ADSORPTION OF LINDANE ONTO WHOLE SOIL, SOIL ORGANIC FRACTIONS AND MICROBIAL BIOMASS

By

POLYCARP SOO HO

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Thesis Approved:

William F. McTernan
Thesis Adviser

Donald R. Snethen

John N. Veenstra

Norman N. Durham
Dean of the Graduate College

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CHAPTER I

INTRODUCTION

Each year, a large number of farm acres receive substantial amounts of pesticides together with other subsidiary materials (1). The widespread use of these chemicals has generated concerns among other things for the injurious effects to groundwater. Numerous instances of groundwater contamination by these chemicals have been shown to be a significant problem in many of the agricultural sections of United States (1,2). Point source pollution such as that from existing and abandoned landfills can contribute to the contamination of water table aquifers (1,2), while, non-point sources such as the leaching of agricultural chemicals can have adverse effects on the aquifers (1,2,3). In order to better control these contamination events, a more complete understanding of the fundamental mechanisms of pesticide transport through the unsaturated zone and eventually to and through water table aquifers is required. Currently, there is incomplete understanding of the transport mechanisms of pesticides. An important component of this transport to the water table is adsorption. It has been shown that synthetic organic materials such as pesticides adsorb onto soil and soil constituents, thereby lowering the solute concentration that is available for leaching (2,4). Solutes that sorb strongly onto soil materials are retarded in their movement through an aquifer or unsaturated layer. The degree of retardation is influenced primarily by the value of the distribution coefficient which is determined by the strength of solute-soil interactions. Assuming singular equilibrium adsorption-desorption models and linear adsorption isotherm, the retardation of the compound with respect to water is (2):

$$R = 1 + (p/i)K = V/Vp \qquad [1]$$

where

p = bulk density of soil (g/cm)
i = volumetric water content (ml/cm)
k = distribution coefficient (ml/gm)
V = interstitial pore velocity (Darcy v/i)
Vp = apparent velocity of the pollutant through the soil

Current groundwater transport models often use a linear isotherm to partially explain the misalignment of the water and contaminant fronts as presented by the retardation equation (equation 1). The working assumptions behind this alteration are that the trace concentration of solute contaminants found in aquifer materials with low adsorptive potentials can be adequately and appropriately described by a linear model (2,3,4,5). However, when presented at trace concentrations under conditions where adsorption rather than precipitation is the controlling mass-transfer process (4), it is suggested that linearity is not an appropriate approximation of the system because the greater the affinity of the solute for the soil phase, relative to its affinity for water, the more strongly the solute will sorb, and the greater the value of the distribution coefficient. De Marsily (3) suggested that in the case of the non-linear adsorption isotherm, where each solute moves independently of its neighbors, other instantaneous relations between F and C are more appropriate than is the linear isotherm. They are the following:

Fruendlich Isotherm:

$$F = KC^{1/n} \qquad K > 0;\ n > 1 \qquad [2]$$

Langmuir Isotherm:

$$F = (K1C)/(1+K2C) \qquad K1,\ K2 > 0 \qquad [3]$$

where:
F = Concentration of adsorbed phase
C = Equilibrium concentration of adsorbate in solution
K,n = constants

Moreover, these constants depend on the direction of the exchange if the phenomena is not strictly reversible.

Thus, solutes that exhibit strongly hydrophobic behaviors will sorb strongly onto soils. Karickhoff, et al. (5) have shown that sorption of organic solutes by soil material is governed by a simple rule: that is, the larger the organic fraction of a soil or sediment, the greater the value of the distribution coefficient. Moreover, Karickhoff, et al. (5) found that the value of the distribution coefficient was approximately proportional to the degree of hydrophobicity of the solute, as measured by the octanol-water partitioning coefficient Kow. These findings are summarized in consistent units in equation 4:

$$(Kd)_i = 6.3\text{E-}07\ (Foc)\ (Kow)_i \qquad [4]$$

where

Foc = fraction of organic carbon in the soil [gram of organic carbon per gram of dry soil]
Kow = octanol:water partitioning coefficient
i = solute index for individual pesticides

If the organic carbon content of the soil is known, the distribution coefficient (Kd) of the system can be determined from the soil organic carbon and the water solubility of the pesticides of concern by equations 5 and 6 respectively.

$$\text{Log Koc} = 3.64 - 0.55 \log WS \text{ (Kenaga, 1980)} \qquad [5]$$

where

WS = water solubility (mg/l)

$$Kd = (Koc) * \%\text{Organic Carbon} \qquad [6]$$

where

Koc of a compound is estimated from its water solubility (5)

As previously mentioned, transport of many compounds through soil is retarded with respect to water due to sorption to soil solids. Sorption of certain pesticides and other relatively complex organic compounds found in contaminated soils frequently follows the Freundlich adsorption isotherm, that is, $S = KC1/n$, where C is the concentration in solution, S is the quantity sorbed and K and n are constants (3,4,5,6). When $1/n$ significantly differs from 1, it has been found that the concentration of the organic compound influences the rate of migration of the compound through soil (1,6). When $1/n$ approaches 1, the equation reduces to a simple linear sorption isotherm, $S = KC$, and the concentration of the compound has little influence on the rate of migration (7).

This research was structured to investigate the different interactions of various pesticides between different whole soils, soil fractions and soil biomass of the type often found in soils. It is suggested that the pesticide and organics infiltrating through the root zone may adsorb onto soil organics and/or onto bacterial biomass as has been shown in previous efforts (2,8,9). This research would evaluate the underlying assumptions that adsorption is proportional to organic carbon content and is abiotic. This project was initiated because of the perceived deficiencies in the linear isotherm approach generally used.

Much of the previous work has been of a correlative nature in which the activity or loss of a pesticide from a series of soils has been compared with numerous soil properties, including parameters such as soil texture, clay mineral type and pH, in addition to soil organic matter content (10). The manner in which a pesticide reacts with the soil organic matter affects adsorption (11). The study of adsorption of any soil-applied herbicides and/or any other pesticide in general, by different fractions of the total soil organic matter, has received little or no attention. Similarly, the role of biotic materials in in these adsorptive processes has not been fully evaluated but preliminary evidence suggests that biotic surfaces have greater adsorptive capacities than do many soils previously evaluated (2,8,9).

Since one of the primary goals of this research was to isolate and subsequently evaluate the role of varying types and concentrations of soil organics in otherwise equal soil systems, a procedure was employed to fractionate the soil organic matter of a single soil into selected residuals and to study the interactions of selected pesticides with these soil fractions. The pesticide used in this initial effort was lindane as it is one of the most commonly used agricultural products in Oklahoma (12). Table 1 shows the solubility of this pesticide used in these studies as well as the toxicity and allowable limits on exposure and use in Oklahoma in a recent survey (12). The solubility of lindane is low and would generally indicate that it would have a great adsorptive affinity for appropriate absorbents.

In this research, the residual soil fractions and collected biomass were used as adsorbents in batch equilibrium

TABLE I

PERTINENT CHARACTERISTICS OF THE INSECTICED LINDANE AND ALLOWABLE LIMITS ON EXPOSURE AND USE

Formula:
1, 2, 3, 4, 5, 6 - Hexachlorocyclohexane

Trade Names: Gammexane
Gammopaz
Kwell
Lindex
Lindust
Lintox

Solubility: 10 mg/l

Toxicity: The acute oral LD value for rats is approximately 90 mg/kg.

Molecular Weight: 290.8

Melting Point: 112.9 ° C

Application: seed treatment

Source: Chemical Week Pesticide Register

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studies to derive adsorption isotherms for lindane.

In principle, this research was structured to permit an evaluation of the relative contribution made by intact and fractionated soil organics to the overall adsorptive capacity of representative abiotic adsorbents of varying organic contents. Similarly, adsorption onto biotic surfaces was also determined to identify the contribution made by soil biomass in the retardation process.

CHAPTER II

MATERIALS AND METHODS

Adsorption studies of this pesticide in water onto whole soil at constant temperature were performed in batch under equilibrium conditions. Equilibrium uptake as well as isotherm studies were completed. The pesticide solution was equilibrated with soil samples for 48 hours at constant temperature on a reciprocating water bath shaker. Samples were taken until equilbrium was achieved. Preliminary evaluations such as the determination of equilibrium times for adsorption of the pesticide onto whole soil were performed in duplicate while final experiments involving pesticide isotherm determinations were carried out in triplicate.

Equilibrium uptake curves of the pesticide onto whole soil were determined by plotting the change in concentration of these pesticides in bulk solution as a function of time. Equilibrium was considered to have been achieved when the amount remained constant for three consecutive samples. Equilibrium rate constant for the pesticide was determined by plotting concentration (log scale) in bulk solution versus time. The slope of this curve is the rate constant in concentration per time. The rate constant is used to determine how fast the pesticide can be adsorbed.

Soil and Soil Derivatives

A large soil sample was obtained from a disturbed site on the Oklahoma State University campus. The soil was air dried and disaggregated to remove gravel and eventually subjected to sequential extractions using the Proximate Analysis Method. This method applies a series of chemical and physical treatments to dissolve specific classes of organic compounds from the soil sample. The constituents dissolved originated with tissues of plants previously growing in the soil (13). Table 2 illustrates the treatments used, together with the fractions recovered.

The Proximate Analysis Method was selected for this investigations because the surface remaining following the various extractions is thought to be unchanged from the original soil particle surface (14). In this way, adsorptive property may be attributable to a lessened organic carbon concentration rather than to the alteration in the soil particle surface.

The amount of fats, waxes and oils of fraction 1, resins of fraction 2, and water-soluble polysaccharides of fraction 3 were determined by estimation of the total ash-free organic matter in ether, alcohol, and hot water respectively. Polyuronides referred to as carbohydrates were removed by 2% hydrochloric acid and estimated by reduction of Fehling's solution. The extraction with 2% hydrochloric acid removed most of the noncellulosic carbohydrates (14).

TABLE II

PROXIMATE ANALYSIS METHOD

Fraction Removed	Treatment
1. Fats, waxes, oils	Ether Extraction
2. Resins (plant substance used in lacquers, varnishes and adhesives)	Alcohol Extraction
3. Water-soluble polysaccharides (branched polymers of high molecular weight)	Hot Water Extraction
4. Hemicellulose (polyuronides)	Hydrolysis with 2% hydrochloric acid
5. Humic matter plus incompletely degraded cellulose, which is not removed by 2% HCl	Hydrogen peroxide

Residual organic matter in the forth extraction consisted primarily of humic acid or humins. These materials were then destroyed by the addition of H_2O_2 (hydrogen peroxide), leaving primarily residual products in the fifth fraction (15).

