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Butachlor, Thiobencarb, and Chlomethoxyfen Movement in Subtropical Soils

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Butachlor [*N*-(Butoxymethyl)-2-chloro-2',6'-diethyl acetanilide], thiobencarb [*S*-(4-chlorobenzyl)-*N*,*N*-diethylthiol carbamate] and chlomethoxyfen (2,4–Dichlorophenyl-3-methoxy-4-nitrophenyl ether) are three of the most common herbicides used in transplanted rice paddies in Taiwan and many other Asian countries. Some research has been conducted on the distribution of these herbicides in soil (Chen and Chen 1979; Chiang *et al.* 1987; 1997; Ishikawa 1976; Niki and Kuwatsuka 1976), but information on their movement in soil is limited. Miscible displacement is a thoroughly researched concept that is useful for explaining the physical properties of soil and for describing the movement of solutes in soil. Theoretical models describing miscible displacement in porous material have been offered for nearly a half-century (Lapidus and Amundson 1952; Neilsen and Biggar 1961; 1962; Amoozegar-Fard 1982; Schnabel and Richie 1987). Incorporating several simplified assumptions, these models can be used to predict solute distribution in soil (Leistra 1973). Other principal parameters controlling herbicide movement in soil include water flux, herbicide diffusibility and water solubility, soil retardability, soil moisture content, and biodegradability (Davidson *et al.* 1968).

The movement of butachlor, thiobencarb, and chlomethoxyfen in two types of subtropical soil Taichung sandy loam and Taoyuan clay loam was investigated. Linear equilibrium sorption and reversible kinetic equilibrium equations were used to predict herbicide movement. A reasonable fit between the analytic and numerical solutions was observed for butachlor and thiobencarb but not for chlomethoxyfen. Butachlor and thiobencarb were eventually distributed to all column layers, but chlomethoxyfen was only detected in the upper layers.

MATERIALS AND METHODS

Soil samples were collected from the cultivated paddies at the experimental farm managed by Chungshing University in Taichung City and the Taoyuan District

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Agricultural Improvement Station in Taoyuan County, Taiwan. Soils were sampled from surface down to a depth of 20 cm. A number of soil properties are described in Table 1. Butachlor (99.2% pure), thiobencarb (100%), and chlomethoxyfen (99.9%) were obtained from the Monsanto (US), Kumiai (Japan) and Ishihara Sangyo (Japan) companies, respectively.

Table 1. Some characteristics of the soils

Location	pH	C.E.C	Organic matter	Mechanical analysis			
	(1:1)	(Meq /100g)	(%)	Clay (%)	Silt (%)	Sand (%)	Texture
Taoyuan	5.3	23.01	2.94	28.6	28.0	43.4	Sandy clay loam
Taichung	6.3	10.94	1.24	9.8	15.4	74.8	Loamy sand

Soil samples were passed through a 2-mm sieve and air-dried at ambient temperature before being packed into several acrylic columns (12 cm x 4.35 cm id). Column tops and bottoms were sealed with acrylic lids and spiral caps, with a spiral line outside of the acrylic column and inside the lid. The spaces between the columns and lids were coated with waterproof gel to prevent leakage. Filter paper, a rubber water seal, and a stainless net were packed inside each lid; a 5 mm layer of glass beads was placed inside each bottom lid (Wang *et al.* 1996). Before conducting the experiments, $CaSO_4$ solution (0.005 *M*) was eluted several times from the bottom lid upward and upper lid downward in order to remove air from the soil columns.

A schematic drawing of our miscible displacement experiment (performed at 25℃) is presented in the previous report (Wang *et al.* 1996). Elution velocities were changed by altering the height of the constant head device. A 0.005 *M* solution of $CaCl_2$ was used as eluant when chloride was used as an ion tracer. Individual herbicide were dissolved in water to concentrations ranging from 8.5 to 232.1 μ g/L; $CaSO_4$ was then added to form a $CaSO_4$ solution concentration of 0.005 *M*. Soil columns were eluted with herbicide-modified $CaSO_4$ solution for 7 days, and eluates were collected in glass tubes at regular intervals. Eluate volumes were recorded and pore velocities were calculated. Chloride ions in eluate were measured with a chloride-elective electrode, and herbicide contents were determined using a GC-ECD apparatus as described previously (Chiang *et al.* 1997). Following miscible displacement experiments, ten 1 cm sections were sliced from each soil column to determine herbicide movement.

