The fumigant 1,3-dichloropropene (1,3-D), in combination with chloropicrin, is considered a major replacement to methyl bromide (MeBr). This study was conducted to better understand phase partitioning of 1,3-D and the role of organic matter in its adsorption to soil. Partition of 1,3-D between air and water ($K_H$), and between soil and water ($K_f$), was determined by quantifying the concentration in both phases upon equilibrium. At 20 °C, the $K_H$ values of (Z)- and (E)-1,3-D were 0.052 and 0.033, respectively. In four California and Florida soils, the $K_f$ values of 1,3-D isomers ranged from 0.39 to 8.55, and the $K_{oc}$ values ranged from 18 to 60. The relatively high $K_H$ and low $K_f$ imply that 1,3-D is highly mobile in most soils after subsurface application. Adsorption of 1,3-D in native soils and soils amended with manure compost increased with increasing soil organic matter content. This suggests that organic wastes may be applied to soil to increase 1,3-D adsorption, thus reducing its potential for offsite movement.

KEYWORDS: Soil fumigation; 1,3-dichloropropene; 1,3-D; adsorption; phase partition; organic amendment

INTRODUCTION

Soil fumigants are heavily used in the production of many food crops to control soil-borne pathogens, nematodes, weeds, and insects. Fumigants are intrinsically volatile, and the volatility is essential for achieving effective pest control. However, the high volatility has often resulted in offsite movement of fumigants and their pollution to air and groundwater. The California Air Resources Board conducted ambient air monitoring of pesticides near application sites in California and found potentially unsafe levels of methyl bromide (MeBr), methyl isothiocyanate (MITC), and 1,3-dichloropropene (1,3-D) (1). Atmospheric emission of MeBr has been linked to the depletion of stratospheric ozone. An international agreement to phase out ozone-depleting chemicals mandates reduction of MeBr supply by 50% in 2001, 70% in 2003, and 100% in 2005 in the United States (2).

With the ban of MeBr, only several alternative fumigants are available: 1,3-D, MITC precursors, and chloropicrin (CP). Overall, 1,3-D, when applied in combination with chloropicrin or MITC precursors, is probably the most important alternative to MeBr. The annual use of 1,3-D from 1987 to 1997 was 13–20 million kg, which ranks fourth to sixth among all pesticides used in the United States (3). During the current transition away from MeBr, it is important to improve the current practices of using 1,3-D so that its potential to impact the environment is minimized. To achieve this objective, a good knowledge of the phase partitioning of 1,3-D in soil is essential.

Distribution of 1,3-D between water and air, and between soil and water, will affect its mobility in soil and thus its potential for offsite movement. Previous studies have shown that adsorption of MeBr in soil is mainly due to organic matter (4), and that organic matter also contributes to 1,3-D adsorption (5). However, most of the previous experiments on fumigant adsorption in soil were carried out using air—soil systems (5–7) instead of a water—soil system. In these studies, the difference in fumigant concentration in the headspace between a soil-less control and a vial containing soil was assumed to be the fraction of fumigant adsorbed to the soil. Because losses due to degradation or volatilization were not differentiated from adsorption in these studies, this indirect approach could be erroneous for estimating adsorption for compounds such as 1,3-D that degrade quickly or volatilize easily in the test system (8).

The main objectives of this study were to determine the air—water and soil—water partition coefficients of fumigant 1,3-D, and to evaluate the response of 1,3-D adsorption to changes in organic matter content caused either by different soil types or by amendment of organic wastes. Concentrations from both the solid and aqueous phases were directly measured when obtaining the partition coefficients.
MATERIALS AND METHODS

Chemicals and Soils. The 1,3-D standard containing 48% Z isomer and 49% E isomer was purchased from Chem Service (West Chester, PA). Telone EC, an emulsifiable formulation of 1,3-D (40% Z and 49% E isomer), was provided by Dow AgroSciences (Indianapolis, IN). Stock solutions were prepared directly in water using Telone EC to avoid the inclusion of solvents in the test systems. Telone EC is being developed for application via drip systems, or chemigation (9).

