

Effect of Formulation on the Behavior of 1,3-Dichloropropene in Soil

Jung-Ho Kim, Sharon K. Papiernik,* Walter J. Farmer, Jianying Gan, and Scott R. Yates

ABSTRACT

The fumigant 1,3-dichloropropene (1,3-D) has been identified as a partial replacement for methyl bromide (CH₃Br) in soil fumigation. 1,3-Dichloropropene is formulated for soil fumigation as Telone II (Dow AgroSciences, Indianapolis, IN) for shank application and as an emulsifiable concentrate (EC) (Telone EC or InLine; Dow AgroSciences) for drip application. This study investigated the effect of formulation on the phase partitioning, transformation rate, and volatilization of 1,3-D isomers. Air-water partitioning coefficients (K_{aw}) were slightly higher for Telone II than for Telone EC, presumably due to the higher apparent water solubility of the EC formulation. Sorption of 1,3-D isomers in two soils was not affected by formulation. Formulation had no significant effect on the rate of 1,3-D transformation in water or soil. In general, differences in the rate of 1,3-D transformation and phase partitioning due to formulation as Telone II or Telone EC were very small. Thus, the effect of formulation on 1,3-D fate may be ignored in transformation and phase partition of 1,3-D in water and soil. Packed soil columns without plastic tarp indicated that with relatively shallow subsurface (10 cm) drip application of Telone EC, emission of 1,3-D isomers was more rapid and produced greater maximum instantaneous flux than deeper (30 cm) shank injection of Telone II. Both application methods resulted in the same cumulative emissions for both isomers, 45% for (*E*)-1,3-D and approximately 50% for (*Z*)-1,3-D. These results suggest that for drip application of fumigants to be effective in reducing emissions, the fumigant must be applied at sufficient depths to prevent rapid volatilization from the soil surface if the water application rate does not sufficiently restrict vapor diffusion.

MODERN SOIL DISINFESTATIONS for controlling soil-borne plant pathogens, parasitic nematodes, weeds, and insects have relied heavily on the use of fumigants. Fumigants are intrinsically volatile; this volatility is essential to achieve effective pest control. However, atmospheric emission of these volatile fumigants from the soil is often a major source of air pollution. Emission of methyl bromide from soil was implicated in stratospheric ozone depletion, and a ban of its production and importation is expected by 2005 in the USA (Anonymous, 2000). The fumigant 1,3-dichloropropene (1,3-D) is considered to be one of the most important alternatives to methyl bromide for control of parasitic nematodes (Noling and Becker, 1994).

To meet the urgent demand of locating and assessing alternative soil fumigants, there is a need to investigate different management methods that may be used to

apply 1,3-D to reduce emissions. In an effort to reduce the negative environmental effects of fumigation, especially the atmospheric emission of fumigants, various improvements to the existing application methods have been proposed. Many of the known approaches to reduce fumigant emission, such as plastic tarping (Wang et al., 1997; Papiernik et al., 2001) and drip application of fumigants (Schneider et al., 1995; Ajwa et al., 2002), are based on the suppression or delay of fumigant transport. Application of fumigants through drip irrigation systems has attracted attention because of its simplicity and low cost for fields that have pre-installed drip systems. Drip fumigation also offers the potential advantage that fumigant rates lower than those used for shank fumigation may be required for effective pest control (Ajwa et al., 2002).

Pesticides are formulated into many usable forms for satisfactory storage, effective application, safety to the applicator and the environment, ease of application with readily available equipment, and economy. Most pesticides are currently applied as water emulsions made from emulsifiable concentrates (EC). Emulsifiable concentrates are concentrated oil solutions of technical-grade material with enough emulsifier added to make the concentrate mix readily with water for application (Ware, 1983, p. 21–32). Application of 1,3-D has been by shank injection of 1,3-D (Telone II) and by drip fumigation using emulsifiable concentrate (EC) formulations of 1,3-D, such as Telone EC and InLine (a mixture of 1,3-D and chloropicrin).

Significant amounts of 1,3-D may be lost following application, with potential cumulative emissions of 30 to 60% of the applied 1,3-D (Gan et al., 1998a, 1998b, 2000a, 2000b). Application of water at the soil surface (water seal) or subsurface drip application of fumigant has the potential to decrease gaseous diffusion and reduce emissions relative to a shank application (Gan et al., 1998b). In drip fumigation, the fumigant is diluted with water to concentrations less than the solubility, then delivered through drip lines. Drip fumigation may improve the uniformity of fumigant distribution, reduce worker exposure, allow for reduced application rates, and reduce air emissions of 1,3-D relative to a standard shank injection (Gan et al., 1998b; Schneider et al., 1995; Wang and Yates, 1999; Ajwa et al., 2002).

Currently, no information is available concerning the effect of formulation on the partitioning and transformation of 1,3-D. This information will help provide the rationale for developing optimized application methods. The main objectives of this study were to (i) evaluate the phase partitioning and transformation of 1,3-D in water and soil when formulated as Telone II and Telone EC and (ii) investigate the volatilization potential of

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Published in J. Environ. Qual. 32:2223–2229 (2003).

