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Movement of Three s-Triazine Herbicides Atrazine, Simazine, and Ametryn in Subtropical Soils

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A partial differentiation equation of convection-dispersion-sorption which reported by Lapidus and Amundson (1952) plus an additional item of chemical decomposition rate is used to simulate the movement of herbicide in soil. The water flux, diffusibility and water solubility of herbicide, soil retardability, soil moisture content and biodegradability are the principal parameters in this simulation (Davidson et al. 1968). Pal and Poonia (1982) suggested that the concept of miscible displacement is important to understand soil physical properties and to describe the movement of a solute in soil. The rate of dissipation of a herbicide from a laboratory experiment under the control of temperature and soil moisture is applied in the field study to predict the dissipation of a herbicide in the soil (Walker, 1976a; 1976b). In that prediction, information such as meteorological data and soil moisture characteristic of the field and sorption of herbicide on soil were necessary. Measurement and simulation of the movement and degradation of atrazine and metribuzin in fallow soil were studied by Nicholls et al. (1982). They reported that the predicted herbicide residues agrees with measurement, but the predicted value was smaller in the short-term period and greater in the long-term period. Wagenet and Huston (1957) developed a model of leaching estimation and chemistry (LEACHM), which is a process-based model of water and solute movement in the unsaturated zone. The influence of climate and soil properties on the degradation of simazine in soils was examined (Chen et al. 1983). A comparison of the persistence of three herbicides---atrazine, simazine and ametryn under various soil temperatures and moisture contents in subtropical soils was reported (Wang et al. 1995). The parameters found from the laboratory test seemed unable to predict directly the rate of dissipation of herbicide in the field in subtropical area.

The present research was designed to investigate the movement of the herbicides in subtropical soils in the laboratory and in the field by measurement of residues and simulation with model. The movement of the herbicides was also elucidated from the effluent breakthrough curves (BTC).

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MATERIALS AND METHODS

Herbicides and soils were the same as previously (Wang et al., 1995). Atrazine and ametryn used in this experiment were provided (Cyanamid Taiwan Corporation) as commercial products with 50 and 80% wettable powders, respectively. Simazine (Ciba-Geigy, Japan) was formulated as a commercial product of 50% wettable powder (Kumiai Chemical Industry Co., Ltd., Japan). Pure herbicides (mp 17.5 °C for atrazine, 227 °C for simazine and 85 °C for ametryn) for reference standards were obtained by extracting the commercial product with chloroform and recrystallizing from hexane. The soil used in the laboratory experiments was collected from the Experimental Farm of Taiwan Agricultural Research Institute, Wufeng, Taichung, and the upland fields of Tucheng near Ta-han River, Taipei county. Soil samples were located in the subtropical area (about latitude 24° N); their physicochemical properties are shown in Table 1.

Table 1. Physicochemical properties of the soils

Location	pH (1:1)	Field capacity(%)	Mechanical analysis Clay	Silt	Sand	Soil texture	Organic matter(%)
Taipei	4.4	10.87	15.6	25.1	59.3	Sandy loam	2.14
Taichung	4.9	28.69	30.8	26.7	42.5	Clay loam	1.45
Taichung	6.5	21.67	21.8	46.2	32.0	Loam	0.94

In laboratory experiments, the collected soils passed a 2-mm sieve, and were dried in air at ambient temperature. Soil of each kind was then packed into three acrylic columns (12 cm x 4 cm id) for experiments with the three herbicides. The acrylic column was sealed with an acrylic lid on the upper and lower sides by a spiral cap, the spiral line outside the acrylic column and inside the lid. Waterproof gel was coated between column and lid to keep the system free of leak. In the lid, the filter paper, rubber water seal and stainless net were packed as shown in Fig. 1. A layer (5mm) of glass beads was placed in the bottom lid. The experiment was preceded by eluting with $CaSO_4$ solution (0.005 M) from the bottom lid upward, and then from the upper lid downward, back and forth for several times to excluding air from the soil column.

