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Sorption of Herbicides Butachlor, Thiobencarb, and Chlomethoxyfen in Soils

H.-C. Chiang,[1] J.-H. Yen,[2] Y.-S. Wang*

[1]Department of Environmental Engineering, National I-Lan Institute of Agriculture and Technology, I-Lan, Taiwan, Republic of China
[2]Department of Agricultural Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

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Three conventioinal herbicides, butaclor [*N*-(Butoxymethyl)-2-chloro-2',6'-diethyl acetanilide], thiobencarb [*S* - (4 - Chlorobenzyl) - *N* , *N* - diethylthiol carbamate] and chlomethoxyfen (2,4-Diclilorophenyl-3-methoxy-4-nitrophenyl ether), are used to control weeds in transplanted rice of paddy fields in tropical and subtropical area, particularly in many Asian countries. Several investigations have examined the behaviors of such herbicides in the soil environment (Chen and Chen 1979; Chen *et al.* 1976; 198l; 1982; Chiang *et al.* 1987; Ishikawa *et al.* 1976). However, information regarding the mobility of the three herbicides in soils is limited. Mobility of a herbicide in soil environment is controlled, to a large extent, by its sorptive interaction with soil constituents. Earlier studies have indicated that soil organic matter is the principal adsorbent for the sorption of nonionic organic compounds on soil from water (Bailey and White 1970; Chiou *et al.* 1985; Hamaker and Thompson 1972). The partition coefficient (K_d, soil organic matter-water partition coefficient (K_{om}), and soil organic carbon-water partition coefficient (K_{oc}) could be used for assessing the strength of soil sorption (Hamaker and Thompson 1972). Chiou *et al,* (1983) suggested that the sorption of nonionic organic compounds by organic matter is essentially a partitioning process.

In this work, we compare the strengths of sorption and investigate the effects of soil properties on sorption of the three herbicides. In addition, an appropriate sorption equation for the three herbicides is derived.. Moreover, discussion is also made of the process of sorption of the three herbicides in soils which guide the behavior of chemicals in soil environments.

MATERIALS AND METHODS

Soil samples, having a wide range of soil characteristics, were collected from nine locations in the cultivated soil of paddy fields around Taiwan. Soils were sampled from surface down to 20 cm depth. Table 1 lists some of the properties of the soils. Pure butachlor of 99.2%, thiobencarb of 100% and chlomethoxyfen of

Correspondence to: Y.-S. Wang

Table 1. Some characteristics of the soils in this experiment.

Soil	Source	pH	clay	Sand	Silt	O.M.	C.E.C.
		(1:1)	%	%	%	%	meq/100g
A	Pintung 1	6.0	28.6	44.0	27.4	2.53	22.76
B	Taoyuan 1	5.3	28.6	43.4	28.0	2.94	23.01
C	Changhua	7.3	24.6	57.4	18.0	1.92	19.51
D	Kaohsiung	8.0	36.6	41.4	22.0	1.70	45.70
E	Tainan	7.3	19.2	43.4	37.4	1.86	22.15
F	Taichung	6.3	9.8	74.8	15.4	1.24	10.94
G	Hualien	7.6	16.6	46.8	36.6	2.55	19.33
H	Pintung 2	4.9	21.2	42.8	36.0	2.61	16.63
I	Taoyuan 2	4.4	33.2	42.8	24.0	2.01	22.14

99.9% purity were obtained from Monsanto Co., U. S. A., Kumiai Chemical Industry Co., Ltd., Japan and Ishihara Sangyo Co., Ltd., Japan, respectively.

Batch tests were used to determine the isotherm adsorption between herbicides and soils. Soil samples (5 g) were placed in 250-mL flasks, which were filled with aqueous solution of herbicide (50 mL) and capped with Teflon-faced silicone septa. All experiments were performed at a constant temperature of 25 ± 0.2 °C. The flasks were then shaked for 24 hrs with a shaking rate of 120 rpm. At the end of the shaking period, the soil-solution mixtures were centrifuged at 3,000 rpm (830 x g) for 10 min, and the supernatant was removed and stored at 4 °C for subsequent analysis. All experiments were conducted in duplicate. In the sorption isotherm studies, six batches were run for testing six different concentrations. Also, the original concentrations of herbicide solution were scattered from 0.12 to 8.67, 0.56 to 6.74 and 0.072 to 0.111 mg/L for butachlor, thiobencarb and chlomethoxyfen, respectively. Effects of pH on sorption of the three herbicide were examined via Tauyuan 1 soil (soil B in Table 1) at concentrations 2.27, 3.35 and 0.0225 mg/L for butachlor , thiobencarb and chlomethoxyfen, respectively, and by adjusting pH value from 2.7 to 9.8 with diluted HCl and NaOH. To determine the equilibration time for the sorption, sorption kinetics were studied in batch mode. Tauyuan clay loam (Soil B) (5 g) were equilibrated from 0.5 hr to 5 d with an aqueous herbicides solution. The concentrations of herbicides in aqueous solution at the beginning were 2.15 mg/L, 3.31 mg/L and 30.40 μ g/L for butachlor, thiobencarb and chlomethoxyfen, respectively.

