

**AN INVESTIGATION INTO THE MASS  
TRANSFER PROPERTIES OF  
A PESTICIDE ONTO  
ABIOTIC MEDIA**

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## AN INVESTIGATION INTO THE MASS TRANSFER PROPERTIES OF A PESTICIDE ONTO ABIOTIC MEDIA

### INTRODUCTION

The contamination of ground water has been a major concern in recent years. The extent and sources of ground water contamination have been the subject of numerous studies and many papers have been published [1,2,3.]. One of the difficulties in ground water contamination assessment is that it occurs underground, out of sight. Due to the slow movement of ground water, the contamination may not be detected until long after the source of the contamination has disappeared. Once ground water is contaminated, it is very difficult to clean. There are generally two approaches to solve ground water contamination problems. First is prevention of the contamination and second is to remove contaminants from the ground water. A knowledge of mass transfer properties of the contaminants in the unsaturated-saturated zone is necessary, whether one wants to prevent ground water contamination, or restore the aquifer after contamination has occurred.

A common source of ground water contamination is the application of synthetic organics to the land's surface. When the applied organics pass through the unsaturated zone, they are subject to evapotranspirations, biodegradation, plant uptake, soil adsorption, or movement into an aquifer. Once in the ground water, the contaminants will move by

advection and dispersion, and be retarded by adsorption. In addition, biodegradation may lower contaminant concentration. Because of the complexity of the transport of ground water contaminants, there remains uncertainty as how to quantify the combined effects of the above processes on the fate of applied organics in the soil environment. However, progress has been made in studies on single effects, such as biodegradation or adsorption. Bower, McCarty, and others have investigated the biodegradability of many halogenated organics under different conditions[4,5,6]. Mathews and Crittenden and others have published papers on abiotic adsorption of organics onto abiotic columns[7,8,9]. However, for the abiotic column study, the previous works mainly focused on activated carbon rather than soil adsorption.

Although very few studies dealing with the kinetics of adsorption onto soil have been conducted, numerous investigations on batch equilibrium adsorption for soil have been made[10,11]. It is generally agreed that the distribution factor "Kd" of hydrophobic organics such as lindane, increases with the soil organic content. Quantitative relationships between Kd and soil organic content have been evaluated by several authors[12,13,14]. One approach is to obtain the water/octanol distribution factor (Kow) for a specific pesticide, then correlate Kow to Koc, and then calculate Kd:

$$K_{ow} = C_o/C_w \quad (1)$$

$$K_{oc} = a \log K_{ow} + b \quad (2)$$

$$K_d = (K_{oc})(f_{oc}) \quad (3)$$

Where:  $C_o$  = equilibrium concentration of pesticide  
in the octanol

$C_w$  = equilibrium concentration of pesticide in  
water

$K_{ow}$  = octanol/water distribution coefficient of  
pesticide

$K_{oc}$  = distribution coefficient of pesticide on  
soil organics and water

$a, b$  = constants

$f_{oc}$  = soil organic content

Drawbacks of the above correlation are that it does not address the specific organic in the soil, nor does it allow for conditions other than equilibrium.

Wershaw [15] proposed a model for humic materials and their interactions with hydrophobic organics. In Wershaw's model, humic materials are described as membrane-like aggregates which are composed of partially decomposed plant derived components. These compounds are held together by weak bondings such as hydrogen bonding. The membrane-like humic structure consist of polar hydrophilic exterior surfaces with hydrophobic interiors. Polar organics will interact with the exteriors of the polar groups of the humic structures while hydrophobic organics tend to partition into, rather than adsorb onto, the hydrophobic interiors of the structure.

There have been many mathematical models incorporating the phenomena of advection, dispersion, adsorption, which occur when a non-biologically reactive organic transports through a saturated or unsaturated medium[16,17,18]. The one dimensional basic mathematical expression for passing through a medium can be expressed as:

$$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial z} + D \frac{\partial^2 C}{\partial z^2} - \frac{\rho_b}{\epsilon} \frac{\partial q}{\partial t} \quad (4)$$

Where: C = Pollutant concentration in aqueous phase, (gm/l).

t = time, (sec)

u = directional velocity, (cm/sec)

z = distance in flow direction

D = dispersion coefficient, (cm<sup>2</sup>/sec)

ε = porosity of the medium

ρ<sub>b</sub> = bulk density of the medium, ( gm/cm<sup>3</sup>)

q = mass of solute adsorbed per unit of dry medium, (gm/gm)

If we ignore axial dispersion, Eq.(1) becomes:

$$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial z} - \frac{\rho_b}{\epsilon} \frac{\partial q}{\partial t} \quad (5)$$

Assuming the adsorption is rapid relative to flow velocity (i.e. local equilibrium always exists), and the adsorption is linear:

$$\frac{\partial q}{\partial C} = K_d \quad (6)$$

Where K<sub>d</sub>=distribution coefficient, (cm<sup>3</sup>/gm)

Eq.(2) becomes:

$$-u \frac{\partial c}{\partial z} = R \frac{\partial c}{\partial t} \quad (7)$$

Where  $R = 1 + \frac{\rho_b K_d}{\epsilon}$ , known as retardation factor.

Equation (7) has been used by some authors [19] to develop models that can predict the transport of hydrophobic organic compounds in ground water.

Equation (7) is valid only if local equilibrium always exists and the adsorption is linear. However, this is not always the case in field situations.

Non-linear adsorption can be expressed by the Freundlich equation:

$$x/m = KC^{1/n} \quad (8)$$

Where:  $x$  = mass of solute adsorbed to the medium, (gm).

$m$  = mass of the medium, (gm).

$C$  = solute concentration in aqueous phase (gm/l)

$K$  and  $1/n$  are constants determined by batch adsorption test.

If  $1/n$  equals to unity, then the adsorption is linear and  $K$  becomes  $K_d$ , as defined in Equation (6). The results of batch tests indicate, in many cases,  $1/n$  is not equal to unity, thus the adsorption is not always linear.

Freeze and Cherry [20] presents concentration profiles for three retardation conditions (see Figure 1). Curve "a" describes the dispersed front of non-retarded solute. In

this case the solute is not adsorbed to the medium. Curve "b" describes the situation that equilibrium partitioning occurs between liquid and solid in the case described by Equation(4). Curve "c" describes the situation that the solute in solid phase is not in equilibrium with the aqueous phase. In this case, the adsorption is relatively slow when compared to the flow velocity and the amount of solute in the solid phase is less than that would be when equilibrium exists. Curve "c" is considered to reflect the actual situation in many cases.

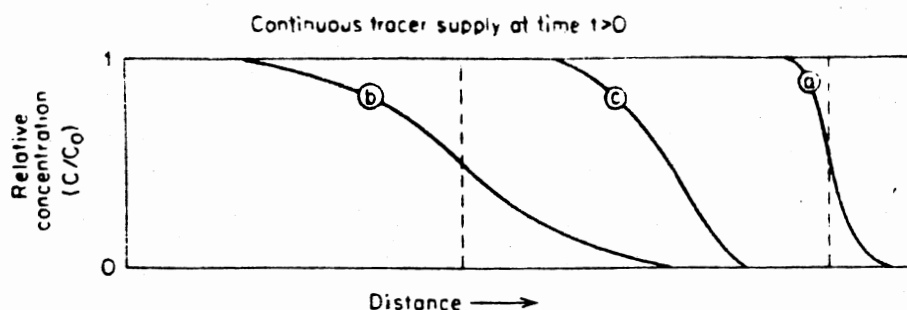


Figure 1. Non-linear Kinetically Limited Retardance (from Freeze and Cherry [5])

From the above discussion, it can be easily seen that Equation(4) will not always address the abiotic continuous flow system appropriately because of improper assumptions. An alternative is to use kinetically based mass transfer approaches to describe the system more adequately.

In a kinetic analysis, adsorption is considered time dependent rather than instantaneous. The overall reaction rate is described by various resistances which individually control the adsorption process. The adsorption of solute

from aqueous phase to the solid medium usually undergoes the following steps:

1. Solute transfer from bulk liquid to the liquid-solid interface.(external resistance)
2. Solute diffuses along any pores and solid surface (internal resistance)
3. Solute adsorbed onto the solid.(adsorption reaction)

The adsorption speed is controlled by the slowest step or resistance of the above. In activated carbon adsorption step 3 (the reaction step) is usually very fast and its effect on the overall resistance is negligible. The adsorption rate is usually controlled by step 1 and/or step 2.

The basic kinetic approach to be applied to a continuous flow abiotic system with advection and adsorption is to solve Equation(4), coupled with the mathematical expression that describes the diffusion into a single particle. This approach is often difficult and requires numerical techniques. Practically, Equation(1) is solved by using a model that represents one or more mass transfer mechanisms, and introducing equilibrium data.

When external mass transfer is the dominant resistance, i.e. the resistance for the solute to pass through the bulk liquid to the liquid-solid interface is far greater than other resistances, the system can be described by an external mass transfer model[9]:



$$\frac{\partial q}{\partial t} = \frac{K_f a}{\rho_b} (C - C_e) \quad (9)$$

Where  $K_f$  = mass transfer coefficient (cm/sec)

$a$  = specific area (cm<sup>2</sup>/cm<sup>3</sup>)

$C_e$  = equilibrium concentration at the liquid-solid interface (mg/l)

Other symbols have been previously described.

When internal mass transfer resistance becomes dominant, i.e. the resistance for the solute to diffuse along the pores and solid surface is far greater than other resistances, the system can be described by the internal mass transfer model[8]:

$$\frac{\partial q}{\partial t} = K_s a (q^* - q) \quad (10)$$

Where:  $K_s$  = mass transfer coefficient (cm/sec)

$a$  = specific area of medium, (cm<sup>2</sup>/cm<sup>3</sup>)

$q^*$  = solute adsorbed per unit of medium when equilibrated with liquid phase concentration.

Other symbols are defined as before

In addition to these models, the system can also be described by surface kinetic model[21]:

$$\frac{\partial q}{\partial t} = K_a C (q^* - q) - k_d q \quad (11)$$

Where:  $K_a$  = mass transfer coefficient, (l/gm-sec)

$k_d$  = desorption rate constant (1/sec)

While the external and internal resistance models can be applied to the adsorption where any parts of the solid

surface have the same affinity to the solute, the surface kinetic model can be used to describe the adsorption where different locations of the solid surface have different affinity to the solute. This model employs a second reversible surface reaction to describe the uptake of solute from liquid to solid. The overall uptake rate,  $\frac{\partial q}{\partial t}$ , is equal to the adsorption rate minus the desorption rate. The adsorption rate in this model is assumed to be proportional to the product of solute concentration in liquid and the difference between the maximum achievable solute uptake and the uptake at time  $t$ , and the desorption rate proportional to the solute uptake at time  $t$ .

Thomas[22] presented an approximate solution to the above equation as follows:

$$C/C_0 = \frac{1}{1 + \exp [k/Q (q_0M - C_0V)]} \quad (12)$$

Where  $C$  = effluent concentration,  $\mu\text{g}/\text{l}$

$C_0$  = influent concentration,  $\mu\text{g}/\text{l}$

$k$  = adsorption rate constant,  $\text{l}/\text{day}-\mu\text{g}$

$V$  = volume of water treated, liter

$M$  = mass of adsorbent,  $\mu\text{g}$

$q_0$  = adsorption capacity,  $\mu\text{g}/\mu\text{g}$

$k$  and  $q_0$  can be obtained from the experimental breakthrough data and the effluent concentration profile,  $C/C_0$  versus time, can be predicted.

In addition to this type of fundamental analysis, two available models were evaluated in this research. These were

the Homogeneous Surface Diffusion Model (HSDM) and Soil Breakthrough Model (SBM). Hand et al [23] derived the Homogeneous Surface Diffusion Model for activated carbon fixed bed adsorber. Basic equations for the model are as follows:

The liquid phase mass balance equation:

$$\frac{\partial \bar{C}(\bar{Z}, T)}{\partial \bar{Z}} = \frac{1}{(D_g + 1)} \frac{\partial \bar{C}(\bar{Z}, T)}{\partial T} + 3 St [\bar{C}(\bar{Z}, T) - \bar{C}_s(\bar{Z}, T)] \quad (13)$$

The intraparticle mass balance equation:

$$\frac{\partial q(\bar{r}, \bar{Z}, T)}{\partial T} = \left(1 + \frac{1}{D_g + 1}\right) \frac{Ed}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left[ \bar{r}^2 \frac{\partial q(\bar{r}, \bar{Z}, T)}{\partial \bar{r}} \right] \quad (14)$$

Where:  $\bar{C}$  = reduced fluid phase concentration, =  $C/C_0$

$\bar{Z}$  = reduced axial coordinate, =  $Z/L$

$D_g$  = Solute distribution parameter

$T$  = Mass throughput

$St$  = Stanton number

$\bar{C}_s$  = reduced fluid phase concentration at exterior surface of adsorbent particle, =  $C_s/C_0$

$\bar{q}$  = reduce adsorbent phase concentration, =  $q/q_e$

$\bar{r}$  = reduced radial coordinate, =  $r/R$

$Ed$  = diffusivity modulus

In the HSDM surface diffusion is assumed to be the predominant intraparticle mass transfer mechanism. The model incorporates liquid and intraparticle mass transfer mechanisms to obtain an effluent concentration profile.

Hutzler [24] developed the Soil Breakthrough Model to predict breakthrough curves in soil columns. Uniform,

spherical soil particles and linear adsorption were the major assumptions in the model. The basic equation for the model is as follows:

$$\frac{\partial C_b(Z,t)}{\partial t} = E \frac{\partial^2 C_b(Z,t)}{\partial Z^2} - v \frac{\partial C_b(Z,t)}{\partial Z} - \frac{3(1-\xi)k_f}{R} [C_b(Z,t) - C(r=R,Z,t)] \quad (15)$$

Where:  $C_b$  = bulk liquid phase concentration

$Z$  = axial position

$t$  = time

$E$  = axial diffusion and dispersion coefficient

$\xi$  = porosity of adsorbent

$k_f$  = mass transfer coefficient

$C$  = liquid phase concentration in  
the aggregate pores

$R$  = aggregate radius

$r$  = radial coordinate

These models are applicable to the abiotic adsorptive system, in which no biological degradation took place. These are especially appropriate for fixed-bed activated carbon adsorbers where adsorption is the dominant mechanism. For soil adsorption, other factors such as interaction between the solute and soil organics may make the system more complicated, as will be discussed later. In this investigation, experimental soil column breakthrough data were used to verify whether the above models were

appropriate to describe the soil system. Hypotheses that explain the results are presented.

