

## Acceleration of 1,3-Dichloropropene Degradation by Organic Amendments and Potential Application for Emissions Reduction

J. Gan,\* S. R. Yates, D. Crowley, and J. O. Becker

### ABSTRACT

Emissions of the fumigant 1,3-dichloropropene (1,3-D) can result in degradation of air quality in certain areas. The high emission potential of 1,3-D is caused by its rapid diffusion and comparatively slow degradation in soil. One approach to reduce the emission is to enhance the surface soil's capacity to degrade 1,3-D. We investigated the capability of two organic amendments, a composted manure (CM) and a biosolid-manure mix (BM), to accelerate 1,3-D degradation in soil. Degradation of 1,3-D was significantly enhanced in amended soils compared to the unamended soil, and the degree of acceleration varied with the type as well as the rate of amendment. Compost manure was more effective in stimulating 1,3-D degradation than the less decomposed BM; even at an amendment/soil ratio as low as 1:40 (w/w), degradation in the CM-amended soil was two times faster than that in the unamended soil. The acceleration in CM-amended soils was a combined result of enhanced chemical and microbial degradation, since sterilization only partially reduced the enhanced degradation. The reduction of 1,3-D emissions by surface application of organic amendments was illustrated in a column experiment: 1,3-D emission loss after injection at 30 cm was 30% from an unamended Arlington sandy loam (a coarse-loamy, mixed, thermic Haplic Durixeralf), but decreased to only 16% in the column containing 5% CM in its top 5-cm layer.

CHEMICAL FUMIGANTS are commonly used for the broad spectrum control of soilborne pathogens, plant parasitic nematodes, and weeds in warm areas such as California and Florida where year-around cultivation of high value crops is conducted. Atmospheric emissions of soil fumigants, however, have caused health and environmental problems (Baker et al., 1996). Recently, emissions of methyl bromide (MeBr) from soil and commodity fumigations were implicated in stratospheric ozone depletion, and a ban of its production and importation is expected by 2001 in the USA (USEPA, 1993). The fumigant 1,3-dichloropropene (1,3-D) is considered to be one of the most important alternatives to MeBr (Noling and Becker, 1994). The vapor pressures of 1,3-D (34.3 mm Hg for *Z*-1,3-D and 23.0 mm Hg for *E*-1,3-D; Batzer et al., 1997), though considerably lower than that of MeBr, are still high enough so that significant atmospheric emissions may result. High 1,3-D concentrations were detected in the ambient air near fumigation areas in 1990 in California, which prompted a 4-yr suspension of the use of Telone II, the commercial formulation of 1,3-D, between 1990 and 1994 (California Department of Food and Agriculture, 1990). Model simulation and field studies predicted that 11 to 77% of the applied dosage would volatilize when the compound

is injected into the subsoil (Basile et al., 1986; van den Burg, 1992; van den Burg et al., 1994; Chen et al., 1995). Although not an ozone-destroying compound, 1,3-D is classified as a toxic air substance in the U.S. Environmental Protection Agency's (USEPA's) Clean Air Act because of its adverse toxicological effects. To minimize the negative impact of 1,3-D on the environment, it is imperative to develop management strategies that enable reduced 1,3-D emissions.

The tendency for 1,3-D to volatilize after soil injection is determined by its transport properties and the degradation characteristics in soil. Transport of 1,3-D in unsaturated soil is very rapid because gas-phase diffusion dominates (McKenry and Thomason, 1974; van den Burg, 1992; van den Burg et al., 1994). In comparison to the rapid diffusion, its degradation in many agricultural soils, with half-lives ranging from a few days to a few weeks (Van Dijk, 1974, 1980; Roberts and Stoydin, 1976; Van der Pas and Leistra, 1987; Smelt et al., 1989; Leistra et al., 1991; Wolt et al., 1993; Ou et al., 1995), is relatively slow. The disparity between diffusion rates and degradation rates is especially great in sandy or fractured (e.g., caused by injection) soils, where upward diffusion (and subsequent volatilization) and downward transport are the main processes for causing fumigant dissipation from the application site. To reduce emissions, Telone II is now required to be injected at depths >45 cm, while some other alternative application methods such as the use of emulsifiable formulations through irrigation systems are also being tested (Schneider et al., 1995; Sipes and Schmitt, 1996; Becker and Mueller, 1997). All of these measures reduce volatilization by encouraging the fumigant's downward movement or limiting its gaseous diffusion.