Supernatant for herbicide analysis was diluted to 500 mL with organic-free deionized water. NaCl (5 g) were added to the solution and the solution was then extracted with benzene (100 mL x 3). After dehydration with anhydrous Na_2SO_4 (8 g), the benzene extracts were evaporated to dryness and the residue was dissolved with *n* -hexane (10 mL) and then analyzed by ECD-GC. ECD gas chromatography was performed through the experiment with Hitachi Gas Chromatography model 663-50. The glass column (2 m x 3 mm I. D.) with 3% OV-1 on 80/100 mesh Chromosorb WHP was employed to analyze butachlor and chlomethoxyfen. To analyze benthiocarb, the liquid phase of the packing material

was replaced by 3% OV-17. Operating temperatures were as follows: injection port, 250 °C; detector, 280 °C; column, 215 °C for analysis of butachlor and benthiocarb, 225 °C for analysis of chlomethoxyfen. Nitrogen was used as a carrier gas.

RESULTS AND DISCUSSION

Equilibrium times for the sorption of butachlor, thiobencarb and chlomethoxyfen on the soil were 5 d, 2 d and 2 hr, respectively. One day was chosen as the equilibrium period in batch test in this studies. By this period, around 90 % of butachlor and 97 % of thiobencarb were sorbed than they were at steady state. No significant pH effects on the sorption of the three herbicides were observed in a pH range from 2.7 to 9.8 (Table 2). This would be expected since changes in pH should not affect sorption of nonpolar organic compounds (Hamaker and Thompson 1972; Lin *et al.* 1970; Weed and Weber 1974).

Table 2. Effects of pH on sorption of the three herbicides in Tauyuan soil*

Butachlor	pH	2.7	4.2	6.0	6.3	7.5	9.6
	Sorbed %	80.3	72.9	74.3	75.8	76.3	77.1
Thiobencarb	pH	3.0	4,4	5.9	6.4	7.2	9.7
	Sorbed %	80.3	81.5	81.7	82.5	82.7	81.3
Chlometh-	pH	2.8	4.4	5.8	6.4	7.2	9.8
oxyfen	Sorbed %	98.5	98.4	98.5	97.8	97.3	97.7

*Original concentrations of butachlor, thiobencarb and chlomethoxyfen in water are 2.27, 3.35 and 0.0225 mg/L, respectively.

The data of the sorption experiments of the three herbicides were calculated for fitting equilibrium sorption equations such as Langmuir, Freundlich and linear equation (Table 3). Above results indicated that the isotherms were well represented by the Freundlich equation and linear equation. Table 4 denotes the sorption coefficient (K_d), and linear correlation coefficients (r) of the three herbicides from the linear equations :

$$S = K_d C \qquad (1)$$

Table 3. Average correlation coefficient of nine soils by linear regressive for describing the sorption of the herbicides with three conventional sorption

Herbicides	Sorption equations					
	Freundlish equation		Linear equation		Langmuir equation	
	Mean*	CV%**	Mean*	CV%**	Mean*	CV%**
Butachlor	0.995	0.22	0.987	1.16	0.574	34.8
Thiobencarb	0.991	1.08	0.972	1.39	0.885	102.8
Chlomethoxyfen	0.989	0.69	0.980	3.68	0.537	9.66

*Mean : Average correlation coefficient of nine soils.

**CV% : Standard error / mean x 100

The K_d values ranged from 11.14 to 33.62 for butachlor, from 13.37 to 54.33 for thiobencarb and from 120.39 to 788.64 for chlomethoxyfen. Above results imply that the order of strength of sorption are chlomethoxyfen > thiobencarb > butachlor. Soil F has the lowest organic matter content (1.236 %) and clay content (9.76 %), and show the lowest of strength of sorption.

