ADSORPTION OF LINDANE, SILVEX AND 2,4-D ONTO WHOLE SOIL AND SOIL ORGANIC FRACTIONS IN SINGLE AND MULTI-SOLUTE SYSTEMS

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PREFACE

The overall objective of this project was to evaluate physical/chemical factors affecting sorption of pesticides by whole soil and soil organic fractions. Experiments with both single and binary mixtures of test compounds were performed in batch aqueous systems. Variations in temperature and concentration was investigated in regard to the effect on sorption.

I wish to acknowledge the fact that this research would not have been possible without the help and inspiration of my major professor and committee members, the challenge and motivation and assistance of my colleagues, the patience and forbearance and the support and understanding of my families.

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CHAPTER I

INTRODUCTION

Each year a large number of farm acres receive substantial amounts of agricultural chemicals, particularly pesticides and fertilizers. The widespread use of these chemicals has generated concerns about impairment of groundwater quality [1]. Although at a more advanced level than just a few years ago, an understanding of the fundamental mechanisms of pesticide transport is clearly lacking. Numerous instances of groundwater contamination by these chemicals underscored the need to better understand the fundamental mechanisms of pesticide transport through the unsaturated zone and eventually to the underlying groundwater aquifers [1-4]. These mechanisms, if properly understood, could be incorporated into contaminant transport models to predict plume migration and the extent of pollution while also assisting in the development of mitigative control measures. Pollution source controls that are not based on sound knowledge of the fate and transport mechanisms of these organic contaminants could result in excessive groundwater contamination or, alternatively, over-regulation.

The mechanisms that affect the fate of these organic chemicals include physical processes, such as transport by advection and dispersion, and adsorption as well as transformation due to chemical and biological reactions [2]. Adsorption is often considered the major controlling factor [2]. Research is therefore needed to characterize the sorptive behavior of these chemicals since the rates of chemical and biological reactions may be relatively low when compared to those of adsorption.

It has been shown that synthetic organic chemicals such as pesticides have adsorbed onto soil and soil constituents, thereby lowering the solute concentration available for leaching [3,4]. Solutes that sorb strongly onto soils are retarded in their movement through an aquifer or unsaturated layer. Retardation is a quantitative index of the chemicals' mobility and is equal to the ratio of the adsorbed and unadsorbed solute fronts in soils [4,5]. 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 a single solute, equilibrium adsorption-desorption model and a linear adsorption isotherm, the retardation of the compound with respect to water is [4]:

$$R = V/V_c = 1 + (P_b/N) * K_d \tag{1}$$

where

V = mean interstitial velocity of water (L/T);

V_c = mean velocity of pollutant front (L/T);

P_b = bulk mass density (solid mass/adsorbent vol);

N = effective porosity (fluid vol/adsorbent vol);

K_d = Distribution coefficient; and

R = retardance factor.

Equation (1) simulates the relative alignment of the mean pollutant front with that of the water. The distribution coefficient describes the partitioning of the solute between the aqueous phase and the soil and results mathematically from a linear isotherm, which is a simplification of an equilibrium process determined in batch systems [6].

Several previous research efforts have used linear isotherms to characterize the adsorption of polynuclear aromatic hydrocarbons (PAH), benzene, carbon tetrachloride, etc., onto sediments [7,8,9]. Many current groundwater transport models also use a linear isotherm to partially explain the misalignments of water and contaminant fronts as presented by the retardation equation (Equation 1) [7-11]. The working assumption behind this approach is that trace amounts of solute contaminants can be adequately and appropriately described by a linear model. Linear isotherms are easy to use and afford less complex mathematical solutions to the transport equations [11]. Moreover, the constant partition coefficient can be correlated with the octanol-water partition coefficient of the solute and the fraction of the organic carbon in the sorbent [11,12,13]. Karickhoff et al. [6,14] have shown that the sorption of organic solutes by soil material was governed by a simple rule: that for any given chemical, the larger the organic fraction of a soil or sediment, the greater the value of the distribution coefficient. Thus, an estimate of the distribution coefficient (K_d) can be calculated if the organic carbon content (%OC) of the adsorbent and the organic carbon partition coefficient (K_{oc}) of the solute are known:

$$K_d = K_{oc} * (\%OC)/100 \quad (2)$$

Where

K_d = partition coefficient;

K_{oc} = organic carbon partition coefficient; and

%OC = percent organic carbon.

Many K_{oc} values reported were based on empirical equations that related the solubility (S) of the solute in water to its organic carbon partitioning coefficient (K_{oc}), such as the expression given by Roy et al. [15]:

$$\log K_{oc} = 3.95 - 0.62 \log S \text{ (mg/1)} \quad (3)$$

where S is solubility of the compound.

When adsorption rather than precipitation is the controlling mass transfer process, the linear isotherm has been shown to be inadequate in addressing practical actual problems [16]. The linear model often used in groundwater contaminant transport models follows the Freundlich isotherm where the exponent 1/N (adsorption intensity) is unilaterally set equal to one. For most soil samples, 1/N is found to be less than one [17-20]. De Marsily et al. [21] further suggested that where each solute moved independently of its neighbors, other instantaneous reactions between the amount adsorbed (F) and its concentration (C) were more appropriate than the linear isotherm.

The partial differential equation generally used to describe pesticide mobility through the saturated zone [22] is:

$$\frac{\partial C_w}{\partial t} = D\partial^2 \frac{(C_w/R)}{\partial Z^2} - \frac{\partial (C_w V/R)}{\partial Z} - (K_s + U)\, C_w \tag{4}$$

where

C_w = pollutant concentration (M/L^3);

t = time (T);

V = direction velocity (L/T);

D = directional dispersion (L^2/T);

K_s = decay coefficient (T^{-1});

R = retardance factor; and

U = plant uptake.

Pollutant concentration at varying points in time and space becomes a function of the hydrodynamic features of velocity and dispersion as well as the physical, chemical and microbial sink terms which are represented in Equation (4). The development of appropriate expressions to discretize and simulate these properties has included extensive effort for the definition of adsorption and biological decay. Much of the knowledge in these areas comes from other applications which include fundamental physical chemistry and microbiology as well as from environmental engineering process research. The retardance factor (Equation 4) describes the physical-chemical attenuation in contaminant transport as shown in Equation (1).

For nonadsorbing solutes, the value of distribution coefficient (K_d) in the retardation equation equals zero; hence, R=1. For R to be greater than unity, the value of K_d should be larger than zero. Thus, a larger R indicates reduced pesticide mobility in the soil and groundwater environments. In those cases where linearity is not appropriate, increased concentrations along the entry boundary can grossly underestimate the amount of pesticide leached.

Research is also needed when two or more of these chemicals are present in soils together. In many instances, multiple pesticides are simultaneously applied or are present from previous applications. Solute adsorption rates can be significantly reduced or enhanced by the presence of another adsorbate [23-25]. While work has been done on multiple solute adsorption onto activated carbon [26-28], there is the need to investigate adsorptive mechanisms inherent in single and multi-solute systems for various soils. Possible adsorptive mechanisms of these chemicals with soil adsorbents include [23-25]:

(a). No competition. That is, adsorption should equal that in single solute systems.

(b). Negative adsorption - adsorption is less than in the single solute systems.

(c). Positive adsorption - adsorption is greater in binary systems than for the single solute systems present.

A plausible explanation for negative adsorption is that compound 1 is less soluble, and when adsorbed, gets more energy than compound 2, that is, it out competes for sites. Whereas for positive adsorption, there is the possibility of synergistic adsorption [23-25]. Synergistic adsorption is defined as an enhancement to adsorption of one solute in the presence of another solute. A workable model to address positive adsorption was similar to that of a typical surfactant adsorption isotherm shown in Figure 1 or to that of a standard chromatography model [29]. That is, when the eluting mobile phase passes through the column, there is a dynamic equilibrium between the fixed and the mobile phases. Molecules remaining on the fixed phase are determined by the distribution coefficient. The molecules remaining on the fixed phase can significantly affect adsorption of other compounds.

Figure 1 can be subdivided into four regions. In region 1, the adsorption obeys Henry's Law i.e. only unassociated, first layer molecules are present. Region II is characterized by a rapid increase in adsorption resulting from lateral interactions which eventually form clusters. These clusters served as centers from which increased adsorption could occur. In region III, the adsorption increases more slowly with concentration than in Region II. In Region IV, adsorp-tion reaches a plateau, occurrings at

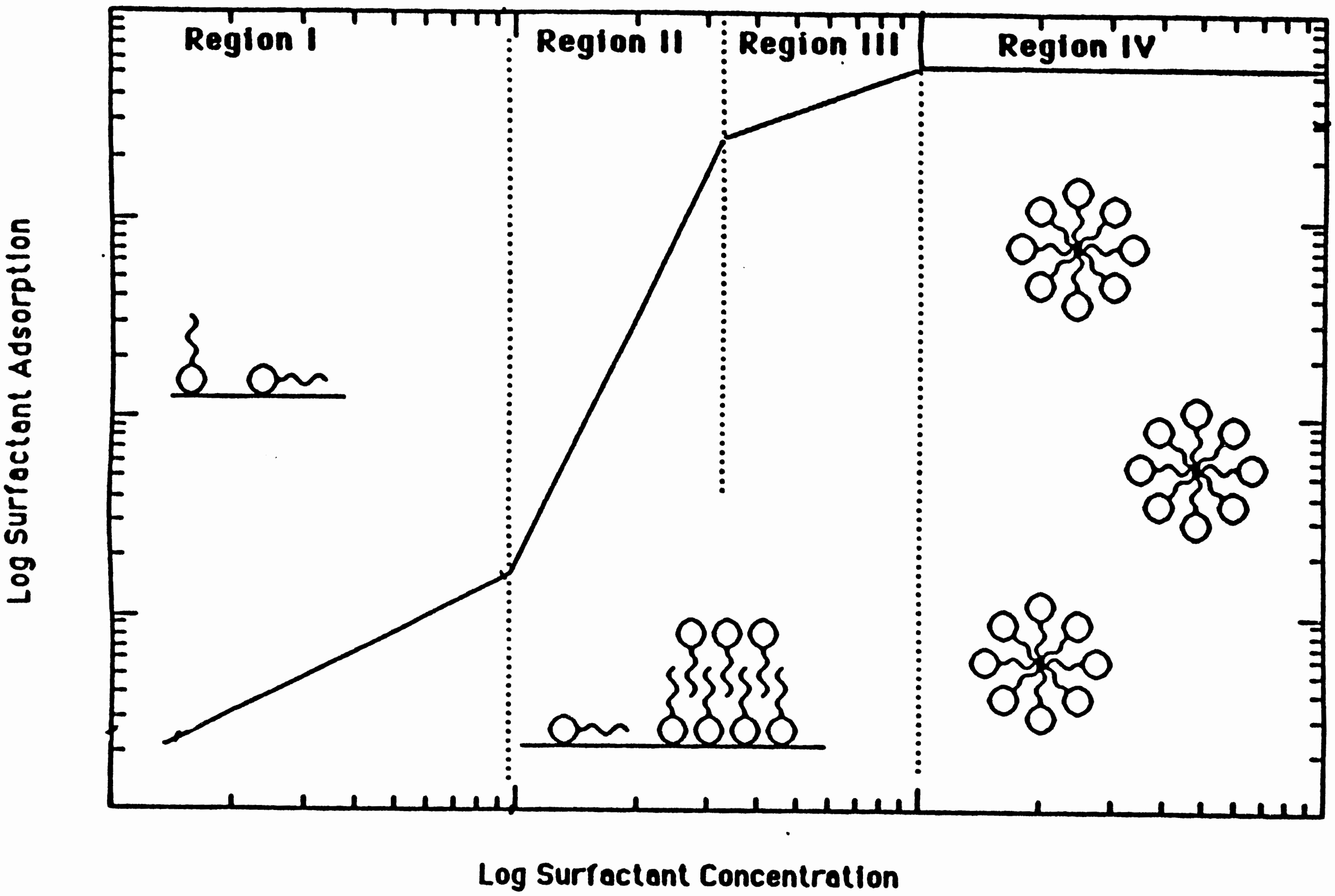


Figure 1 .. A schematic of a typical surfactant adsorption isotherm.
(Source: Surfactants Workshop at University of Oklahoma December, 1991.)

high concentrations above the critical micelle concentration[59-61]. Other possibilities for synergistic adsorption include [30-31]:

1. The environment in the proximity of a solid surface was different from that in the bulk solution. Small changes in the nature of the surface or the environment around it may strongly affect the affinity of adsorption even if the active sites remains unaltered [30].
2. In some cases, the surface may be modified during the reaction with a pesticide. Both the spatial distribution within the charged species are strongly influenced by the electric field emanating from charged surfaces. Charged surfaces can enhance the adsorption of the pesticides that are found in the vicinity of the surface but are not adsorbed at specific sites [31].
3. Soil organic matter contains many reactive groups that are known to enhance chemical changes in several families of organic adsorbates [32].
4. It is also possible that synergistic adsorption could be attributed to surface acidity - the ability of the surface to act as a Browsted or Lewis acid. This could be enhanced by an increase in proton concentration as the surface of a negatively charged solid is approached [30,31].
5. A sufficiently large adsorbate (as most pesticides are) can interact with multiple sites on the surface simultaneously. These interactions may strongly modify

the orientation of the adsorbate species relative to the surface by affecting the electron distribution in that part of the molecule in which the surface-catalyzed adsorption occurs. The various simultaneous interactions between the surface and the pesticides can hinder or enhanced adsorption [31].

6. Because of the competition for adsorption sites with water molecules (due to the solubility of the adsorbate), the pesticides, may in the presence of a liquid phase, not adsorb at those sites with which they interact most strongly. Under this condition, the soil may expand or at least swell. Large solute molecules may interact with interlayer sites, that under normal conditions, were inaccessible to these molecules [30] and as a result, as adsorption of the pesticides proceeds, site coverage increases to the extent that lateral interaction occurs between the adsorbed molecules.
7. The competition with the polar water molecule may considerably reduced adsorption. Yet, the pesticide molecules that do reach the vicinity of the solid may undergo a strong electro-static interaction, which may, in turn, perturb the adsorbate's electron charge distribution and thus weaken some bonds in the adsorbate, making it more likely to be adsorbed [30,31].
8. Adsorptive properties of surface-adsorbed pesticides

can be altered by a strong interactions with the solid or with another adsorbed species. In either case, the intrinsic properties of the surface, can enhance or hinder adsorption [31].

Objectives

The main objectives of this research were to identify different interactions of various pesticides between whole soil and various soil organic fractions. The effort evaluated the underlying assumptions that adsorption is proportional to soil organic carbon content and is linear. This work has also been of a correlative nature in which the activity or loss of a pesticide from solution to a series of soils has been compared with numerous soil properties including specific surfaces, organic carbon content and cation exchange capacity and molecular weight of the soil organics. The approach of selective removal of different organic components from the soil matrix followed by adsorption studies on the residues permits evaluation of the contribution of a given fraction to the overall adsorptive capacity of the soil. This work investigated the premise that soil organic matter is/is not a good predictor for determining the distribution coefficient and subsequently, adsorption.

This work is also an extension of single pesticide uptake studies to multicomponent systems involving different soil organic fractions as the adsorbent. This research subsequently investigated the effects of competitive adsorption from multiple solutes onto various soil organic fractions. Other specific project objectives include:

1. Characterization of the homogeneity or heterogeneity of the surface soils based on isosteric heats of adsorption and the evaluation of isosteric heats of adsorption in determining the distribution of surface site energies that existed on the soil. This information can be used in conjunction with previously developed methods to define multiple solute adsorption onto soils.
2. To evaluate various multisolute adsorptive systems models for their capacities to explain the data collected.

CHAPTER II

MATERIALS AND METHODS

Introduction

Experiments in this study were designed to observe the sorption of three organic pesticides (lindane, Silvex and 2,4-D) onto two different types of soils, and onto various soil organic fractions. Another aspect of this study was to observe the competitiveness of two pesticides in binary systems under similar conditions. Experiments were conducted utilizing aqueous slurries of soil and water shaken in batch reactors. Various concentrations of pesticides were added to the batch reactors, shaken until equilibrium was attained, and then centrifuged. Aliquots of the supernatant were extracted with hexane and iso-octane for lindane and the acidic herbicides, respectively. The extracts were analyzed by gas chromatography and subjected to additional analyses. A more detailed description of this investigation follows:

Equilibrium Uptake Studies

Adsorption studies of individual pesticides onto whole soil at constant temperature were performed in batch under equilibrium conditions. Equilibrium uptake curves and isotherm studies were completed. A pesticide solution of ten parts per billion was equilibrated for 24 hours at a constant temperature on a reciprocation water bath shaker. Samples were taken until equilibrium was achieved. Preliminary evaluations such as the determination of equilibrium times for adsorption of the pesticide were performed in duplicate while final experiments involving pesticide isotherm determinations were carried out in triplicate.

Equilibrium uptake curves of the pesticides 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 solute concentration remained constant for three consecutive sampling periods. Samples were collected daily.

Soil and Soil Derivatives

The soils used in this study included materials collected from a disturbed site on Oklahoma State University campus hereafter called the NRC soil and a sample tentatively identified as being of the Port series which was collected from a field north of Stillwater, Oklahoma. The soils were air-dried at 22 to 25°C and disaggregated to remove gravel and eventually subjected to sequential extractions using the Proximate Analysis Method (PAM) to dissolve specific classes of organic compounds from the soil samples. The constituents dissolved originated with tissues of plants previously grown in the soils [32]. Table I

TABLE I

CHEMICAL TREATMENTS AND SOIL ORGANIC FRACTION REMOVED BY THE PROXIMATE ANALYSIS METHOD

Fraction Removed	Treament
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

illustrates the treatments used combined with the fractions recovered.

The Proximate Analysis Method was selected for these investigations as the surface remaining following the various extractions was reported to be unchanged from that of original soil particle [32]. In this way, modifications to adsorptive properties may be attributable to a lessened organic carbon content rather than to the alteration of the original soil particle.

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 ashfree 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 noncellulose carbohydrates [20,32]. Residual organic matter in the fourth fraction consisted primarily of humic acid or humins. These materials were then destroyed by the addition of hydrogen peroxide, leaving primarily residual inorganic or mineral products in the fifth fraction [20]. Other investigators have reported that a large part of the soil organic matter could be decomposed by hydrogen peroxide [20,32] and that treatment with hydrogen peroxide would not affect or appreciably change the weight of the inorganic material. In principle, these would permit evaluation of the contribution of a given fraction of the organic matter to the overall adsorptive capacity.

Molecular Weight Characterization and Identification of Specific Classes of Compounds on the Soil Organic Fractions by GC/MS

Following these extractions, samples were injected in a gas chromatograph (GC) with a capillary column for separation and quantification. After separation, an integration time rate of two scans per second was used, and the mass spectrometer was scanned over a range of 20 to 200 atomic mass units (amu) for quantitative analysis. Duplicates were completed for each sample. The compounds represented by the GC peaks were identified by recalling the mass spectra from the data storage through the appropriate spectrum numbers [33]. Identification of the compounds was then confirmed based on the comparison of the sample mass spectrum with that of a standard derived from the suspected compound. This effort was limited to the Port soil and its extracts. The NRC sample was used to define procedures and evaluate initial hypothesis.

Soil Organic Carbon Concentration

Portions of the soil and fractionated soil samples were analyzed for organic carbon content by the potassium dichromate method (34). This inexpensive titration method utilized exothermic heating and oxidation of the sample with potassium dichromate and concentrated sulfuric acid. Excess dichromate was backtitrated with 0.5 N ferrous ammonium sulfate solution to a sharp one drop endpoint. The results of the analysis were calculated by the following equation:

$$\%OC = 10\,(1-T/S)[1.0N(0.003)(100/W)] \tag{7}$$

where

T = sample titration, ml ferrous solution;

S = standardization blank titration, ml ferrous solution;

0.003 = meq weight of carbon;

1.0 N = normality of potassium dichromate; and

W = weight of sediment sample in grams.

The procedure has been previously summarized [34]. A 0.2 to 0.5 g dried soil sample was placed in a 500 ml Erlymeyer flask. Exactly 10 mls of 1 N potassium dichromate solution was added to the sample followed by intermittent mixing. Twenty mls of concentrated sulfuric were then added and mixed by gently rotating the flask for 1 minute. The mixture was allowed to stand for 30 minutes. A standardization blank without the soil was processed with each new set of samples. After 30 minutes, the solution was diluted to 200 mls with distilled water. Ten mls of 85% phosphoric acid, 0.2 g sodium fluoride, and 15 mls of diphenylamine indicator were then added. The solution was back-titrated with 0.5 N ferrous ammonium sulfate solution to a sharp brilliant green endpoint.

Cation Exchange Capacity

Cation exchange capacity was determined for each fractionated soil preparation by a wet chemical method [35], which 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 cm. Buchner funnel and the leachate 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 analyzed for the milliequivalents 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 as follows:

Milliequivalents of Calcium/100g - Milliequivalents of Chloride/100g = Cation Exchange Capacity (CEC)/100g (8)

Cation exchange monitors mineral rather than organic partitioning surfaces. Cation exchange capacity in this case was determined to compare the levels in the extracted adsorbents with removals of pesticides from solution by an increasingly prevalent mineral surface.

Surface Area Analysis

Portions of the original soil and selected soil derivatives were analyzed for surface area using the Quantochrome filling method [36]. The sample to be intruded with mercury was first cleaned of adsorbed species by degassing the material under vacuum in a dilatometer. The evacuation of the sample was to remove air from the adsorbed species from the sample and the dilatometer. The removal of adsorbed species cleaned the surface of the solid, which assisted in obtaining the expected contact angle with mercury. The test was continued until the pressure was lowered to less than 0.1 Torr. While under vacuum, the dilatometer was then filled with mercury and placed in the pressurizing instrument where pressure was gradually increased.

During the pressure increase, the mercury intruded the pores of the sample, resulting in the lowering of the mercury level. The capacitance in an autoscan porosimeter then converted the height of the mercury level into an electrical signal. It did this by measuring the drop in the mercury level as a function of the pressure. These values were then automatically recorded as surface area.

The total surface area of the soil samples was also obtained using the ethylene glycol monoethyl ether (EGME) procedure of Cihacek and Bremner (1979) [37] as a check to that of the Quantachrome filling method. Consistent results were obtained by the two methods. Subsequent discussion will utilize the Quantachrome method.

Reagents, Pesticides, and Other Laboratory Protocols

Lindane, Silvex, and 2,4-D were selected as adsorbate for investigations as they have been reported to be common and persistent in the environment [38-40]. They were selected for use as representative of low solubility, nonionic hydrophobic solutes in the case of lindane, and of high solubility, negatively charged hydrophillic solutes (the acidic herbicides). Extractions of these compounds for subsequent processing allowed the use of a similar gas chromatography instrument and column. Tables II and III show the pertinent characteristics of the pesticides used in this research. The nonionic nature of lindane allowed the evaluation of the sorption of uncharged nonpolar compounds as opposed to polar or ionic compounds as was the case with the acidic herbicides.

The organic chemicals used in the adsorption experiments were 99% purity. Organic solvents used for the extraction were pesticide grade. Varying concentrations of pesticides were made with distilled water. All reagents were used as received.

All glassware and microsyringes were prewashed with hot water, followed by cold water, and eventually by distilled water. After prewashing, 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 glassware was sealed, capped, and stored for later use.

TABLE II

PERTINENT CHARACTERISTICS OF THE INSECTICIDE LINDANE AND ALLOWABLE LIMITS ON CHEMICAL EXPOSURE AND USE

Formula : 1,2,3,4,5,6 - Hexacholocyclohexane
Trade Names : Gammexane
Gammopaz
Kwell
Lindex
lindust
Lintox
Solubility : 10 mg/l
Toxicity : The acute oral LD value for rats is approximately 90 mg/l

Molecular Weight : 290.8
Melting point : 112.9°C
Application : Seed treatment

Source : Chemical Week Pesticide Register.

TABLE III

PERTINENT CHARACTERISTICS OF THE TWO ACIDIC HERBICIDES AND THEIR HERBICIDAL PROPERTIES

Formula :	2,4 Dichlorophenoxy acetic acid 2,(2,4 Trichoropropionic acid)
Trade Names :	2,4-D Silvex
Solubility :	900 mg/l 600 mg/l
Toxicity :	The acute oral toxicity of a single dose of the phenoxy herbicides to mammals ranges from LD^{50} values of 100 mg/kg to 2000 mg/kg. This is equivalent to doses of 1 oz or more of chemical for a matured human male.

Source : The Phenoxy Herbicides (2nd Ed.). Council for Agricultural Science and Technology. Report No.77, Aug. 1978

Pesticides Extraction and Identification

Lindane

After shaking, the vials were centrifuged on an International Equipment Co. model Centra-7 centrifuge at 1200 rpm for one hour. In these experiments, the centrifuge speed was found to be limited to 1200 rpm or less due to breakage of the vials.

After centrifugation, equal aliquots of the clear supernatant solutions were removed and concentrated using a microextraction procedure [41]. This extraction procedure was unique because it required only small sample aliquots extracted with 10 mls of solvent. After agitation, the phases were allowed to separate with the solvent phase subsequently withdrawn with 5.25-inch disposable borosilicate glass pipettes and transferred to 5 ml storage vials which were capped with Teflon-lined screw caps. The samples were then stored at less than 4°C until analyzed by gas chromatography. The peak areas from these extracted samples were compared to those from reference standards obtained from Supelco Company. Separate percent recovery determinations were performed and the mean of five replicates was found to be 97%. This means there was a reasonable certainty that any differences noted between trials were due to variations in the experimental conditions rather than analytical procedures. All data gathered during the study were subsequently corrected using the extraction efficiencies generated for the individual experiments.

2,4-D and Silvex

Methods used in these experiments are listed below and have been found to be very effective for the analysis of acidic herbicides [42]:

1. A well-mixed representative 100-ml sample was added to a previously washed 8 ounce glass bottle.
2. One gm of potassium hydroxide was added to the sample and was shaken for 10 minutes at approximately 135 excursions/minute.
3. Forty mls of diethyl ether were added and shaken for 5 minutes. As much ether as possible was carefully removed without disturbing the aqueous layer. The ether was discarded.
4. Four mls of 18 N sulfuric acid, 35 to 40 gm of sodium chloride, and 100 mls diethyl ether were titrated into the remaining sample which was shaken at about 270 excursions/min for 5 minutes.
5. Following the phase separation, a 25-ml aliquot of the ether was pipetted into a 12 dram vial.
6. One ml of 5% ammonium hydroxide in methanol and several boiling chips were added. The sample was evaporated in a 70 C water bath until the liquid just wet the vial base (approximately 0.5 ml remained).
7. Two mls of boron trifluoride methanol reagent were added to the vial and reimmersed into the 70 C water

bath to a depth of approximately 4 cm for 20 minutes.

8. The methanol was evaporated under a gentle stream of nitrogen in the water bath again until the bottom was just wet (approximately 0.5 ml remained). Caution was taken to keep the sample from drying.
9. Five mls of 5% aqueous sodium sulfate solution and 5 mls of iso-octane were added to the vial and handshaken in an inverted position for 2 minutes.
10. Three uls of the iso-octane phase were subsequently injected into the GC with a column packed with a Supelco 3 % SP2100.
11. The concentration of each of the esters in the final solution was determined by comparing peak areas to those of a reference standard which were obtained from Supelco Company.

The recovery efficiencies were found to be 85 and 80% for laboratory grade 2,4-D and Silvex, respectively. All data gathered were subsequently corrected using the extraction efficiencies generated for the individual experiments.

Isotherm Analysis

The adsorption of certain pesticides and other relatively complex organic compounds applied to soil in batch reactors can be compared by several adsorption equations or models. These include the Freundlich, linear, and Langmuir equation/models among others (43-45).

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 volatilization or other, nonadsorptive phenomena.

Freundlich Isotherm Analysis

The Freundlich adsorption isotherm is basically an empirically-derived relationship between the mass of solute sorbed per mass of adsorbent (X/M) and the equilibrium concentration of the solute in solution (C). The Freundlich isotherm has often been used by researchers to describe the sorption of compounds to soils and is expressed as [43]:

$$F = X/M = KC^{1/N} \tag{9}$$

where

X = amount of adsorbate adsorbed (mass);

M = weight of soils (mass);

C = Concentration of solute remaining in solution at equilibrium (mass of solute per volume of water);

K = Freundlich distribution or partitioning coefficient between the solute adsorbed and the solute remaining in solution (intercept, i.e., amount adsorbed per unit weight at C = 1). It indicates a rough measure of sorption capacity of the adsorbent; and

1/N = slope of the line. The slope is an approximate measure of the intensity of an adsorption. Adsorption intensity is an indicator of the energy of sorption and is independent of the partitioning coefficient [15].

Taking the log of both sides:

$$\log X/M = \log K + 1/n \log C \qquad (10)$$

An equation of a straight line with the slope equal to 1/N and an intercept of K. Therefore, if X/M is plotted against C on a log-log paper, a straight line should be obtained if a reasonable data fit is observed.

Linear Isotherm Model Analysis

The linear model often used in groundwater contaminant transport models follows the Freundlich isotherm where the exponent 1/n is unilaterally set equal to 1:

$$X/M = S = KC \qquad (11)$$

Such an equation is termed linear and a plot of S versus C is a straight line if a reasonable fit is observed. The slope of this type of plot yields K. In this case, coefficient K becomes K_d, the distribution coefficient and represent adsorption intensity.

Langmuir Equation Analysis

The Langmuir equation was originally derived for the adsorption of gases by smooth solid surfaces, and the derivation was based upon three assumptions [45]:

1. Energy of adsorption is constant and independent of the extent of surface coverage;
2. Adsorption is at localized sites with no interaction between adsorbate molecules; and
3. The maximum adsorption possible is that of a complete monomolecular layer.

This isotherm can be expressed as:

$$1/q = 1/b + 1/KbC \qquad (12)$$

where

q = amount of adsorbate adsorbed per unit mass of adsorbent

C = equilibrium concentration of the adsorbate in solution

K = a constant related to bonding energy of the adsorbate to adsorbent

b = maximum adsorption or capacity factor

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, where the slope is equal to (1/Kb) and the intercept at 1/b.

Freundlich Multicomponent Isotherm

The Freundlich multicomponent isotherm was derived by Shendorf and Rebun [46] and has been widely used to describe experimental data. This equation was used to predict the competition and the adsorption of the various pesticides described above in binary systems. The derivation of the isotherm was similar to that of a monocomponent system where it was assumed that each component individually obeyed the Freundlich isotherm, and that for each component in a multicomponent system, an exponential distribution of adsorption energies existed which being equivalent to the energy distribution in the monosystem [46,47].

For a binary system, the adsorption by each component is given by:

$$q_1 = K_1C_1(C_1+a_{12}C_2)^{n_1-1} \tag{13}$$

$$q_2 = K_2C_2(C_2+a_{21}C_1)^{n_2-1} \tag{14}$$

where:

K and N = the Freundlich intercept obtained at C = 1, and slope in a monosystem, respectively; and

C_1 and C_2 = equilibrium concentrations of solutes 1 and 2, respectively, and

a_{12} and a_{21} = determined from the intercept of a straight line by plotting C_1/C_2 versus B_1/C_2,

where

$$B_1 = K_1C_1/q_1)^{1/(1-n_1)} \tag{15}$$

The competitive coefficient constant was defined by Sheindorf et al. [46,47] as a positive-value term and values ranged from zero (complete lack of competition) to less than 10 which corresponded to the degree of competition. The application of the multiple-type Freundlich isotherm necessitated experimental work to construct competitive adsorption isotherms that measured the amount of solute adsorbed in the presence of competing species. These measurements were then used to derive the competitive coefficient [46-48].

Polanyi Adsorption Potential Theory

Polanyi Potential theory, originally applied to gas-phase adsorption and subsequently to liquid-phase adsorption [49,50] has recently been applied to aid in the prediction of adsorption of organic contaminants from the vapor phase of gas onto soil [49]. "Characteristic Curves" developed with the Polanyi theory can be established for single and multiple mixtures of organic solutes onto activated carbon and these curves can be used to predict sorption potential of other organic chemicals or to correct for the effects of temperature on the adsorption capacity for organic compounds. They can also be used to test/explain which compounds have greater adsorptive retention on the adsorbent [49,50]. Traditional applications of the Polanyi theory have assumed a fixed pore volume within a given granular activated carbon (GAC) [51,52] and have generally not been considered applicable to determine adsorption onto heterogeneous materials such as soil.

The effective application of Polanyi theory however may be of considerable utility in the prediction of adsorption isotherms for a wide variety of chemicals onto soil because of the capability to predict multicomponent competitive adsorption. Single solute adsorption models do not adequately define conditions common to pesticide transport beneath typical farm fields which may have many organic compounds present. This information is of paramount importance when conducting investigations of chemical contaminant and fate and transport analyses at contaminated waste sites [49]. An attempt will be made in this research to identify conditions where Polanyi theory may be applied to determine the adsorption of multiple pesticides onto different soil surfaces. The decisive factor in determining if Polanyi Potential theory is applicable to heterogeneous sorbents, such as soil, is the evaluation of whether or not a "characteristic curve" can be developed.

The theory assumes adsorptive forces originate from van der Waals' interactions [50-52]. The force of attraction for a compound in solution depends on its proximity to the adsorptive surface. The highest adsorbate concentrations within the pores of the particle will condense first if Polanyi Theory holds [50]. The theory also assumes that molecules will concentrate at high-energy sites on the particle surface and will crystallize as a solid or condense as a liquid [50,51]. The Polanyi theory defined the adsorption potential (E) as the free energy that was needed to remove any compound from the bulk liquid to the adsorption space. The value of E in the adsorption space varies continuously from some maximum value to zero [52]. By plotting the natural log of the space volume adsorbed (W) versus the adsorption potential per molar volume (E/V), a single characteristic curve can be defined for a specific adsorbent. The space volume adsorbed is defined as [52]:

$$W\ (ml/g) = q * 1/density * 1/10^{6} \qquad (16)$$

$$q = X/M_{co}\ (ug/g) \qquad (17)$$

and

$$E/V\ (cal/mol) = [RT\ \ln\ (C_{s}/C)]/(MW/density) \qquad (18)$$

where

R = ideal gas constant, 1.987 cal/gmol (°K);

T = temperature in Kelvin;

C_{s} = solute concentration at saturation (ug/l); and

C = equilibrium concentration from isotherm (ug/l).

X/M_{co} = ultimate capacity at $C = 100$ ug/l.

Isosteric Heat of Adsorption

The isosteric heat of adsorption was calculated at different temperatures to evaluate the surface characteristics of the soils used in the experiment. It was also used in this study to measure the energy potential available during adsorption. These measurements are potentially useful in determining the distribution of surface site energies and can be used in conjunction with Polanyi Potential Theory to define multiple solute adsorption onto soils. As used, isosteric heats of adsorption can provide a direct measure of the bonding strength between associating species. This bonding strength varies with surface coverage of the adsorbent by the adsorbate and is a function of heterogeneities in the adsorbent as well as local interactions between multiple solutes.

The isosteric heat of adsorption (dH) is the differential molar quantity which gives a measure of the heat adsorbed or released during the adsorption process [53] and was obtained by collecting adsorption data at various temperatures and applying the Clausius-Claperon equation to the system where the coverage was maintained constant. The relationship is defined as [54,55]:

$$dH = R \ln C_2/C_1 * [1/T_2-1/T_1] \qquad (19)$$

where:

dH = isosteic heats of adsorption in Kcal/Mole

C_1 and C_2 are equilibrium concentrations at temperatures T_1 and T_2, respectively; and

R = the molar gas constant.

By plotting dH versus surface coverages (ppb), the heterogeneity of the soil surface can be evaluated. That is, a curve approaching a constant heat of adsorption is indicative of a soil surface with homogeneous adsorptive properties while varying heats indicate heterogeneity of the adsorbent surfaces.

Statistical Analysis

The Pearson Correlation Model (PCM) procedure found in the Statistical Analysis System (SAS) program [56,57] was applied to statistically address the significance of select independent variables on adsorption. PCM computes correlation coefficients between variables and performs hypothesis testing about linear models. In this case, a linear model between the soil independent variables investigated (surface area, cation exchange capacity, organic carbon, molecular weight of the organics) and the dependent variable, adsorption, was completed. It should be noted that those independent variables were actually not independent of each other when presented in soil. But for the sake of analyses, they were referred to as independent. The output presented the correlation and the significance of the independent variables to adsorption. Two numbers will appear on the output in a given row and column. The upper number is the estimated correlation coefficient between the row variable and the column variable. The lower number is the significance probability for testing that the corresponding population correlation is zero. That is, the p-value.

The general Linear Model (GLM) procedure found in the Statistical Analysis System (SAS) program was also applied to statistically address the significance of independent variables on adsorption. This procedure established a linear model between between the soil variables (surface area, cation exchange capacity, organic carbon content, molecular weight of the organics) and adsorption. In this analysis, adsorption was referred to as the dependent variable (response variable) and OC, CEC, SA, and MW were referred to as independent variables. The F-value is the ratio produced by dividing mean square value by mean square error. It tests how well the model as a whole (after adjusting the mean) accounts for the dependent variable's behaviour. If the significant probability label Pr>F, is small, it indicates significance. Similar analysis for the distribution coefficient was also performed to addressed the relationship between the soil variables.

Research Structure

Two soils were tested in either duplicate or triplicate for their performance as adsorbents. The soil samples were collected from a site on the Oklahoma State University campus and from a site north of Stillwater, Oklahoma, hereafter called the NRC soil and the Port soil respectively. Soil physical and chemical properties were determined to define the underlying mechanisms explaining variations in adsorption noted for single and multiple solute systems. An assortment of isotherm models were applied to collected data as were statistical methods used to identify the effects and magnitudes of the contribution exerted by the critical soil and/or solute properties. Tables IV and V summarize the research completed.