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Abbreviations: 1,3-D, 1,3-dichloropropene; EC, emulsifiable concentrate; GC, gas chromatography.

1,3-D when applied to untarped soil via drip irrigation as Telone EC compared with a conventional shank injection of Telone II. This knowledge will be useful in designing application protocols that achieve more consistent and uniform pest control and minimize fumigant emissions.

MATERIALS AND METHODS

Chemicals and Soils

A standard containing 48% (*Z*)-1,3-D and 49% (*E*)-1,3-D was purchased from Chem Service (West Chester, PA). Two commercial formulations of 1,3-D, Telone II [0.61 g mL⁻¹ (*Z*)-1,3-D and 0.58 g mL⁻¹ (*E*)-1,3-D] and Telone EC [0.40 g mL⁻¹ (*Z*)-1,3-D and 0.40 g mL⁻¹ (*E*)-1,3-D] were provided by Dow AgroSciences and Dow Elanco (Indianapolis, IN), respectively. Telone II is used for conventional shank injection, and Telone EC is an emulsifiable concentrate of 1,3-D formulated for drip application.

Two soils, an Arlington sandy loam (coarse-loamy, mixed, active, thermic Haplic Durixeralf) and a Carsitas loamy sand (mixed, hyperthermic Typic Torripsamment), were used in this study. Arlington sandy loam was acquired from the University of California Agricultural Experiment Station in Riverside, CA. Carsitas loamy sand was collected from the University of California Coachella Valley Research and Extension Center in Thermal, CA. Before use, moist soils were passed through a 2-mm sieve. The Arlington soil had a pH of 7.2 and an organic carbon content of 9.2 g kg⁻¹, and consisted of 74.6% sand, 18.0% silt, and 7.4% clay. The Carsitas soil had a pH of 7.3 and an organic carbon content of 3.2 g kg⁻¹, and was comprised of 84.2% sand, 12.8% silt, and 2.9% clay. The water content was adjusted to 10.0% (w/w) for transformation experiments.

Air–Water Partitioning

Air–water partitioning of 1,3-D formulated as Telone II and Telone EC was determined at 20 and 40°C. For each formulation, six aqueous solutions containing 150 to 450 mg L⁻¹ (Telone II) or 250 to 900 mg L⁻¹ (Telone EC) were prepared and 10-mL aliquots (triplicate samples) of each solution were transferred to 21.6-mL headspace vials (Supelco, Bellefonte, PA). A broader range in concentration was possible for Telone EC because of its higher apparent solubility. Vials were immediately sealed with Teflon-faced butyl rubber septa and aluminum seals, and then vortexed for 2 min. The vials were equilibrated in the dark at 20 ± 0.2 or 40 ± 0.2°C for 16 h.

To determine the concentration of 1,3-D in air (C_a), a 1-mL sample of the headspace was withdrawn using a gas-tight syringe and transferred into a gas chromatography (GC) vial containing 1 mL of hexane. To determine the concentration of 1,3-D in water (C_w), 0.5 mL of the aqueous phase was withdrawn with a gas-tight syringe and transferred into a 10-mL headspace vial containing 5 mL of hexane. The vials were vortexed for 2 min and a portion of the hexane phase was then transferred into a GC vial. Analysis of 1,3-D was conducted using a Hewlett-Packard (Palo Alto, CA) 6890 GC equipped with an electron capture detector. The conditions were set as follows: 30-m × 0.25-mm × 1.4-μm RTX-624 capillary column (Restek Co., Bellefonte, PA); 1.5 mL min⁻¹ carrier gas (N₂); 110°C isothermal oven temperature; 230°C inlet temperature; and 280°C detector temperature. The measured C_a and C_w (both in mg L⁻¹) were used to calculate the dimensionless Henry's law constant (K_H) using $K_H = C_a/C_w$.

Soil–Water Partitioning

Sorption of 1,3-D formulated as Telone II and Telone EC to Arlington and Carsitas soil was determined by batch equilibration. Aqueous solutions containing 50, 100, 200, 350, and 600 mg L⁻¹ 1,3-D were prepared in deionized water with 200 mg L⁻¹ of HgCl₂, which was added to inhibit biological degradation of 1,3-D. Twenty milliliters of each solution was added to 5.0 g of soil (dry weight) in a 50-mL centrifuge tube (triplicate samples). The centrifuge tubes were tightly capped and mechanically shaken for 16 h at room temperature. A preliminary experiment showed that the 16-h period was sufficient to achieve equilibrium. The samples were then centrifuged for 5 min at 12 000 × *g* and 4°C.

To determine the concentration of 1,3-D in the solution phase (C_w), a 0.5-mL aliquot of the supernatant was withdrawn with a gas-tight syringe, extracted with ethyl acetate, and the 1,3-D concentration was quantified by GC. After the supernatant was decanted, the centrifuge tube (with soil) was weighed to determine the amount of solution remaining in the soil pellet. To determine the concentration of 1,3-D in the solid phase (C_s), 10 mL of ethyl acetate and 7 g of anhydrous sodium sulfate were added to the centrifuge tubes. The sample tubes were tightly capped and mechanically shaken for 30 min. Following centrifugation, an aliquot of the ethyl acetate phase was transferred into a GC vial and analyzed by GC using the conditions described above. The measured C_s (mg kg⁻¹) and C_w (mg L⁻¹) were fitted to a linear isotherm $C_s = K_d C_w$, where K_d is the linear sorption coefficient (L kg⁻¹). Linear isotherms were forced through the origin (no sorption at zero concentration).

