韓國環境科學會誌 第4卷(第4號), 379~386, 1995
J. of the Korean Environmental Sciences Society

Adsorption and Leaching of *cis* and *trans*-Permethrin in the Soil

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(Manuscript received 26 April 1995)

Abstract

Permethrin[3-phenoxybenzyl(1RS)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate] insecticides were selected to study adsorption and leaching potentials related to pollution on Commerce silty clay loam soil near Baton Rouge, Louisiana, USA. GLC-ECD chromatogram of permethrin included 32.5 % of *cis*-permethrin and 67.4 % of *trans*-permethrin. Extraction efficiencies of *cis* and *trans*-permethrin were 92.5 % and 92.3 % in fortified water, respectively and 85.9 % and 88.8 % in fortified soil, respectively. At a 1:10 soil/water ratio,the Koc values for *cis* and *trans* isomers of permethrin were 938 and 877, respectively. Leaching of permethrin was evaluated in soil columns(5.4 cm i.d. × 26 cm length). Total recoveries of the permethrin applied to the soil column were 84.5 ± 3.1 %. When the soil columns were leached with three pore volumes of water, the distributions of *cis*-permethrin leached were 6.10 % and 0.07 % of amount applied in the untreated zone soil and leachate water, respectively. *Trans*-permethrin distributions were 5.20 % in the untreated zone soil and 0.05 % in leachate water. *Cis* and *trans*-permethrin was strongly adsorbed to soil. The results of the study showed the strong relationship between adsorption and leaching. *Cis* and *trans*-permethrin to be leached into the groundwater in soils with shallow aquifers were suggested a low leaching potential.

Key Words : Pesticides, Permethrin, Adsorption, Leaching, Movement.

1. INTRODUCTION

The recently developed synthetic pyrethroids were appeared to be more effective aginst some insect species than the natural compounds, and were even less hazardous to mamals(Elliott, 1970).

Permethrin[3-phenoxybenzyl(1RS)-*cis,trans*-3-(2, 2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] is a contact insecticide against a broad range of pests(Fig.1.). It controls leaf and fruit eating pests in vegetables at 40-70 g a.i./ha, in fruit at 25-50 g, other crops at 50-200 g/ha(Tomlin, 1994).

The environmental fate of pesticides has attracted recent attention because of their pollution potential to the environment. Lake and river water can undoubtedly be contaminated with runoff water from adjacent agricultural fields if pesticides are not managed properly. The permethrin losses from the fields was < 0.01 % of the amount applied in Louisiana (Carroll *et al.*, 1981).

When pesticides are applied to soil, it comes into contact with a variety of surfaces to which it may adsorb. Because adsorption processes can influence leaching, translocation, volatilization, and persistence, it is a major factor in the behavior of a pesticides. Adsorption is a complex phenomenon involving interactions between the solute, solvent, and solid phases. A simple equilibrium distribution coefficient has often been used to quantify the adsorption characteristics. The adsorption distribution coefficient is usually determined in batch equilibrium tests in which a solute is allowed to partition between a solvent and a solid phases. Adsorption directly affects the rate at which a pesticide leaches in soil and potentially to the ground water.

Soil-adsorbed pesticides are subject to leaching by water percolating downward in the soil profile. The extent of leaching is generally dependent on climate, soil, pesticide, and management that influence leaching and the amount of leachate water(Leonard, 1989). Several pesticide properties that influence leaching include partition coefficient, water solubibity, vapor pressure, hydrophobic-hydrophilic character, ionic state, and chemical, photochemical, and biological properties(Himel *et al.* 1989 ; Kim *et al.*, 1992). It is commonly accepted that pesticides which are strongly adsorbed to soil particles and have low water solubilities, are relatively immobile in soil.

The objectives of this study were to evaluate the adsorption behavior and leaching properties of *cis* and *trans* isomers of permethrin in soil columns and to predict their movement under natural conditions.

2. MATERIALS AND METHODS

2.1. Materials

A Commerce silty clay loam soil (fine-silty, mixed, nonacid, thermic Aeric Fluvaguent) was used for the study. Soil was collected from the top 20 cm of the soil profile, air-dried at room temperature, lightly crushed, and passed through a 2 mm sieve. Selected characteristics of the soil include : sand of 48%, silt of 21%, clay of 31%, pH of 6.1. bulk density of 1.41 Mg/m^3, soil poposity of 47%, and organic C content of 1.14% (Bleyerveld and Kim, 1989). The initial concentrations of permethrin in this soil were below detection limits.