TABLE IV

SUMMARY OF RESEARCH STRUCTURE EVALUATING LINDANE, 2,4-D AND SILVEX ADSORPTION ONTO SOILS FROM THE NRC PORT SOILS

Adsorbents	Replications	Test Type	Concentration (ppb)
Whole Soil	2	Equilibrium	10
Whole Soil	3	Isotherm	10, 20, 50 100, 200, 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	"
Control	5		10, 20, 30,* 50, 100

Experiment conditions: 2 gms of soil in 10mls stock solution for lindane and 5 gms of soil in 150mls of stock solution.

* Note: Concentrations for control trials for 2,4-D and Silvex were 10, 50 and 100 ppb.

TABLE V

SUMMARY OF COMPETITIVE ADSORPTION RESEARCH FOR LINDANE AND SILVEX, AND SILVEX AND 2,4-D AND LINDANE AND 2,4-D ON PORT SOIL AT T = 25, 30 AND 35 DEGREES C

Adsorbents	Replications	Test Type	Initial Concentration (ppb)
Whole Soil	3	Isotherm	100, 20, 50 100, 200, 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	"
Control			10, 50, 100

Experimental conditions: 5 gms of soil in equal aliquots of stock solution of 100mls each.

CHAPTER III

RESULTS--SINGLE SOLUTE UPTAKE INVESTIGATIONS

Adsorbent Data

General soil properties which may influence compound sorption are soil particle charges, ion exchange capacity, expanding lattice structures of clays, soil organic matter, pH, and surface area [58]. Agronomists and environmentalists concerned with the efficacy and persistence of pesticides in soil systems have investigated a variety of sorption properties of soil detailed in Table VI for soils and soil fractions used as adsorbents in this study. This table shows that, as expected, the percent organic carbon in each of the soils decreased after each sequential extraction of the organic fraction.

Cation exchange capacity within the soil fraction series stayed relatively constant until the forth and fifth extraction, with final reductions of 96 and 78 percent for the NRC and Port soils series respectively. Surface area generally increased after each treatment, however, until the fifth extraction where significant reductions were observed.

Equilibrium Uptake Data

Relatively little information is available regarding

TABLE VI

PROPERTIES OF NRC AND PORT SOILS AND SOIL FRACTIONS USED IN THE EXPERIMENT

Adsorbent	Cation Exchange Capacity (meq/100gm)	Surface Area (m^2/gm)	% Organics Carbon
NRC			
Whole Soil	12.3	15.0	1.5
Fraction 1	11.7	21.0	1.2
Fraction 2	11.9	20.0	1.1
Fraction 3	10.5	22.5	1.0
Fraction 4	2.5	24.0	0.9
Fraction 5	0.4	15.0	0.7
Port			
Whole Soil	17.5	8.9	2.3
Fraction 1	16.1	25.4	1.8
Fraction 2	15.8	27.1	1.7
Fraction 3	15.2	28.7	1.7
Fraction 4	12.3	32.8	1.6
Fraction 5	3.7	17.3	0.5

the kinetics of sorption of pesticides onto soils. An equilibrium uptake study was performed to determine how much contact time was needed for these systems to reach equilibrium. Equilibrium uptake curves were obtained for all three pesticides on NRC and Port soil. Contact times for lindane and the acidic herbicides from the equilibrium screening trials were established at approximately 8 and 12 hours respectively for these soils, but were subsequently shaken for 24 hours to ensure that equilibrium had been achieved. Figures 2 through 4 present equilibrium curves for Lindane, Silvex, and 2,4-D, respectively, for both soils. The amount of the compound remaining in solution versus time is shown.

The sorption of all three pesticides was rapid with the majority of uptake within the first few hours of shaking. This was most prevalent with lindane. The uptake rates subsequently decreased, slowly diminishing to a steady minimum where equilibrium was assumed to occur.

Isotherm Data--Single Solute

Lindane

Tables VII, VIII and IX present the initial and final concentrations for each of the adsorbents and for each of the solutes used in this study. The data in table VII indicated that the relative removal of lindane in the undisturbed whole soil was higher at the lower influent concentrations of 10, 20 and 50 micrograms per liter (ug/l)

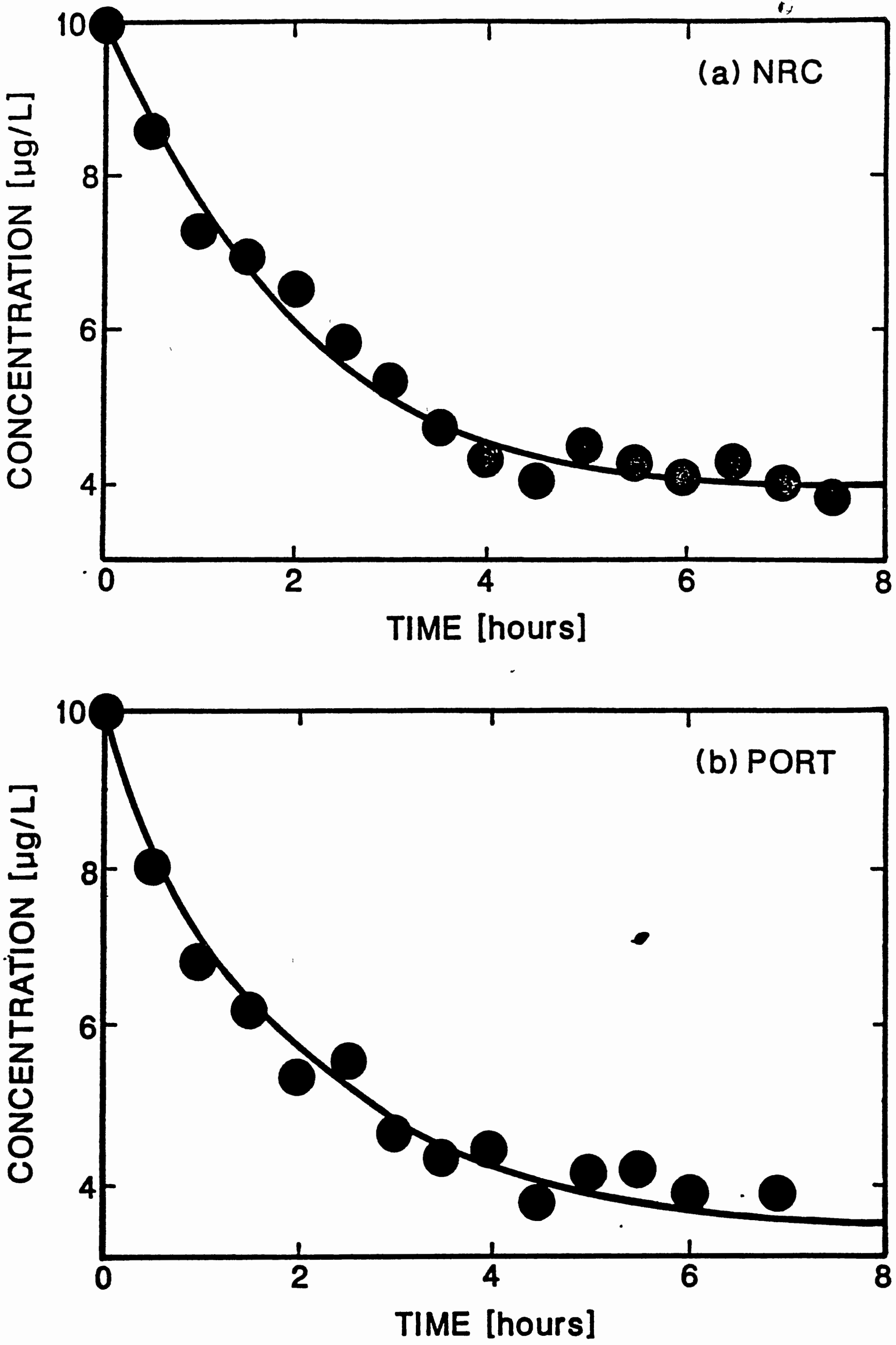


Figure 2. Equilibrium Uptake Studies of Lindane on
(a) NRC, (b) Port soil

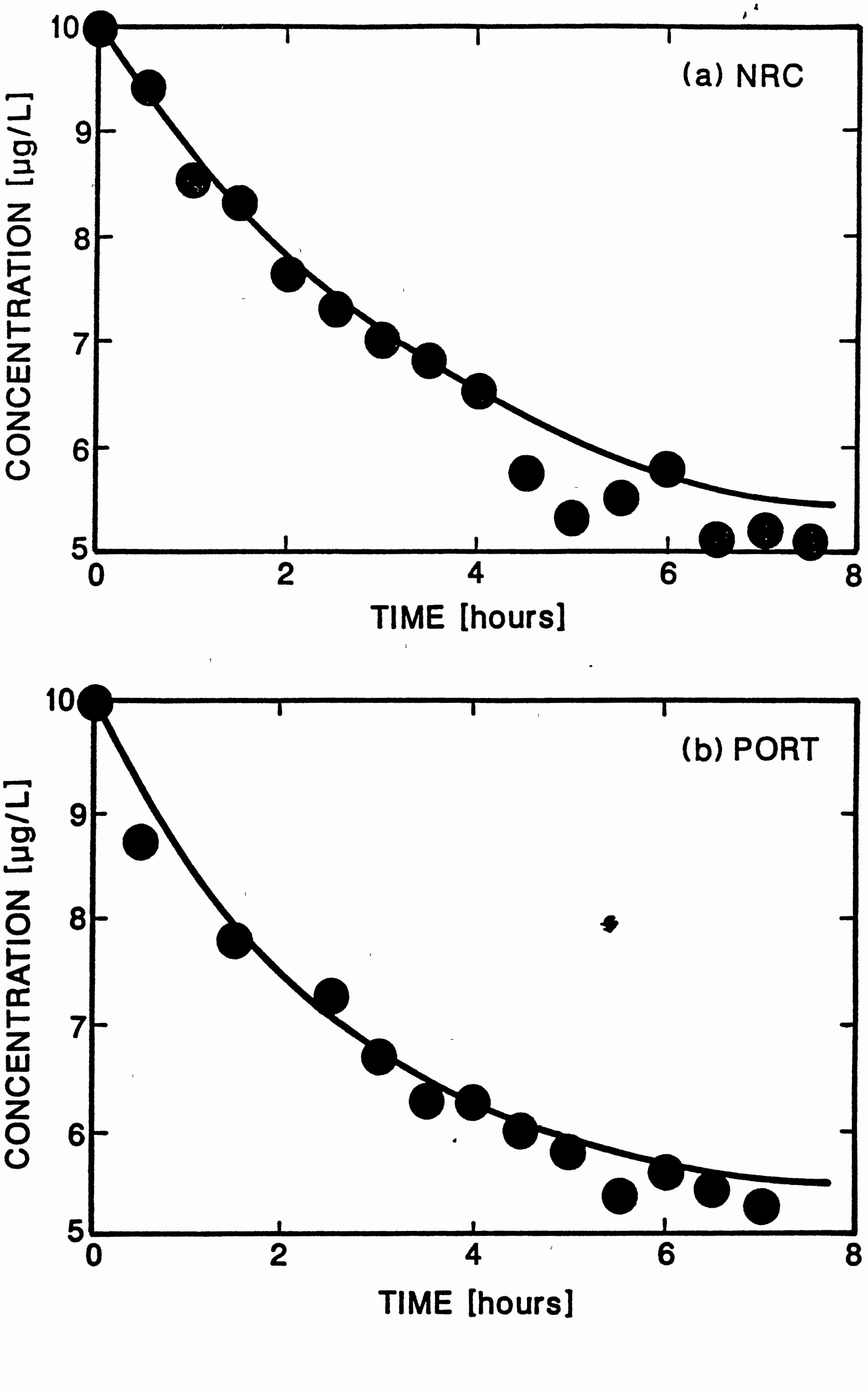


Figure 3. Equilibrium Uptake Studies of Silvex on
(a) NRC, (b) Port soil

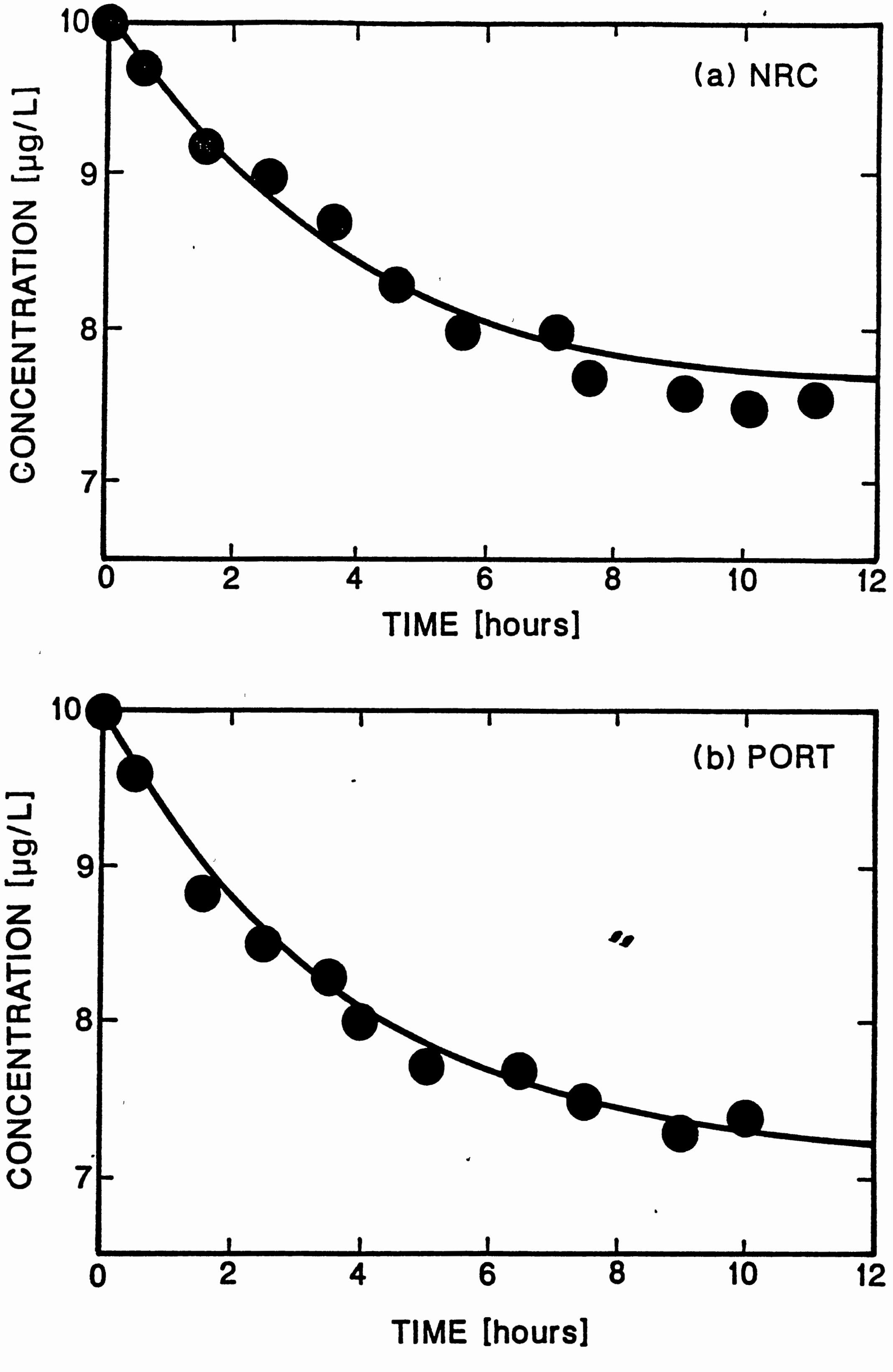


Figure 4. Equilibrium Uptake Studies of 2,4-D on (a) NRC, (b) Port soil

TABLE VII

INITIAL AND FINAL LIQUID CONCENTRATION (AVERAGES OF TRIPLICATES) OF LINDANE FOR ALL TEST ADSORBENTS USED IN THE EXPERIMENT UNDER EQUILIBRIUM CONDITION AT T = 25° C

	Lindane Doses (ug/l)					
Adsorbents	10	20	50	100	300	500
NRC						
Whole Soil	3.5	7.9	36.9	87.7	276.0	491.7
Fraction 1	8.4	17.0	32.4	50.0	276.5	473.2
Fraction 2	1.2	2.5	17.0	44.0	265.8	157.0
Fraction 3	7.9	12.4	25.0	32.0	240.0	398.1
Fraction 4	1.6	3.5	7.4	10.0	43.2	256.7
Fraction 5	1.5	14.0	19.8	88.5	166.0	232.0
Port	10	20	50	100	200	500
Whole Soil	8.2	13.7	35.6	89.2	140.4	326.0
Fraction 1	5.1	12.3	36.0	68.0	120.0	320.0
Fraction 2	5.3	12.5	45.3	69.4	147.9	380.0
Fraction 3	9.7	11.9	43.0	37.1	165.9	385.3
Fraction 4	8.4	13.7	36.6	60.0	125.9	355.0
Fraction 5	10.0	17.2	47.0	96.2	189.5	493.0

TABLE VIII

INITIAL AND FINAL LIQUID CONCENTRATION (AVERAGES OF TRIPLICATES) OF SILVEX FOR ALL TEST ADSORBENTS USED IN THE EXPERIMENT UNDER EQUILIBRIUM CONDITION AT T = 25° C

	Silvex Doses (ug/l)					
Adsorbents	10	20	50	100	300	500
NRC						
Whole Soil	8.2	14.2	25.5	96.8	278.0	492
Fraction 1	4.8	14.6	39.8	79.8	264.0	355
Fraction 2	6.9	16.6	38.5	76.8	283.0	475
Fraction 3	4.5	14.8	32.8	93.6	149.0*	365
Fraction 4	6.8	14.2	29.9	69.8	286.0	328
Fraction 5	8.8	16.2	47.5	82.4	285.0	480
Port	10	20	50	100	200	500
Whole Soil	7.4	13.3	46.6	83.0	155.0*	450
Fraction 1	5.8	14.0	45.8	80.0	150.0*	420
Fraction 2	5.8	13.8	39.2	85.2	176.0*	408
Fraction 3	4.2	13.8	25.3	82.0	194.6*	401
Fraction 4	7.5	18.9	38.0	99.0	176.0*	400
Fraction 5	9.8	18.8	47.0	98.8	195.0*	496

*200 Silvex doses.

TABLE IX

INITIAL AND FINAL LIQUID CONCENTRATION (AVERAGES OF TRIPLICATES) OF 2,4-D FOR ALL TEST ADSORBENTS USED IN THE EXPERIMENT UNDER EQUILIBRIUM CONDITION AT T = 25°C NRC AND PORT

	2,4-D Doses (ug/l)					
Adsorbents	10	20	50	100	200	500
<u>NRC</u>						
Whole Soil	9.2	18.5	42.8	86.6	170.0	472.0
Fraction 1	8.5	14.2	38.6	78.6	177.6	70.0
Fraction 2	8.2	15.5	37.8	78.0	173.5	51.0
Fraction 3	7.6	16.2	35.4	75.4	170.2	468.0
Fraction 4	8.2	16.0	29.9	68.8	155.0	454.0
Fraction 5	9.3	19.0	44.5	88.6	173.0	475.0
<u>Port</u>						
Whole Soil	9.3	19.7	49.3	85.0	163.0	487.3
Fraction 1	7.7	17.2	44.3	82.6	197.4	497.4
Fraction 2	8.2	17.7	41.0	86.0	189.8	491.1
Fraction 3	9.3	16.2	46.1	83.0	166.2	479.7
Fraction 4	9.3	18.4	41.7	75.0	187.3	425.0
Fraction 5	9.0	18.5	48.0	95.0	196.6	491.0

than at the higher solute concentrations especially those from the 300 and 500 ug/l samples. The Port soil series exhibited less removal of lindane at the lower solute concentrations than did the NRC soil but exhibited higher uptake at the higher concentrations. Approximately 34 percent of the initial lindane concentration was removed with the Port soil from the 500 ug/l concentration in the NRC systems versus only about 9 percent with the Port soil.

The NRC soil fraction 1 exhibited generally lower lindane adsorption than was noted with the whole soil. The Port soil following the removal of the first organic fraction, showed lindane uptake to be similar or better than the whole soil.

Soil fraction 2 of the NRC soil showed lindane uptake to be higher than either the first soil fraction or the whole soil at all concentrations evaluated while the Port soil exhibited inconsistent adsorptive behaviour over the range of the adsorbate. The second fraction derived from the Port soil consistently showed lower uptake of lindane than did the comparable NRC soil or the previous Port soil fraction at all concentrations evaluated.

The third fraction of both soils again exhibited inconsistent adsorptive potentials. In some cases adsorption at select concentrations was greater for this soil than for either the whole soil or the previous fractions. At other concentrations, however, this was not observed.

Significantly higher removals of lindane at all but two concentrations were observed in the fourth NRC fraction when compared with the previous soils. This was not continued with the similar Port soil fraction, but nevertheless, improved lindane uptake at select influent solute concentrations was observed. Apparent exposure of this material (humic layer) by the previously applied sequential treatments accounted for the increase in adsorptive capacity, particularly on the NRC adsorbent. A similar but not totally consistent trend was observed for the Port soil series soils.

Removal of the humic materials during the fifth extraction by hydrogen peroxide resulted in lowered adsorptive capacities of the soils. The soil surface remaining after the removal of the liable organic matter by these treatments still exhibited a degree of adsorption affinity. This may be attributable to a change in the structure of residual organic matter due to the rigorous reaction of hyrdogen peroxide and/or the exposure of inorganic surfaces, where the adsorbate was able to sorb through interactions with the metal cations of the soil surfaces through water of hydration [57]. The effects of the residual organics measured at 0.73 and 0.52% for the Port and NRC soils can not be totally guaged. The lowest concentration of lindane adsorbed onto the NRC mineral matter actually exceeded the adsorption noted with the humic layer found in Fraction 4.

Silvex

Comparison of Table VIII with that of Table VII showed that lindane generally exhibited greater sorption than Silvex on similar soils. There were inconsistencies in the data as on soil fraction 1 of the NRC soil, it was observed that at the 10 and 20 ug/l concentration ranges, Silvex exhibited higher uptake than lindane on similar soils. This perhaps can be explained by soil surface properties such as cation exchange capacities, surface areas and organic carbon content. With some exceptions, less Silvex was adsorbed onto the NRC whole soil than onto any other fraction while the first four Port soil fractions exhibited slightly increased herbicide uptake over the concentration ranges applied when compared to the NRC materials. The last two Port fractions, the humic and the mineral surface adsorbents, however, consistently removed less than the comparable NRC soils.

Both soils in fraction 1 exhibited similar characterisitcs of higher Silvex removals at the lower influent concentrations than at the higher herbicide levels. The Port soil series, however, exhibited lower adsorption than did the NRC soil for this fraction.

Soil fraction 2 of the Port soil had generally higher pesticides removal than did either the first soil fraction, the whole soil or the comparable NRC fraction. This was also observed among the highest influent concentration range in studied. Fraction 2 of the NRC soil, however, behaved somewhat like fraction 1 in that it had higher removals at the lower influent concentrations than at the higher levels.

Both soils in fraction 3 showed significantly higher removals of Silvex at lower concentrations and lower relative uptakes at higher concentrations. The Port soil series exhibited a slightly higher removal of the herbicide than the NRC at the lower concentrations but was less effective at the higher concentration levels.

The exposed humic layer of the fourth fraction did not yield significantly higher Silvex removals when compared to the other soil fractions for both soils at the low and intermediate adsorbate concentrations. This fraction, however, exhibited the greatest removal at the higher concentration ranges evaluated for both soils. Similarly, the destruction of the humic layer in the fifth fraction of both soils greatly reduced the uptake capacity for the herbicide, particularly at higher concentrations.

2,4-D

Table IX showed that the removals of 2,4-D by various soils and soil fractions was not significant. There was a general increase in adsorption, however, with increased solute concentration; unlike the other systems evaluated but the relative removals were never exceeded 15 percent at the highest herbicide concentration. This state is numerically represented by the NRC whole soil depicted in Table IX. The data indicated relatively less removal of 2,4-D at the 10 and 20 ug/l concentration ranges. However, at the intermediate concentration ranges of 50 to 200 ug/l, it was shown that 2,4-D removal increased significantly with the highest percentage removal at the 200 ug/l range.

Isotherm Plots

Isotherms for the collected data were fitted to the Freundlich and Langmuir equations and to the Linear model by a linear regression function as presented in Figures AI-4 through AI-24 in the appendix. Table X presents the correlation coefficients for the Freundlich and Langmuir equations and for the linear model as determined by linear regression, least squares. An important observation can be made based on these data: The Freundlich and Langmuir equations alternatively produced better descriptions than did the linear model of the adsorption responses over the measured test ranges. In some cases, the lack of conformity to Langmuir versus the Freundlich equation may be due to the lack of homogeneity of the soil surface or that there were interactions among the molecules at localized sites. Correlations coefficients for both the Freundlich and the Langmuir equations among the pesticides evaluated across the various soil fractions varied quite significantly. This was perhaps attributed to both the adsorbate and adsorbent differences. That is, the variations in the coefficients of correlation can be present for reasons such as the solubility of the pesticides and or microscopic roughness or microporosity within the various soil adsorbents.

TABLE X

COMPARISON OF COEFFICIENT OF CORRELATION TO ADSORPTION MODEL FOR LINDANE, SILVEX AND 2,4-D RESPECTIVELY

Adsorbent	Lindane, Silvex and 2,4-D respectively		
	Freundlich	Langmuir	Linear
	R^2	R^2	R^2
<u>NRC</u>			
Whole Soil	88, 87, 95	70, 77, 99	30, 47, 79
Fraction 1	93, 92, 91	97, 82, 93	28, 88, 83
Fraction 2	81, 90, 93	97, 86, 98	42, 72, 78
Fraction 3	85, 81, 92	91, 62, 98	82, 79, 76
Fraction 4	91, 80, 97	99, 96, 98	69, 70, 26
Fraction 5	74, 87, 95	72, 89, 98	29, 79, 80
<u>Port</u>			
Whole Soil	91, 87, 80	93, 76, 48	78, 68, 35
Fraction 1	92, 90, 93	96, 69, 45	48, 95, 20
Fraction 2	96, 80, 90	68, 95, 94	75, 79, 34
Fraction 3	86, 90, 88	83, 50, 91	77, 85, 55
Fraction 4	95, 88, 94	87, 65, 98	76, 59, 49
Fraction 5	91, 82, 95	72, 90, 96	51, 65, 39

The linear isotherm model was less satisfactory in fitting these data as observed in figures AI-4 through AI-24 presented in the appendix. This state was pictorially represented by figure 5. The results shown graphically in figure 5, include also the plots of the Freundlich and Langmuir isotherm. As presented, the model worked well in the lower concentration ranges but not in the higher ranges. It is therefore consistent with the data to conclude that this model has been generally accepted for low pesticide concentrations because it simplifies mathematical calculations [4], but it may not appropriately describe the misalignments of water and contaminant fronts in an equilibrium process as presented by the retardation. (equation 1).

Adsorptive Capacity

Comparisons of ultimate adsorption capacities of these pesticides for both soils and their derivatives are presented in Table XI. Included in this table are the soil organic carbon, cation exchange capacity, and surface area for both soils and their extracts. Molecular weight of the extracted organics from the Port series is also listed. These were done to determine possible causative relationships between adsorption and select properties of the adsorbent. In these cases, the frequently applied underlying assumption that adsorption was proportional to

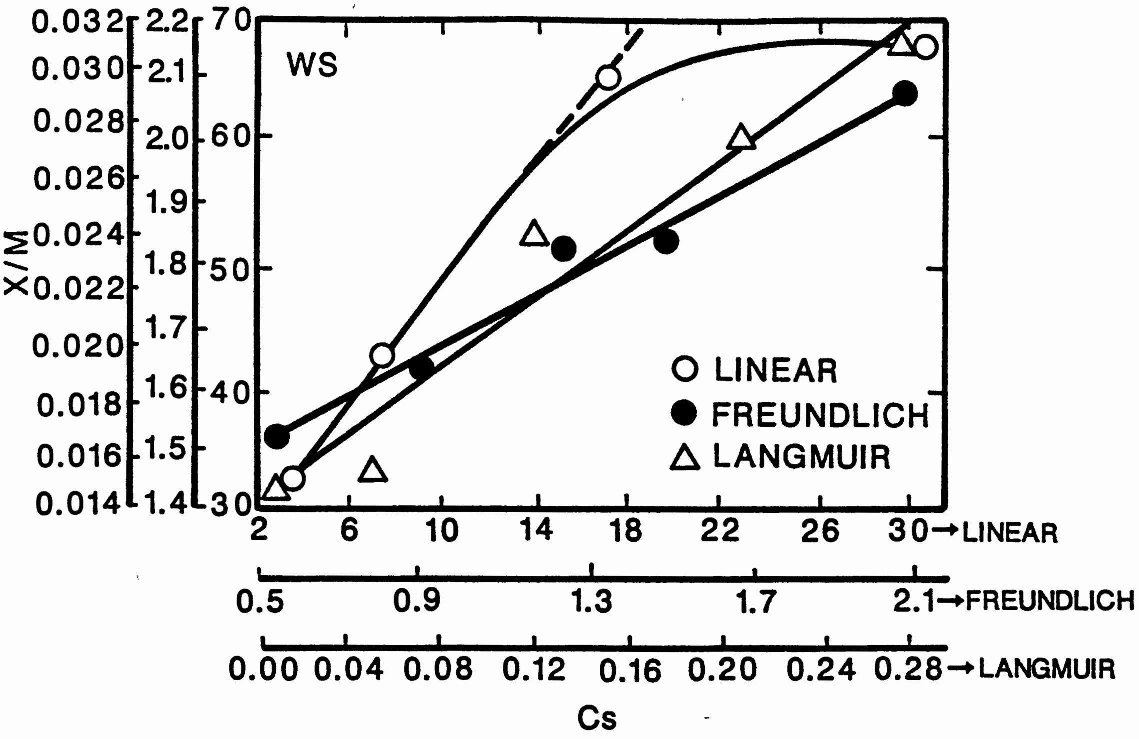


Figure 5. Lindane Adsorption Isotherms (Whole Soil) on NRC soil

TABLE XI

COMPARISON OF ULTIMATE CAPACITY OF LINDANE, SILVEX AND 2,4-D VERSUS PERCENT ORGANIC CARBON, CATION EXCHANGE CAPACITY, AND SURFACE AREA TO ADSORPTION ON NRC AND PORT SOILS

Adsorbent	CEC	SA	%OC	Ultimate Capacity (ng/g) Lindane	Silvex	2,4-D
NRC						
Whole Soil	12.3	15.0	1.54	89.1	158.48	199.52
Fraction 1	11.7	21.0	1.21	199.5	630.95	251.10
Fraction 2	11.9	20.0	1.15	223.8	316.12	316.20
Fraction 3	10.5	22.5	1.09	251.18	794.32	398.10
Fraction 4	2.50	24.0	0.98	1000	707.94	1023.29
Fraction 5	0.40	15.0	0.73	199.5	199.5	158.48
Port						
Whole Soil	17.5	8.90	2.35	199.5	354.81	158.48
Fraction 1	16.1	25.4	1.85	316.22	630.95	158.48
Fraction 2	15.8	27.1	1.75	316.22	1258.92	354.81
Fraction 3	15.2	28.7	1.70	354.8	707.94	446.68
Fraction 4	12.3	32.8	1.63	398.1	707.94	501.68
Fraction 5	3.72	17.3	0.52	56.23	70.79	100.00

organic carbon content was also evaluated. The ultimate capacities (X/Mco) at 100 ppb for each of the adsorbents were used in these comparisons. A constant level of adsorbate assured that differences due to solute concentrations were eliminated when calculating an ultimate capacity. The determination of the ultimate capacity value was done by reading the amount adsorbed per unit adsorbate from the origin of a Freundlich isotherm plot when the abscissa equaled 100 parts per billion.

Table XI showed that after each sequential treatment, the ultimate capacity of lindane and 2,4-D increased until the forth soil fraction was removed. These data also showed that even though the percent organic carbon of the soil fraction decreased, adsorption of these two pesticides increased until the humic layers in the fifth fraction were removed. Similar trends were observed for cation exchange capacity. As the cation exchange capacities decreased, adsorption increased in each of the various adsorbents as compared to the whole soil.

With the exception of one measurement conducted on the NRC soil, surface area increased with each sequential treatment until the fourth fraction was removed. Increases in surface area of over 30 percent were observed. These increases paralled the trend for ultimate capacity.

Silvex adsorption, however, showed increased adsorption through the first soil extraction for both the soils followed by a significant reduction in the NRC soil fraction

2. The Port soil series, however, showed increased adsorption capacity through soil fraction 2. This fraction had the highest adsorption of Silvex of all of the adsorbents evaluated. In contrast, the highest uptake capacity of Silvex in the NRC soil series was found to be in soil fraction 3. The exposed humic layer in the forth fractions on both soils did not exhibit the highest uptake for Silvex which were otherwise shown by lindane and 2,4-D trials. It's removal did, however, result in a significant reduction in the ultimate capacity. The ultimate capacity of the mineral surfaces however, was still greater than that observed for the NRC whole soil. In general, a comparison of surface area in Table XI to adsorption indicated that surface area was better correlated to adsorption for both soils and soil fractions. Other parameters such as cation exchange capacites and the organic cabon content did not mirror the same trend for their ultimate capacities.

In order to more fully quantify the effects of soil organic carbon on pesticide adsorption, GC/MS was completed for the Port soil series. Table XII presents these data. The samples presented in this table did not contain high molecular weight species as expected. This was perhaps due to some of the highly water soluble compounds such as water soluble polysaccharides and hemicellulose which could not be captured by the solvents used in the standard extraction process. These results, however, were consistent with the early work of Hayes [59].

TABLE XII

CHARACTERIZATION AND SEPARATION OF SOIL ORGANIC FRACTION COMPONENTS BY MOLECULAR WEIGHT USING GC/MS

Component	Extract	MW	Possible Structure
Fraction 1	Ether	219	Aromatic Amine
Fraction 2	Alcohol	177	? (Aromatic)
Fraction 3	Hot Water	256	Fatty Acid
Fraction 4	Acid	101	Aliphatic Amine

Statistical Analysis and Interpretation of Data

The Pearson Correlation Model (PCM) procedure found in the Statistical Analysis System (SAS) program [56,57] was applied to statistically address the significance of the important independent variables on ultimate capacities. A linear model was first established to show any dependence or statistical significance which applies the probability level. Table XIII presents the result of similar analyses which identified the statistical significance of the effects exerted by the independent variables: soil organic carbon, cation exchange capacity, surface area and molecular weight of the soil fractions on adsorption. The dependent variable was expressed as ultimate capacities. In these initial analyses, adsorption was defined as the dependent or response variable.

Results from this analysis showed that all three pesticides adsorption efforts exhibited high correlations for surface areas. Cation exchange capacities and organic carbon content had negative correlations for lindane adsorption with molecular weight second to surface area. In the case of Silvex and 2,4-D, the analysis indicated that cation exchange capacities were better correlated to adsorption than were organic carbon content of the soil. The molecular weight of the organics had no correlation at all for both herbicides. The results confirmed to the previous observation presented in Table XI that adsorption was directly correlated to surface area for all three

TABLE XIII

PEARSON CORRELATION COEFFICIENTS FOR SURFACE AREA, MOLECULAR WEIGHT, CATION EXCHANGE CAPACITY, AND ORGANIC CARBON ON ADSORPTION

Simulation Results	Significance of independent Variables
	Lindane
CEC	-0.23534 0.6535
SA	0.921 0.009
OC	-0.227 0.664
MW	0.731 0.098
	Silvex
CEC	0.580 0.227
SA	0.690 0.129
OC	0.418 0.408
MW	-0.106 0.841
	2,4-D
CEC	0.360 0.482
SA	0.982 0.0004
OC	0.271 0.602
MW	-0.256 0.623

pesticides. In general, Table XIII indicated that surface area was statistically most significant to adsorption of lindane with molecular weight of the organics second. Organic carbon and cation exchange capacity did not contribute as much but some significance was indicated. Cation exchange capacity had minimal impact in this investigations. However, for Silvex and 2,4-D, it was determined that surface area was still the statistically most significant variable with cation exchange capacity and organic carbon following.

A summary of the GLM comparisons is presented in Table XIV. In this table, the significance probability label Pr>F for surface area, was found to be 0.0005, the smallest amount the rest of the other independent variables. As mentioned earlier, the smaller the Pr>F value, the higher the significance. Molecular weight of the organics also indicated a significance probability label of 0.0819, a value far smaller than either the organic carbon concent or the CEC significane probability label. It was concluded that surface area was statistically most significant to adsorption, with molecular weight of the organics second. Organic carbon and CEC did not contribute as much when compared to surface area and molecular weight, but some significance was indicated.

Further analysis by the General Linear Model provided an equation for each pesticide that was useful for predicting the distribution coefficient based on the various

TABLE XIV

STATISTICALLY ANALYSIS OF ANOVA COMPARISONS FOR SURFACE AREA, MOLECULAR WEIGHT OF THE ORGANICS, CATION EXCHANGE CAPACITY, ORGANIC CARBON CONTENT ON THE BASIS OF ADSORPTION

Simulation Results	Significance of Independent Variables	
SA	Significant	Pr > F 0.0005
MW	Significant	Pr > F 0.0819
OC	Less Significant	Pr > F 0.2474
CEC	Less Significant	Pr > F 0.5862

independent variables as shown in Table XV. These results included the statistical weights assigned to each of the independent variables that contributed to the behaviour of the dependent variable, distribution coefficient, Kd. It can be noted that unlike the data presented in tables XIII and XIV which showed that adsorption was most strongly correlated with soil surface area, organic carbon and CEC had the most significant impact on Kd. This is attributed to the method used to calculate the partition coefficient; where the slope of the fitted isotherm in the linear range (lowest adsorbate concentration) was used to find the measured value. As previously discussed, however, the total isotherms were decidedly nonlinear in higher solute concentration ranges. At these lower concentrations, surface area was not critical because there was no limitation in adsorption sites.