Transformation in Soil and Water

The degradation rate of 1,3-D formulated as Telone II and Telone EC was determined in aqueous solution and in soil. Aqueous and soil samples containing 30 mg L⁻¹ 1,3-D were prepared by adding 10 μL of Telone II and Telone EC stock solution (30 000 mg L⁻¹ 1,3-D) to 10 mL of deionized water or 10 g of soil in 21.6-mL headspace vials. Vials were immediately sealed with septa and caps. Aqueous samples (triplicates) were equilibrated for 0.4, 2, 3, 5, 10, 15, 25, and 48 d at 25 ± 0.2 and 35 ± 0.2°C. The 1,3-D concentration remaining in solution at each time was determined by removing a 0.5-mL aliquot from each vial using a gas-tight syringe, which was extracted by transferring the aqueous solution into a 10-mL headspace vial containing 3 mL of ethyl acetate and 3 g anhydrous sodium sulfate. Soil samples (triplicates of Arlington and Carsitas soil) were equilibrated for 0.25, 1, 2, 3, 4, 6, 13, 20, and 35 d at 20 ± 0.2°C. For extraction, each vial was decapped and 10 mL ethyl acetate and 7 g anhydrous sodium sulfate were added. The vial was tightly capped and mechanically shaken for 30 min.

Aliquots of the ethyl acetate extracts were transferred into GC vials and analyzed by GC using the conditions described above. The transformation of 1,3-D was described by first-order kinetics, using $C = C_0 \exp(-kt)$, where C is 1,3-D concentration (mg kg⁻¹) at time t (h), C_0 is the initial 1,3-D concentration (mg kg⁻¹), and k is the first-order rate constant (h⁻¹).

Diffusion and Volatilization Following Soil Application

Volatilization and diffusion of 1,3-D formulated as Telone II and Telone EC were determined in columns packed with the Arlington soil at room temperature. The columns were made of stainless steel and were 70 cm in length with a 12-cm i.d. Columns were packed with fresh soil at a bulk density of 1.55 g cm⁻³ and a moisture content of 4.75% (w/w). A sampling

chamber (4 cm in length with a 12-cm i.d.) was sealed onto the top of the soil column. The design and use of the columns is described in detail elsewhere (Gan et al., 2000b).

Telone II (284.8 μL) was injected 30 cm below the soil surface using a gastight syringe. Telone EC was first dissolved in water to produce a solution containing 1200 mg L^{-1} 1,3-D, then 282.4 mL of this solution was delivered at 2 mL min^{-1} at a 10-cm depth using a syringe pump. This water application rate corresponds to 25 mm of water applied uniformly across the column cross-sectional area. For both formulations, the application rate was equivalent to 300 $\text{kg of 1,3-D ha}^{-1}$ with 150 kg ha^{-1} of each isomer. A constant air flow of 100 mL min^{-1} was established by connecting the outlet to a stable vacuum source.

A computerized relay system was used to automate the introduction of an aliquot of the headspace from each column into the GC at 11-min intervals for 14 d. The GC conditions used for on-line monitoring were as follows: 100- μL gas sampling valve; 60-m \times 0.53-mm \times 3.0- μm AT624 capillary column (Alltech Associates, Deerfield, IL); 20 mL min^{-1} column flow (N_2); 100°C isothermal oven temperature; and 280°C detector temperature. Volatilization fluxes of 1,3-D were calculated as $\text{mg m}^{-2} \text{min}^{-1}$ and cumulative volatilization losses as the percentage of applied 1,3-D.

To compare the diffusion of 1,3-D from Telone II and Telone EC, soil air (1.0 mL) was withdrawn from the soil columns at different depths (5, 10, 20, 30, 40, 50, 60, and 70 cm) using a gastight syringe at 1, 2, 4, 8, 24, 48, 72, and 144 h after application. Soil-air samples were transferred to 8.7-mL headspace vials and analyzed by GC–electron capture detection (ECD) using an automated headspace sampler (Teledyne Tekmar, Mason, OH). The conditions of the headspace sampler were set as follows: 90°C equilibration temperature; 90°C valve temperature; 90°C line temperature; 2-min equilibration time; 1.0-mL sample loop; 1700-Pa (0.25-psi) vial pressurization pressure; and 0.1-min pressure equilibrium time. The conditions of the GC–ECD were set as follows: 30-m \times 0.25-mm \times 1.4- μm RTX-624 capillary column (Restek); 0.71 mL min^{-1} carrier gas (N_2); 120°C isothermal oven temperature; 230°C inlet temperature; and 280°C detector temperature.