## **MATERIALS AND METHODS**

### solute

The pesticide lindane ( $C_6H_6Cl_6$ ) was used in this investigation as it is a commonly used agricultural chemical in Oklahoma. It is a non-ionic, non-polar hydrophobic chlorinated hydrocarbon pesticide. Solid lindane for this investigation was obtained from the Supelco Company. Lindane of 2.5 milligrams were dissolved in 1 liter of distilled water. To make lindane dissolve more rapidly, magnetic agitation was used. This solution was diluted with distilled water to a total volume of 25 liters. This resulted in a final solution of 100 ug/l which was used as influent to the soil columns.

### Adsorbents

Original and serially extracted soils were used as adsorbents in this investigation. The purpose of using serially extracted soils was to identify the roles of adsorption by different types of soil organics. The extraction method was given by Stevenson[25]. The soil was first sieved using a US No. 200 sieve with 0.0075 mm openings (passing materials were used). The first extraction removed lipids (oils, waxes, greases) by using diethyl ether as a solvent. Diethyl ether is a non-polar solvent which can be used to concentrate nonpolar organics. The second extraction removed resins by using ethyl alcohol. Resins are

amorphous mixtures of carboxylic acids and terpenes occurring as exudations of many varieties of trees and shrubs. They are polar and soluble in alcohols. Ethyl alcohol was chosen to remove these materials, organic matter in the original and the serially extracted soils was determined by the titration method proposed by Gaudette[26]. The properties of the soils used for this study are shown in Table I.

Table I Properties of Soil Adsorbents Used for This Study

	Original Soil	Lipids-free Soil	Resins-free Soil
Total organic carbon (%)	1.54	1.21	1.15
Lipids (%)	0.1157	0	0
Resins (%)	0.0122	0.0122	0
Water Soluble Polysaccharides(%)	0.48	0.48	0.48
Hemicellulose(%)	0.0024	0.0024	0.0024
Cation Exchange Capacity (me/100gm)	12.3	11.7	11.9
Surface Area m <sup>2</sup> /gm	15	21	20

Source[27]

To reduce the interference of biological activities, all soil adsorbents were autoclaved at 15 psi and 250°F for 30 minutes before filling the columns.

#### Columns

Plexiglass columns 9 inches long and 2.5 inches in diameter were used in this investigation. Sample ports at 3 inch intervals were made in each column.

### System Construction and Operation

The original and sequentially extracted soils were placed in three plexiglass columns. Glass beads of 3 mm in diameter were mixed with the soil to increase hydraulic conductivity. Columns were operated in the same manner with the exception of the different soil adsorbents. Powered by a peristaltic pump with multiple heads set to deliver 10 ml/hr of solution, the columns were operated in downflow mode. Calibration of the pump delivery rates was accomplished by pumping distilled water through the columns and measuring the flow rate with a stop watch and a volumetric flask. The flow rate was checked daily. It was found that the flow rate slowly decreased with time during the initial stages of the experiment before becoming constant. Lindane was pumped into the systems after a steady flow rate was established. Effluent samples from the bottom and sample ports were collected daily for lindane analysis. The configuration of the experimental system is shown in Figure 2. Physical operation parameters for the columns were as follows:

Column Size: Inside Diameter: 2.5 inch. Length: 9 inch

Soil Weight: 285.1 gram

Soil Volume: 271.5 cm<sup>3</sup>

Flow rate: 10 ml/hr

Empty Bed Contact Time: 27.15 hours

Superficial Velocity:  $2.3 \times 10^{-4}$  cm/sec

pH = 6.2

Influent Concentration: 100 ug/l

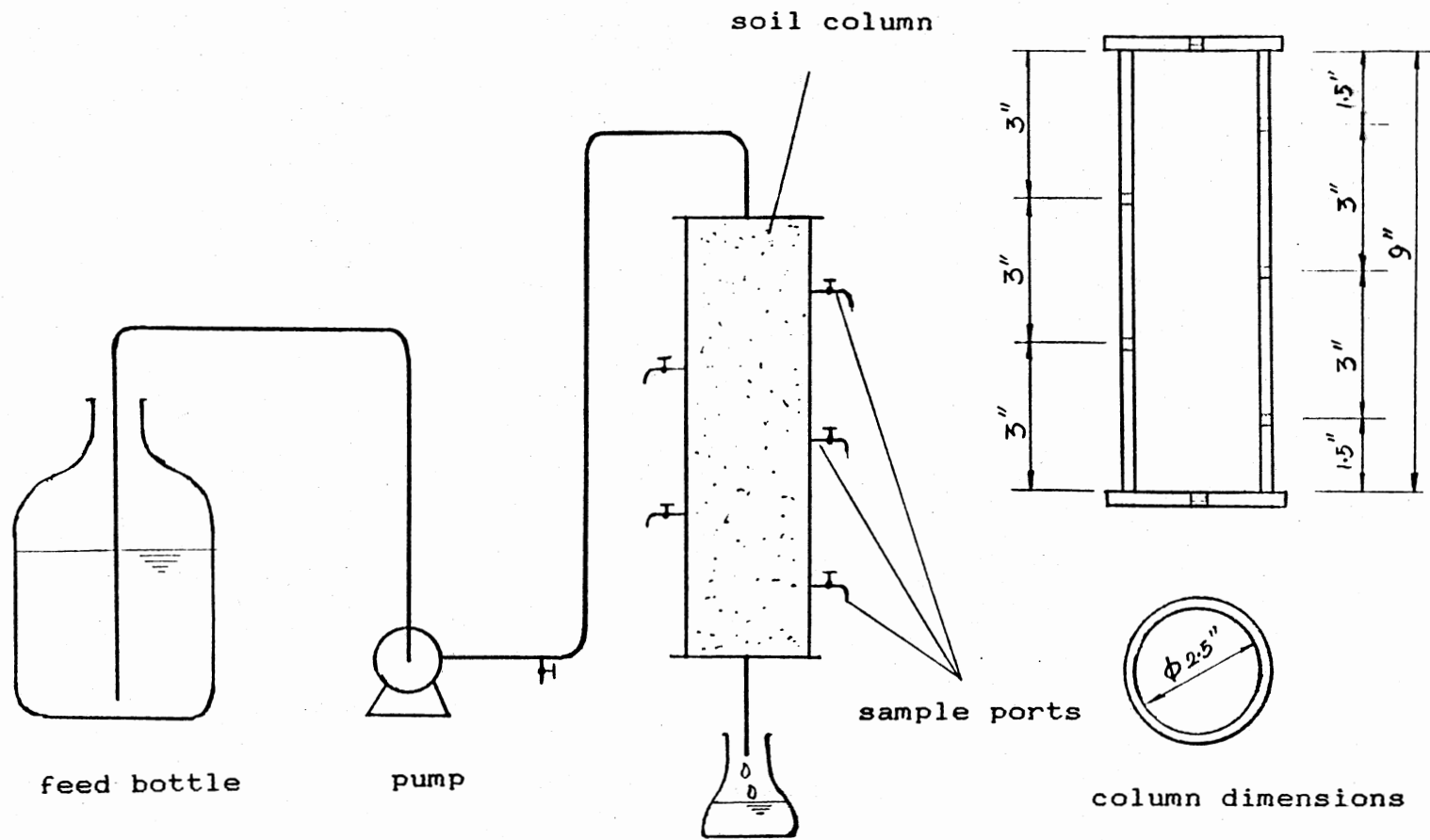


Figure 2. Configuration of the Experimental System



### Analytical Methods

The lindane concentration was analyzed by Gas Chromatography with an electron capture detector (Ni<sup>63</sup>) (Perkin-Elmer Sigma 2000). Triplicates of effluent samples were obtained from soil column for GC analysis. The mean value of concentration for the three samples was used. The packed column (1.5%-SP-2250) in the GC was obtained from Supelco Company. The data were processed and printed out by a digital integrator (Perkin-Elmer LCI-100).

The operation parameters of the GC were as follows:

Column: 1.5 %-SP-2250, from Supelco Company

Carrier Gas: 95% Argon and 5% methane

Oven Temperature: 185°C

Gas Flow Rate: 40 ml/min

Lindane standards in iso-octane were obtained from Supelco Company and were diluted with iso-octane to proper concentrations for use. A microextraction technique was employed to extract the pesticide from the water into a solvent (hexane). This method has been widely employed recently for non-ionic hydrophobic materials because of its relative simplicity as well as requiring considerably less sample volume than other extraction procedures[28]. Average recoveries of about 90% for lindane were noticed in this work. Recovery is the percentage of pesticide extracted from water to hexane in the extraction process. To calculate the recovery, lindane-water solutions of known concentration were prepared. These solutions were extracted by hexane and

injected into the GC for analysis. The "obtained" concentrations for these solutions were derived by comparing the peak areas of the solutions with those of the lindane standards. Then the recovery was calculated by dividing the "obtained" concentration by the real known concentration of lindane-water sample.

The concentration of the effluent from the soil columns was determined by comparing the area from extracted effluent samples with those from the standards.

Finally, Analysis of Variance (ANOVA) and Duncan's Multiple-Range Test were employed to compare and analyze the experimental and simulated data. ANOVA is a statistical method that can be used to compare several data sets and determine whether there are statistical differences among the data. If statistical differences exist, Duncan's Multiple-Range Test can be employed to further identify the difference between any two of the data sets tested. In this study, the data to be compared were the absolute values of the difference between the experimental concentration and the concentration predicted by each of the five kinetic models. ANOVA was applied using the computer software developed by Yee [29], while Duncan's method was calculated using a calculator.

## RESULTS

The experimental breakthrough data for the three soil columns are shown in Table II, Table III, and Table IV. Breakthrough curves showing the concentration versus time

are presented in Figure 3 and breakthrough curves showing the concentration versus the pore volume are presented in Figure 4.

Table II. Experimental Breakthrough Data  
for Original Soil

Time (days)	Volume fed (liters)	Effluent Concentration. ( $\mu\text{g}/\text{l}$ )	C/Co (%)
0	0	0	0
2	0.48	7.1	7.1
4	0.96	12.3	12.3
6	1.44	19.8	19.8
8	1.92	44.9	44.9
10	2.40	50.2	50.2
12	2.88	65.4	65.4
14	3.36	75.7	75.7
16	3.84	79.9	79.9
18	4.32	80.5	80.5
20	4.80	80.0	80.0
22	5.28	79.4	79.4
24	5.76	81.1	81.1

Table III. Experimental Breakthrough Data  
for Lipid-free Soil

Time (days)	Volume fed (liters)	Effluent Concentration ( $\mu\text{g}/\text{l}$ )	C/Co (%)
0	0	0	0
2	0.48	4.1	4.1
4	0.96	8.3	8.3
6	1.44	11.8	11.8
8	1.92	19.2	19.2
10	2.40	34.7	34.7
12	2.88	68.2	68.2
14	3.36	80.0	80.0
16	3.84	80.9	80.9
18	4.32	81.1	81.1
20	4.80	81.8	81.8

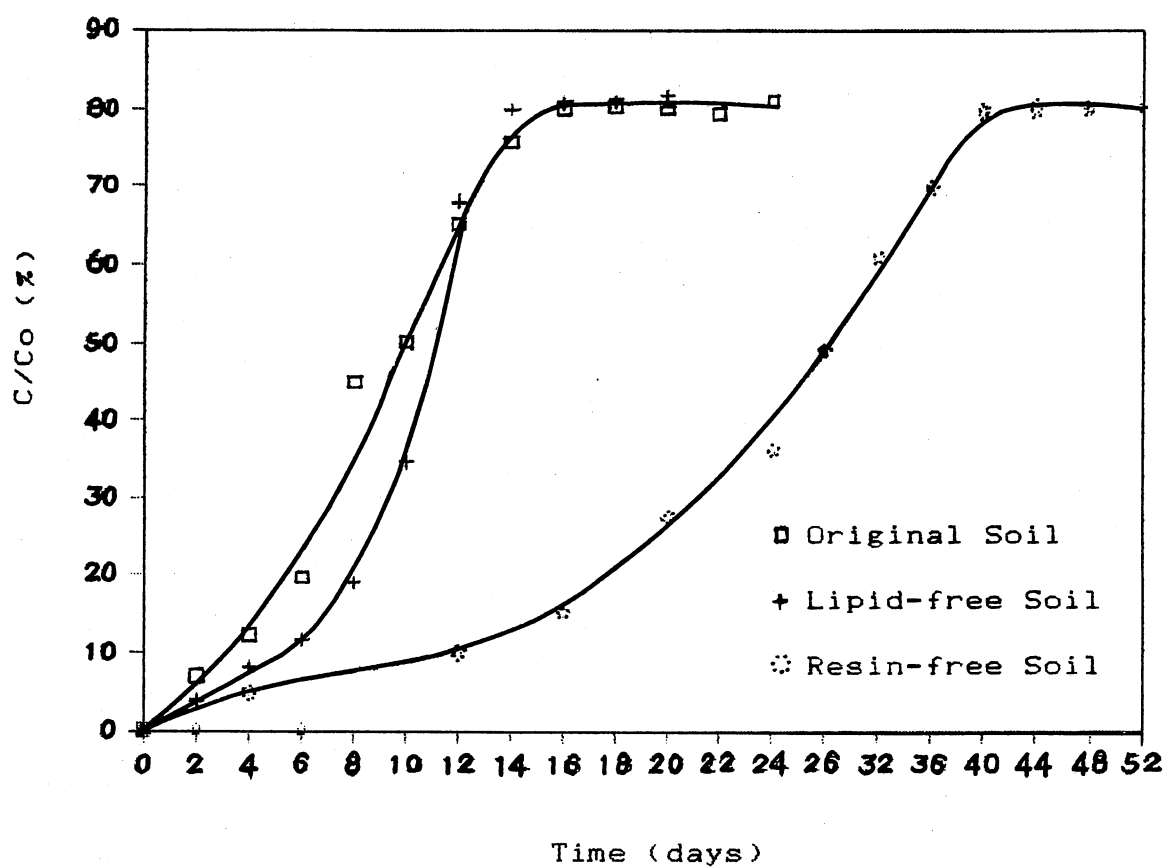


Figure 3. Experimental Breakthrough Curves For Three Soil Adsorbents ( $C/C_0$  versus Time)