Four soils were used in this study: Arlington sandy loam, Chualar clay loam, Mocho silty clay loam, and Pahokee muck. The Arlington sandy loam (Coarse-loamy, Mixed, Thermic, Haplic Durixeralf) was taken from the top 30 cm of a field at the University of California, Riverside, Agriculture Experimental Station. The Chualar clay loam (Fine-loamy, Mixed, Thermic, Haplic Durixeralf) was taken from an agricultural field near Salinas, CA. The Mocho silty clay loam (Fine-loamy, Mixed, Thermic, Fluventic Haploxerolls) was sampled from an agricultural field near King City, CA. The Pahokee muck (Eutic, Hyperthermic Lithic Medisaprists, Muck) was provided by the Everglades Research and Education Center in Bellegla, FL. A compost made of steer manure and biosolids was purchased from a local Home Depot store. The soils and manure were passed through a 2-mm sieve prior to their use. To study the effect of organic matter addition on 1,3-D adsorption, Arlington sandy loam was amended with the manure compost at 10, 20, 60, and 100% (w/w; dry weight). The organic matter content of the amended soils was 3.8, 6.1, 15.1, and 24.2%, respectively. The Arlington sandy loam was also oxidized with 30% H2O2 (90 °C; three times) to remove native organic matter, and the oxidized soil was used for adsorption measurement (9).

The physiochemical properties of the soils and manure are listed in Table 1. The soil texture was determined by the hydrometer method (10). The organic carbon content (OC) was estimated by subtracting the total inorganic carbon content (TIC) from the total carbon content (TC). The TC in oven-dried soils (115 °C for 18 h) was measured using the dry combustion method (11). The TIC in the oven-dried soils was determined by reacting the soil with HCl and measuring the change of pressure in a closed vessel due to the release of CO2 (11). The organic matter content (OM) was derived from OC using a multiplication factor of 1.724.

Aqueous Transformation Experiment. Prior to the partition experiments, an aqueous transformation experiment was conducted to evaluate the rate of 1,3-D transformation in water. Briefly, aqueous samples containing 1,3-D at 30 mg L−1 was made by adding 10 μL of Telone EC stock solution (30 000 mg L−1 in deionized water) to 10 mL of deionized water in a 21.6-mL headspace vial (Supelco, Bellefonte, PA). The headspace vials were immediately sealed with Teflon-faced butyl rubber septa and aluminum seals and equilibrated at 25 ± 0.2 and 35 ± 0.2 °C. After 0.4, 2, 3, 5, 10, 15, 25, and 48 days, a 0.5-mL aliquot (triplicate samples) was withdrawn from each vial using a gastight syringe and transferred to a 10-mL headspace vial containing 3 mL of ethyl acetate and 3 g of anhydrous sodium sulfate. The sample vials were sealed and shaken for 30 min, and a portion of the ethyl acetate was transferred to a 2-mL gas chromatography (GC) vial for analysis.

Analysis of 1,3-D was conducted using a HP 6890 GC equipped with an electron capture detector (ECD). The conditions were set as follows: capillary column, 30 m × 0.25 mm × 1.4 μm RTX-624 (Restek Co., Bellefonte, PA); carrier gas, N2, 1.5 mL min−1; oven temperature, isothermal at 110°C; inlet temperature, 230 °C; and detector temperature, 280 °C.

Air–Water Partition Experiment. An air–water partition experiment was conducted to determine the distribution of 1,3-D isomers between air and water at 20 and 40 °C. Aqueous solutions containing 200, 400, 600, 800, 1200, and 1400 mg L−1 of 1,3-D were prepared using Telone EC, and 10 mL of each solution was transferred into a headspace vial (triplicate samples), sealed with septa and caps, and then vortexed for 2 min. The vials were kept in the dark and equilibrated at 20 ± 0.2 or 40 ± 0.2 °C for 16 h. To determine the concentration of 1,3-D in air (Ca), a 1.0-mL sample of the headspace was withdrawn using a gastight syringe and transferred to a GC vial containing 1 mL of hexane. To determine the concentration of 1,3-D in water (Cw), 0.5 mL of the aqueous phase was withdrawn with a gastight syringe and transferred to a 10-mL headspace vial containing 5 mL of hexane. The vials were vortexed for 2 min, and a portion of the aqueous phase was then transferred to a GC vial and analyzed using the conditions given above. The measured Ca and water Cw were used to calculate the dimensionless Henry’s law constant KHW using KHW = Ca/Cw.