RESULTS AND DISCUSSION

Air–Water Partitioning

Air–water partitioning was linear over the concentration range tested for both formulations ($R^2 = 0.99$; Table 1). The K_H values for both 1,3-D isomers formulated as Telone II were 1.07 to 1.16 times greater than those for Telone EC (Table 1). The slightly higher K_H of Telone II may be due to the emulsifier in Telone

Table 1. Air–water partition coefficients (K_H) of 1,3-dichloropropene (1,3-D) isomers in Telone II and Telone emulsifiable concentrate (EC) formulations.

Temperature °C	Isomer	Formulation	K_H	R^2 †
20	(Z)-1,3-D	II	0.058	0.99
		EC	0.051	0.99
	(E)-1,3-D	II	0.037	0.99
		EC	0.032	0.99
40	(Z)-1,3-D	II	0.113	0.99
		EC	0.106	0.99
	(E)-1,3-D	II	0.077	0.99
		EC	0.071	0.99

† The term R^2 indicates the coefficient of determination for linear regression to the concentration data (six concentration points used to calculate each K_H value).

EC, which is a detergent material that allows the suspension of microscopically small oil droplets in water (formation of an emulsion). The increased apparent water solubility of the Telone EC formulation compared with the Telone II formulation may result in a higher K_H for Telone II.

The K_H of (Z)-1,3-D was significantly greater than that of (E)-1,3-D (Table 1), which is expected due to the higher vapor pressure and lower water solubility of (Z)-1,3-D compared with (E)-1,3-D (Goring, 1962). Other researchers have reported higher K_H for (Z)-1,3-D than for (E)-1,3-D (Goring, 1962; Leistra, 1970). The results reported in Table 1 are in agreement with previously reported values of K_H for 1,3-D isomers. For example, Goring (1962) reported K_H of 0.056 and 0.041 for (Z)- and (E)-1,3-D, respectively, at 20°C. As a result of the higher K_H and vapor pressure of (Z)-1,3-D, it can be expected that vapor phase diffusion of (Z)-1,3-D will be more rapid than that of (E)-1,3-D following 1,3-D application to soil.

Soil–Water Partitioning

Sorption of 1,3-D isomers was not strongly affected by formulation, as evidenced by nearly equivalent K_d values for both formulations (Table 2). Sorption of (Z)-1,3-D to both soils was similar, with slightly less sorption of (E)-1,3-D to Carsitas soil than Arlington soil (Table 2). Sorption of 1,3-D may be affected by pH, exchangeable cations, and other environmental conditions (Singhal and Kumar, 1976). In Carsitas soil, the (Z) isomer demonstrated slightly more sorption than the (E) isomer. The low K_d observed (≤ 0.7) for both isomers in both soils suggests that 1,3-D is present predominantly in the vapor and liquid phases, as has been previously observed (Wolt et al., 1993). Sorption isotherms were well-described using a linear model ($R^2 \geq 0.97$; Table 2). Fitting a nonlinear (Freundlich, $C_s = K_f C_w^n$) model to the soil–water partitioning data resulted in a slightly improved fit for some isotherms. Isotherm nonlinearity parameters (n) ranged from 0.88 to 0.95. The slight differences in the K_H and K_d values of 1,3-D isomers in Telone II compared with Telone EC suggest that formulation may have small effects on 1,3-D fate and transport.

Transformation in Soil and Water

Degradation of Telone II and Telone EC in aqueous solution at both temperatures followed first-order kinetic

Table 2. Linear isotherm parameters for sorption of 1,3-dichloropropene (1,3-D) isomers in Telone II and Telone emulsifiable concentrate (EC) formulations to Arlington and Carsitas soils.

Soil	Isomer	Formulation	K_d	R^2 †
Arlington	(Z)-1,3-D	II	0.63	0.98
		EC	0.70	0.98
	(E)-1,3-D	II	0.68	0.98
		EC	0.67	0.98
Carsitas	(Z)-1,3-D	II	0.65	0.98
		EC	0.66	0.98
	(E)-1,3-D	II	0.61	0.97
		EC	0.60	0.97

† The term R^2 indicates fit to linear model forced through the origin.

Table 3. First-order transformation rates (*k*) in water and half-lives of 1,3-dichloropropene (1,3-D) isomers formulated as Telone II and Telone emulsifiable concentrate (EC).

Temperature	Isomer	Formulation	<i>k</i>	Half-life	<i>R</i> ² †
°C			d ⁻¹	d	
25	(Z)-1,3-D	II	0.078	8.83	0.99
		EC	0.077	8.90	0.99
	(E)-1,3-D	II	0.084	8.20	0.99
		EC	0.083	8.25	0.99
35	(Z)-1,3-D	II	0.297	2.33	0.99
		EC	0.287	2.40	0.99
	(E)-1,3-D	II	0.334	2.06	0.99
		EC	0.321	2.15	0.99

† The term *R*² indicates fit to first-order kinetic model.

