

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

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### **ABSTRACT**

The effects of mass transfer properties on pesticide transport through a lab scale soil-water system were evaluated with alternative kinetically based model formulations. External and Internal Resistance as well as Surface Kinetic approaches were employed. Statistical procedures were used in subsequent data analysis to identify model conformance to collected data. The results of the experimental phase of the research indicated that the soil adsorptive capacity increased significantly with the removal of lipids and resins, suggesting that specific types rather than the sum of soil organics affected the adsorption process. While all three models satisfactorily predicted the ultimate capacity, only the Surface Kinetic approach simulated the shape of the breakthrough curves. The low soil organic contents and inherent surface heterogeneities apparently resulted in incomplete coatings of the soil particles and diminished the utility of the External and Internal Resistance Models. These are based upon the assumption of constant adsorptive potentials. The Surface-Kinetic Model effectively addressed this problem. In contrast to traditional adsorption theory, the transfer of an organic solute from liquid to soil may be due to several mechanisms resulting in the adsorption of solute onto the mineral surface as well as a partitioning of adsorbate into the soil humic materials themselves. Further studies on these processes are necessary for a better understanding of the solute transport process in the soil-water system.

Adsorption to farm soils is one of the more important factors used to assess the environmental impact of pesticides applied to the land's surface. The transport of pesticides in the saturated or unsaturated zones is advanced by fluid advection and dispersion and retarded by soil adsorption. The pesticides retained by the soil as well as those in the soluble phase may be further available for biodegradation or chemical decomposition. By way of background, current analysis approaches makes several simplifying assumptions to allow for more readily usable mathematics; adsorption of pesticides and tangentially other soluble organics is linear, reversible and at equilibrium. In contrast, the research reported here employed kinetically based mass transfer approaches to evaluate fundamental transport processes. These diffusion based approaches offer greater potentials for more accurately predicting the sorption of contaminants onto agricultural soils than do the equilibrium based methods traditionally included in retardance equations. By way of background, the basic one-dimensional mathematical expression for solute transport through a porous medium has been expressed as:

$$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial z} + D \frac{\partial^2 C}{\partial z^2} - \frac{\rho_b}{\epsilon} \frac{\partial q}{\partial t} \quad (1)$$

If axial dispersion is ignored, Equation (1) becomes:

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

Further assuming that the adsorption is rapid relative to flow velocity (i.e., local equilibrium between the aqueous and solid phases always exists) and that the adsorption is linear:

$$\frac{\partial q}{\partial C} = Kd \quad (3)$$

Then, substituting  $\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C} \frac{\partial C}{\partial t}$  and Equation (3) into Equation (2):

$$-u \frac{\partial C}{\partial z} = \left( \frac{1 + \rho_b Kd}{\epsilon} \right) \frac{\partial C}{\partial t} \quad (4)$$

where:

$$1 + \frac{\rho_b Kd}{\epsilon} \text{ is known as the retardation factor.}$$

The distribution coefficient in Equation (3) describes the partitioning of solute between the aqueous phase and the solid medium. This coefficient may be derived

<sup>1</sup> Variables are defined in the nomenclature listing at the end of this article.

from the linear adsorption isotherm, which is a simplification of the original Freundlich model, or from empirically generated regression equations. If derived from the non-linear Freundlich model, the exponent, usually denoted as  $1/N$ , is set equal to unity and the coefficient  $K$  becomes  $K_d$ .

Should laboratory evaluation prove impractical, numerous previous investigations of batch equilibrium adsorption for soil have been made [1, 2]. It is generally held that the distribution factor  $K_d$  of hydrophobic organics such as lindane, increases with the soil organic content. Quantitative relationships between  $K_d$  and soil organic content have been evaluated by several authors [3-5]. One approach is to obtain the water/octanol distribution factor ( $K_{ow}$ ) for a specific organic material, correlate  $K_{ow}$  to  $K_{oc}$ , and then calculate  $K_d$ :

$$K_{ow} = C'/C_w \quad (5)$$

$$K_{oc} = x \log K_{ow} + y \quad (6)$$

$$k_d = (K_{oc}) (f_{oc}) \quad (7)$$

Some drawbacks of the above correlations are that they do not address specific organics in the soil, nor do they allow for conditions other than equilibrium.

While models based upon the retardation approach have reportedly been successful in predicting the transport of hydrophobic compounds in ground water [6], it is not considered appropriate for all situations. Freeze and Cherry described the concentration profiles of solute transported through a porous medium [7]. When the medium is non-adsorptive, the dispersed front of solute may move ahead of the water front while the retardation effect makes the front of solute lag behind that of the non-adsorptive system when the medium is adsorptive and equilibrium occurs. If the medium is adsorptive but non-equilibrium adsorption exists, the front of solute is somewhere between those of the non-adsorptive and equilibrium systems. Non-equilibrium adsorption is considered to reflect actual situations in many cases.