Soil–Water Partition Experiment. Adsorption of 1,3-D from aqueous solution to soil was determined by batch equilibration at 20 ± 1 °C (12). Aqueous solutions containing 1,3-D at 50, 100, 200, 350, and 600 mg L−1 were prepared by adding Telone EC and 200 mg L−1 of HgCl2 in deionized water. Addition of HgCl2 was done to inhibit the 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 Teflon centrifuge tube, and three replicates were used for each concentration. 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 for achieving equilibrium. The centrifuge tubes were then centrifuged for 5 min at 10 000 rpm and 4 °C. To determine the concentration of 1,3-D in the solution phase (C1), a 0.5-mL aliquot of the supernatant was withdrawn with a gastight syringe and extracted with ethyl acetate using the procedures given above. An aliquot of the ethyl acetate extract was transferred for 1,3-D concentrations on 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 (Cs), 10 mL of ethyl acetate and 10 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 to a GC vial and analyzed by GC using conditions as given before. The measured Cs and Cw were fitted to the Freundlich equation

\[
C_s = K_f C_w^n
\]

where Kf is the Freundlich adsorption coefficient, and n is a constant indicating the nonlinearity of the adsorption isotherm (13).

To evaluate the reversibility of 1,3-D adsorption, a single-step desorption experiment was conducted using soils samples derived from the previous adsorption experiment (14, 15). Only Chualar clay loam and Mocho silty clay loam were used in this experiment. After the supernatant was decanted, 20 mL of deionized water with 200 mg L−1 HgCl2 was added to the centrifuge tubes, and the soil was resuspended and shaken for 16 h. The soil slurry was centrifuged, and the supernatant and soil were analyzed for 1,3-D concentrations using the same procedures as described for the adsorption experiment. The measured Cs and Cw were fitted to the Freundlich equation, and the estimated Kf is denoted as KHW and n is denoted as nHW.

RESULTS AND DISCUSSION

Degradation in Water. Degradation is an important factor to consider for accurately determining KHW and Kf. Figure 1 shows the disappearance of 1,3-D in water at 25 and 35 °C in a closed system. Disappearance of 1,3-D isomers at both temperatures followed the first-order decay model (r2 = 0.99). At 25 °C, the first-order rate constants of (Z)- and (E)-1,3-D were 0.077 and 0.083 d−1, respectively, and at 35 °C the corresponding values were 0.286 and 0.321 d−1, respectively. From the rate constant, the half-life of (Z)-1,3-D was 9.0 and

Table 1. Selected Properties of Soils and Manure Compost

<table>
<thead>
<tr>
<th>soil name</th>
<th>texture</th>
<th>silt (%)</th>
<th>clay (%)</th>
<th>sand (%)</th>
<th>OC (%)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chualar</td>
<td>clay loam</td>
<td>55.4</td>
<td>28</td>
<td>16.6</td>
<td>0.8</td>
<td>8.4</td>
</tr>
<tr>
<td>Arlington</td>
<td>sandy loam</td>
<td>74.6</td>
<td>18</td>
<td>7.4</td>
<td>0.92</td>
<td>7.2</td>
</tr>
<tr>
<td>Mocho</td>
<td>silty clay loam</td>
<td>10.5</td>
<td>43.3</td>
<td>46.1</td>
<td>1.28</td>
<td>7.3</td>
</tr>
<tr>
<td>Pahokee</td>
<td>muck</td>
<td>46</td>
<td>7.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>manure</td>
<td></td>
<td>14.0</td>
<td>8.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.4 d, respectively, at 25 and 35 °C, while that of (E)-1,3-D was 8.3 and 2.2 d, respectively, at 25 and 35 °C. These half-life values agreed with McCall (16), who reported an overall 1,3-D half-life of 51, 11.3, and 3.1 d in water at 10, 20, and 30 °C, respectively. The relatively rapid degradation of 1,3-D in water would cause overestimation of K_H and underestimation of K_0 if the fumigant concentration were measured only from the air phase in the headspace.

