

## Isomeric Effects on Volatilization of 1,3-Dichloropropene Fumigant in Soil

Jung-Ho Kim and Megharaj Mallavarapu\*

Department of safety & Environmental Prevention, Daegu Haany University, Gyeongbuk 712-715, Korea  
\*Centre for Environmental Risk Assessment and Remediation, University of South Australia, SA 5095, Australia  
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### Abstract

The fumigant 1,3-dichloropropene (1,3-D) was recently proposed as a direct replacement for methyl bromide ( $\text{CH}_3\text{Br}$ ) in soil fumigation. This study was conducted to better understand behavior phase partitioning, diffusion and volatilization of 1,3-D as affected by isomer. The Henry's law constant ( $K_H$ ) of *cis*-1,3-D and *trans*-1,3-D was 0.058 and 0.037 at 20°C, respectively.  $K_H$  of *cis* form of 1,3-D was higher than that of *trans* form of 1,3-D. To compare with volatilization of 1,3-D isomer, soil column [70 cm (length) × 12 cm (i.d.)] included a shank injection at 30 cm with 300 kg ha<sup>-1</sup>. Maximum *cis*-1,3-D and *trans*-1,3-D concentration reached 57 mg L<sup>-1</sup> and 39 mg L<sup>-1</sup> at 30 cm depth at 1h after application. Cumulatively, after 10 days, 51.8% and 43.57% of applied *cis*-1,3-D and *trans*-1,3-D was emitted via volatilization, respectively. The total losses of *cis*-1,3-D were significantly greater than that of *trans*-1,3-D. Finally, *cis*-1,3-D and *trans*-1,3-D, such as isomer are dominant of 1,3-D fates in soil.

**Key Words :** Fumigant, Ozone-depleting chemicals, Isomer, 1,3-dichloropropene, Phase partitioning, Diffusion, Volatilization

### 1. Introduction

Soil fumigants are heavily used in the production of many food crops to control soilborne pathogens. Fumigants are intrinsically volatile, and the volatility is essential for achieving effective pest control. However the high volatility of fumigants has often been associated with the pollution of ambient air<sup>1-3</sup>.

Atmospheric emission of MeBr has been linked to the depletion of stratospheric ozone. By an international agreement to phase out ozone-depleting chemicals, MeBr was eliminated in 2005 in the USA<sup>4</sup>. With the ban of MeBr, only several alternative fumigants such as 1,3-dichloropropenes(1,3-D), MITC and chloropicrin(CP) are available. Overall, 1,3-D is probably the best alternative to MeBr<sup>5</sup>.

Dichloropropenes are synthetic chemicals made of a chain of three carbon atoms with a double bond connecting the first two carbons. Two chlorine atoms are attached at varying positions on this carbon chain generating five different types (or isomers) of dichloropropene molecules. The names of the isomers are 1,1-D, 1,2-D, 1,3-D, 2,3-D, and 3,3-D. 1,3-D dissolves in water and evaporates easily, and is used mainly in farming as a pesticide. Because 1,3-D is used in much higher amounts than the other isomers and released to the environment as a fumigant, most of the data available are for 1,3-D. Therefore, the focus of this research is the 1,3-D isomer<sup>6</sup>.

To meet the urgent demand of locating an alternative soil fumigant, there is a need to investigate different management methods that may be used to apply 1,3-D which would reduce its emission loss. In an effort to reduce the environmental effects of fumigation, especially the atmospheric emission of fumigants, various improvements to the existing application methods

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Corresponding Author : Jung-Ho Kim, Department of safety & Environmental Prevention, Daegu Haany University, Gyeongbuk 712-715, Korea  
Phone: +82-53-819-1416  
E-mail: kim@dhu.ac.kr

have been proposed<sup>7,8</sup>). The movement of a fumigant in the soil is mainly a result of diffusion in the vapor phase. During this diffusion process there is a tendency to establish a concentration equilibrium in the vapor, water and soil<sup>9</sup>). Characterization of the air-water partition coefficient ( $K_H$  Henry's law constant) of 1,3-D is essential for understanding the migratory behavior of 1,3-D in the air, water and soil compartments of the environment. The  $K_H$  is one of the most important physical properties in determining the volatilization of 1,3-D between the air and water phases<sup>10,11</sup>). The information that is available concerning the isomeric effects of 1,3-D for the air and water phases on soil is useful for interpreting volatilization, as well as for providing the rationale for developing optimized application methods<sup>12-14</sup>).