Soil Organic Carbon Concentration

Portions of the fractionated soil samples were analyzed for organic carbon content by a modified Walkley-Black titration method (16) adopted and modified by Jackson (17). This method utilizes exothermic heating and oxidation with potassium dichromate and concentrated sulfuric acid of the sample and the titration of excess dichromate with 0.5N ferrous ammonium sulfate to a sharp endpoint (18). The results of the analysis were calculated by the following equation:

$$\%O.C. = 10(1-[T/S])[1N * (0.003)(100/W)] \qquad [7]$$

where

T = sample titration, ml of ferrous solution
S = standardization blank titration, ml of ferrous solution
0.003 = 12/400 = milliequivalent weight of carbon
1N = normality of potassium dichromate
W = weight of sediment samples in grams

Cation Exchange Capacity

Exchangeable cations were also determined for each fractionated soil preparation by using the wet chemical method (19). This method consisted of adding 50 mls of 1N calcium chloride to a soil sample which was then shaken intermittently for 4 hours. The soil salt mixture was then filtered on a 5.5 centimeter Buchner funnel and the leachate was titrated with Ethylene Diamine Tetraacetic Acid (EDTA) to determine the milliequivalents of calcium per 100 grams of soil. Another portion of the soil was then saturated with 1N sodium nitrate and the leachate was analyzed for the milliequivalent of chloride by using the Mohr titration which consisted of silver nitrate as the titrant with potassium chromate as the indicator. The total cation exchange capacity was given by: milliequivalents of calcium/100 grams minus milliequivalents of chloride/100 grams = Cation Exchange Capacity (CEC)/100 grams. The fifth extractions with hydrogen peroxide reportedly removes all of the residual cover. Cation exchange capacity monitors mineral rather than organic partition surfaces. Cation exchange capacity were completed to compare their levels in the extracted adsorbents with removals of pesticide from solution by an increasingly prevalent mineral surface.

Surface Area Analysis

Portions of the original soil, selected soil derivatives and processed bacterial cells were analyzed for surface area by the Quatachrome filling method. This consists of forcing mercury under pressure into the sample to determine pore and surface volume by the mercury removed. The system consisted of outgasing the sample, filling the sample cell with mercury and measuring the volume of pore radii to a limit of about 4 microns. The relation between pore radius and pressure was given by:

$$Pr = -2Y \cos i \qquad [8]$$

where P was the absolute pressure in psi, r was the pore radius in microns, Y was the surface tension in dyne/cm (480) and i (140°) was the contact angle between the mercury and pore wall. Thus, the above equation reduced to:

$$r = 106.7/P \qquad [9]$$

As intrusion occurred, the height of mercury in the measurement apparatus decreased. The capacitance detector in the autoscan porosimeter converted the height of the mercury column into an electrical signal. It did this by measuring the volume and pressure outputs of the autoscan porosimeters, and the filling apparatus at discrete pressure intervals. These values were used to calculate the user defined quantity such as surface area which was then immediately plotted versus pressure. The system measured pressure and volume at least 5 times a second but utilized only those values which were separated by a minimum pressure difference.

Bacterial Biomass

Bacterial mass was obtained by collecting return bacterial cells from a 2.5 liter bench top reactor maintained in the School of Civil Engineering at Oklahoma State University. This reactor was fed a constant concentration of a buffered, low energy substrate to provide a genetically consistent bacterial population for subsequent experiments. Collected cells were settled and the supernatant water was decanted. Washing with distilled water was repeated several times to remove residual substrate. The cells were recovered by centrifugation, followed by drying at 110^{o}C to remove water. The bacterial material was then ground and screened to obtain equal sieve sizes of 40-mesh size fraction. These techniques were similar to those employed by Shin, et al. (20) in related experiments.

Activated Carbon

Adsorption studies of selected pesticides onto powdered and granular activated carbon were also completed to provide data for comparison to other adsorbents. That is, activated carbon adsorption in these experiments was used as a comparison media against which these soil systems and bacterial biomass could be evaluated.

Reagents, Pesticides and Other Laboratory Protocols

The organic chemicals used in the adsorption experiments were +99% purity. Organic solvents used for extraction were pesticide grade. Varying concentrations of pesticide solutions were made with distilled water that was prepared in the Oklahoma State University laboratory.

All glassware as well as microsyringes were prewashed with hot water, followed by cold water and eventually by distilled water. After prewashings, the glassware was then rinsed repeatedly with methanol to remove any water prior to a methylene chloride rinse. The methylene chloride was used to remove residual methanol. The glassware was then dried with nitrogen gas to drive off the methylene chloride. Immediately following the nitrogen gas drying, the bottles were sealed and capped and stored for later use.

Pesticide Extractions

Extractions of lindane were performed by using a microextraction procedure developed by Junk and Svee (20). This approach was developed for use in the U. S. Environmental Protection Agency verification sampling and analysis program and was chosen because it uses small sample volumes (10 milliliters) and has a reported detection limit in nanograms per liter (21).

All samples were extracted into hexane and shaken by hand in the inverted position. After agitation, the phases were allowed to separate. Three microliters were then removed by a precleaned microsyringe and injected directly on the gas chromatograph.

Pesticide Identification

The pesticide in the solvent extract was identified by elution time and estimated by peak area, using a Perkin-Elmer gas chromatograph (Sigma 2000) with an electron capture detector (Nickel-63) plus a Perkine Elmer digital integrator (LCI-100) and a glass column packed with 3% SP2100. Five percent methane - 95% argon was used as the carrier gas. Optimum gas flow, voltage and temperature parameters gave a retention time of 3 minutes. This corresponds to values from EPA standards that were processed prior to each set of sample injections.

Separate percent recovery determinations were performed and the mean recovery of five replicates for this compound was determined to be 97 percent. This means that there was reasonable certainty that any differences noted between trials were due to variations in the experimental condition rather than in analytical procedures.

Isotherm Analysis

The adsorption of certain pesticides and other relatively complex organic compounds applied to soil in batch reactors can be analyzed by several adsorption equations or models. These include the Freundlich, the linear and the Langmuir equation/models (22). Experimentally, the amount of pesticide adsorbed was determined as the difference between the total pesticide concentration originally placed in the system and that in the supernatant at equilibrium. Controls were used in each set of the tests to determine losses, if any, by volatization.

Freundlich Isotherm Analysis

The Freundlich equation has the form:

$$F = X/M = KC^{1/n} \qquad [10]$$

where

X = amount of adsorbate adsorbed
M = weight of soils
X/M = concentration of adsorbed phase
C = equilibrium concentration of adsorbate in solution after adsorption
K,N = constants

Taking the log of both sides we obtain:

$$\log x/m = \log k + 1/n \log c \qquad [11]$$

which is the equation of a straight line whose slope is 1/n and whose intercept is k. Therefore, if x/m is plotted against c on log-log paper, a straight line should be obtained, if a reasonable data fit was observed (22). Observed K and 1/n values for each of the soil derivatives, bacterial samples and activated carbons with individual pesticides were determined from the graphs. The graphically determined K values were then compared to a theoretical Kd values resulting from applications of equations 5 and 6 for the whole, and for the fractionated soil samples as well as for the bacterial biomass. These comparisons were also completed for each of the other two models selected for evaluation.

Linear Isotherm Model Analysis

The often used linear model is the Freundlich isotherm where the exponent 1/n is unilaterally set equal to 1. The equation can then be plotted on normal paper where the slope equals 1 and the intercept K. In this case, coefficient K becomes Kd, the distribution coefficient, if a reasonable fit can be observed.

Langmuir Equation Analysis

The Langmuir adsorption equation (equation 3) was initially derived for the adsorption of gases by solids, the derivation being based upon three assumptions (3):

1. energy of adsorption is constant and independent of the extent of surface coverage
2. adsorption is on localized sites and there is no interaction between adsorbate molecules
3. maximum adsorption possible is that of a complete monomolecular layer

In order for the Langmuir equation to be considered applicable to a given set of data, a straight line plot must be obtained by plotting 1/q versus 1/C.

Research Structure

Table 3 is a summary of how this research was structured.

Analysis of Variance (ANOVA)

The purpose of using ANOVA in this research was to evaluate statistically any differences in the adsorptive capacity of each of the adsorbents. This was done by utilizing a statistic package (STAT) developed by Yee, et al. (24). ANOVA is essentially an arithmetic process for partitioning a total sum of squares into components associated with recognized sources of variations.

Duncan's New Multiple-Range Test

When the Anova results indicated that there are differences between various data sets, the Duncan's multiple range test was used to separate these differences and determine which sample data set varied. The procedure for this is called the Duncan's T-test. The basic computational formula for the Duncan's multiple-range test is:

$$\text{C. diffs.} = Kr^{*}(\text{Mean square within group error}/n) \quad [12]$$

where k values are obtained from statistic tables and n is the number of groups.

TABLE III

SUMMARY OF RESEARCH STRUCTURE

Adsorbents	Replications	Test Type	Initial Concentration (ppb)
Whole Soil	2	Equilibrium	100
Whole Soil	3	Isotherm	10, 30, 50, 100, 300, 500
Soil Fraction 1	3	Isotherm	"
Soil Fraction 2	3	Isotherm	"
Soil Fraction 3	3	Isotherm	"
Soil Fraction 4	3	Isotherm	"
Soil Fraction 5	3	Isotherm	"
Microbial biomass	3	Isotherm	"
Powdered Activated Carbon	3	Isotherm	"
Granular Activated Carbon	3	Isotherm	"
Control	5		10, 20, 30, 50, 100

CHAPTER III

RESULTS

Adsorbent Data

Table 4 presents a summary of selected properties for the soil, soil fractions, biomass and activated carbon used as adsorbents in this study. This table shows that within the soil fraction series, the percent organic carbon in each of the soils decreases after each sequential treatment. Cation exchange capacity within the soil fraction series were reduced significantly, on the order of about 96 percent reduction after the fifth sequential treatment. However, surface area among the soil fraction series increased after each treatment until the fifth extraction. Significant reductions in surface area were then observed.

The table also shows that the microbial biomass has the highest organic carbon content of the soil constituents. The surface area of the biomass was significantly higher than the soil fraction series. The cation exchange capacity of the microbial biomass was observed to be less than most of the soil fractions but was significantly higher than the fifth soil fraqction, the hydrogen peroxide extraction.