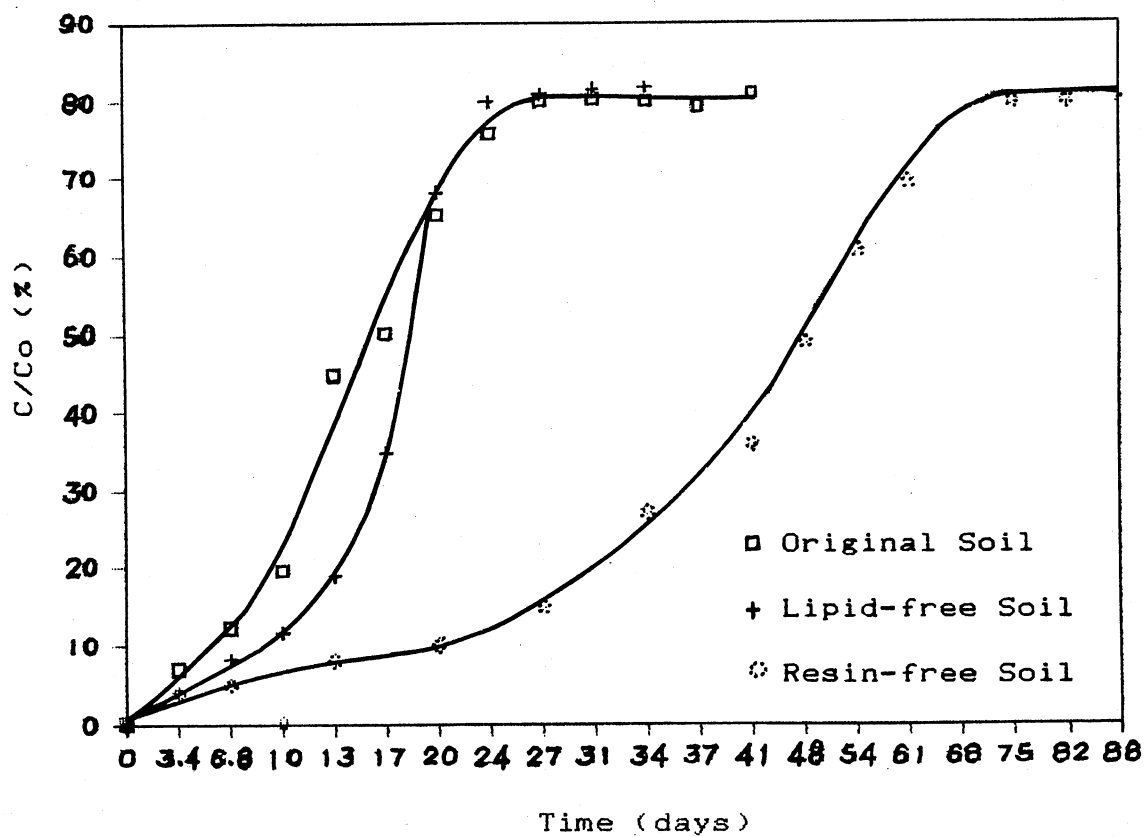


Figure 4. Experimental Breakthrough Curves For Three Soil Adsorbents ( $C/C_0$  versus pore volume)

Table IV. Experimental Breakthrough Data  
for Resin-free Soil

Time (days)	Volume fed (liters)	Effluent Concentration ( $\mu\text{g}/\text{l}$ )	C/Co (%)
0	0	0	0
2	0.48	3.9	3.9
4	0.96	5.1	5.1
8	1.92	8.3	8.3
12	2.88	10.2	10.2
16	3.84	15.2	15.2
20	4.80	27.4	27.4
24	5.76	36.1	36.1
28	6.72	49.7	49.7
32	7.68	61.2	61.2
36	8.64	69.7	69.7
40	9.60	79.8	79.8
44	10.56	80.1	80.1
48	11.52	80.0	80.0
52	12.48	80.2	80.2

The ultimate adsorption capacity (referred to the influent concentration of 100  $\mu\text{g}/\text{l}$ ) for each soil was calculated by integrating the area above the breakthrough curve. The integrated capacities of the soils are shown in Table V.

Table V. Experimental Ultimate Adsorption Capacity

	Ultimate Adsorption Capacity ( $\mu\text{g}/\text{gm}$ )
Original Soil	0.92
Lipids-free Soil	1.22
Resins-free Soil	3.37

It can be seen that the adsorption capacity increases with a decrease in the amount of organic carbon, especially for the second extracted soil (alcohol extraction of

resins). The results contradict other studies [10,11], which showed that adsorption capacity increase with increasing total organic content in the soil. The results are similar to the DDT adsorption study conducted by Shin et al [30], which showed that the equilibrium uptake of DDT by soil increases with the amount of lipids and resins extracted.

Five Models were employed in this study in an attempt to predict these breakthrough curves. The simulated curves were then compared to the experimental data. The results are shown as follows:

1. External Model:

Mass transfer coefficients in this model were calculated using correlations presented by Hines and Maddox [31]. The solution to Equation(6) was also from the same authors. These mass transfer coefficients are shown in Table VI, while a comparison of the breakthrough curves predicted by this model with the experimental data are shown in Figures 5, 6, and 7, for the three soil adsorbents respectively. Theoretical ultimate adsorption capacity was calculated by integrating the area above the simulated curves. The results are shown in Table VII.

Table VI. Mass Transfer Coefficients for External Model

Mass Transfer Coefficients (cm/s)	
Original Soil	0.060
Lipids-free Soil	0.075
Resins-free Soil	0.072

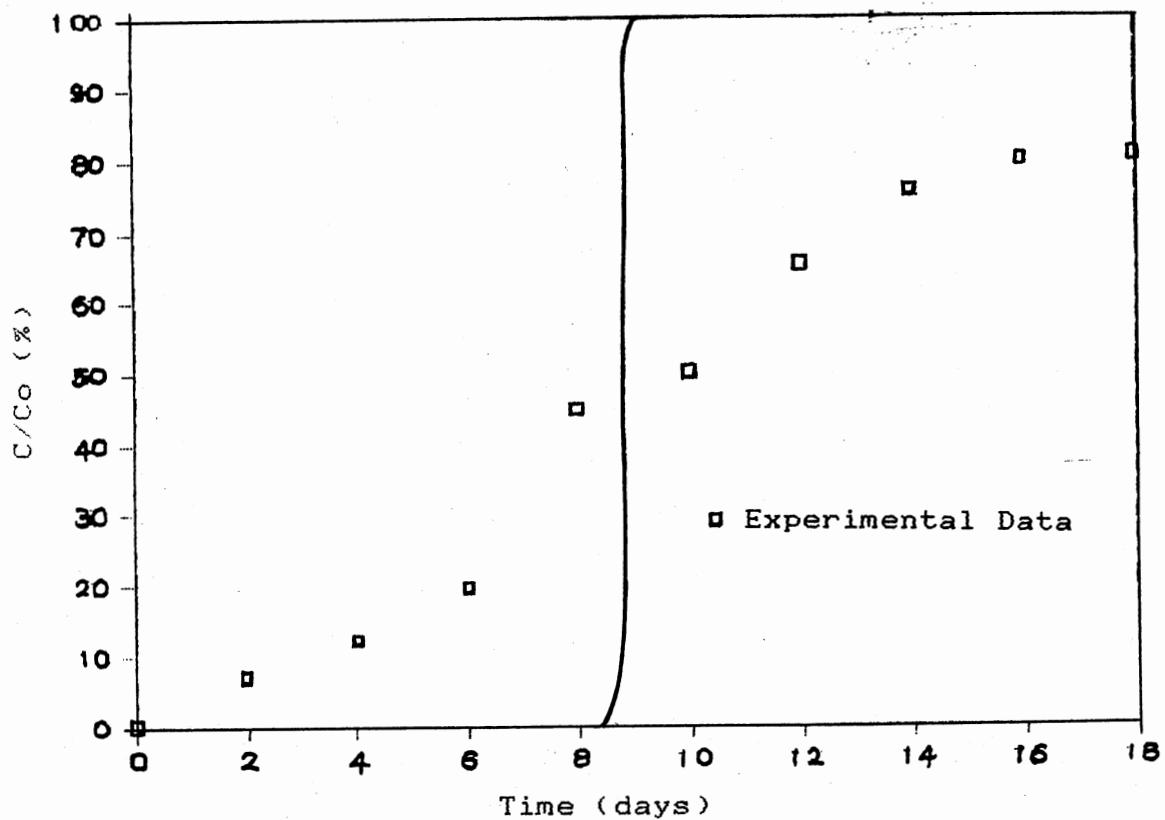


Figure 5. Experimental Data versus Breakthrough Curve predicted by External Model for Original Soil



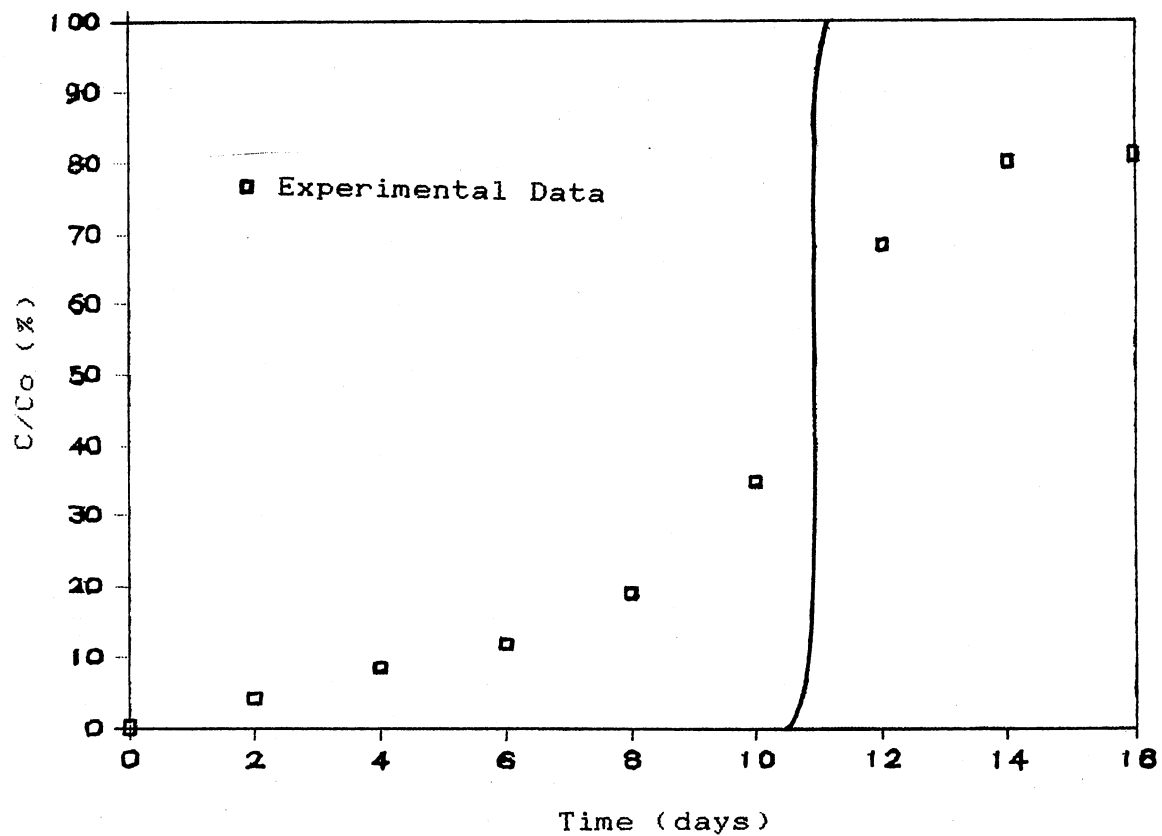


Figure 6. Experimental Data versus Breakthrough Curve Predicted by External Model for Lipid-free Soil

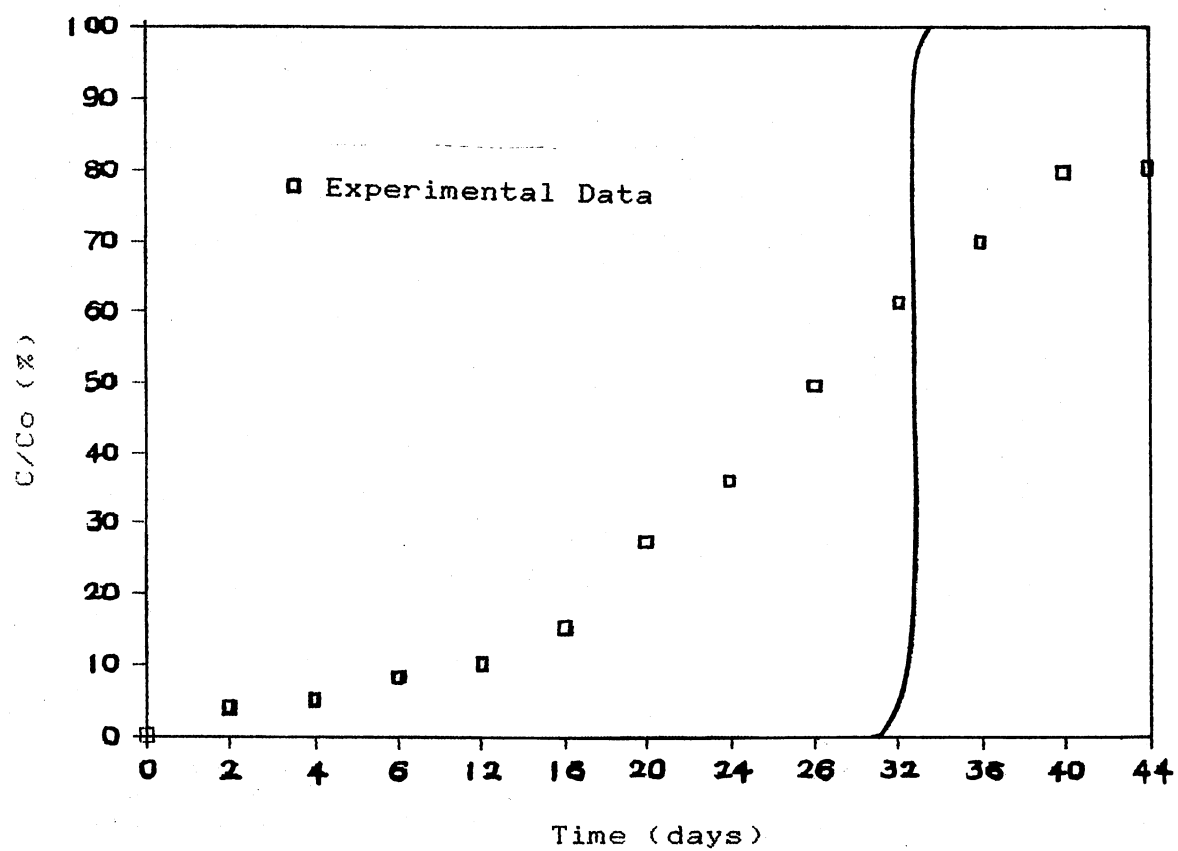


Figure 7. Experimental Data versus Breakthrough Curves Predicted by External Model for Resin-free Soil

It can be seen that the model predicted curves do not fit the experimental data well but the ultimate capacities obtained from the experimental data and from the models are closer (Table VII with Table V). The experimental capacity while always relatively close to that predicted by the external resistance model was always larger, however.

