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Received for review May 19, 1986. Revised manuscript received October 21, 1986. Accepted January 15, 1987. Mention of trademark or proprietary product does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval to the exclusion of other products that may also be suitable.

Adsorption of Butachlor to Soils

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The adsorption of butachlor [α -chloro-2,6-diethyl-*N*-(butoxymethyl)acetanilide] from water to rice paddy soils in Japan was studied with use of high-pressure liquid chromatography in order to better understand its behavior. The adsorption to most of the soils was better described by the Freundlich isotherm than by the Langmuir isotherm. The adsorption increased with butachlor concentration, soil organic carbon, and temperature. The positive temperature dependence of adsorption implies that the adsorption is endothermic and the heat of adsorption is positive. The heat of adsorption, ΔH , calculated from the Clausius-Clapeyron equation was 5-7 kcal/mol, indicating that the adsorption is physical and reversible. The kinetics of adsorption and the effect of molecular weight of the herbicide on adsorption were also studied. The adsorption of alachlor (α -chloro-2,6-diethyl-*N*-(methoxymethyl)acetanilide) was measured to study the molecular weight effect.

Adsorption of herbicides to soil from water is an important factor affecting their fate, biological activity, and persistence in soil. Better understanding of these processes will permit more effective weed control with minimum residues.

Adsorption of herbicides to soils can be described either by the Freundlich equation, where A = amount adsorbed, C = equilibrium concentration, and K , $1/n$ = constants

$$A = KC^{1/n} \quad (1)$$

$$\log A = 1/n \log C + \log K \quad (2)$$

or by the Langmuir equation (Bailey and White, 1970), where A_∞ = adsorption maximum and K_1, K_2 = constants.

$$A/A_\infty = K_1 C / (K_2 C + 1) \quad (3)$$

$$C/A = K_2 C / K_1 A_\infty + 1 / K_1 A_\infty \quad (4)$$

The Freundlich equation is purely empirical and imposes no limiting adsorption, while the Langmuir equation is based on theoretical consideration and shows maximum adsorption when a monolayer of molecules has covered all surfaces. Conformity of isotherms to the Freundlich or the Langmuir equation can be tested by measuring the linearity of plotting $\log A$ vs. $\log C$ for the Freundlich or plotting C/A vs. C for the Langmuir, respectively.

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Table I. Properties of Herbicides

common name	butachlor	alachlor
chemical name	α -chloro-2,6-diethyl- <i>N</i> -(butoxymethyl)acetanilide	α -chloro-2,6-diethyl- <i>N</i> -(methoxymethyl)acetanilide
mol wt	311.9	269.8
solubility in water, ppm		
10 °C	22	164
20 °C	23	212
35 °C	34	338

Adsorption of butachlor has been studied by Brightwell and Rueppel (1978). They found that the adsorption of butachlor followed the Freundlich isotherm and the Freundlich coefficient K value ranged from 3.5 to 20.0. They concluded that butachlor adsorption is reversible but butachlor would not be readily desorbed into water.

The purpose of this work was to study the butachlor adsorption in more detail to better understand the behavior of butachlor in a rice paddy field. Parameters studied were butachlor concentration, rate of adsorption, temperature effect, and molecular weight effect. Correlations with the Freundlich and the Langmuir isotherms were also determined.

MATERIALS AND METHODS

Herbicides. Technical-grade butachlor (93.1%) and alachlor (93.6%) produced by Monsanto were used as received. The molecular weight and the solubility in water of butachlor and alachlor at various temperature are shown

Table II. Soil Properties

soils ^a	carbon content, %	soil constituents, %			surface area, ^b m ² /g
		coarse sand	fine sand	silt	
A	5.86	25.0	21.4	43.7	0.10
B	2.92	28.5	26.4	23.4	0.42
C	4.04	11.0	28.1	23.2	0.83
D	1.17	1.3	17.5	53.6	0.76
E	6.19	7.0	29.5	03.3	0.67

^a Soil classification: A, paddy soil, alluvial ando soil; B, paddy soil, alluvial grey lowland soil; C, upland soil, diluvial ando soil; D, paddy soil, alluvial grey lowland soil; E, paddy soil, alluvial humic ando soil. ^b Calculated from the average surface area of each soil constituent (Yamane, 1975).

in Table I. The solubility data were obtained from Monsanto Agricultural Research, St. Louis, MO.