Alternatively, 1,3-D emissions can also be minimized if 1,3-D is degraded near the surface before volatilizing into the air. The degradation of a pesticide in soil is influenced by soil chemical and biological conditions, both of which can be modified by addition of organic matter amendments. In situations where soil organic matter fortuitously promotes the growth and activity of selected pesticide degrading microorganisms, the addition of organic matter to soil may cause accelerated degradation of the target compound (Gan et al., 1996a; Kästner and Mahro, 1996; Topp et al., 1996). The effect of organic amendments on fumigant degradation, however, has not been reported, and altering management practices to manipulate pesticide degradation to reduce its negative environmental impact has been largely untested.

The primary objectives of this study were to measure the acceleration of 1,3-D degradation in soil by common

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**Abbreviations:** 1,3-D, 1,3-dichloropropene; CM, compost manure; BM, biosolid-manure mix; GC, gas chromatography; ECD, electron capture detector.

organic amendments, and the effect of amendment types and application rates on the degree of acceleration. The potential applicability of using this phenomenon to reduce 1,3-D emissions was tested in soil columns by comparing 1,3-D emissions from unamended and surface-amended soils.

## MATERIALS AND METHODS

### Soil, Organic Amendments, and Chemicals

The soil used in this study, an Arlington sandy loam, was taken from the top 20 cm in a field at the Univ. of California, Riverside Agricultural Experimental Station. The soil had a pH of 7.4 and an organic matter content of 0.92%. Moist soil was passed through a 2-mm sieve and stored at room temperature before use. Two different organic amendments were used: CM (The Home Depot, Moreno Valley, CA) and a 1:1 (w/w) BM (Recyc Inc., Corona, CA). Compost manure represents a more decomposed amendment, while BM is a less degraded amendment that is allowed for direct application in farm fields. Moist CM and BM contained 20% (w/w) and 73% of water, respectively. Dried CM and BM contained 25 and 15.4% of total C, and 2.4 and 1.6% of total N, respectively. The total C and N contents were determined by flash combustion of dried materials on an NA 1500 Nitrogen Analyzer (Carlo Erba, Italy).

The 1,3-D standard containing 48% (*Z*) isomer and 50% (*E*) isomer was purchased from Chem Service (West Chester, PA). Telone II containing 50% (*Z*) isomer and 45% (*E*) isomer was provided by DowElanco (Indianapolis, IN).

### Degradation in Nonsterilized and Sterilized Soil-Amendment Mixes

Degradation of 1,3-D was first determined in nonsterilized and sterilized 1:2 (w/w) amendment-soil mixes to elucidate the mechanism of enhanced degradation. Nonsterilized mixes were prepared by directly mixing CM or BM with soil, and sterilized mixes were obtained by autoclaving the mixes twice at 121°C for 60 min each time. The sterilized mixes were handled aseptically prior to and during the incubation. Before incubation, the water content was adjusted with deionized water to 18% for all CM-soil mixes, and to 26% for all BM-soil mixes. A higher water content was used for the BM-soil mix because of the high original water content in BM. Nonsterilized or sterilized soil (unamended) was adjusted to 18% water content and used as control. The water potentials of different amendment-soil combinations were measured using tensiometers (Table 1).

Thirteen grams (dry wt.) of the prepared soil or amendment-soil mixes were placed in 21-mL headspace vials (Supelco Inc., Bellefonte, PA), and 5  $\mu$ L of acetone solution containing 100  $\mu$ g  $\mu$ L<sup>-1</sup> 1,3-D was then added to give a concentration of 38  $\mu$ g kg<sup>-1</sup> for each sample. The treated vials were immediately sealed with aluminum caps and Teflon-faced butyl rubber septa and placed in an incubator at 25  $\pm$  0.5°C. The sealing prevented 1,3-D vapor from diffusing out of the vial and also kept the sterilized samples under sterile conditions during incubation. At different time intervals after the treatment, three replicates from each treatment were removed and the vials chilled to -15°C. The sample vials were opened while still cold, and 10 mL of ethyl acetate was quickly added, after which the vials were recapped and shaken for 1 h. After the removal of residual water in the sample by anhydrous sodium sulfate, an aliquot of the ethyl acetate supernatant was analyzed by gas chromatography (GC) with an HP5890

**Table 1. Carbon, N, and water contents and 6-d cumulative CO<sub>2</sub> evolution of unamended soil and soils amended with organic matters at different ratios (number of replicates = 3).**