Table VII. Ultimate Adsorption Capacity Derived from Breakthrough Curves Predicted by External Model

=====	
Ultimate Adsorption Capacity ( $\mu\text{g}/\text{gm}$ )	
Original Soil	0.712
Lipids-free Soil	0.905
Resin-free Soil	2.710
=====	

2. Internal Model: Intraparticle mass transfer coefficients were calculated by correlations proposed by Helfferich [32], where the solution of Equation 7 was obtained from Hines and Maddox [31]. The mass transfer coefficients for three soil columns are shown in Table VIII. Breakthrough curves for the three soil adsorbents predicted by this model are shown in Figures 8, 9 and 10 respectively. The ultimate adsorption capacity for three soil adsorbents were calculated by integrating the area above the simulated breakthrough curves. These results are shown in Table IX.

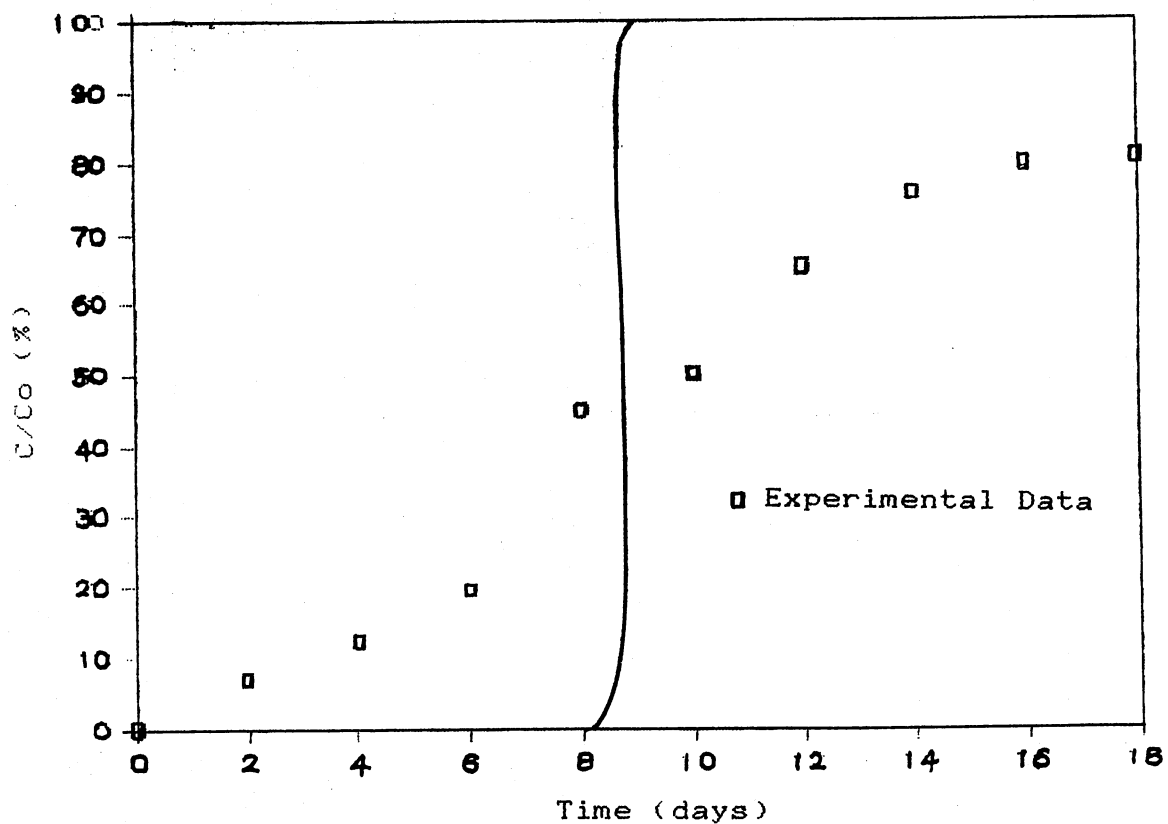


Figure 8. Experimental Data versus Breakthrough Curve Predicted by Internal Model for Original Soil

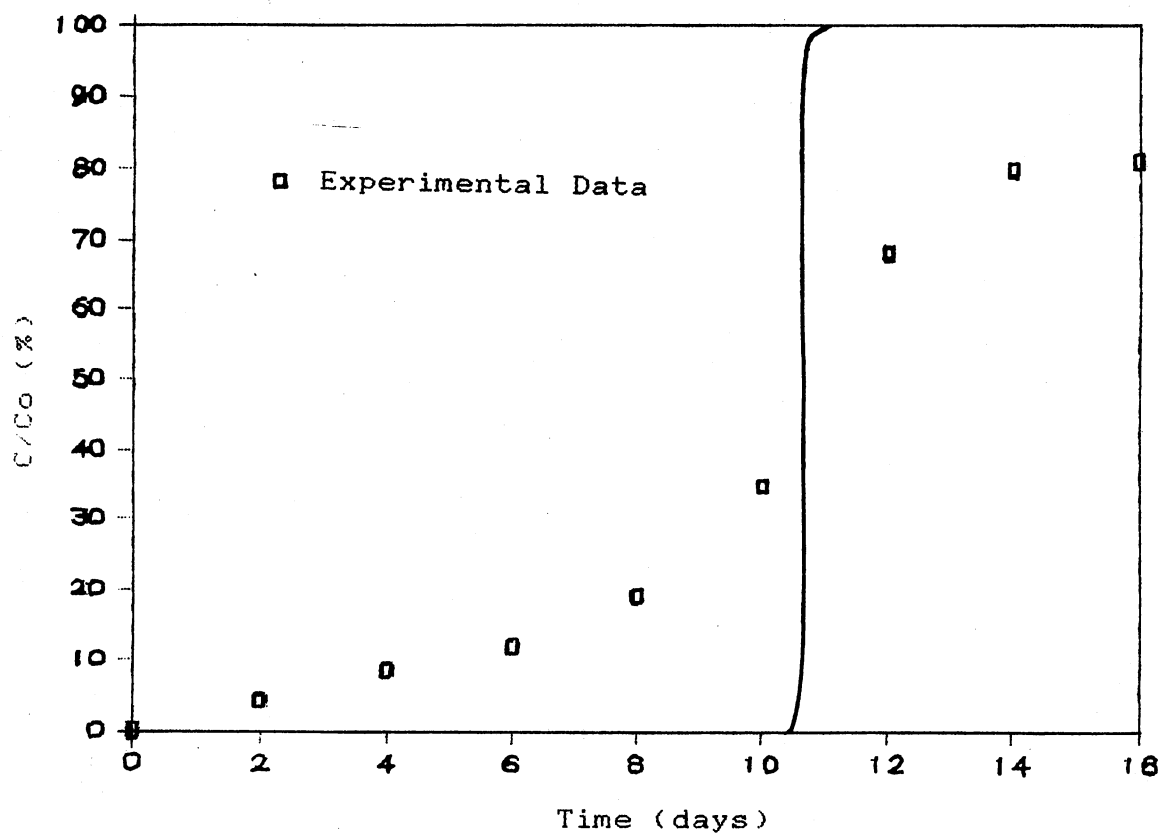


Figure 9. Experimental Data versus Breakthrough Curve Predicted by Internal Model for Lipid-free Soil

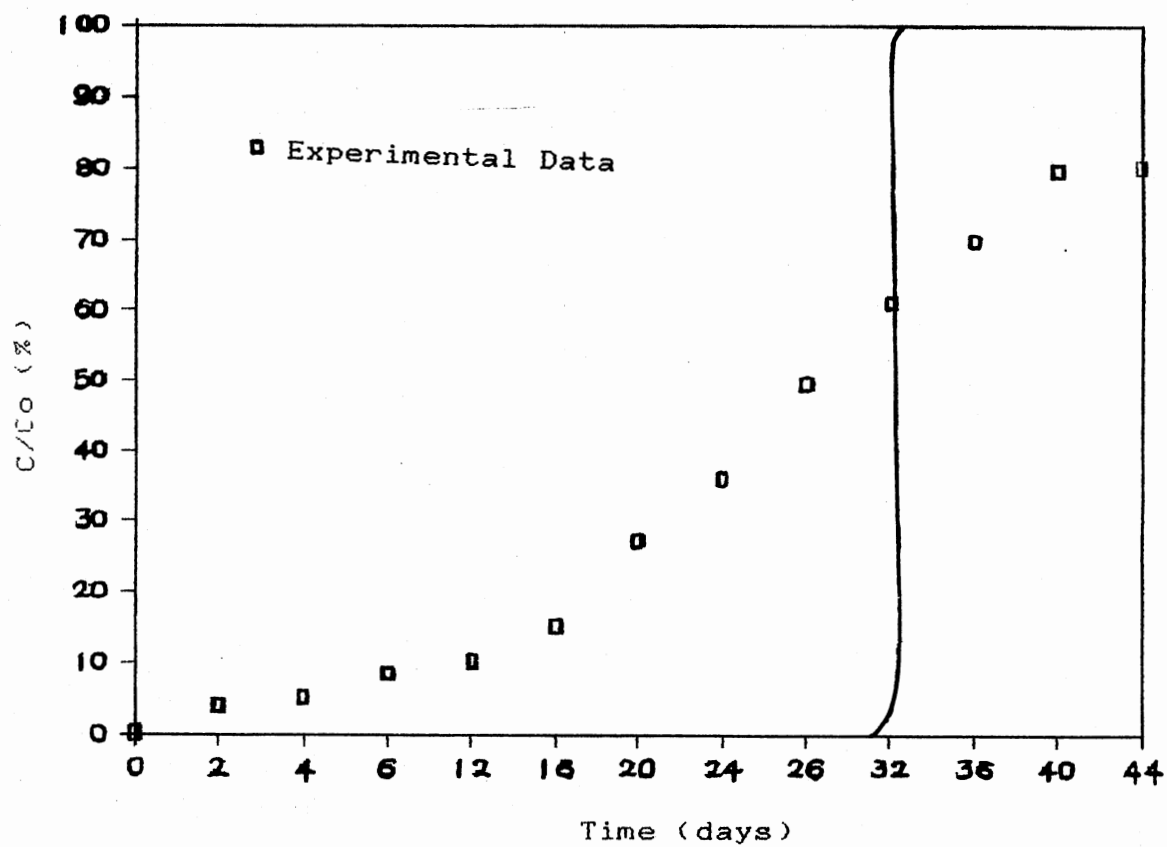


Figure 10. Experimental Data versus Breakthrough Curve Predicted by Internal Model for Resin-free Soil

Table VIII. Mass Transfer Coefficients for Internal Model

Mass Transfer Coefficients (cm/sec)	
Original Soil	1.49
Lipids-free Soil	1.60
Resin-free Soil	0.48

Table IX. Ultimate Adsorption Capacity Derived from Breakthrough Curves predicted by Internal Model

Ultimate Adsorption Capacity( $\mu\text{g/gm}$ )	
Original Soil	0.713
Lipids-free Soil	0.890
Resins-free Soil	2.71

It can be seen that the mass transfer coefficients decreased with the lipids and resins removed. Compared to those of the external resistance model, the mass transfer coefficients for this model are larger (Table VII with Table VI). The ultimate adsorption capacities derived from the model predicted curves are similar to those from the external model. An obvious discrepancy between the model predicted breakthrough curves and experimental data was also observed.

3. Homogeneous Surface Diffusion Model (HSDM): In this model developed by Hand et al [22], surface diffusivity is

calculated from an empirical correlation developed by Dobrzilewski, Crittenden and Hand[33]. Batch type Freundlich adsorption isotherm constants required for this model ( $k$  and  $1/n$ ) were obtained from Ho [27]. Mass transfer constants for this model are shown in Table X.

Table X. Mass Transfer Constants for HSDM

	Intraparticle Diffusivity (cm <sup>2</sup> /sec)
Original Soil	1.30x10 <sup>-6</sup>
Lipids-free Soil	1.00x10 <sup>-6</sup>
Resins-free Soil	3.18x10 <sup>-7</sup>

Breakthrough curves for the three soil columns are shown in Figures 11, 12 and 13, while the ultimate adsorption capacities calculated by integrating the area above the predicted breakthrough curves are presented in Table XI.

Table XI. Ultimate Adsorption Capacity derived from Breakthrough Curves predicted from HSDM

	Ultimate Capacity (µg/gm)
Original Soil	0.689
Lipids-free Soil	0.875
Resins-free Soil	2.664



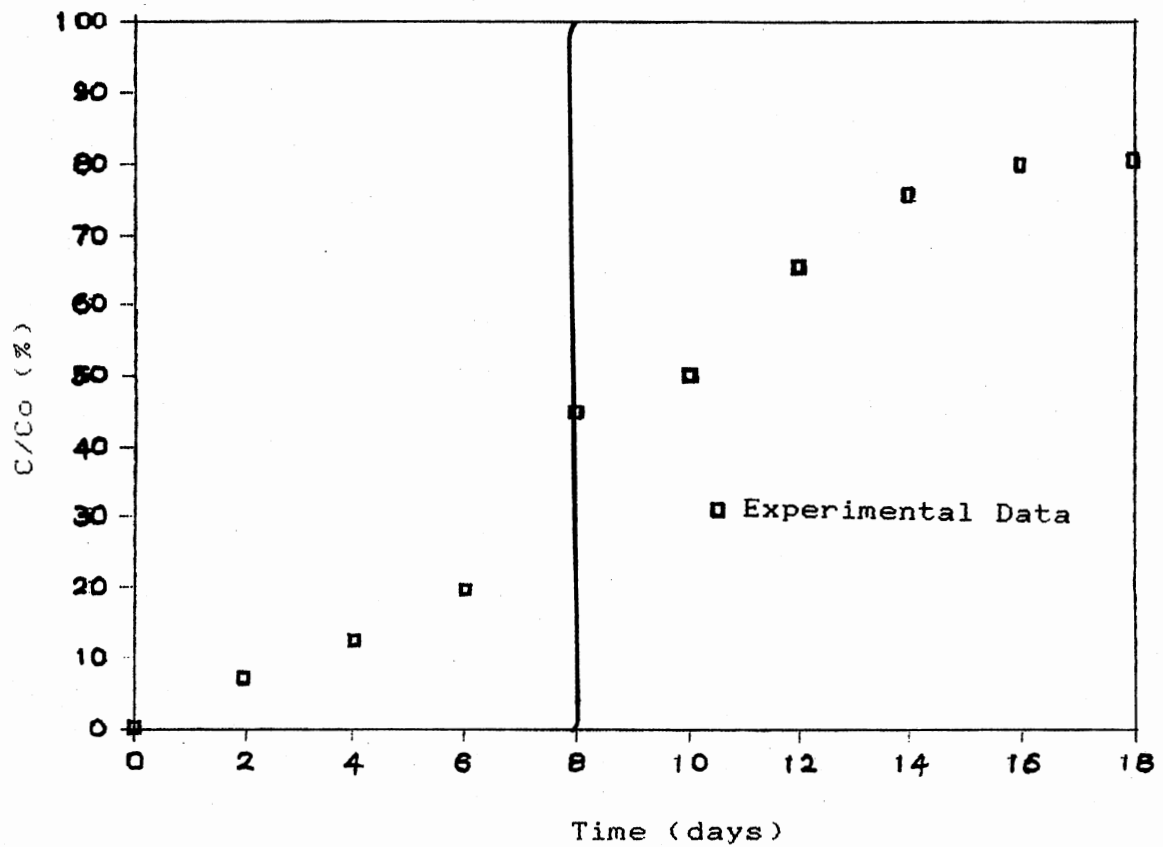


Figure 11. Experimental Data versus Breakthrough Curve Predicted by HSDM for Original Soil