Experiment on miscible displacement were performed at 20 ± 1 °C. A schematic drawing appears in Fig. 2. Eluting velocities were varied by altering the height of constant head device. The $CaCl_2$ solution (0.005 M) was used as influent liquid when use chloride ion as tracer. With the herbicide as solute, herbicide was dissolved in water to a concentration 2 ppm and appropriate $CaSO_4$ was added to the solution to make a $CaSO_4$ solution of 0.005 M concentration. The soil column was eluted with herbicide modified $CaSO_4$ solution (0.005 M) for five to nine days depending upon the velocity of effluent. Eluates were collected in flasks at constant intervals; the volumes of eluate were recorded and the pore velocity was calculated. Chloride ions in eluate were measured with a chloride-elective electrode, and the herbicide in the eluate was analyzed with a GC pre-

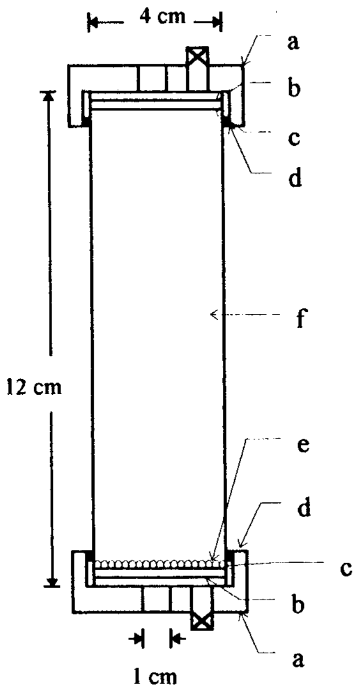

Figure 1. **The apparatus of the soil column.**
a. Upper lid b. Stainless net,
c. Filter paper, d. Rubber water seal,
e. Glass beads, f. Soil, g. Lower lid

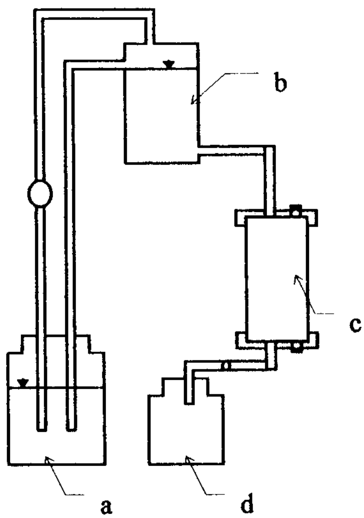

Figure 2. **The schematic drawing of the experimental design.**
a. Reservoir, b. Constant head device,
c. soil column, d. Fraction collector

ceded by extraction twice with chloroform. After experiment on miscible displacement, the soil from each column was sliced into five successive sections (2 cm). In each section, soil (20g) was taken to determine the herbicide.

The method of analysis of herbicide in soils was the same as that described previously paper (Wang et al., 1995). The soil (20 g) was extracted with methanol (80%, 50 mL) in a rotary shaker for 1 h, and filtered; the residue was washed with methanol (80% 2 x 25 mL). The filtrates were combined and concentrated to dryness at 70 °C on a rotary evaporator, dissolved in chloroform (2 mL), and passed through an Al_2O_3 column (6 g, 1.2 x 15 cm) and then washed with hexane (50 mL). The hexane eluate was discarded and the column was then eluted with chloroform (75 mL). The chloroform eluate was collected and concentrated to dryness; the residue was dissolved in benzene for GC analysis. The ECD gas chromatograph (Varian 3700) was equipped with an integrator (CDS 111) and a recorder (Varian Model 9176). A glass column (2 m x 2 mm id) packed with equal proportions of a mixture of SE-30 (2%) and QF-1 (3%) coated on 100/200 mesh Chromosorb G-HP was employed. Operating temperatures were as follows: injection port and detector 240 °C, column 200 °C. Nitrogen was used as a carrier gas at a flow rate 40 mL/min.

The locations and experimented design in the field experiments were the same as in previous work (Wang et al. 1995) Field experiments were performed at the Experimental Farm of Taiwan Agricultural Research Institute, Wufeng, Taichung, in the winter from Nov. 1989 to Mar. 1990 (16 weeks). Sixteen plots (four each) were treated with atrazine (50%), simazine (50%), ametryn (80%) wettable powder (at rates 2, 2, 1.25 kg ai/ha, respectively) and control. The control plots were hand weeded. The size of each plot was 1.5 m x 5 m. Meteorological data such as temperature and precipitation in the Taichung area during the experimental period were showed in the previous paper. The soil in treated plots were sampled by 20 cores per plot of diameter 1.5 cm to a depth 20 cm by random sampling at 28, 56 and 84 days after application of herbicide. Soils in each core were divided into eleven layers, i.e. 0 - 0.5, 0.5 - 1, 1 - 1.5, 1.5 - 2, 2 - 3, 3 - 4, 4 - 5, 5 -7, 7 - 10, 10 - 15, 15 - 20 cm from the upper side. The same layer of the cores from each plot were mixed and passed through a sieve (2 mm). The soil was stored at - 10 °C while awaiting chemical analysis. Subsamples of each layer from each plot were analyzed in duplicate.