Soils. Four soil samples from rice paddies and one from an upland field in Japan were provided by Professor S. Kuwatsuka of Nagoya University along with data for organic carbon content and soil constituents (Table II). The total carbon content was determined by a C-N Corder (Yanagimoto MT-500, Tokyo). According to Professor Kuwatsuka, organic carbon content in the total carbon in the provided soil samples is negligible. The approximate surface area was calculated from the average particle size of each soil constituent (Yamane, 1975).

Reagent. Methanol used for extractions and HPLC analysis was HPLC grade (Merck).

Adsorption Measurements. Amounts ($1/4$ -g) of soil samples were weighed into 20-mL glass jars, and 5 mL of aqueous herbicide solution of known concentrations was added to each jar. The jars were sealed with Teflon-lined screw caps and mechanically shaken (Taiyo Recipro Shaker R-1, Taiyo Co., Tokyo) for various lengths of time (usually 17 h) at the desired temperature. After shaking, the solutions were centrifuged at the same temperature for 15 min at 3600 rpm. Of the supernatant 2.5 mL was then extracted with methanol on a reversed-phase octadecyl (C_{18}) extraction column (J. T. Baker Chemical Co.) to remove soil artifacts that could interfere with the LC analysis. The herbicide concentrations in the supernatant were then determined by high-pressure liquid chromatography (HPLC) using a Shimadzu LC4A equipped with UV detector and the 25-cm stainless-steel tube column packed with octadecylsilane silica gel (Ultron C-18 of Shinwa Kako, Tokyo). The column temperature was 65 °C. The mobile phase was an isocratic solution of methanol/water (77.5/22.5%, v/v), and the flow rate was 1.0 mL/min. After C_{18} column cleanup, both butachlor and alachlor could be successfully measured at 215-nm UV wavelength without interference.

For each measurement, a fortified blank was included to measure the effect of adsorption of the herbicides to the wall of the jar. The amount of herbicides adsorbed on soil was calculated by eq 5, where A is the amount adsorbed

$$A = (C_0 - C)V/m \quad (5)$$

(microgram/gram of soil), C and C_0 are the equilibrium concentration of herbicides after shaking with no soil and with soil (ppm), V is the volume of the solution (5 mL), and m is the weight of the soil (0.25 g). At least two replications were carried out for each measurement. A typical HPLC chromatogram for alachlor and butachlor after the extraction with methanol/water is shown in Figure 1.

RESULTS AND DISCUSSION

1. Rate of Adsorption. The adsorption of butachlor onto three soils at various shaking times up to 96 h is

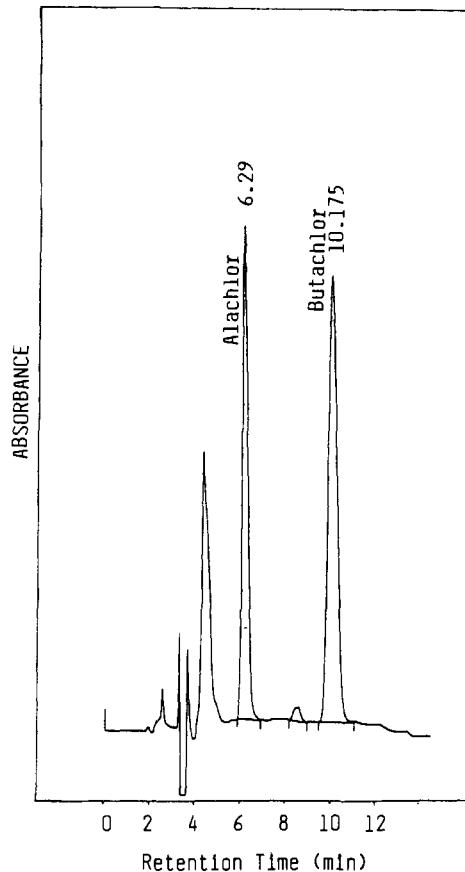


Figure 1. Typical HPLC diagram for alachlor and butachlor after extraction with methanol/water.

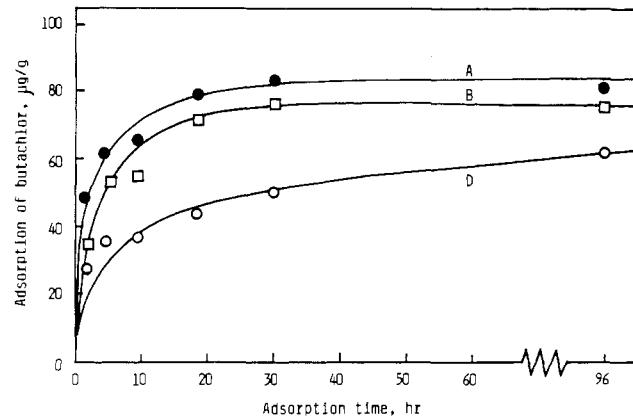


Figure 2. Rate of adsorption of butachlor to soils A, B, and D at 20 °C.