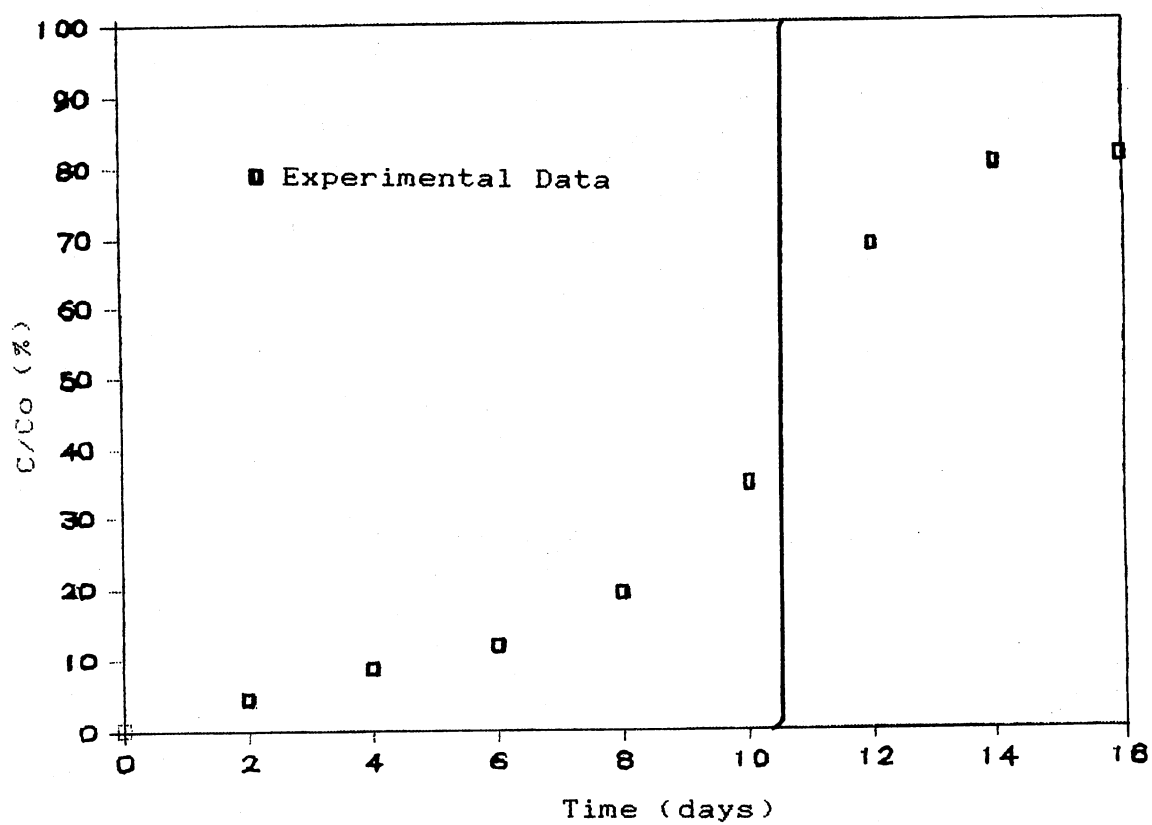


Figure 12. Experimental Data versus Breakthrough Curve Predicted by HSDM for Lipid-free Soil

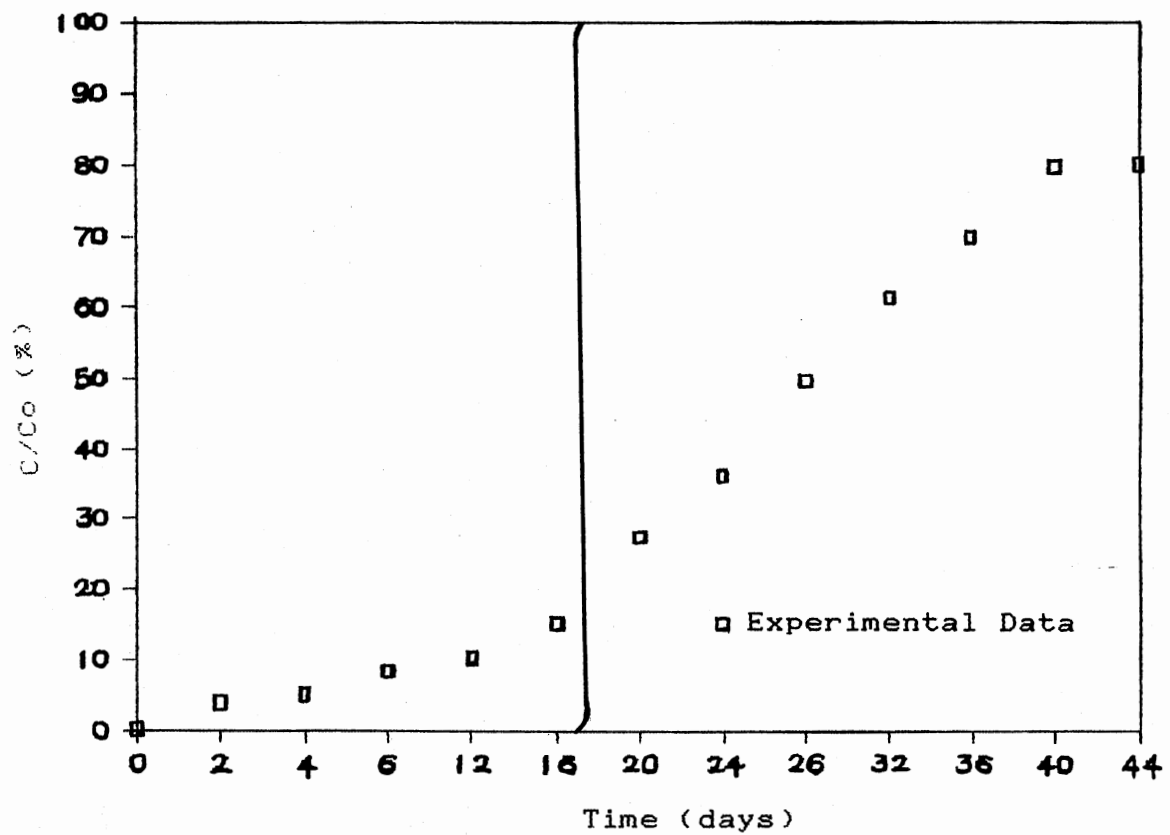


Figure 13. Experimental Data versus Breakthrough Curve Predicted by HSDM for Resin-free Soil

It can be seen that the intraparticle diffusivity decreases with the extraction of lipids and resins. The ultimate capacity calculated from the modeled curves was similar to those from the External and Internal Models. The HSDM predicted curves appear vertical, showing an obvious discrepancy from the experimental data. As before, there is a reasonable correlation between the various models and the total amount of pesticide adsorbed but little apparent agreement between the rates of adsorption.

4. Soil Breakthrough Model: This model was developed by Hutzler [24] and uses mass transfer coefficients calculated using correlations proposed by Dobrzilewski et. al. [33]. The calculation method for mass transfer coefficients is the same as that used for HSDM. The results are shown in Table XII. Breakthrough curves for the three respective soil columns predicted by this model are shown in Figures 14, 15, and 16. The ultimate adsorption capacities calculated by integrating the area above the breakthrough curves predicted by this model are shown in Table XIII.

Table XII. Mass Transfer Coefficients for Soil  
Breakthrough Model

Intraparticle pore diffusivity(cm <sup>2</sup> /sec)	
Original Soil	1.30x10 <sup>-6</sup>
Lipids-free Soil	1.00x10 <sup>-6</sup>
Resins-free Soil	3.18x10 <sup>-7</sup>

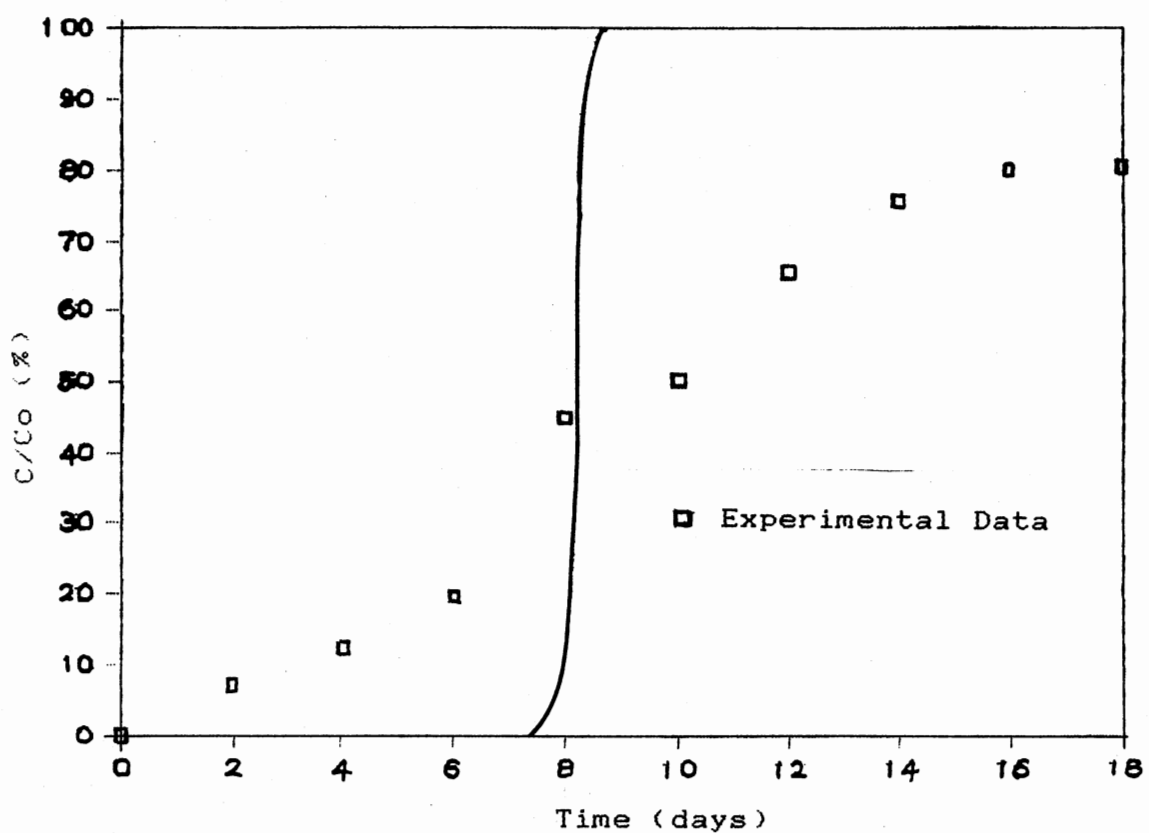


Figure 14. Experimental Data versus Breakthrough Curve Predicted by Soil Breakthrough Model for Original Soil

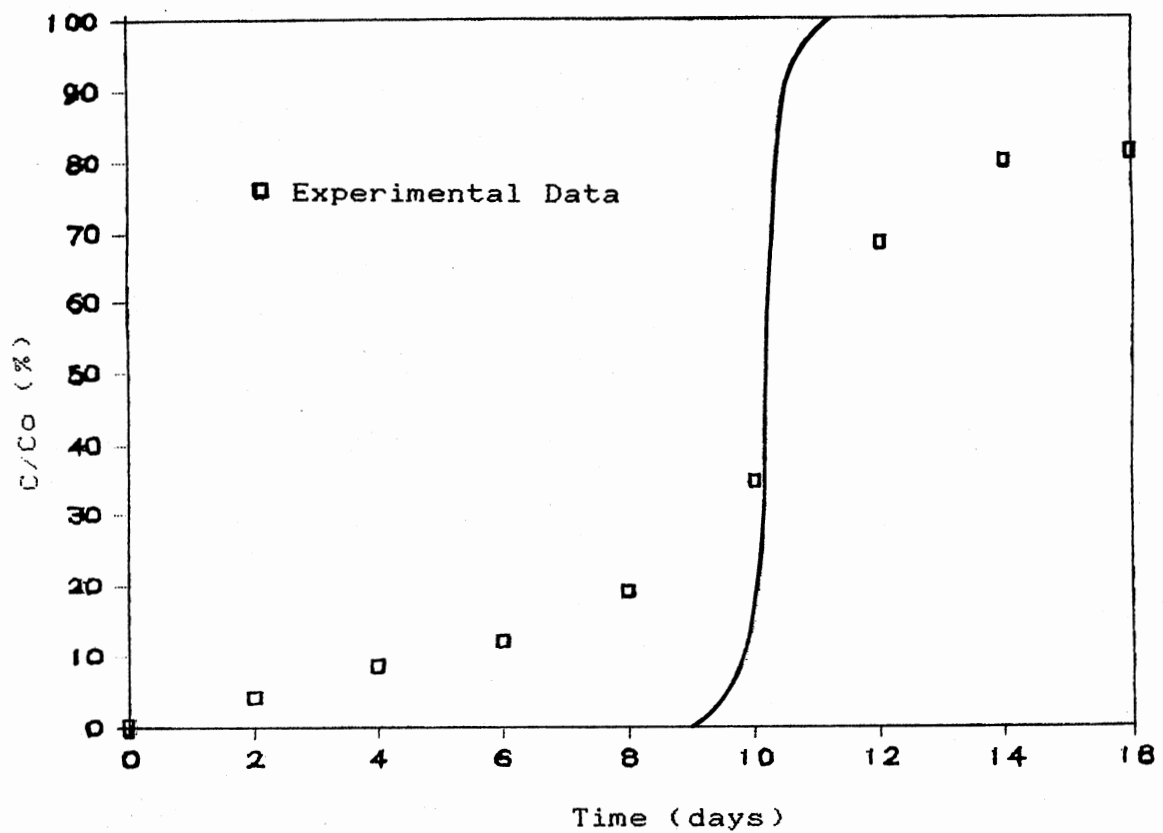


Figure 15. Experimental Data versus Breakthrough Curve Predicted by Soil Breakthrough Model for Lipid-free Soil