Table XVI presents a summary of K_d (distribution coefficient) values obtained graphically from the linear models presented in figures AI-4 through AI-24 and from Equations (2) and (3), respectively as well as value obtained from the simulated equation model. These data indicated that, in general, the distribution coefficients obtained from the collected data differed from those obtained from correlations. If $Kd_{measured}$ was greater than Kd_{model}, it means that there was much more adsorption than predicted. In the case of lindane, the distribution coefficients obtained from models (Kd_{model}) consistently

TABLE XV

MODEL PREDICTIONS FOR THE DISTRIBUTION COEFFICENTS BASED ON THE VARIOUS INDEPENDENT VARIABLES BY THE GENERAL LINEAR MODEL

$$KD_{Lindane} = 0.516 - 0.1247(CEC) - 0.00549(SA) + 2.424(OC) - 0.0023(MW)$$

CEC = Pr>F = 0.445
OC = Pr>F = 0.329
SA = Pr>F = 0.419
MW = Pr>F = 0.403

$$KD_{Silvex} = -3.033 + 0.894(CEC) + 0.1416(SA) - 4.838(OC) - 0.000814(MW)$$

CEC = Pr>F = 0.0347
OC = Pr>F = 0.0841
SA = Pr>F = 0.0884
MW = Pr>F = 0.4986

$$KD_{2,4-D} = -3.30 - 1.04(CEC) + 0.334(SA) + 8.350(OC) + 0.001164(MW)$$

CEC = Pr>F = 0.0056
OC = Pr>F = 0.0106
SA = Pr>F = 0.0072
MW = Pr>F = 0.0840

TABLE XVI

COMPARISONS OF DISTRIBUTION COEFFICIENTS OBTAINED FROM GRAPHS AND FROM MODELS CALCULATED FOR K_{oc} ON VARIOUS SOIL FRACTIONS FOR LINDANE, SILVEX AND 2,4-D ON NRC SOIL

Adsorbent	$K_{d\,measured}$	$K_{d\,model}$	$K_{d\,simulated}$
Lindane			
Whole Soil	0.085	32.92	0.120
Fraction 1	0.050	25.86	0.2565
Fraction 2	0.482	24.58	0.3110
Fraction 3	0.396	23.30	0.0253
Fraction 4	1.561	21.12	1.029
Fraction 5	3.160	15.60	1.4116
Silvex			
Whole Soil	0.531	2.61	2.600
Fraction 1	9.730	6.41	4.330
Fraction 2	1.101	5.03	4.696
Fraction 3	10.95	4.78	6.846
Fraction 4	9.45	4.11	6.8096
Fraction 5	1.052	3.03	4.520
2,4-D			
Whole Soil	1.750	2.02	1.866
Fraction 1	1.560	1.58	1.654
Fraction 2	1.520	1.51	0.816
Fraction 3	1.670	1.43	2.693
Fraction 4	26.26	1.29	10.41
Fraction 5	1.594	0.96	1.380

overpredicted the actual distribution coefficient values measured whereas for Silvex, Kd_{model} underpredicted in soil fractions 1, 3 and 4. With 2,4-D adsorption on soil fractions 1, 2 and 3, the original approach more closely approximated the distribution coefficient, while the opposite occurred for the whole soil and the mineral surface (fraction 5). These comparisons indicated that as with the adsorption data previously presented, soil organic level was not a consistently good predictor for determining the distribution coefficient. While the simulated model ($Kd_{simulated}$) was able to predict the distribution coefficents better than did the underlying Kd model, neither approach was wholly satisfactory. These comparisons further substantiated the underlying observations that soil organic content alone was not a good predictor for determining either the distribution coefficent or ultimate adsorptive capacity. Other variables should also be taken into account.

RESULTS--COMPETITIVE ADSORPTION

Competitive Adsorption Studies

When one or more solutes are present in a solvent, the adsorption of the solute is unpredictable due to many possible interactions among the solutes, between the solvent and the adsorbent and the solute and the adsorbent. Solute characteristics, such as solubility and molecular weight, the presence of various functional groups, and the steric relationships and concentration may all simultaneously affect adsorption of multiple solutes [58]. Since soil is such a complex system relative to activated carbon or other traditional adsorbents, adsorption of more than one solute is difficult to fully define. It is vitally important to understand and characterize these processes, however, when developing conceptual and mathematical models of transport.

The results of the analyses conducted to determine the competition between two pesticides in solution when adsorbed onto Port soil and soil fractions are tabulated in Tables XVII and XVIII for 25, 30, and 35°C for systems involving lindane and Silvex.

Lindane data: Comparison to Single Solute System.

The data presented in Table XVII indicated that adsorption of lindane with Silvex as the potentially competiting pesticide at 25°C within the Port whole soil fraction, was generally, higher than when present in single

TABLE XVII

COMPETITIVE ADSORPTION OF LINDANE WITH SILVEX IN SOLUTION: INITIAL AND FINAL CONCENTRATION (AVERAGES OF TRIPLICATES) OF LINDANE FOR FOR ALL TEST ADSORBENTS (5 GMS) IN THE EXPERIMENT UNDER EQUILIBRIUM CONDITIONS

	Lindane Doses (ug/l)					
Adsorbents (Port Soil)	10	20	50	100	200	500
T = 25°C						
Whole Soil	5.9	12.8	25.2	93.9	113.7	400.4
Fraction 1	5.0	11.5	19.0	68.9	152.0	469.4
Fraction 2	7.9	17.3	24.5	53.8	102.1	432.0
Fraction 3	3.0	16.0	29.4	72.2	102.5	451.7
Fraction 4	3.9	14.3	27.7	66.4	155.0	458.0
Fraction 5	5.2	15.3	36.7	77.5	160.9	462.0
T = 30°C						
Whole Soil	5.6	13.8	25.3	87.6	164.7	485.7
Fraction 1	3.1	7.1	27.4	85.4	154.7	464.7
Fraction 2	2.1	13.3	25.7	87.2	156.7	487.5
Fraction 3	3.0	18.8	37.9	81.5	165.0	464.3
Fraction 4	3.6	13.7	28.8	71.7	164.6	399.6
Fraction 5	4.4	17.0	28.0	87.0	180.1	403.0
T = 35°C						
Whole Soil	5.0	15.9	39.9	81.0	174.8	432.0
Fraction 1	5.1	16.1	30.4	87.1	171.0	468.0
Fraction 2	4.9	15.9	29.0	86.6	173.8	446.0
Fraction 3	4.9	14.0	29.9	86.5	178.0	458.0
Fraction 4	4.7	12.0	39.7	88.3	173.9	459.5
Fraction 5	5.6	17.3	37.5	82.7	189.0	483.0

TABLE XVIII

COMPETITIVE ADSORPTION OF SILVEX WITH LINDANE IN SOLUTION: INITIAL AND FINAL CONCENTRATION (AVERAGES OF TRIPLICATES) OF SILVEX FOR FOR ALL TEST ADSORBENTS (5 GMS) IN THE EXPERIMENT UNDER UNDER EQUILIBRIUM CONDITIONS

	Silvex Doses (ug/l)					
Adsorbents (Port Soil)	10	20	50	100	200	500
<u>T = 25°C</u>						
Whole Soil	7.5	17.3	46.3	83.4	188.4	465.3
Fraction 1	7.3	18.2	46.3	86.3	151.7	435.3
Fraction 2	5.3	12.3	47.2	86.3	192.7	482.6
Fraction 3	9.0	14.3	41.4	86.8	186.4	424.3
Fraction 4	9.6	18.6	43.7	80.7	187.2	475.2
Fraction 5	9.1	18.8	41.3	91.3	194.7	492.6
<u>T = 30°C</u>						
Whole Soil	8.9	16.9	42.9	89.8	190.6	440.0
Fraction 1	9.5	16.9	31.1	89.5	179.1	482.6
Fraction 2	9.1	14.8	38.7	85.5	174.7	469.4
Fraction 3	5.8	16.0	43.3	86.0	178.7	469.8
Fraction 4	4.3	14.3	21.7	84.5	185.2	450.1
Fraction 5	5.7	17.8	42.0	88.0	159.6	422.9
<u>T = 35°C</u>						
Whole Soil	8.4	16.3	38.5	94.0	163.0	433.3
Fraction 1	7.2	14.5	46.8	88.3	158.4	433.3
Fraction 2	7.1	14.0	43.3	85.5	194.6	410.0
Fraction 3	5.8	16.5	38.6	82.8	192.0	414.0
Fraction 4	9.7	18.4	36.6	90.5	184.0	388.0
Fraction 5	8.7	18.5	46.8	97.5	185.0	470.0

solute systems as shown in Table VII. Lower rates of removal of lindane in the binary system was observed as the concentration increased to the 500 ug/l range.

Soil fraction 1 for the binary systems showed Lindane removal to be significantly higher at the lower solute concentrations than removal in lindane alone systems. The single solute system exhibited a slightly improved lindane uptake at the 200 ug/l concentration with a significant increase at the 500 ug/l trial.

The Port soil fraction 2 in the binary systems showed lower removal of the pesticide at low solute concentrations but higher adsorptive affinities of the pesticide at the 50, 100 and 200 ug/l concentration ranges than did the single solute systems. When the adsorbate concentration was increased to 500 ug/l, adsorption in the single solute systems again was considerably improved when compared to the binary trials. This suggests that a maximum capacity for solute existed on the soil surfaces but that complex interactions between solutes occurred at lower concentrations.

The third soil fraction of the binary systems exhibited the highest removal of lindane at the 10 ug/l trials when compared with the lindane alone systems. However, higher affinities of the pesticide at 20, 100 and 500 ug/l concentration ranges were observed in the single solute systems. The binary system for this fraction, on the other hand, showed a slightly higher lindane uptake at the 50 and

200 ug/l range.

The fourth soil fraction for the binary systems behaved similarly to the first soil fraction where higher uptake of lindane was observed at the lower solute concentrations. The single solute systems showed improved lindane adsorption at the higher concentrations of 100, 200 and 500 ug/l concentration range than did the binary systems.

The removal of the humic layer in the fifth fraction still allowed a degree of adsorption affinity with the binary systems yielding a higher uptake of the pesticide over the majority of the concentrations evaluated. That is, the single solute systems showed less removal of lindane.

Silvex data: Comparison to Single Solute System.

The data presented in Table XVIII indicated that adsorption of Silvex when lindane was present as a potentially competiting pesticide (T = 25°C) on whole soil was generally lower than when Silvex was present alone as presented in Table VIII. Only in the 50 ug/l concentration did Silvex exhibit greater adsorption in binary systems than in the single solute trials.

Soil fraction 1 exhibited similar characteristics of higher Silvex removal in the single solute systems than at in the binary systems while Soil fraction 2 of the Port soil series, indicated a higher removal of Silvex in the binary systems at lower concentrations and relatively lower removals of the herbicide at higher concentrations. Only in the 10 and 20 ug/l concentrations did Silvex exhibit greater adsorption in binary systems than in the single solute trials. The lower removals of Silvex were observed at the rest of the solute concentration trials and indicated that some of the Silvex may have undergone either cosolvation or competition.

Soil fraction 3 of the single solute system was similar to soil fraction 1 in that it exhibited similar Silvex adsorption characterisitcs for a single solute.

Soil fraction 4 of the binary systems exhibited a slightly higher uptake of Silvex at the 20 and 100 ug/l pesticide concentration ranges, but the majority of the data evaluated still showed a lower removal of the herbicides when presented in binary systems.

Following the removal of the liable humic layers in the fifth fractions, a degree of adsorption affinity for the herbicide for both systems, was still present. Higher removals of Silvex were observed for this soil fraction in the binary systems over the entire concentrations evaluated than in Silvex systems alone.

In general, the removals of Silvex among the various soil fractions indicated that adsorption, while highly variable, was more significant in the single solute systems than where lindane was also present. This contradicted many of the lindane observations where higher removals of lindane in the binary systems were observed. This suggests that the properties (that is, solubility, polarity etc.) of lindane contributed to overall adsorption. Similarly, the interactions between Silvex and lindane suggested that a maximum capacity for the solute existed on the soil surface which resulted in a competition for sites between the two pesticides giving rise to a lower removal of Silvex in the binary systems.

The competitive effect of each solute (Silvex and lindane) in a bisolute system on the adsorption of the other solute is shown in Table XIX. The adsorptive capacities of the various soil fraction for each of the pesticides at 100 ppb equilibrium concentration is presented in this table. From Table XIX, it can be seen that the equilibrium adsorption of Silvex from a bisolute solution on the various soil fractions was reduced in the presence of lindane. For a pure Silvex solution for example on the whole soil (WS), the uptake capacity reached an equilibrium value of 354.81 ng/g at the equilibrium concentration of 100 ppb. Under the same conditions, in a bisolute systems containing equal concentrations of both Silvex and lindane, the Silvex uptake was 181.97 ng/g, about 48% lower. Similarly, for the other soil fractions, uptake capacities of Silvex in the bisolute systems were less than were observed in single systems, indicating a reduction in the uptake capacity.

The results also showed that lindane uptake in the presence of Silvex, acted to increase the adsorption of lindane for all the soil fractions evaluated. A hypothesis suggested here to account for the increase of lindane adsorption was that synergistic or increased adsorption occurred. That is, the adsorbed lindane molecules formed small enough two-dimensional micelles or hemimicelles (clusters) due to lateral energy productive interations similar to that of surfactants adsorption onto iron oxide [60]. The term hemimicelle or micelle is used here to describe the densely adsorbed phase present on an adsorbed site at high concentration at or above that corresponding to phase transition [61]. If that is the case, the monomer concentration increase as observed may caused increased adsorption.

Although the amount of Silvex adsorbed on the various soil fractions was found to be reduced significantly relative to its value in pure solution, the combined capacity for the two pesticides was greater than that for either of the pure substances alone. It is less than either of the pure solutes would have shown at twice the concentration. It thus appears that the total adsorptive capacity of the various soil fractions may be increased with mixed solutes. This revealed the more important principles which are shown later to have quite general applicability in explaining synergistic adsorption taking place.

Competitive adsorption data: Lindane competing with 2,4-D.

Table XX summarizes the adsorption of lindane at various temperatures with 2,4-D as a possible competiting adsorbent. Equal sample aliquots of both lindane and 2,4-D

TABLE XIX

COMPARISON OF ADSORPTION CAPACITY AT 100 ppb EQUILIBRIUM CONCENTRATION IN SINGLE AND BISOLUTE SYSTEMS FOR LINDANE AND SILVEX

	Compound		Adsorption Capacity at 100 ppb in ng/g	
			Bisolute System	
Adsorbent	Lindane (L)	Silvex (S)	L - S	
WS	199.50	354.81	Lindane	616.59
			Silvex	181.97
S1	316.22	630.95	Lindane	621.58
			Silvex	274.42
S2	316.22	1258.92	Lindane	446.68
			Silvex	165.97
S3	354.80	707.94	Lindane	449.77
			Silvex	257.03
S4	398.10	707.94	Lindane	489.77
			Silvex	79.43
S5	56.23	70.79	Lindane	363.07
			Silvex	91.20

at various concentrations were introduced into an erlymeyer flask the various soil samples and shaken until equilibrium. The results obtained were in agreement with the trends previously observed in Tables XVII and XVIII for the lindane-Silvex systems. That is, adsorption of lindane did not increase consistently within the fractionated soil fractions. However, the removal of lindane was generally higher for systems utilizing lindane and 2,4-D than with lindane and Silvex. The systems with lindane and 2,4-D exhibited higher adsorption than did the lindane-Silvex trials. This was apparently due either to solvent effects or to lessening of competition between solutes for sites on the adsorbent.

Lindane data: Comparison to Single Solute System.

Whole soil

The data presented in Table XX when compared to those in Table VII of the Port soil indicated that adsorption of lindane in the presence of 2,4-D at 25°C within the whole soil fraction, was generally, higher than when present in single solute systems. As compared to the single uptake data of lindane, adsorption of lindane in the binary solute system exhibited higher lindane adsorption untill the 100 ug/l range. Relatively less removal of lindane was observed, however, as the concentration increased to 500 ug/l range.

TABLE XX

COMPETITIVE ADSORPTION OF LINDANE WTIH 2,4-D IN SOLUTION: INITIAL AND FINAL CONCENTRATION (AVERAGES OF TRIPLICATES) OF LINDANE FOR ALL TEST ADSORBENTS (5 GMS) IN THE EXPERIMENT UNDER EQUILIBRIUM CONDITIONS

	Lindane Doses (ug/l)					
Adsorbents (Port Soil)	10	20	50	100	300	500
T = 25°C						
Whole Soil	2.7	8.7	28.9	66.0	183.0	448.9
Fraction 1	5.0	8.4	19.7	42.7	169.0	378.2
Fraction 2	5.0	13.2	33.0	72.7	161.4	351.5
Fraction 3	3.3	5.0	19.2	49.4	109.4	372.3
Fraction 4	2.7	5.4	23.5	52.5	180.7	452.5
Fraction 5	4.6	10.6	21.2	87.2	159.4	473.6
T = 30°C						
Whole Soil	4.3	18.9	30.7	76.3	163.1	447.5
Fraction 1	6.4	17.1	32.9	62.9	174.4	470.3
Fraction 2	5.6	9.7	29.0	89.2	185.4	399.7
Fraction 3	6.4	10.3	22.7	91.0	176.7	389.3
Fraction 4	7.6	11.5	25.2	66.1	124.3	390.6
Fraction 5	7.3	12.0	35.6	49.9	175.6	421.2
T = 35°C						
Whole Soil	8.3	10.5	33.5	84.0	171.0	450.0
Fraction 1	4.4	18.2	36.1	58.0	179.0	466.0
Fraction 2	5.3	18.3	23.1	86.6	174.0	441.0
Fraction 3	4.2	14.7	27.5	75.1	176.3	474.0
Fraction 4	5.1	9.1	36.7	78.9	185.6	477.0
Fraction 5	4.8	18.7	46.6	88.0	190.4	472.8

Soil fraction 1

Soil fraction 1 exhibited similar characterisitcs to those of the whole soil fraction in that lindane removal was higher in binary systems until the 100 ug/l concentration where the single solute system exhibited a slightly improved uptake through the 200 and 500 ug/l ranges.

Soil fraction 2

Port soil fraction 2 showed lower removal of the pesticide at the 20, 100 and 200 ug/l concentration ranges than was observed in the lindane single systems. Higher lindane adsorption in the binary systems was observed among the rest of the concentrations evaluated.

Soil fraction 3

The third soil fraction of the binary solute systems again, exhibited higher uptake of lindane over most of the concentrations evaluated than did the lindane single systems. However, the single solute systems showed improved lindane adsorption over the binary trials at only the 100 ug/l trials.

Soil fraction 4

The forth fraction in the binary systems behaved similarly to the whole soil and soil fraction 1 in that the single solute systems showed a higher removal of lindane at the 300 and 500 ug/l range than did the binary systems. The binary systems showed consistently better removals of lindane for this fraction as the concentration increased to the 100 ug/l range.

Soil fraction 5 of the binary system exhibited a lessened degree of adsorption affinity for the lindane when compared to the previous soil fractions. As before, this was attributed to the loss of the remaining organic layers on the adsorbent. There was a higher uptake of the pesticide over the entire concentration range evaluated in the binary solute systems than for the single lindane trials.

2,4-D data: Comparison to Single Solute System Whole soil

The data presented in Table XXI indicated that relative adsorption of 2,4-D with lindane as the secondary adsorbent, on whole soil, was generally higher at the lower influent solute concentrations than was observed in the 2,4-D single systems presented in Table XIX. Less removal of 2,4-D in the binary system, however, than the single solute system was observed as the concentration increased from 100 to 500 ug/l range.

Soil fraction 1

Soil fraction 1 showed lower removals of 2,4-D at the 10 and 20 ug/l ranges for the binary system than did the single 2,4-D trials but higher removals of the herbicide as the concentration increased to the 500 ug/l.

TABLE XXI

COMPETITIVE ADSORPTION OF 2,4-D WITH LINDANE IN SOLUTION: INITIAL AND FINAL CONCENTRATION (AVERAGES OF TRIPLICATES) OF 2,4-D FOR ALL TEST ADSORBENTS (5 GMS) IN THE EXPERIMENT UNDER EQUILIBRIUM CONDITIONS

	2,4-D Doses (ug/l)					
Adsorbents (Port Soil)	10	20	50	100	300	500
T = 25°C						
Whole Soil	8.1	17.2	44.7	91.3	187.2	478.2
Fraction 1	7.8	17.5	43.2	90.2	181.2	484.3
Fraction 2	6.2	17.3	40.2	82.6	180.7	474.2
Fraction 3	8.7	17.2	40.2	82.5	180.3	473.5
Fraction 4	8.8	17.3	42.2	83.7	171.2	433.4
Fraction 5	7.7	16.7	44.3	88.6	193.5	486.3
T = 30°C						
Whole Soil	8.5	17.5	42.5	83.8	180.5	468.0
Fraction 1	8.5	18.4	46.6	87.6	179.9	474.2
Fraction 2	6.2	15.7	45.4	94.5	176.4	478.0
Fraction 3	8.6	13.2	42.6	86.6	191.5	475.0
Fraction 4	8.8	14.9	44.6	84.7	182.5	476.7
Fraction 5	8.1	17.5	46.7	89.5	186.4	488.0
T = 35°C						
Whole Soil	8.31	18.16	40.7	87.6	188.3	461.7
Fraction 1	8.43	17.29	35.0	85.0	190.0	479.0
Fraction 2	5.91	17.20	44.1	88.4	186.0	484.7
Fraction 3	7.73	16.13	45.7	93.8	183.5	486.2
Fraction 4	7.87	16.94	46.7	94.5	182.2	473.3
Fraction 5	4.53	17.06	43.6	89.6	197.5	488.9

Soil fraction 2

Port soil fraction 2 of the single solute system showed consistently slightly higher removals of 2,4-D than did the binary 2,4-D trials over the majority of concentrations evaluated.

Soil fraction 3

Soil fraction 3 of the binary systems behaved similarly to the first soil fraction where lower removals of 2,4-D over the single 2,4-D systems were observed at the 200 ug/l trials. The majority of the concentrations evaluated showed higher removals of 2,4-D for the binary systems than in the single solute systems.

Soil fraction 4

Soil fraction 4 of the binary solute systems again indicated higher removals of 2,4-D at the lower solute concentration over the single solute systems. Less removal of the herbicide was observed for the binary systems at the 50, 100 and 500 ug/l concentration ranges than the single solute systems.

Soil fraction 5

Soil fraction 5 behaved more like soil fraction 2 in the binary systems in that it exhibited significantly higher removals of 2,4-D than did the single solute systems over the entire concentration ranges evaluated.

Competitive adsorption data: Comparison of Lindane to 2,4-D.

With reference to both Tables XX and XXI, the Port data presented in Table XX indicated that the removals of lindane in whole soil fractions, 1, 2 and 3 were significantly higher than 2,4-D over the entire concentration ranges evaluated. These observations corresponded well with the single solute adsorption data presented in Tables VII and IX where lindane adsorption was consistently higher that than for 2,4-D.

Soil fraction 4

The exposure of the humic layers in the forth soil fraction did not significantly lower the removals of lindane or 2,4-D because the humic layer was considered to be the primary site of adsorption in soil organic matter. The removal of lindane over 2,4-D was still predominantly greater in this soil fraction for all the concentrations evaluated.

Soil fraction 5

Soil fraction 5 indicated that the adsorption of lindane in the binary systems was greater than 2,4-D for all concentrations evaluated.

The competitive effect of each solute in a bisolute system on the adsorption of other solute is shown in Table 21. From Table XXII, it can be seen that with the exception of soil fractions 2, 3 and 4, the equilibrium adsorption of

TABLE XXII

COMPARISON OF ADSORPTION CAPACITY AT 100 ppb EQUILIBRIUM CONCENTRATION IN SINGLE AND BISOLUTE SYSTEMS FOR LINDANE AND 2,4-D

	Compound		Adsorption Capacity at 100 ppb in ng/g	
Adsorbent	Lindane (L)	2,4-D (D)	Bisolute System L - D	
WS	199.50	158.48	Lindane	446.68
			2,4-D	162.18
S1	316.22	158.48	Lindane	575.43
			2,4-D	169.82
S2	316.22	354.81	Lindane	602.55
			2,4-D	239.88
S3	354.80	446.68	Lindane	933.25
			2,4-D	208.92
S4	398.10	501.68	Lindane	501.18
			2,4-D	323.59
S5	56.23	100.00	Lindane	407.38
			2,4-D	134.89

2,4-D from a bisolute solution on the various soil fractions was increased in the presence of lindane. That is, an increased adsorption of 2,4-D in the binary systems versus the single pesticide systems was found. For a pure 2,4-D solution, for example, the whole soil (WS) uptake capacity reached an equilibrium value of 158.48 ng/g at the equilibrium concentration of 100ppm. Under the same conditions, in a bisolute system containing equal concentrations of both 2,4-D and lindane, 2,4-D uptake capacity was 162.18, or about 2.2% higher. Similarly for lindane, uptake capcities of 199.50 and 446.68 ng/g were observed for the single and bisolute systems, respectively, at an equilibrium concentration of 100 ppb, indicating a 55% increased in uptake capacity. It is noteworthy that the less soluble compound was more favorably adsorbed in the lindane-2,4-D binary solute systems studies. That is, lindane was adsorbed more strongly of the two competitors.

Although the amount of 2,4-D adsorbed on soil fractions 2, 3 and 4 were found to decrease relative to their value in pure solution, the combined capacity of lindane and 2,4-D for the binary systems were greater than that for either of the pure substances alone. That is, in general, the results indicated that, in multispecies systems, cumulative adsorption exceeded the adsorption of individual species in the single-species systems. It thus appeared that total adsorptive capacity of the various soil fractions may be increased with mixed solutes. It would appear that the addition of a second solute either lowered the solubility of the compound or the formation of ideal mixed micelles/hemimicelles (or clusters) occurred. This interaction would tend to increase adsorption [61-63]. Also, the micelles/hemimicelles (clusters) would serve as centers for which increased adsorption could occur. It is therefore suggested that this behaviour is caused by the specificity of synergistic effects that gives rise to increased adsorption of lindane. The continued increased of 2,4-D was again, potentially attributable to synergistic adsorption. These assumptions are, however, a priori, reasonable, and so can be counted on as leading to a valid predictions of the trends.

Competitive adsorption data - Silvex competing with 2,4-D.

Table XXIII summarizes the adsorption of Silvex at various temperatures with 2,4-D as a possibly competiting adsorbate. The conditions for the experiments were the same as that of the other binary solute systems mentioned previously.

Adsorption data: Comparison of Silvex to Single Solute System.

Whole soil

The data presented in Table XXII indicated that adsorption of Silvex with 2,4-D as the secondary adsorbent at 25°C within the whole soil fraction was generally lower at the 10, 20 and 200 ug/l range when compared to the single solute adsorption data in Table VIII. Less removal of the herbicide was observed in the single solute systems as the concentrations increased from 50 to 100 ug/l and to the 500 ug/l range where lower removal of Silvex was further observed.

Soil fraction 1

Soil fraction 1 of the Port soil series in binary solute systems indicated that the removal of Silvex was generally, lower than when Silvex was present alone in similar trials. Relatively higher removals of the herbicide in the binary systems was observed only at the 50 ug/l range.

Both soil fractions 2 and 3 of the binary systems indicated lower removals of Silvex generally over the entire concentration ranges than were observed in the single solute systems. The single solute systems showed decreased Silvex adsorption at only the 50 and 200 ug/l ranges respectively.

Soil fraction 4

Soil fraction 4, however, indicated higher removals of the herbicide for the binary system at the 20 and 100 ug/l concentration range over the single Silvex trials. The rest of the concentrations evaluated, however, showed lower relative removals of the herbicide than did the single solute systems.

Soil fraction 5

Removals of the humic layer in the fifth fraction did not completely stop adsorption of these pesticides. An affinity for the herbicide was present and attributed to interactions between the mineral soil surface and the organic pesticides. These trials also showed higher removals of Silvex over the entire concentration ranges for the binary system than was observed for the single solute systems.

In general, the data in Table XXIII, with comparisons to Table 8, indicated that the removal of Silvex was higher in single solute systems than when 2,4-D was present as a competiting adsorbate. This implies that a maximum capacity for the solute existed on the soil surfaces.

Adsorption data: Comparison of 2,4-D to Single Solute System

Adsorption of 2,4-D in the binary systems with Silvex as as the secondary adsorbate as shown in Table XIV, followed the same trend as that of Silvex when 2,4-D was present as the competitng adsorbate in that there was a general decrease in adsorption for 2,4-D in the binary solute systems when compared to the pure 2,4-D solute systems depicted in Table IX for all the soil fractions evaluated. This indicated that either the sites were saturated or that insufficient energy was available to complete adsorption and were thus unable to retain additional pesticides.

TABLE XXIII

COMPETITIVE ADSORPTION OF SILVEX WITH 2,4-D IN SOLUTION: INITIAL AND FINAL CONCENTRATION (AVERAGES OF TRIPLICATES) OF SILVEX FOR ALL TEST ADSORBENTS (5 GMS) IN THE EXPERIMENT UNDER EQUILIBRIUM CONDITIONS

Adsorbents (Port Soil)	Silvex Doses (ug/l)					
	10	20	50	100	300	500
T = 25°C						
Whole Soil	8.4	17.2	35.4	78.7	187.0	431.0
Fraction 1	8.6	16.9	43.8	80.3	163.5	443.0
Fraction 2	7.6	18.7	44.7	84.2	152.7	458.5
Fraction 3	8.4	18.2	41.2	87.5	164.7	463.7
Fraction 4	8.3	15.4	40.3	82.1	177.8	471.8
Fraction 5	8.3	17.3	45.1	85.4	169.5	482.5
T = 30°C						
Whole Soil	8.4	16.1	37.8	80.5	160.0	438.6
Fraction 1	8.6	16.8	41.2	82.7	165.1	445.4
Fraction 2	9.1	17.6	41.2	88.0	160.6	465.5
Fraction 3	9.4	17.7	43.2	89.5	160.4	472.4
Fraction 4	9.8	15.5	40.7	87.1	164.0	480.8
Fraction 5	8.8	16.4	42.7	85.1	179.0	474.5
T = 35°C						
Whole Soil	9.2	15.6	36.7	75.2	176.0	457.9
Fraction 1	9.1	16.9	42.2	80.0	167.3	446.7
Fraction 2	8.9	16.5	42.0	76.8	188.3	440.3
Fraction 3	9.3	16.6	48.1	76.8	162.3	474.0
Fraction 4	8.7	17.4	45.2	82.1	173.3	471.0
Fraction 5	8.2	18.6	46.4	87.1	184.2	482.0

TABLE XXIV

COMPETITIVE ADSORPTION OF 2,4-D WITH SILVEX IN SOLUTION: INITIAL AND FINAL CONCENTRATION (AVERAGES OF TRIPLICATES) OF 2,4-D FOR ALL TEST ADSORBENTS (5 GMS) IN THE EXPERIMENT UNDER EQUILIBRIUM CONDITIONS

	2,4-D Doses (ug/l)					
Adsorbents (Port Soil)	10	20	50	100	300	500
T = 25°C						
Whole Soil	9.7	18.7	47.5	96.8	193.5	467.7
Fraction 1	9.7	17.1	44.7	93.6	182.7	478.2
Fraction 2	9.3	16.0	45.3	95.3	190.2	467.5
Fraction 3	9.7	18.1	41.3	92.1	177.5	463.3
Fraction 4	9.4	15.8	43.8	88.7	174.6	468.9
Fraction 5	9.7	18.3	48.2	91.6	187.5	487.0
T = 30°C						
Whole Soil	9.5	18.9	49.3	91.3	161.7	462.0
Fraction 1	6.4	17.4	43.9	97.4	185.3	474.0
Fraction 2	9.8	16.3	47.5	88.4	183.4	482.3
Fraction 3	9.0	15.8	47.7	87.5	176.2	471.8
Fraction 4	9.5	16.3	43.0	80.5	172.1	472.0
Fraction 5	8.8	18.8	49.2	87.5	181.2	476.6
T = 35°C						
Whole Soil	9.8	17.5	44.8	87.5	184.2	481.7
Fraction 1	9.7	16.4	45.1	95.7	193.3	466.8
Fraction 2	9.3	16.8	43.1	82.0	179.4	472.2
Fraction 3	8.9	17.9	47.4	87.1	187.4	468.3
Fraction 4	9.8	16.6	44.6	85.2	182.4	484.5
Fraction 5	9.0	17.6	47.6	86.7	183.4	489.5

The competitive effect of each solute in a bisolute system on the adsorption of the other solute is shown in Table XXV. The adsorption capacity at 100 ppb equilibrium concentration for both solutes is presented in this table. From Table XXIV, it can be seen that equilibrium adsorption of each solute from a bisolute solution on the various soil fractions was reduced in the presence of a second solute. For a pure 2,4-D solution, for example, the whole soil (WS) uptake capacity reached an equilibrium value of 158.48 ng/g at the equilibrium concentration of 100 ppb. Under the same conditions, in a bisolute system containing equal concentrations of both 2,4-D and Silvex, 2,4-D uptake capacity was 85.11 ng/g, or about a 46% reduction. Similarly for Silvex, uptake capacities of 354.81 and 269.15 ng/g were observed for the single and bisolute systems, respectively, at an equilibrium concentration of 100 ppb, indicating a 24% reduction in uptake capacity.

Although the amount of each solute adsorbed on the various soil fractions wase found to be reduced significantly relative to its value in pure solution, the combined capacity, for most cases, was greater than that for 2,4-D alone but was less than either of the pure solutes exhibited at twice the concentration. It appears that total adsorptive capacity of the various soil fractions was still increased adsorption with mixed solutes, this implies that the increased adsorptive capacity was potentially attributable to energy producing lateral interactions

TABLE XXV

COMPARISON OF ADSORPTION CAPACITY AT 100 ppb EQUILIBRIUM CONCENTRATION IN SINGLE AND BISOLUTE SYSTEMS FOR 2,4-D AND SILVEX

	Compound		Adsorption Capacity at 100 ppb in ng/g	
Adsorbent	2,4-D (D)	Silvex (S)	Bisolute System D - S	
WS	158.48	354.81	2,4-D	85.11
			Silvex	269.15
S1	158.48	630.95	2,4-D	134.89
			Silvex	389.04
S2	354.81	1258.92	2,4-D	141.25
			Silvex	309.00
S3	446.68	707.94	2,4-D	181.97
			Silvex	245.47
S4	501.68	707.94	2,4-D	199.52
			Silvex	354.81
S5	100.00	70.79	2,4-D	89.12
			Silvex	190.54

between the pesticides and with the adsorbent where clusters or micelles were formed which served as centers for which synergistic adsorption or increased adsorption occured [64-68]. Both the surfactant and chromatography model were able to explain the increased adsorption of either of the pesticides but the surfactant model was much more appropriate in defining the increased adsorption of both pesticides since it predicted lateral interactions among the molecules resulting in cluster formation. These clusters can act as centers for which increased adsorption can occur.

Competitive Adsorption

The Sheindorf-Rebhun-Sheintuch (SRS) equation was applied to each of the binary solute combinations evaluated. The SRS equation is a multicomponent Freundlich-type adsorption equation (equations 13 & 14). The derivation of the SRS equation was based on the assumption that there was an exponential distribution of adsorption energies available for each solute [46-47].