TABLE IV

PROPERTIES OF SOIL, SOIL FRACTIONS, BIOMASS AND ACTIVATED CARBON

Adsorbents	Cation Exchange Capacity (meq/100 gm)	Surface Area (m^2/gm)	% Organic Carbon
Whole Soil	12.3	15	1.54
Fraction 1	11.7	21	1.21
Fraction 2	11.9	20	1.15
Fraction 3	10.5	22.5	1.09
Fraction 4	2.50	24	0.988
Fraction 5	0.40	15	0.73
Biomass	1.50	30	38.0
PAC	----	1100	----
GAC	----	800	----

Equilibrium Uptake Data

Relatively little is known regarding the kinetics of sorption of pesticides onto soils. An equilibrium uptake study was initiated primarily to determine operating times for the subsequent isotherm determinations. That is, the time when a true equilibrium is achieved where desorption equals adsorption is required to establish proper conditions for an isotherm study. Equilibrium uptake curves of the pesticide onto whole soil were determined by the change in concentration of these pesticide in bulk solution as a function of time. An equilibrium rate constants for the pesticide was determined by plotting the natural logarithm of the pesticide concentration in the bulk solution versus time. The slope of this curve was the rate constant (base e) in concentration per reciprocal time.

Figure 1 presents the equilibrium uptake curve determined for lindane while figure 2 shows the data used to determine the rate constant K. Figure 1 shows that the times to equilibrium for lindane uptake by the whole soil is approximately 15 hours, which could be explained by the fact that lindane is highly insoluble in water. The equilibrium rate constant was determined from Figure 2 was found to be approximately 1.68/day.

Isotherm Data

Table 5 illustrated the initial and final concentration

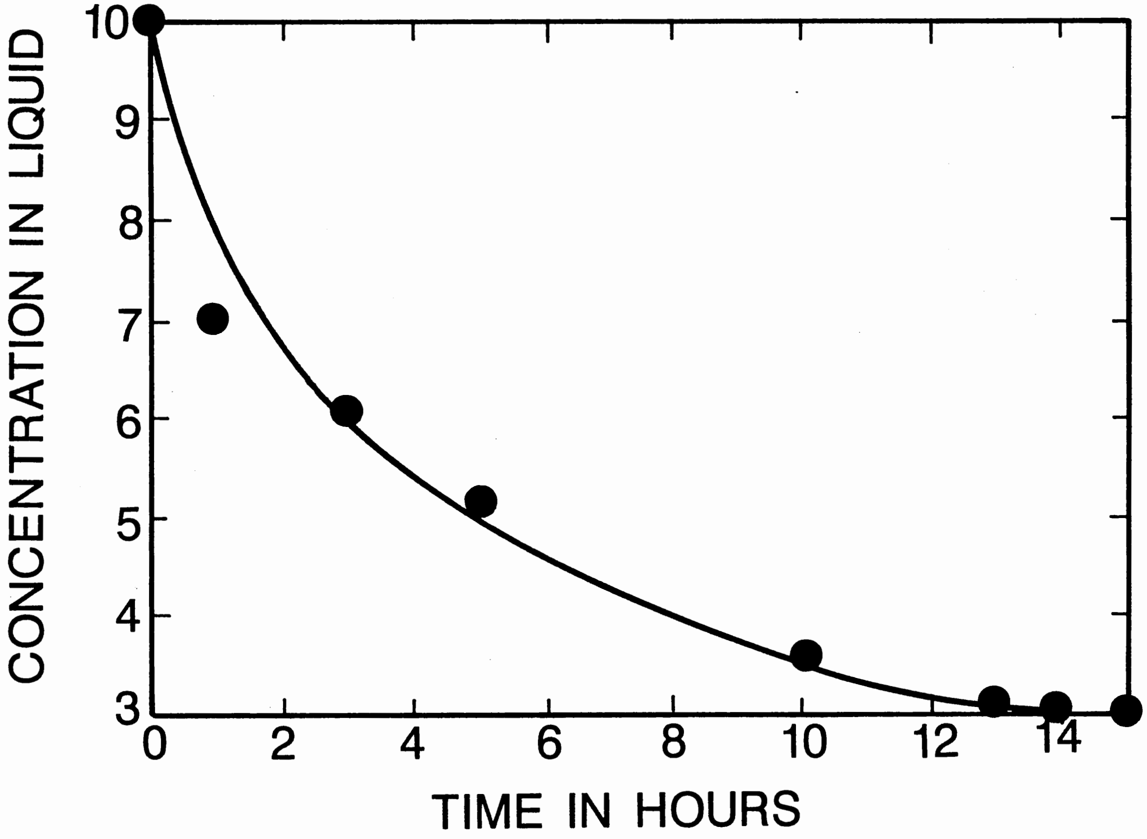

Figure 1. Equilibrium Uptake Studies: Lindane onto whole soil

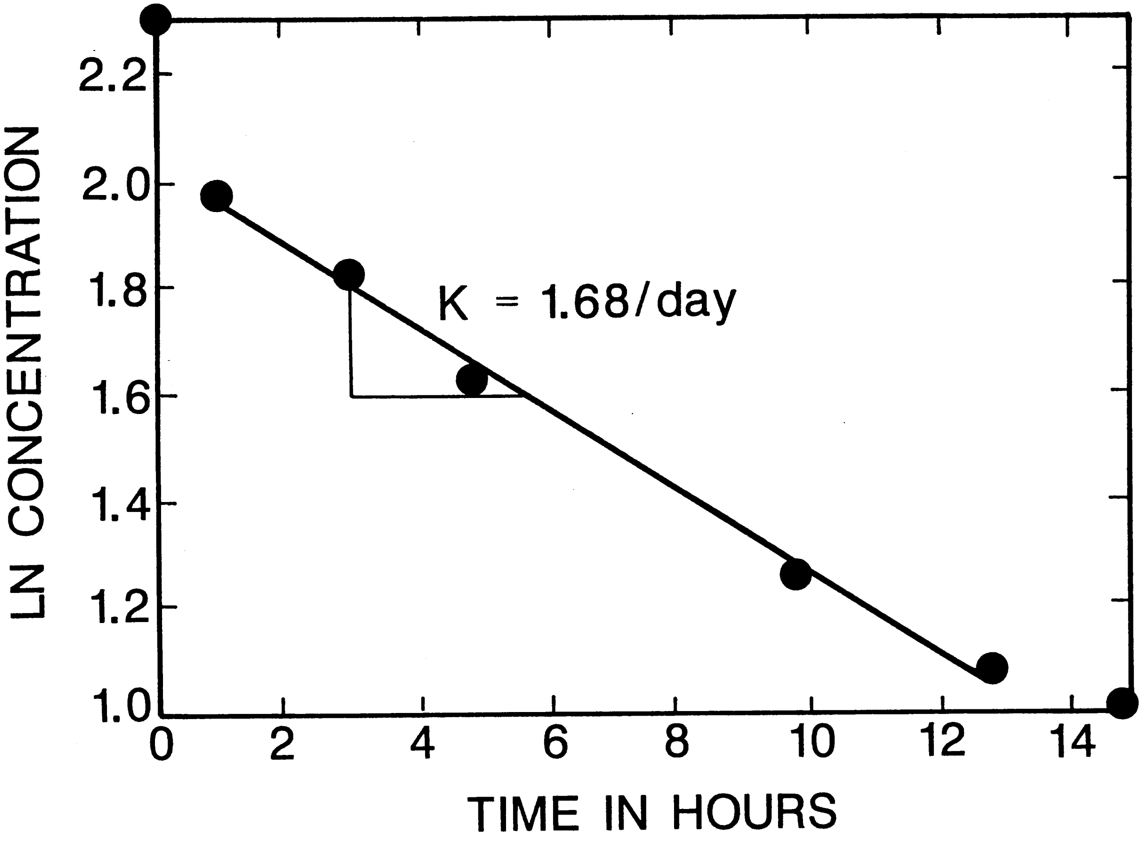

Figure 2. Determination of uptake rate constants: Lindane onto whole soil

TABLE V

INITIAL AND FINAL LIQUID CONCENTRATION (AVERAGES OF TRIPLICATES) FOR ALL TEST ADSORBENT (2 GMS) IN THE EXPERIMENT UNDER EQUILIBRIUM CONDITIONS

Adsorbents	Lindane Doses (micrograms per liter)						
	10	20	30	50	100	300	500
Whole Soil	3.50	7.94	17.9	36.9	87.7	---	---
Fraction 1	8.43	17.0	21.8	32.4	50.0	---	---
Fraction 2	1.20	2.50	---	17.0	44.0	---	157.0
Fraction 3	7.91	---	17.3	25.0	32.0	24.0	398.1
Fraction 4	1.63	3.50	5.20	7.40	10.0	43.2	256.7
Fraction 5	1.50	14.0	---	19.8	---	166.0	232.0
Biomass	BDL*	---	2.46	3.00	6.72	43.6	74.47
PAC	0.05	---	0.20	2.00	5.00	3.80	4.20
GAC	0.03	---	0.18	0.05	3.50	2.43	17.37
Control	9.92	---	---	49.87	99.76	---	498.5

* BDL represents below detection limits

for each of the adsorbents and for each of the solute concentrations used in this study. The data in table 5 showed that removal of lindane in the whole soil was approximately 65 percent at the lower influent concentration, while exhibiting significantly less removal at higher solute concentrations for the whole soil adsorbent. This could be explained by assuming that the pore space of this soil had been fully filled with the pesticide at the lower solute concentrations, leaving little available space for additional pesticide adsorption.

The soil in fraction 1 had a slightly lower removal capacity for lindane at the lower concentrations as compared to the whole soil but a significantly higher removal at higher concentrations. Soil fraction 2 showed lindane removal to be higher than either the first soil fraction or the whole soil at low but exhibited greater adsorptive affinities than any of the three previous adsorbents at the highest concentration. Soil fraction 3 was more like fraction 1 than 2 in terms of the solute adsorbed at low as well as high influent concentrations.

Significantly higher removal of the pesticide at low as well as high concentrations were observed in soil fraction 4 when compared with the other soil fractions or with the whole soil. Soil fraction 4, where the hemicellulose was removed, exhibited the greatest adsorptive behavior of any of the five soil fraction or whole soil groups over the 10 to 100 ppb range. The prevailing hypothesis is that greater adsorptive capacity was exposed in these four sequential extractions leaving only the humic layer on each soil particle. Wershaw, et al. (1987) presented a model of partitioning into humic lattices rather than adsorption onto a particular material (25). Exposure of this material by sequential extractions is thought to increase the adsorptive capacity. Therefore, removal of this material during the fifth extraction by hydrogen peroxide exposes the mineral surface of the soil by removing the final organic coat on the soil grains and lowering the adsorptive capacity at high solute concentrations.

Removal of lindane by microbial biomass was higher than that achieved by any of the soil based adsorbents at low and high solute concentration. Reference to table 4 shows that while the cation exchange capacity of the biomass was lower than all but one of the adsorbents, it's surface area was the largest measured. This appears to account for the increased adsorption.