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

In a kinetic analysis, the adsorption process is considered as 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 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 surfaces (internal resistance).
3. Solute is adsorbed onto the solid (adsorption reaction).

The adsorption speed is controlled by the slowest step or the highest resistance of the above. In activated carbon adsorption, step 3 (the reaction step) is unusually very fast and its effect on the overall resistance is negligible. The adsorption rate has often been considered to be controlled by step 1 or step 2 [8].

The basic kinetic approach to be applied to a continuous flow abiotic system with advection and adsorption is to solve Equation (1) when it is coupled with a mathematical expression that describes diffusion into a single adsorptive particle. This approach is difficult to solve mathematically and requires that numerical techniques be applied [9]. An alternative approach is to substitute one or more mass transfer mechanisms into Equation (1) and introduce equilibria data.

If external mass transfer controls the phase change, the resistance for the solute to pass through the bulk liquid to the liquid-solid interface is far greater than other resistances and the system can be described by an external mass transfer model [10]:

$$\frac{\partial a}{\partial t} = \frac{K_f a}{\rho_b} (C - C_e) \quad (8)$$

When internal mass transfer becomes dominant, the resistance for the solute to diffuse along the pores and solid surface is far greater than other adsorptive properties and the system can be described by an internal mass model [11]:

$$\frac{\partial q}{\partial t} = K_s a (q^* - q) \quad (9)$$

In addition to these models, the system can also be described by a surface kinetic model [8]:

$$\frac{\partial q}{\partial t} = K_a C (q^* - q) - k_d q \quad (10)$$

While the external and internal resistance models can be applied to describe adsorption where all of the adsorbent surface has equal affinities to the solute, the surface kinetic model can be used when locations along the solid surface have different affinities to the solute. This approach employs a second reversible surface reaction to describe the uptake of solute from liquid to solid. The overall uptake rate,  $\partial q/\partial t$ , 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  $t$ , while the desorption rate is proportional to the solute uptake at time  $t$ .

Thomas presented an approximate solution to Equation (10) [12]:

$$C/C_0 = \frac{1}{1 + \exp [k/Q (q_0M - C_0V)]} \quad (11)$$

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

These models have been shown to be applicable to abiotic adsorptive systems, where no biological degradation has occurred. They were developed especially for fixed-bed activated carbon processes where adsorption is the dominant mechanism [8], but recent developments have indicated that soil-based adsorption may include comparable mechanisms [13]. Humic materials have been described as membrane-like aggregates which are composed of partially decomposed plant derived components. These compounds are held together by weak attractions such as hydrogen bonding. The membrane-like humic structure consists of polar, hydrophilic exterior surfaces with hydrophobic interiors. Polar organics may interact with the exteriors of the humic structures while hydrophobic organics tend to partition into rather than adsorb onto the interiors of the humic molecule. Karichhoff proposed that the adsorption process in soil is controlled by a two-step process of rapid surface sorption followed by slower diffusive transport into the interior of the solid [14]. This model would correspond to an initial surface kinetic limited step followed by a diffusion based internal resistance model. Internal resistance, in this application, describes either partitioning into humic materials or adsorption onto mineral surfaces. It has been shown that attractions to mineral surfaces may exceed those to soil organics at low soil organic levels [15]. Other factors, however, such as an uneven organic coating on the soil surface may affect the applicability of the internal resistance model to describe adsorption onto soils. Similarly, there are organics other than humics in soils receiving pesticides. These organics may not exhibit similar partition properties and may also not best be described by an internal resistance approach.

In this investigation, experimental column breakthrough data were obtained to evaluate the utility of these three kinetic approaches to laboratory scale soil adsorption systems. These soil systems can be characterized as having relatively low organic contents, which were not exclusively humic materials. Further, serial extractions of select portions of these soil organics were made to produce similar, but altered, adsorptive surfaces. In this way, the fundamental hypothesis relating adsorption to total soil organic content was evaluated as were the several hypotheses of mass transfer.