Matrix	C†	N†	Water content	Total CO <sub>2</sub> ‡
	%		kPa	mg
Soil, unamended	1.08	0.11	1	0.46
CM-Soil, 1:2	8.70	0.83	30	8.34
CM-Soil, 1:4	5.65	0.54	20	7.61
CM-Soil, 1:8	3.62	0.35	7	6.61
CM-Soil, 1:20	2.17	0.21	4	6.11
CM-Soil, 1:40	1.63	0.16	3	5.81
BM-Soil, 1:2	5.48	0.56	18	4.54

† Total C/N contents were measured using the flash combustion method on a NA-1500 Nitrogen Analyzer (Carlo Erba, Italy).

‡ Total soil respiration measured as CO<sub>2</sub> evolution from 50-g matrix in closed flasks during 6-d incubation at 25°C.

GC (Hewlett Packard, San Fernando, CA) equipped with an electron capture detector (ECD). The GC column and conditions were: RTX-624 capillary column (30 m by 0.25 mm by 1.4  $\mu$ m, Restek Co., Bellefonte, PA) with 240°C inlet temperature, 270°C detector temperature, 1.1 mL min<sup>-1</sup> column flow rate (He), and 100°C isothermal oven temperature.

### Reaction with Aniline

To understand the potential pathway of chemical degradation of 1,3-D in amended soil, the reaction of 1,3-D with aniline was determined at 25°C in solution. The NH<sub>2</sub> group on aniline functions as a nucleophile and was found to react readily with CH<sub>3</sub>Br and CH<sub>3</sub>I in a previous study (Gan and Yates, 1996). Water solution containing 5 mM aniline and 0.2 mM 1,3-D was prepared and transferred to 21-mL headspace vials and the vials were immediately sealed. Disappearance of 1,3-D isomers from the solution was determined by periodically analyzing the ethyl acetate extract by GC-ECD. At the end of reaction, an aliquot of ethyl acetate extract was injected into an HP5890 GC in tandem with an HP5971 Mass Selective Detector to obtain mass spectra of the reaction products. The GC column and conditions were: RTX-624 or HP-5MS column (cross-linked 5% phenyl methyl silicone, 30 m by 0.25 mm by 0.25  $\mu$ m, Hewlett Packard), 0.9 mL min<sup>-1</sup> He flow rate, 80°C initial oven temperature (2 min) ramping at 5°C min<sup>-1</sup> to 200°C, 70 eV in EI mode, and 14 to 200 m/z scanning range.

### Degradation in Soils with Different Amendment Rates

The effect of amendment/soil ratios on the degree of acceleration of 1,3-D degradation was determined in soil amended with CM at decreasing ratios: 1:2, 1:4, 1:8, 1:20, and 1:40 (w/w). The 1:20 and 1:40 ratios were included because they represent feasible field application rates. To evaluate the relative contribution of biological and chemical degradation, 1,3-D degradation was also determined in matrices of the same mixing ratios that were autoclaved prior to incubation. Similar sample preparation and incubation procedures as described above were followed. The combined dry mass of amendment and soil was 13.0 g in each sample vial and the water content in the matrix was 18%. Disappearance of parent 1,3-D isomers was followed by extracting samples with ethyl acetate and analyzing an aliquot for the remaining concentration at various time intervals.

To correlate 1,3-D degradation with amendment-induced changes of soil microbial activity, CO<sub>2</sub> evolution were measured for each mixing ratio. Fifty grams (dry wt.) of nonsterilized soil or soil-amendment mix was placed in a 125-mL Erlenmeyer flask, and the closed flask was incubated at 25°C

for 6 d. The total CO<sub>2</sub> production from the matrix inside the flask was trapped in 4 mL 0.5 M NaOH solution in a glass vial in the flask. The amount of CO<sub>2</sub> was estimated from the change of NaOH concentration as determined by titration with diluted HCl standard solution at the end of incubation. The results of these measurements are given in Table 1.