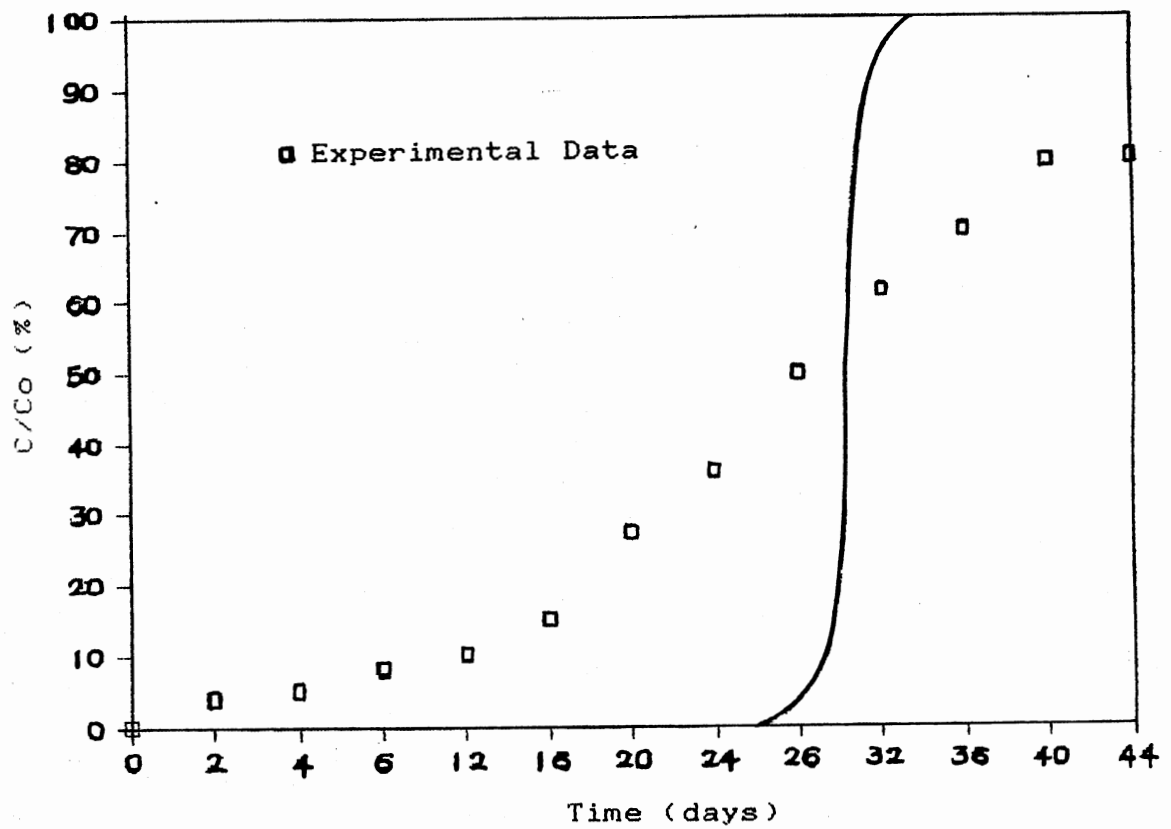


Figure 16. Experimental Data versus Breakthrough Curve Predicted by Soil Breakthrough Model for Resin-free Soil

The mass transfer coefficients decrease with the extraction of lipids and resins, while the ultimate adsorption capacities derived from the model predicted breakthrough curves are similar to other models considered. Comparing the shape of the curves, the simulated breakthrough curves apparently fit the experimental data better than the above three models but still show noticeable deviation.

Table XIII. Ultimate Adsorption Capacity Derived from Break-through Curves Predicted by Soil-Breakthrough Model

Ultimate Adsorption Capacity ( $\mu\text{g}/\text{gm}$ )	
Original Soil	0.665
Lipids-free Soil	0.833
Resins-free Soil	2.512

5. Surface Kinetic Model: Mass transfer coefficients for this model were calculated from experimental data by the method given by Thomas[22]. A solution to Equation (8) was also obtained from the same author. Mass transfer coefficients for this model are shown in Table XIV. Breakthrough curves for three soil columns are shown in Figure 17, 18 and 19. The ultimate capacities calculated by integrating the area above the breakthrough curves predicted by this model are shown in Table XV.



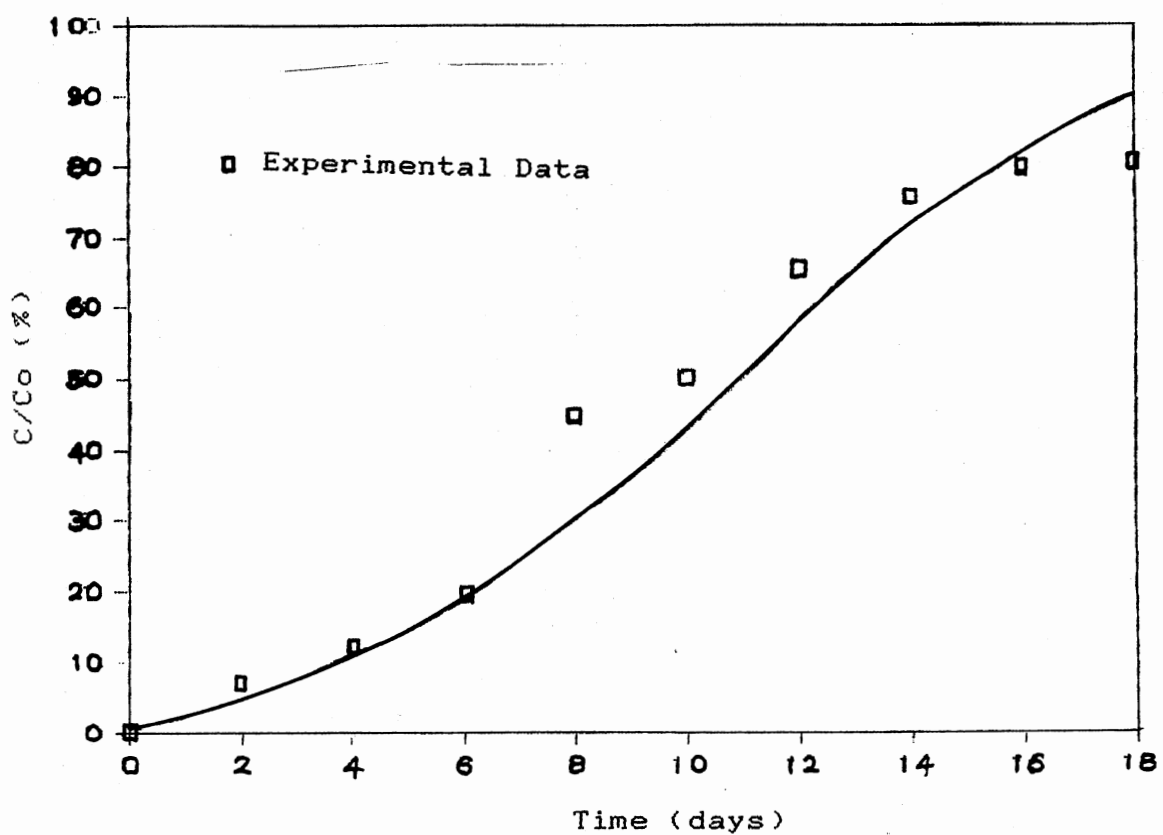


Figure 17. Experimental Data versus Breakthrough Curve Predicted by Surface Kinetic Model for Original Soil

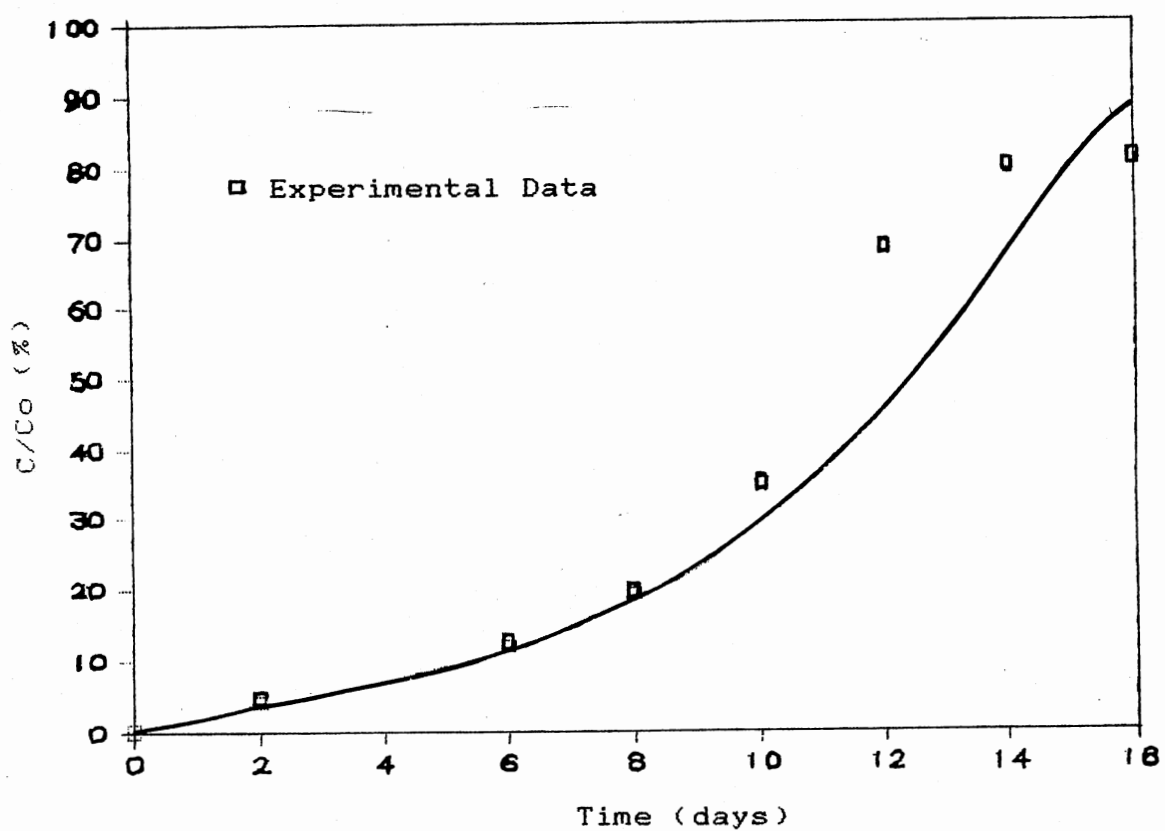


Figure 18. Experimental Data versus Breakthrough Curve Predicted by Surface Kinetic Model for Lipid-free Soil

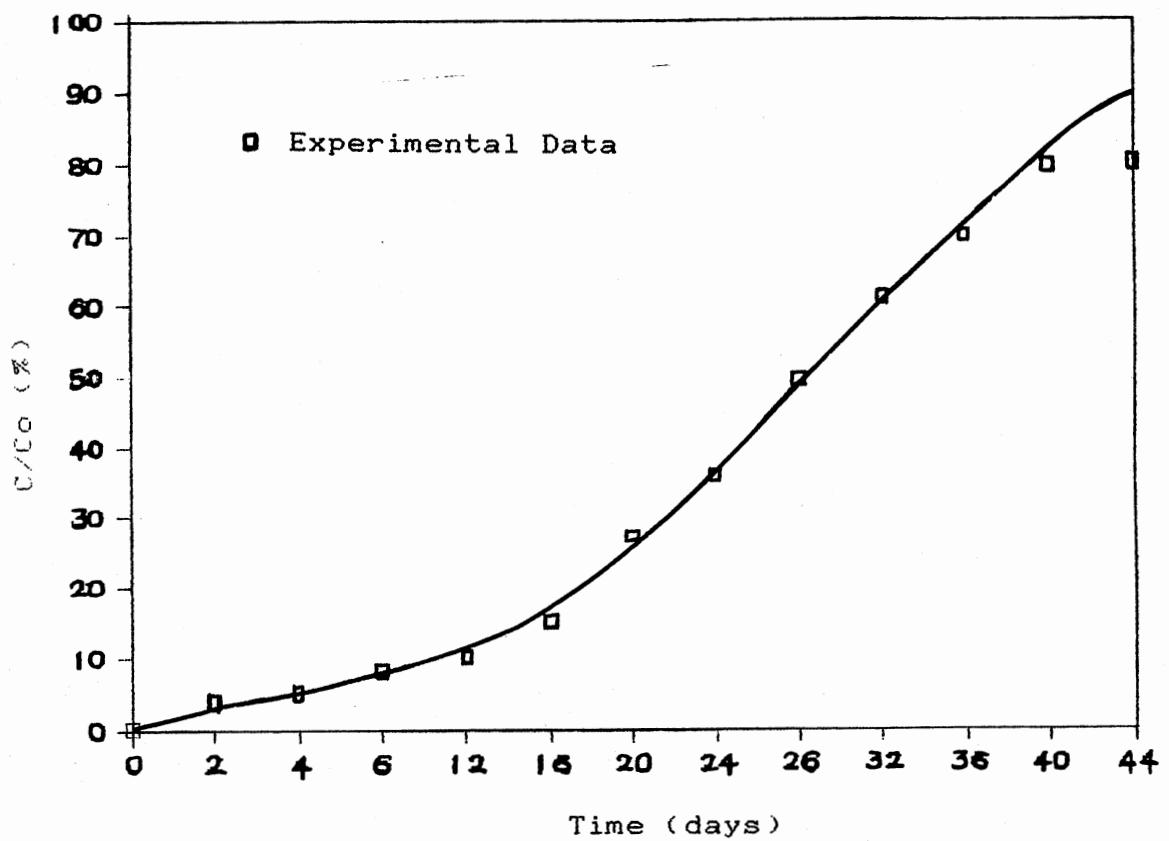


Figure 19. Experimental Data versus Breakthrough Curve Predicted by Surface Kinetic Model for Resin-free Soil

It was found that mass transfer coefficients for original and lipid-free soils were similar while that calculated for the resin-free soil was smaller. Ultimate adsorption capacities appear to be similar to those from other models and to the experimental data set. Among the five models, the breakthrough curves predicted by this model, however, appeared to best fit the experimental data.