ics (*R*² > 0.99). There was little difference in the half-life between Telone II and Telone EC formulations (Table 3), which suggests that the formulations did not affect 1,3-D hydrolysis. Abiotic degradation of 1,3-D in water is mainly attributed to hydrolysis (McCall, 1987; Roberts and Stoydin, 1976) via nucleophilic substitution where water or OH⁻ serves as the nucleophile, forming 3-chloroallyl alcohol. Nucleophilic groups such as -NH₂, -NH, -SH, and -OH may contribute to the S_N2 type of reaction when they are present at sufficiently high concentrations (Schwarzenbach et al., 1993). Addition of Telone EC into water increased the concentration of surfactant, which may include hydrophobic groups, such as -C_nH_{2n+1}, C_nH_{2n-1}, -phenyl, -CH₂OR, and -COOR, and hydrophilic groups, such as -OH, -COOH, -CN, -NHCONH₂, -SO₃⁻H⁺(Na⁺), -OSO₃⁻H⁺(Na⁺), -COO⁻Na⁺, and -N⁺X⁻ (Ware, 1983, p. 21–32). This study showed that the surfactant in Telone EC does not significantly affect the rate of 1,3-D hydrolysis at 1,3-D concentrations of approximately 30 mg L⁻¹.

The transformation rate of both 1,3-D isomers in aqueous solution increased with increasing temperature (Table 3). The hydrolysis half-life values of 1,3-D reported in Table 3 are similar to those of McCall (1987), who reported 1,3-D half-lives of 11.3 and 3.1 d in water at 20 and 30°C, respectively, and Wang et al. (2001), who reported hydrolysis half-lives of 9 and 13 d for (*E*)- and (*Z*)-1,3-D, respectively, at 20°C. The (*E*) isomer showed slightly higher reaction rates in aqueous solution than the (*Z*) isomer (Table 3), in agreement with previous reports (Wang et al., 2001).

Transformation of 1,3-D in Arlington and Carsitas soil in a closed system followed first-order kinetics for both formulations (*R*² > 0.99) (Table 4). No significant

Table 4. First-order transformation rates (*k*) and half-lives of 1,3-dichloropropene (1,3-D) isomers applied as Telone II and Telone emulsifiable concentrate (EC) formulations to Arlington and Carsitas soils at 20°C.

Soil	Isomer	Formulation	<i>k</i>	Half-life	<i>R</i> ² †
			d ⁻¹	d	
Arlington	(Z)-1,3-D	II	0.094	7.35	0.99
		EC	0.101	6.84	0.99
	(E)-1,3-D	II	0.099	6.96	0.99
		EC	0.105	6.54	0.99
Carsitas	(Z)-1,3-D	II	0.097	7.12	0.99
		EC	0.103	6.69	0.99
	(E)-1,3-D	II	0.099	6.96	0.99
		EC	0.104	6.61	0.99

† The term *R*² indicates fit to first-order kinetic model.

differences in the degradation rate due to formulation were observed (Table 4), so the surfactant in Telone EC did not appear to influence the rate of 1,3-D transformation in these soils. The degradation rate of both 1,3-D isomers was unaffected by soil type (Table 4). The half-life values we observed in Arlington soil are similar to those reported by other researchers (Dungan et al., 2001; Gan et al., 1998a, 2000c), who report 1,3-D half-lives in unamended Arlington soil ranging from approximately 4 to 10 d at approximately 20°C. In both soils, (*E*)-1,3-D was degraded slightly more rapidly than (*Z*)-1,3-D (Table 4), in agreement with previous research (Ou et al., 1995; Gan et al., 1998a, 2000c; Dungan et al., 2001).

Volatilization and Diffusion following Soil Application

Comparison of fumigant distribution following drip application and shank injection has indicated that both methods of application are reasonably effective in distributing the fumigant through the soil (Schneider et al., 1995; Wang and Yates, 1999). Packed soil columns were used to compare the diffusion of 1,3-D applied as Telone II (simulated shank injection) and Telone EC (simulated drip application). For both formulations, the maximum vapor-phase 1,3-D concentration occurred at the depth of injection (30 cm for Telone II, 10 cm for Telone EC) for the first 24 h (Fig. 1). The concentration of 1,3-D measured in the soil air 1 h after simulated shank application of Telone II was 57.6 mg L⁻¹ for (*Z*)-1,3-D and 39.3 mg L⁻¹ for (*E*)-1,3-D (Fig. 1A). For drip application of Telone EC, the vapor-phase 1,3-D concentrations were much lower, 17.0 mg L⁻¹ for the (*Z*) isomer and 11.0 mg L⁻¹ for the (*E*) isomer at 1 h after application (Fig. 1B). The maximum measured vapor-phase concentration of 1,3-D in the application without water (Telone II) was approximately 3.5 times greater than that for drip application of Telone EC at 1 h after the treatment.

The rapid transport of Telone II was demonstrated by its distribution pattern with time. The 1,3-D gas distributions decreased uniformly with distance from the source when Telone II was applied by direct injection (Fig. 1A). Movement of Telone EC in the soil column was more restricted than that of Telone II, and most of the applied mass of Telone EC remained near the application point (10 cm) for a prolonged time (Fig. 1B). Diffusion of 1,3-D was more rapid after simulated shank injection of Telone II than simulated drip application of Telone EC. The retarded movement of Telone EC was apparently a result of the reduced vapor diffusion caused by the increased water content and decreased air porosity in the soil. At 1 h after application, maximum vapor-phase concentrations of (*Z*)-1,3-D were 1.4 to 1.5 times greater than those of (*E*)-1,3-D (Fig. 1). The distribution of the (*Z*) and (*E*) isomers of 1,3-D in soil was consistent with the relative differences in the air–water partition coefficient *K*_H of the two isomers in this study (Table 1).