### Application of Surface Amendment for Emissions Reduction

A column experiment was conducted to test the effect of surface incorporation of CM on 1,3-D emission losses from the Arlington sandy loam. The same column system has been used previously for measuring MeBr volatilization and has been shown to be a reliable method for estimating fumigant emissions (Gan et al., 1996b, 1997). In brief, four large soil columns were prepared by uniformly packing the soil into closed-bottom glass columns (60 cm high by 12.5 cm [i.d.]) to a bulk density of 1.5 g cm<sup>-3</sup> with 20% volumetric water content. Two columns were not amended with any CM, while the top 5-cm soil layer of the other two columns was replaced with 1:20 CM-soil mix. A sampling chamber (4 cm high by 12.5 cm [i.d.], top-sealed) with an outlet and inlet was then sealed onto the soil column. A constant airflow of 150 mL min<sup>-1</sup> was established using a vacuum source to sweep 1,3-D volatilizing off the soil surface into activated C sampling tubes (ORBO-32, Supelco) installed at the outlet. To apply 1,3-D, 100 µL of Telone II (120 mg 1,3-D) was injected into the center of the columns at 30 cm below the soil surface, through a septum-sealed sampling port located at that position on the column wall. The time that Telone II was applied was considered as time zero. The sample tubes were replaced every 6 h, and 1,3-D recovered in these tubes was analyzed on GC after the charcoal granules were extracted with 3 mL ethyl acetate in closed headspace vials. Similar GC conditions as given above were used for analyzing C tube samples. Volatilization fluxes of 1,3-D in µg h<sup>-1</sup> were obtained by dividing the amount of 1,3-D recovered in the sample tubes over the sampling interval. Cumulative volatilization losses, in percentage of applied chemical, were estimated by integrating volatilization fluxes over the total sampling period.

**Table 2. First-order rate constants  $k$  (d<sup>-1</sup>) of 1,3-d degradation in soil and manure-amended soil and relative contribution of biodegradation to amendment-induced degradation (number of observations = 12-18).**

Matrix	Nonsterilized $k \pm SE$ ( $r^2$ )	Sterilized $k \pm SE$ ( $r^2$ )	Biodegradation, % †
<b>(Z) 1,3-D</b>			
Soil, unamended	0.15 ± 0.01 (0.96)	0.13 ± 0.00 (0.99)	-
BM‡-soil, 1:2	0.37 ± 0.02 (0.97)	0.48 ± 0.00 (1.00)	0
CM‡-soil, 1:2	0.98 ± 0.04 (0.96)	0.38 ± 0.01 (1.00)	71
CM-soil, 1:4	0.84 ± 0.01 (1.00)	0.36 ± 0.01 (1.00)	68
CM-soil, 1:8	0.83 ± 0.03 (0.99)	0.39 ± 0.02 (0.98)	63
CM-soil, 1:20	0.62 ± 0.03 (0.97)	0.24 ± 0.01 (0.99)	78
CM-soil, 1:40	0.47 ± 0.03 (0.93)	0.19 ± 0.01 (0.99)	82
<b>(E) 1,3-D</b>			
Soil, unamended	0.19 ± 0.01 (0.97)	0.15 ± 0.00 (1.00)	-
BM-soil, 1:2	0.33 ± 0.02 (0.95)	0.38 ± 0.00 (1.00)	0
CM-soil, 1:2	1.16 ± 0.04 (0.96)	0.51 ± 0.02 (0.99)	64
CM-soil, 1:4	1.42 ± 0.05 (0.99)	0.50 ± 0.01 (1.00)	72
CM-soil, 1:8	1.88 ± 0.12 (0.95)	0.50 ± 0.01 (1.00)	80
CM-soil, 1:20	1.13 ± 0.06 (0.96)	0.34 ± 0.02 (0.98)	81
CM-soil, 1:40	0.64 ± 0.03 (0.97)	0.27 ± 0.01 (1.00)	76

† The contribution of biodegradation to the total degradation induced by the addition of manure, calculated as difference of  $k$  between nonsterilized and sterilized treatments divided by difference of  $k$  between the measured (nonsterilized) and the soil contribution.