Table 4. Sorption constant (K_d) and correlation coefficient (r) of herbicides butachlor, thiobencarb and chlomethoxyfen on nine soils by the linear equation

Soils	Herbicide					
	Butachlor		Thiobencarb		Chlomethoxyfen	
	K_d*	r	K_d*	r	K_d*	r
A	25.78	0.992	37.05	0.992	663.9	0.988
B	33.62	0.993	41.81	0.976	649.0	0.984
c	16.10	0.986	24.16	0.971	505.3	0.997
D	20.06	0.959	22.78	0.959	435.8	0.988
E	22.99	0.986	28.69	0.995	436.2	0.980
F	11.14	0.997	13.37	0.883	120.4	0.977
G	30.07	0.995	43.39	0.997	788.6	0.986
H	29.23	0.993	54.33	0.989	778.0	0.949
I	19.02	0.986	27.08	0.984	624.8	0.971

*Each K_d value was calculated by six batch tests of different concentrations (duplicate in each concentration) scattering from 0.12 to 8.67 mg/L, 0.56 to 6.74 mg/L and 0.072 to 0.111 mg/L for butachlor, thiobencarb and chlomethoxyfen solution, respectively.

Soil properties such as organic matter content, clay content and type, pH value and cation exchange capacity (CEC) exert a significant effect on the sorption of solute (Bailey and White 1970; Khan *et al.* 1979). Table 5 presents the linear correlation coefficients between K_d and soil properties in this studies. The K_d values of nine soils are highly correlated with organic matter content, whereas other soil properties including pH, clay content, and CEC are not. Fig. 1 displays the relationship between K_d and organic matter content of the soils. The slopes in Fig. 1 are equivalent to the experimental K_{om} value by the following equation:

$$K_d = K_{om} / 100 \times \% \text{ organic matter} \quad (2)$$

Table 5. Correlation coefficient between sorption coefficient and soil properties for three herbicides

Herbicides	Soil properties			
	pH	O.M.	Clay	CEC
Butachlor	0.2122	**0.9380	0.1674	0.0689
Thiobencarb	0.3578	*O.8991	0.0405	0.1380
Chlomethoxyfen	0.3082	*O. 8840	0.3130	0.0282

* P = 0.05 (>0.8114)

** P = 0.01 (>0.9172)

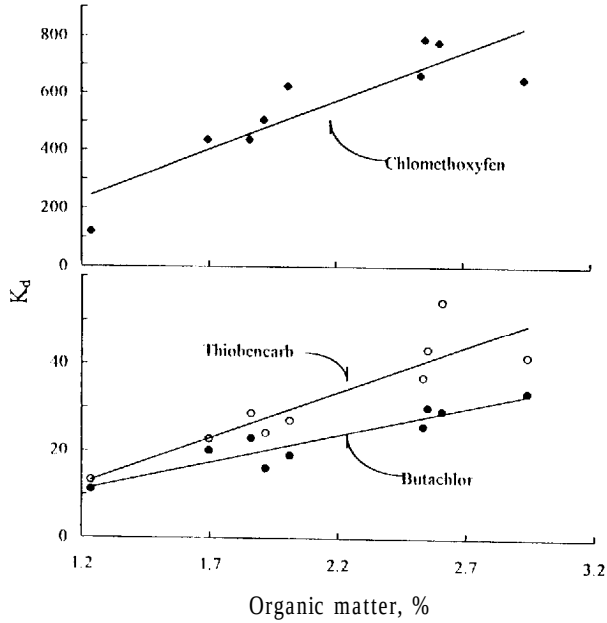

Figure 1. Relationship between K_d and organic matter content

K_{om} is soil organic matter-water partition coefficient. Relationship between water solubility (S_w, in μ mole/L in equation 3, and in mole/L in equation 4) and K_{om} of nonionic organic compounds have been reported by Chiou *et al.* (1979; 1983).

$$\log K_{om} = 4.04 - 0.557 \log S_w \qquad r^2 = 0.988 \qquad (3)$$

$$\log K_{om} = -0.729 \log S_w + 0.001 \qquad r^2 = 0.996 \qquad (4)$$

Table 6. A comparison of experimental and estimated values of K_{om}

Herbicides	Water solubility, S_w	K_{om}		
	(20 °C, μ g/ml)	Experimental	Estimated	
Butachlor	20	1,084	1,001*	1,033**
Thiobencarb	30	1,544	776*	741**
Chlomethoxyfen	0.39	26,291	11,065*	23,988**

* Estimate with equation 3.

** Estimate with equation 4.

Table 6 compares experimental and estimated values of K_{om}. Experimental K_{om} closely corresponded to the values calculated from the herbicide's water solubility. In particular, the K_{om} values of butachlor and chlomethoxyfen could be accurately predicted by their water solubility by fitting equation 4. Based on above evidence, the sorption of the three herbicides in soils seems to be a highly promising partitioning process.

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