RESULTS AND DISCUSSION

Constant eluting velocity in the experiments on miscible displacement of chloride breakthrough curve, is attributed to the shorter experimental period and non-reactive solute. But in the case of the herbicide, the eluting velocity varies during the experiment, and is, hence, expressed with average pore velocity (v) (Table 2). The influent concentrations are also averaged for the reason of the difficulty to maintain constancy, and are shown as 1.20, 1.36 and 1.05 ppm for atrazine, simazine and ametryn, respectively.

Table 2. Average pore velocities of soil columns in miscible displacement experiments for herbicides

Soil type	Average pore velocity v ($cm\ hr^{-1}$)		
	Simazine	Atrazine	Ametryn
Taipei sandy loam	7.265	5.656	5.654
Taichung loam	0.646	0.936	0.306
Taichuns clay loam	1.566	1.661	1.203

The parameters of the soil columns in the miscible displacement experiment are shown in Table 3.

Because the experiment is in continuous influent and supposing the system to be semi-infinite system, according to Van Genuchten and Parker (1984), the initial and

Table 3. Parameters of soil columns in miscible displacement experiment.

Soil type	Herbicide	Bulk density ($g\ mL^{-1}$)	Water content ($mL\ mL^{-1}$)	Flux ($cm\ h^{-1}$)
	Atrazine	1.460	0.431	2.438
Taipei sandy loam	Simazine	1.489	0.442	3.211
	Ametryn	1.454	0.424	2.397
	Atrazine	1.466	0.531	0.497
Taichung loam	Simazine	1.444	0.527	0.340
	Ametryn	1.387	0.503	0.154
	Atrazine	1.277	0.563	0.935
Taichung clay loam	Simazine	1.283	0.558	0.874
	Amletryn	1.264	0.545	0.656

boundary conditions of non-reactive solute of the miscible displacement are

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

after making dimensionless, the analytic solution of the chloride, a non-reactive solute, is as follows (Lapidus and Amundson, 1952):

$$C_e = \{erfc[(P_e / 4 R_e T_v)^{1/2} (R_e - T_v)] + \{exp(P_e) erfc[(P_e / 4 R_e T_v)^{1/2} (R_e + T_v)]\} / 2$$

in which C_e is the relative concentration of the effluent; T_v is the number of pore volumes, $T_v = vt/L$, L is the soil column length; P_e is the Peclect number that corresponds to vL/D; R_e is a retardation factor, $R_e = 1 + r K_d / q$, r is the soil bulk density, q is the soil moisture, K_d is distribution coefficient. The dispersion coefficient D is obtained from the chloride breakthrough curve (by plotting T_v vs C_e), D is the sum of molecular diffusion and mechanical dispersion.

When the solute is degradable, like the herbicide in this work, and supposing the solute to be sorbed on the sorbate according to a linear equilibrium sorption and to be degraded according to a reaction of first order, the analytic solution is (Parker and Van Genuchten, 1954)

$$C_e = \{exp[(v - u) x / 2D\} erfc[(R_e x - ut)/2(DR_e t)^{1/2}] + exp[(v + u) x / 2D] erfc[R_e x + ut)/2(DR_e t)^{1/2}]\} / 2$$

in which $u = (v^2 + 4kD)^{1/2}$, v is the average pore velocity (cm/h), k is the first-order kinetic degradation coefficient. This equation is suitable to predict the movement of pesticide in a soil column.