To measure herbicide levels in eluate, samples were diluted to 500 mL with organic-free deionized water. Five grams of NaCl were then added to the solution and then extracted thrice with benzene (100 mL each). Following dehydration with 8 g anhydrous Na_2SO_4, the benzene extracts were evaporated to dryness and the residue was dissolved with *n*-hexane to a volume of 10 mL prior to GC-ECD analysis. In 250-mL flasks, soil samples were extracted with three 50 mL of acetone in a shaker (200 rpm) for 30, 15 and 15 min, respectively. Acetone extracts were separated from soil by centrifugation at 3000 rpm for 10 min, then evaporated on a rotary evaporator at a temperature below 40 ℃ to a volume of approximately 8 mL. Finally, 10% NaCl solution was added to a final concentration of 1% NaCl and extracted thrice with benzene (40 mL each). Herbicides were analyzed in the same manner as water samples.

ECD gas chromatography was performed with Hitachi Gas Chromatograph (model no. 663-50). Glass column (2 m × 3 mm id) with 3% OV-1 on 80/100 mesh chromosorb WHP were used to analyze butachlor and chlomethoxyfen; for thiobencarb, the liquid phase of the packing material was replaced by 3% OV-17. Operating temperature were as follows: injection port, 250 ℃; detector, 280 ℃; column, 215 ℃ for butachlor and benthiocarb analysis and 225 ℃ for chlomethoxyfen analysis. Nitrogen was used as the carrier gas.

RESULTS AND DISCUSSION

Soil column parameters for the miscible displacement experiment are shown in Table 2. Dispersion coefficients (*D*) were estimated according to the miscible displacement of the chloride tracer. Based on the breakthrough curves (BTCs) of the chloride tracer, the relationship between average pore velocity (*v*) and dispersion coefficient (*D*) for the two soil types were estimated using the method of Gupta and Greenkorn (1974). Values were

$D = 3.992v + 0.21$ for Taoyuan clay loam and
$D = 0.425v$ for Taichung sandy loam

Table 2. Parameters of soil columns in miscible displacement experiment

Soil type	Bulk density (g/cm^3)	Water content (mL/mL)	Flux (cm/h)	Herbicide
Taoyuan clay loam	1.23	0.467	0.358	Butachlor
	1.24	0.464	1.020	Chlomethoxyfen
	1.23	0.474	1.376	Thiobencarb
Taichung sandy loam	1.48	0.440	3.676	Butachlor
	1.49	0.405	2.415	Chlomethoxyfen
	1.51	0.401	2.884	Thiobencarb

where D is the sum of molecular diffusion and mechanical dispersion. Results from the tracer experiments revealed a negligible effect of molecular diffusion in Taichung sandy loam.

Herbicide concentration in soil column (12 cm) effluent and individual soil layers were predicted according to the one-dimensional convective-dispersive sorption equation:

$$\frac{\partial C}{\partial t}+\frac{\rho}{\theta}.\frac{\partial S}{\partial t}=D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x}$$

where C is the chemical concentration in solution (μ g/cm^3), S is the chemical amount adsorbed per gram of soil (μ g/g), D is the dispersion coefficient (cm^2/hr), v the average pore-water velocity (cm/hr), ρ is the bulk density (g/cm^3), θ the saturated water content (cm^3/cm^3), x the linear distance in flow direction (cm), and t the time (hrs). An instantaneous equilibrium model

$$S = K_d \times C$$

and a reversible kinetic model (Oddson *et al.* 1970)

$$\partial S/\partial t = K_{Kin}(K_d \times C - S)$$

were used to describe the solute sorption term (δ S/ δ t). In sorption equilibrium equations, K_d and K_{kin} are constants. An analytical solution was used for the equilibrium model equation and a numerical solution was used for the equilibrium and kinetic model equations.

The parameters used for describing breakthrough curves for the miscible displacement of the three herbicides are listed in Table 3.