shown in Figure 2. For soils A and B, the adsorption initially increased rapidly and reached a plateau in about 30 h. The soil D adsorption was still increasing after 96 h and is probably due to the higher surface area and higher porosity of soil D (Table II). Adsorption of pesticides to porous adsorbents is generally very slow because the diffusion process of solute molecules into pores is very slow. This is particularly evident when the solute molecule is large (Sato and Ruch, 1980). According to Freed et al. (1973), kinetics of adsorption of pesticides can be explained on the basis of a diffusion-controlled process.

A standard adsorption time of 17 h was used to reduce experimental time although a thermodynamically stable equilibrium was not yet completely attained. The concentration of herbicide solution after 17 h (overnight) of shaking is termed "equilibrium concentration" for convenience. This approach is generally accepted for ad-

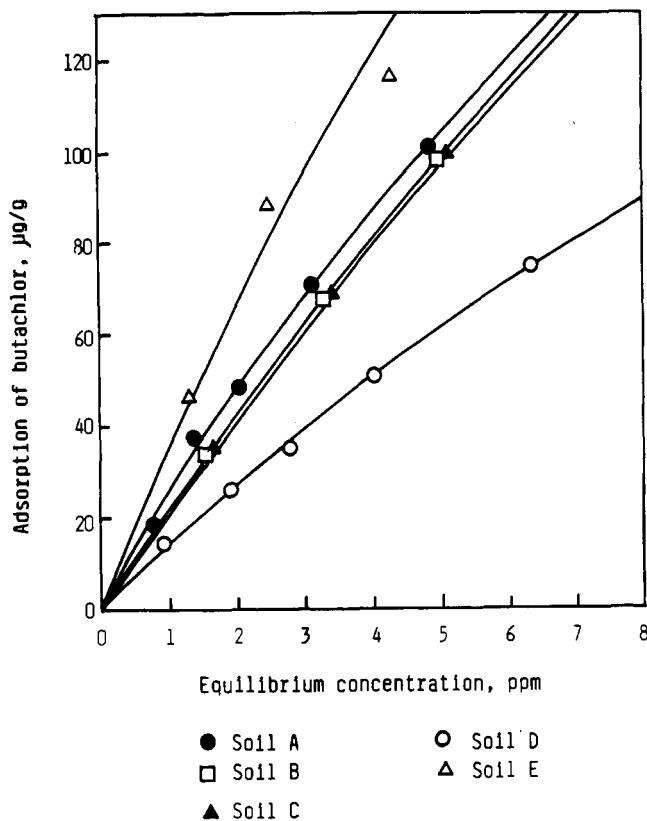


Figure 3. Adsorption isotherm for butachlor after 17 h at 20 °C.

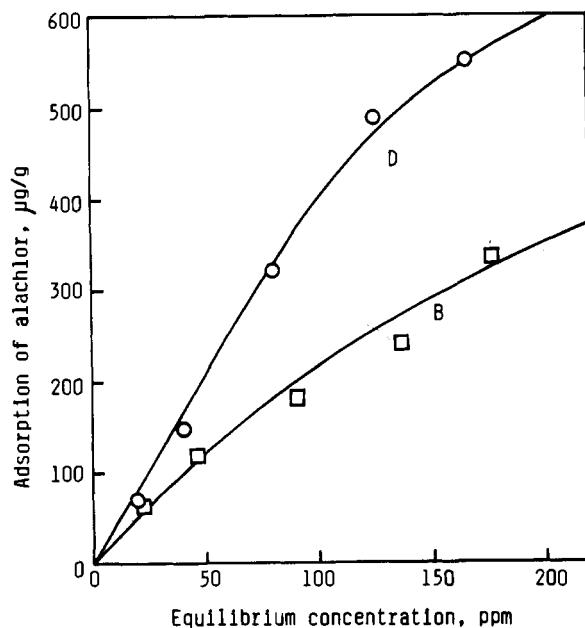


Figure 4. Adsorption isotherm for alachlor to soils B and D after 17 h at 20 °C.

sorption studies (Luce and Robertson, 1961).