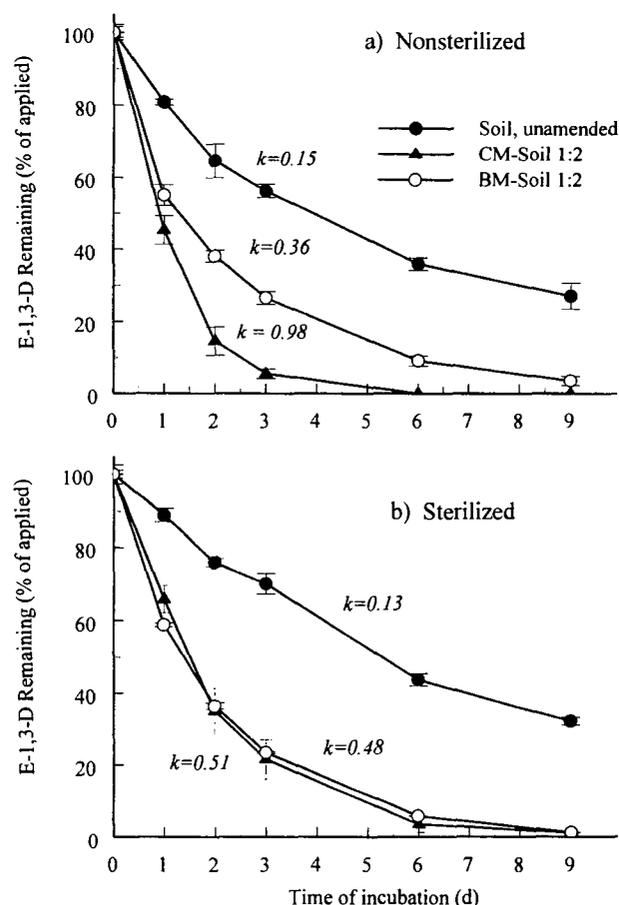
‡ CM = compost manure; BM = biosolid-manure mix.

## RESULTS AND DISCUSSION

### Mechanism of Enhanced 1,3-D Degradation in Amended Soil

Degradation of both (*Z*) and (*E*) 1,3-D isomers in nonsterilized, unamended soil exhibited a first-order kinetics, with the constant  $k$  of 0.13 to 0.19 d<sup>-1</sup>, or half-life ( $t_{1/2}$ ) of 3.5 to 5 d (Table 2). At this degradation rate, it can be expected that a significant fraction of the applied 1,3-D will volatilize into the air due to the rapid gas-phase diffusion. Similar rates of degradation in the sterilized and nonsterilized soil (Fig. 1b) further indicated that chemical rather than microbial transformation is the major degradation process in this soil (Table 2).

Degradation of 1,3-D was substantially enhanced by the addition of CM or BM at 1:2 ratio and the enhancement was greater with CM than with BM (Fig. 1 and Table 2). For example, degradation of (*Z*) 1,3-D in nonsterilized, CM-amended soil was six times faster than that in the nonsterilized soil; with a first-order  $t_{1/2}$  of 4.6 d in the unamended soil as compared to 0.7 d in the CM-soil mix (Fig. 1a). Sterilization of the matrix resulted in significantly ( $P < 0.01$ ) reduced degradation in the CM-soil mix, but had no effect in the BM-soil mix (Fig. 1, Table 2). Enhanced degradation of 1,3-D in



**Fig. 1. Degradation of (*Z*) 1,3-dichloropropene in unamended and organic matter amended Arlington sandy loam at 25°C under (a) nonsterilized and (b) sterilized conditions.**

CM-amended soil was thus attributable to both chemical and microbial degradation whereas in BM-amended soil, the enhanced degradation was chiefly a result of chemical degradation.

When organic wastes are being composted, successional changes in microbial populations and community structures occur (Hoitink and Fahy, 1986). Our results suggest that composting allowed the development in CM of those microbial species that were able to metabolize 1,3-D, while the lack of 1,3-D biodegradation in BM-amended soil may be attributed to a low population of these degraders in the undecomposed biosolid-manure product. Microbial degradation of 1,3-D has been reported for some soils, mainly loamy soils after repeated fumigant applications (Smelt et al., 1989; Ou et al., 1995). In these soils, degradation of 1,3-D became more rapid after a lag phase of 3 d or longer. The adaptation of the soil microflora to 1,3-D was suggested to be due to the selection of a microbial population with 1,3-D degradative capacity (Lebbink et al., 1989). Several bacterial strains capable of degrading 1,3-D have been isolated from adapted soils, including certain *Pseudomonas* spp. (Lebbink et al., 1989; Verhagen et al., 1995).