Adsorption Properties

Table 6 is a summary of ultimate capacity ($X/M_{Co\ at\ 100ppb}$) for each of the adsorbents used in this study. The reason for using 100 ppb was to determine the adsorptive capacity of all of the adsorbent at a consistant adsorbate level. This assures that differences due to solute concentration

TABLE VI

ULTIMATE CAPACITY OF SOIL, SOIL FRACTIONS AND MICROBIAL BIOMASS AT 100 PPB SOLUTE CONCENTRATION

Adsorbents	Ultimate Capacity
Whole Soil	102.33
Fraction 1	707.90
Fraction 2	1000.00
Fraction 3	1000.00
Fraction 4	3981.07
Fraction 5	269.10
Biomass	25118.90

were controlled when interpolating linear models. The determination of these ultimate capacity value was done by reading the amount adsorbed per unit adsorbate from the ordinate of a Freundlich isotherm plot when the abscissa equals 100 parts per million.

Table 6 shows that after each sequential treatment, the ultimate capacity of the adsorbent increases until the fifth soil fraction when the ultimate capacity is significantly reduced. This values is still greater than that for the whole soil, however. Microbial biomass had the highest uptake capacity when compared to the whole soil or to the various fractions.

Statistical Analysis

Table 7 illustrates a summary of the data used in the ANOVA to statistically test whether the ultimate capacities of the various adsorbents used in this research differed from one another.

Using an alpha level of 0.05, the $f_{(6,14,0.05)}$ textbook value equals 2.85. Since the F-test of 56.3117 is greater than 2.85, the H_o is rejected and it was concluded that the ultimate capacity of some of the adsorbents were statistically different from others. The source of these differences was further evaluated.

TABLE VII

ANALYSIS OF VARIANCE DETERMINATION TO STATISTICALLY TEST THAT THE ULTIMATE CAPACITIES OF THE SELECTED ADSORBENTS DIFFERED

H_0 (Null hypothesis): the means of the ultimate adsorptive capacities at a solute concentration equal to 100 ppb for soil, soil fractions and biomass are equal.

H_A (Alternative hypothesis): they (the means of the ultimate capacities) are not equal to each other.

Critical region: reject H_0 if F-test is greater than $f_{(df,\alpha)}$.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	F-test
Among Samples	1.1E+09	6	1.88E+08	
Within Replicates	4.68E+07	14	3.34E+06	56.3117
Total Variation	1.18E+09	20		

Duncan's Multiple-Range Test

The Duncan's multiple-range tests involves the so-called layer or stairstep approach to the making of multiple comparisons. Instead of making all comparisons in relation to a single critical difference, the size of the critical difference is adjusted depending upon whether one or more of the means falls between those being compared as shown in table 8.

The basic computational formula for the Duncan's multiple-range test is:

$$C_{diffs} = Kr\ (ms/n)^{1/2}$$

where the K values are obtained from statistics tables. In all cases, if the difference between the means was larger than the minimum for that range, it was considered to be significant. The results for these comparisons are contained in table 8.

It was concluded from this analysis that the ultimate capacity of the various adsorbents were statistically different from one another except for whole soil and soil fraction 5 and for soil fraction 2 and soil fraction 3.

Isotherm Plots

Isotherms for the collected data were fitted to the Freundlich and Langmuir equations and to the linear model as shown in Figures 3 to 9. These figures show that the

TABLE VIII

DUNCAN'S MULTIPLE-TEST TO STATISTICALLY DETERMINE WHETHER ONE OR MORE OF THE MEANS FALLS BETWEEN THOSE BEING COMPARED EQUILIBRIUM CONDITIONS

	Whole	Soil1	Soil2	Soil3	Soil4	Soil5	Biomass
Whole	---	sig	sig	sig	sig	nonsig	sig
Soil1	sig	---	sig	sig	sig	sig	sig
Soil2	sig	sig	---	nonsig	sig	sig	sig
Soil3	sig	sig	nonsig	---	sig	sig	sig
Soil4	sig	sig	sig	sig	---	sig	sig
Soil5	nonsig	sig	sig	sig	sig	---	sig
Biomass	sig	sig	sig	sig	sig	sig	---

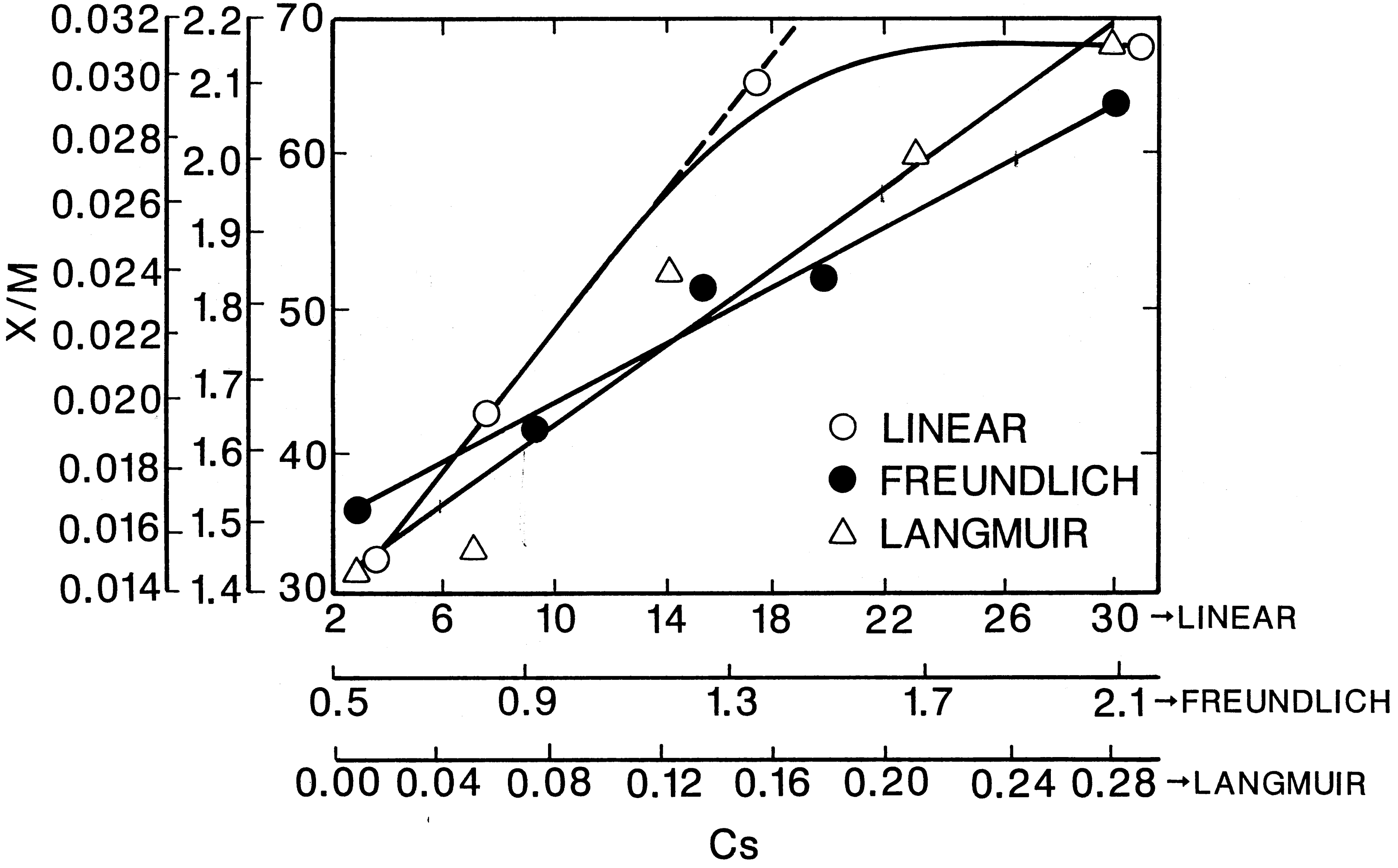

Figure 3. Lindane Adsorption Isotherms (whole soil)

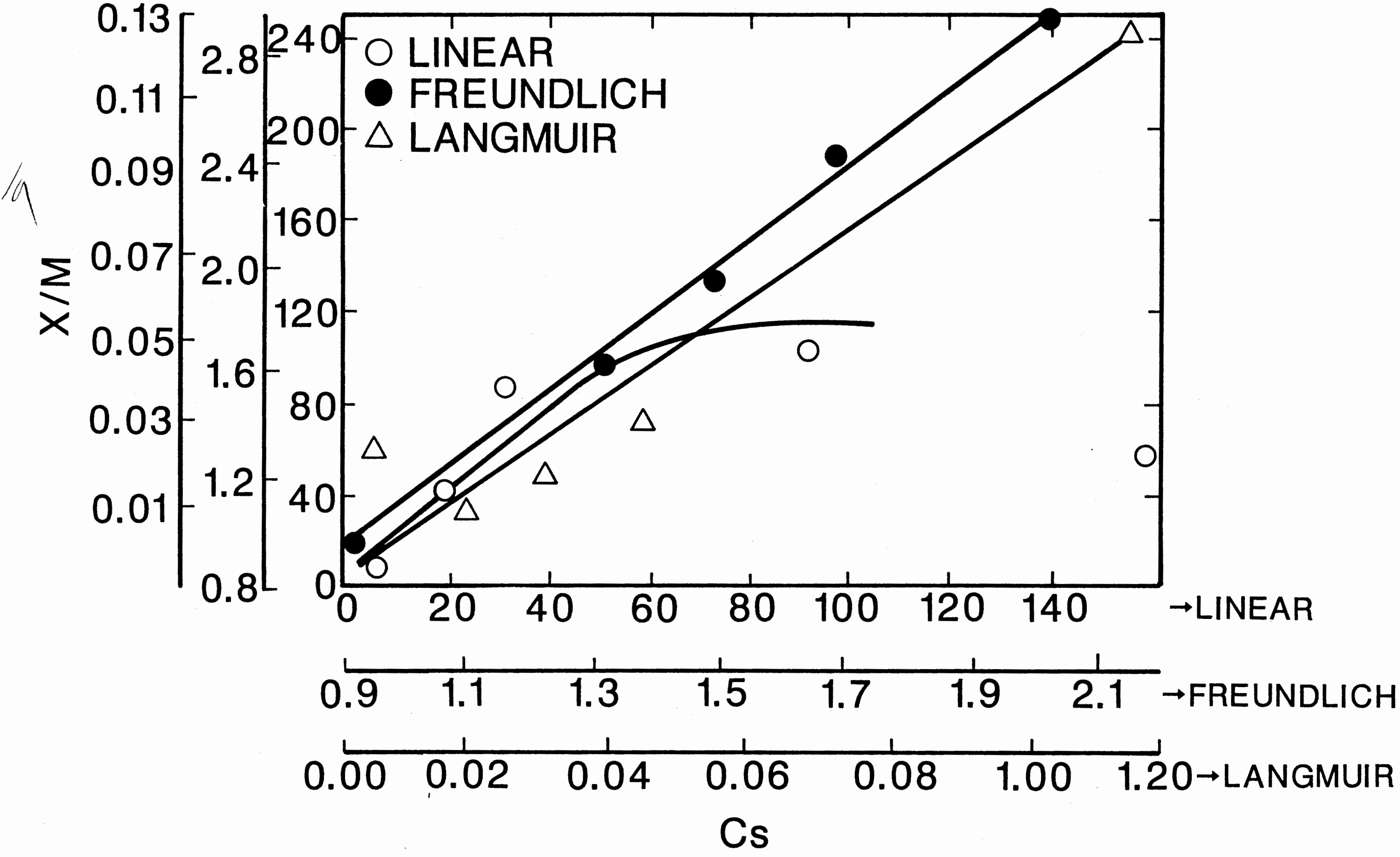

Figure 4. Lindane Adsorption Isotherms (soil fraction 1)