2. Adsorption Isotherm. Adsorption isotherms for butachlor and alachlor are shown in Figures 3 and 4, respectively. The adsorption of alachlor was measured at higher concentration because the solubility in water is much higher than that of butachlor. The comparison of butachlor and alachlor adsorption at the same concentration is shown in Figure 5. In both cases, the adsorption increases steeply at low concentration and then rises more slowly at higher concentration. No limiting adsorption was observed within the range of concentrations used. In all of the above experiments, because of the limited solubility of the herbicides, a state where the surface was completely

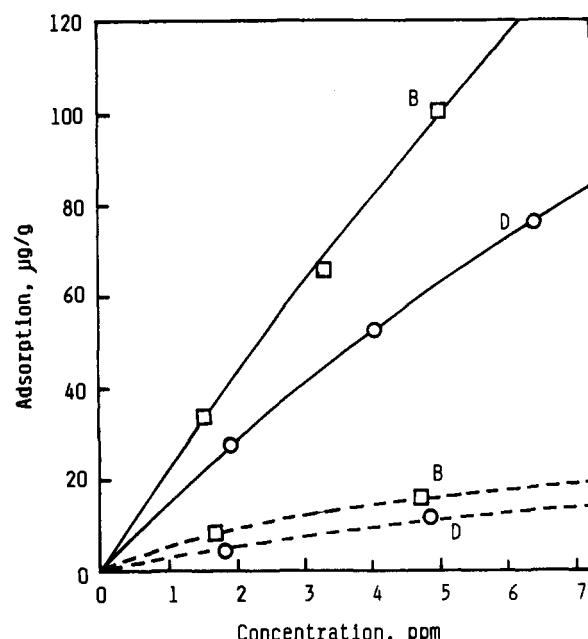


Figure 5. Adsorption of butachlor (solid lines) and alachlor (dotted lines) onto soils B and D after 17 h at 20 °C.

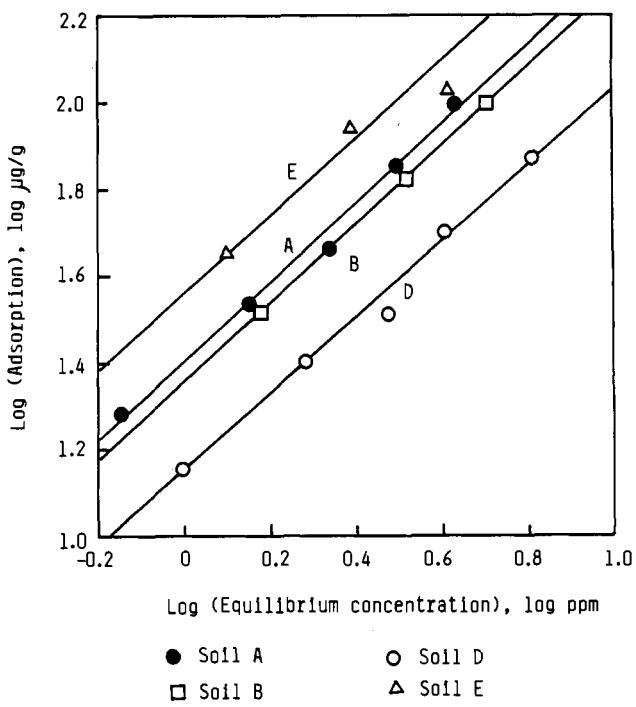


Figure 6. Freundlich plots for butachlor adsorption.

Table III. Freundlich Constants and Correlation Coefficients (*r*) for Butachlor and Alachlor Adsorption at 20 °C

soils	butachlor			alachlor		
	<i>r</i>	<i>K</i>	<i>1/n</i>	<i>r</i>	<i>K</i>	<i>1/n</i>
A	0.987	25.2	0.905			
B	0.940	23.4	0.885	0.996	7.91	0.71
D	0.999	14.8	0.870	0.996	3.42	1.01
E	0.982	38.9	0.798			

covered was never reached. Figures 6 and 7 and Figures 8 and 9 show the Freundlich plots and the Langmuir plots for butachlor adsorption and alachlor adsorption, respectively. The figures show that adsorption of butachlor and alachlor is better described by the Freundlich equation than by the Langmuir equation, which agrees well with the results of most herbicide adsorption studies (Bailey and