Chemical reactions contributed 30 to 35% to the enhanced 1,3-D degradation in the CM-soil mix, and were entirely responsible for enhanced degradation in the BM-soil mix (Table 2). Chemical degradation of 1,3-D in soil is mainly attributed to its hydrolysis in H<sub>2</sub>O (Castro and Belser, 1966; Roberts and Stoydin, 1976; McCall, 1987). The fact that degradation of 1,3-D in sterilized CM- or BM-soil mixes was many times faster than that in sterilized, unamended soil implies that pathways other than the H<sub>2</sub>O-catalyzed hydrolysis might be involved. From its structure, 1,3-D should readily undergo bimolecular (S<sub>N</sub>2) nucleophilic substitution (Schwarzenbach et al., 1993), in which 3-chloroallyl alcohol is formed where water serves as the nucleophile. Nucleophiles such as inorganic SH<sup>-</sup> and OH<sup>-</sup> and functional groups such as -NH<sub>2</sub>, -NH, -SH, and -OH on organic matter (e.g., proteins, amino acids, or phenolic compounds) may contribute to the S<sub>N</sub>2 type of reaction when they are present at sufficiently high concentrations (Schwarzenbach et al., 1993; Oremland et al., 1994; Gan and Yates, 1996). At a 1:2 amendment/soil ratio, the increase in total C or N was about eight times in the CM-soil mix, and five times in the BM-soil mix (Table 1). Since addition of organic amendment into soil increased the concentration of some of these nucleophiles, enhanced 1,3-D degradation could thus also occur via the S<sub>N</sub>2 pathway.

The possible involvement of S<sub>N</sub>2 mechanism was illustrated from the rapid disappearance of 1,3-D isomers in 5 mM aniline solution that was five times faster than that in water (Fig. 2). As aniline was present in abundance to 1,3-D, the second-order reaction followed a pseudo first-order ( $r^2 = 1.00$ ). Compared to MeBr degradation under the same conditions ( $k = 0.24 \text{ d}^{-1}$ ) (Gan and Yates, 1996), disappearance of 1,3-D isomers ( $k = 0.55\text{--}0.59 \text{ d}^{-1}$ ) was about 2.3 times as fast. GC/MS analysis of the ethyl acetate extract showed two peaks after

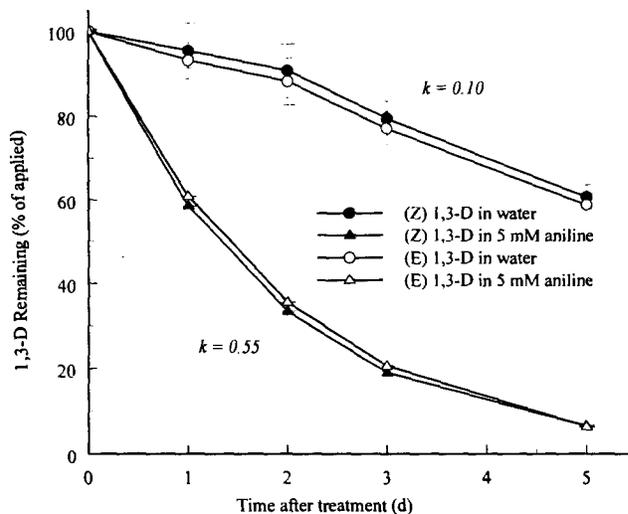


Fig. 2. Disappearance of 1,3-dichloropropene isomers from deionized water and 5 mM aniline solution at 25°C.

aniline: peak 1 had a retention time of 25.7 min on the RTX-624 column and 16.4 min on the HP-5MS column, and peak 2 had respective retention times of 26.6 and 17.0 min. Both peaks on either column gave identical spectra, indicating that they were likely isomers to each other. From the spectrum, it was tentatively determined that the reaction products were isomers of 3-chloroallyl aniline (MW = 167), the product of S<sub>N</sub>2 substitution at the N position of aniline by chloride on C3 of the 1,3-dichloropropene molecule.

### Effect of Amendment Rates on the Degree of Acceleration

The potential use of soil organic matter amendments for reducing 1,3-D emissions on a management scale must consider amendment rates that are practical for field applications. To determine the dependence of enhanced degradation on amendment rates, 1,3-D degradation was measured in soils amended with different proportions of CM. Degradation of both 1,3-D isomers in nonsterilized amendment-soil mixes was essentially unaffected when the mixing ratio was reduced from 1:2 to 1:8. It then decreased, but not proportionally, as the ratio further decreased from 1:8 to 1:40 (Table 2). The nonproportional response of degradation to the mixing ratio was reflected in that, at 1:40, the degradation of the (E) or (Z) isomer was still about three times as fast as that in the unamended soil (Table 2). The rapid degradation of 1,3-D at such a low amendment/soil ratio implies that significantly enhanced degradation can be achieved with typical field application rates of amendments (10–50 t ha<sup>-1</sup>).