The isotherm was compared with the experimental results by plotting the equilibrium concentration for each adsorbate at each soil load computed. This is pictorially represented in figures AII-01 through AII-54 in the appendix, where it was generally shown that good correlations existed especially at the lower and

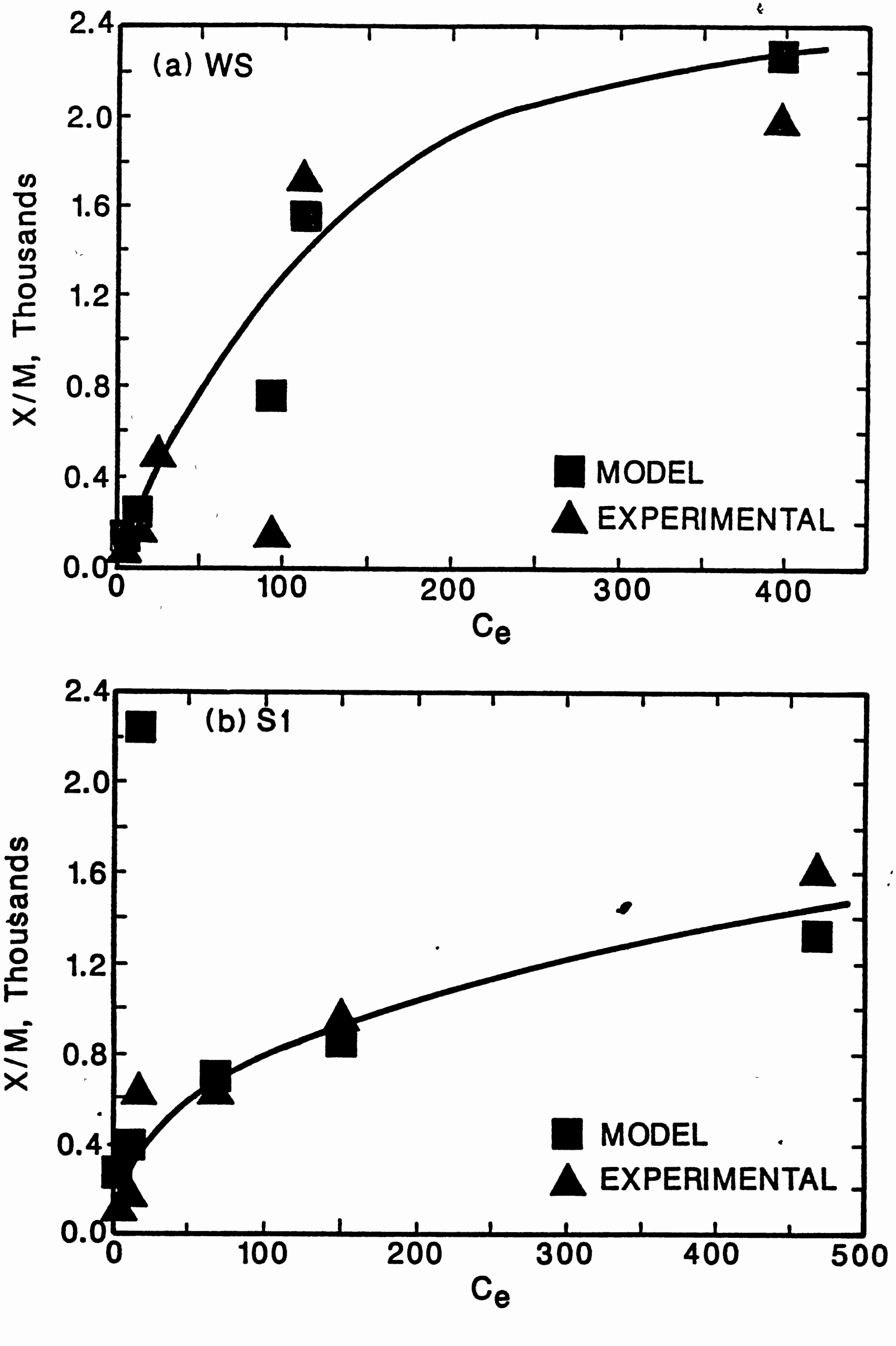


Figure 6. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) WS and (b) S1 at 25°C

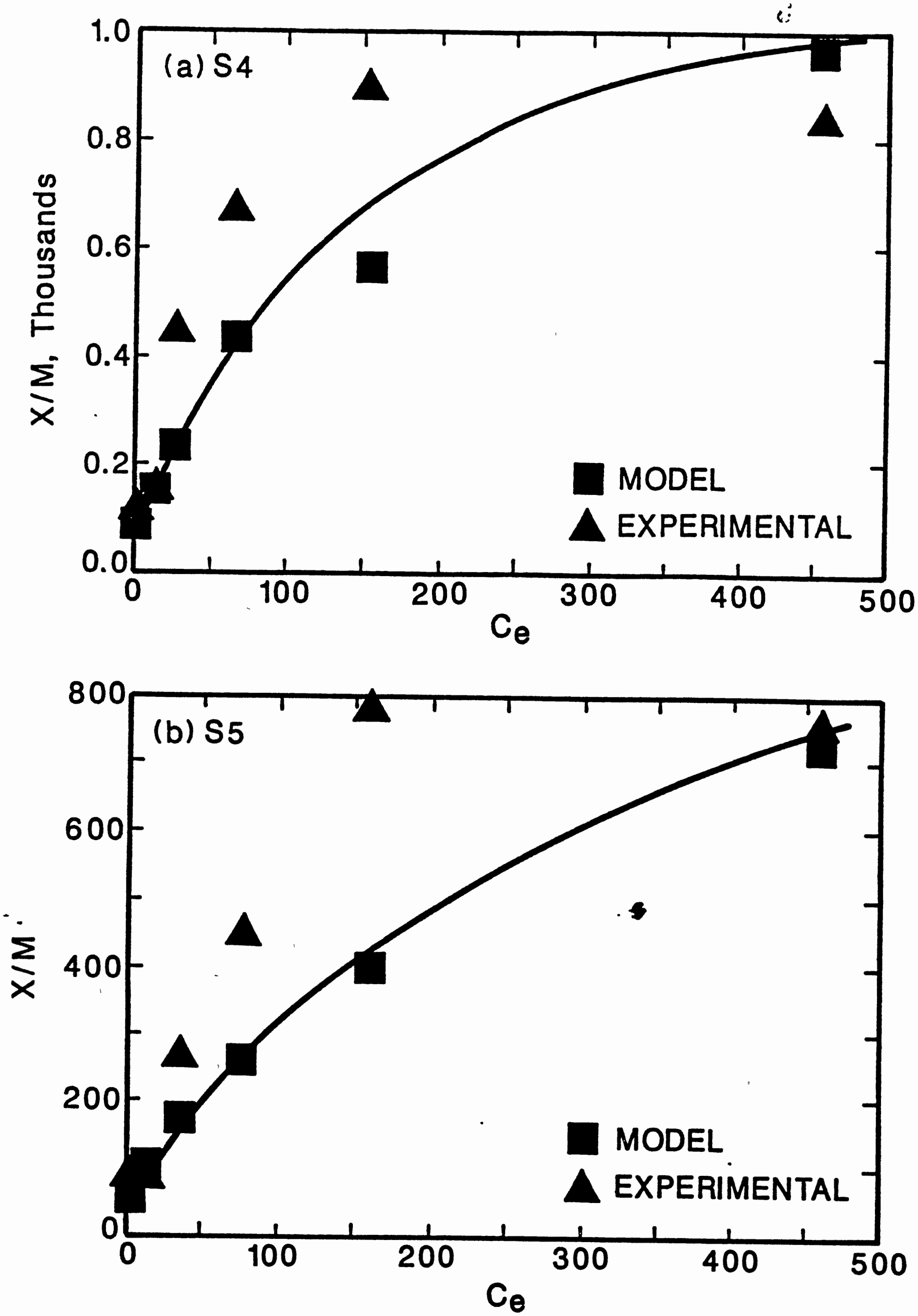


Figure 7. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) S4 and (b) S5 at 25°C

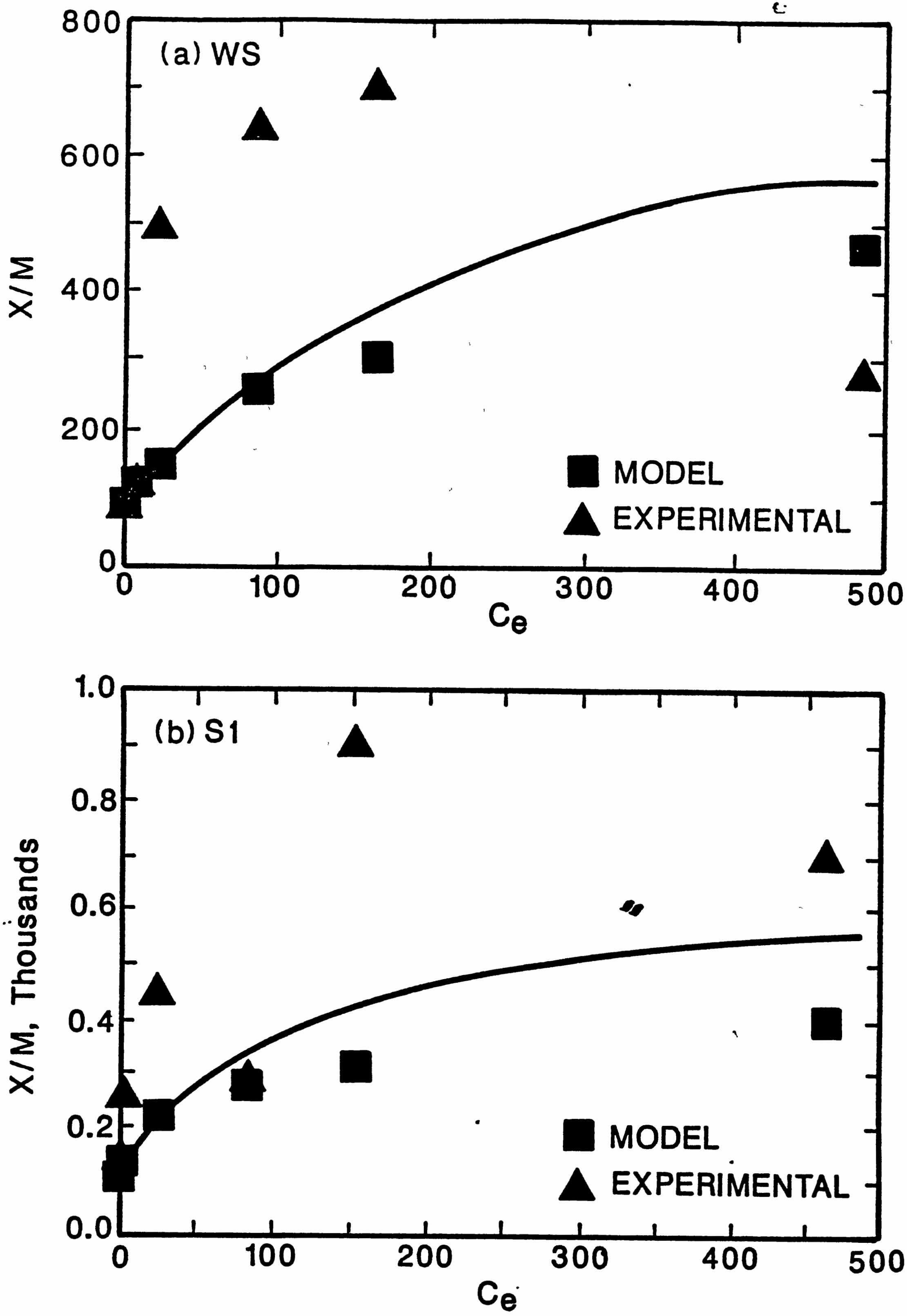


Figure 8. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) WS and (b) S1 at 30°C

intermediate solute concentrations, between the experimental and computed data. This is presented in Figure 6 which indicated conformity of the experimental data to computed results for lindane in the presence of Silvex at T = 25°C on whole soil and soil fraction 1 respectively. Some of the selected soil fractions in figure 7 indicated that conformity of the SRS equation for lindane with Silvex present as the competiting adsorbate, on soil fractions 4 and 5 respectively, was only apparent at the lower solute concentrations. This indicates that the sites were saturated by adsorbate and were unable to retain additional pesticide.

Figures AII-04 through AII-06 (in the appendix) depict adsorption where systems utilizing lindane and Silvex were compared at T = 30°C. The figures indicated that the experimental data conformed well to the SRS especially for soil fraction 1 through 5 but followed a decrease in adsorption as predicted by the SRS equation at higher solute concentration ranges. This is represented by figure 8(a) which indicated that conformity of the SRS equation by the whole soil data describing lindane adsorption with Silvex present, was good only at the 10 to 50 ug/l concentration range. Again, the model did not predict the upper solute concentration ranges well.

The competition of lindane with Silvex as the competiting adsorbate at 35°C among the soil fractions closely followed the SRS equation as depicted in figures AII-07 through AII-09 in the appendix. This is represented by figure 9. Figure 9(a) showed that the adsorption of lindane with Silvex as the competiting adsorbate on whole soil, closely followed the SRS equation. Figures 9(b) also showed that again, the SRS equation did not adequately describe the experimental data except for the 50 and 200 ug/l concentration range.

The data in figures AII-10 through AII-18 (in the appendix) presented the Silvex and lindane systems at temperatures 25, 30 and 35°C respectively. Again, these figures showed that the predictions by the SRS equations were generally in accord with the experimental results at the lower and intermediate concentration ranges but did not properly describe the higher concentration data. At higher concentrations, the equation seemed to underpredict the amount of solute adsorbed as depicted in figure 10(b). This figure showed Silvex adsorption with lindane present as the competiting adsorbate on soil fraction 1.

Figures AII-19 through AII-27 (in to the appendix) depict competition of lindane with 2,4-D at 25, 30 and 35°C respectively. The figures indicated that the experimental data generally conformed well to the SRS equation. This is represented by figure 11. Again, figure 11 indicated comformity at the lower to intermediate concentration ranges and less conformance at the higher solute concentrations. The SRS equation underpredicted the amount of lindane adsorbed in the presence of 2,4-D on soil fraction 4 and 5 respectively, for these cases. This indicates the model was

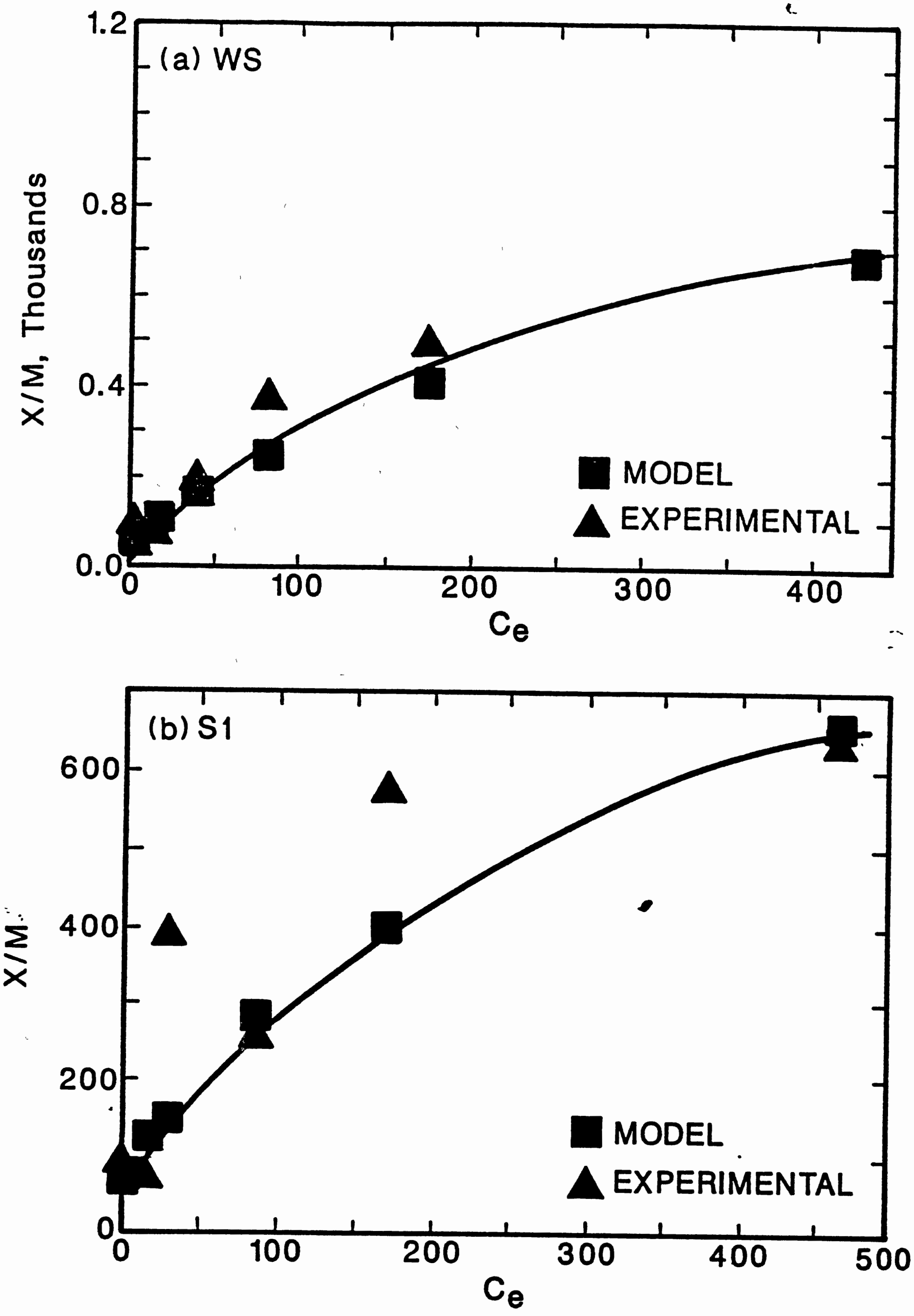


Figure 9. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) WS and (b) S1 at 35°C

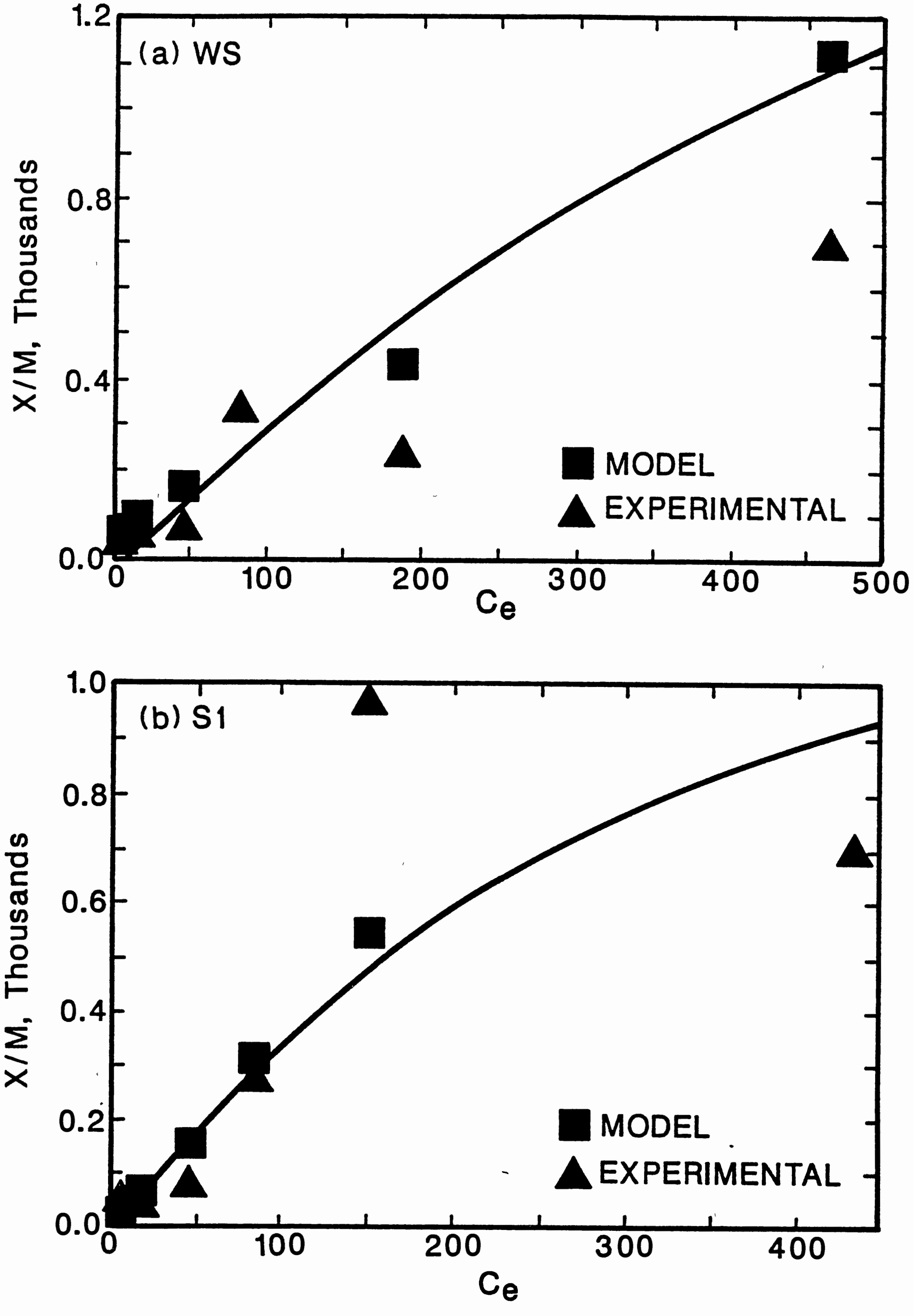


Figure 10. SRS Multiple Freundlich-Type Isotherms of Silvex with Lindane present on (a) WS and (b) S1 at 25°C

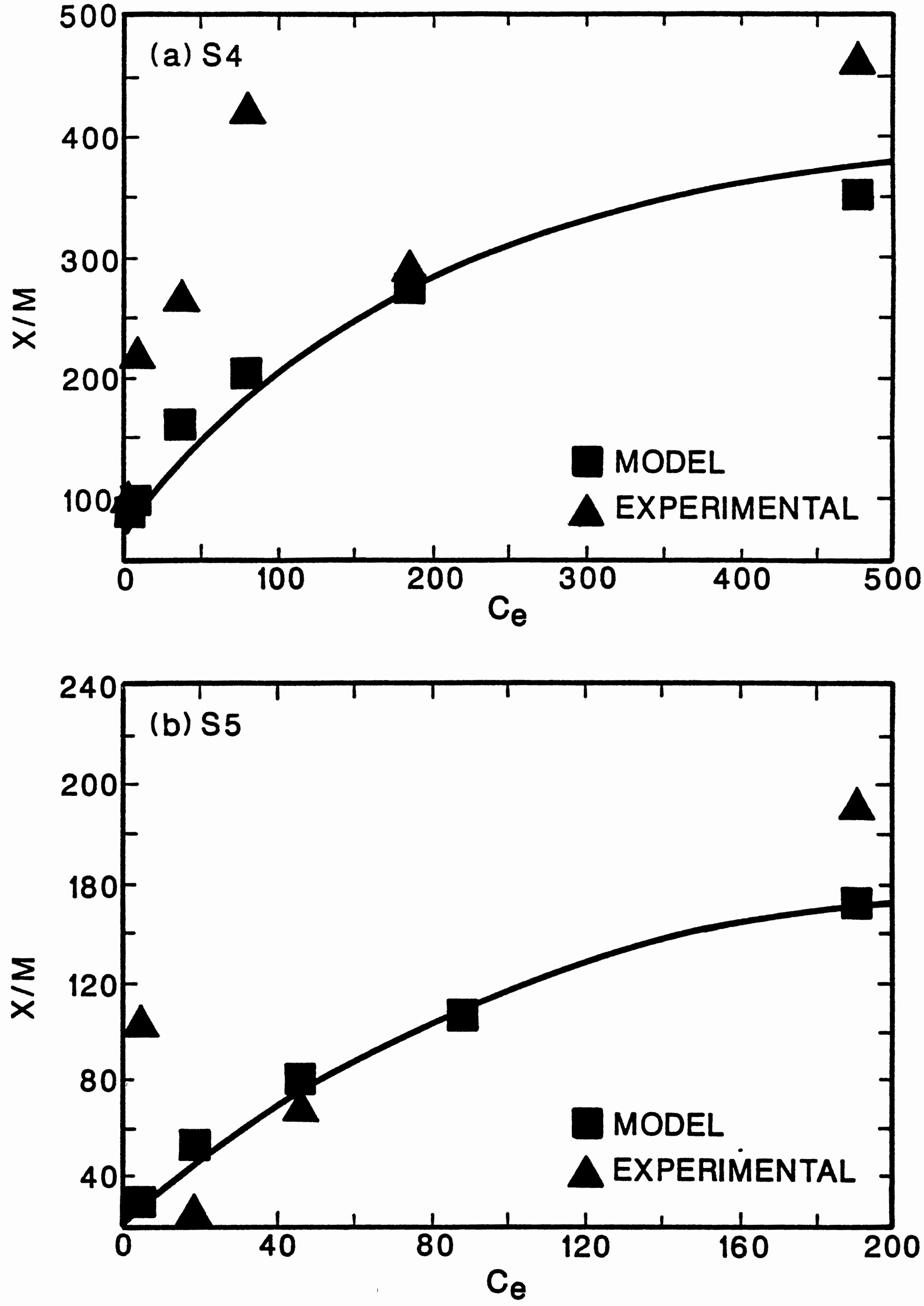


Figure 11. SRS Multiple Freundlich-Type Isotherms of Lindane with 2,4-D present on (a) S4 and (b) S5 at 35°C

unable to consider synergistic or other energy effects.

The competition of 2,4-D with lindane as the competitng adsorbate at various temperatures was presented in figures AII-28 through AII-36 (refer to appendix). Again, the data conformed generally well to the SRS equation at the lower and intermediate ranges. At higher concentration ranges, the equation again underpredicted the experimental data in almost all cases. This is represented by figure 12 which showed the adsorption of 2,4-D with lindane present on whole soil and soil fraction 1 at 35°C. An exception to figures 13(a), 14(b), and 15(b) indicated that the SRS equation overpredicted the adsorption of 2,4-D at the highest concentration while also indicating an acceptable conformance at the lower solute concentrations.

Silvex with 2,4-D present also conformed generally well to the SRS equation for all of the soil fractions at the various temperature evaluated as depicted in figures AII-37 through AII-45 (refer to appendix). The figures, again showed that general conformance to the equation at the lower and intermediate concentration ranges. At higher solute concentrations however, the equation again seemed to underpredict the experimental data most of the cases. This is presented in figure 16. Figure 16 indicated that the adsorption of Silvex with 2,4-D present on whole soil and soil fraction 1 respectively, conformed well with the SRS at the lower and intermediate concentration ranges. As before, significantly less conformance was observed at the highest

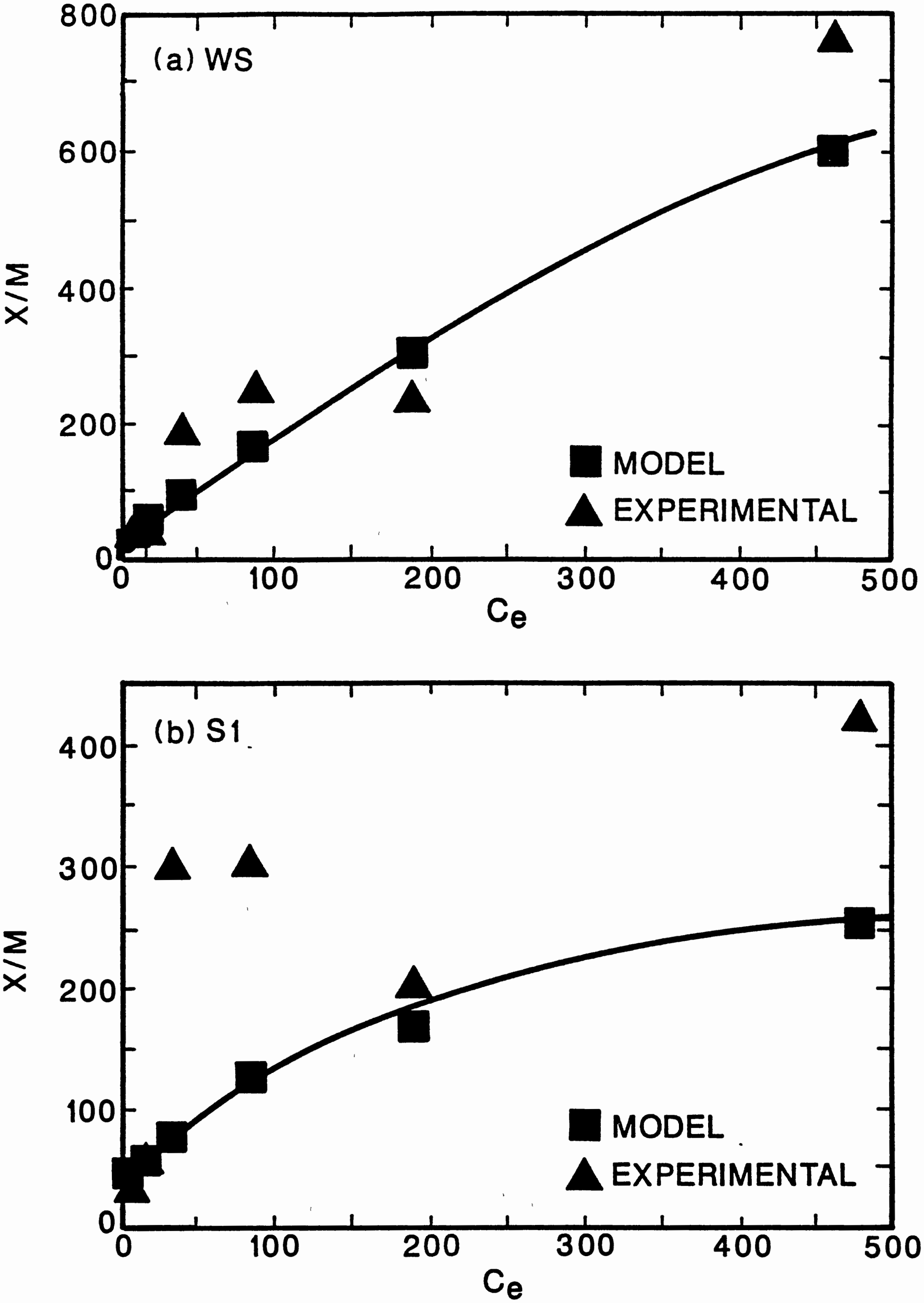


Figure 12. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Lindane present on (a) WS and (b) S1 at 35°C

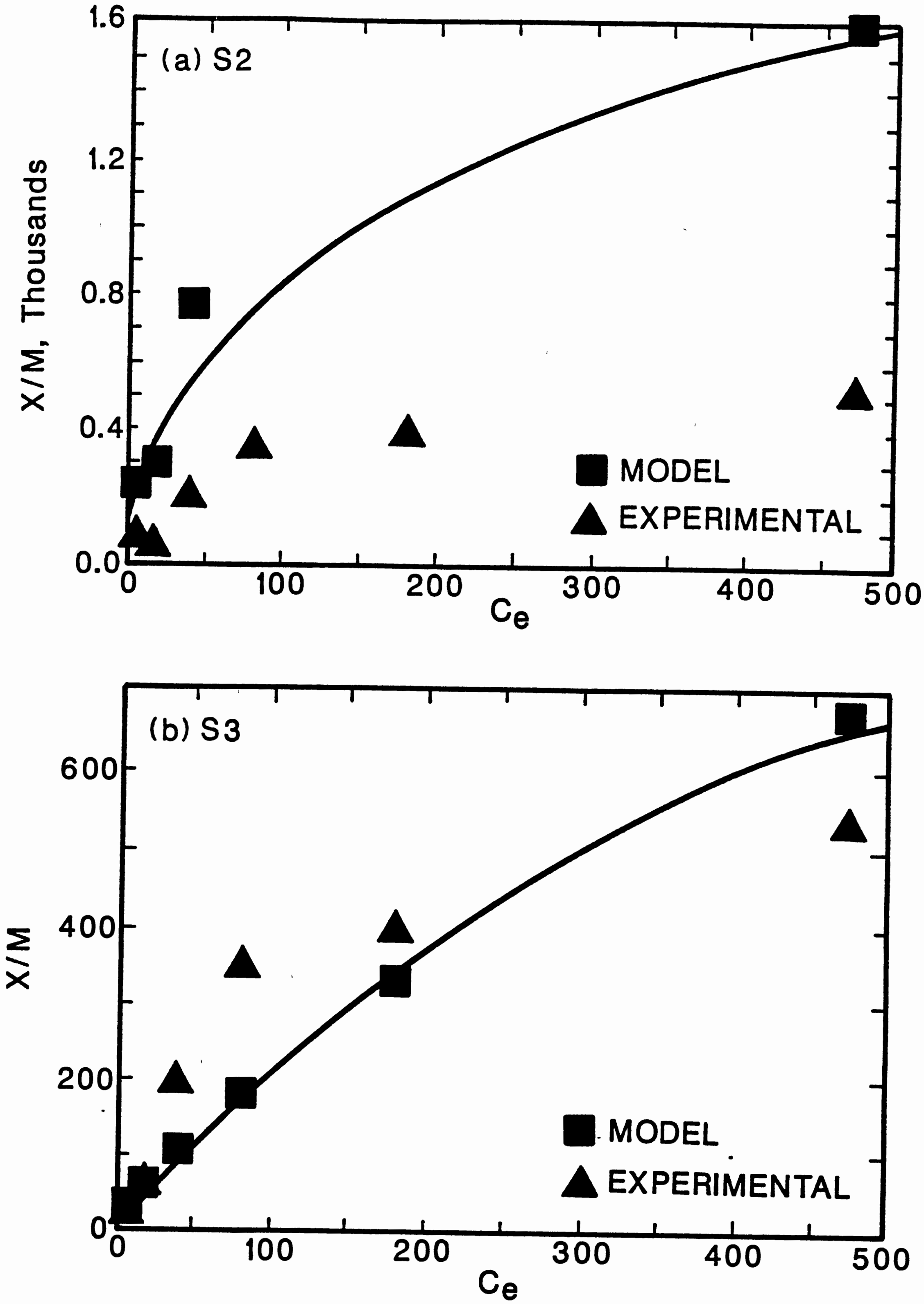


Figure 13. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Lindane present on (a) S2 and (b) S3 at 25°C

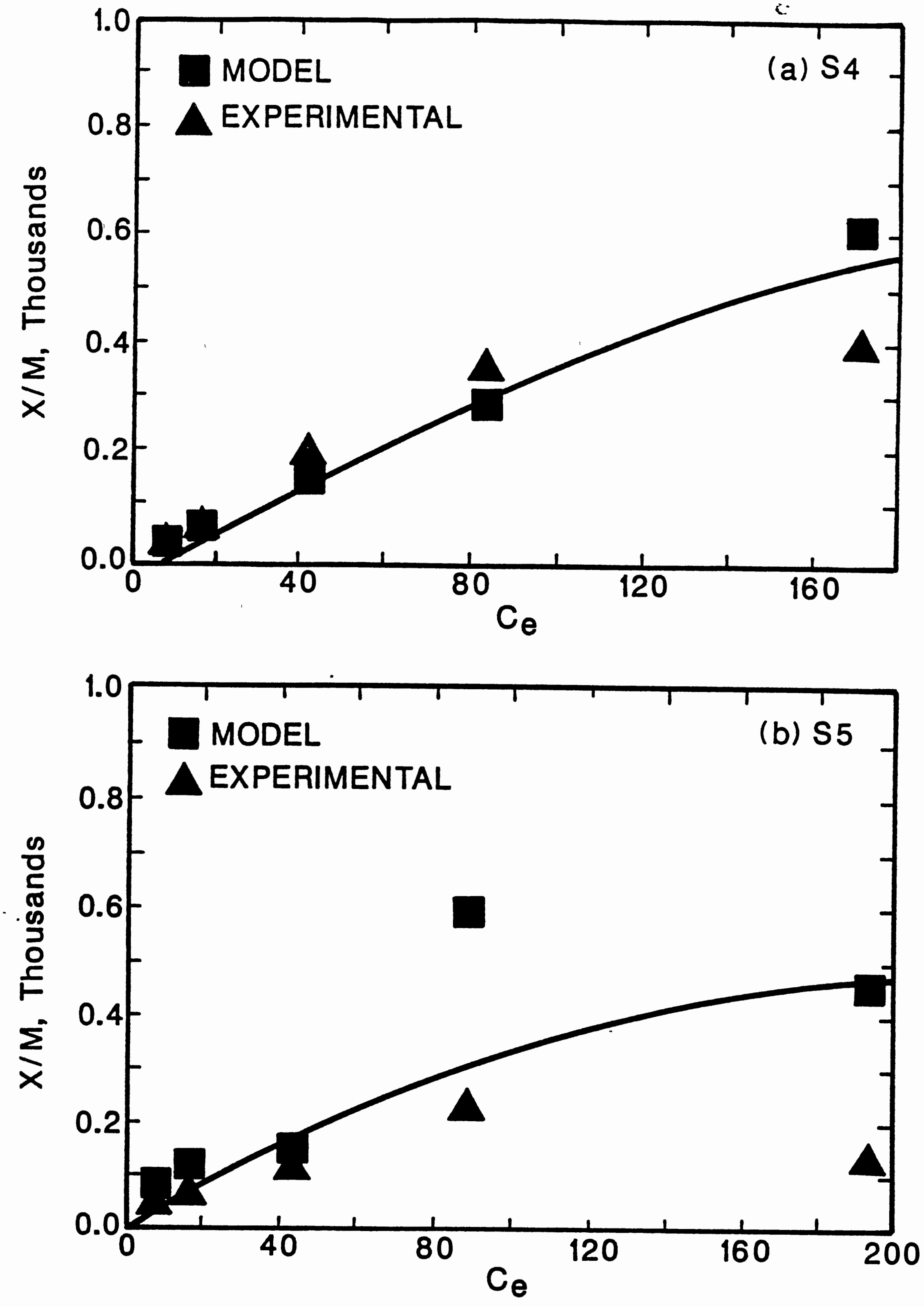


Figure 14. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Lindane present on (a) S4 and (b) S5 at 25°C

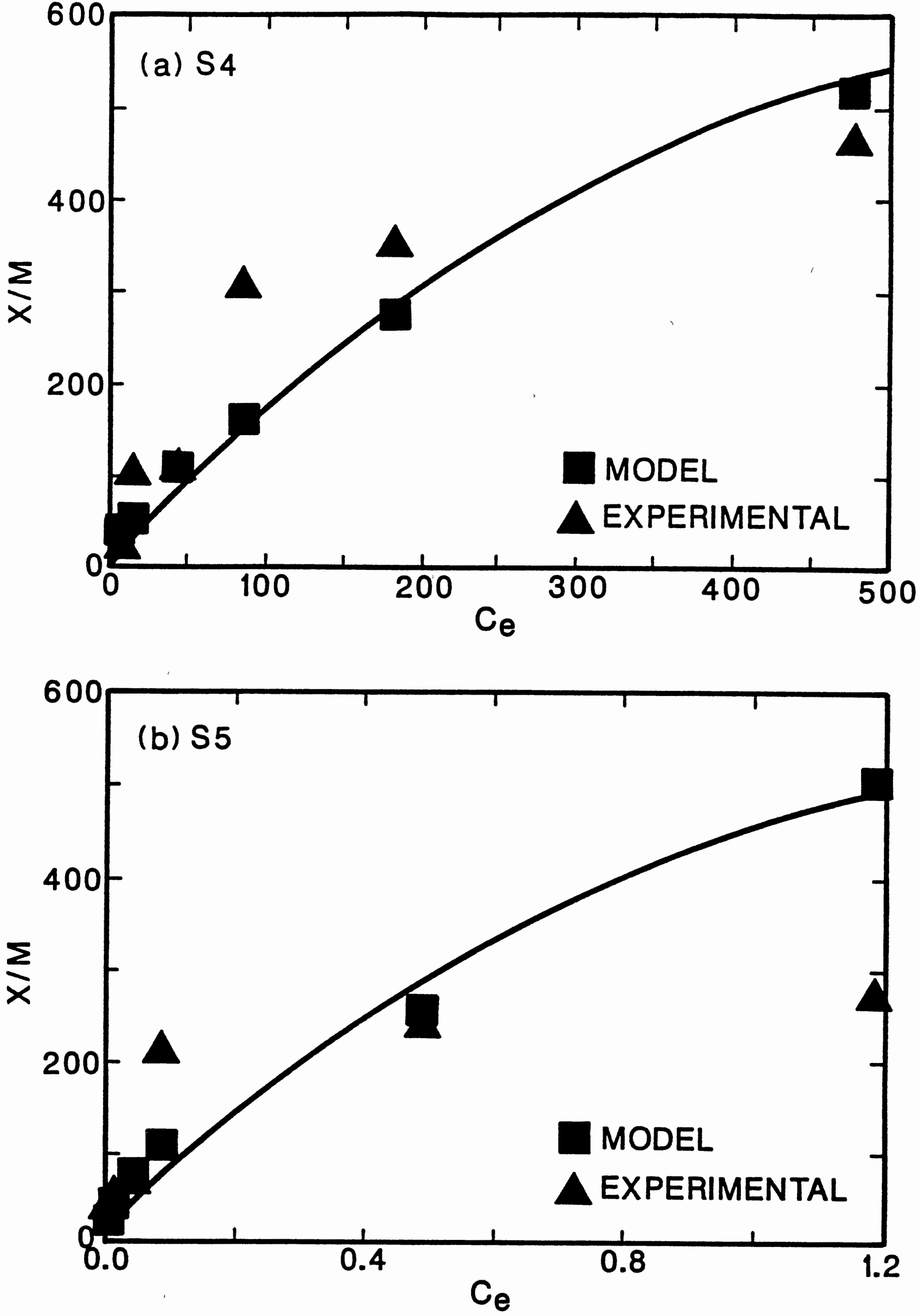


Figure 15. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Lindane present on (a) S4 and (b) S5 at 30°C

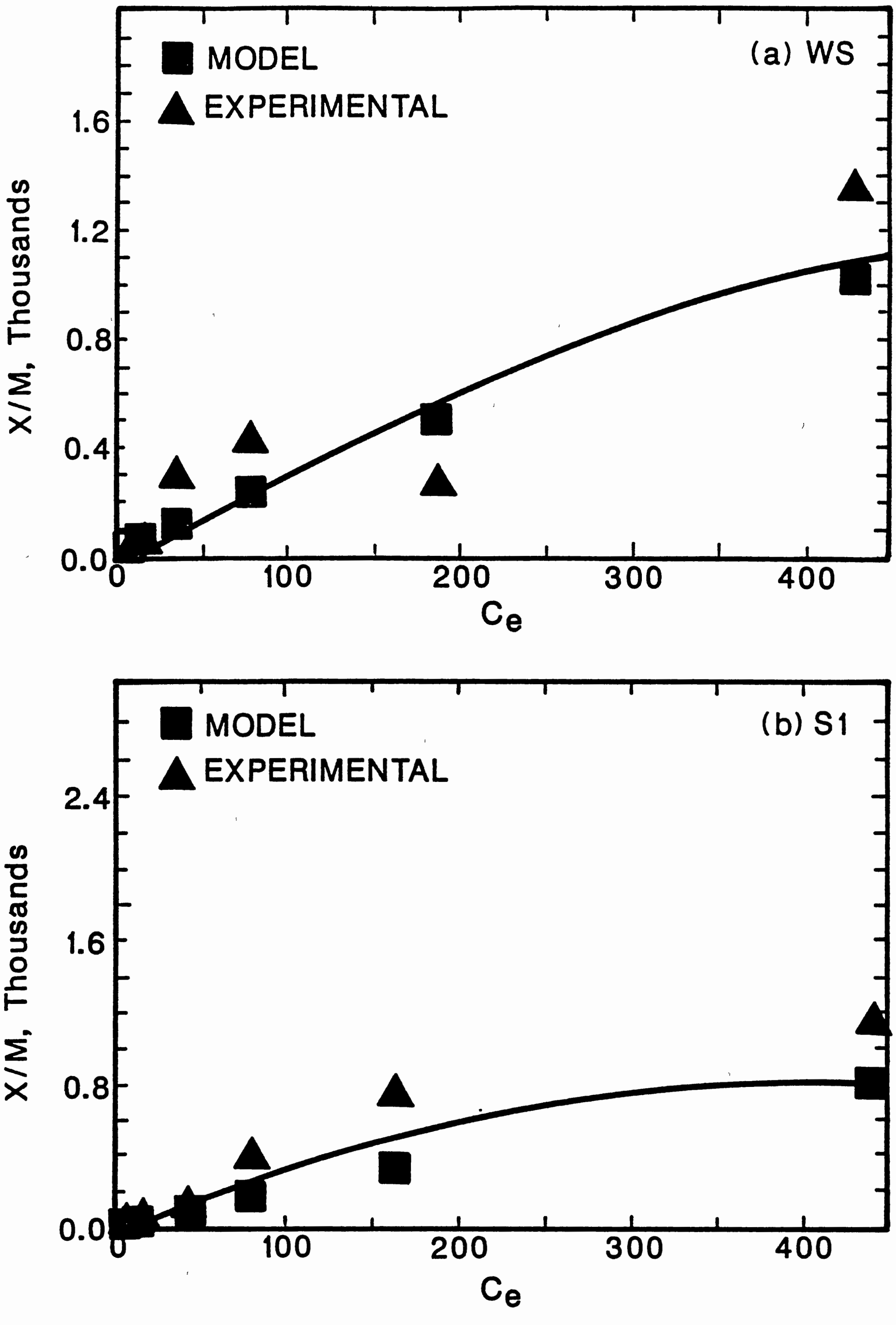


Figure 16. SRS Multiple Freundlich-Type Isotherms of Silvex with 2,4-D present on (a) S4 and (b) S5 at 30°C

solute concentration range.