The objectives of this study were to investigate whether the  $K_H$  of 1,3-D is affected by isomer. The specific purpose was also to research the isomeric effect of 1,3-D on volatilization. This knowledge will be used to design application protocols that will achieve more consistent and uniform pest control while minimizing intrinsic emissions.

## 2. Materials and Methods

### 2.1. Chemicals

The 1,3-D standard containing 48% *cis* isomer and 49% *trans* isomer was purchased from Chem Service (West Chester, PA). Telone II (0.61 g mL<sup>-1</sup> *cis*-1,3-D and 0.58 g mL<sup>-1</sup> *trans*-1,3-D) that is a 1,3-D formulation used for conventional shank injection was provided by Dow AgroSciences (Zionsville, IN).

### 2.2. Gas-liquid Phase Partition Coefficient

An air-water partition experiment was conducted to determine the distribution of 1,3-D between air and water at 20°C. Aqueous solutions, containing approximately 200, 400, 600, 800, 1,200 and 1,400 mg L<sup>-1</sup> of 1,3-D, were prepared in deionized water. Ten milliliters of each stock solution was transferred into a 21.6-mL headspace vial (triplicate samples), sealed with Teflon-faced butyl rubber septa and then vortexed for 2 min. The vials were kept in the dark at 20°C, and allowed to equilibrate for 16 h. A preliminary

study showed that a 16 h period was adequate for achieving equilibrium. To determine the concentration of 1,3-D in the air phase ( $C_a$ ), a 1 mL sample of the headspace was withdrawn with a gas-tight syringe and transferred into a GC vial containing 1 mL of hexane at 20°C. The GC vials were then vortexed for 2 min. To determine the concentration of 1,3-D in the water phase ( $C_w$ ), 0.5 mL of aqueous phase was withdrawn with a gas-tight syringe and transferred into a 10-mL headspace vial containing 5 mL of hexane at 20°C. The headspace vials were vortexed for 2 min, and a portion of the hexane phase was then transferred into a 2-mL gas chromatography (GC) vial.

Analysis of 1,3-D in the GC vial was conducted using a HP 6890 gas chromatograph equipped with an electron capture detector. The conditions were set as follows: capillary column, 30 m × 0.25 mm × 1.4 μm RTX-624 (Restek Co., Bellefonte, PA); carrier gas, N<sub>2</sub>, 1.5 mL min<sup>-1</sup> oven temperature, isothermal at 110°C; inlet temperature, 230°C; and detector temperature, 280°C. Under these conditions, the retention time of *cis*-1,3-D and *trans*-1,3-D were 5.60 and 6.31 min, respectively.

### 2.3. Diffusion and Volatilization

Volatilization of 1,3-D was simultaneously determined from columns packed with the Arlington sandy loam soil passed through a 2-mm sieve at room temperature. The Ar soil had a pH of 7.2, organic carbon of 0.92%, sand of 74.6%, silt of 18.0% and clay of 7.4%<sup>15</sup>). The columns were made of stainless steel and had a dimension of 70 cm (length) × 12 cm (i.d.). Columns were packed with fresh soil at a bulk density of 1.55 g cm<sup>-3</sup> and a moisture content of 4.75% (w/w). A sampling chamber of 4 cm (length) × 12 cm (i.d.) was sealed onto the top of the soil column.

The 284.8 μL of Telone II is injected at 30 cm below the surface by gastight syringe. The application rate of 1,3-D was equivalent to 300 kg ha<sup>-1</sup> with *cis*-1,3-D of 153.8 kg ha<sup>-1</sup> and *trans*-1,3-D of 146.2 kg ha<sup>-1</sup>. A constant air flow of 100 mL min<sup>-1</sup> was established by connecting the outlet to a stable vacuum source into a HP 5890 GC.

A computerized relay system was used to automate

the introduction of a 1,3-D from the headspace from each column into the GC at an 11-min interval during 10 days. The GC conditions used for on-line monitoring were as follows: 100  $\mu\text{L}$  gas sampling valve, 60  $\text{m} \times 0.53 \text{ mm} \times 3.0 \mu\text{m}$  AT624 capillary column (Ailtech, Deerfield, IL), 20  $\text{mL min}^{-1}$  column flow ( $\text{N}_2$ ), 100°C isothermal oven temperature, and 280°C detector temperature. Volatilization fluxes were calculated as  $\text{mg min}^{-1} \text{ m}^{-2}$  and cumulative volatilization losses as percentage of applied 1,3-D.