## MATERIALS AND METHODS

### Experimental

*Solute* — The pesticide lindane ( $C_6H_6Cl_6$ ) was used in this investigation as the adsorbate. It is a commonly used agricultural chemical, a non-ionic, non-polar hydrophobic chlorinated hydrocarbon. Regent grade lindane for this investigation was obtained from the Supelco Company. 2.5 milligrams of solid pesticide was dissolved in 1 liter of distilled water with magnetic agitation. This solution was

Table 1. Properties of Soil Adsorbents Used for This Study

	<i>Original Soil</i>	<i>Lipids-Free Soil</i>	<i>Resins-Free Soil</i>
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/100 gm)	12.3	11.7	11.9
Surface area m <sup>2</sup> /gm	15	21	20

Source: Ho [18].

then diluted with distilled water to a total volume of 25 liters, resulting in a final concentration of 100 µg/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 played by different types of soil organics in adsorption. The extraction method used can be found in Stevenson [16]. The soil was initially sized using a US No. 200 sieve with 0.0075 mm openings. The materials passing this sieve size were then extracted to remove lipids as well as resins. Lipid fractions contained oils, waxes, greases and were extracted from these samples by using diethyl ether as a solvent while a second extraction with ethyl alcohol removed resins. 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. Residual organic matter in the original and the serially extracted soils was determined by the titration method proposed by Gaudette [17]. The properties of the soil and soil extracts used for this study were presented by Ho [18] and are shown in Table 1. To reduce the interference of biological activity, all soil adsorbents were autoclaved at 15 psi and 250°F for 30 minutes before filling the columns.

*System construction and operation* — The original and sequentially extracted soils were placed in three plexiglass columns shown in Figure 1. Glass beads of 3 mm in diameter were mixed with the soil to increase hydraulic conductivity. All columns were operated in downflow mode at 10 mL/hr. Flows were delivered by a multihead peristaltic pump which was recalibrated daily by pumping distilled water into a volumetric flask. 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. The physical conditions for these experiments were:

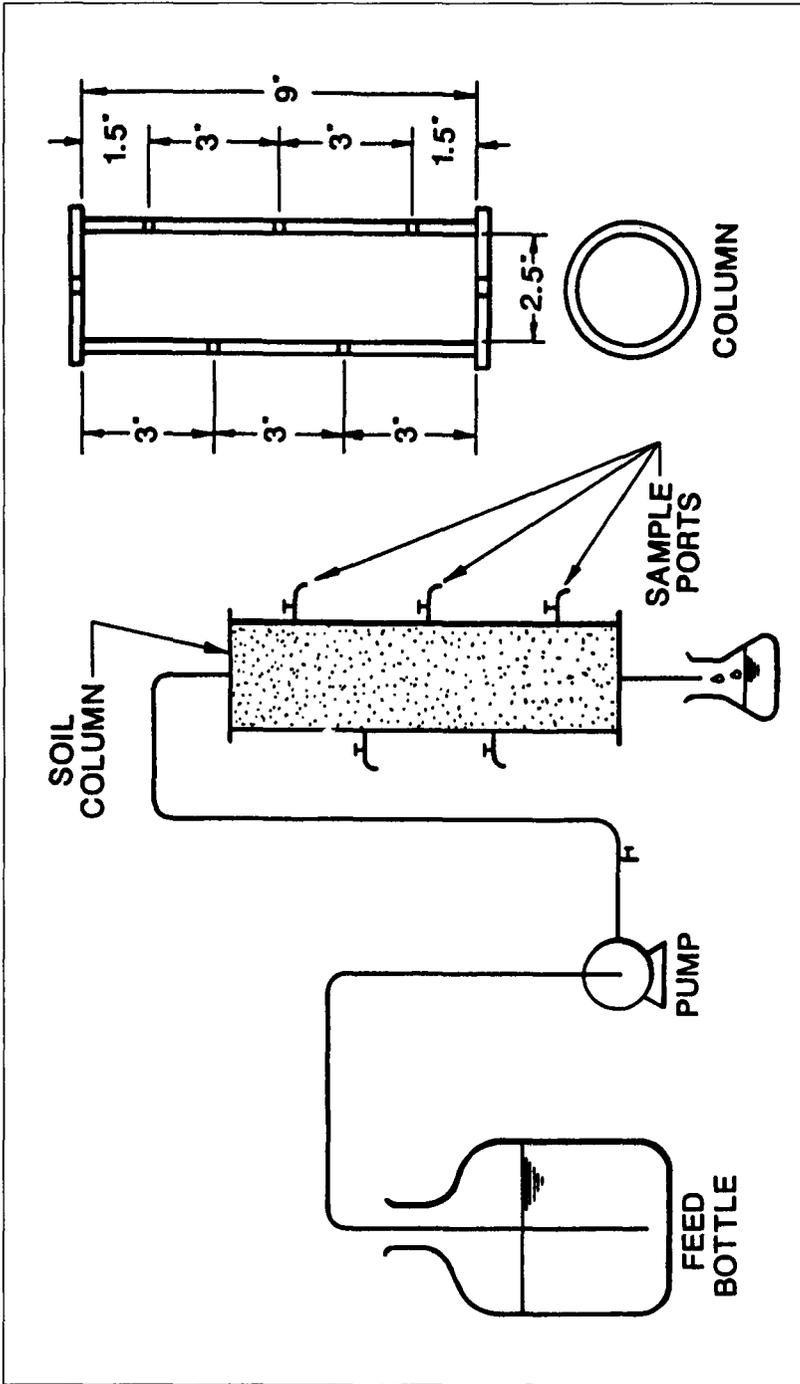


Figure 1. Schematic of laboratory column system.