Figures AII-46 through AII-54 in the appendix depicted 2,4-D with Silvex as the probable competitng adsorbate. It was noted, in the previous trials, that the SRS equation tended to underpredict the adsorption of the herbicides at the higher solute concentration ends. This observation continued in the 2,4-D with Silvex systems on soil fractions 2 to 5 and whole soil and soil fraction 1 at 30 and 35°C respectively as presented in figures 17-19.

The findings described thus far indicated that in general, all of the data conformed well to the SRS equation basically at the lower and intermediate concentration ranges. At higher concentrations, however, the SRS equation usually underpredicted the experimental data with some exception where it overpredicted. The SRS equation was relatively unstable in simulating adsorption at higher solute concentrations in that it was unable to examine adsorption mechanisms other than competition. Several researchers have attributed altered adsorption in multisolute systems to "lateral interactions" or to the formation of clusters or micelles [55,61-64]. These descriptions refer to energies of adsorption brought about by complex interactions between the solutes and between the adsorbent.

It possible to derive SRS based competitive coefficients on a concentration basis for each binary solute system [46-48]. These coefficients are convenient single

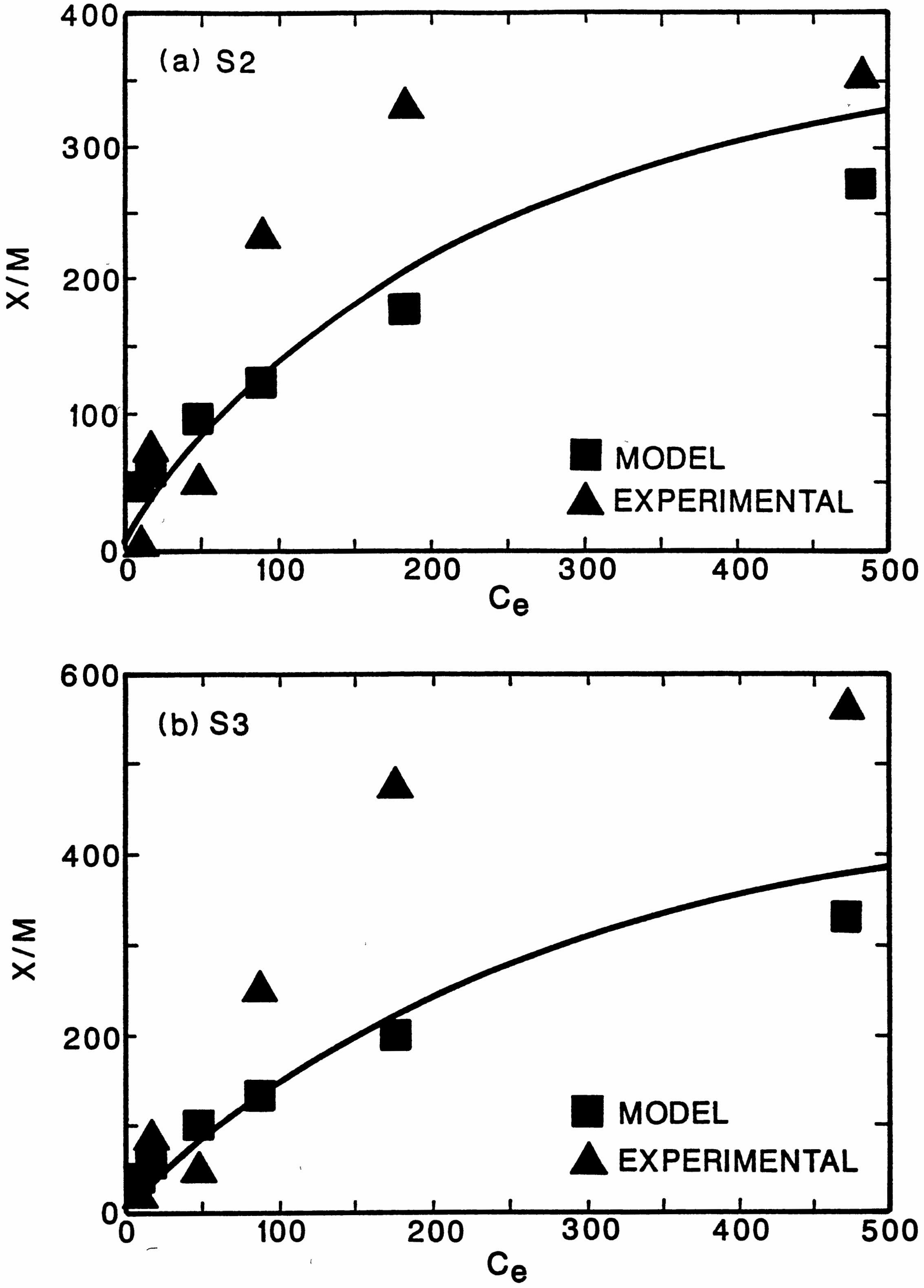


Figure 17. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Silvex present on (a) S2 and (b) S3 at 30°C

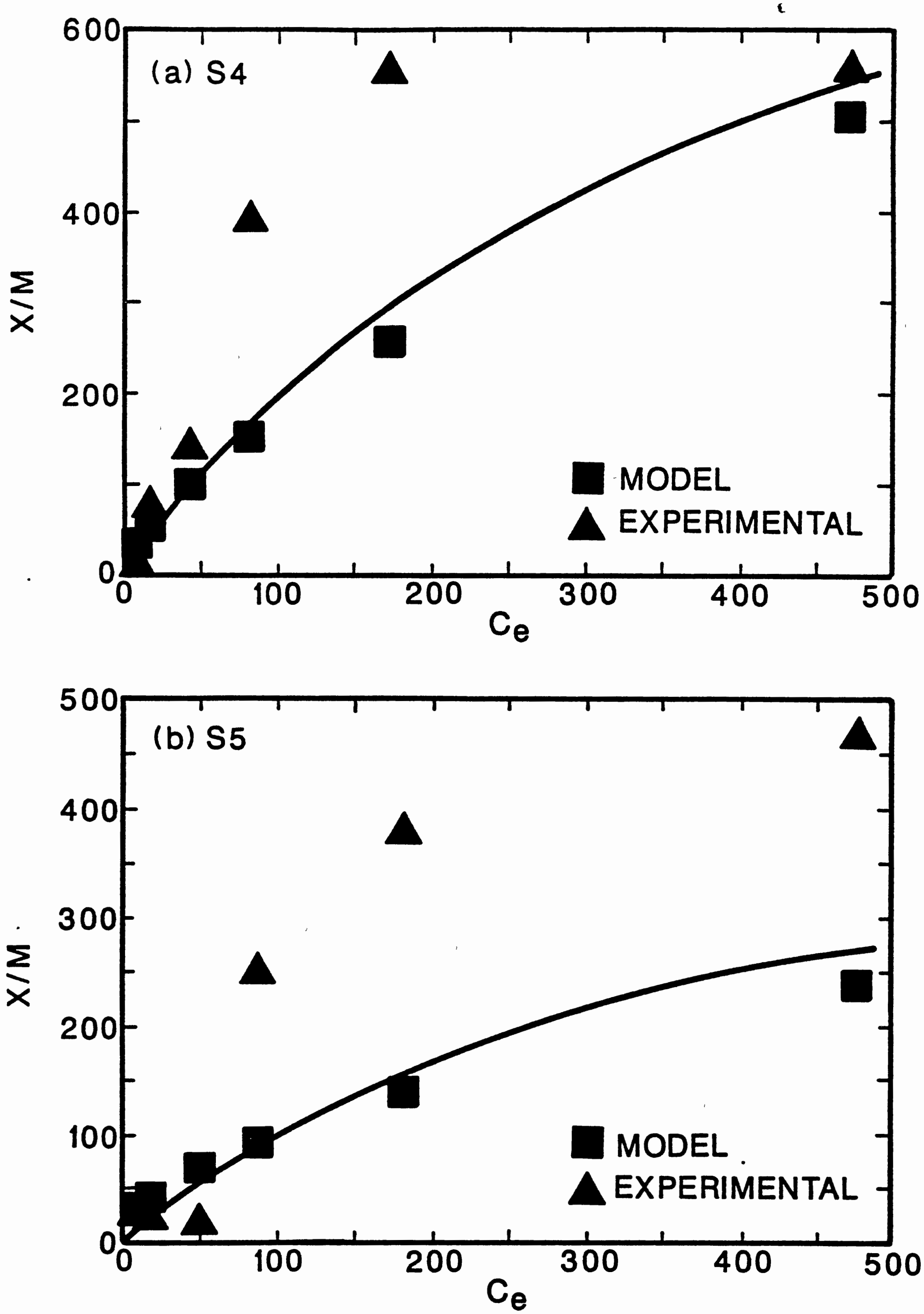


Figure 18 **. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Silvex present on (a) S4 and (b) S5 at 30°C**

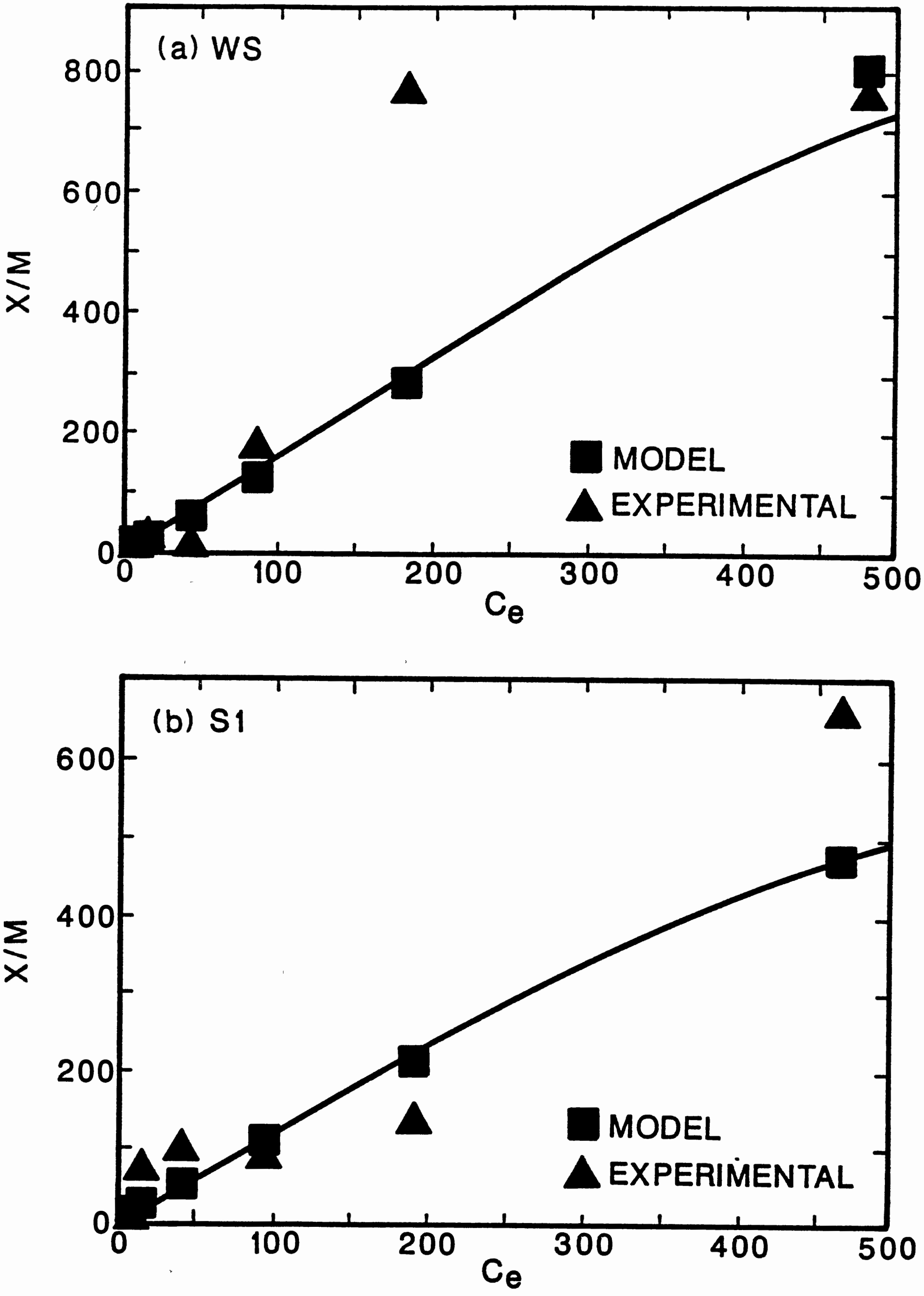


Figure 19. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Silvex present on (a) WS and (b) S1 at 35°C

value terms that can be used to describe the degree of competition in the specific systems under these experimental conditions. This competition includes the interactions among the solute, and between the solvent and the adsorbent and the solute and the adsorbent but does not consider synergistic or other energy effects according to the original SRS derivation. The competitive coefficient constant was defined as a positive-value term and range from zero (a complete lack of competition) to higher values (typically less than 10) corresponding to the degree of competition. A summary of competitive coefficients of lindane and Silvex obtained at various temperatures is given in Table XXVI. These data indicated that the competitive coefficients of lindane evaluated under various temperatures were generally smaller than those of Silvex. That is, the magnitude of lindane competition with Silvex for sites onto various soil fractions was higher than for Silvex. The competitive coefficients ranged from 0.932 to 1.428 for Silvex; whereas the values for lindane were lower, ranging from 0.4 to 0.867. This was in agreement with the qualitative observations previously made that adsorption of lindane was more profound than Silvex. The results were found to conform to the data shown in Tables XVII and XVIII.

Table XXVII presents the competitive adsorption coefficients for lindane and 2,4-D respectively, on various soil fractions. It can be observed that the competitive

TABLE XXVI

COMPETITIVE ADSORPTION COEFFICIENTS OF THE LINDANE AND SILVEX IN BINARY SOLUTE SYSTEMS ON VARIOUS SOIL FRACTIONS

	Competitive Coefficients		
	25° C	30° C	35° C
Silvex			
Whole soil	0.98	1.200	0.953
Fraction 1	1.10	1.428	1.030
Fraction 2	1.01	1.403	0.969
Fraction 3	1.10	1.332	1.040
Fraction 4	0.98	0.932	1.050
Fraction 5	1.10	1.111	1.070
lindane			
Whole soil	0.56	0.768	0.825
Fraction 1	0.40	0.504	0.799
Fraction 2	0.50	0.487	0.812
Fraction 3	0.41	0.844	0.789
Fraction 4	0.50	0.746	0.600
Fraction 5	0.83	0.867	0.801

TABLE XXVII

COMPETITIVE ADSORPTION COEFFICIENTS OF THE LINDANE AND 2,4-D IN BINARY SOLUTE SYSTEMS ON VARIOUS SOIL FRACTIONS

	Competitive Coefficients		
	25° C	30° C	35° C
<u>2,4-D</u>			
Whole soil	0.950	0.989	1.020
Fraction 1	1.482	1.180	0.980
Fraction 2	1.175	1.067	0.841
Fraction 3	1.897	1.270	0.814
Fraction 4	2.070	1.100	1.300
Fraction 5	0.930	0.911	0.970
<u>lindane</u>			
Whole soil	0.043	0.785	0.830
Fraction 1	0.506	0.788	0.818
Fraction 2	0.443	0.701	0.844
Fraction 3	0.360	0.720	0.641
Fraction 4	0.336	0.721	0.540
Fraction 5	0.545	0.740	0.999

TABLE XXVIII

COMPETITIVE ADSORPTION COEFFICIENTS OF THE 2,4-D AND SILVEX IN BINARY SOLUTE SYSTEMS ON VARIOUS SOIL FRACTIONS

	Competitive Coefficients		
	25° C	30° C	35° C
<u>Silvex</u>			
Whole soil	0.85	0.84	0.73
Fraction 1	0.87	0.90	0.76
Fraction 2	0.84	0.92	0.95
Fraction 3	0.94	0.98	0.96
Fraction 4	0.95	0.98	0.97
Fraction 5	0.90	0.91	0.95
<u>2,4-D</u>			
Whole soil	0.50	1.09	1.10
Fraction 1	0.74	1.00	1.15
Fraction 2	1.02	1.10	1.02
Fraction 3	1.03	0.99	1.06
Fraction 4	1.04	1.01	1.03
Fraction 5	1.06	1.02	0.98

coefficients for 2,4-D evaluated at various temperatures were consistently greater than those of lindane with the exception of soil fractions 2 and 5 at T = 35°C, which indicated higher values. As mentioned previously, larger values of competitive coefficients indicated more competition for adsorption sites. This means that more of the primary adsorbate would be adsorbed than would the secondary compound. In these trials, lindane was the primary adsorbate while 2,4-D would be the secondary compound.

In general, the magnitude of lindane competiting with 2,4-D adsorption on these soil fractions was lower than for 2,4-D competiting with lindane as indicated by these adsorption coefficients. Comparison of the competitive coefficients of lindane in Table XXVII to those presented in Table XXVI revealed that these values were generally lower when lindane competed for adsorption sites with 2,4-D than when Silvex was the competitng solute. Again, this was in agreement with the qualitative observations made in this study that adsorption of lindane was more profound in the the 2,4-D system than when Silvex was the secondary adsorbate. Higher removals of the pesticide would mean greater competition for the competiting adsorbate.

Table XXVIII shows the results of competitive coefficients for Silvex and 2,4-D, respectively, on the various soil fractions. These data indicated that the competitive coefficients of Silvex were generally smaller than the 2,4-D coefficients among the various soil fractions. Values range from 0.50 to 1.10 and 0.73 to 0.98 respectively, for 2,4-D and Silvex. The slight differences in the competitive coefficients for the two herbicides again indicated that they were possibly competing for the same sites with only a slightly higher preference of these sites for Silvex or that they were so soluble as to not compete.

In general, the competitve coefficients from the above tables indicated that though there was some competition between the various pesticides, the competition as indicated was minimal or negligible. Competition coefficients varied from 0.40 to 0.867 for lindane in the presence of Silvex and 0.043 to 0.999 for lindane in the presence of 2,4-D. 0.98 to 1.428 and 0.814 to 2.070 for Silvex with lindane and 2,4-D present respectively. These values suggest heterogeneous interactions between ions and adsorption sites: Silvex and 2,4-D did not compete for adsorption sites as much as lindane did on the various soil fractions. The predictive capability of these coefficients can reduce experimental effort and provide a more realistic representation of these pesticide adsorption in soils.

Isosteric Heats of Adsorption

The isosteric heats of adsorption were determined to evaluate the surface characteristics of the soil and soil fractions as they have been shown to yield information as to the homogeneity of the adsorptive surface. The isosteric heat of adsorption is the differential molar quantity which gives a measure of the heat adsorbed or released by the pesticides during the adsorption process. That is, this test serves as a surrogate for the solute-adsorbent energy components inherent in adsorption. These data were collected to address dynamic interactions between solutes and between the solutes and the adsorbent. Together with the physical and chemical measurements such as surface area, CEC and soil organic materials, the isosteric heats of adsorption more completely defined the adsorptive system.

The measurement was obtained by collecting adsorption data at various temperatures and applying the Clausius-Clapeyron equation to the system. The relationship is defined as [53,54]:

$$DH = R\ \text{Ln}\ (C_2/C_1)_{theta}/(1/T2-1/T_1) \qquad (7)$$

The isosteric heats of adsorption is also a potentially powerful method for determining the distribution of surface site energies between association species [38,39,55,].

The heats of adsorption at different temperatures were plotted in Figures AIII-79 through AIII-95 (refer to appendix) while a typical plot is presented in figure 20. The curve can be subdivided into 2 regions. In region 1, the adsorption obeys Henry's Law (i.e. only unassociated, first layer molecules are present) while region 2 was characterized by a rapid increase in adsorption. These 2 regions were defined by Scamehorn, Schechter and wade [60] and have been observed in other studies [61-63]. Still others have reported the rapid increase in adsorption at a

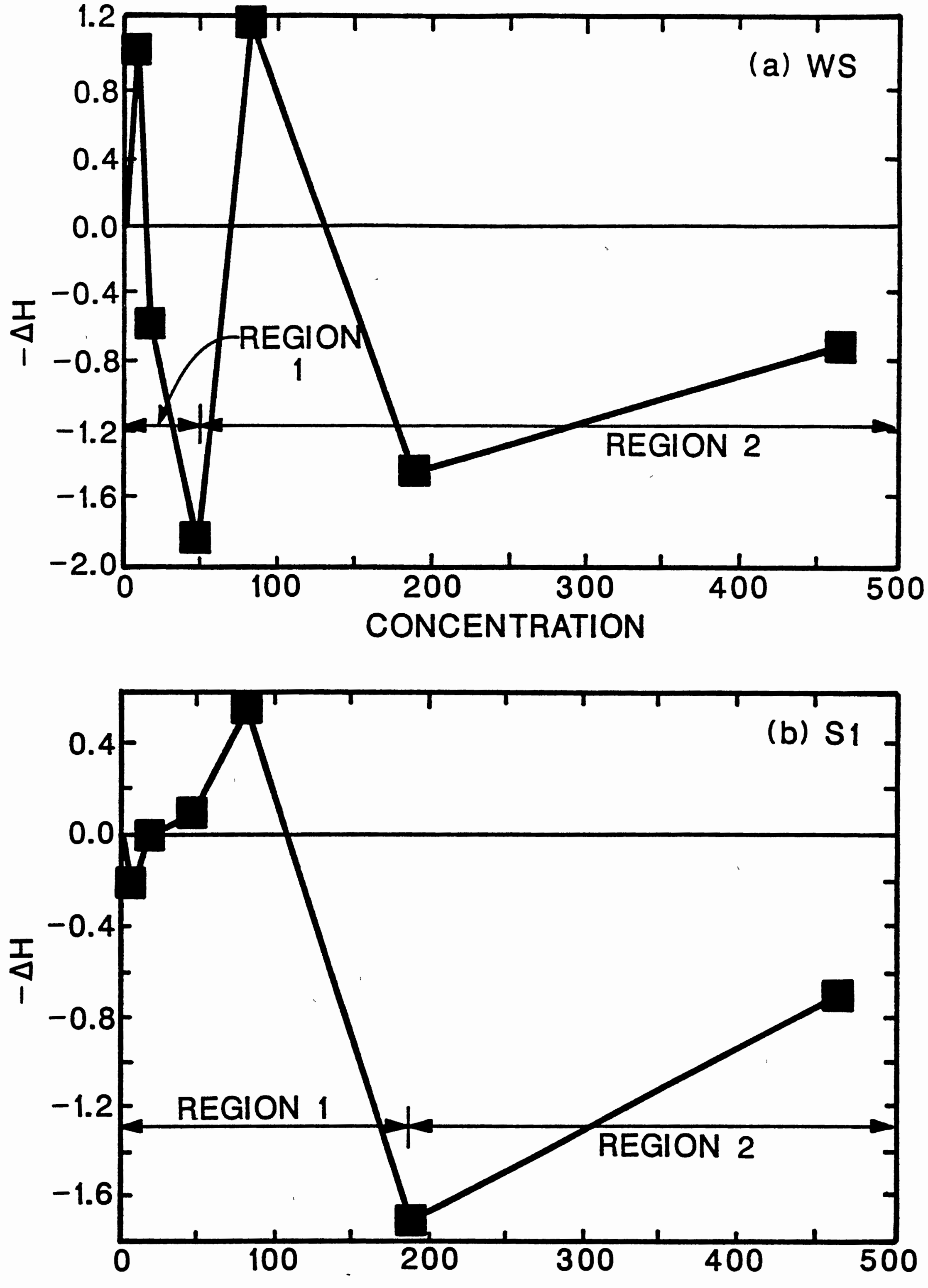


Figure 20. Isosteric Heats of Adsorption of Silvex with Lindane present on (a) WS, (b) S1

specific concentration, which is characteristic of the transition from region 1 to 2 [64-68].

The graphs represented by figure 21 showed that the heats of lindane adsorption with Silvex present for these soils were not constant. This indicates that the soil surfaces were heterogenous as to adsorption. This implies that the variations in the heats of adsorption were caused by increasing interactions between adsorbate molecules on the surface and in solution as the solute concentration increased. Such interactions were unlikely at low surface saturation since, the sorbed molecules located themselves at positions far removed from each other to maximized mutual repulsions. These apparent heats of adsorption suggested that the adsorbate first sorbs on the most energetic adsorption sites and then sorbs on sites with lower energies. That is, a gradual increase in the isosteric heat of adsorption at low surface coverage was followed by a leveling and descent, i.e. the enthalpies became less exothermic as X/M (surface coverage) increased. This state is denoted by "region 1" on the graph represented in figure 20 where lindane was absorbed onto soil fractions 1 and 2 respectively. The first important feature of these plots is the sharp increase in the heats of adsorption which was interpreted as corresponding to the initial rapid surface adsorption of lindane which precedes critical cluster/micelle formation. The second feature is the less dramatically decreasing slope which corresponds to the

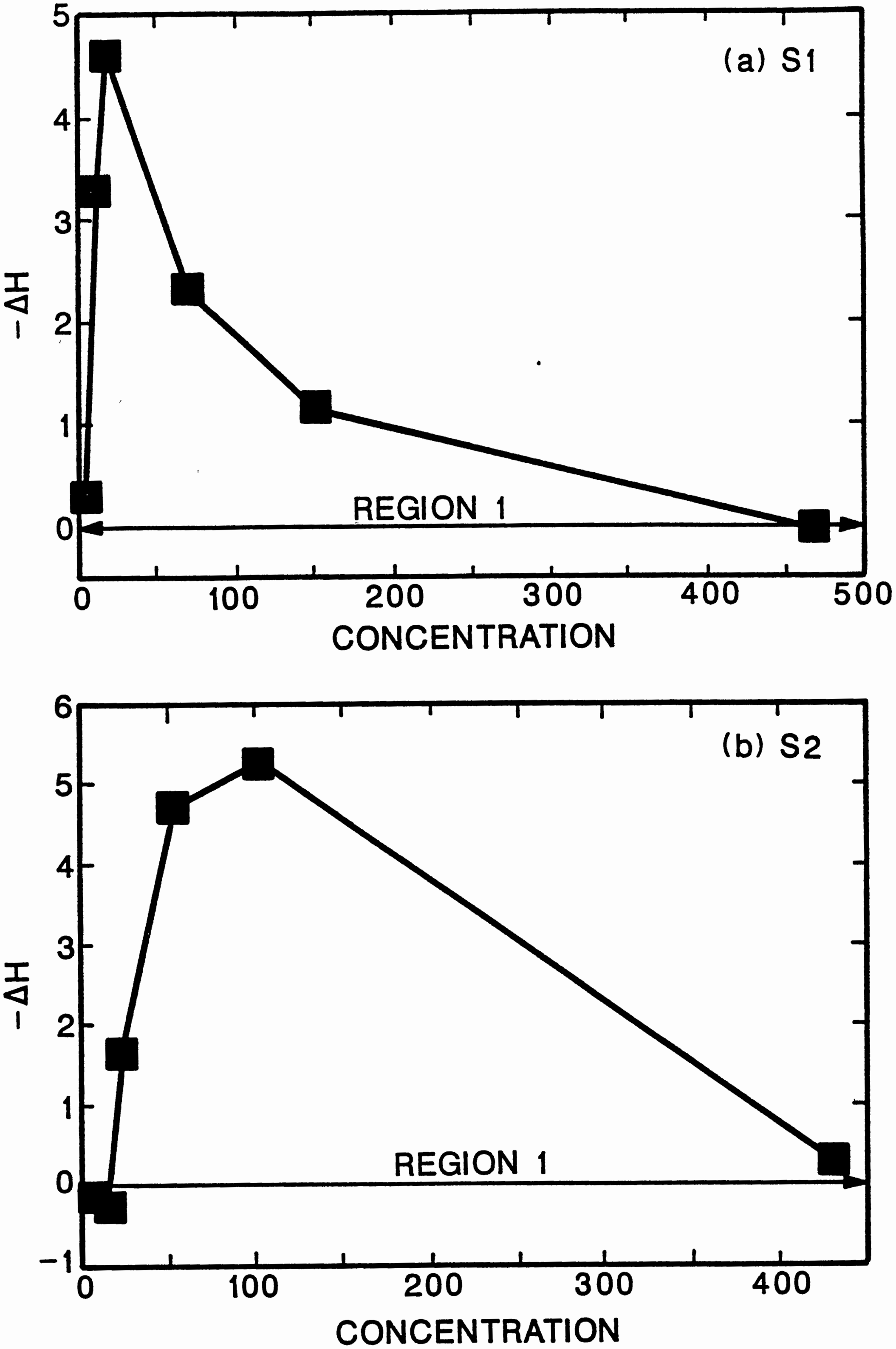


Figure 21. Isosteric Heats of Adsorption of Lindane with Silvex present on (a) S1, (b) S2

induction period associated with clusters formation. This is considered "typical" response and is presented in figure 21. The decreasing slope has, by analogy to gas adsorption, been misinterpreted to mean that all the adsorption sites are filled (i.e., all layers present are in close-packed state). While it is possible for this to happen, this generally does not occur for the soil studied here as indicated by region 2 shown in figure 20.

With increasing surface coverage, adsorbate molecules encountered fewer unoccupied adsorption sites and more adsorbed molecules. Adsorption onto lower energy sites possibly including multilayer adsorption then occured and the corresponding interaction energies were reduced. Multilayer adsorption is physically very reasonable. The existence of multilayer adsorption has been previously suggested by other workers, based on adsorption density data [55,69-70] where they observed a horizontal step in adsorption isotherm at about monolayer coverage, before adsorption increased to multilayer coverages. This step did not occurs in the isosteric heats of adsorption suggesting monolayer coverage at multiple heterogeneous adsorption sites.

The results given in the example figure 22 showed that during the adsorption of the Silvex with lindane as the probable competing adsorbate on whole soil and soil fraction 1, the value of the isosteric heats of adsorption decreased as expected, with increasing surfaces coverages, in region

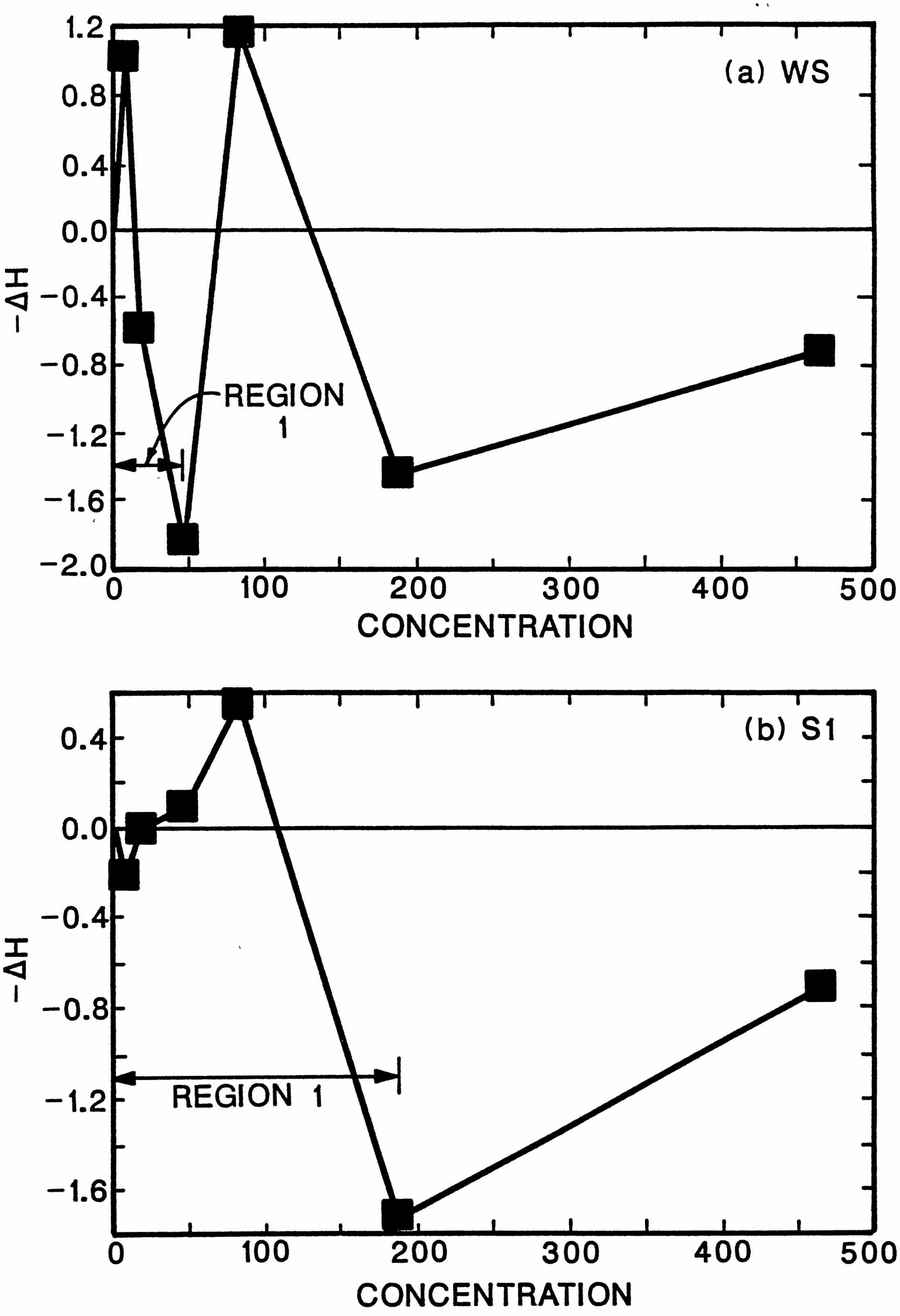


Figure 22. Isosteric Heats of Adsorption of Silvex with Lindane present on (a) WS, (b) S1

1. With the completion of adsorption in region 1, however, a discontinuity occured when the heats of adsorption suddenly increased. The reversal probably indicated the onset of synergistic adsorption where the increased energy required to orient the adsorbed molecules into surface clusters/micelles was achieved. It is common to liken adsorption from solution to that of gas phase transfer although there are several major differences between the two. There are large lateral attractions between adsorbed species, whereas species accessible to vapor adsorption studies must be of such low molecular weight that van der Waals lateral interactions are weak [55,63]. These lateral interations of the adsorbed species form clusters or micelles which serve as centers from which synergistic or increased adsorption occurs. The discontinuities in the isosteric heats of adsorption curves substantiated the hypothesis that synergistic adsorption did occur as the increased in energy measured paralleled increased adsorption.