**Air—Water Partition.** The air—water partition coefficient K_H is important in determining how easily 1,3-D moves through soil air and its potential for offsite movement. Three methods have been used to measure K_H of pesticides: (i) direct measurement of concentrations in both air and water; (ii) measurement of concentrations only in one phase, and inference of concentrations for the second phase by assuming 100% mass recovery; and (iii) calculation from vapor pressure and solubility (6, 17). In this study, 1,3-D concentrations were directly measured in air and water upon equilibrium. To determine whether partition of 1,3-D obeys Henry’s law, the linearity of K_H was evaluated over an initial aqueous concentration range of 200–1400 mg L^{-1} (Figure 2). It appears that a linear correlation between C_a and C_w was present for the entire concentration range (r^2 = 0.99), which allows the estimation of K_H from the slope of the linear regressions. The K_H values of (Z)- and (E)-1,3-D were 0.052 and 0.033, respectively, at 20 °C, and 0.108 and 0.073, respectively, at 40 °C. These K_H values at 20 °C agreed well with those of Leistra (5) for the same temperature. The K_H values of both 1,3-D isomers increased with increasing temperature. It can be expected that at higher temperatures, the movement of 1,3-D in soil will be dominated by gas-phase diffusion via soil air, and as a result, 1,3-D will move very rapidly. Gan et al. (18) reported that 56% of the 1,3-D injected at the 20-cm depth in a soil column was lost to emission over a 20-d period, with 80% of the emission occurring during the first 4 days.

The K_H of (Z)-1,3-D was greater than that of (E)-1,3-D, which corresponds with the higher vapor pressure for (Z)-1,3-D (3.5 kPa at 20 °C) than for (E)-1,3-D (2.3 kPa at 20 °C) (19). These differences were tested to be statistically different at p = 0.05 using the t-test. 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. Gan et al. (18) observed that the cumulative loss of (Z)-1,3-D (64%) was slightly greater than that of (E)-1,3-D (60%) from soil columns over a 20-d period.

**Soil—Water Partition.** The soil—water partition coefficient has long been established as an important parameter in determining pesticide movement in soil. The coefficient is typically measured using batch equilibrium procedures, and C_D is inferred from the difference between the initial and final solution concentration. However, this approach ignores losses of sorbate due to volatilization and degradation, which could lead to overestimated K_H values (6). This may be especially true for 1,3-D isomers, as our studies showed that 1,3-D had relatively rapid degradation and high volatility in water.

Adsorption isotherms of 1,3-D isomers in Chualar clay loam and Pahokee muck are shown in Figure 3. The n was always close to 1 (Table 2), suggesting that the Freundlich isotherms could be also approximated by linear isotherms. This implies that 1,3-D concentrations up to an initial aqueous concentration range of 600 mg L^{-1} did not saturate the potential sorption sites of the soils.

The K_f values of (Z)-1,3 were 0.47, 0.55, and 0.60 in the Chualar clay loam, Arlington sandy loam, and Mocho silty clay loam, respectively, and the respective K_f values of (E)-1,3-D...
were 0.39, 0.41, and 0.45 (Table 2). The fact that $K_f$ was $<1$ suggests that 1,3-D was very weakly sorbed to these soils. In the Pahokee muck and manure compost that contained substantially more organic matter, $K_f$ values increased to 8.55 and 6.96, respectively, for (Z)-1,3-D, and to 8.55 and 7.33, respectively, for (E)-1,3-D. Therefore, a distinct effect was observed in the role of organic matter for enhancing 1,3-D adsorption. This observation allowed the expression of adsorption on the basis of soil organic carbon content ($f_{oc}$), using $K_{oc} = K_{f/oc}$. The $K_{oc}$ values for the Arlington sandy loam, Chualar clay loam, Mocho silty clay loam, and Pahokee muck ranging from 18 to 60, generally smaller than the $K_{oc}$ value of 68 reported by McCall et al. (20). The $K_{oc}$ value has been used for predicting the environmental behavior of pesticides. Pesticides with a $K_{oc}$ ranging from 50 to 150 are classified as highly mobile in soil, and 1,3-D falls within this group. Due to its relatively high diffusive mobility and low retention in soil, 1,3-D should move readily through the soil, resulting in excessive emissions and likely movement to groundwater.