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 E-4 cm/sec

pH = 6.2

Influent Concentration: 100 µg/L

*Analytical methods* — Lindane 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 each soil column. The top and bottom ports of the reactor vessel were sampled for GC analysis. A 1.5%-SP-2250 packing was used in the GC column which was obtained from Supelco Company. The data were processed and printed by a digital integrator (Perkin-Elmer LCI-100).

The operational parameters of the GC were:

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 further diluted with this solvent to obtain proper concentrations for subsequent use. A microextraction technique was employed to remove 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 [19]. Average recoveries of about 90 percent for lindane were recorded 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. The recovery was then calculated by dividing the "obtained" concentration by the 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.

*Models* — Three kinetic models (External, Internal, and Surface Kinetic Models) were employed to compare the experimental data. If the measured data could be described by a particular formulation based upon one of the features previously discussed, the adsorptive system evaluated was then said to be controlled by the type of resistance or other mechanisms inherent in the model. The mass transfer coefficients in the External Model were calculated using

correlations presented by Hines and Maddox [9]. The solution to Equation (8) was also from these same authors. The intraparticle mass transfer coefficients for the Internal Model were calculated by correlations proposed by Helfferich [20], while the solution of Equation (9) was obtained from [9]. Mass transfer coefficients for the Surface Kinetic Model and solution to Equation (10) were obtained using the method given by [12]. Predicted effluent concentrations versus time for the three soil columns were calculated using these kinetic models.

*Statistics* — The breakthrough data from the laboratory experiments and those from the predictive models were analyzed by Analysis of Variance (ANOVA) and Duncan's Multiple-Range Test. ANOVA was used to compare several data sets to determine whether there were differences among the data. If statistical differences existed, Duncan's Multiple-Range Test was employed to further identify these differences between any two of the data sets tested. In this study, the data to be compared were the ultimate adsorption capacities determined for experimental as well as theoretically predicted breakthrough curves and the measured concentrations and those simulated by each of the three kinetic models. ANOVA

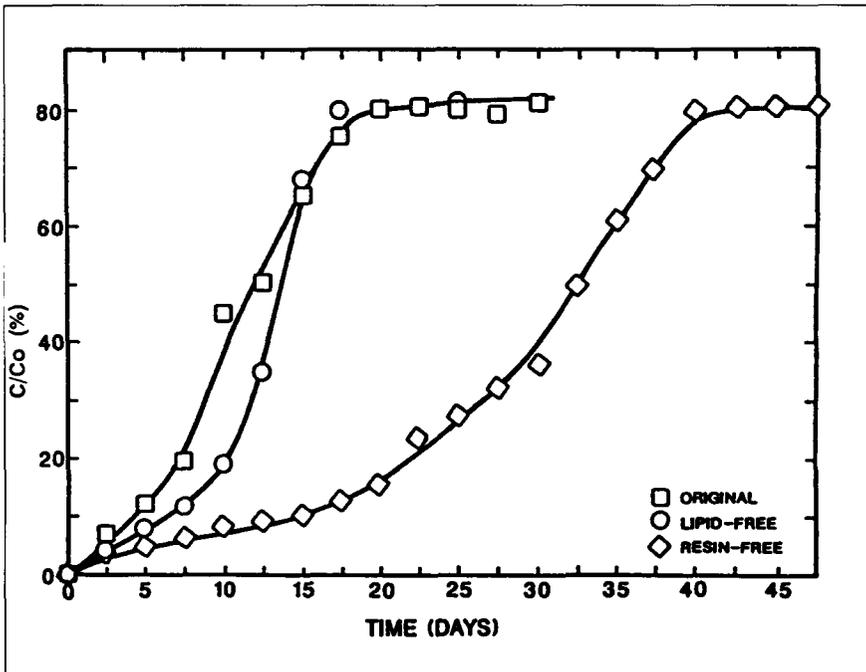


Figure 2. Experimental breakthrough curves for original, lipid-free, and resin-free soil adsorbents.