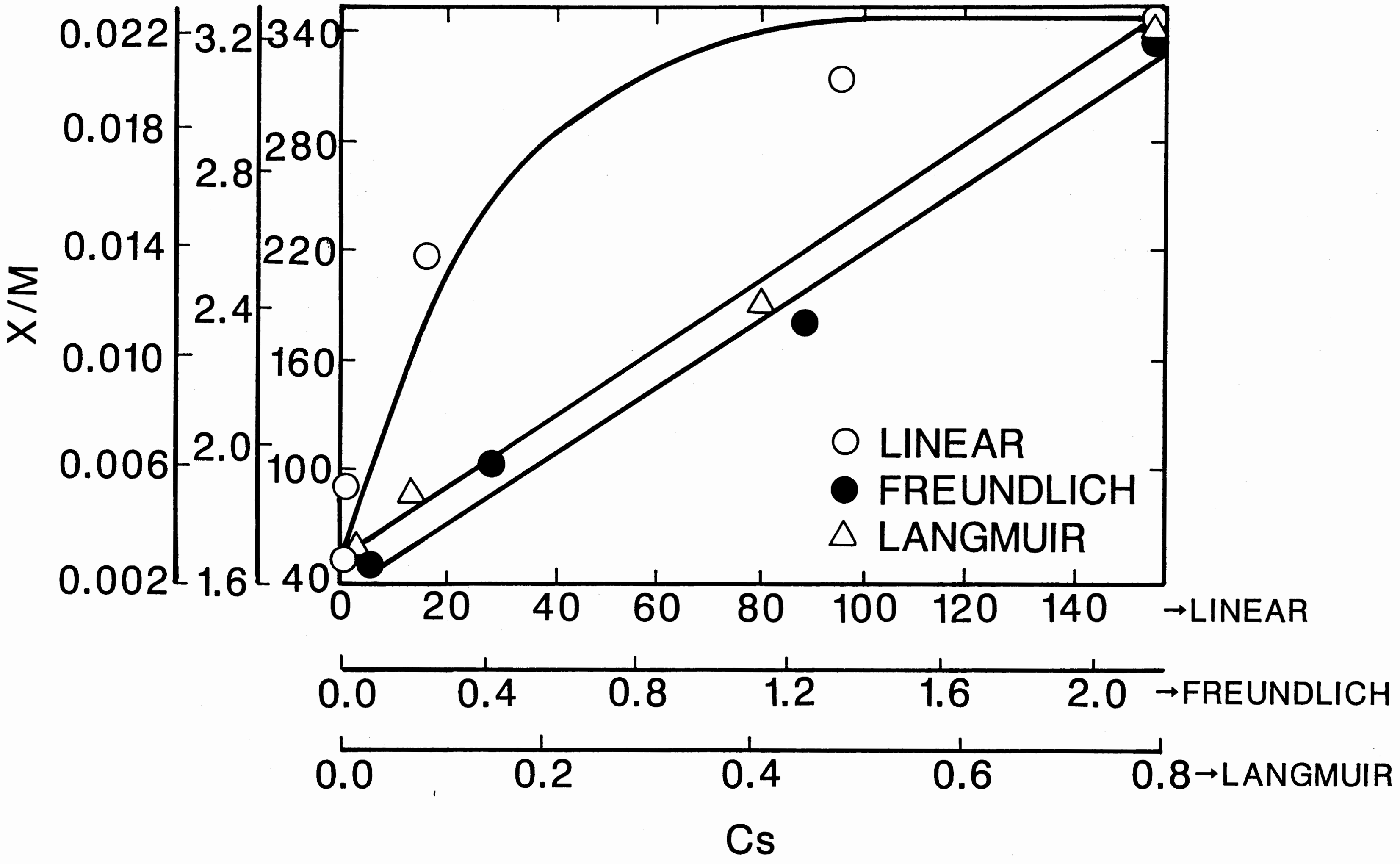

Figure 5. Lindane Adsorption Isotherms (soil fraction 2)

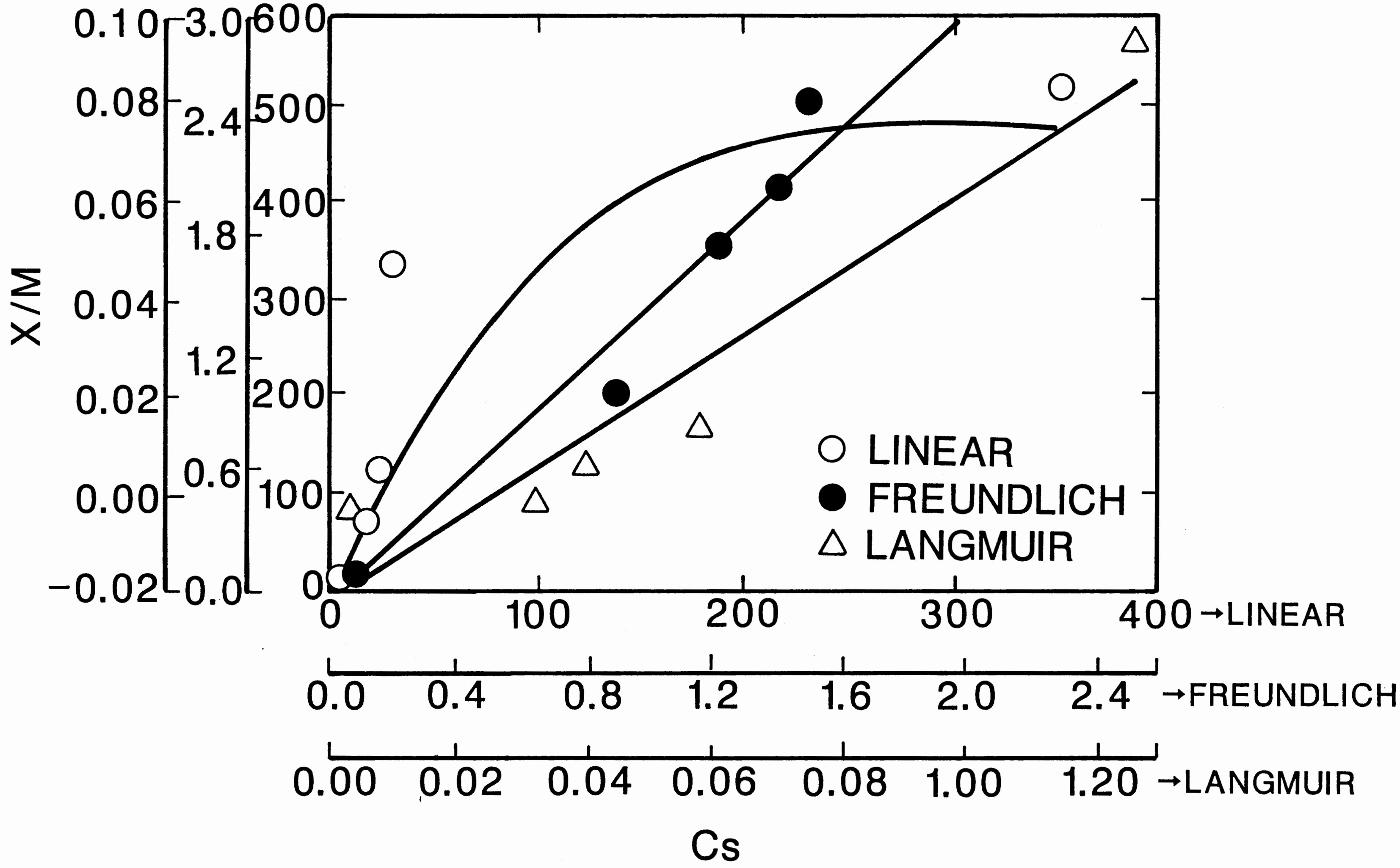

Figure 6. Lindane Adsorption Isotherms (soil fraction 3)