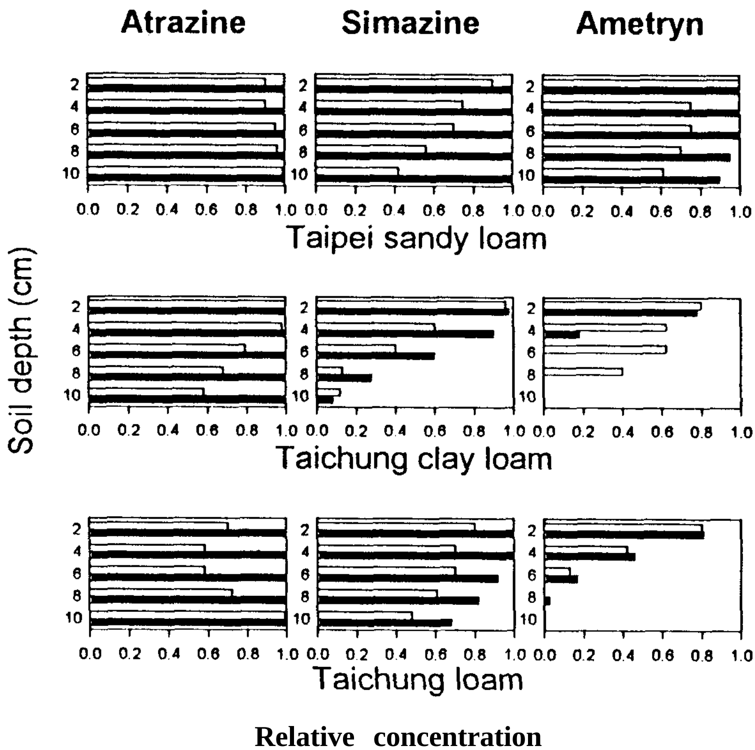

Figure 3. Herbicide residues in each layer of soil columns in the laboratory experiment
▭ Measured ▬ Predicted

The predicted and measured residues of three herbicides in the soil column in the laboratory experiments are shown in Fig. 3. All three herbicides were distributed to all layers in a sandy loam column, but in clay loam and loam soil column only atrazine and simazine were distributed to all layers, no ametryn was detected in the lower layer of the clay loam and loam column. The herbicide content decreased obviously with depth of the soil column when packed with loam and clay loam soils,

Water flow in soil under unsaturated conditions are found according to Darcy's law and the equation of continuity

$$\partial \theta / \partial t = \partial [K_y(\theta) \partial H_y / \partial x] / \partial x - U(x, t)$$

in which *q* is soil moisture (mL/mL), H_y is the hydraulic head (mm), K_y is the hydraulic conductivity (mm/d), t is time (d), x is depth (mm) downward and U is the loss of moisture by evaporation per day. In the unsaturated field conditions in this work, the herbicides moved to the various depths in field soil after 26, 56 and 84 days as shown in Table 4. The deepest movements are 7, 5 and 4 cm for atrazine, simazine and ametryn, respectively, in the field experiments. For simulation with the LEACHP model, a submodel of the LEACHM model, with the rates of dissipation from the laboratory test (Table 5), the maximum movement of herbicide were 15, 12 and 8 cm for atrazine, simazine and ametryn, respectively. With the rates of dissipation from the field test (Table 5), the meteorological data, soil moisture (calculated from the soil moisture characteristics), latitude and sorption coefficient are introduced to the LEACHP model, the maximum movements of the three herbicides in unsaturated moisture field condition were 11, 9 and 4 cm for atrazine, simazine and ametryn, respectively. Both movement

Table 4. Movement of atrazine, simazine and ametryn in Taichung loam soil under field experiment

Soil depth (cm)	Residues (%)								
	Atrazine			Simazine			Ametryn		
	28	56	84	28	56	84	28	56	84
0 - 0.5	9.52	2.24	2.01	19.47	2.29	2.19	2.31	0.83	0.83
0.5 - 1.0	3.23	1.41	0.86	2.63	1.34	0.64	1.28	0.26	0.31
1.0 - 1.5	1.22	0.96	0.71	0.36	0.79	0.42	0.90	0.01	0.14
1.5 - 2.0	0.61	0.67	0.56	0.30	0.41	0.26	0.01	0.01	0.01
2 - 3	0.78	0.91	0.65	0.61	0.35	0.25	0.03	ND	0.01
3 - 4	0.31	0.37	0.47	0.45	0.01	0.01	0.01	ND	0.01
4 - 5	0.27	0.01	0.39	0.09	ND	ND	ND	ND	ND
5 - 7	0.02	ND	ND	ND	ND	ND	ND	ND	ND
7 - 10	ND	ND	ND	ND	ND	ND	ND	ND	ND
10 - 15	ND	ND	ND	ND	ND	ND	ND	ND	ND
15 - 20	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND: Not detected.

Table 5 Dissipation coefficient of three s-triazine herbicides in Taichung loam in the laboratory and field experiments

	Dissipation coefficient (per day)	
	In the laboratory*	In the field**
Atrazine	0.0115	0.0423
Simazine	0.0100	0.0483
Ametryn	0.0141	0.1070

* Regression from data in Table 6 of the previous report and **from Table 5 of the previous report (Wang et al. 1995)

depth and residues showed greater predicted values than measured; this effect is attributed to dissipation rate of herbicide. The predicted values are improved when the rate coefficient for dissipation from the field experiments are considered instead of that from the laboratory.

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