The diffusion of 1,3-D in the soil columns was determined by withdrawing from the soil air at different depths using a gastight syringe at 1, 2, 4 and 8 h after application. Then a 1.0 mL soil air was transferred by gas tight syringe into 8.7 mL headspace vial and analyzed with GC-ECD equipped with automated headspace sampler (Tekmar Co., Cincinnati, OH). The conditions of headspace sampler were set as follows: equilibration temperature at 90°C valve temperature at 90°C line temperature at 90°C equilibration time at 2 min sample loop of 1.0 mL vial pressurization pressure at 0.25 psi press equilibrium of 0.1 min. The conditions of GC-ECD were set as follows: capillary column, 30  $\text{m} \times 0.25 \text{ mm} \times 1.4 \mu\text{m}$  RTX-624 (Restek Co., Bellefonte, PA); carrier gas,  $\text{N}_2$ , 0.71  $\text{mL min}^{-1}$  oven temperature, isothermal at 120°C; inlet temperature, 230°C; and detector temperature, 280°C<sup>14</sup>.

### 3. Results and Discussion

#### 3.1. Gas-Liquid Phase Partition

The air-water partition coefficient ( $K_H$  Henry's law constant) is extremely important in determining how easily 1,3-D moves in soil and enters the atmosphere through volatilization<sup>16</sup>. The direct measurement of equilibrium concentrations of 1,3-D in the air ( $C_a$ ) and liquid ( $C_w$ ) phases was used to measure  $K_H$ . The dimensionless  $K_H$  is then obtained using  $K_H = C_a / C_w$ <sup>17</sup>. To determine whether 1,3-D follows Henry's law, the linearity of  $K_H$  was determined over the aqueous concentration range of 100  $\text{mg L}^{-1}$  to 500  $\text{mg L}^{-1}$  (Fig. 1). From the slope of these lines, the  $K_H$  values of *cis*-1,3-D and *trans*-1,3-D were 0.058 and 0.037, respectively.

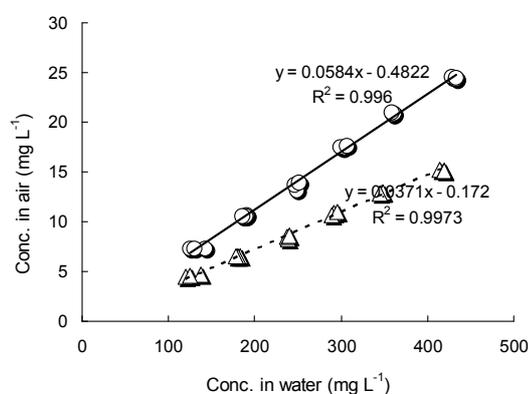


Fig. 1. Air-water partition of *cis*- (○) and *trans*- (△) 1,3-dichloropropene at 20°C.

At a relatively higher  $K_H$  it can be expected that the movement of 1,3-D will be dominated by gas-phase diffusion in the air and, as a result, will move greater distances in the soil profile by diffusion from the vapor phase. The  $K_H$  value of 0.058 for *cis*-1,3-D is substantially higher than that of 0.037 for *trans*-1,3-D, which correlates well with the higher vapor pressures of 3500 Pa for *cis*-1,3-D than that of 2300 Pa for *trans*-1,3-D at 20°C<sup>16</sup>. As a result of the higher  $K_H$  and vapor pressure of *cis*-1,3-D than *trans*-1,3-D, it can be expected that vapor phase diffusion of *cis*-1,3-D will be higher than that of *trans*-1,3-D. Our high  $K_H$  of *cis*-1,3-D may be attributed to the rapid and high volatilization in the field.

#### 3.2. Diffusion in Soil Column

The potential contribution of the fumigant to air pollution via volatilization may be illustrated using soil column<sup>18,19</sup>. We used packed soil columns to compare the diffusion between *cis*-1,3-D and *trans*-1,3-D. The *cis*-1,3-D and *trans*-1,3-D diffusion as different isomer are shown in Fig. 2. The 1,3-D gas distributions decreased uniformly with distance from the source when the 1,3-D was applied with direct shank injection. At 1 h after application, the highest *cis*-1,3-D vapor concentration was compared with a *trans*-1,3-D concentration peak. Maximum *cis*-1,3-D and *trans*-1,3-D concentration reached 57  $\text{mg L}^{-1}$  and 39  $\text{mg L}^{-1}$  at 30 cm depth of injection.