Disappearance of 1,3-D at various mixing ratios generally followed first-order kinetics, with better fits in the 1:2 to 1:8 range than at the lower ratios, and in the sterilized mixes as compared to the nonsterilized mixes (Table 2). When the disappearance of 1,3-D in the nonsterilized mixes was depicted on a logarithmic scale, it becomes apparent that two phases began to develop as the mixing ratio was decreased from 1:8 to 1:40; and

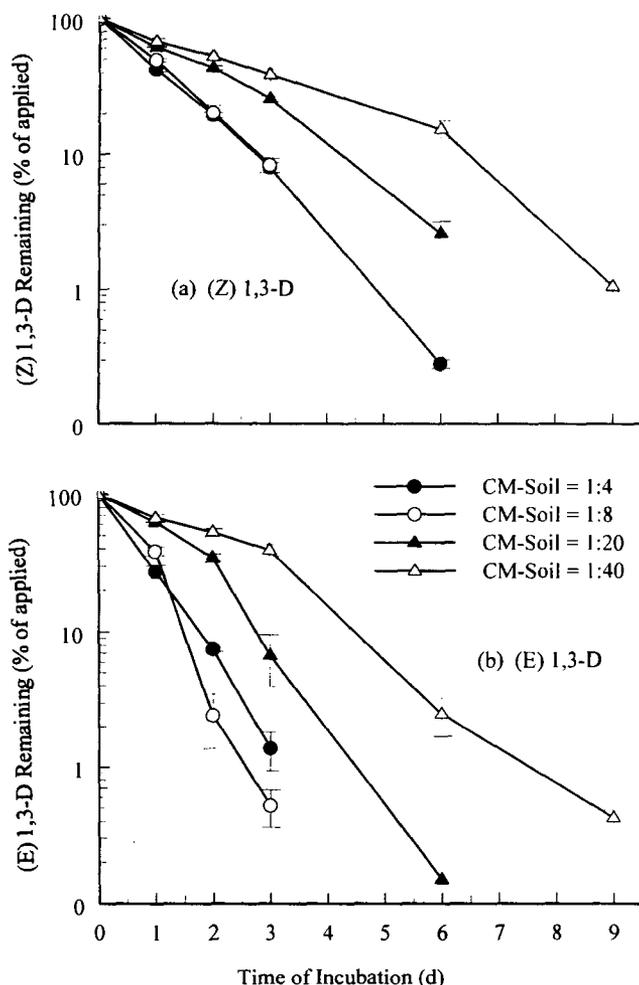


Fig. 3. Degradation of 1,3-dichloropropene isomers in compost manure-amended Arlington sandy loam at various amendment rates. (a) (Z) 1,3-dichloropropene; and (b) (E) 1,3-dichloropropene.

the degradation during the second phase was consistently more rapid than during the first phase (Fig. 3). The beginning of the second phase was prolonged as the ratio decreased, and the biphasic phenomenon was more evident for (E) 1,3-D than that for (Z) 1,3-D (Fig. 3). It is likely that at high CM rates, stimulated biodegradation occurred immediately after the treatment, and the first phase was too short to be visible. Microbial activity measured as  $\text{CO}_2$  evolution showed a similar response to the mixing ratio as did the 1,3-D degradation (Table 1). For instance, the total amount of  $\text{CO}_2$  evolved from 50 g of the 1:40 mix during the 6-d incubation was 5.8 mg, which was almost 70% of that from the 1:2 mix, or 12 times greater than that from the unamended soil.

The contribution of biodegradation to the overall 1,3-D degradation as induced by amendment addition was calculated for various mixing ratios from the difference of degradation rate constant  $k$  ( $\text{d}^{-1}$ ) between the sterilized and nonsterilized treatments (Table 2). For (Z) 1,3-D, biodegradation contributed about 60 to 70% of the induced degradation for mixing ratios ranging from 1:2 to 1:8, but this figure increased to about 80%