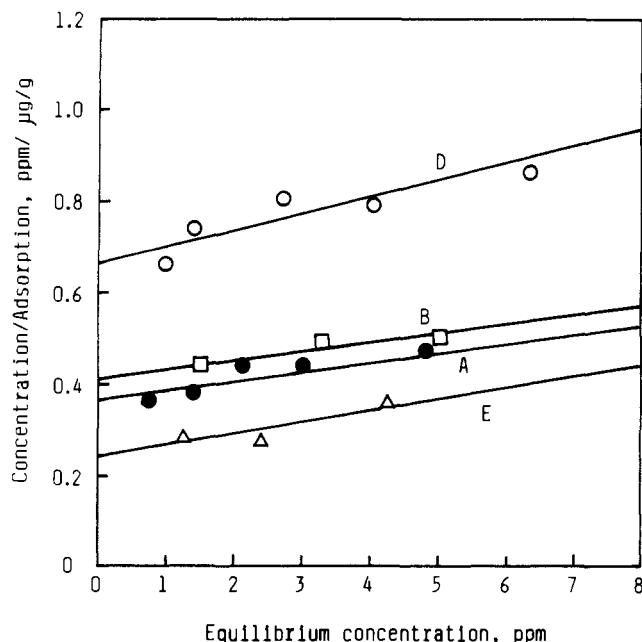


Figure 7. Langmuir plots for butachlor adsorption.

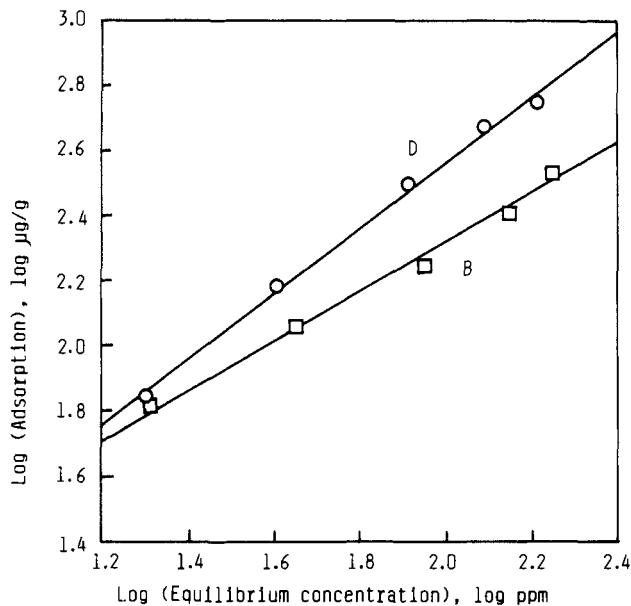


Figure 8. Freundlich plots for alachlor adsorption (17 h, 20 °C).

White, 1970; Freed and Haque, 1973; Kozak and Weber, 1983). The Freundlich plots show that the correlation coefficient is high ranging from 0.94 to 0.99 for all systems. The K values for butachlor are much higher than those for alachlor as shown in Table III, which agrees well with the results of Brightwell and Rueppel (1978) and Suba and Pearson (1979).

3. Comparison of Adsorption of Butachlor and Alachlor. The adsorption of butachlor is several times greater than that of alachlor at the same concentration as shown in Figure 5. This result supports the premise that the adsorption increases with the molecular weight of adsorbate in the same series of molecular structure (Sato and Ruch, 1980). The lower adsorption of alachlor to soils in comparison with butachlor accounts for the higher soil mobility of alachlor observed by Takematsu et al. (1971).

It is interesting to note that the alachlor adsorption to soil B is lower than that to soil D at high alachlor concentration (20–200 ppm) as shown in Figure 4, but lower than that to soil D at lower concentration (0–7 ppm) as shown in Figure 5. This is attributed to the higher value

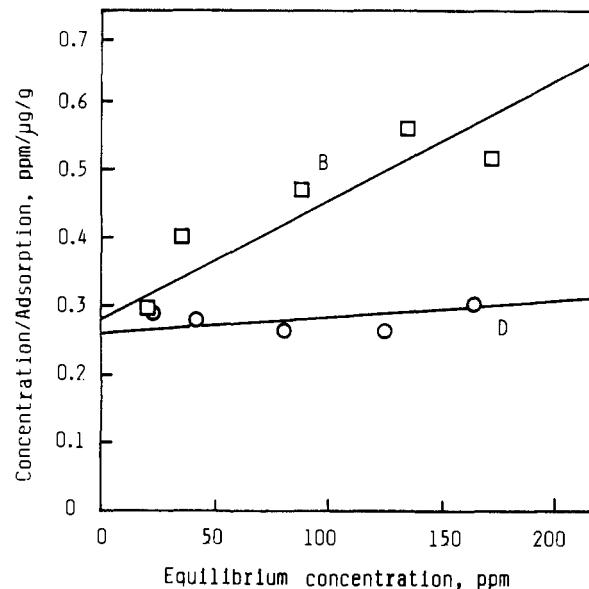


Figure 9. Langmuir plots for alachlor adsorption to soils B and D (17 h, 20 °C).