### Influence of Organic Matter on Adsorption

Figure 4 shows adsorption of 1,3-D in Arlington sandy loam amended with different levels of a manure compost. When the overall organic matter content was 3.8, 6.1, 15.1, and 24.2%, the $K_f$ values of (Z)-1,3-D were 1.10, 1.41, 3.85, and 6.96, respectively, and those of (E)-1,3-D were 1.05, 1.40, 3.73, and 7.33, respectively. The relationship between $K_f$ of (Z)-1,3-D and soil OM followed

$$K_f = 0.31[OM (%)] - 0.43 \quad (r^2 = 0.98) \quad (2)$$

The relationship between $K_f$ of (E)-1,3-D and soil OM followed

$$K_f = 0.29[OM (%)] - 0.25 \quad (r^2 = 0.99) \quad (3)$$

Therefore, soil organic matter content could potentially be used as an indicator to predict the adsorption capacity for 1,3-D. Arvieu (4) reported that MeBr adsorption in soil was largely due to organic matter that provided sites for ion exchange and van der Waals interactions. Similar mechanisms may also be applicable to 1,3-D adsorption in soil (21).

The dependence of 1,3-D adsorption on organic matter was further demonstrated from the decrease in adsorption after removal of soil organic matter through H$_2$O$_2$ oxidation (Figure 5). The $K_d$ values of (Z)-1,3-D in natural and H$_2$O$_2$-oxidized Ar soils were 0.74 and 0.50, respectively, and the respective values for (E)-1,3-D were 0.70 and 0.47. These differences were tested to be statistically different at $p = 0.05$ using the $t$-test.

As H$_2$O$_2$ oxidation could remove up to 78% of the total soil organic matter (9), it may be concluded that adsorption of 1,3-D isomers was reduced by $\sim 50\%$ due to organic matter removal.

### Desorption

Desorption was selectively measured for the Chualar loam and the Mocho silty clay loam, and the ratio of $K_{d}/K_f$ was calculated (Table 3). The $K_{d}/K_f$ ratio was consistently $>1$, indicating that hysteresis occurred during desorption. This implies that as the time increased, some of the initially adsorbed 1,3-D became irreversibly bound to the soil, probably due to stronger bond interactions. The $K_{d}/K_f$ ratio of 1,3-D was also greater in the Mocho silty clay loam than in the Chualar loam. The Mocho silty clay loam, with 1.28% organic C, was more difficult to desorb 1,3-D than Chualar loam, with 0.80% organic C. These results further suggest the role of soil organic matter in adsorbing 1,3-D.

### Conclusions

The fumigant 1,3-D is a major replacement for MeBr that will be phased out by the year 2005. To develop practices that are more environmentally compatible, the distribution of 1,3-D among the air, water, and soil phases needs to be better understood. The measured $K_{oc}$ and $K_f$ values of 1,3-D isomers in a number of California and Florida soils suggests that 1,3-D is extremely mobile in soil and has a high potential for offsite transport, e.g., emission into the air and movement to groundwater. This study showed that adsorption of 1,3-D increased with increasing soil organic matter content and was enhanced after addition of organic wastes. Therefore, organic amendment may be an option for reducing 1,3-D emissions during soil fumigation.

### ACKNOWLEDGMENT

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Phase Partition of 1,3-Dichloropropene in Soil


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