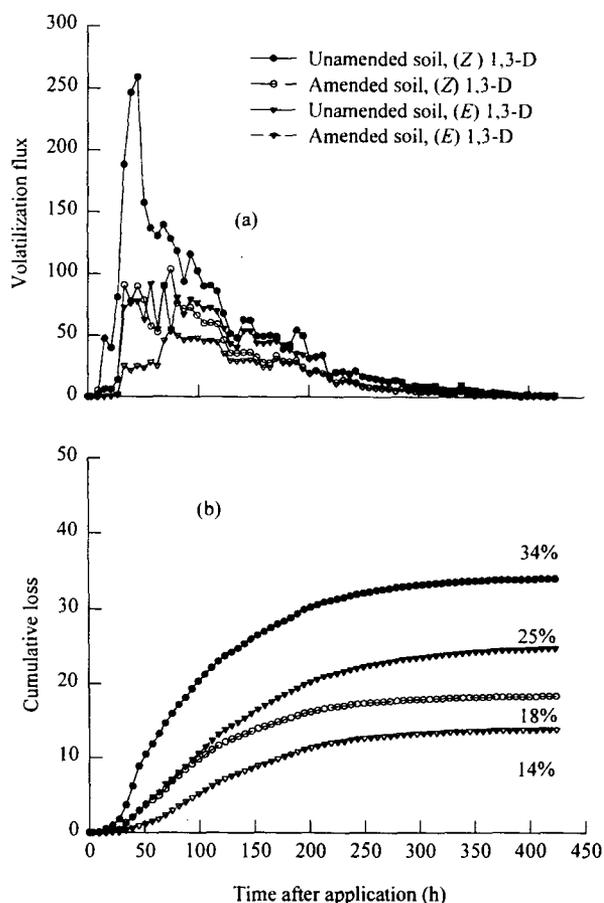


Fig. 4. Volatilization of 1,3-dichloropropene isomers from columns packed with the Arlington sandy loam with and without the amendment of a compost manure at 5% (w/w) after Telone-II was injected at the 30 cm depth. (a) Volatilization fluxes in  $\mu\text{g h}^{-1}$ ; and (b) Cumulative volatilization losses in percent of applied 1,3-D.

when the mixing ratio was decreased to 1:20 or 1:40 (Table 2). Similar trends were also found among the different mixes for (E) 1,3-D (Table 2). Therefore, it can be concluded that while chemical degradation was significant (30–40% of the enhanced degradation) for soils amended with CM at high rates, its role gradually decreased and microbial degradation gained more dominance as the amendment/soil ratio was further reduced.

### Reduction of 1,3-D Emissions by Surface Amendment

Volatilization losses of 1,3-D from unamended and CM-amended soil columns were determined for 432 h (or 18 d) after Telone-II was injected at the 30-cm depth. The averaged volatilization fluxes in  $\mu\text{g h}^{-1}$  and the cumulative losses in percentage of applied fumigant are given for both isomers in Fig. 4. The volatilization fluxes of (Z) or (E) 1,3-D during the first 200 h were much greater from the unamended columns than columns containing 1:20 CM-amended soil in the top 5 cm, though the difference gradually diminished thereafter (Fig. 4a). For instance, the maximum flux for (Z) 1,3-D from the unamended treatment was >2.5 times that from the amended treatment. Cumulatively, about 34% of the

applied (*Z*) and 25% of the (*E*) 1,3-D were lost from the unamended columns at the end of the experiment. In comparison, the total loss of (*Z*)- and (*E*) 1,3-D from the CM-amended columns was only 18 and 14% of the applied amount, a reduction of >40% of that from the unamended soil (Fig. 4b).

As column packing, fumigant treatment, sampling and sample analysis were kept under the same conditions for all four columns, the difference in 1,3-D emissions between the two treatments can be mainly attributed to the incorporation of 5% CM into the top 5-cm soil layer. The results from this experiment are therefore indicative of the potential usefulness of surface amendment as a management practice for minimizing 1,3-D emissions. More studies, such as emission monitoring and efficacy tests under field conditions, however, should be conducted to validate these laboratory observations. Longevity of soil organic matter amendments for causing enhanced degradation, and interactions of amendments and fumigant leaching should be also investigated.

## CONCLUSIONS

This research demonstrates that integrating organic amendments with 1,3-D fumigation may significantly reduce 1,3-D atmospheric emissions by causing enhanced fumigant degradation. Rapid degradation occurred at amendment rates low enough to allow realistic applications under field conditions, where the amended surface layer may act as a "filter" to reduce the emission and the fumigant concentration in the soil below the surface is not lowered to compromise the efficacy. This approach could be especially beneficial for sandy-textured soils, where gas-phase diffusion is very rapid and degradation is relatively slow. As the negative environmental and toxicological effects of chemical fumigants are being realized, but applicable nonchemical methods are yet to be developed, environment-benign and yet effective strategies that integrate multiple approaches are urgently needed for soilborne pest control. The findings from this study indicate a promising integration of 1,3-D fumigation and organic amendment application that warrant further research on larger scales and under different conditions.

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