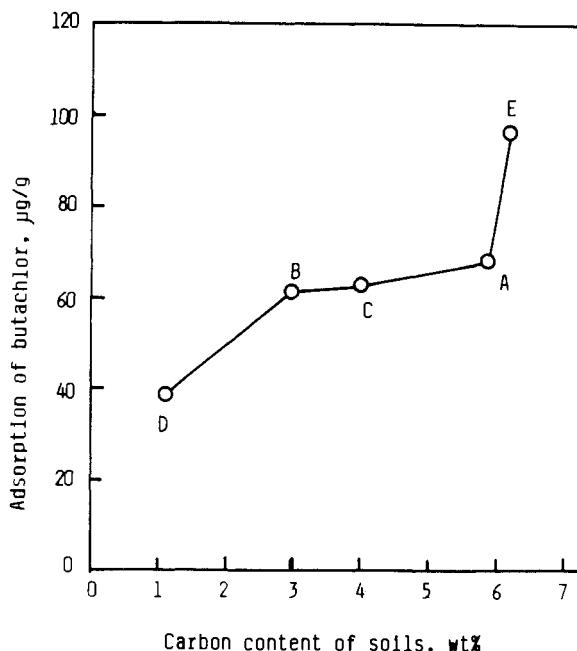


Figure 10. Carbon content in soils vs. butachlor adsorption at 3 ppm equilibrium concentration (17 h, 20 °C).

of $1/n$ of the Freundlich isotherm for soil D than for soil B (Table III).

4. Effect of Soil Properties. Adsorption of butachlor increased with an increase in organic carbon content in soils as shown in Figure 10, which agrees well with the results by Brightwell and Rueppel (1978). Weber and Peter (1982) demonstrated that organic matter was the primary adsorbing surface in soils for adsorption of acetanilide herbicides. These results support the fact that herbicide activity decreases as organic matter in soils increases (Carringer et al., 1975).

5. Effect of Temperature. The adsorption of butachlor at 10, 20, and 35 °C was measured by shaking the solution for 17 h at each temperature and centrifuged at the same temperature. In general, herbicide adsorption onto soils from aqueous solution decreases with temperature because the solubility of most herbicides in water increases with temperature (Freed and Haque, 1973; Harris and Warren, 1964; Mills and Bigger, 1969; Weber et al.,

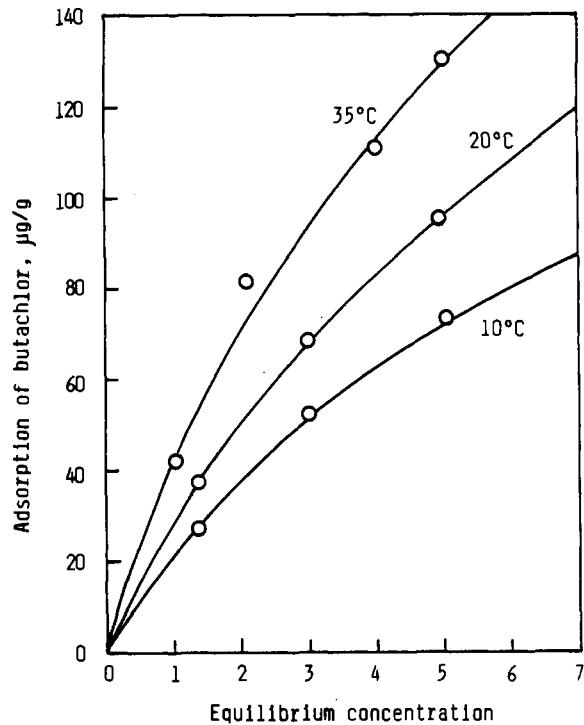


Figure 11. Adsorption of butachlor to soil A at 10, 20, and 35 °C.

Table IV. Effect of Temperature on Adsorption of Alachlor to Soil A (17 h)

temp, °C	equil concn, ppm	adsorp, µg/g
10	84.1	255
20	84.8	299
35	81.4	391

1965). However, butachlor adsorption increased significantly with temperature as shown in Figure 11 and 12, although the solubility increases slightly with temperature as shown in Table I. The same trend on the temperature dependence was observed on alachlor adsorption as shown in Table IV, although the solubility increased significantly with temperature.

The increase in adsorption with temperature had been reported for polymer adsorption (Luce and Robertson, 1961; Koral et al., 1958) and nonionic surfactant adsorption (Corkill et al., 1966), but little is known for herbicide adsorption (Haque and Sexton, 1968; Pradip and Fuerstenau, 1985).