Volatilization flux and cumulative volatilization of

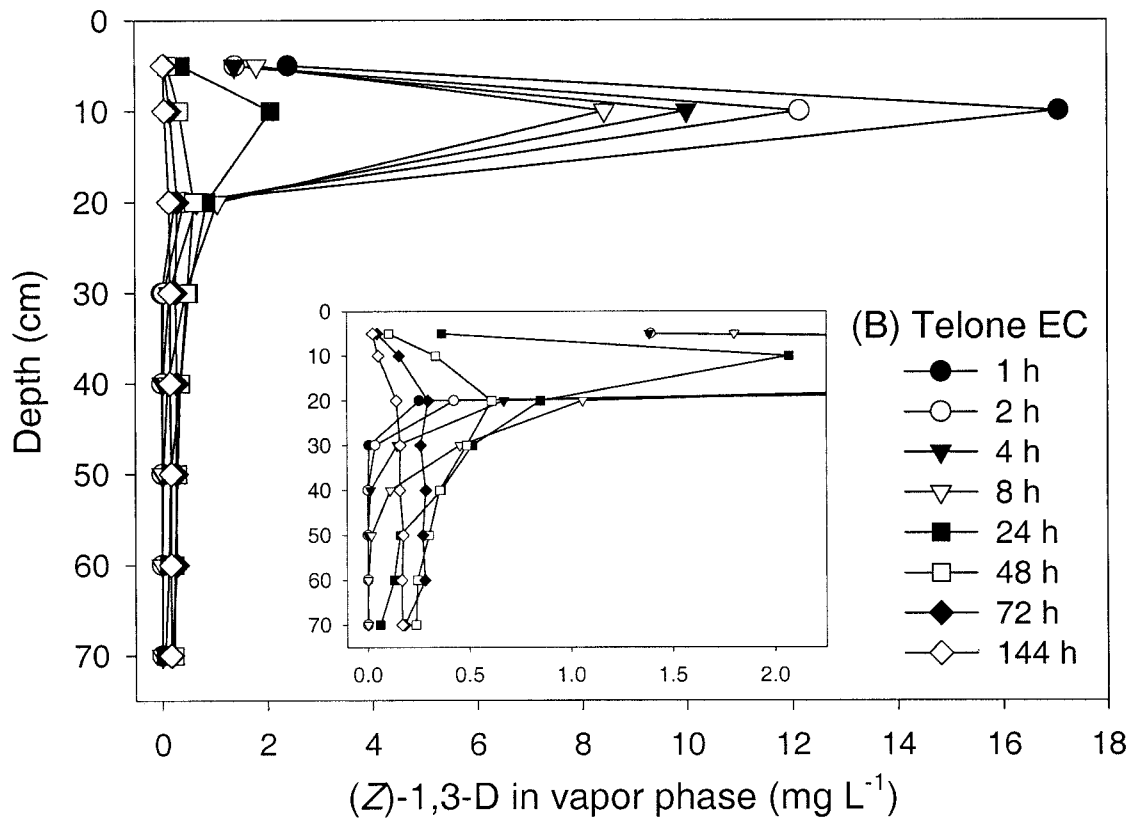
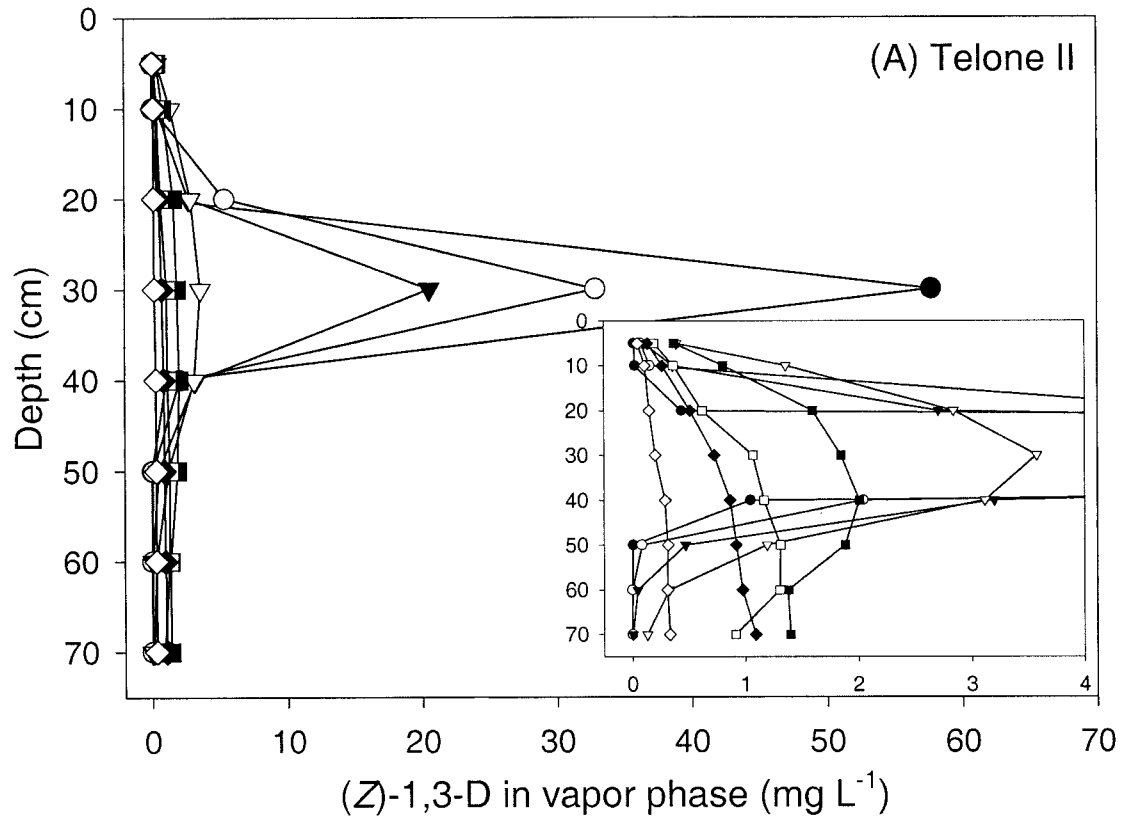