Table 2. Experimental Breakthrough Data for Original Soil  
(Influent Concentration = 100 µg/L)

<i>Time (Days)</i>	<i>Volume Fed (Liters)</i>	<i>Effluent Concentration (µg/L)</i>		
		<i>Original Soil</i>	<i>Lipid-Free Soil</i>	<i>Resin-Free Soil</i>
0	0	0	0	0
2	0.48	7.1	4.1	3.9
4	0.96	12.3	8.3	5.1
6	1.44	19.8	11.8	6.5
8	1.92	44.9	19.2	8.3
10	2.40	50.2	34.7	9.1
12	2.88	65.4	68.2	10.2
14	3.36	75.7	80.0	12.6
16	3.84	79.9	80.9	15.2
18	4.32	80.5	81.1	23.7
20	4.80	80.0	81.8	27.4
22	5.28	79.4		31.9
24	5.76	81.1		36.1
28	6.72			49.7
32	7.68			61.2
36	8.64			69.7
40	9.60			79.8
44	10.56			80.1
48	11.52			80.0
52	12.48			80.2

was applied using the computer software developed by Yee [21], while Duncan's method was calculated using an internal program prepared for this effort.

## RESULTS

The experimental breakthrough data for the three soil columns are presented in Table 2, while breakthrough curves of concentration versus time are found in Figure 2. These data showed that the time to breakthrough initially decreased and then increased with the respective soil extractions completed. A comparison of the breakthrough curves predicted by the External Model with the experimental data are shown in Figure 3 for the three soil adsorbents, while similar comparisons for the internal Model and the Surface Kinetic Model are presented in Figures 4 and 5 respectively. It can be seen that the External and Internal Models did not fit the

Table 3. Ultimate Adsorptive Capacities Calculated from Experimental and Model-Predicted Breakthrough Curves ( $\mu\text{g}/\text{gm}$ )

<i>Models</i>	<i>Original Soil</i>	<i>Lipids-Free Soil</i>	<i>Resins-Free Soil</i>
Experimental	0.92	1.22	3.37
External model	0.712	0.905	2.71
Internal model	0.713	0.890	2.71
Surface kinetic model	0.85	0.96	2.65

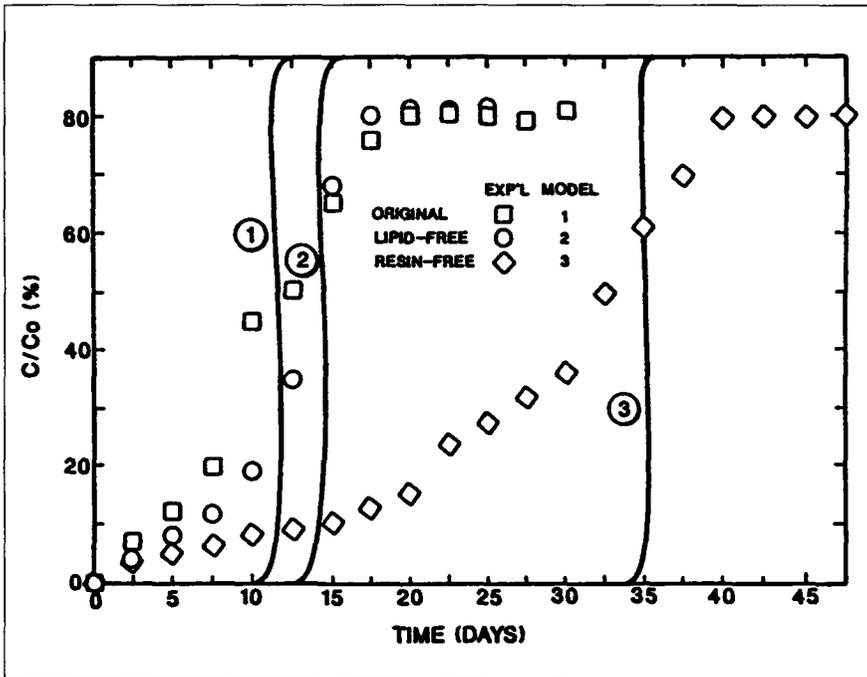


Figure 3. Simulated and experimental breakthrough data for original, lipid-free and resin-free soils. Model used: external resistance.

collected data well but that the breakthrough curves predicted by the Surface Kinetic Model appeared to better explain these data.

The ultimate adsorption capacities calculated with a fixed influent concentration of  $100 \mu\text{g}/\text{L}$  for each soil were calculated by integrating the area above the individual experimental breakthrough curves. Adsorption capacities for the theoretical curves were calculated similarly. These results are presented in Table 3.