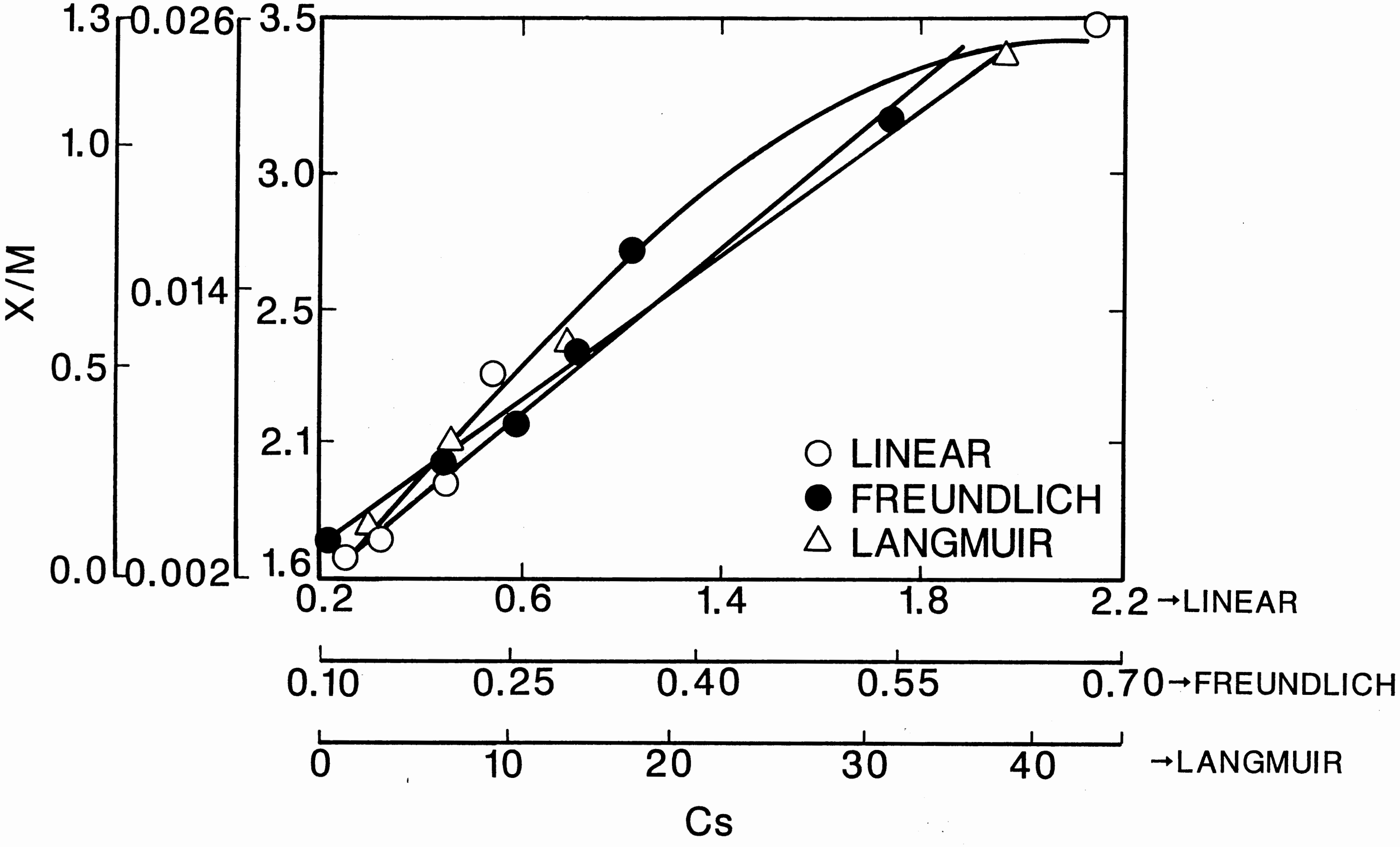

Figure 7. Lindane Adsorption Isotherms (soil fraction 4)

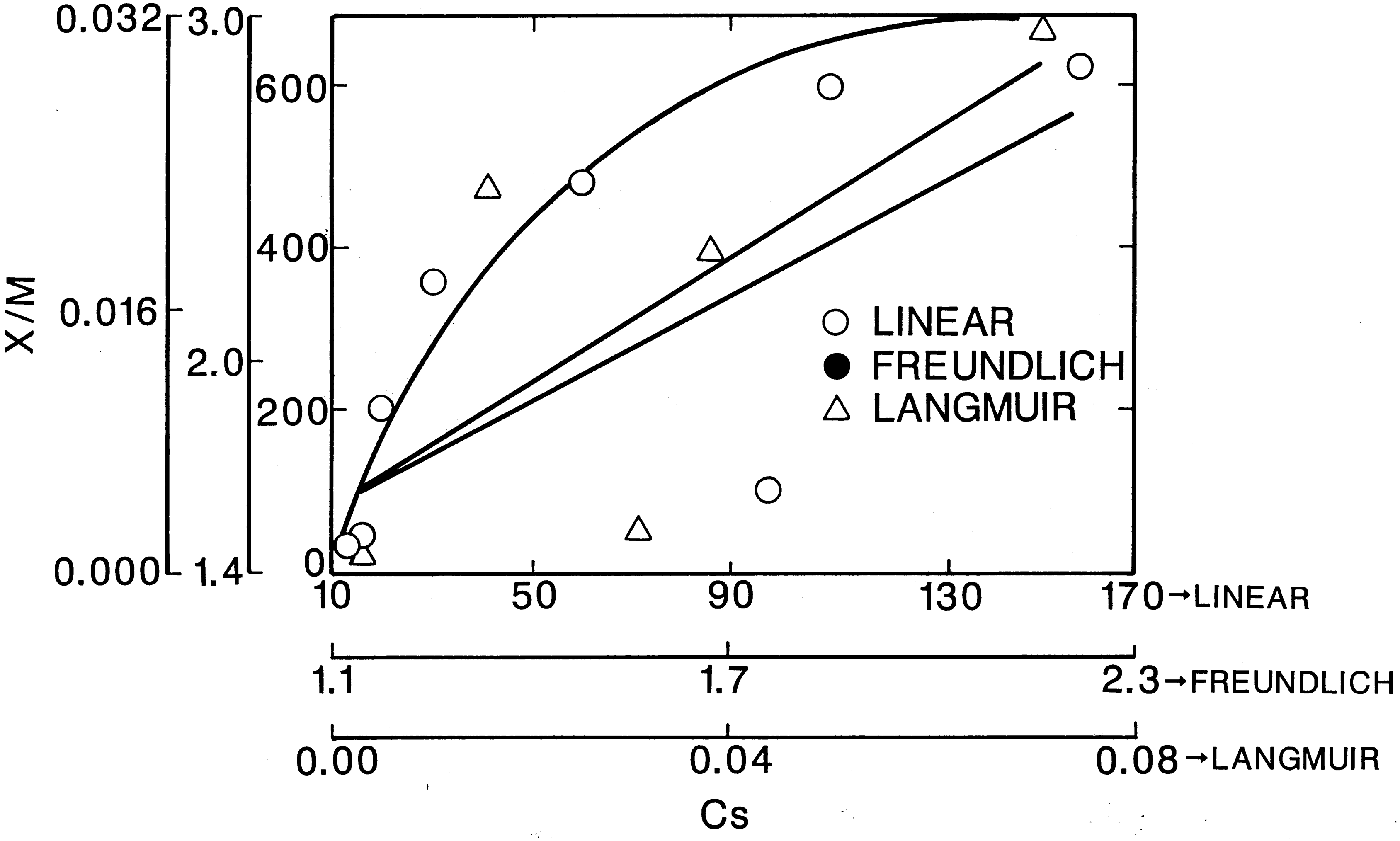

Figure 8. Lindane Adsorption Isotherms (soil fraction 5)

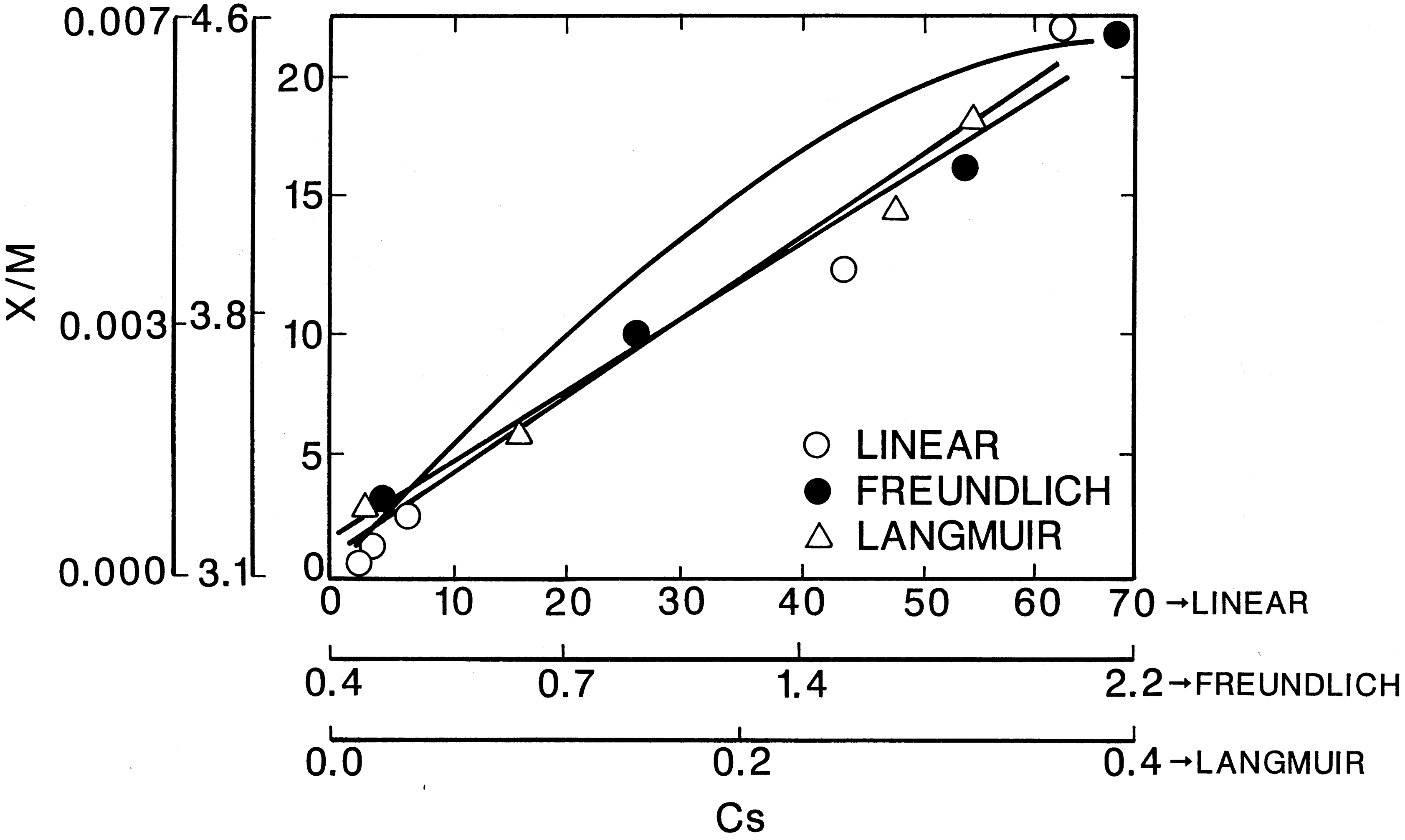

Figure 9. Lindane Adsorption Isotherms (bacterial biomass)

Freundlich and Langmuir equations described the adsorption response over the appropriate test ranges. These figures also show that the linear assumptions of the adsorption model were less satisfactory in fitting these data. Table 9 presents a comparison of coefficient of correlations and equations for the Freundlich, Langmuir and linear models when compared to the means of the collected data. The correlation coefficients for the linear equation further indicated that the linear adsorption model was less satisfactory in fitting these data or in predicting adsorption response.