Table XIV. Mass Transfer Coefficients for  
Surface Kinetic Model

Mass Transfer Coefficients (1/day-ug)	
Original Soil	0.003
Lipids-free Soil	0.0033
Resins-free Soil	0.0012

Table XV. Ultimate Adsorption Capacity Derived from Breakthrough Curves Predicted by Surface Kinetic Model

Ultimate Adsorption Capacity ( $\mu\text{g}/\text{gm}$ )	
Original Soil	0.85
Lipids-free Soil	0.96
Resins-free Soil	2.65

The effects of serial extraction on ultimate adsorption capacity can be easily seen from data presented in figure 2: the removal of lipids increases the ultimate adsorption

capacity by a small amount while the removal of resins increases the capacity significantly.

The mass transfer coefficients for the five models are summarized in Table XVI. Ultimate Adsorption Capacities for different Models and different soil types are summarized in Table XVII.

Table XVI. Mass Transfer Coefficients in Five Models

	Original Soil	Lipids-free Soil	Resins-free Soil
External(cm/sec) Model	0.060	0.075	0.072
Internal(cm/sec) Model	1.49	1.60	0.48
HSDM (cm <sup>2</sup> /sec)	1.30x10 <sup>-6</sup>	1.00x10 <sup>-6</sup>	3.18x10 <sup>-7</sup>
Soil Breakthrough Model (cm <sup>2</sup> /sec)	1.30x10 <sup>-6</sup>	1.00x10 <sup>-6</sup>	3.18x10 <sup>-7</sup>
Surface Kinetic Model(l/day-μg)	0.003	0.0033	0.0012

Table XVII Ultimate Capacities Calculated from Experimental and Model-predicted Breakthrough Curves (μg/gm)

Models	Original Soil	Lipids-free Soil	Resins-free Soil
Experimental	0.92	1.22	3.37
External Model	0.712	0.905	2.71
Internal Model	0.713	0.890	2.71
HSDM	0.689	0.875	2.664
Soil Break-through Model	0.665	0.833	2.512
Surface Kinetic Model	0.85	0.96	2.65

As discussed in the introduction, if the soil column system is described by equilibrium and linear adsorption, the retardation factor,  $R$ , is a function of distribution factor,  $K_d$ , which represents the amount of unadsorbed solute. The distribution factors for the three different soil columns were calculated from the experimental data, then were compared to those calculated from data of batch study conducted by Ho [27], as well as those calculated by soil organic correlation method provided by Karichhoff [12]. The results are shown in Table XVIII.

Table XVIII Comparison of Distribution Factors from Column Study, Batch Study, and Organic Correlations

	Column Study	Batch Study	Organic Correlations
Original Soil	6.5	20.84	18.9
Lipid-free Soil	8.3	4.27	14.8
Resin-free Soil	26.2	38.00	14.1

It can be observed that for original and resin-free soils, the experimental distribution factors from the column study were smaller than those from batch study. For lipid-free soil, the result were opposite.

ANOVA was employed to analyze the differences among the

breakthrough concentrations predicted by the five kinetic models. The analysis was completed on the residuals obtained from the absolute value of the observed minus the simulated for each of the models. The critical value of F distribution used in ANOVA was based on the alpha value of 0.05. In order to further investigate any statistical differences which might occur in the predictive performance of these models, Duncan's Multiple-Range Test was also employed for the data describing adsorption in these soil systems. The results of ANOVA are shown in Table XIX.

Table XIX Results of ANOVA for Three Soil Columns

	Original Soil	Lipid-free Soil	Resin-free Soil
Sum of Squares	32204.44	3702.15	14484.54
Degree of Freedom	55	45	60
Mean Squares	585.54	82.27	241.41
Value of F-test	2.48	3.81	4.67
Critical F value ( $\alpha = 0.05$ )	2.53	2.61	2.53

It can be seen by comparing the value of F-test and the critical F value that statistically, there was no substantial differences among the five models for the original soil, but for lipid-free and resins-free soils, significant differences occurred. Duncan's test was then applied to the lipid-free and resin-free soils, Results of the test are shown in Tables XX, and XXI.

Table XX Statistical Comparison Among Models for  
Lipids-free Soil

	Ext. Model	Int. Model	HSDM	Soil Break- through Model	Surface kinetic Model
Ext. Mode.	*	S	S	S	D
Int. Model	S	*	S	S	D
HSDM	S	S	*	S	D
Soil Break- through Model	S	S	S	*	D
Surface Kinetic Model	D	D	D	D	*

(S = Not significantly different.  
D = Significantly different.)

Table XXI Statistical Comparison Among Models for  
Resins-free Soil

	Ext. Model	Int. Model	HSDM	Soil Break- through Model	Surface kinetic Model
Ext. Mode.	*	S	S	S	D
Int. Model	S	*	S	S	D
HSDM	S	S	*	S	D
Soil Break- through Model	S	S	S	*	D
Surface Kinetic Model	D	D	D	D	*

The results for the statistically different soils indicated that only the Surface Kinetic Model was different



from other models. This, together with the plotted data comparing the experimental with the simulation results, shows that the surface kinetic model more closely approximated the experimental data set.

## DISCUSSION

The effects of serial extraction of soil on the adsorption capacity and kinetic factors influencing adsorption may result from different mechanisms. The experiments showed that the ultimate adsorption capacities increased with the removal of lipids ( 1st extraction ) and resins ( 2nd extraction ). Lipids in the soil may coat the soil particle surface as well as clog the pores of the soil. Pierce et al [34] suggested that non-ionic chlorinated hydrocarbons can be adsorbed to lipids by hydrophobic bonding. The overall effect of lipid removal on adsorption is that of decreasing the adsorptive capacity associated with lipids and increasing the adsorption capacity associated with soil clay and humic aggregates, because the removal of lipids leads to the exposure of lindane to the clay, resins, and humic aggregates, which were previously coated by the lipids. In this investigation, the removal of lipids increased the ultimate adsorption capacity from 0.92ug/gm to 1.22ug/gm. The overall increase of ultimate adsorption capacity after lipid removal implies that the increased adsorption of lindane by humic aggregates is greater than the decreased adsorption by lipids.

The removal of resins raised the ultimate adsorption capacity from  $1.22\mu\text{g}/\text{gm}$  to  $3.37\mu\text{g}/\text{gm}$ . This dramatic increase may be caused by the following reasons: the resins are more polar than lipids thus have a smaller affinity and low adsorption capacity to lindane. The removal of resin further increased the exposure of lindane to humic aggregates and clay, while the loss of adsorption capacity associated with resin appears minimal.

The experimental data in this investigation did not fit some of the kinetic models chosen for evaluation. With all of the models employed in this study, the general assumption was that the pesticide could be adsorbed onto the particle surface evenly. This may not have been the case for soil adsorption. The humic substances were not removed after the extraction of lipids and resins. As proposed by Wershaw[15], the apparent adsorption of lindane was actually a partitioning of lindane into the hydrophobic interior of humic aggregates. Walker and Crawford[35] indicated that when the soil organic content is less than 6%, the organics do not cover the soil particles entirely, and both mineral and organic surfaces are involved in adsorption. In this situation, not every part of the soil surface has the same adsorption attraction to lindane. The aggregates may also stick to each other to form less available surface than if they are separate. The above may explain the general tendency of the deviation between experimental and modeled breakthrough curves: low concentration of lindane in the

effluent was detected earlier than some of the models predicted, but while the simulation curves reach 100% breakthrough, the experimental curves do not reach the top, showing that adsorption was still progressing.

In the external model, the mass transfer resistance from bulk liquid to liquid-solid interface was assumed to be dominant. In Hines and Maddox's correlation, the mass transfer coefficient was a function of free liquid diffusivity and Reynold's number. The mass transfer surface used in the model was the soil particle surface, which did not necessarily represent the effective surface area on which the adsorption took place. The breakthrough curves predicted by this model showed a noticeable deviation from the experimental data.

In the internal model, mass transfer resistance of diffusion along the solid surface was assumed to dominate. In this model the mass transfer coefficients decreased with the soil extraction. This may have been caused by the creation of "roughness" in the solid surface by extraction, which increased the resistance for organic to travel. Another explanation was that the total effective surface for adsorption after extraction may have been increased by removing the "clogging materials". The breakthrough curves predicted by this model were similar to those predicted by the external model. Noticeable deviation between the model and experimental curves was also observed. The results showed that neither the external nor internal models used in

this investigation described the soil adsorption appropriately.

The Homogeneous Surface Diffusion Model has been successfully used to predict the performances of activated carbon adsorbers[36]. The important assumption of this model is that surface diffusion is the predominant intraparticle mass transfer mechanisms. The major difference between this model and that based upon internal resistance is that it employs parameters from the non-linear Freundlich adsorption equation instead of linear approximations. The surface diffusivity is calculated from an empirical correlation developed by Dobrzelewski, Crittenden and Hand[22]. The model predicted breakthrough curves were "steep", while the experimental ones were gently sloping. This deviation may have been caused by the use of correlations designed for activated carbon to calculate mass transfer coefficients for soil. The mechanisms for adsorption of lindane to activated carbon and to soil may also be different. The mass transfer coefficients calculated by the correlations may not be appropriate for soil systems. Unfortunately, there are no correlations suitable to calculate mass transfer coefficients for soil.

The Soil Breakthrough Model was developed by Hutzler[23]. The assumptions in this model were uniform, spherical soil particles and linear adsorption. The breakthrough curves predicted by this model were closer to the experimental ones than those from the Homogeneous

Surface Diffusion Model, but obvious deviations between the model and experimental curves existed. According to Wershaw's model for soil humic materials[15], the hydrophobic groups of humic materials responsible for adsorption are in the interior of membrane-like aggregates, not distributed evenly along the soil particle surface. The assumptions inherent in the Soil Breakthrough Model clearly do not comply with Wershaw's Model and may be the cause for the significant deviation from the experimental data.

Breakthrough curves obtained from the Surface Kinetic Model agreed with the experimental most closely of the models evaluated. The solution of Equation (8) was given by Thomas[32]. As discussed in the introduction section, this model was based on a second order surface reaction theory. Thomas' solution derived an effluent concentration expression, in which two constants must be calculated from the experimental data. By a more precise definition, it may not be a "true" predictive model because it required experimental data to calculate the constants. Since the overall effect of factors such as structural change after soil extraction were finally reflected by the experimental breakthrough data, better prediction could be expected.

Another possible factor accounting for the earlier experimental breakthrough than the predicted curves was free liquid dispersion. In most of the kinetic models, the dispersion term was neglected, partially because it was easier to solve the partial differential equation, and

partially because it was negligible for activated carbon adsorber, where both superficial velocity and adsorption rate were relatively high. But in soil columns, the situation was the opposite. The neglect of dispersion term may cause noticeable errors.

It is apparent that kinetic mass transfer analysis was more appropriate to describe the solute's transport through fixed adsorptive media than the equilibrium retardation model. A major factor impeding the kinetic study was the heterogeneous character of the soil surface. For high organic content soils (e.g. > 6%), the organic may entirely coat the soil surface and would result in adsorption evenly over the organic coating. Under these conditions the various kinetic models suitable to other adsorptive systems may be also applicable to soil columns. But in many cases, the soil organic content was low and the soil particles were partially coated by the organics. Some humic aggregates may form their own individual particles. The adsorption in this situation may take place simultaneously onto the soil clay, the organic coating, and the humic aggregate particles. A detailed mathematical description of this complicated situation becomes difficult.

## CONCLUSIONS

In this investigation, three columns filled with different soil adsorbents were evaluated in a kinetic study. Five kinetic models were employed in an attempt to simulate the experimental data. The experimental data showed that the

ultimate adsorption capacity increases with the removal of lipids and resins. The results suggested that different types of organics play different roles in the interaction with hydrophobic pesticides. The general term of "soil organic content", which does not address specific types of organic, may not be adequate to describe the adsorption process. The presence of lipids and resins in the soil hinders rather than enhances the pesticide-soil interaction. The reason may be that the lipids and resins clog the pores of the soil and/or cover the surface of "responsible organics" for adsorption, which prevents the contact of pesticide and the "responsible organics".

Among the five kinetic models employed in this study, the Surface Kinetic Model best fit the experimental data. The Soil Breakthrough Model while exhibiting lower conformity with the experimental data than did the Surface Kinetic Model was better than other approaches evaluated. The External Model, Internal Model, and Homogeneous Surface Diffusion Model displayed similar discrepancies. There are several possible reasons for these inadequacies in fitting the experimental data. The organic content of the soil adsorbents used in this study was less than 6%, which is the minimum amount to completely cover the surface of the spherical soil particles. The inability to model these data may be caused by the uneven pesticide-soil organics interaction on the surface of the soil particles. That is, the adsorbents used in this effort were not ideal in that

the measured mass of the soil used in these experiments was not available for adsorption. Until there is at least a monolayer of appropriate organics covering each soil particle, the fundamental reactions described by the internal and external models as well as those in the surface diffusion code are not readily observed. The amount of available surface rather than a specific resistance limits adsorption rate. The Surface Kinetic Model, better than the others, begins to address these deficiencies.

In addition to the uneven adsorption on the soil surface, neglecting the dispersion term in the mass balance differential equation may have also contributed to the observed discrepancy between that predicted by some approaches and the experimental data.

Due to different adsorption mechanisms and complex soil-organic structure, kinetic models suitable for a activated carbon fixed bed adsorber may not without modification, necessarily describe the transport of organic solutes through porous soil. Further research to understand these adsorption mechanisms and the role of the soil-organic structure is suggested in order to establish a proper kinetic model coupling the factors that were not included in models for activated carbon.



