

환경 화학-P1 Organic Matter Effects on Adsorption of Soil Fumigant 1,3-Dichloropropene in Soil

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1. 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 of air and groundwater. Atmospheric emission of MeBr has been linked to the depletion of stratospheric ozone. An international agreement to phase out ozone-depleting chemicals will reduce MeBr supply by 70% in 2003 before a complete elimination in 2005 in the United States.

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 the amendment of organic wastes. Partition coefficients were determined by simultaneously measuring the concentrations in the different phases at equilibrium.

Table 1. Selected properties of soils and manure compost

Samples	Soil texture	Silt (%)	Clay (%)	Sand (%)	O.C (%)	pH
Salinas	Loam	55.4	28	16.6	0.8	8.4
Arlington	Sandy loam	74.6	18	7.4	0.92	7.2
King city	Silty clay	10.5	43.3	46.1	1.28	7.3
Florida	Muck	-	-	-	46	7.1
Manure	-	-	-	-	14.02	8.8

2. MATERIALS AND METHODS

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* isomer and 40% *E* isomer), was provided by Dow AgroSciences (Indianapolis, IN).

Four soils were used in this study: Arlington (Ar), Salinas (Sa), King City (Ki), and Florida muck (Fl). The Ar soil (Coarse-loamy, Mixed, Thermic, Haplic Durixeralf) was taken from the top 30 cm of a field at the University of California, Riverside, Agricultural Experiment Station. The Sa (Fine-loamy, Mixed Thermic Typic Argixerroll) and Ki (fine loamy, mixed, Thermic Fluventihaploxeroll) soils were taken from agricultural fields near Salinas and King City, CA, respectively. The Fl soil (Euic, Hyperthermic Lithic Medisaprists, Muck) was provided by the Everglades Research and Education Center in Belle Glade, Fl. A compost made of steer manure and biosolids was purchased from a local hardware store. The physicochemical properties of the soils and manure are listed in Table 1. Adsorption of 1,3-D from aqueous solution to soil was determined by batch equilibration.

Table 2. Freundlich adsorption coefficients of 1,3-dichloropropene in soils and a manure compost

Samples	1,3-D isomer	Freundlich coefficients		
		<i>K_f</i>	<i>n</i>	<i>r²</i>
Salinas	(<i>Z</i>)	0.47	0.97	0.99
	(<i>E</i>)	0.39	0.95	0.99
Arlington	(<i>Z</i>)	0.55	0.95	0.99
	(<i>E</i>)	0.41	0.91	0.99
King city	(<i>Z</i>)	0.60	0.95	0.99
	(<i>E</i>)	0.45	0.92	0.99
Florida	(<i>Z</i>)	8.55	1.03	0.99
	(<i>E</i>)	8.55	0.99	0.99
Manure	(<i>Z</i>)	6.96	1.02	0.99
	(<i>E</i>)	7.33	1.02	0.99

3. RESULTS AND DISCUSSION

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_s* 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 can lead to overestimated *K_f* values. This may be especially true for 1,3-D isomers, as our study showed that 1,3-D had relatively rapid degradation and high volatility in water.

Isotherm parameters for all soils are given in Table 2. The *n* was always close to 1 (Table 2), suggesting that the Freundlich isotherms could be also approximated by linear isotherms. This also implies that 1,3-D concentrations up to an initial aqueous concentration of 600 mg L⁻¹ did not saturate the potential sorption sites of

the soils.

The K_f of (*Z*)-1,3 was 0.47, 0.55, and 0.60 in the Sa, Ar and Ki soils, respectively, and that of (*E*)-1,3-D was 0.39, 0.41, and 0.45, respectively (Table 2). The fact that K_f was < 1 suggests that 1,3-D was extremely weakly sorbed in these soils. In the Florida muck and manure compost, which contained substantially more organic matter, K_f 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 based on soil organic carbon content (foc), using $K_{oc} = K_f/foc$. The K_{oc} for the Ar, Sa and Ki soils ranged from 35 to 60, which compares well with the K_{oc} value of 68 reported by McCall et al.. K_{oc} 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, and may result in excessive emissions and movement to groundwater if it is not degraded prior to offsite transport.

Influence of Organic Matter on Adsorption

When the overall organic matter content was 3.8, 6.1, 15.1, and 24.2%, the K_f of (*Z*)-1,3-D were 1.10, 1.41, 3.85 and 6.96, respectively, and that of (*E*)-1,3-D were 1.05, 1.40, 3.73 and 7.33, respectively. The K_f of both (*Z*)- and (*E*)-1,3-D was linearly correlated with soil OM ($r^2 = 0.98$). Therefore, increasing the soil organic matter content through the addition of organic amendments could potentially be used as an option to reduce 1,3-D offsite movement by increasing its adsorption. Arvieu 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.

The dependence of 1,3-D adsorption on organic matter was further demonstrated by the decrease in adsorption after removal of soil organic matter through H_2O_2 oxidation. The K_f of (*Z*)-1,3-D in natural and H_2O_2 oxidized Ar soils were 0.55 and 0.40, respectively, and the respective values for (*E*)-1,3-D were 0.41 and 0.33. These differences were tested to be statistically different at $p = 0.05$ using a t -test. As H_2O_2 oxidation could remove the majority of the native soil organic matter, it may be concluded that adsorption of 1,3-D isomers was reduced by 20% due to the removal of organic matter.

Desorption.

Desorption was selectively measured for the Sa and Ki soils, and the ratio of K_{fd}/K_f was calculated. The K_{fd}/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 was resistant to desorption. The K_{fd}/K_f ratio of 1,3-D was also greater in the Ki soil than the Sa soil, suggesting that adsorbed 1,3-D was more resistant to desorption from the Ki soil (1.28% organic C) than from the Sa soil (0.80% organic C). These results further suggest the importance of soil organic matter in adsorbing 1,3-D.

4. CONCLUSIONS

The fumigant 1,3-D is a major replacement for MeBr that will be phased out by the year 2005. In order 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_f values of 1,3-D isomers in a number of California 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 was influenced by soil organic matter and was enhanced after addition of organic wastes. Therefore, organic amendment may be an option for reducing 1,3-D emissions during soil fumigation.

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