The results given in these figures also showed that the isosteric heats of adsorption were highest with increasing coverages. This is represented by figure 23 where showed the isosteric heats of adsorption of lindane with Silvex as the competiting adsorbate on soil fractions 3 and 4 respectively are shown. The graphs indicated that the isosteric heats of adsorption were highest at the 50 and 100 ug/l concentration range respectively. It was assumed that the soil surfaces

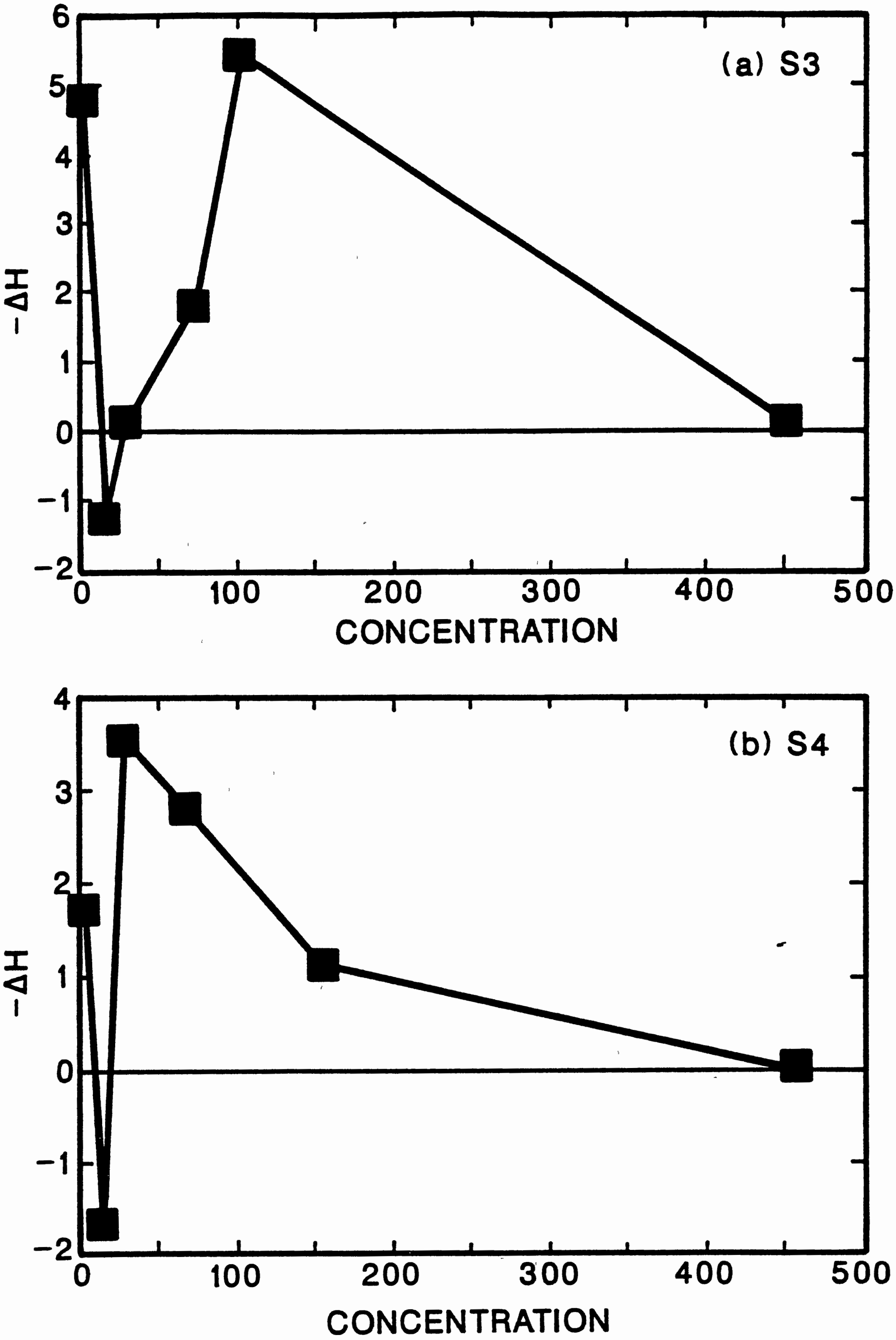


Figure 23. Isosteric Heats of Adsorption of Lindane with Silvex present on (a) S3, (b) S4

were composed of patches with different adsorption energies, with the adsorption energy of each site within a given patch being uniform. These homogeneous patches must be large enough so that boundary effects between them are neglible. Therefore at some concentration, the most energetic patches undergo a phase transition (i.e. formation of clusters), initiating the onset of region 2 as shown in the figure with the less energetic phase undergoing phase transition as well.

Some of the soil fractions evaluated, gave an almost constant heat of adsorption with increasing surface coverage. Figure 24 presents the isosteric heats of adsorption of 2,4-D with lindane presented as the competing adsorbate on soil fractions 4 & 5 respectively. The data presented in figure 24(b) gave an almost constant heat of adsorption of 2,4-D with lindane present on soil fraction 5, with increasing coverages but differed from figure 24(a) in that the heats of adsorption of 2,4-D on soil fraction 4 changed from endothermic to exothermic.

It would be rather anomalous for the isosteric heats of adsorption to have a positive surface free energy. This is probably due to lateral chemical interactions between the mixtures which adsorbed energies to form clusters and which then served as centers from which synergistic adsorption can occur. It is of interest to note that some of the figures evaluated (figures 25 and 26) did revealed anomalies suggesting that the overall process of adsorption of Silvex

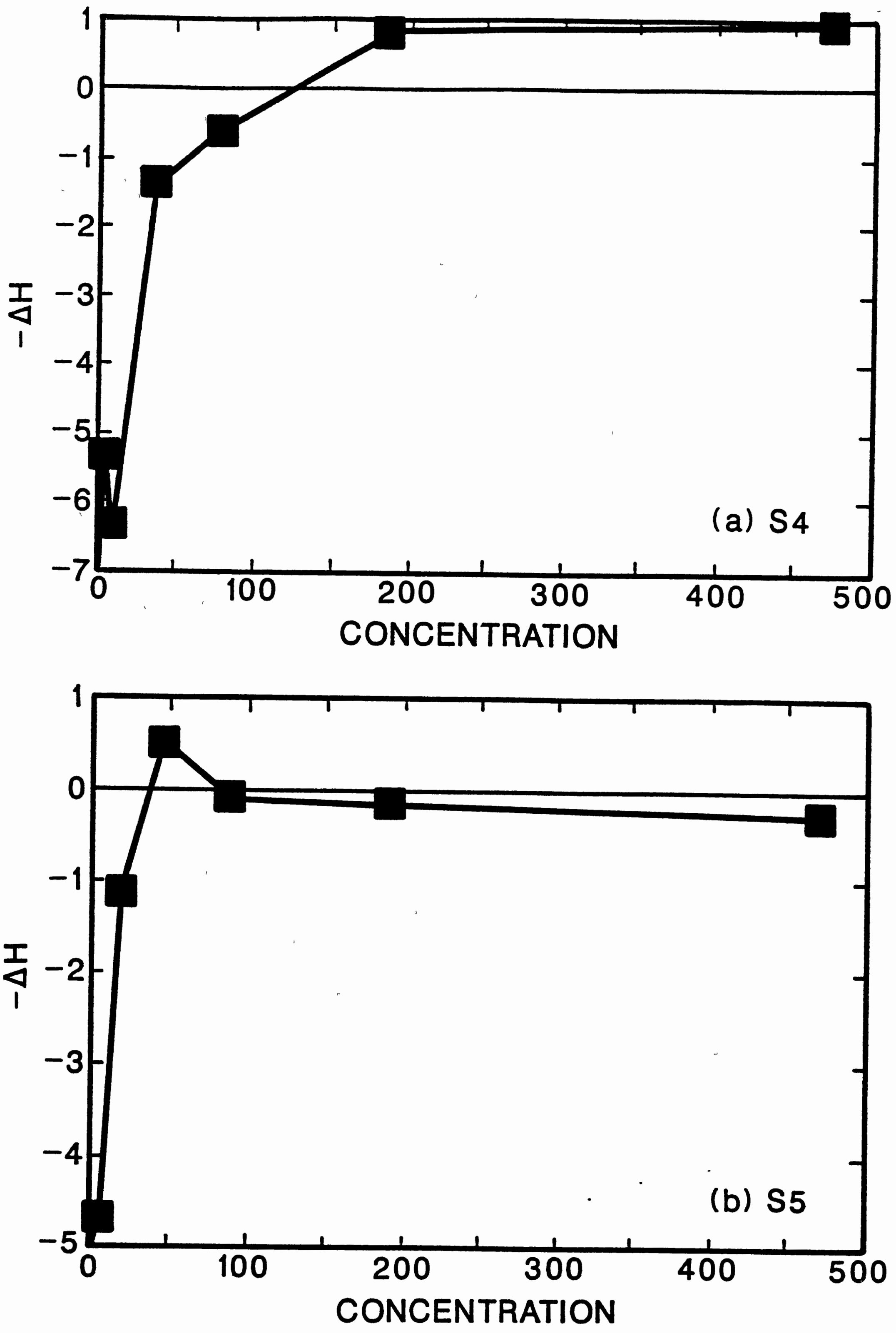


Figure 24. Isosteric Heats of Adsorption of 2,4-D with Lindane present on (a) S4, (b) S5

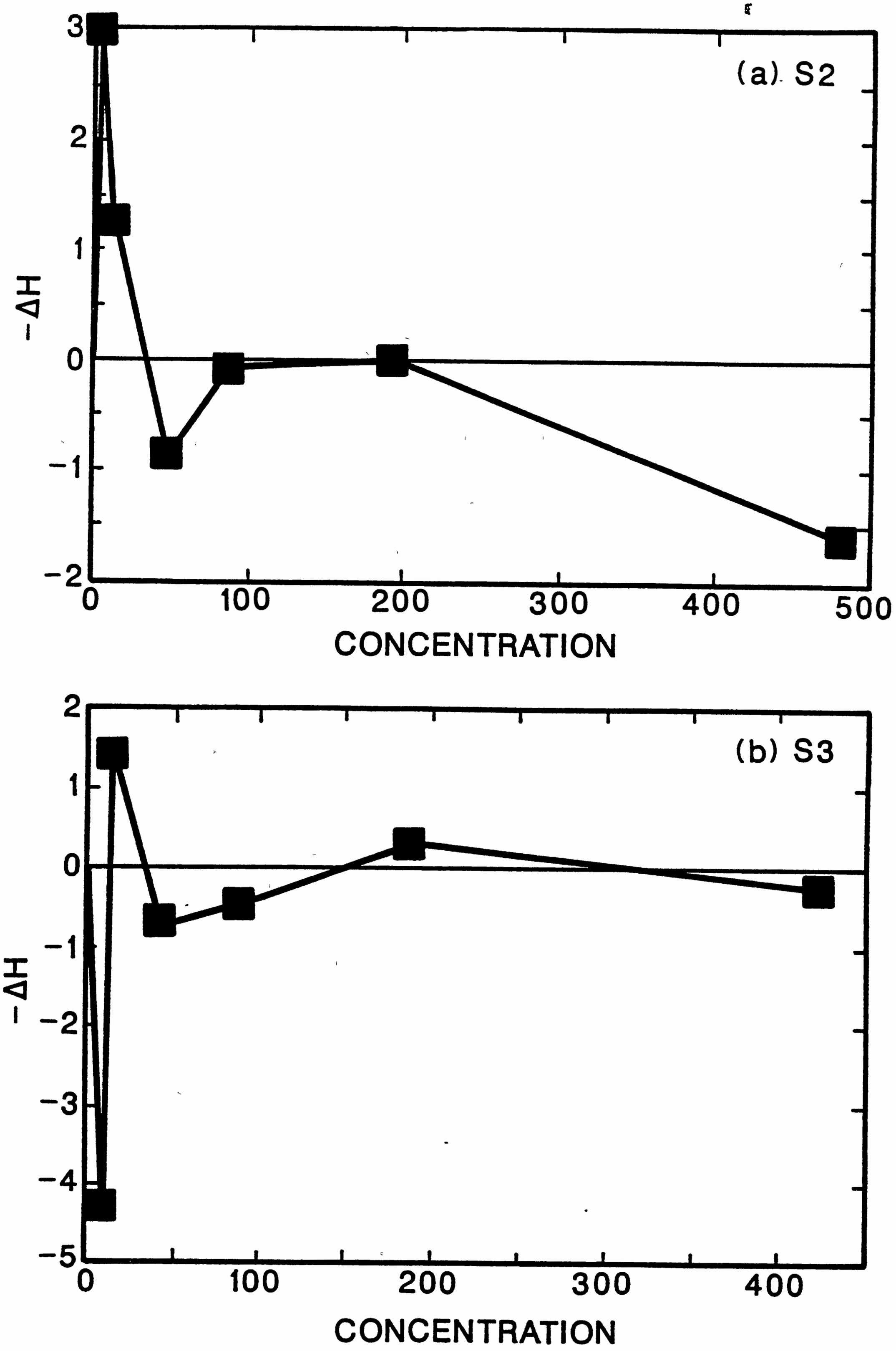


Figure 25. Isosteric Heats of Adsorption of Silvex with Lindane present on (a) S2, (b) S3

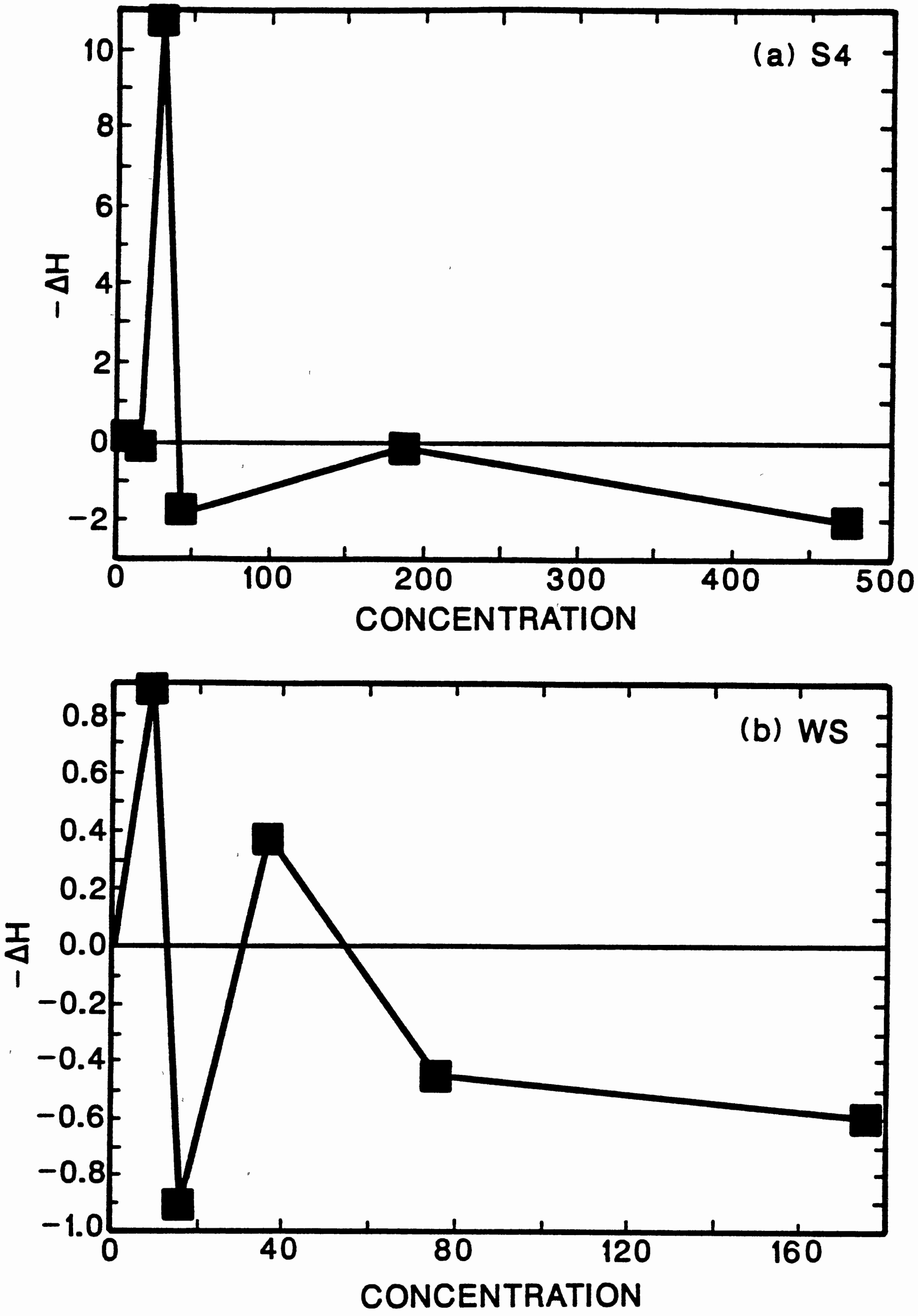


Figure 26. Isosteric Heats of Adsorption of Silvex with Lindane and with 2,4-D present on (a) S4, (b) WS respectively

with lindane present on soil fractions 3 and 4 respectively, changed from exothermic to endothermic at a certain coverage or concentration range. From the graphs in figures 25 and 26 respectively, it appears that the isosteric heats tend to be more positive at low surface coverage. In another system as depicted in figure 26, isosteric heats appeared to be negative at low coverage and positive at higher coverages. That is, at higher surface coverages, the amount of adsorption energy decreased more rapidly and even appeared to become slightly endothermic. This decreased energy paralleled directly a corresponding reduction in adsorption. This was especially true for the acidic herbicides, 2,4-D and Silvex and corroborates the low competitive adsorption coefficients previously discussed as well as explaining some of the inconsistencies found in the data themselves (refer to figures 25 and 26).

As a test of the hypothesis that synergistic adsorption did occur in the binary systems, it was instructive to compare the SRS plots with that of the isosteric heats of adsorption. A comparison of the isosteric heats of adsorption was made to that of the data obtained by the SRS equation in the preceding section. The results represented graphically in the figure 27 included also the data from the SRS relation for Silvex with 2,4-D present on soil fraction 1. The data presented in the preceding section with the SRS figures indicated that conformance of the adsorbate data occurred only at the lower solute concentration ranges. The

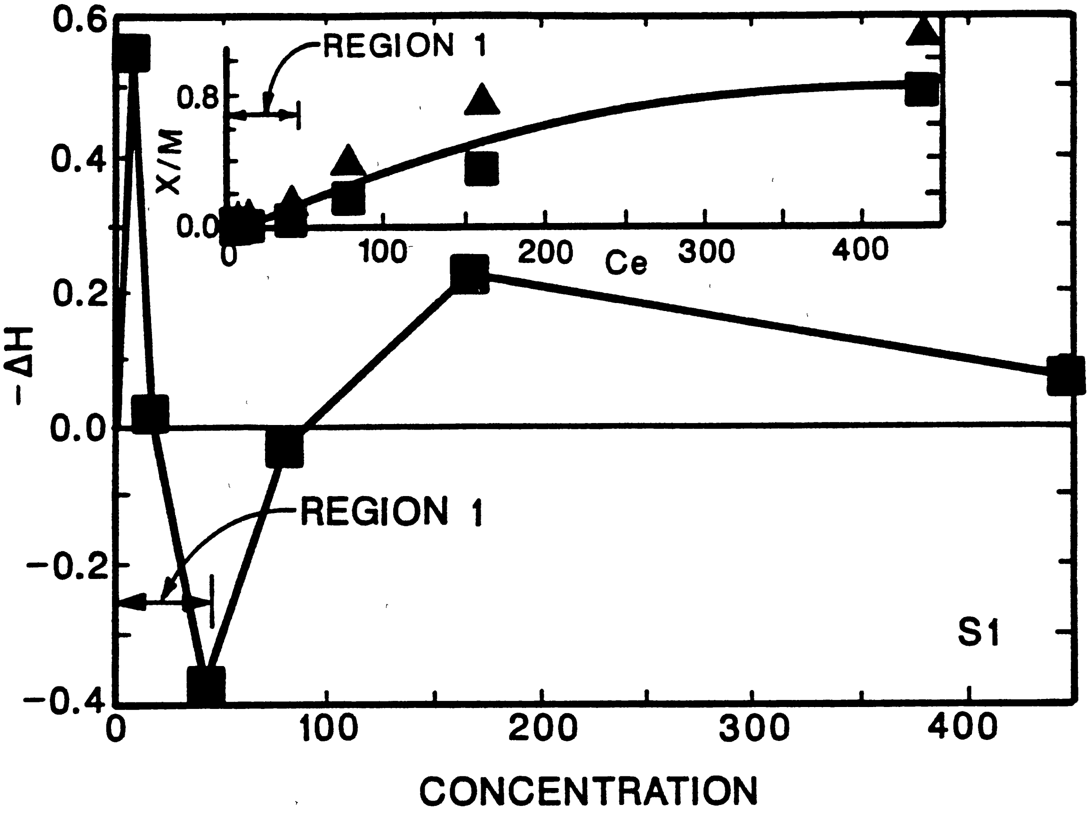


Figure 27. Comparison of the Isosteric Heats of Adsorption plots with the SRS Multiple Freundlich-Type Isotherm of Silvex with 2,4-D present on S1

comparison suggested that there was a relationship between the apparent heats of adsorption within region 1 and that of the SRS data at the lower solute concentrations since at the lower solute concentration ranges, the adsorbate first sorbed at the highest energy sites and was evident of "pure adsorption", i.e adsorption obeys Henry's law. The relationship between SRS equation and the isosteric heats of adsorption may be represented by region 1.

To obtain further evidence of the nature of synergistic adsorption, better agreement between the "discontinuity" region in the isosteric heats of adsorption and that of the SRS data at the higher solute ends was also obtained. The comparisons indicated that beyond the discontinuity region, the adsorbate data did not conform to the SRS equation at this region. The SRS equation generally underpredicted the experimental data in this region. The behaviour is apparently related to the increased energy required for the molecules to orient themselves into surface clusters. As described earlier, the discontinuity was interpreted as signifying the increased energy required to orient the adsorbed molecules into surface clusters which served as centers for synergistic adsorption to occur and which SRS equation probably could not address.

Further comparisons were made between the SRS equation and the isosteric heats of adsorption with that of the equilibrium uptake data in the binary systems. This is presented in figure 28. Figure 28 showed the comparison of

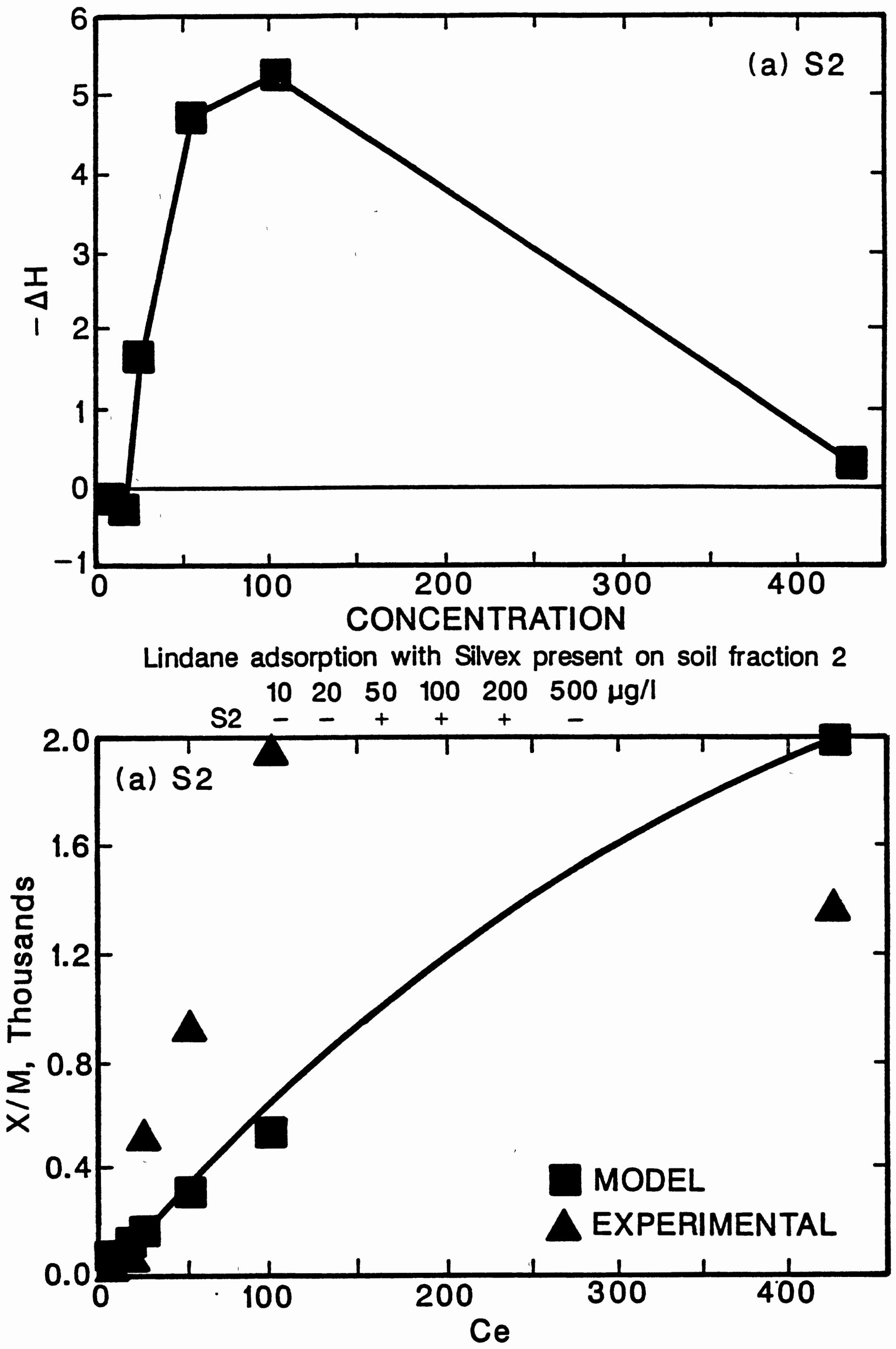


Figure 28. Comparison of the SRS Multiple Freundlich-Type Isotherm and the Isosteric Heats of Adsorption plots of Lindane with Silvex present on S2 to the equilibrium data

the SRS and the isosteric heats of lindane with Silvex present on soil fraction 2 with that of the equilibrium data. The equilibrim uptake data were denoted by pluses (+) and minuses (-) sign. The plus sign would indicate those data that were greater than that of the single solute system (i.e synergistic adsorption) while the negative sign represents equilibrium uptake data that were smaller than the lindane alone systems, which could be either competition or sites saturation. From the figure, it was noted that the isosteric heats of adsorption consistently corresponds to that of the equilibrium uptake data with every increase in the isosteric heats in the plots corresponding to the plus sign. This behaviour is apparently related to the increased energy required for the molecules to orient themselves into surface clusters. As described earlier, the increase in the isosteric heats of adsorption was interpreted as signifying the increased energy required to orient the adsorbed molecules into surface clusters which served as centers for synergistic adsorption to occur. The minus sign similarly, indicates a decrease in the isosteric heats of adsorption.

The SRS equation, on the other hand, conformed only to the negative sign of the data. This is because the SRS is predicated on the premise that "pure" adsorption occurred and that the SRS equation was unable to consider synergistic or other energy effects. Again this substantiated the hypothesis that synergistic adsorption did occur as revealed by the data in the isosteric heats of adsorption.

Polanyi Theory

The Polanyi adsorption potential theory is defined as the work done by adsorptive forces in bringing a molecule from the bulk solution phase to a point near the adsorbent surface where it may subsequently precipitate or coalesce [34,35,36]. The theory, originally widely applied to gas phase adsorption and subsequently to liquid-phase adsorption onto activated carbon [34,35,], has recently been used to aid in the prediction of adsorption of vapor phase organic contaminants onto soil [36].

This work evaluated the effectiveness of applying the theory for adsorption onto various soil fractions previously discussed. The decisive factor in determining if Polanyi theory was applicable to the various soil fractions, was the evaluation of whether the theory could predict the adsorptive capacity of the individual pesticides within the binary systems evaluated. These applications of the Polanyi model to multiple soils were intended to supplement the previously presented competitive adsorption model which frequently was inadequate in describing adsorption at higher solute levels. The fundamental property of concern within the Polanyi model was its basis in having sufficient concentration present to enable precipitation on the solid surface. This was considered equivalent to the "clusters" or micelles identified in the isosterics heats of adsorption phase of this research and was intended to address an alternative mechanism of mass transfer.

TABLE XXIX

COMPARISON OF UPTAKE CAPACITY OF POLANYI ADSORPTION THEORY TO EXPERIMENTAL DATA IN LINDANE-SILVEX SYSTEMS WHERE %ERROR ((EXPT - POLANYI)/EXPT) * 100

Lindane	Whole Soil			Soil 3			
	Polanyi	Expt.	%Error		Polanyi	Expt.	%Error
10 ug/l	257.33	398.10	35.3	10 ug/l	159.23	138.72	14.79
20 ug/l	333.80	416.86	19.9	20 ug/l	320.66	78.40	309.0
50 ug/l	415.88	630.95	34.0	50 ug/l	415.88	411.20	1.140
100 ug/l	645.74	501.18	28.8	100 ug/l	608.13	949.60	35.96
200 ug/l	685.67	660.69	3.78	200 ug/l	706.55	965.60	1.130
500 ug/l	1043.56	354.80	194.1	500 ug/l	934.86	900.00	3.870
Soil 1				Soil 4			
10 ug/l	167.40	99.88	67.6	10 ug/l	151.47	121.00	24.18
20 ug/l	252.24	168.80	49.4	20 ug/l	287.26	154.00	86.50
50 ug/l	323.88	618.60	47.6	50 ug/l	395.59	445.80	11.26
100 ug/l	608.13	612.60	0.73	100 ug/l	614.24	671.60	8.540
200 ug/l	898.20	960.00	6.44	200 ug/l	934.86	900.00	3.870
500 ug/l	155.81	611.40	74.5	500 ug/l	632.95	760.00	16.72
Soil 2				Soil 5			
10 ug/l	228.24	41.20	453.9	10 ug/l	90.95	94.40	3.650
20 ug/l	311.18	52.80	489.3	20 ug/l	144.08	93.00	54.92
50 ug/l	357.95	509.00	29.60	50 ug/l	210.69	265.20	20.55
100 ug/l	488.04	924.00	14.71	100 ug/l	290.15	448.20	35.26
200 ug/l	632.95	1956.6	67.60	200 ug/l	399.57	780.80	48.82
500 ug/l	1119.23	1360.0	17.70	500 ug/l	632.95	760.00	16.72

Silvex	Whole Soil			Soil 3			
	Polanyi	Expt.	%Error		Polanyi	Expt.	%Error
10 ug/l	90.73	48.40	87.40	10 ug/l	60.21	18.40	227.2
20 ug/l	121.20	53.60	126.12	20 ug/l	74.28	114.00	34.84
50 ug/l	172.00	74.00	132.43	50 ug/l	120.05	172.00	30.20
100 ug/l	212.29	332.0	36.00	100 ug/l	168.67	264.00	36.11
200 ug/l	283.71	232.0	22.20	200 ug/l	239.35	272.00	12.00
500 ug/l	394.63	694.0	43.10	500 ug/l	346.28	1513.4	77.11
Soil 1				Soil 4			
10 ug/l	38.39	52.80	27.29	10 ug/l	43.70	70.00	227.3
20 ug/l	62.05	35.80	73.30	20 ug/l	63.30	28.00	126.0
50 ug/l	101.28	73.40	37.98	50 ug/l	99.281	24.80	20.45
100 ug/l	140.88	273.40	80.31	100 ug/l	139.48	138.60	0.630
200 ug/l	190.17	966.00	48.47	200 ug/l	216.58	256.00	15.40
500 ug/l	329.23	694.00	52.56	500 ug/l	353.52	496.00	28.73
Soil 2				Soil 5			
10 ug/l	48.81	41.20	18.47	10 ug/l	26.52	17.00	56.00
20 ug/l	69.96	55.80	25.38	20 ug/l	36.89	24.00	53.71
50 ug/l	123.71	153.60	19.46	50 ug/l	53.40	174.00	69.31
100 ug/l	160.44	146.00	9.890	100 ug/l	77.32	174.00	55.56
200 ug/l	227.00	274.00	17.10	200 ug/l	110.82	106.00	4.550
500 ug/l	336.28	348.00	3.370	500 ug/l	170.36	148.00	15.11

TABLE XXX

COMPARISON OF UPTAKE CAPACITY OF POLANYI ADSORPTION THEORY TO EXPERIMENTAL DATA IN LINDANE-2,4-D SYSTEMS WHERE %ERROR EQUALS ((EXPT.-POLANYI)/EXPT) * 100

Lindane	Whole Soil			Soil 1			
	Polanyi	Expt.	%Error		Polanyi	Expt.	%Error
10 ug/l	270.53	144.40	87.35	10 ug/l	483.18	132.40	264.94
20 ug/l	347.37	225.60	53.98	20 ug/l	550.26	299.20	83.91
50 ug/l	450.51	420.60	7.11	50 ug/l	829.14	614.80	34.86
100 ug/l	539.36	679.00	20.57	100 ug/l	1108.9	1011.2	9.66
200 ug/l	672.09	338.20	98.73	200 ug/l	1408.6	1811.0	22.22
500 ug/l	812.72	1021.0	77.53	500 ug/l	2059.0	2554.0	19.38
Soil 1				Soil 4			
10 ug/l	399.57	98.40	306.07	10 ug/l	361.54	145.80	147.97
20 ug/l	455.04	231.20	96.82	20 ug/l	420.06	290.00	44.85
50 ug/l	572.72	605.00	5.34	50 ug/l	572.72	529.00	8.26
100 ug/l	706.55	1145.4	38.31	100 ug/l	678.84	950.00	76.72
200 ug/l	1022.9	618.40	65.42	200 ug/l	889.26	385.00	130.98
500 ug/l	706.50	618.40	14.25	500 ug/l	1075.0	950.00	13.16
Soil 2				Soil 5			
10 ug/l	376.30	99.80	277.05	10 ug/l	252.24	106.80	136.18
20 ug/l	450.51	136.00	231.26	20 ug/l	293.06	187.40	56.38
50 ug/l	534.00	339.80	57.15	50 ug/l	333.75	574.40	41.90
100 ug/l	620.42	545.80	13.67	100 ug/l	432.85	811.80	46.68
200 ug/l	713.65	771.60	7.51	200 ug/l	483.18	526.40	8.21
500 ug/l	713.00	771.60	7.59	500 ug/l	590.00	526.40	12.08
2,4-D							
	Polanyi	Expt.	%Error		Polanyi	Expt.	%Error
10 ug/l	64.79	36.80	76.06	10 ug/l	63.50	25.40	150.00
20 ug/l	79.93	54.80	45.86	20 ug/l	82.36	55.40	49.10
50 ug/l	102.63	105.60	2.810	50 ug/l	114.56	195.00	0.870
100 ug/l	125.30	174.00	27.99	100 ug/l	150.07	348.40	56.93
200 ug/l	151.58	255.80	40.74	200 ug/l	202.58	394.00	48.58
500 ug/l	196.50	36.00	54.93	500 ug/l	293.28	530.00	44.66
Soil 1				Soil 4			
10 ug/l	58.62	43.401	2.03	10 ug/l	91.05	23.60	285.81
20 ug/l	76.79	50.00	50.53	20 ug/l	108.97	53.20	104.83
50 ug/l	103.66	136.00	23.78	50 ug/l	138.53	155.0	11.89
100 ug/l	131.78	196.00	32.77	100 ug/l	165.86	324.80	48.93
200 ug/l	167.52	376.00	55.45	200 ug/l	200.56	576.00	65.18
500 ug/l	233.00	314.00	25.80	500 ug/l	257.53	1332.0	80.67
Soil 2				Soil 5			
10 ug/l	63.50	76.00	16.45	10 ug/l	67.43	44.40	51.87
20 ug/l	115.71	54.00	114.2	20 ug/l	79.93	65.40	22.22
50 ug/l	141.33	196.00	27.89	50 ug/l	100.59	113.00	10.98
100 ug/l	167.52	348.00	51.86	100 ug/l	118.05	227.40	48.09
200 ug/l	200.56	386.00	48.04	200 ug/l	139.93	130.00	7.640
500 ug/l	293.28	530.00	44.66	500 ug/l	139.90	130.00	7.620

TABLE XXXI

COMPARISON OF UPTAKE CAPACITY OF POLANYI ADSORPTION THEORY TO EXPERIMENTAL DATA IN 2,4-D-SILVEX SYSTEMS WHERE %ERROR EQUALS ((EXPT - POLANYI)/EXPT)*100

2,4-D	Whole Soil			Soil 1			
	Polanyi	Expt.	%Error		Polanyi	Expt.	%Error
10 ug/l	28.53	56.00	49.00	10 ug/l	237.70	44.00	440.23
20 ug/l	35.55	26.00	36.70	20 ug/l	344.17	37.60	815.35
50 ug/l	48.96	49.20	0.400	50 ug/l	556.21	172.60	222.50
100 ug/l	62.24	63.80	2.450	100 ug/l	889.93	150.00	493.29
200 ug/l	79.13	130.00	39.10	200 ug/l	1301.3	450.00	189.18
500 ug/l	106.82	606.00	82.30	500 ug/l	2218.0	734.00	202.18
Soil 1				Soil 4			
10 ug/l	19.51	5.60	248.3	10 ug/l	43.43	112.00	61.22
20 ug/l	27.41	57.00	51.91	20 ug/l	53.50	82.40	35.07
50 ug/l	48.48	104.80	53.74	50 ug/l	81.54	123.00	33.71
100 ug/l	74.52	128.00	41.78	100 ug/l	108.97	226.00	50.46
200 ug/l	111.18	346.00	67.87	200 ug/l	144.19	507.40	71.58
500 ug/l	196.59	436.00	54.91	500 ug/l	251.11	622.00	59.63
Soil 2				Soil 5			
10 ug/l	25.30	13.40	88.81	10 ug/l	16.70	5.60	198.2
20 ug/l	33.15	79.00	58.04	20 ug/l	23.59	33.00	28.52
50 ug/l	55.76	92.40	39.65	50 ug/l	39.69	36.00	10.25
100 ug/l	81.54	94.00	13.83	100 ug/l	56.32	168.00	66.48
200 ug/l	114.56	196.00	41.55	200 ug/l	83.19	250.00	66.72
500 ug/l	179.67	650.00	72.36	500 ug/l	138.0	260.00	46.92
Silvex							
	Polanyi	Expt.	%Error		Polanyi	Expt.	%Error
10 ug/l	85.45	31.60	53.85	10 ug/l	162.05	33.80	379.4
20 ug/l	105.42	56.00	88.25	20 ug/l	222.60	35.00	122.8
50 ug/l	130.05	292.00	161.9	50 ug/l	335.40	175.00	47.31
100 ug/l	165.33	425.00	61.10	100 ug/l	490.40	250.00	2.040
200 ug/l	212.29	260.00	18.35	200 ug/l	675.40	705.00	7.480
500 ug/l	272.58	1380.0	30.43	500 ug/l	670.00	564.00	0.660
Soil 1				Soil 4			
10 ug/l	128.76	27.40	369.9	10 ug/l	92.56	33.40	177.1
20 ug/l	182.72	61.80	195.5	20 ug/l	201.93	90.60	122.8
50 ug/l	295.29	124.00	138.1	50 ug/l	283.71	192.60	47.31
100 ug/l	402.60	394.00	2.180	100 ug/l	364.29	357.00	2.040
200 ug/l	577.06	730.00	20.95	200 ug/l	477.21	444.00	7.480
500 ug/l	960.00	1140.0	15.79	500 ug/l	606.00	610.00	0.660
Soil 2				Soil 5			
10 ug/l	122.00	47.40	157.3	10 ug/l	67.43	44.40	51.87
20 ug/l	179.10	25.80	594.1	20 ug/l	130.05	33.40	289.3
50 ug/l	261.89	106.00	147.0	50 ug/l	201.93	52.40	285.3
100 ug/l	343.07	316.00	8.540	100 ug/l	272.58	610.00	55.31
200 ug/l	444.95	946.00	52.97	200 ug/l	371.65	350.00	6.190
500 ug/l	711.00	830.00	14.34	500 ug/l	139.90	130.00	7.620

The adsorptive capacity obtained with the Polanyi adsorption potential theory was compared to the experimental adsorption capacity data of the individual pesticide in binary systems contained in Tables XXIX, XXX and XXXI respectively to test the applicability.