Adsorption

A comparison of adsorption of lindane as a function of soil organic carbon, cation exchange capacity and surface area is shown in table 10. These comparisons were done to determine possible relationships between adsorption and percent organic carbon, cation exchange capacity or surface area.

Table 10 shows that even though the percent organic carbon of the soil fraction series decreased, adsorption of the pesticide increased for all the soil adsorbents when compared to the whole soil. The same trends were observed for cation exchange capacity because as the cation exchange capacities decreases, adsorption increases in all the various soil adsorbents. However, in the case of surface

TABLE IX

COMPARISONS OF R^2 (100%) ON VARIOUS ADSORBENTS WITH EQUATIONS FOR THE GIVEN MODEL

Adsorbent	Freundlich Equation $F = KC^{1/n}$ R^2	Langmuir Equation $F = (K_1C)/(1+K_2C)$ R^2	Linear Equation $F = KC$ R^2
Whole Soil	97	97	90
Fraction 1	95	99	2
Fraction 2	99	99	44
Fraction 3	83	94	74
Fraction 4	98	99	45
Fraction 5	98	70	83
Biomass	99	99	29
PAC	85	97	63
GAC	92	99	55

TABLE X

COMPARISON OF ADSORPTION VERSUS PERCENT ORGANIC CARBON, CATION EXCHANGE CAPACITY AND SURFACE AREA

Adsorbent	% Organic Carbon	CEC	Surface Area	Ultimate Capacity
Whole Soil	1.54	12.3	15	102.33
Fraction 1	1.21	11.7	21	707.90
Fraction 2	1.15	11.9	20	1000.00
Fraction 3	1.09	10.5	22.5	1000.00
Fraction 4	0.988	2.50	24	3981.00
Fraction 5	0.73	0.40	15	269.10
Biomass	38.0	1.50	30	25118.00

area comparisons, adsorption increases with increasing surface area. Figures 10, 11 and 12 are plots of percent organic carbon, cation exchange capacity and surface area versus the ultimate capacity of adsorption respectively. From the figures, there appeared to be a definative correlation between surface area and adsorption while the other two plots did not produce a linear relationship when adsorption was compared with the parameter values of concern. Correlation coefficients describing these relationships were calculated as 0.26, 0.42 and 0.70 for ultimate ultimate capacity versus percent organic carbon, cation exchange capacity and surface area, respectively.

These results further indicate that there is a possible linear relationship between ultimate capacity and surface area while the correlation coefficients of 0.26 and 0.42 respectively, for percent organic carbon and cation exchange capacity indicated no strong relationship between adsorption and these parameters.

Table 11 presents a summary of Kd (distribution coefficient) values obtained from the graphs and from equations 5 and 6 respectively. These comparisons were done to determine whether the two distribution coefficients obtained are similar.

Table 11 shows that the distribution coefficients that were obtained from the graphs differ from the Kd value obtained from the model for some of the soil fractions while

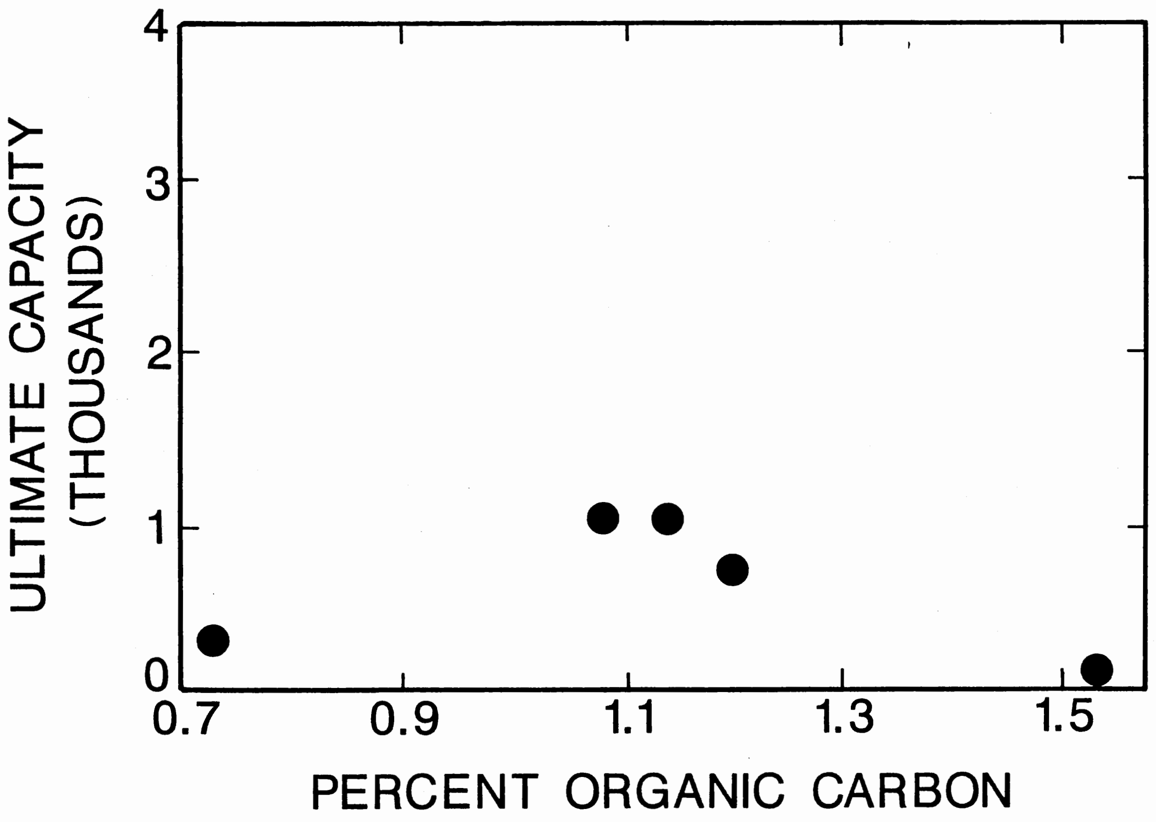

Figure 10. A Comparison of Ultimate Capacity to Percent Organic Carbon for all Soil Adsorbents (Average of Replicates)

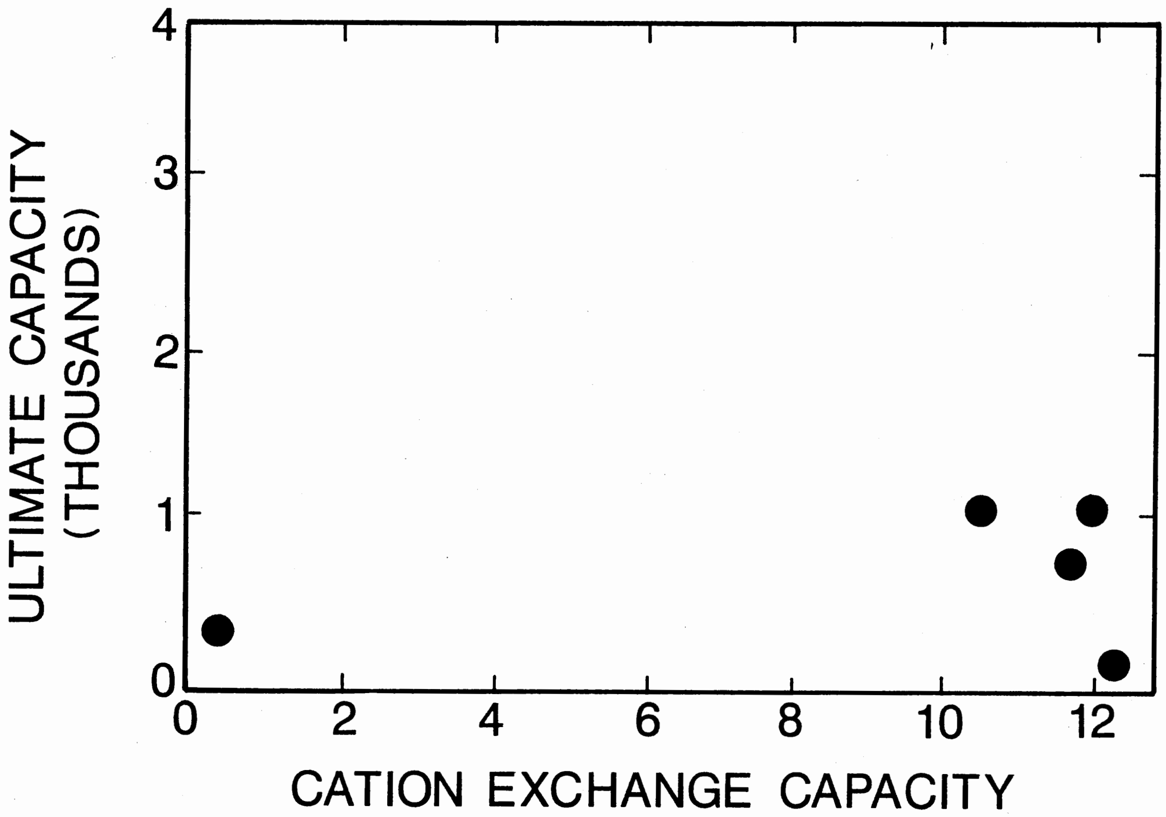

Figure 11. A Comparison of Ultimate Capacity to Cation Exchange Capacity for all Soil Adsorbents