2.2. Analysis

Permethrin extraction of water was accomplished by mixing water with 100 mL hexane by a magnetic stirrer for 2 hr. The mixture was quantitatively transferred to a 1L separatory funnel, the water discarded, and the hexane dried over anhydrous Na_2SO_4 for GC analysis. Extractions of soil were accomplished by soxhlet extracting 30 g air-dried soil for 3 hr with 200 mL n-hexane : acetone(41 : 59, v/v) azeotrope(Southwick and Willis, 1990). The extract was partitioned in a separatory funnel, washed three times with 200mL volumes of distilled water to remove the acetone and dried over anhydrous Na_2SO_4. A 2 mL aliquot of nujol(2% in hexane) was added to the hexane. The hexane volume was then reduced by using a gentle N_2 flow.

Permethrin concentrations in the extracts were analyzed using a Tracor 540 GC equipped with ^{63}Ni electron capture detectors. A Megabore column(15 m long×0.53 mm i.d.) of DB210 was used. The column oven temperatures were 220℃. Detector and inlet temperatures were 240℃ and 230℃, respectively. Flow rates of He(99.995% minimun purity) carrier gas and N_2 (99.995% minimum purity) make-up gas were 10mL/min and 40mL/min, respectively. Standard permethrin(purity 97%) was furnished Crescent chemical Co..

2.3. Adsorption experiment

Adsorption isotherms were determined by placing 4 g of air-dried soil and 40 mL of permethrin solution (ranging from 500 to 10000 ng/mL) into 50mL sealed centrifuge tubes. The samples were shaken (135 strokes per minute) for 24 hr, a period that preliminary studies had shown were sufficient to attain equilibrium. Samples were then centrifuged at 3000 rpm for 30 min and the supernatant was used for permethrin analysis. Differences between the added amounts of permethrin and the remaining amounts of permethrin in the supernatant was considered to be the amounts adsorbed.

2.4. Leaching experiment

Each column, which consisted of 13 stacked and taped steel ring, (5.4 cm i.d.×3cm in length) was fitted with a Büchler funnel containing Whatman filter paper and mounted on a stand with a 500 mL Erlenmeyer flask for leachate collection (Smith and Willis, 1985). The columns were uniformly packed to a depth of 23 cm (bulk density 1.23 Mg/m^3, soil porosity of 41.1%) with untreated soil and saturated with distilled water prior to applying the permethrin. It was then covered with a depth of 3 cm (84.92 g) of soil treated 297mg/g of permethrin. Amounts of permethrin added to column was 112 g/ha of permethrin, the same rate of permethrin applied in cotten field studies in Lousiana, USA (Southwick *et al.*, 1983).

The soil column was leached with either 245 mL of distilled water (water depth of 10.69 cm, one pore volume) or 735 mL distilled water (water depth of 32.10 cm, three pore volumes). The 224 ± 6.76 mL of leachate from one pore volume of water was collected during 33.0 ± 8.8 hr (rate of 7.41 ± 1.98 mL/hr). The soil samples were divided into 0-5, 5-8, 8-11, 11-14, 14-20 and 20-26 cm after leaching. Each segment was air-dried for one week and crushed for permethrin analysis.

3. RESULTS AND DISCUSSION

3.1. Analysis of *cis* and *trans* isomers of permethrin

Retention times of *cis*-permethrin and *trans*-permethrin were 6.99 min and 7.18 min, respectively. The ratio of *cis* and *trans* isomers of permethrin may vary with the manufacturing process(Worthing, 1979). GLC-ECD chromatogram of permethrin showed 32.5% of *cis*-permethrin and 67.4% of *trans*-permethrin(Fig.2). The quantitative detection limit was 0.04 ng/mL of *cis*-permethrin and 0.09 ng/mL of *trans*-permethrin in water and 0.40 ng/g of *cis*-permethrin and 0.84 ng/g of *trans*-permethrin in soils. Extraction efficiencies of cis and *trans*-permethrin were 92.5 %, and 92.3 % in fortified water, respectively and 85.9 %, and 88.8 % in fortified soil, respectively(Table 1).

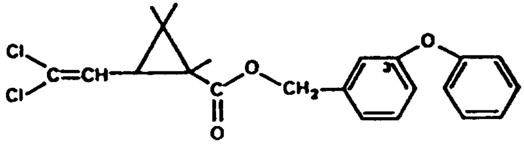

Fig. 1. Chemical structure of permethrin [3-phenoxybenzyl(1RS)-*cis*,*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate].