The results from the application of the Polanyi model presented here indicated that the theory was inconsistent in addressing adsorption for all three chemicals. This is shown in Tables XXIX, XXX and XXXI respectively where predictions of lindane, Silvex and 2,4-D in the presence of the other corresponding solute were in accord with the experimental results about 50% of the time. There were data, however, that were within a +/- 100 ng/g. The differences between the observed and the simulated data, expressed as percent errors, showed that some of the data were inadequately described by the Polanyi model but that many sets were inconsistent with the model theory. additional discussion follows a more complete introduction to these data.

Table XXIX shows the predictions by Polanyi Theory of both lindane and Silvex with the presence of the corresponding solute. From the values in Table XXIX, it is shown that the predictions of both lindane and Silvex with the presence of the corresponding solute were in accord with the experimental results at only certain concentration ranges evaluated.

Predictions of lindane adsorption capacity on the whole soil appeared to be represented by the Polanyi Adsorption

Theory only for the 200 ug/l concentration data. This was because as adsorption of the pesticide proceeded, site coverage increased to the extent that lateral interactions occurred between the adsorbed molecules. These lateral interactions eventually formed clusters. These were considered equivalent to the Polanyi model property where sufficient concentration must be present to allow precipitation on the solid surfaces.

Significant differences were observed with the rest of the concentration ranges evaluated. This is because, in region 1, there was insufficient concentration to allow precipitation.

Soil fraction 1 was more like the whole soil in that the predictions of lindane adsorption capacity again appeared to be represented by the Polanyi Theory at the 100 and 200 ug/l concentration ranges.

Soil fraction 2 consistently showed lower lindane adsorption than was predicted by the Polanyi Theory at the lower solute influent concentration ranges. However, the trend was reversed within the intermediate concentration ranges in that the theory predicted lower lindane adsorption than was observed. The theory closely predicted lindane adsorption at the highest solute concentration. This, again, is in accord with the above observation that as adsorption proceeds, lateral interactions occur and eventually lead to cluster formation or precipitation on the solid surface.

Soil fraction 3 showed Polanyi Theory to closely predict lindane adsorption at the 50 and 500 ug/l concentration ranges. The theory overpredicted adsorption capacity of lindane at the 20 ug/l concentration range and underpredicted its adsorption capacity at the 200 ug/l concentration ranges respectively.

Soil fraction 4 showed that the theory could closely address the experimental data of lindane adsorption at all of the concentrations evaluated. However, on soil fraction 5, the theory again showed that it could closely predict lindane adsorption at the 10, 50 and 500 ug/l concentration data. Considerably lower agreement than that obtained for the experimental results were observed at the other solute concentration ranges.

Predictions of Silvex adsorption with lindane present as the competiting adsorbate on both the whole soil and soil fraction 1 indicated that considerably lower agreement was obtained between the model and the collected data at the higher solute concentrations. Close predictions by the model were observed at the 200 ug/l for the whole soil fraction and at the 10, 20 and 50 ug/l concentrations for soil fraction 1.

Soil fractions 2 showed that the theory could closely predict the experimental results on all concentrations up evaluated. Whereas on soil fraction 3, the theory showed close approximations of Silvex adsorption at only the 50 and 200 ug/l concentration data. Considerably lower predictions of Silvex adsorption were observed at the rest of the concentration ranges evaluated.

On soil fraction 4, the theory showed close approximations of Silvex adsorption at the 100 and 200 ug/l concentrations. Considerably lower predictions of Silvex adsorption by the theory were observed at the highest concentration.

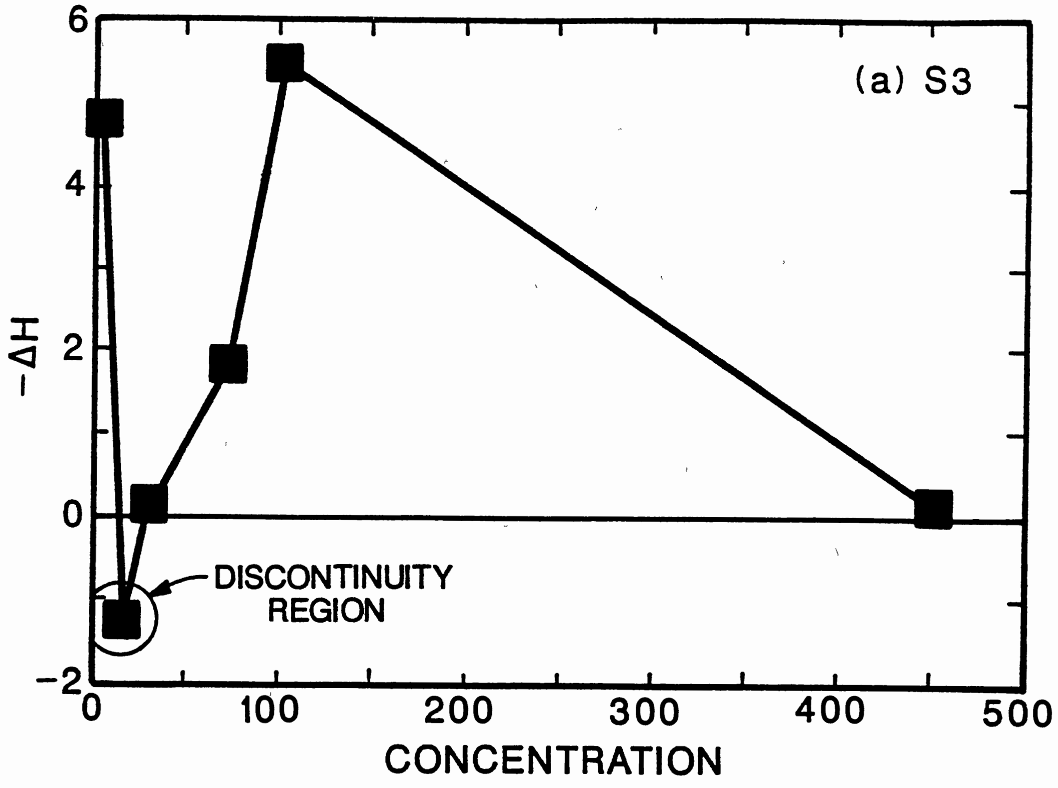
The theory again showed close approximations of Silvex adsorption to experimental results only at the lower and highest influent concentrations. At the intermediate concentration ranges, the theory showed considerably lower agreements to experimental results.

In general, the results of the application of Polanyi theory presented in Table XXIX indicated that the theory was found to be fairly inconsistent in predicting adsorption capacity of both lindane and Silvex respectively at a +/- 100 ng/g margin of error. Predictions of lindane and Silvex in the presence of the corresponding solute were adequate only about 50 percent of the time. This same trend was also observed for lindane-2,4-D and Silvex-2,4-D systems as shown in Table XXX and XXXI respectively.

Since adsorption potential is the work done by adsorptive forces in bringing a molecule from the bulk solution phase to a point near the adsorbent surface where it precipitates or coalesces, it was considered fundamentally equivalent to the energy clusters or micelles identified in the isosteric heats of adsorption phase of theis effort. Indeed, it was observed that the Polanyi theory, often predicted the transitional regions between regions 1 and 2 respectively as described by the isosteric heats of adsorption plots. Beyond that, the Polanyi theory was unstable to predict the trend of competition and showed considerable lower adsorption capacity values as compared to the actual data.

Figure 29 showed a comparison of the isosteric heats of adsorption to that of the Polanyi model predictions. The figure showed that the Polanyi model predicted the trend of competition of lindane with Silvex present on soil fraction 3, with close approximations at the transitional zone between region 1 and 2 of the isosteric heats of adsorption curve. This transitional/discontinuity region indicated lateral interations which eventually formed energy clusters which were taken to be equivalent to the precipitation of the pesticide on the solid surface as predicated by the Polanyi model.

Table 32 presents a summary of the trends of competition for the various pesticides as predicted by the Polanyi model at the discontinuity regions identified from the isosteric heats of adsorption plots. The table showed that at the discontinuity regions, the Polanyi model consistently predicted the trends of competition for the various pesticides. This was in accord with the observation presented in figure 29 that at the discontinuity region, there were lateral interactions which eventually formed energy clusters which were considered equivalent to the



<u>LINDANE</u>

SOIL 3	POLANYI	EXPT.	
10 µg/l	159.23	138.72	
20 µg/l	320.66	78.40	
50 µg/l	415.88	411.20	←DISCONTINUITY REGION
100 µg/l	608.13	949.60	
200 µg/l	706.55	965.60	
500 µg/l	934.86	900.00	

Figure 29. Comparison of the Isosteric Heats of Adsorption of Lindane with Silvex present on S2 to Polanyi Model predictions

precipitation of the pesticide on the solid surface. Table XXXII also showed that Polanyi model was able to consistently predict the trend of competition at the higher solute concentrations. This was because as concentrations increased, surface coverages increased to the extent where solute coalesed or precipitated as required by the model.

This is again in accordance with the observation that the surfactant model was more appropriate in explaining the synergistic effects of adsorption in binary systems than was the chromatography model. The fundamental basis of the surfactant model was the formation of clusters which were identified by the isosteric heats of adsorption plots. This was considered functionally equivalent to the precipitation of the pesticides and to micelle formation in surfactant applications. The Polanyi model was able to consistently predict competition at this region.

TABLE XXXII

PREDICTING THE TRENDS OF COMPETITION OF THE PESTICIDES (ng/g) BY POLANYI THEORY AT THE DISCONTINUITY REGIONS OF THE ISOSTERIC HEATS OF ADSORPTION PLOTS AND AT THE HIGHER SOLUTE CONCENTRATIONS FOR THE VARIOUS SOIL FRACTIONS

Lindane-Silvex System

Soil	Conc.	Polanyi	Expt.
WS	*10ug/l	257.33	398.10
	*20ug/l	333.80	416.86
	*200ug/l	685.67	660.69
S1	100ug/l	608.12	612.60
	200ug/l	898.20	960.00
S2	*50ug/l	357.95	509.00
	500ug/l	1119.2	1360.0
S3	*50ug/l	415.88	509.00
	200ug/l	706.55	965.60
	500ug/l	934.86	900.00
S4	*50ug/l	395.59	445.80
	100ug/l	614.24	671.60
	200ug/l	934.86	900.00
S5	*50ug/l	210.69	265.20
	500ug/l	632.95	760.00

Silvex-Lindane System

Soil	Conc.	Polanyi	Expt.
WS	*100ug/l	212.29	332.00
	*200ug/l	283.71	232.00
S1	*10ug/l	38.39	52.80
	*50ug/l	101.28	73.40
S2	*50ug/l	123.71	153.60
	*100ug/l	160.44	146.00
	200ug/l	227.00	274.00
	500ug/l	336.28	348.00
S3	*50ug/l	120.05	172.00
	*200ug/l	239.35	272.00
S4	*50ug/l	99.28	124.80
	*100ug/l	139.48	138.60
	*200ug/l	216.58	256.00
S5	200ug/l	110.82	106.00
	500ug/l	170.36	148.00

Silvex-2,4-D System

Soil	Conc.	Polanyi	Expt.
WS	*200ug/l	212.29	260.00
S1	*100ug/l	402.60	394.00
	200ug/l	212.29	260.00
S2	*100ug/l	343.07	316.00
	500ug/l	960.00	1140.0
S3	*200ug/l	675.40	705.00
	500ug/l	670.00	564.00
S4	*200ug/l	477.21	444.00
	*500ug/l	606.00	610.00
	100ug/l	364.29	357.00
S5	*10ug/l	67.43	44.40
	*200ug/l	371.65	350.00
	500ug/l	139.90	130.00

2,4-D-Silvex System

Soil	Conc.	Polanyi	Expt.
WS	*20ug/l	35.55	26.00
	*200ug/l	79.13	130.00
S1	*100ug/l	74.52	128.00
S2	*100ug/l	81.54	94.00
	*200ug/l	114.56	194.00
S3	-	-	-
S4	*50ug/l	81.54	123.00
S5	*20ug/l	23.59	33.00
	500ug/l	138.0	260.00

*Data at the discontinuity region

CHAPTER IV

DISCUSSION

Results--Single Uptake

Summary

From Figures 1 through 3, the uptake rates following the initial adsorption period decreased over time, slowly diminishing to a steady constant concentration, with the majority of the uptake within the first few hours of contact. This was most obvious in the case of lindane. As postulated by Hayes et. al. [59], it appeared that, at longer times, adsorption is governed by the diffusion of the pesticide molecules from the exterior surface to the interior pores of the soil, i.e., a higher rate of solute movement through macropores followed by much slower passage through the micropores [58,59]. This type of behavior conformed to various type of organic uptake by soils as described by other researchers [71-81]. The relatively faster rate of equilibrium exhibited by lindane could be explained by the fact that lindane is less soluble than either Silvex or 2,4-D in water [72,74].

The data in Table VII indicated that removal of lindane on most of the soil fractions for both soils was slightly higher at the lower influent concentrations while exhibiting significantly less removal at the higher solute concentrations. This could be explained by assuming that pore spaces of the soil had been filled with the pesticide at the lower end of the concentration, thus leaving behind considerably less space for further uptake.

Significantly higher removal of lindane at low and high concentrations was observed in the NRC soil fraction 4 when compared with other soil fractions or with the whole soil. The Port soil for these fraction, did not appear to remove the pesticide as much at the lower influent concentration as did the NRC soil, but did exhibit higher uptake at the highest solute concentration. The prevailing hypothesis is that greater adsorptive capacity was exposed in these four sequential extractions leaving only the humic layer on each soil particle. The humic layer has been shown by several workers [82-84] to be highly adsorptive to nonionic pesticides, primarily because this layer is considered to be the primary site of adsorption in soil organic matter [81-84].

The soil surface after the removal of the remaining liable organic matter by hydrogen peroxide treatment still exhibited some degree of adsorption of lindane for both soils. The NRC soil had the highest adsorptive levels at the 10, 300 and 500 ug/l range. More adsorptive sites were then exposed. The pretreatment also could have altered the structures of the remaining organics or have exposed inorganic surfaces, where the compounds sorbed by interacting with the metal cations through waters of hydration at general hydrogen bonding sites [58].

The data in Table VIII indicated the removal of Silvex by both soils and their derivatives was significantly less when compared to the removal of lindane. Apparently this was because Silvex was more soluble. Both soils and fractions 1, 2 and 3 showed higher removals of Silvex at lower concentrations than lindane with a much lower removal of Silvex at higher solute concentrations. This, too, could be explained by assuming that the pore space of this soil had been filled with pesticides at lower solute concentrations, leaving little available space for additional pesticide adsorption.

The exposed humic layer of the fourth fraction did not provide significant removal of Silvex especially for the Port soil as compared to other soil fractions. This agrees with other research [85-99] which suggested that even though humic micelles and membranes could react in a number of sorption and binding reactions, most of the exterior of the micelles are negatively charged due to ionized carboxyl and hydroxyl functional groups. This would decrease the removal of Silvex, or any other acidic herbicide, since like charges repel. At the same time, the solvent-like exterior of the micelle could allow some incorporation of the herbicides into the micelle [85-99] as shown by the data in Table VIII for the forth soil fractions of these soils.

Both soils in fraction 5 indicated decreased removals of Silvex with the destruction of the humic layers by hydrogen peroxide. This was apparently because the mineral exposed surfaces had lowered adsorptive capacities. Adsorption with this fraction was attributed to the interaction with the metal cations through waters of hydration and at general hydrogen bonding sites [58].

The slight removal of 2,4-D itself by the various soil fractions as shown in Table IX could be attributed again to high solubility as well as the structure of the compound as illustrated in Table III. That is, under saturated condition, competition with the polar water molecule may considerably reduced adsorption. The competition of adsorption sites with water molecules (due to the solubility of 2,4-D), may in the presence of a liquid phase, interfere with adsorption at those sites with the strongest interactions [84]. The adsorption of water into these sites may determine whether acidic groups in the soil fraction of the soil will preferentially interact with the adsorbate molecules [85,86].

The soil extractions by various destructive treatments also exposed more pore spaces (based on increased surface area within the soil fractions) where competition between water and the herbicides may have occured. That is, the competition with the water polar molecules resulted in dislodged 2,4-D molecules from the adsorptive sites. This could mean less available adsorption space for 2,4-D [86].

The slightly higher removals of 2,4-D in the fourth fraction for the NRC soil as compared with the other soil fractions could be due to the presence of hydrogen ions during the acid treatment and that the hydrogen ions influenced the deionization of the functional groups. Thus, a weak hydrogen bonding could occur between the OH groups of the humic surface and the oxygen group from the acidic herbicides [58]. Additional possible mechanisms for the increased 2,4-D adsorption by this soil fraction have been explained by physical adsorption, coordination through the carbonyl, association of the carbonyl by bridging to coordinated water on the exchange ions and hydrogen bonding from the carbonyl to a clay surface may occur [87-89].

The data in Table IX also indicated a slightly higher removal of 2,4-D in the NRC soil than in the Port soil even though the extracted Port soil had higher measured surface areas. It can be assumed that since the Port soil had a higher organic matter content, sequential removal of the organic fractions made possible a number of additional sites which allowed water to compete with the acidic herbicides for the sites as well, leaving a higher concentration of the pesticides in the solution. Frissel [87] reported negative adsorption of 2,4-D onto various soil types. Negative adsorption was defined as having a higher concentration of the adsorbate in solution than what was initially present, after equilibrium. He attributed his results to competition from water. Also, as mentioned earlier, the higher organic matter content of the Port soil might have influenced the lower uptake of 2,4-D due to the abundance of negative charges [90,91], since like charges repel.

Table XI showed that after each sequential treatment, the ultimate capacity of lindane and 2,4-D increased until the forth soil fraction was removed. Silvex adsorption, however, showed increased adsorption through the first soil extraction for both of the soils followed by a significant reduction in NRC soil fraction 2. The Port soil, however, showed increased adsorption through soil fraction 2. This fraction had the highest adsorption of Silvex of all of the adsorbents. In contrast, the highest uptake of Silvex in the NRC soil was found to be in soil fraction 3. Overall, the removal of the materials that are soluble in ether and alcohol increased the adsorptive capacity of the soil based adsorbents.

The removal of these derivatives during a sequence of extractions may have promoted disruptions of the soil aggregates, exposure of occluded surfaces, and a progressive increase in adsorption [20]. Essentially, the adsorptive surface was cleaned by the extraction and was better able to exhibit its intrinsic adsorptive capacities [20]. The removal of these materials (lipids, waxes, and resins) may have increased the wettability of the soil surface for fractions 1,2, and 3, thereby allowing full penetration of these pesticide solution into the available sites [20].

The highest removal of the pesticides was in soil fraction 4. Humic acid has been described by Khan and Schnitzer [75,91,93] as having cross-linked, open structures with cavities capable of retaining organic compounds. This structure is affected by pH and ionic strength. Since hemicellulose in the fourth fraction is removed by hydrochloric acid at lowered pH and increased ionic strength, these materials began to coil, forming rigid spherocolloids and aggregations of spheresocolloids with hydrophobic interiors [78,92,93]. These hydrophobic portions of the humic molecules have the potential to bind pesticides [78,92,93]. The enhanced formation of hydrophobic interiors caused by lowered solution pH would also helped to explain the results of some researchers, which indicated that nonionizable, nonpolar compounds bind to a somewhat greater degree to humic materials at lowered pH than at higher values [93-95]. This same theory could also apply to lindane. On the other hand, since "like dissolves like", the hydrophillic constituents of humic acid layer would probably be most reactive to the more soluble compounds, as in the case of phenoxyalkanioc (i.e., the acidic herbicides would be bound to this hydrophillic constituents).

Table X indicated better conformance of the Freundlich isotherm and the Langmuir equation over the linear isotherm model. The data showed that the Freundlich and Langmuir equations described the adsorption response over the appropriate test ranges. However, conformity to a lesser extent to the Langmuir equation over the Freundlich isotherm may be due to the lack of homogeneity of the soil mineral surfaces or multilayer adsorption occuring on the adsorbent.

Contrary to the frequent assumption, the linear isotherm model was less satisfactory in fitting these data as shown in figures 5 through 25 in the appendix as well as in Table X. Most of the linear isotherms exhibited a convex-type function. This kind of isotherm indicates that as adsorption sites were filled, it became increasingly more difficult for the adsorbate molecules to fill the vacant sites because the sites were saturated at the lower influent solute concentration. That is, a finite surface area-adsorbate potential [44]. This means that in those cases where linearity is not appropriate, increased concentrations along the entry boundary can grossly underestimate the amount of pesticide leached.

The distribution coefficients obtained from collected data differed from those obtained from correlation as presented in Table 16. In some cases, however, such as 2,4-D adsorption on selected soil fractions, were described by the appropriate correlation. The difference between the observed and predicted values implies a substantial contribution to sorption by more specific sorbate-sorbent interactions than by general hydrophobic forces. The mechanism of sorption is likely, therefore, to involve extensive hydrogen-bond formation between the sorbate and hydrogen-bonding sites on the sediment organic matter. The discrepancy noted in the distribution coefficients was also probably 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 [97,98]. The model assumes a correlation between organic carbon and K_d, which did not exist for all of the soil fractions used in this work. The models presented in Equations (2) and (3) were formulated for soils high in humic acids and humins. Means et al. [100] also found significant differences in experimental and predicted data for the sorption of polycyclic aromatic amines. Schellenberget et al. [101] showed that the model was applicable only to a limited degree to compounds which were fully or partially ionized at natural pH values such as carboxylic acids and phenols. Another possible reason for these results may be due to the way soils were extracted and exposure of occluded surfaces to allow further uptake of the pesticides [20, 99].

The simulated distribution equation, however, was able to show better approximations of the distribution oceffiicients to the measured value than the underlying distribution model because the simulated equation took into accounts all the variables that contributed to the behaviour of the dependent variable, i.e. Kd, instead of just organic carbon content alone.

Table XI also showed that after each sequential treatment, the ultimate capacity of the adsorbent increased until the the forth fraction when the ultimate capacity was significantly reduced. The table also showed that even though the percent organic carbon of the soil fraction decreased, adsorption of the pesticide increased until the forth fractions were removed. This same trend was observed for surface cation exchange capacity as the cation exchange capacity decreased, adsorption increased in all various adsorbent as compared to the whole soil. In the case of surface area, it increases with each sequential treatments until the forth fraction. This same trend was observed for ultimate capacity.

Further statistically analysis indicated that surface area was most significant in terms of contibution to adsorption. A summary of the General Linear Model (GLM) is presented in Table XIV. In this analysis, adsorption was referred to as the dependent variables (response variable) and organic carbon content, CEC, MW and surface area were referred to as independent variables. If the significance probability label Pr >F, was small, it indicated significance. It was concluded that surface area was statistically most significant to adsorption with molecular weight of the organics second. Organic carbon content and cation exchange capacity did not contribute as much, but some significance was indicated. Again, this is in accord with the previous observation made with the comparisons of surface area to ultimate capacity as shown in Table X. It should be noted the sequentially extracted organic carbon stated above should not be regarded as representatives of the organic matter in the soil.

Conclusions

Results from these efforts showed that adsorption of all three pesticides was not linear and that removal of hydrophobic materials such as lipids, waxes and oils, generally increased the adsorptive capacity of the soil. The subsequent removal of humic materials by hydrogen peroxide reversed this trend resulting in decreased adsorption capacity. Statistical analysis of soil variables indicated that surface area was the most significant variable in terms of contribution to adsorption while cation exchange capacity and organic carbon were less significant or were insignificant. The underlying hypothesis for these findings is that the removal of these derivatives during a sequence of extractions, may have promoted disruptions of the soil aggregates, exposure of occluded surfaces and therefore, progressive increase in adsorption. Comparisons of distribution coefficients obtained from experimental data differed from coefficients obtained from theoretical models. The discrepancy noted was probably due to the way soil organics were extracted as well as the effects of the treatments in opening pore structure and increasing surface area, or a model format that was not appropriate for varying soil organic levels. Finally, the data also showed that molecular weight, the aliphatic and aromatic portion of each portion of each fraction which can also influence the adsorption of pesticide in use.

CHAPTER V

DISCUSSION

Results--Competitive Adsorption

The results presented in Table XIX, showed that the equilibrium adsorption of Silvex from the bisolute systems was reduced in the presence of lindane. The results also showed that lindane uptake in the presence of Silvex, increased for all of the soil fractions evaluated. Although the amount of Silvex adsorbed on the various soil fractions was found to be reduced relative to its value in pure solution, the combined capacity for both pesticides was greater than that for either of the pure substances alone. Further, it was less than either of the pure solutes would have shown at twice the concentration. It appeared that the total adsorptive capacity of the various soil fractions may be increased with mixed solutes.

Table XXII showed adsorption of lindane and 2,4-D in the lindane and 2,4-D binary systems was greater than when present singly. From Table XXII, it can be seen that with the exception of soil fraction 2, 3 and 4, the equilibrium adsorption of 2,4-D from a bisolute solution on the various soil fractions was increased in the presence of lindane. Similarly, for lindane in the binary systems with 2,4-D, uptake capacities increased among the various soil fractions evaluated. That is, in general, the results in Table XXII indicated that, in multispecies systems, cumulative adsorption exceeded the adsorption of individual species in the single-species systems. It appeared that the total adsorptive capacity of the various soil fractions increased with mixed solutes.

A hypothesis previously suggested to account for the increased of both lindane and 2,4-D and lindane in the lindane-Silvex binary systems was based on the assumption that there was some form of synergistic adsorption occurred [102]. Interactions between the solutes and between the solutes and the adsorbents produced lateral interactions with the associated increases in available adsorptive energies. These increased energies, documented with the isosteric heats of adsorption plots, produced larger individual and summed adsorption capacities than when compared to single solute isotherm data.

An extension of this explanation was given in the example of figure 22 which showed that during the adsorption of Silvex with lindane as the competing adsorbate, the value of the isosteric heat of adsorption first increased and then decreased as expected with increasing coverage. With the completion of adsorption, however, in region 1, a discontinuity occured. That is, the heats of adsorption suddenly increased indicating the onset of synergistic adsorption. This discontinuity was interpreted as signifying the presence of the increased energy required to orient the adsorbed molecules into a critical surface cluster, thus allowing the synergistic adsorption to proceed. This is consistent with work done by Griffin and Jurinak [69].

This could only be explained by assuming that with increasing surface coverage, adsorbate molecules encountered fewer unoccupied adsorption sites and more adsorbed molecules. Adsorption onto lower energy sites including multilayer adsorption then occurred. Lateral interactions among the adsorbed species formed clusters or micelles which served as centers for synergistic adsorption. This, coupled with the observation that there was increased adsorption in the binary systems as compared to the single solute systems, was evidence that there was increased/synergistic adsorption taking place. For this reason, the discontinuity in the isosteric heats of adsorption validated the observation of increased adsorption as the energy necessary to bring about the increase/synergistic adsorption was present.

The energies available for adsorption were inconsistent with prevailing hypothesis regarding surface coverages as shown in region 1 of figure 22. That is, Langmuir model of adsorption does not account for these discontinuities in available adsorptive energies. Rather, as a finite level of coverage is achieved, adsorption will cease. This increase in the heats of adsorption was interpreted as corresponding to initial rapid surface adsorption which preceded critical cluster formation. This was consistent with the work done on the interactions of phosphate on calcite and sediments by Griffin and JurinaK and Stumm and Leckie respectively [69,70,103]. The decrease in the heats of adsorption was attributed to the induction period associated with cluster formation. These clusters served as centers from which synergistic adsorption could occur.

A comparison was made between the SRS equation models and the isoteric heats of adsorption as presented in figure 26. The data presented by the SRS figures indicated that conformance of the adsorbate data occurred only at the lower solute concentration ranges. An explanation is that the adsorbate first sorbed at the highest energy sites and was evidence of high energy adsorption associated with low surface coverage saturation. This was consistent with the the work of Kuo et al [104,105] where he investigated the interactions of phosphate on sediments. The isosteric heats of adsorption in region 1 indicated an initial rapid adsorption at the lower solute concentration ranges corresponding to low-surface coverage by the adsorbate. The SRS equation closely approximated the uptake of these compounds in these regions. This behavior directly corresponded to isotherms representative of surfactant from aqueous solutions on mineral oxide surfaces on the first region shown in figure 1. At this region, for very dilute solution and sparse surface coverages, Henry's law is obeyed.

Further comparisons involving the discontinuity region of the isosteric heats of adsorption and that of the SRS data at the higher solute levels indicated that the adsorbate data did not conform to the SRS equation. The SRS equation generally underpredicted the experimental data in this region. This behaviour was apparently related to the increased adsorption indicated by the isosteric heats. As described earlier, the discontinuity was interpreted as signifying the increased energy required to orient the adsorbed molecules into critical surface clusters, thereby allowing synergistic adsorption to proceed [106-113]. The discontinuity is taken directly corresponded to the first and second region of the isotherms representing surfactant adsorption. The isotherm deviated markedly from the linear behavior, signaling the transition from the first to the second region, with adsorption increasing rapidly as the solution concentration increased. Therefore, since the SRS equation is predicated on the premise that the solutes have a "pure adsorption" behavior, i.e. no enchanced/increased adsorption behavior, the failure of the SRS equation to conform with the experimental data plots at the higher solute concentration ranges was attributed to this particular limitation of the method.

According to Tables XXIX through XXXI, the Polanyi Adsorption Potential theory could in some cases, predicted accurately the ultimate capacity of the pesticides for the various binary systems evaluated. Ultimate capacities were calculated and compared for all three chemicals for the soils. The results indicated that the theory was found to be inconsistent for all three chemicals over the concentration ranges evaluated.

The inability to predict the ultimate capacity at the solute concentration ranges evaluated was probably due to having insufficient concentrations to cause precipitation as this model is based upon a coalescence mechanism [51,52].

Figure 29, however, showed that the Polanyi model was able to approximate the trend in the transitional zone between regions 1 and 2 (i.e. the discontinuity region). and also conformed by the data presented in Table XXXII. This was because the discontinuity region, as described earlier, was attributed to lateral interaction which eventually formed clusters or micelles [106-113]. This was considered equivalent to the precipitation of the pesticides on the solid surface as predicated by the Polanyi model. Beyond this region, the Polanyi model was unable to adequately predict the trend of competition between the pesticides. The inability to predict adsorption for some of the soil fractions indicated that adsorption of pesticides by soils was a function of mechanisms other than coalesce or precipitation. Rather solubility effects and interactions with organic matter appeared to dominate adsorption in regions beyond the discontinuity. The model only measures pure adsorption and other interactions among the soil fractions.

At the lower solute concentration levels, as depicted by the initially rapid increase and eventually decrease heats of adsorption depicted in region 1, the Polanyi model was unable to predict the trend of competition among the pesticides. Again, this was to be expected because region 1 corresponded to high energy adsorption associated with low surface coverage saturation by the adsorbate. Since the fundamental property of concern within the Polanyi model was its basis in having sufficient concentration present to enable precipitation on the solid surface, the inability for the Polanyi model to predict the trend of competition at lower solute levels was attributed to having insufficient concentration of the adsorbate for precipitation to occur.

Conclusions

The results of this study verified or confirmed the results of previous research on single component adsorption as well as providing results and conclusions for multicomponent systems. The verifications and conclusions drawn from this study are presented below.

* Adsorption of both lindane and 2,4-D as well as lindane in the lindane-Silvex binary systems showed greater adsorption of the pesticides than when presented singly. This was probably caused by the onset of increased adsorption taking place due to interactions between the solutes and between the solutes and adsorbents (synergistics effects) resulting in increased available adsorptive energies. These

increased energies, documented with the isosteric heats of adsorption plots, produced larger individual and summed adsorptive capacities when compared to single solute isotherms.

- A discontinuity in the isosteric heats of adsorption curve, not commonly noted in more homogeneous adsorbents was interpreted as signifying the increased energy required to orient the adsorbed molecules into a critical surface cluster, thus allowing increased adsorption to proceed. These increased energies provided reasons for synergistic adsorption that did occur.
- The figures presenting the SRS Multiple Freundlich-Type Isotherms showed that the model could closely simulate the uptake of these compounds at the lower and intermediate solute concentrations. This was expected since the isosteric heats of adsorption from the preceding section indicated that the initial rapid adsorption at the lower solute concentration ranges was probably a high energy adsorption associated with low surface saturation, thereby causing the SRS equation to closely simulate the uptake of these compounds.
- A comparison between the discontinuity region and that of the SRS data at the higher solute ranges indicated that beyond the discontinuity region, the adsorbate data did not conform to the SRS equation. This is is apparently related to the increased energy required to

orient the adsorbed molecules into a critical surface cluster which the SRS equation could not address. The discontinuity point marks the end of "pure adsorption" where mass transfer of the solute is limited, chiefly by solubility.

* The results indicated that the Polanyi Potential theory were inconsistent in predicting the trend of competition for all three chemicals over the various concentration ranges evaluated. The Polanyi model, however, was able to closely predict the trend of competition at the discontinuity region relative to region 1 and 2. This was because the discontinuity region was formed by lateral interactions between the pesticides and between the pesticides and the adsorbent. Energy was diverted from mass transfer to cluster formation. These clusters were considered equivalent to the precipitation of the pesticide on the solid surface.