Diffusion of *cis*-1,3-D was rapid after shank in-

jection than *trans*-1,3-D. This indicated that *cis*-1,3-D was present in higher proportions in soil profiles. The distribution of the *cis*-1,3-D and *trans*- 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.

### 3.3. Volatilization in Soil Column

Emission of flux for *cis*-1,3-D and *trans*-1,3-D as different isomer as determined by column study is shown in Fig. 3. Volatilization fluxes of 1,3-D were determined for 10 d (240 h) from soil columns that 1,3-D was injected at the 30 cm depth. The *cis*-1,3-D in the vapor phase reached peak concentrations at 13.9

h after injection compared with a peak at 19.0 h for the *trans*-1,3-D. The maximum flux was  $2.82 \text{ mg m}^{-2} \text{ min}^{-1}$  for the *cis*-1,3-D and  $1.86 \text{ mg m}^{-2} \text{ min}^{-1}$  for the *trans*-1,3-D. The flux of *cis* and *trans*-1,3-D isomers were  $2.73 \text{ mg m}^{-2} \text{ min}^{-1}$  and  $1.33 \text{ mg m}^{-2} \text{ min}^{-1}$  at 12 h after injection, respectively. The flux for the *cis*-1,3-D and the *trans*-1,3-D were  $1.85 \text{ mg m}^{-2} \text{ min}^{-1}$  and  $1.61 \text{ mg m}^{-2} \text{ min}^{-1}$  for on 24 h after injection, respectively (Table 1).

The volatilization losses of applied 1,3-D are given for both isomers in Fig. 4. In comparison, 29.2, 40.4, 46.7, 49.9 and 51.8% of *cis*-1,3-D was emitted via volatilization after 2, 4, 6, 8, and 10 d, respectively. At same time, the volatilization loss for *trans*-1,3-D were

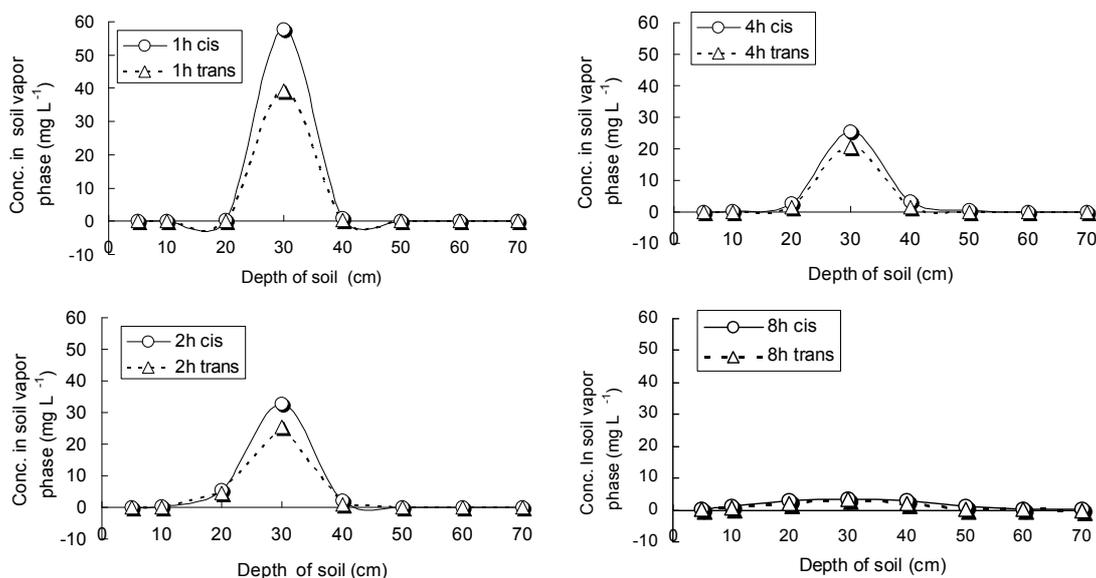


Fig. 2. Diffusion of *cis*- (○) and *trans*- (△) 1,3-dichloropropene in soil column applied with 30 cm depth.