Table 3. Parameters used to describe the breakthrough curves (BTCs) of the three herbicides using the transport model

Herbicide	*Re*	*v* (cm/hr)	*D* (cm^2/hr)	Peclet no.	*V/Vo*	Time (days)
			Taoyuan clay loam			
Butachlor	89.6	0.77	3.27	2.81	10.69	7.05
Chlome.	1735.3	2.20	8.99	2.94	39.93	7.00
Thiobencarb	109.5	2.90	11.79	2.95	45.02	7.00
			Taichung sandy loam			
Butachlor	38.5	8.36	3.55	28.24	71.41	6.96
Chlome.	443.9	5.96	2.53	28.24	84.91	7.00
Thiobencarb	51.4	7.19	3.06	28.24	102.92	7.00

The Peclet numbers (Pe, $Pe = vL/D$) for Taichung sandy loam were much larger than those of Taoyuan clay loam in indication that molecular diffusion may be an important factor in herbicide movement in the latter soil type but not in the former. The Re order in the soil samples was chlomethoxyfen > thiobencarb > butachlor. A comparison of a single herbicide in the two soil types revealed a higher Re value in Taoyuan clay loam.

According to Van Genuchten and Parker (1984), the initial and boundary solute conditions in terms of miscible displacement are

$$C(x, t) = 0 \quad \text{for} \quad x > 0 \quad \text{and} \quad t = 0$$

$$C(x, t) = \text{Co} \quad \text{for} \quad x = 0 \quad \text{and} \quad t > 0$$

$$\text{Lim}\, C(x, t) = 0 \quad \text{for} \quad t > 0$$

assuming a semi-infinite column. The three herbicides tested in this study were sorbed according to linear equilibrium sorption (Chiang *et al.* 1997), the analytical solution is

$$C/Co = \{\text{erfc}[(Re-V/Vo)/\sqrt{V/Vo*4D\,\text{Re}/v'L}\,] + \exp(v'L/D')\text{erfc}[(Re+V/Vo)/\sqrt{V/Vo*4D\,\text{Re}/v'L}\,]\}/2$$

where C/Co is the relative concentration of the effluent; V/Vo the pore volume number; Re the retardation factor ($Re = 1+\rho K_d/\theta$, $v' = v/Re$, $D' = D/Re$) and L the soil column length.

The above analytical solution assumed instantaneous adsorption and a linear, single-valued adsorption-desorption relation assumptions that may not be valid for all of the conditions occurring in this study. In order to improve the predictions of herbicide movement, a reversible kinetic equilibrium equation was also used. Due to the low pore velocities in the soil column, it is difficult to evaluate the suitability of two solute sorption models. However, based on the effluent BTCs for butachlor and thiobencarb in the Taoyuan clay loam soil columns (Figs. 1A and 1B, respectively), it appears that a reasonable fit was achieved between the analytical and numerical solutions.

Breakthrough curves for butachlor and thiobencarb in Taichung sandy loam are presented as Figs. 1C and 1D, respectively. The curve computed from the reversible kinetic model agreed more with the experimental BTC than the curve computed from the instantaneous equilibrium model. Although reasonable predictions were achieved by the kinetic model for both BTC position and shape, a significant discrepancy was found between the experimental and computed values unlike the agreement between the analytical and numerical solution for the instantaneous equilibrium model equation. In the case of chlomethoxyfen, herbicide residue was not detected at all in soil column effluents.