Table 1. Recovery of *cis* and *trans*-permethrin in soil and water

Samples	Pesticides	Concen.(μg/g)	Recovery(%) (Mean±SD)
Water	*cis*-permethrin	0.01	98.1±3.2[1]
		0.10	91.2±12.4
		0.20	88.4±4.2
	trans-permethrin	0.01	96.0±3.4
		0.10	92.2±11.0
		0.20	88.7±5.3
Soil	*cis*-permethrin	0.10	90.8±3.4
		0.50	81.7±9.1
		2.00	85.2±5.7
	trans-permethrin	0.10	91.8±10.2
		0.50	86.8±6.2
		2.00	88.0±7.9

1) n = 5

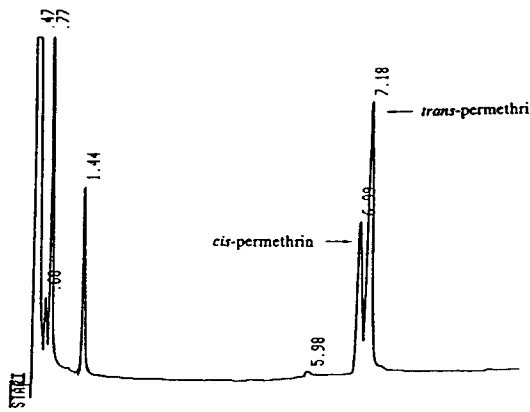

Fig. 2. Chromatogram of *cis* and *trans*-permethrin by GC-ECD in the soil.

3.2. Adsorption kinetics

Pesticide adsorption isotherms were calculated using the Freundlich equation(Green and Karickhoff 1989):

$$A=Kd\ C^{1/n} \qquad (1)$$

where A is the amount adsorbed (ng/g), C is the equilibrium solution concentration (ng/mL) after adsorption equilibrium and Kd and 1/n are Freundlich equilibrium constants. Model parameters were determened by fitting the experimental data to the linear forms of Freundlich(Guo *et al.* 1993):

$$\log A = \log Kd + (1/n) \log C \qquad (2)$$

Graphs of experimental data fitted to equation (2) were presented in Fig.3. Model parameters for adsorption were shown in Table 2.

The Kd value, representing the amount of pesticide adsorbed at an equilibrium concentration of 1 μg/mL, is the linear partitioning coefficient (soil/water). The Kd values for cis and trans isomers of permethrin were 10.7 and 10.0, respectively(Table 2). The Kd's showed that permethrin is strongly adsorbed on the soil. The Kd's also indicate that permethrin suggested a low leaching potential from soil columns.

These values of Kd were divided by the organic C content to calculate the adsorption paramether known as Koc. The Koc was expressed (Wood *et al.* 1987) as :

$$Koc=(Kd/\text{organic carbon content})\times 100. \qquad (3)$$

Koc is a soil-water partitioning constant based on the organic C fraction (0.0114) of a soil. The Koc values for cis and trans isomers of permethrin were 938 and 877, respectively (Table 2).

Table 2. Kinetics of Freundlich equation for the adsorption of *cis* and *trans*-permethrin in soil

Pesticides	Kd1)	Koc2)	1/n1)
cis-permethrin	10.7	938	0.96
trans-permethrin	10.0	877	0.96

1) log A = log Kd + (1/n) log C.
where A : amount adsorbed (ng/g)
C : equilibrium concentration (ng/mL)
2) Koc = Kd/Foc
where : Foc is the fraction by weight of organic carbon in the soil (0.0114)

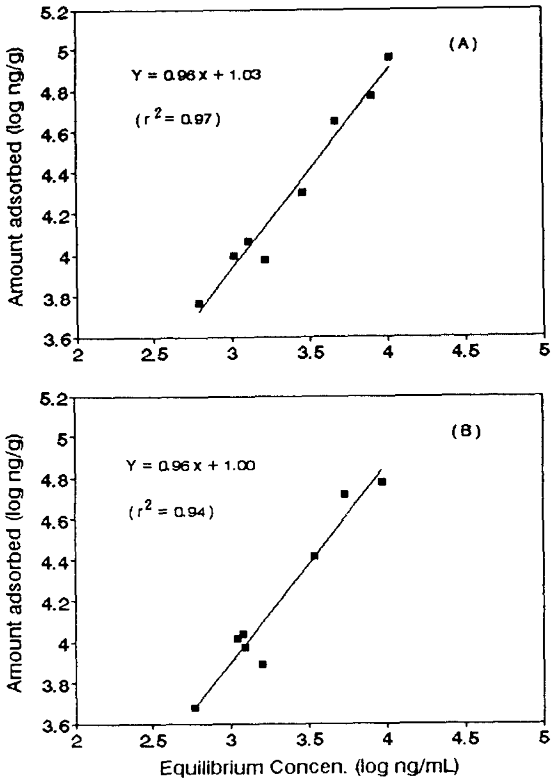

Fig. 3. Batch adsorption of (A)*cis*-permethrin and (B)*trans*-permethrin from a Commerce silty clay loam.