Table 1. Emission flux and cumulative volatilization of *cis*-1,3-D and *trans*-1,3-dichloropropene in soil column applied with 30 cm

Time(day)	Emission flux ( $\text{mg min}^{-1} \text{ m}^{-2}$ )		Cumulative volatilization (% of applied)	
	<i>cis</i> -1,3-D	<i>trans</i> -1,3-D	<i>cis</i> -1,3-D	<i>trans</i> -1,3-D
0.5	2.733	1.335	5.89	2.15
1	1.857	1.610	17.52	10.53
2	0.789	0.785	29.21	21.82
4	0.433	0.393	40.42	32.67
6	0.214	0.208	46.74	38.52
8	0.119	0.117	49.98	41.66
10	0.063	0.066	51.82	43.54

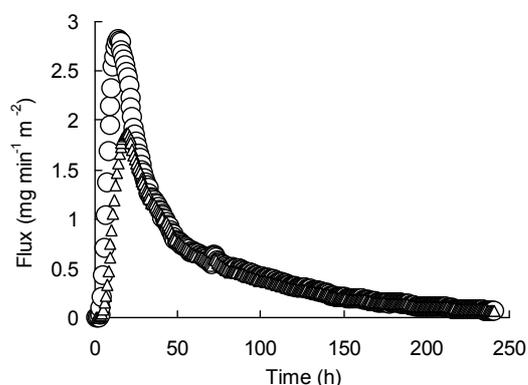


Fig. 3. Emission flux of *cis*- (○) and *trans*- (△) 1,3-dichloropropene in soil column applied with 30 cm depth.

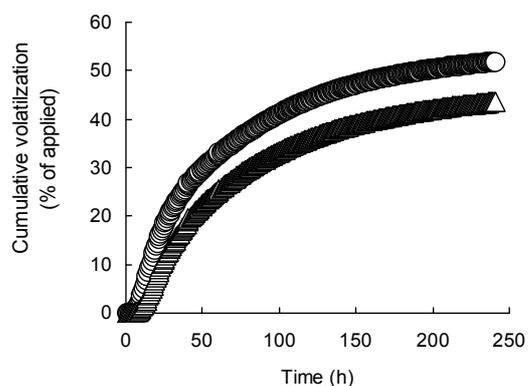


Fig. 4. Cumulative volatilization losses of *cis*- (○) and *trans*- (△) 1,3-dichloropropene in soil column applied with 30 cm depth.

the 21.8, 32.6, 38.5, 41.6 and 43.5% after 2, 4, 6, 8, and 10 d, respectively (Table 1). The total losses of *cis*-1,3-D was significantly greater than that of *trans*-1,3-D.

After shank injection, a fumigant rapidly vaporizes and the vapor diffuses through unfilled air pores in soil. This process allows the fumigant to quickly emit throughout the soil. Therefore, 1,3-D emission is likely to be determined by its type of isomers. The rapid emission may be attributed to the rapid diffusion with *cis*-1,3-D than *trans*-1,3-D. This result showed that *cis*-1,3-D in ambient air was higher than *trans*-1,3-D, owing to differences within its isomers. The differ-

ences may be explained by their different physical-chemical properties of 1,3-D isomer. In comparison to *trans*-1,3-D, the *cis*-1,3-D isomer has a lower boiling point (*cis* vs *trans* : 104.1 vs. 112. 6°C) and solubility (*cis* vs *trans* : 2180 vs. 2320 mg L<sup>-1</sup> at 25°C), but a higher vapor pressure (*cis* vs *trans* : 5700 vs. 4500 Pa at 25°C) and Henry's Law constant (*cis* vs *trans* : 0.058 vs. 0.037 at 20°C in this study)<sup>20</sup>. The different physical-chemical properties of 1,3-D isomer were also evident from the volatilization behaviour 1,3-D which increased with *cis*-1,3-D than *trans*-1,3-D<sup>21</sup>.

#### 4. Conclusion

In order to develop more environmentally sustainable practices, the isomeric effects of 1,3-D fumigant in the soil needs to be better understood.

Factors such as isomer of *cis*-1,3-D and *trans*-1,3-D can affect  $K_H$ , and thus play an important role in fumigant volatilization. Diffusion and volatilization of *cis*-1,3-D was found to be higher than the *trans*-1,3-D in soil columns. Finally, the *cis*-1,3-D and *trans*-1,3-D, such as isomer are dominant of the environmental fate and transport of 1,3-D. Distribution of 1,3-D isomer will affect its mobility in soil and thus its potential for offsite movement to the ambient air is significant.

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