Fig. 1. Soil-gas concentrations of (Z)-1,3-dichloropropene applied as (A) Telone II (no water, 30-cm depth) and (B) Telone emulsifiable concentrate (EC) (drip application, 10-cm depth) in untarped soil columns packed with Arlington sandy loam.

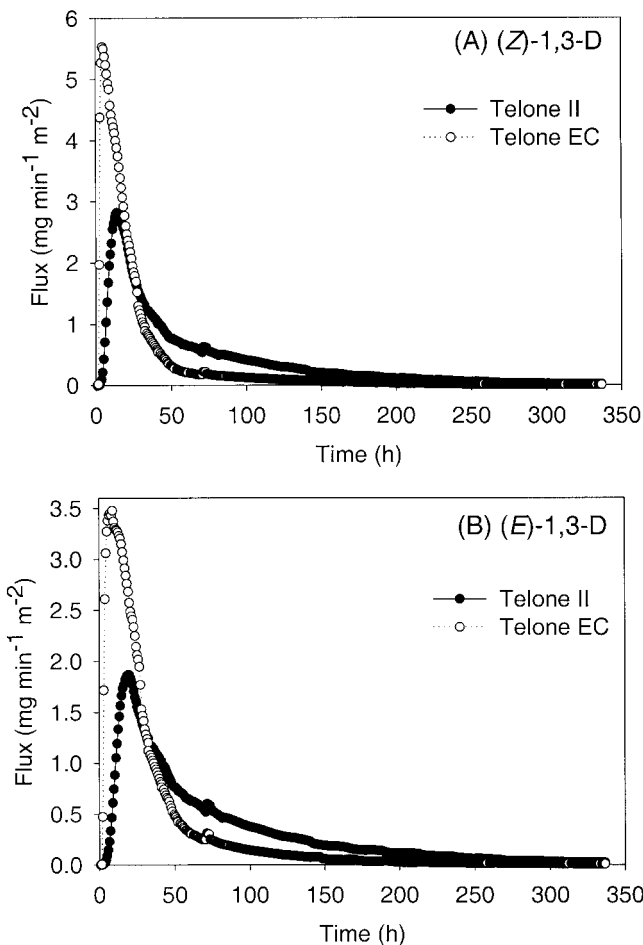


Fig. 2. Volatilization flux of (A) (Z)-1,3-dichloropropene (1,3-D) and (B) (E)-1,3-D in untarped soil columns receiving shank injection of Telone II (30-cm depth) or drip application of Telone emulsifiable concentrate (EC) (10-cm depth).

1,3-D were determined for 14 d (336 h) from untarped soil columns treated with Telone II and Telone EC at 30- and 10-cm depths, respectively. The volatilization flux of both 1,3-D isomers during the first 24 h were much greater from the Telone EC-treated column than from the Telone II-treated column (Fig. 2). Flux of (Z)-1,3-D peaked 14 h after injection in the Telone II treatment while maximum flux from the Telone EC treatment occurred 4.4 h after application (Fig. 2A). Similar trends were observed for (E)-1,3-D, for which the maximum flux occurred at 19 and 8.8 h after injection for Telone II and Telone EC, respectively (Fig. 2B). The maximum flux of both 1,3-D isomers was approximately two times higher for the Telone EC treatment than for the Telone II treatment (Fig. 2). Drip application of 1,3-D at 10 cm with 25 mm of water resulted in higher maximum flux occurring shortly after application, while deeper (30 cm) shank application of Telone II resulted in a more prolonged flux of lower intensity (Fig. 2).

Cumulative losses in 14 d were similar for both formulations (Fig. 3), despite the differences in instantaneous flux (Fig. 2). In these experiments, cumulative volatilization in 14 d accounted for 45 to 53% of the applied 1,3-D.