To confirm this unusual temperature dependence of adsorption, two additional experiments were conducted. First, all of the solutions were centrifuged at room temperature (20 °C) after being shaken at various temperature to nullify the effect of temperature on centrifugation. Second, the adsorption time was extended to 45 h in order to confirm the results at equilibrium adsorption. In all cases, the butachlor adsorption increased with temperature.

The positive temperature dependence of adsorption indicates that the adsorption process is endothermic and the isosteric heat of adsorption, ΔH , is positive. However, the free energy of adsorption, $\Delta G(\Delta H - T\Delta S)$, must be negative for adsorption to take place. Since ΔH is positive as determined, $T\Delta S$ must be positive and greater than ΔH . Koral et al. (1958) observed the same behavior of adsorption and explained this on the basis that, during the adsorption of the adsorbate, some solvent molecules are released from the surface of adsorbent and go into solution, which increases the translational degree of freedom and consequently increases the entropy change, ΔS . It is quite

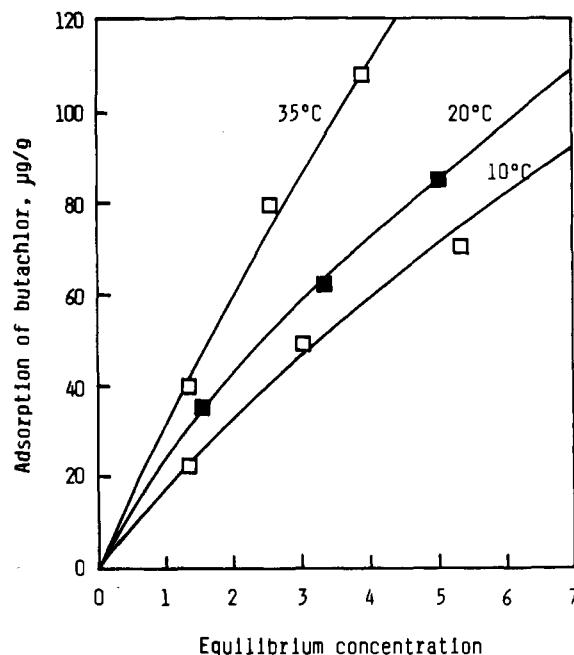


Figure 12. Adsorption of butachlor to soil B at 10, 20, and 35 °C (17 h).

likely that the same mechanism is also applicable to the present system to account for the positive temperature dependence of adsorption since the soil surface must be highly hydrated and a large number of water molecules must be displaced by the herbicide molecules. The entropy change is thereby fairly large in the herbicide adsorption from the aqueous solution.

The isosteric heat of adsorption, ΔH , can be calculated from these data (Koral et al., 1958; Freed and Haque, 1973; Yamane and Green, 1972). Assuming that the activity of the herbicide molecules at the soil surface does not change if the amount of adsorption is kept constant, ΔH can be expressed by eq 6, where R is the gas constant (1.987

$$\frac{\Delta H}{R} = \frac{\Delta H_0^s - H_0^l}{R} = \frac{\partial}{\partial} \left(\frac{\ln C}{1/T} \right)_x \quad (6)$$

cal/deg·mol), C is the equilibrium concentration of adsorbate at a fixed amount of herbicides adsorbed X , and H_0^s and H_0^l are the partial molal enthalpies of the herbicide on the soil surface and in the liquid, respectively. This expression requires that the chemical potential of the adsorbate in solution, μ_0^l , is equal to the chemical potential of the adsorbate at the surface, μ_0^s , and then one may write

$$\mu_0^l + RT \ln a_1 = \mu_0^s + RT \ln a_s \quad (7)$$

where a_1 and a_s are activities of the adsorbate in the solution and on the surface, respectively. Equation 6 is obtained by differentiating eq 7. Since the herbicide concentrations of the present work are very dilute, the activities can be replaced by the concentration.

The equilibrium butachlor concentrations, C , at a given adsorption to soils A and B vs. the reciprocals of the absolute temperature are shown in Figures 13 and 14. $\partial \ln C / \partial (1/T)$ can be determined from the slope of the straight lines. The isosteric heats of adsorption, ΔH , of butachlor to soil B and soil A calculated from eq 6 were 5 and 7 kcal/mol, respectively, indicating that the absorption of butachlor onto soils is physical and reversible. The reversibility between adsorption and desorption of butachlor plays an important role in controlling its concentration in rice paddy water when the amount of water varies due to dry weather or rain.