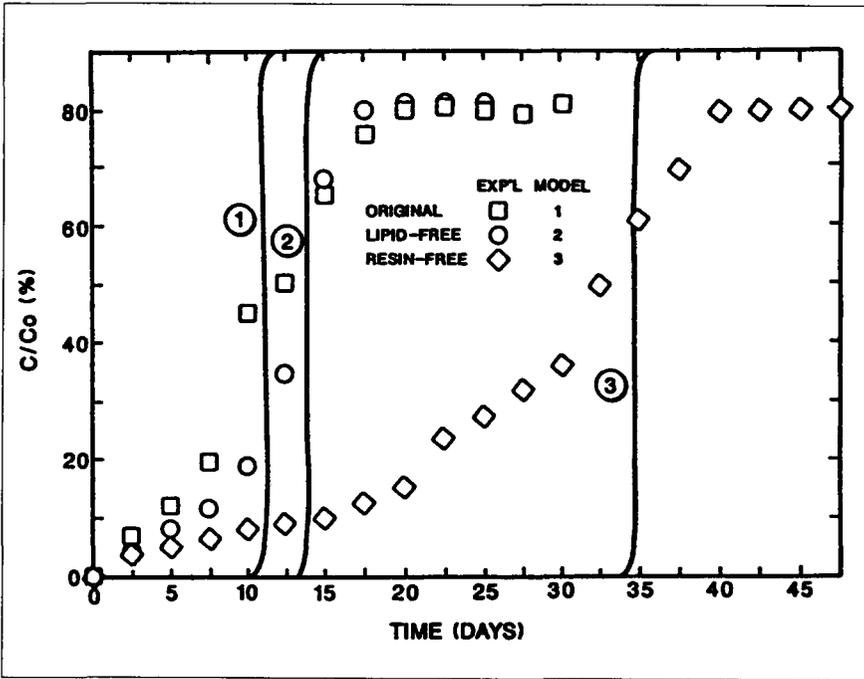


Figure 4. Simulated and experimental breakthrough data for original, lipid-free and resin-free soils. Model used: internal resistance.

These data show that the experimental adsorption capacity increases with a decrease in the amount of soil organic carbon. A 33 percent gain in adsorption capacity was noted following lipid extraction, while an overall gain of over 250 percent was realized when both soil organic components were extracted. These results contradict other studies [1, 2], which showed that adsorption capacity increased with increasing total organic content in the soil. These results are, however, similar to the DDT adsorption study conducted by Shin et al. [22], which showed that the equilibrium uptake of DDT by soil increases with the amount of lipids and resins extracted.

The theoretical adsorption capacities determined from the curves predicted by the process models, while relatively close to the experimental values, were always similar. The theoretical adsorption capacity predicted by the Surface Kinetic Model was closer to the experimental values for the whole and first soil extract than those predicted by other models. Analysis of variance calculations for the data presented in Table 3 showed that ultimate adsorption capacities could be successfully predicted by each of these kinetic models.

Table 4. Mass Transfer Coefficients Calculated for the Three Models Evaluated in the Investigation

<i>Models</i>	<i>Original Soil</i>	<i>Lipids-Free Soil</i>	<i>Resins-Free Soil</i>
External model (cm/sec)	0.060	0.075	0.072
Internal model (cm/sec)	1.49	1.60	0.48
Surface kinetic model (1/day- $\mu$ g)	0.003	0.0033	0.0012

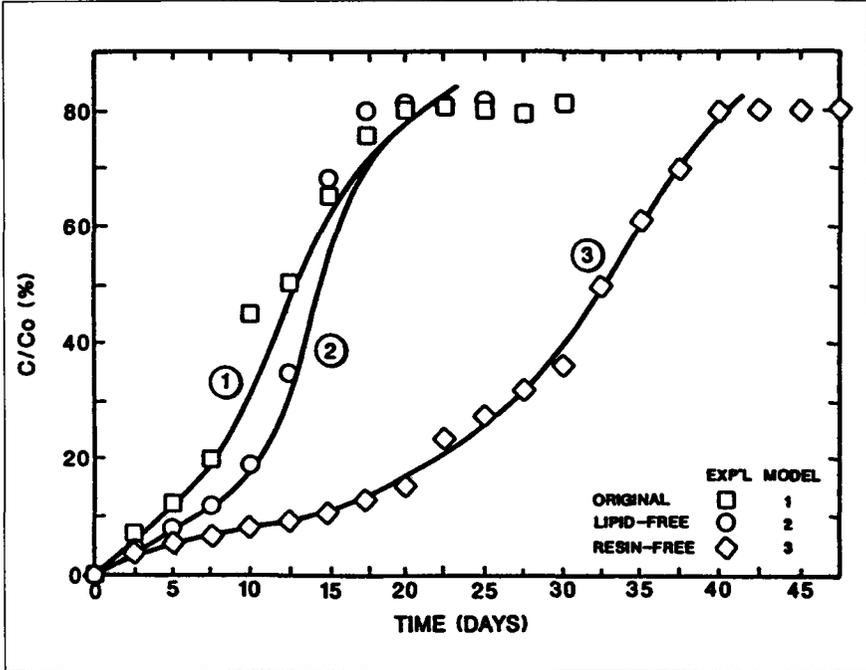


Figure 5. Simulated and experimental breakthrough data for original, lipid-free and resin-free soils. Model used: surface kinetic.