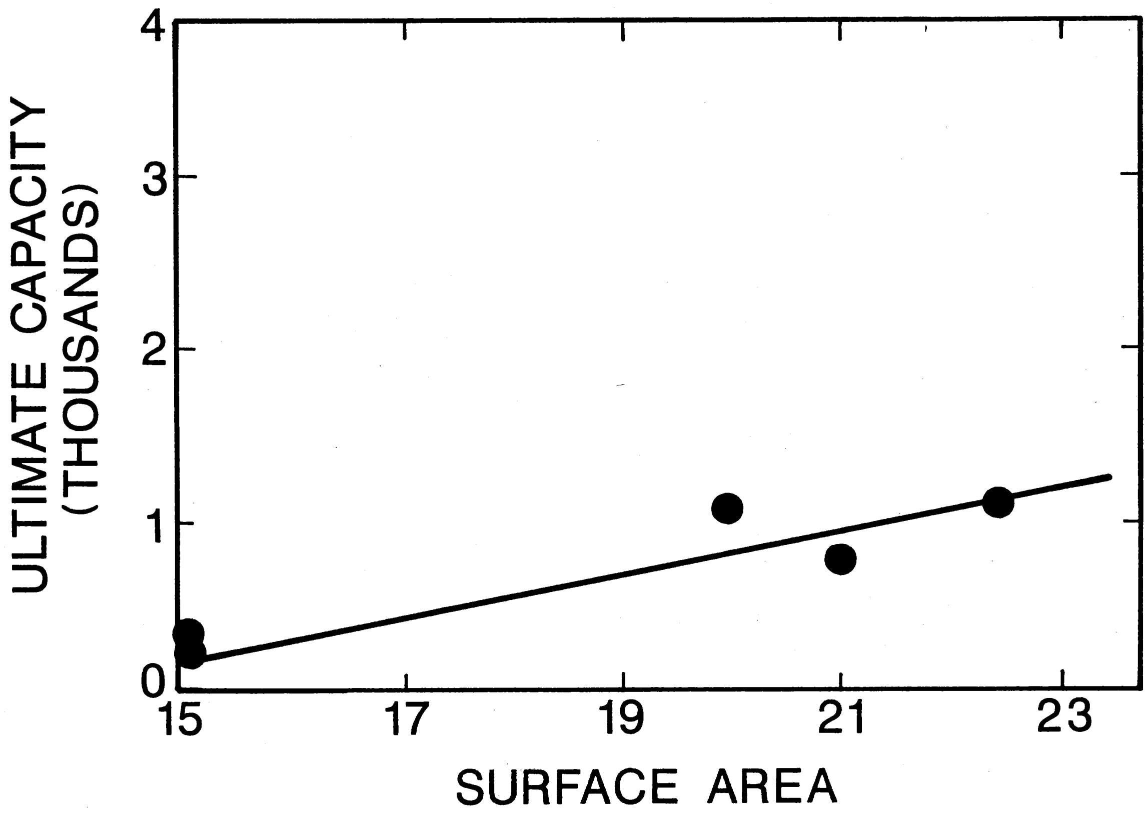

Figure 12. A Comparison of Ultimate Capacity to Surface Area for all Soil Adsorbents

TABLE XI

COMPARISON OF DISTRIBUTION COEFFICIENTS OBTAINED FROM GRAPHS AND FROM MODELS CALCULATED FOR K_{oc} = 1230

Adsorbent	K_{graph}	K_{model}
Whole Soil	20.84 (3)	18.9
Fraction 1	4.27 (4)	14.8
Fraction 2	38.00 (5)	14.1
Fraction 3	9.77 (6)	13.4
Fraction 4	12.00 (7)	12.1
Fraction 5	3.16 (8)	8.97
Biomass	691.0 (9)	467.4
GAC	316.0 (-)	----
PAC	1023.0 (-)	----

others such as for the whole soil and soil fraction 4 achieved a good approximation between the models and experimental values. The discrepancy noted in the distribution coefficient for some of the soil fractions was possibly due to the way the treatments removed the organics or the type of organics that were removed or a model format that was inappropriate for varying soil organic levels. Since it was shown that no linear relationship between percent organic carbon and adsorption exists. The Kd value obtained from the graph differs significantly from the Kd value determined by the model. The model assumes a correlation between organic carbon and Kd, which did not exist for all of the soil fractions used in this work. The model presented in equations 5 and 6 was formulated for soils high in humic acids and humins. These materials dominated the whole soil as well as soil fraction 4. Not surprisingly, the theoretical model best approximates the experimental distribution coefficient for the soil fraction reportedly containing humic materials. Similarly, the humics seem to exert the most dominant response in terms of adsorption capacity when viewed on ultimate capacity basis.

CHAPTER IV

DISCUSSION

The removal of materials that are soluble in ether and alcohol (soil fraction 1 and 2 respectively) increased the adsorptive capacity of these soil based adsorbents. Lipids, fats, resins have all been implicated in the stabilization of soil aggregate (14,15). That is, the hydrophobic materials may prevent access to adsorptive sites. Therefore, the removal of these derivatives during a sequence of extractions promotes disruption of the soil aggregates, exposure of occluded surfaces and progressive increase in adsorption (14,15). Essentially, the adsorptive surface was apparently cleaned by extraction and able to better show its intrinsic adsorptive capacity. Hayes reported similar results (11). The removal of these materials (lipids, waxes and resins) may result in an increase in the wettability of the soil surface for fraction 1, 2 and 3, thereby allowing full penetration of the pesticide solution into the available sites. Furthermore, the reduction in organic carbon content by these extractions was only a few tenths of percent, so that soils could differ greatly in these initially extracted components (fats, waxes, oils and resins) without differing significantly in total organic carbon available for adsorption. This could was supported by the increases the increases in surface area of the soil fractions after treatments with ether, alcohol and hot water, respectively. These extractions removed material which blocks surface sites sites allowing a greater adsorptive capacity to be manifested.

In fraction 4, adsorption of the pesticides was enhanced by HCl extraction. This extraction with 2% HCl removed most of the noncellulosic carbohydrates (20). Therefore, the residual organic matter in the forth fraction consisted chiefly of humic acid or humins. It was expected that humic acid exposed in this fraction would be strongly adsorptive (6). Total surface area may have increased by aggregate breakdown or relaxation of humic acid structure due to the removal of stabilizing acid structure and minerals (20). This was confirmed by the reduction of CEC in this fraction as a result of the destruction of mineral exchange colloids (6) and by increases in surface area after the extractions.

It appears that the effect of pH on HCl treatments in the fourth extractions was somehow manifested in the adsorption of the pesticide. That is, the acidicity of this treatment affected the amount of pesticide which was adsorbed and the strength with which it was held since the energy of adsorption vastly differs with varying pH's. The work of Hamaker (6), Hayes (19) and Shin (20) indicated that the degree of acidity or basicity influenced the total charge on the soil colloids. That is, the adsorption of the pesticide was likely to occur as a result of catalytic action of the clay diluent. The rate of reaction of these pesticides in the presence of clay diluents with decreasing acidity increases, thereby increasing the rate of adsorption of the pesticides.

It was found that removal of extracted humic acids from soil fractions decreased the adsorption of lindane significantly. According to Shin, et al. (6), the effect of destroying the organic matter with hydrogen peroxide could result in a reduction of total surface area, thus decreasing the adsorptive capacity of the soil. Data in table 3 shows that surface area was reduced after the hydrogen peroxide treatment. Reductions in surface area in the humic removed soil fraction was probably due to the rigorous reaction of hydrogen peroxide possibly destroying the lattice structure of the humic materials or possibly affecting the clay particles themselves (10,11,13,14,15,20,22).

The adsorptive capacity of bacterial biomass was greater than each of the soil fractions as well as the whole soil but was less than activated carbon. This was probably because the bacterial cells have a larger surface area than the soil fractions as shown in table 4 or because of the greater organic carbon found in the biomass based adsorbents.

Isotherms for the collected data fitted to the Freundlich and Langmuir equations and the linear model showed that the Freundlich and Langmuir equations better described the experimental adsorption response than did the linear model. Data fitted to the linear equation showed that there was reduced conformance to conditions of the model. Thus, the linear model cannot be used to adequately explain the misalignment of the water and contaminate fronts as presented by the retardation equation.

Statistical analysis of individual ultimate capacities for the various adsorbents showed that there were significant differences between some of the soil adsorbents. These were assumed to be due to the removal of the soil organics by the fractionation schemes utilized. These fractionations progressively lowered cation exchange capacity, raised surface area, and lowered residual organic carbon. In addition, these fractionations appeared to open pore surfaces to allow greater solute penetration.

Comparisons of adsorption to percent organic carbon, cation exchange capacity and surface area of various adsorbents showed that there was no linear relationship between ultimate capacity and % O.C. as well as CEC while adsorption and surface area indicated a possible linear relationship. It was found that a key element of those properties evaluated which affected adsorption was surface area rather than other measurable soil conditions.

CHAPTER V

CONCLUSION

This work was structured to look at interactions of lindane with different soil organic and inorganic fractions. It was found that the analysis techniques employing linear models to describe partitioning and ultimately retardation were inappropriate to data collected in this effort. Data presented in table 9 and in figures 3 to 9 showed that adsorption was not linear but actually deviated from linearity. It was found that the Freundlich and Langmuir equations better described the appropriate adsorption response than did the linear model.

The removal of hydrophobic materials generally increases the adsorptive capacity of the soil. The removal of hemicellulose by the hydrolysis of 2% HCl also increases the adsorptive capacity of the soil. Finally, the removal of organic matter by H_2O_2 in the fifth soil fraction shows that adsorption capacity of the soil decreases, probably due to the removal of the humics which previously were shown to have the highest adsorptive affinities for the solute.

Comparisons of distribution coefficient obtained from the graphs differed from the Kd value obtained from the theoretical models available for most of the soil fractions.

Others such as whole soil and soil fraction 4 (the humic materials) achieved a good approximation between the model and experimental values. These differences seemed due to the types of organics removed as well as the effects of the treatments in opening pore structure and increasing surface area.

Statistical analysis of ultimate capacity of the various adsorbent indicated significant differences among the various adsorbents. Duncan's multiple range comparison test showed that the ultimate capacities of the various adsorbents were statistically different from one another except for whole soil and soil fraction 5 and for soil fraction 2 and soil fraction 3. This indicated that the removal of all of the soil organic residue produce an adsorptive surface which was statistically indistinguishable from the whole soil. The surface areas of both whole soil and the soil fraction 5 adsorbent were equal. This seems to account for these adsorptive similarities.

Microbial biomass had the highest organic carbon content of any of the non-activated carbon adsorbents tested. The cation exchange capacity was observed to be less than most of the soil fractions but was significantly higher than that observed in the soil fraction series. The adsorptive capacity of the bacterial biomass was greater than each of the soil fractions as well as the whole soil but was less at high solute concentration than that of the activated carbon. This appears due to the observed greater surface area or organic carbon of the microbial biomass.

Finally, comparisons of ultimate capacity to percent organic carbon, cation exchange capacity and surface area indicated a linear relationship between ultimate capacity and surface area with a poorly defined relationship to either cation exchange capacity or percent soil organic carbon.

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VITA

Polycarp Soo Ho

Candidate for the Degree of

Master of Science

Thesis: ADSORPTION OF LINDANE ONTO WHOLE SOIL, SOIL ORGANIC FRACTIONS AND MICROBIAL BIOMASS

Major Field: Environmental Engineering

Biographical:

Personal Data: Born in Sibu, Sarawak, Malaysia, January 29, 1963, the son of Mr. and Mrs. Andrew Ho

Education: Graduated from Sacred Hearts Secondary School, Malaysia, in December, 1981; received the degree of Bachelor of Science in Civil Engineering from Oklahoma State University, Stillwater, Oklahoma, in July, 1986; completed requirements for the degree of Master of Science in Environmental Engineering at the Oklahoma State University in July, 1988.

Professional Experience: Research Assistant, Department of Civil Engineering, Oklahoma State University, August, 1986 to May, 1988.