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## APPENDIX A

CALCULATION OF EXTERNAL MASS TRANSFER COEFFICIENTS  
FOR THREE DIFFERENT SOILS

Mass transfer coefficients are calculated using correlations given by Hines et al.

$$j_D = \frac{K_f}{U'} (Sc)^{2/3}$$

Where:

$j_D$  = Chilton and Colburn j-factor

$K_f$  = mass transfer coefficient, cm/sec

$U'$  = superficial velocity, 0.00023 cm/sec

$Sc$  = Schmidt Number

$$Sc = \frac{\mu}{\rho_{DAB}}$$

Where,  $\mu$  = viscosity of water, 0.01 gm/cm-sec=1.00 cp

$\rho$  = density of water, 0.998 gm/cm<sup>3</sup>

$D_{AB}$  = diffusivity calculated by Wilde and Chang

(Hines p 29)

$$D_{AB} = \frac{1.17 \times 10^{-13} (\rho_B M_B)^{1/2} T}{V_A^{0.6} \mu}$$

Where  $\mu$  = defined as above, 1.00 cp

$V_A$  = molar volume of lindane, 0.23 m<sup>3</sup>/kg-mol

$M_B$  = molecular weight of water, 18

$\beta_8$  = association factor of water, 2.6

T = absolute temp., 293°C

$$D_{AB} = \frac{1.17 \times 10^{-13} (2.6 \times 18)^{1/2} \times 293}{0.23^{0.6} \times 1.00}$$

$$= 5.65 \times 10^{-10} \text{ m}^2/\text{sec}$$

$$Sc = \frac{0.01}{0.998 \times 5.65 \times 10^{-6}} = 1773$$

$$j_D = 1.09 \text{ Re}^{-2/3}$$

Where:  $\epsilon$  = porosity of soil, 0.52

Re = Reynold's number

$$Re = \frac{U'd}{\mu}$$

where d = diameter of adsorbent

U', and  $\mu$  are defined as above.

For original soil:

$$d = 1.82 \times 10^{-5} \text{ cm}$$

$$Re = \frac{0.998 \times 0.00023 \times 1.82 \times 10^{-5}}{0.01}$$

$$= 4.1 \times 10^{-7}$$

$$K_f = \frac{0.52}{0.00023} \times 1773^{2/3} = 1.09 \times (4.1 \times 10^{-7})^{-2/3}$$

$$K_f = 0.06 \text{ cm/sec}$$

For lipid-free soil:

$$d = 1.3 \times 10^{-5} \text{ cm}$$

$$Re = \frac{0.998 \times 0.00023 \times 1.3 \times 10^{-5}}{0.01}$$

$$= 2.9 \times 10^{-7}$$

$$K_f = \frac{1.09 (2.9 \times 10^{-7})^{-2/3} \times 0.00023}{0.52 \times 17732^{2/3}}$$

$$= 0.075 \text{ cm/sec}$$

For resin-free soil:

$$d = 1.37 \times 10^{-5} \text{ cm}$$

$$Re = \frac{0.998 \times 0.00023 \times 1.37 \times 10^{-5}}{0.01}$$

$$= 3.1 \times 10^{-7}$$

$$K_f = \frac{1.09 (3.1 \times 10^{-7})^{-2/3} \times 0.00023}{0.52 \times 17732^{2/3}}$$

$$= 0.072 \text{ cm/sec}$$

Sample calculation of C/Co versus time for original soil:

$$\beta = \frac{Z K_f a}{U_z}$$

$$\tau = \frac{K_f a}{K_d \rho_b} \left( t - \frac{Z}{U_z} \right)$$

$$C/C_o = \frac{1}{2} \left( 1 - \operatorname{erf} \left( \sqrt{\frac{\tau}{\beta}} - \sqrt{\tau} \right) \right)$$

Where:

Z = column length, 22.86 cm

K<sub>f</sub> = mass transfer coefficient, 0.06 cm/sec

a = surface area, 1.58 x 10<sup>3</sup> cm<sup>2</sup>/cm<sup>3</sup>

ξ = porosity of soil, 0.52

U<sub>z</sub> = interstitial velocity, 4.423 x 10<sup>-4</sup> cm/sec

K<sub>d</sub> = distribution factor, 6.5 cm<sup>3</sup>/gm

ρ<sub>b</sub> = bulk density of soil, 1.05 gm/cm<sup>3</sup>



$\xi$  = length parameter, dimensionless

$\tau$  = time parameter, dimensionless

erf = error function

$$\xi = \frac{22.86 \times 0.06 \times 1.58 \times 10^5}{0.52 \times 4.423 \times 10^{-4}}$$

$$= 9.42 \times 10^8$$

$$\sqrt{\xi} = 30692$$

$$\tau = \frac{0.06 \times 1.58 \times 10^5}{6.5 \times 1.05} \left( t - \frac{22.86}{4.423 \times 10^{-4}} \right)$$

$$= 1389 ( t - 51683 )$$

For a given time  $t$ ,  $C/C_0$  can be calculated. For example, when  $t = 8.446$  days = 729734.4 seconds,

$$\tau = 1389 ( 729734.4 - 51683 )$$

$$= 9.418 \times 10^8$$

$$\sqrt{\tau} = 30689$$

$$\sqrt{\xi} - \sqrt{\tau} = 30692 - 30689 = 3$$

erf ( 3 ) = 1 ( from Table 4-1 in reference [31] )

$$C/C_0 = \frac{1}{2} ( 1 - 1 ) = 0$$

For another example, when  $t = 8.448$  days, using the same procedure, we get:

$$\sqrt{\xi} - \sqrt{\tau} = -0.89$$

erf ( -0.89 ) = -0.79

$$C/C_0 = \frac{1}{2} [ 1 - (-0.79) ] = 0.89 = 89 \%$$

## APPENDIX B

CALCULATION OF INTERNAL MASS TRANSFER COEFFICIENTS  
FOR THREE DIFFERENT SOILS

Internal mass transfer coefficients are calculated using correlations given by Hines et al.

$$K_s = \frac{10 D_A}{d (1 - \xi)}$$

Where:  $K_s$  = intraparticle mass transfer coefficient, cm/sec

$D_A$  = intraparticle diffusivity, cm<sup>2</sup>/sec

$d$  = diameter of soil particles

$\xi$  = porosity of soil, 0.52

For original soil:

$$D_A = 1.3 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$d = 1.82 \times 10^{-5} \text{ cm}$$

$$K_s = \frac{10 \times 1.3 \times 10^{-6}}{1.82 \times 10^{-5} (1 - 0.52)} = 1.49 \text{ cm/sec}$$

For lipid-free soil:

$$D_A = 1.0 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$d = 1.82 \times 10^{-5} \text{ cm}$$

$$K_s = \frac{10 \times 1.0 \times 10^{-6}}{1.3 \times 10^{-5} (1 - 0.52)} = 1.6 \text{ cm/sec}$$

For resin-free soil:

$$D_A = 3.18 \times 10^{-7} \text{ cm}^2/\text{sec}$$

$$d = 1.37 \times 10^{-5} \text{ cm}$$

$$K_s = \frac{10 \times 3.18 \times 10^{-7}}{1.37 \times 10^{-5} \times (1-0.52)} = 0.48 \text{ cm/sec}$$

Sample calculation of  $C/C_0$  versus time for original soil:

$$\beta = \frac{Z K_s a K_d \rho_b}{\epsilon U_z}$$

$$\tau = K_s a \left( t - \frac{Z}{U_z} \right)$$

$$C/C_0 = \frac{1}{2} \left( 1 - \text{erf} \left( \frac{\tau}{\sqrt{\beta}} - \sqrt{\tau} \right) \right)$$

Where:

$Z$  = column length, 22.86 cm

$K_s$  = mass transfer coefficient, 1.49 cm/sec

$a$  = surface area,  $1.58 \times 10^8 \text{ cm}^2/\text{cm}^3$

$\epsilon$  = porosity of soil, 0.52

$U_z$  = interstitial velocity,  $4.423 \times 10^{-4} \text{ cm/sec}$

$K_d$  = distribution factor,  $6.5 \text{ cm}^3/\text{gm}$

$\rho_b$  = bulk density of soil,  $1.05 \text{ gm/cm}^3$

$\beta$  = length parameter, dimensionless

$\tau$  = time parameter, dimensionless

erf = error function

$$\beta = \frac{22.86 \times 1.49 \times 1.58 \times 10^8 \times 6.5 \times 1.05}{0.52 \times 4.423 \times 10^{-4}}$$

$$\rho_3 = 1.59696 \times 10^{11}$$

$$\sqrt{\rho_3} = 399620$$

$$\begin{aligned} \tau &= 1.49 \times 1.58 \times 10^5 \left( t - \frac{22.86}{4.423 \times 10^{-4}} \right) \\ &= 235420 ( t - 51684 ) \end{aligned}$$

For a given time  $t$ ,  $C/C_0$  can be calculated. For example, when  $t = 8.4493$  days = 730019.5 seconds,

$$\begin{aligned} \tau &= 235420 ( 730019.5 - 51684 ) \\ &= 1.59693 \times 10^{11} \end{aligned}$$

$$\sqrt{\tau} = 399617.00$$

$$\sqrt{\rho_3} - \sqrt{\tau} = 399620 - 399617.00 = 3.0$$

$$\text{erf} ( 3.0 ) = 1 \text{ ( from Table 4-1 in reference [31] )}$$

$$C/C_0 = \frac{1}{2} ( 1 - 1 ) = 0$$

For another example, when  $t = 8.4494$  days, using the same procedure, we get:

$$\sqrt{\rho_3} - \sqrt{\tau} = 0.16$$

$$\text{erf} ( 0.16 ) = 0.17$$

$$C/C_0 = \frac{1}{2} ( 1 - 0.17 ) = 0.42 = 42 \%$$

## APPENDIX C

CALCULATION OF MASS TRANSFER COEFFICIENTS  
FOR SURFACE KINETIC MODEL

Thomas[32] solved Equation 8 and obtained the following expression for effluent concentration of the column:

$$C/C_0 = \frac{1}{1 + \exp[(k/Q)(q_0 M - C_0 V)]}$$

Where: C = effluent concentration,  $\mu\text{g/l}$

$C_0$  = influent concentration, 100  $\mu\text{g/l}$

k = adsorption rate constant, 1/day- $\mu\text{g}$

V = Volume of water treated, liter

M = mass of soil,  $285.1 \times 10^6 \mu\text{g}$

$q_0$  = adsorption capacity,  $\mu\text{g pesticide}/\mu\text{g soil}$

k and  $q_0$  were calculated from the slope and intercept of the graph obtained by plotting  $\ln(C_0/C)$  versus V:

$$\text{Slope} = - \frac{k C_0}{Q}, \quad k = - \frac{\text{slope} \times C_0}{C_0}$$

$$\text{Intercept} = \frac{k q_0 M}{Q}, \quad q_0 = \frac{\text{intercept} \times Q}{k \times M}$$

For original soil:

$$\text{Slope} = - 1.26 \text{ l}^{-1}, \quad \text{Intercept} = 3.25$$

$$k = \frac{1.26 \times 0.24}{100} = 0.003 \text{ (1/day-}\mu\text{g)}$$

$$q_0 = \frac{3.25 \times 0.24}{0.003 \times 285.1 \times 10^6} = 9.1 \times 10^{-7} \mu\text{g}/\mu\text{g}$$

For lipid-free soil:

$$\text{Slope} = - 1.38 \text{ l}^{-1}, \quad \text{intercept} = 4.0$$

$$k = \frac{1.38 \times 0.24}{100} = 0.0033 \text{ (1/day-}\mu\text{g)}$$

$$q_0 = \frac{4.0 \times 0.24}{0.0033 \times 285.1 \times 10^6} = 1.02 \times 10^{-6} \mu\text{g}/\mu\text{g}$$

For resin-free soil:

$$\text{Slope} = - 0.507 \text{ l}^{-1}, \quad \text{intercept} = 3.55$$

$$k = \frac{0.507 \times 0.24}{100} = 0.0012 \text{ (1/day-}\mu\text{g)}$$

$$q_0 = \frac{3.55 \times 0.24}{0.0012 \times 285.1 \times 10^6} = 2.4 \times 10^{-6} \mu\text{g}/\mu\text{g}$$

Sample calculation of C/Co versus time for original soil:

$$\begin{aligned} C/Co &= \frac{1}{1 + \exp [(k/Q) (q_0 M - Co V)]} \\ &= \frac{1}{1 + \exp [(0.03/0.24)(0.91 \times 285.1 - 100 V)]} \\ &= \frac{1}{1 + \exp [0.0125 (259.4 - 100 V)]} \end{aligned}$$

when  $t = 2$  days,  $V = 0.48 \text{ l}$

$$\begin{aligned} C/Co &= \frac{1}{1 + \exp [0.0125 (259.4 - 100 \times 0.48)]} \\ &= 0.07 = 7 \% \end{aligned}$$

Using the same procedure, C/Co can be calculated for any given time  $t$ .

## APPENDIX D

**CONCENTRATIONS OF THE EFFLUENT  
TAKEN FROM SAMPLE PORTS**

Concentrations of the effluent taken from sample ports of the three soil columns are shown in Tables XXII, XXIII, and XXIX. The data and subsequent analysis presented in the body of this thesis are the concentrations of influent and effluent from the bottom of the columns.

Table XXII Concentration of Effluent Taken from  
Sample Ports of Original Soil Column

Time (days)	port 1	port 2	port 3	port 4	port 5
0	0	0	0	0	0
2	12.3	11.6	11.1	10.5	9.99
4	20.4	19.8	17.7	14.3	14.2
6	35.7	30.5	34.4	32.2	20.3
8	50.4	51.2	48.3	32.3	40.2
10	77.3	76.5	63.9	64.1	49.8
12	80.4	79.4	78.3	73.5	60.1
14	80.7	80.1	79.4	76.8	70.1
16	87.5	84.4	80.8	77.5	75.4
18	88.3	87.5	83.4	84.3	79.8
20	89.6	86.9	86.5	81.6	80.1
22	90.0	89.5	88.4	86.3	79.9
24	89.9	90.0	89.3	85.4	81.

Table XXIII Concentration of Effluents Taken from  
Sample Ports of Lipid-free Soil

Time (days)	concentration ( $\mu\text{g}/\text{l}$ )			
	port 1	port 2	port 3	port 4
0	0	0	0	0
2	10.2	11.0	10.9	9.8
4	18.1	17.5	17.3	12.3
6	31.2	29.5	28.4	25.0
8	48.8	47.3	45.5	35.4
10	76.4	68.3	60.4	55.3
12	79.4	79.5	77.3	56.3
14	81.3	82.1	80.1	75.4
16	84.7	83.2	79.5	78.1
18	85.3	84.3	80.3	80.2
20	86.1	85.3	82.9	81.3

Table XXIV Concentration of Effluents Taken from  
Sample Ports of Resin-free Soil Column

Time (days)	concentration ( $\mu\text{g}/\text{l}$ )		
	Port 1	Port 2	Port 3
0	0	0	0
2	5.1	4.9	4.0
4	7.4	6.5	6.4
8	25.8	19.3	10.4
12	37.0	29.2	14.8
16	47.3	34.3	20.4
20	51.2	46.2	34.2
24	60.3	54.3	50.1
28	78.5	77.3	67.4
32	80.8	80.3	75.2
36	83.2	79.4	79.8
40	84.2	83.2	81.8
44	85.1	84.2	80.3
48	85.9	83.8	81.1
52	85.2	84.5	80.4



## VITA

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