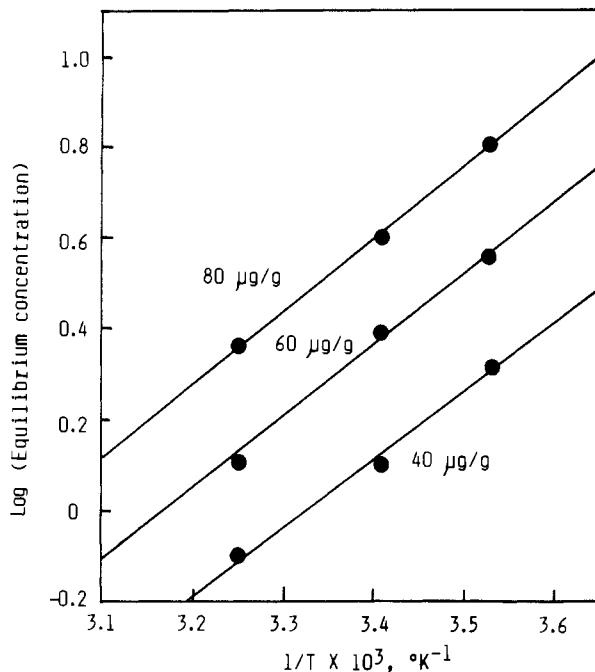


Figure 13. Equilibrium concentration of butachlor at a given surface coverage to soil A vs. the reciprocal of absolute temperature.

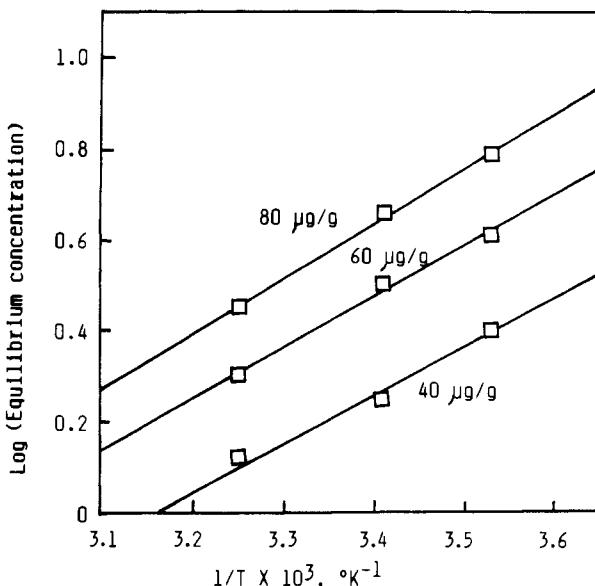


Figure 14. Equilibrium concentration of butachlor at a given surface coverage to soil B vs. the reciprocal of the absolute temperature.

CONCLUSIONS

The rate of adsorption of butachlor was very rapid initially and then decreased with time. The time needed for achieving "equilibrium" depends on the soil texture, usually 30 h at 20 °C.

The adsorptions of butachlor increased markedly with increasing organic carbon content. This accounts for the fact that the optimum application rate of butachlor in rice paddies tends to increase as the organic matter content in soils increases.

The adsorption of both butachlor and alachlor was better described by the Freundlich isotherm than by the Langmuir isotherm. Butachlor was adsorbed up to about 7 times as much as alachlor was by the same soil as expected from the lower solubility in water.

The adsorption of butachlor and alachlor increased with the increase in temperature, which implies that the adsorption is endothermic. The heat of adsorption of butachlor to soils calculated from the Clausius-Clapeyron equation was 5–7 kcal/mol, indicating that the adsorption is physical and reversible.

The reversibility of adsorption plays an important role in controlling its concentration in rice paddy water. As the concentration in rice paddy water increases, the adsorption onto soils increases as shown in Figures 3–5, while as the concentration decreases, desorption takes place. Therefore, the herbicide concentration in rice paddy water can be maintained in narrow desired range by the reversibility between adsorption and desorption.

ACKNOWLEDGMENT

We are grateful to Prof. S. Kuwatsuka, Department of Agricultural Chemistry, Nagoya University, Japan, for providing us with soil samples with physical data and for helpful suggestions during the course of this work. We also thank W. R. Udell, Monsanto Agricultural Research Station, Ibaraki, Japan, for his guidance in the project.

Registry No. Butachlor, 23184-66-9; alachlor, 15972-60-8.

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Received for review December 26, 1985. Revised manuscript received June 9, 1986. Accepted December 8, 1986.