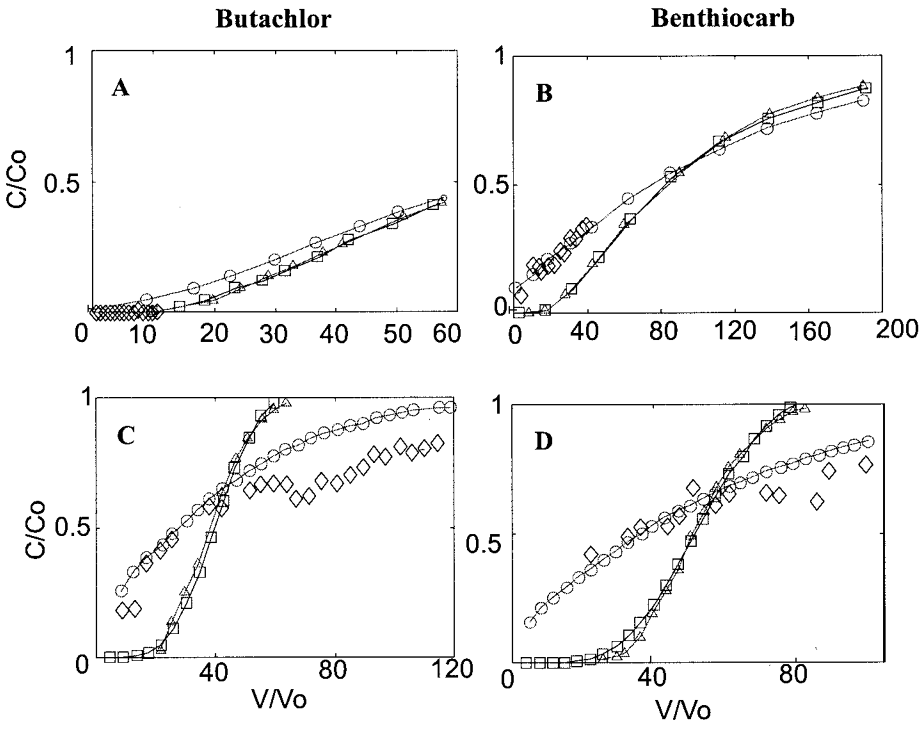

Figure 1. The effluent breakthrugh curves of butachlor and thiobencarb in the Taoyuan clay loam (**A, B**) and Taichung sandy loam (**C, D**) soil column. □ Equilibrium model (Analytical solution); △ Equilibrium model (Numerical solution); ○ Kinetic model (Numerical solution); ◇ Measured.

Predicted and measured herbicide residues determined from soil columns during the miscible displacement experiments are show in Fig. 2. It was found that models based on instantaneous equilibrium or reversible kinetic process simulated the measured herbicide concentrations in each soil column layer reasonably well. Butachlor and thiobencarb were distributed to all layers in both soil types, especially average distributed in Taichung sandy loam soil column, but chlomethoxyfen was not detected in the lower layer of either the clay loam or sandy loam soil columns. Of the three herbicides, chlomethoxyfen showed the lowest mobility, with almost complete retention in the top 4 cm of soil. Herbicide distribution is clearly dependent on soil type. A partial differential single-dimensional convective-dispersive sorption equation with reversible kinetic sorption model is capable of describing butachlor and thiobencarb movement reasonably well in the laboratory. In contrast, chlomethoxyfen mobility is very limited.

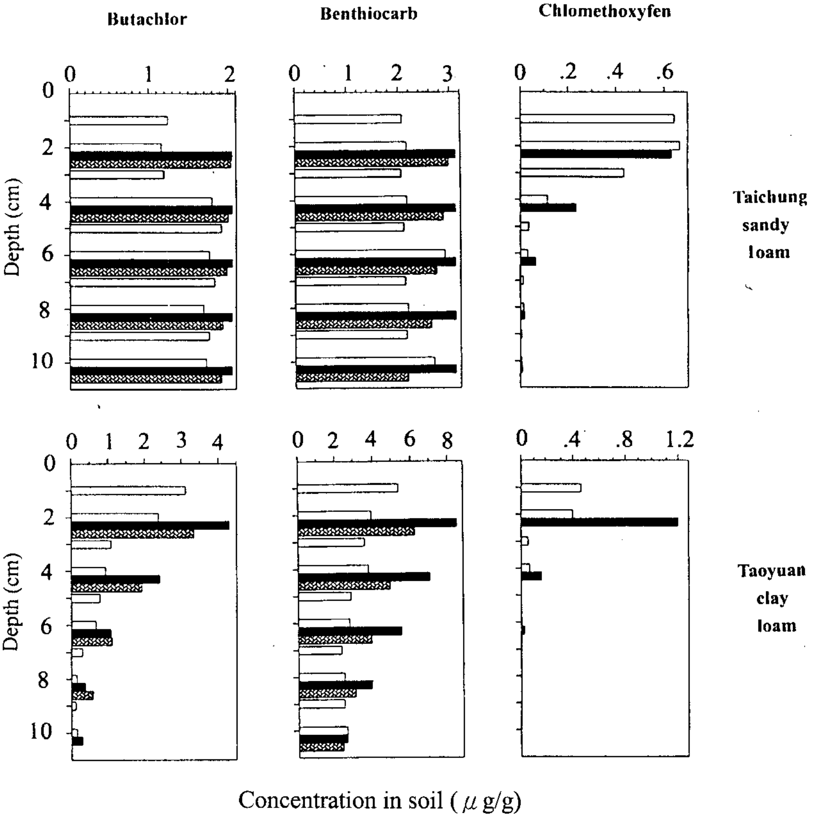

Figure 2. Predicted and measured residues and distribution of herbicide in the Taichung sandy loam and Taoyuan clay loam soil columns. □ Measured; ■ Predicted by equilibrium model; ▨ Predicted by kinetic model.

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