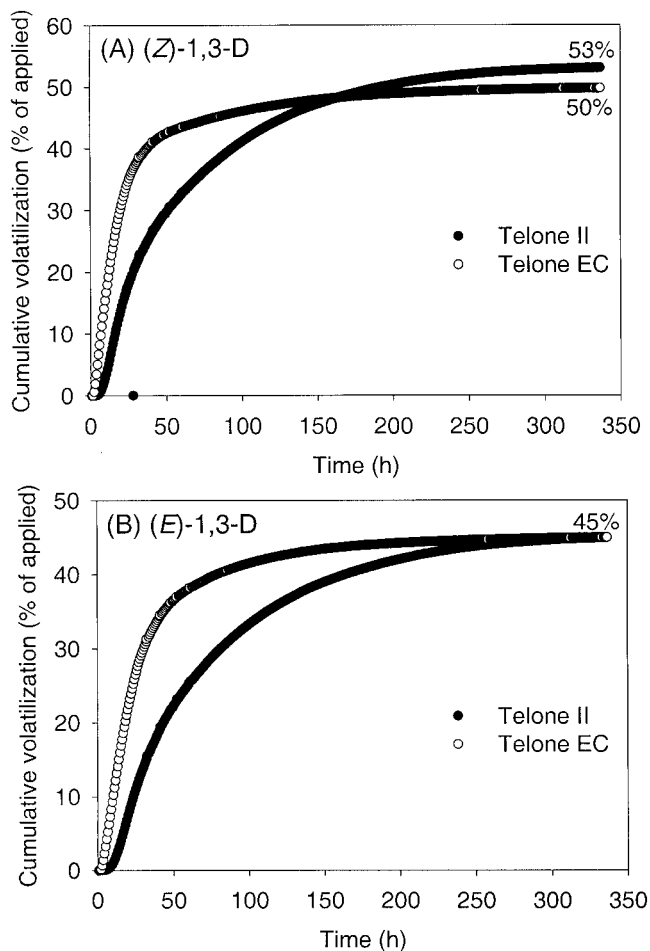


Fig. 3. Cumulative emission losses of (A) (Z)-1,3-dichloropropene (1,3-D) and (B) (E)-1,3-D in untarped soil columns receiving shank injection of Telone II (30-cm depth) or drip application of Telone emulsifiable concentrate (EC) (10-cm depth).

These results are similar to those reported by other researchers in laboratory and field experiments. Gan et al. (1998b, 2000b) reported measured cumulative losses of 48 to 51% for (Z)-1,3-D and 40 to 43% for (E)-1,3-D following application at a 30-cm depth with no surface tarp (the same conditions used in the application of Telone II in these experiments). Gan et al. (2000a) report that in field experiments measuring volatilization following drip application (10-cm depth) of Telone EC to untarped soil, cumulative volatilization was 32% for both isomers. Wang et al. (2001) reported cumulative 1,3-D losses of 57% following subsurface (20 cm) drip application of Telone EC.

In these experiments, both the instantaneous flux (Fig. 2) and cumulative flux (Fig. 3) were greater for (Z)-1,3-D than for (E)-1,3-D. These results are consistent with the results of other laboratory studies, which also indicated more volatilization of the (Z) isomer (Gan et al., 1998a, 1998b, 2000a, 2000b). The differences may be explained by their different physicochemical properties, with the (Z) isomer having a lower boiling point (104.1 vs. 112.6°C) and solubility (2180 vs. 2320 mg L⁻¹ at 25°C), but a higher vapor pressure (5700 vs. 4500

Pa at 25°C) and Henry's law constant (0.051–0.058 vs. 0.032–0.037 at 20°C; Table 1) than the (*E*) isomer.

Previous research indicated that application of 1,3-D with water in subsurface drip application could significantly reduce cumulative emissions. In laboratory experiments, Gan et al. (1998b) determined cumulative volatilization rates of 1,3-D isomers following subsurface drip application of Telone SL (an emulsifiable formulation) and simulated shank injection of Telone II, both at a 20-cm depth. Subsurface drip application using water application rates similar to those used in these experiments produced cumulative emissions of 24 and 20% for (*Z*) and (*E*)-1,3-D, respectively; for simulated shank injection, cumulative volatilization of both isomers was nearly 60%. Apparently, when 1,3-D is drip-applied deep in the soil, restriction of vapor-phase diffusion contains most of the fumigant mass within the soil, where it may be degraded before emission from the soil surface. When 1,3-D is applied by drip application nearer the soil surface with a relatively low water application rate, as in these experiments, vapor and water transport allow rapid fumigant transport to the soil surface and high-intensity flux occurs shortly after application (Fig. 2). These results suggest that when the amount of water added in drip application of fumigants is insufficient to impede gas-phase diffusion, the fumigant must be applied at sufficient depths to prevent rapid volatilization from the soil surface to effectively reduce emissions.

ACKNOWLEDGMENTS

We thank Fred Ernst, Christian Taylor, and Qiaoping Zhang for assistance in obtaining some of the data. This study was supported by the USDA-CSREES Methyl Bromide Transition Program (Award no. 00-51102-9551).

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