The Freundlich adsorptant constant, 1/n, represents the degree of non-linearity of adsorption isotherms. Values of 1/n for organic matter rich soils are less than unity, Organic matter poor soils show values greater than unity (Hata and Nunoshige, 1982). A large value of 1/n in this experiment may be attributed mainly to the adsorption of the permethrin on clay minerals.

3.3 Leaching in soil columns

Distribution of permethrin in soil columns and leachate water are given in Fig.4 and 5. Total recoveries (soil + leachates) after leaching with control (no leaching), one, and three pore volumes were 86.00 %, 86.10 %, and 80.17 % of applied amount for *cis*-permethrin(Fig. 4) and 87.00 %, 87.10 % and 81.25 % for *trans*-permethrin(Fig.5), respectively.

For *cis*-permethrin after leaching with one pore volum, 83.00 % of applied amount was in the 0- to 5-cm depth (3 cm of treated zone plus 2 cm of untreated zone), while the cis-permethrin amounts in the untreated zone (below the 5-cm depth) were 3.10 % of the applied amount. With three pore volumes of leachate, 74.00 %, 6.10 %, and 0.07 % of applied *cis*-permethrin were appeared in the treated zone soil, the untreated-zone soil and leachate water, respectively(Fig.4). The low mobility of cis-permethrin in the soil column resulted from undoubtedly strong adsorption to the soil (Kd=10.7) and low water solubility(0.2 mg/L). Leaching of *trans*-permethrin was concurred with *cis*-permethrin in soil column(Fig.5).

Smith and Willis investigated that *cis* and *trans*-permethrin in the leachates was 0.08 % and 0.04 % of that applied by three pore volumes, respectively (Smith and Willis, 1985).

Carroll *et al.* reported that concentration and losses of permethrin in runoff were low. The concentration of permethrin never exceeded 0.20

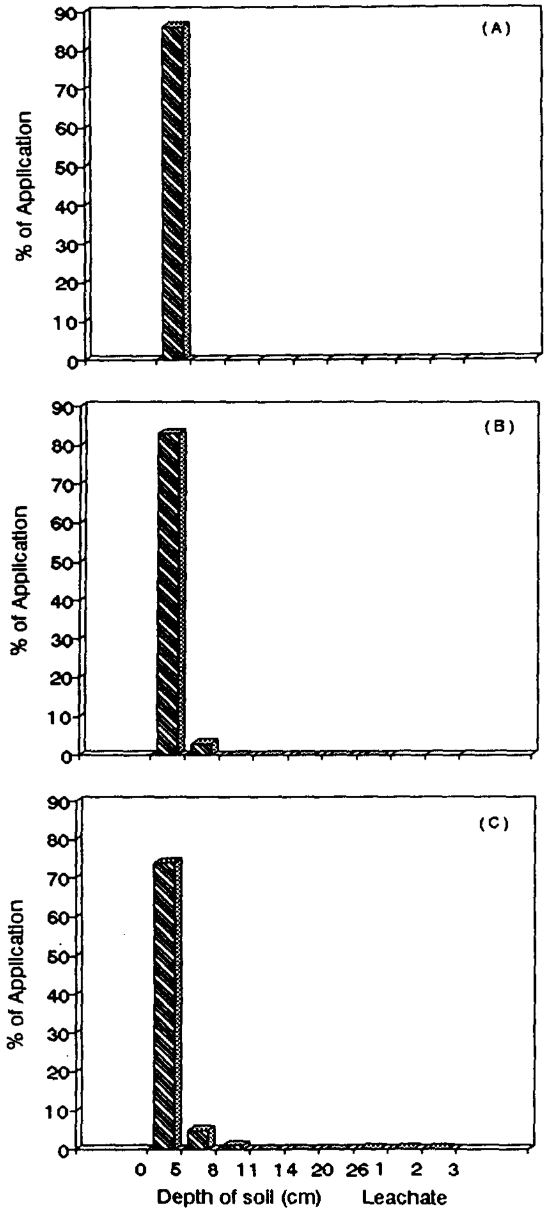

Fig. 4. Distribution of *cis*-permethrin in soil column and leachate after leaching with (A)no leaching (B)one pore volume and (C)three pore volume of water.