Mass transfer coefficients calculated for the three kinetic models for each soil system are presented in Table 4. It can be seen that for all three models, the removal of lipids increased the mass transfer coefficients to a small extent, while the subsequent removal of resins resulted in a significant decrease for these values.

As discussed in the introduction, if the soil column system was described by equilibrium and linear adsorption, the retardation coefficient,  $R$ , became a function of the distribution coefficient  $K_d$ . These distribution coefficients for the three

Table 5. Comparison of Distribution Coefficients (Kd) from Column and Batch Study Experiments, and from Available Organic Correlations

	<i>Column Study</i>	<i>Batch Study</i>	<i>Organic Correlations</i>
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

Table 6. Statistical Comparisons among Model Results for Three Soil Adsorbents (Duncan's Multiple Range Test)<sup>a</sup>

	<i>External Model</i>	<i>Internal Model</i>	<i>Surface Kinetic Model</i>
External model	-	S	D
Internal model	S	-	D
Surface kinetic model	D	D	-

**Note:** S means there is no significant difference and D means significant difference exists.

<sup>a</sup> Results were the same for all the three soil adsorbents.

different soil conditions were calculated from the experimental data and were compared to those calculated from batch study data conducted by Ho [18], as well as those calculated by the soil organic correlation method provided by Karichhoff [14]. The results are shown in Table 5.

The values of Kd were generally greater from batch evaluations than from column determinations, while those from organic correlation calculations were intermediate. As before, however, the lipid-free soil tended to behave differently than either of the other two adsorbents. These differences in the values of the distribution coefficients appeared to result from the columns being operated at non-equilibrium conditions.

The statistical evaluations (Table 6) indicated that the conformance of the Surface Kinetic Model to the actual data was different from that observed for the other models. This, together with the plotted data comparing the experimental with the simulation results, indicated that the Surface Kinetic Model more closely approximated the experimental data and would be a better approach for the conditions of this investigation; to predict the shape and timing of the experimental breakthrough curve.

Table 7. Results of ANOVA for Three Sets of Soil Column Experiments

	<i>Original Soil</i>	<i>Lipid-Free Soil</i>	<i>Resin-Free Soil</i>
Sum of Squares			
among models	2208.91	1068.50	4577.73
within models	3964.26	2013.64	8652.70
total	6173.17	3082.14	13230.43
Mean Squares			
among models	1104.45	534.25	2288.86
within models	120.13	74.58	160.24
Degree of Freedom			
among models	2	2	2
within models	33	27	54
total	35	29	56
Value of F-Test	9.19	7.16	14.28
Standard F Value (alpha - 0.05)	3.316	3.354	3.183

## DISCUSSION

These experiments showed that adsorption capacity increased and the magnitude of the mass transfer coefficient decreased when lipids and subsequently resins were removed from the soil matrix. The effects of these serial extractions of soil organics on these adsorption properties may result from different mechanisms. Lipids in the soil may have coated the soil particle surface as well as clogged the pores of the soil. Pierce et al. suggested that non-ionic chlorinated hydrocarbons can be adsorbed to lipids by hydrophobic bonding [23]. The overall effect of lipid removal on adsorption appeared to be that of decreasing the adsorptive capacity associated with lipids while simultaneously increasing those associated with mineral and humic aggregates, which were previously coated by the lipids. In this investigation, the removal of lipids increased the ultimate adsorption capacity from 0.92  $\mu\text{g}/\text{gm}$  to 1.22  $\mu\text{g}/\text{gm}$ . This increase was accompanied by a 40 percent increase in soil particle surface area (Table 1). The overall increase of ultimate adsorption capacity after lipid removal implied that the increased adsorption of lindane by humic aggregates was greater than the decreased adsorption by lipids.

The removal of soil resins additionally raised the ultimate adsorption capacity from 1.22  $\mu\text{g}/\text{gm}$  to 3.37  $\mu\text{g}/\text{gm}$ , while a minor decrease in surface area was

measured. This dramatic increase appeared to be caused by the resins, which had an increased polarity relative to the lipids and exhibited a smaller affinity and lower adsorptive capacity to the non-polar adsorbate. The removal of resins further increased the exposure of the lindane to humic aggregates which had higher adsorptive capacities (or partitionings) as well as to clays, while the loss of adsorption capacity associated with the resin fraction appeared minimal.