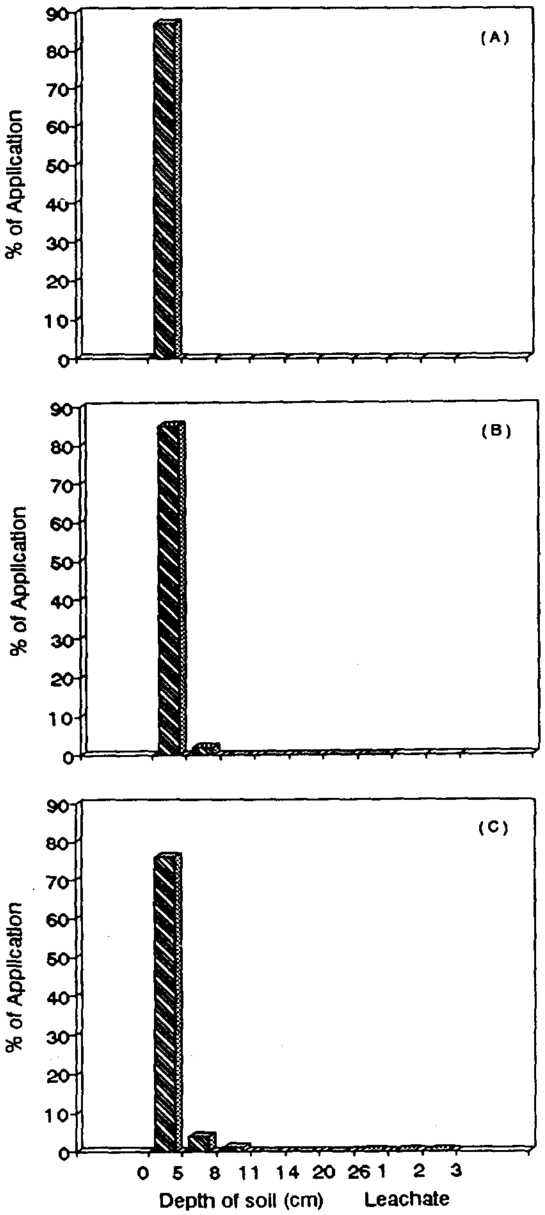

Fig. 5. Distribution of *trans*-permethrin in soil column and leachate after leaching with (A)no leaching (B)one pore volume and (C)three pore volume of water.

μg/L. The total permethrin losses was < 0.01 % of that applied in Louisiana(Carroll *et al.*, 1981). The trends observed in the soil column studies was confirmed by report of Smith and Carroll(Smith and Willis, 1985 ; Carroll *et al.*, 1891).

4. CONCLUSIONS

GLC-ECD chromatogram of permethrin was showed 32.5 % of *cis*-permethrin and 67.4 % of *trans*-permethrin.

Batch equilibrium studies with a Commerce silty clay loam soil resulted in Koc values of 938, and 877, respectively for *cis*-permethrin and *trans*-permethrin. The expected leaching by these Koc was confirmed with soil column leaching studies using three pore volumes of leachate. The experimental results confirmed the relationship between adsorption and leaching. Permethrin was strongly adsorbed by sediment, and erosion control can be important in controlling losses of permethrin. Permethrin movement under natural conditions was suggested a low leaching and run off potential.

ACKNOWLEDGMENTS

This research was a contribution from USDA-ARS, Louisiana and supported by LSU Agricultural Center, Louisiana Agricultural Experiment Station in USA and Korea Science & Engineering Foundation in Korea.

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土壤 中 *cis* 및 *trans*-Permethrin의 吸着 및 浸出

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合成 Pyrethroid系 permethrin[3-phenoxybenzyl(1RS)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate]은 直接接觸 殺蟲劑로서, 哺乳動物에는 매우 底毒性이므로 使用量이 增加되고 있다. 따라서 土壤中 permethrin의 動態를 豫測할 必要가 있다. Permethrin을 GC-ECD로 分析하였으며, *cis*-permethrin은 32.5%였고 *trans*-permethrin은 67.4%였다. Commerce silty clay loam 土壤에서 Koc값은 *cis* 및 *trans*-permethrin이 각각 938 및 877였다. 土壤 컬럼(5.4 cm i.d. × 26 cm length)을 利用한 溶脫實驗을 하였다. 3배의 pore 부피에 해당하는 물로 cis-permethrin을 浸出할 경우, 處理된 土壤層에 74.00%였고 6.10%만 아래층으로 移動되었으며, 0.07%의 微量만 浸出水로 浸出되었다. Permethrin은 土壤에 강하게 吸着되기 때문에, 土壤 column에서의 浸出量도 매우 적었다. 따라서 自然系에서의 浸出(Leaching) 및 유거(Runoff)농도는 매우 낮을 것으로 豫測된다.