Walker and Crawford indicated that when the soil organic content is less than 6 percent, the organics do not entirely cover the soil particles, and both mineral and organic surfaces may be involved in adsorption [24]. In this investigation where soil organics were considerably less than 6 percent and where much of this material was less adsorptive than were humic materials it was assumed that the soil surface had spatially varying adsorptive attractions to the lindane. As these less adsorptive materials were extracted, the relative adsorptive capacity as well as the rate of phase transfer increased. Karichhoff has suggested that adsorption onto soils is a two-part process [14]; an initial surface interaction followed by an internal transport. Wershaw has proposed that a partitioning of the adsorbate into the hydrophobic interiors of the humics occurs rather than a true adsorption [13]. This partitioning may be equivalent to an internal transport, and while neither the internal nor external model was totally appropriate in terms of fitting the collected data, the magnitude of the mass transfer coefficients showed that these systems were at least partially controlled by external resistance. A parallel effort did show, however, that additional serial extractions beyond those utilized in this work exposed an increasing percentage of humic material which resulted in increased adsorption. Subsequent removal of the humic layer decreased adsorption [18].

Breakthrough curves simulated by the Surface Kinetic Model agreed with the experimental data most closely of the models evaluated. As discussed in the introduction, this model was based on a second order surface reaction theory, which appears to best account for the natural heterogeneity encountered in the original soil as well as allowing for the structural changes resulting from the serial soil extractions. If the adsorbents utilized in this effort exceeded 6 percent total organic carbon and were predominantly humic, a different model may have proven to be more appropriate.

## CONCLUSIONS

In this investigation, three columns filled with different soil adsorbents were used to evaluate the time dependent nature of pesticide adsorption. Three kinetic models were utilized in an attempt to simulate the experimental data which showed that the ultimate adsorption capacity increased with the removal of lipids and subsequently resin fractions. The results suggested that different types of organics play different roles in the interaction with hydrophobic pesticides. The general terms of "soil organic content," which does not address specific types of soil organics, proved to be inadequate to describe the adsorption process. The

presence of lipids and resins in the soil hindered rather than enhanced the pesticide-soil interactions. It appears 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 three kinetic models employed in this study, the Surface Kinetic Model best fit the experimental data. This model is based upon unequal potentials on the adsorbent surface. The External Model and Internal Model displayed similar discrepancies in that while they adequately simulated total adsorption, they improperly defined the shape of the experimental breakthrough curves. The magnitude of the mass transfer coefficients calculated for the more fundamentally based External and Internal Resistance models, showed that the systems were more predominantly dominated by internal mass transfer processes. The surface heterogeneity encountered in these soils appeared to limit the utility of the Internal model, as written, to simulate the collected data, but the predominance of humic-based adsorption/partitioning did appear to feature internal mass transfer. A detailed understanding of these adsorption systems would seem best explained by a heterogeneous surface controlled initial reaction followed by an internal mass transfer into the incomplete humic layer.

The amount of available surface as well as a specific resistance apparently limits the adsorption rate. The Surface Kinetic Model best addressed this system where numerous organics with varying adsorptive affinities only partially coated the soil-mineral surface.

Further research is needed to better understand the appropriate adsorption mechanisms and the role that the soil-organic structure played in the transfer of organic contaminants onto soil particles.

## NOMENCLATURE

- C = pollutant concentration in aqueous phase (mg/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)
- K<sub>d</sub> = distribution coefficient (cm<sup>3</sup>/gm)
- C' = equilibrium concentration of the pesticide or other organic compound in octanol (mg/L)
- C<sub>w</sub> = equilibrium concentration of the pesticide or other organic compound in water (mg/L)
- K<sub>ow</sub> = octanol/water distribution coefficient of the pesticide or other organic compound

- Koc = distribution coefficient of the pesticide or other organic compound between soil organics and water
- Kf = external mass transfer coefficient (cm/sec)
- Ce = equilibrium concentration at the liquid-solid interface (mg/L)
- x,z = constants
- foc = soil organic content (Decimal Fraction)
- Ks = internal mass transfer coefficient (cm/sec)
- a = specific area of the medium (cm<sup>2</sup>/cm<sup>3</sup>)
- q\* = solute adsorbed per unit of medium when equilibrated with liquid phase concentration (gm/gm)
- Ka = mass transfer coefficient (1/gm-sec)
- kd = desorption rate constant (1/sec)
- Co = influent concentration (mg/L)
- k = adsorption rate constant (1/day-μg/L)
- V = volume of water treated (liter)
- M = mass of adsorbent (μg)
- qo = Thomas solution adsorption capacity (μg/μg)
- Q = flow rate (liter/day)

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