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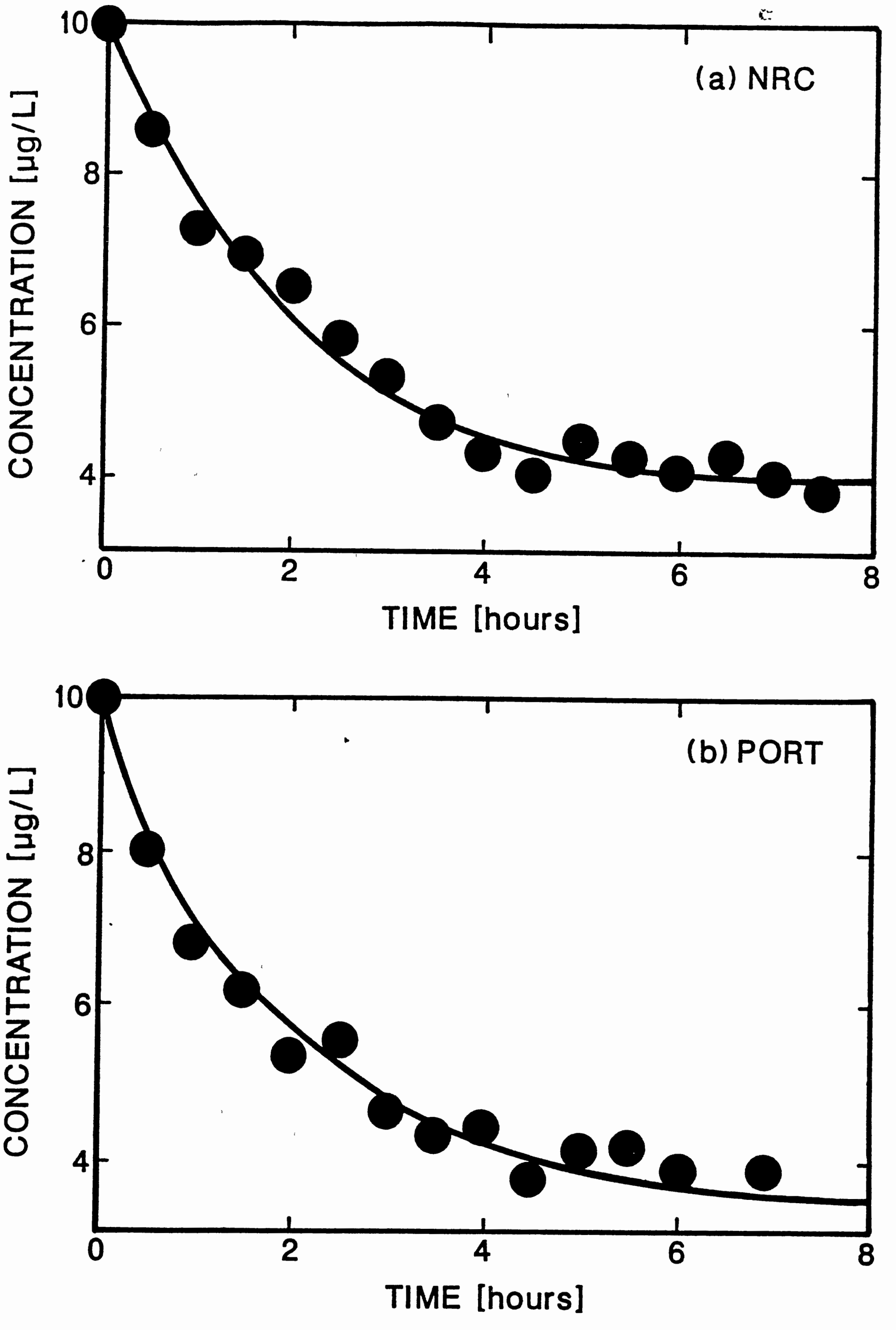
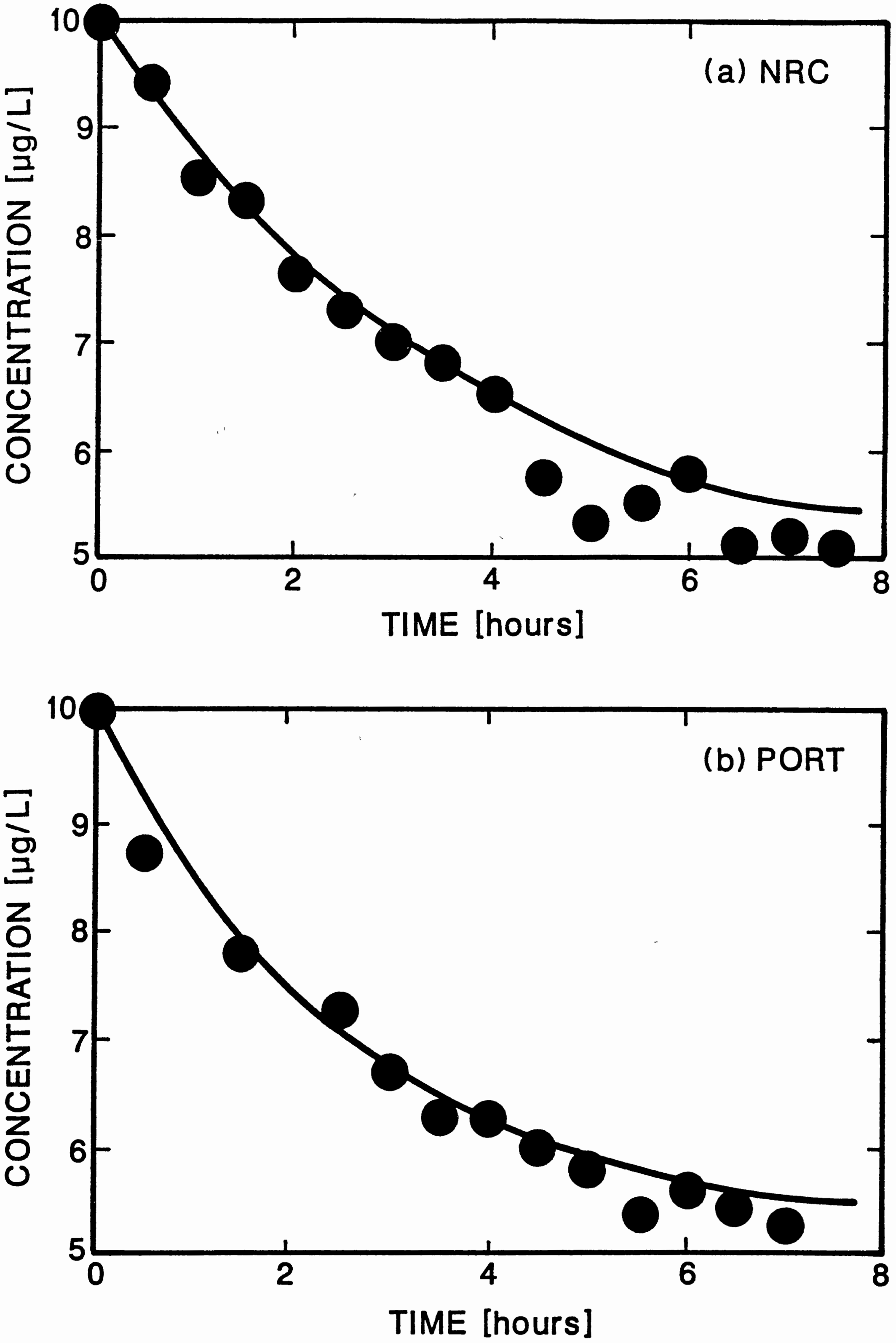
APPENDIX A

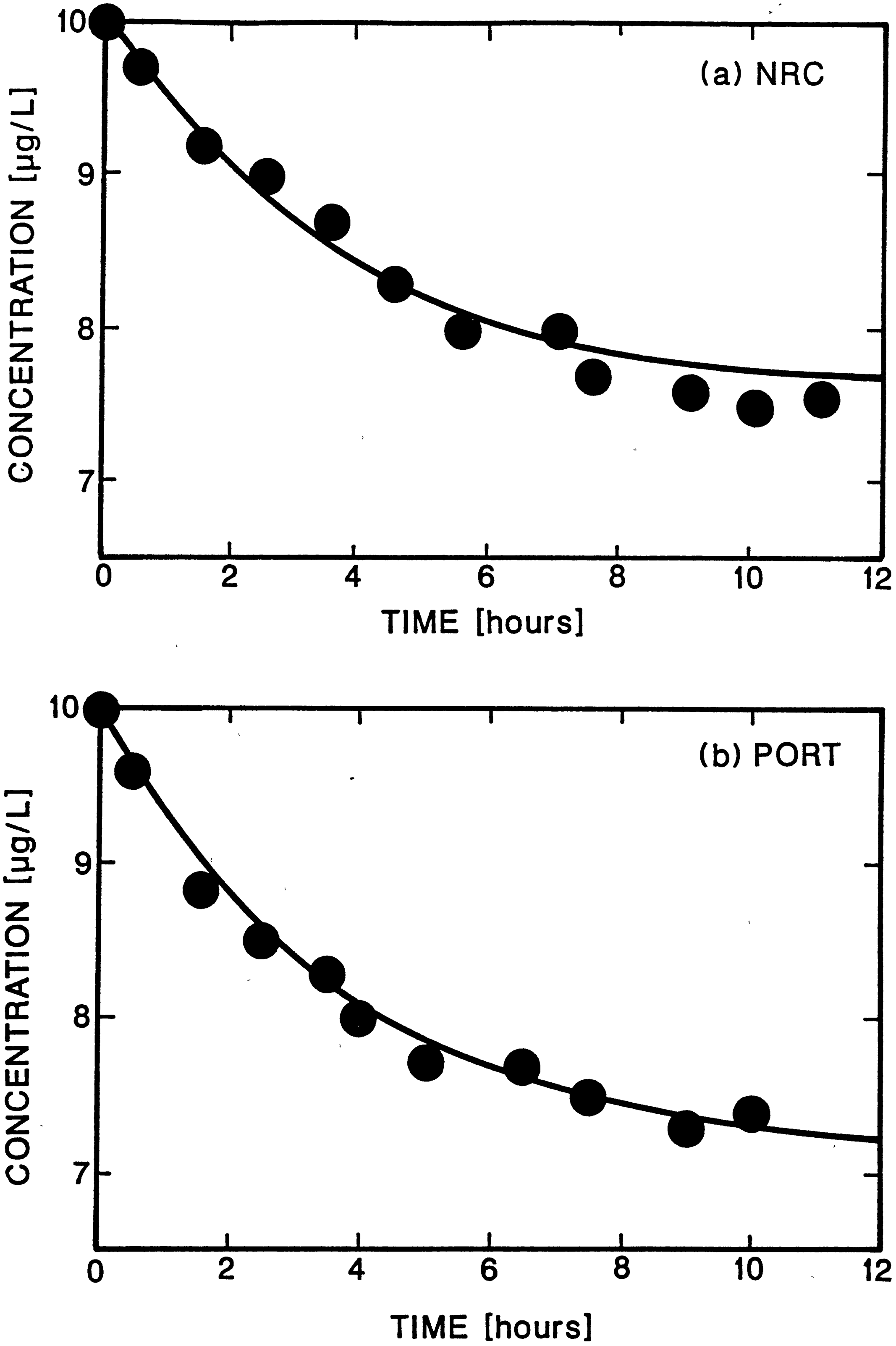
EQUILIBRIUM UPTAKE CURVES AND ADSORPTION ISOTHERMS FOR LINDANE, SILVEX AND 2,4-D ON NRC AND PORT SOIL AND SOIL FRACTIONS



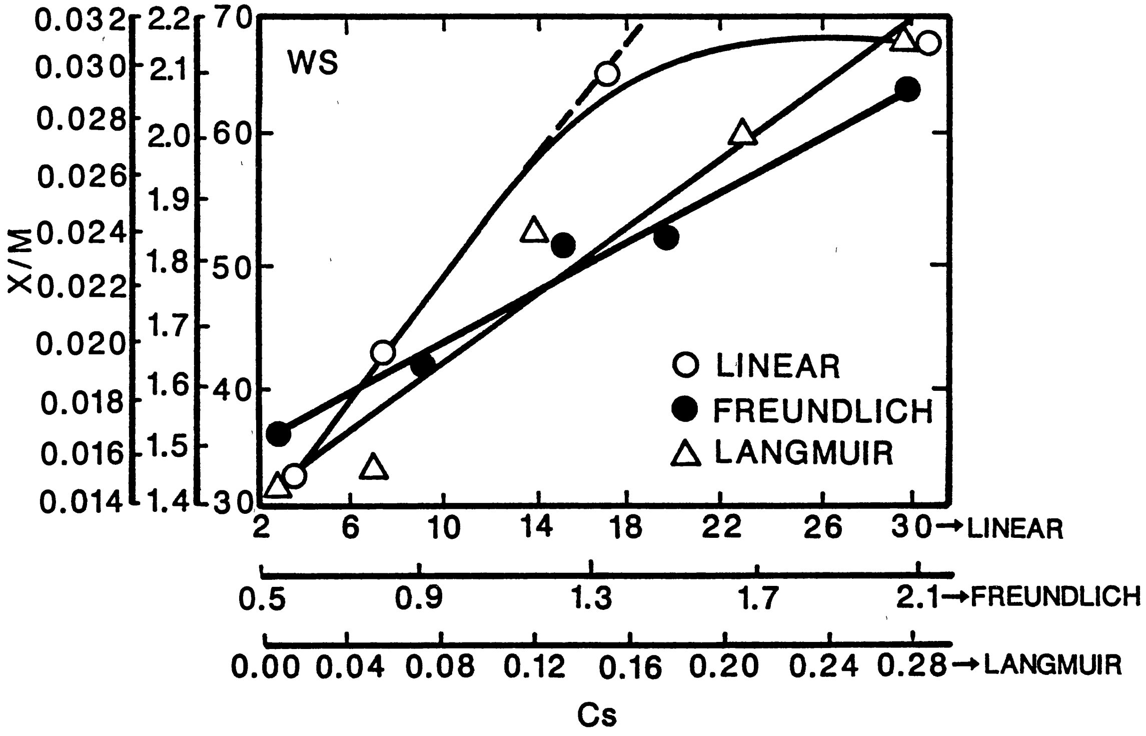
AI-1. Equilibrium Uptake Curves of Lindane on NRC and Port Soil



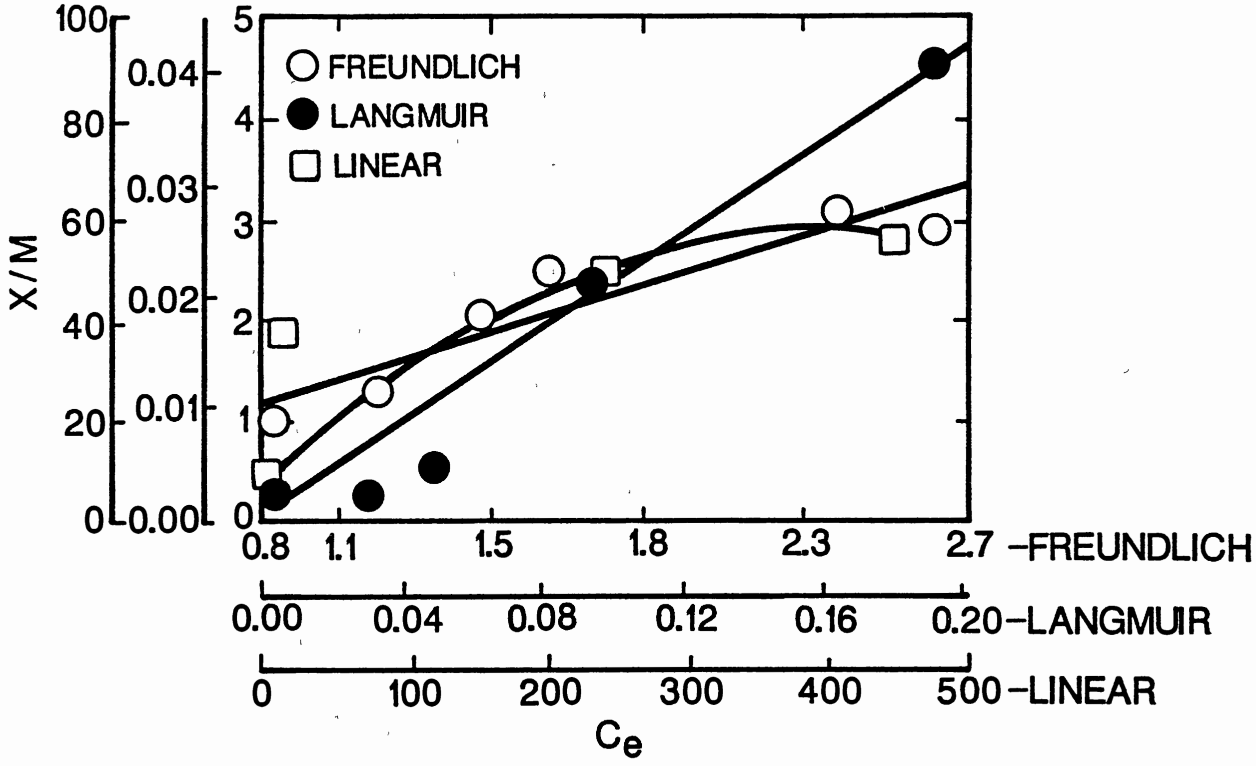
AI-2. Equilibrium Uptake Curves of Silvex on NRC and Port soil



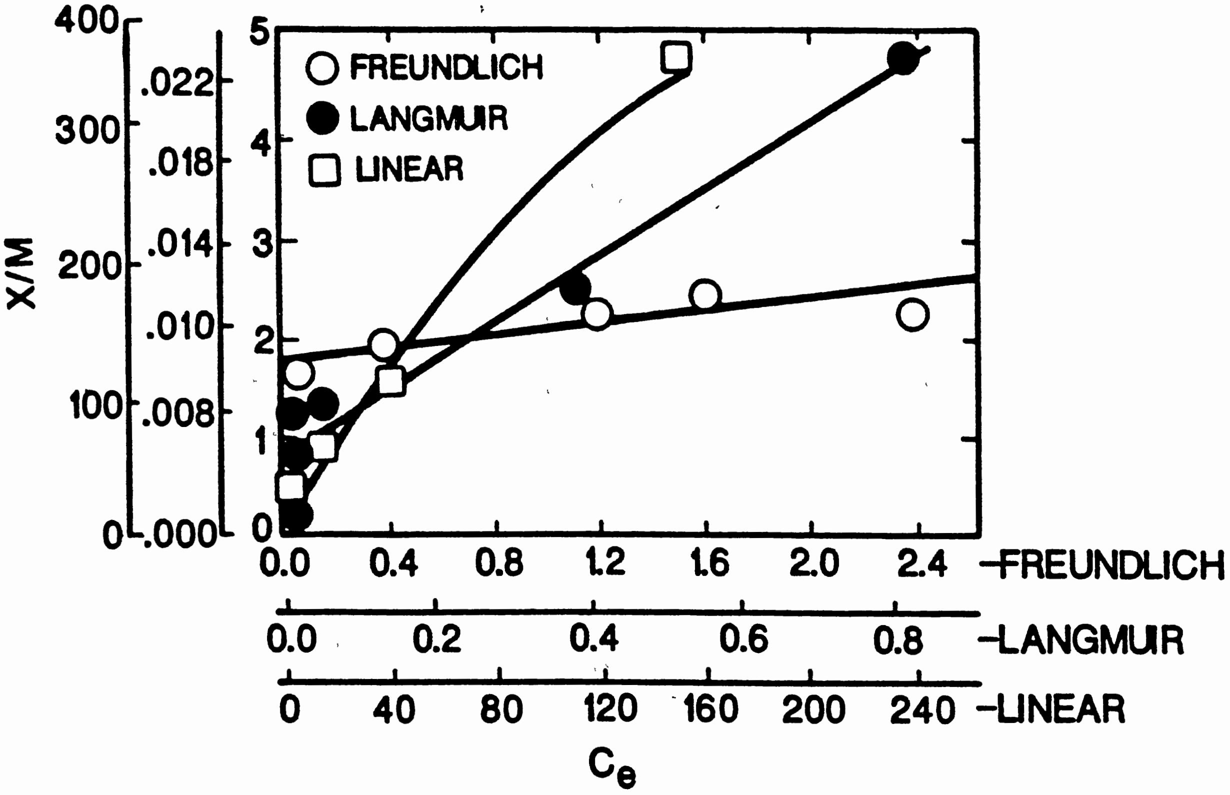
AI-3. Equilibrium Uptake Curves of 2,4-D on NRC
and Port Soil



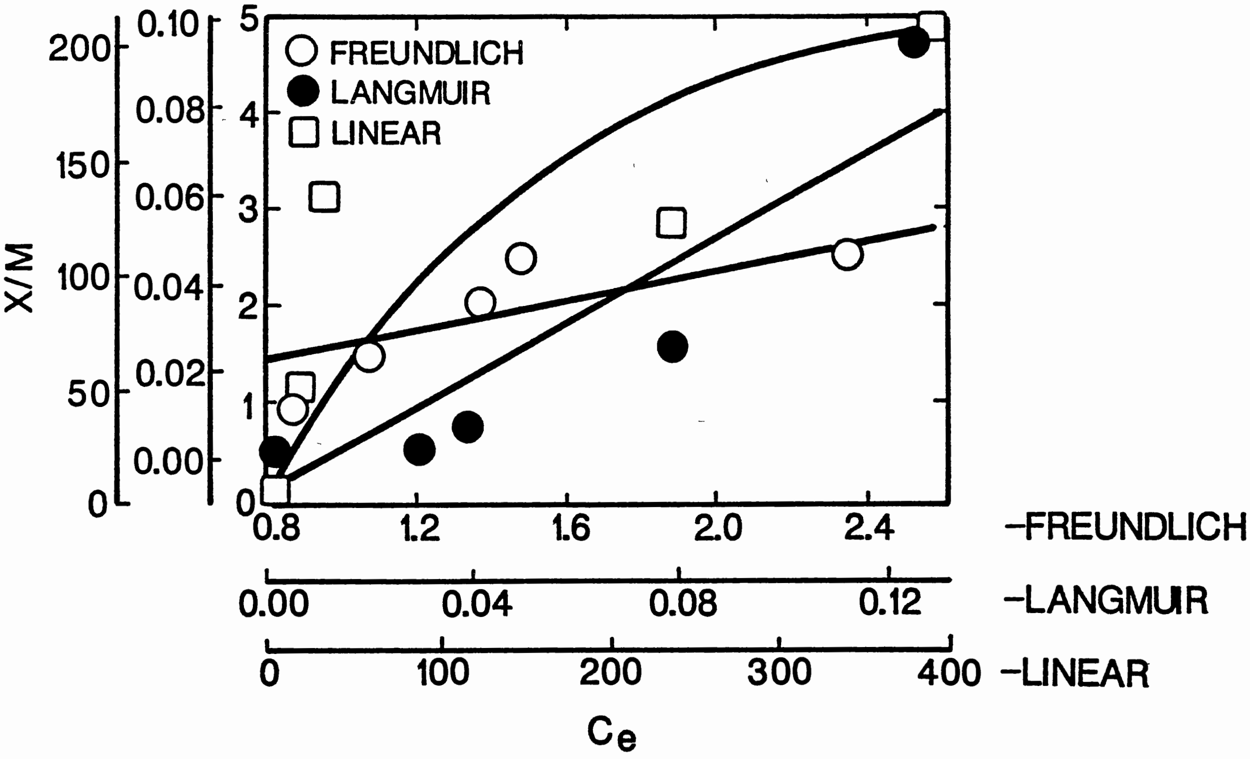
AI-4. Lindane Adsorption Isotherms (Whole Soil) on NRC Soil



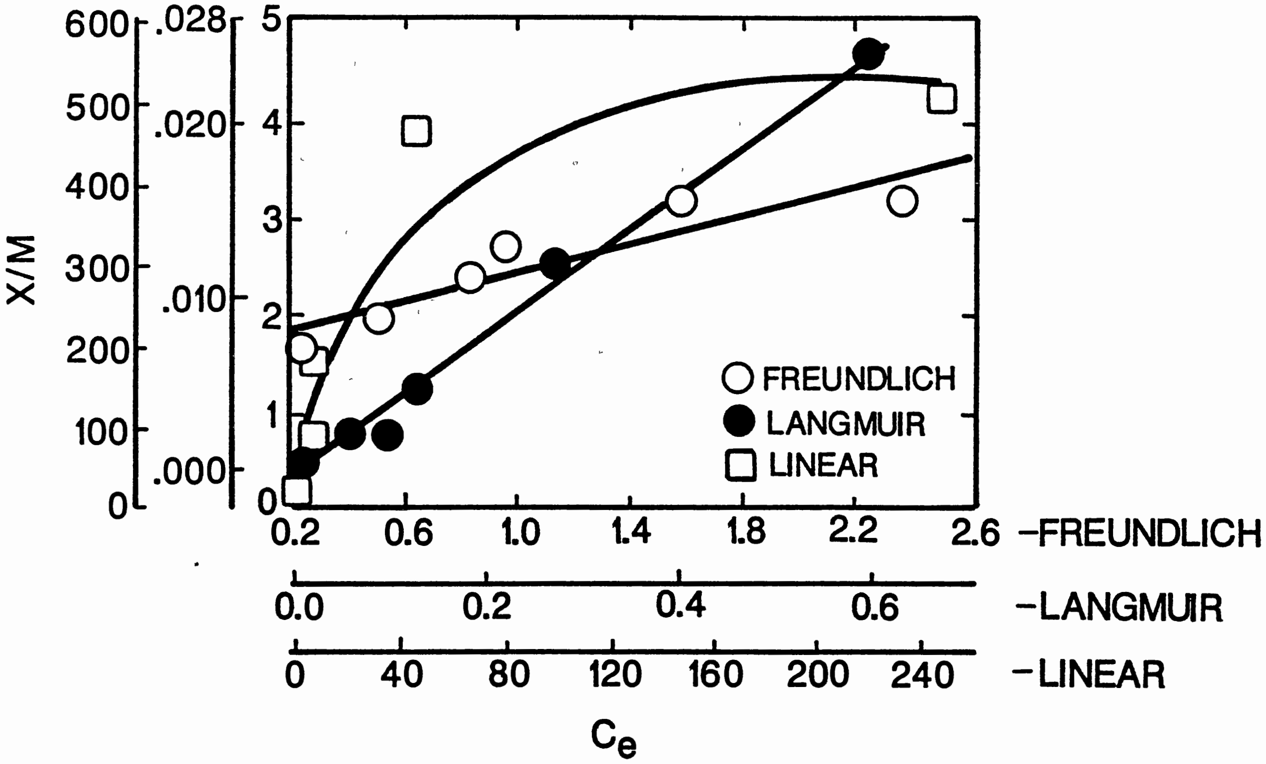
AI-5. Lindane Adsorption Isotherms (Soil 1) on NRC Soil



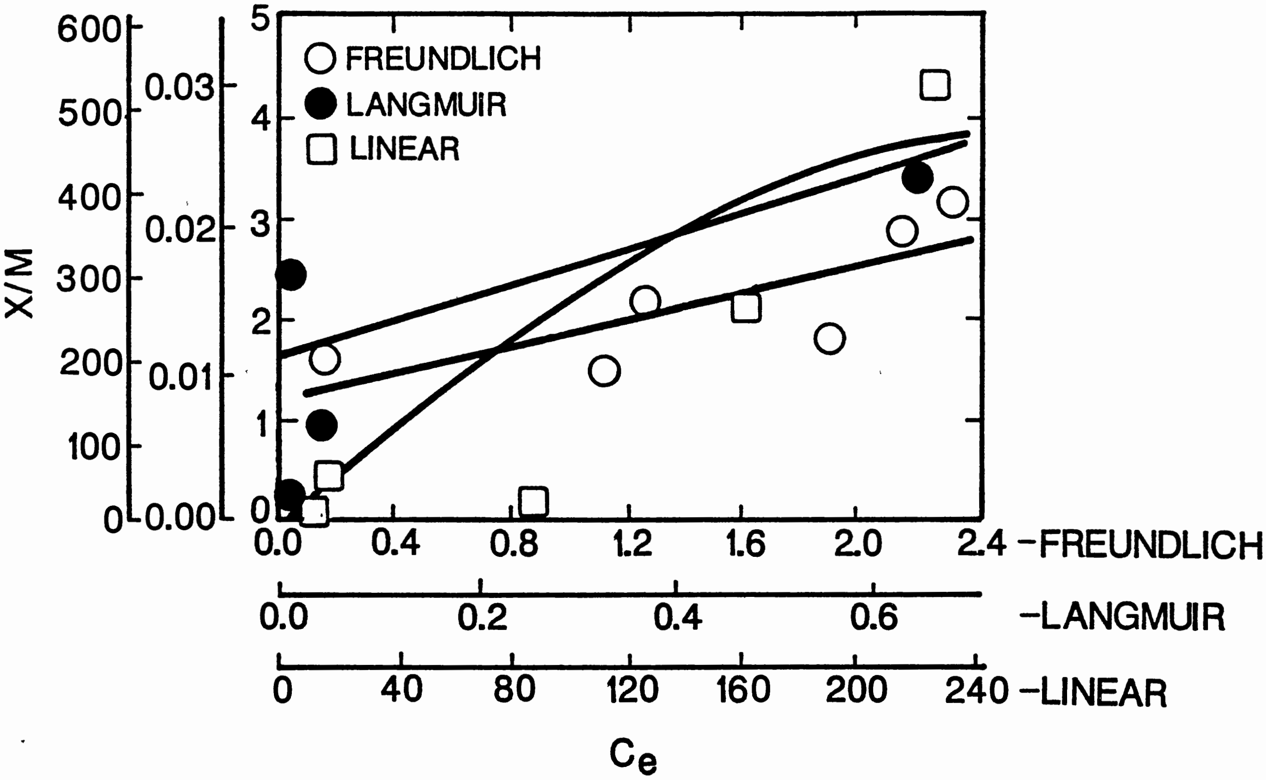
AI-6. Lindane Adsorption Isotherms (Soil 2)
on NRC Soil



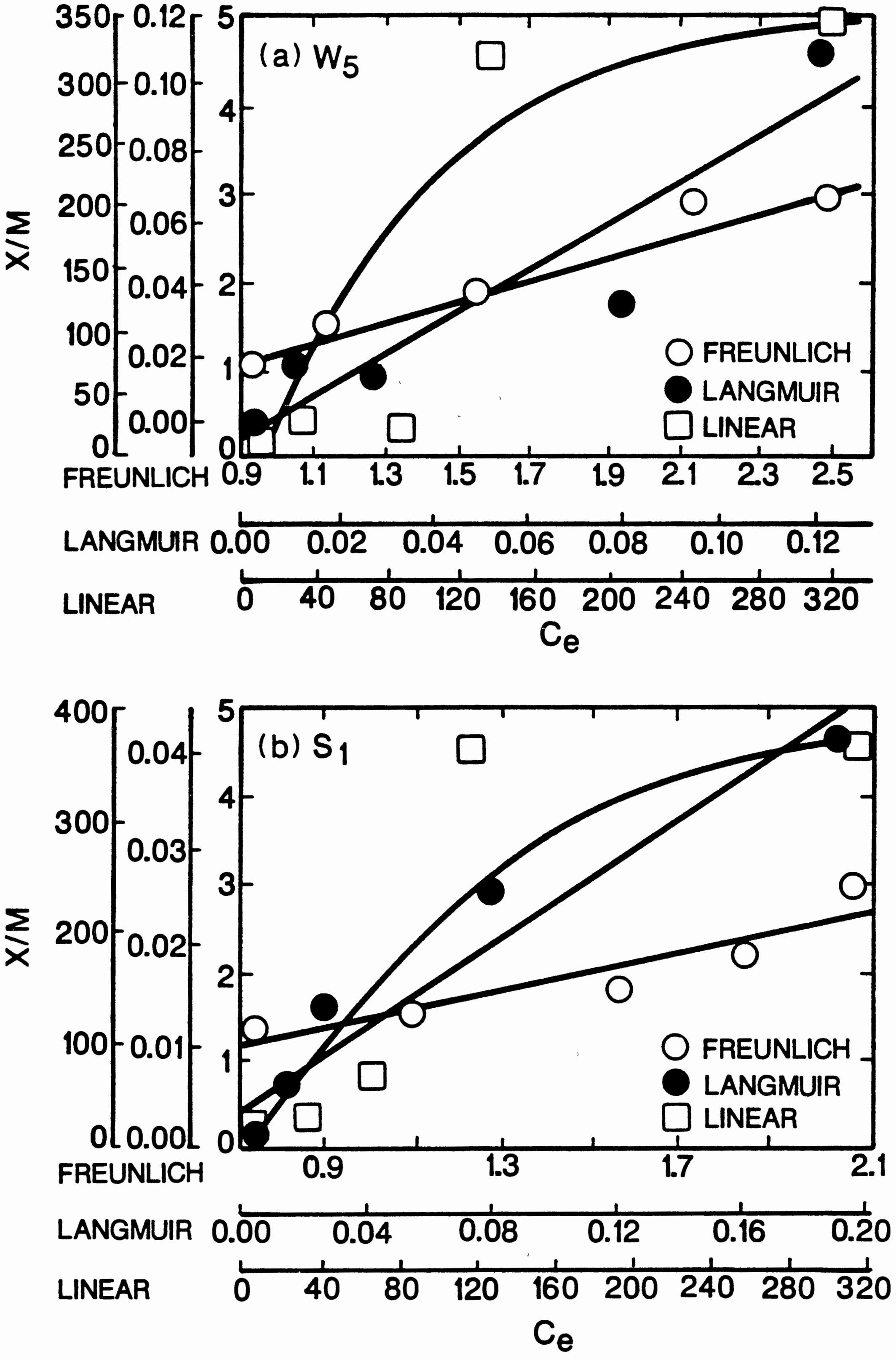
AI-7. Lindane Adsorption Isotherms (Soil 3)
on NRC Soil



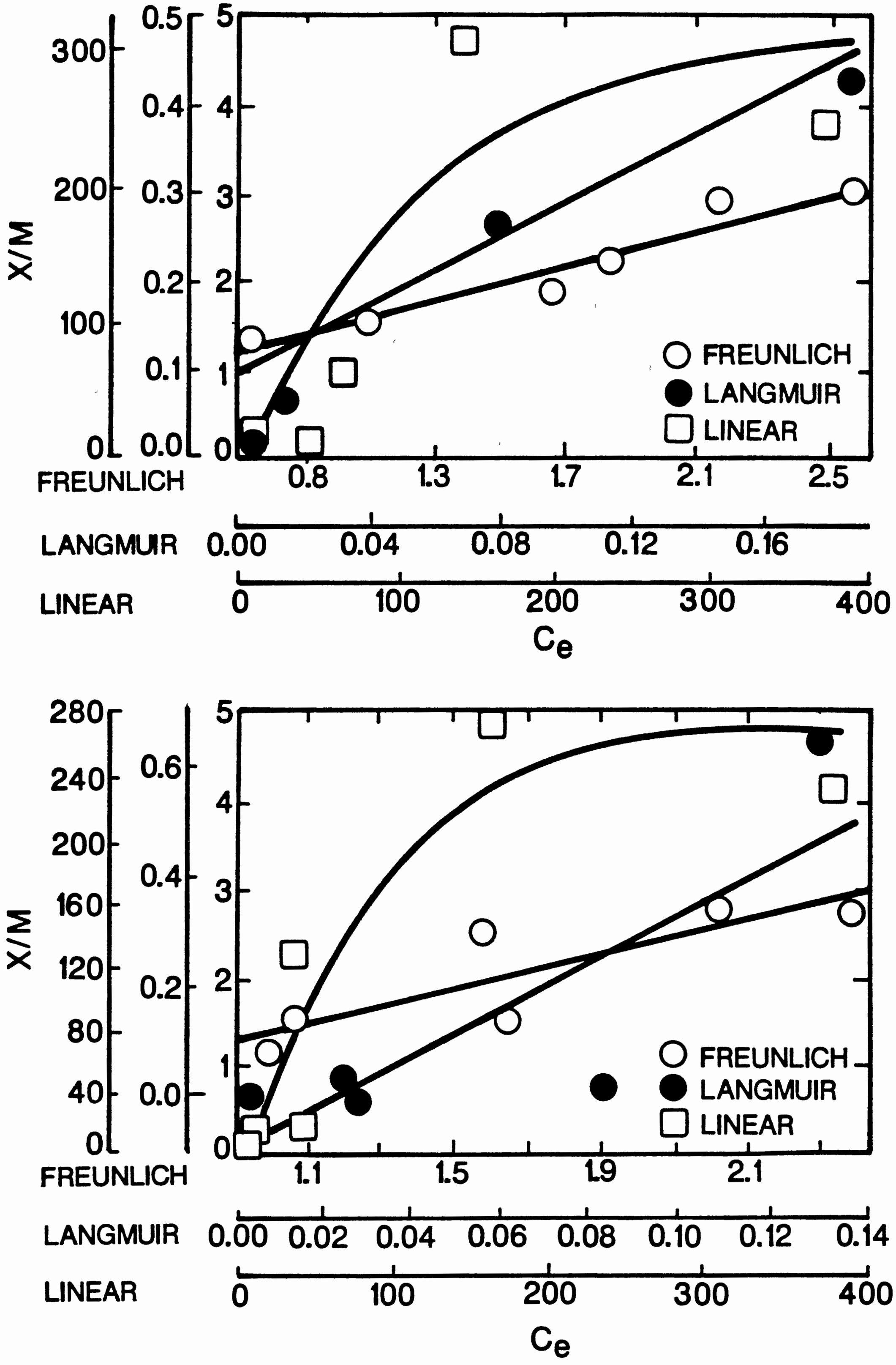
AI-8. Lindane Adsorption Isotherms (Soil 4) on NRC Soil



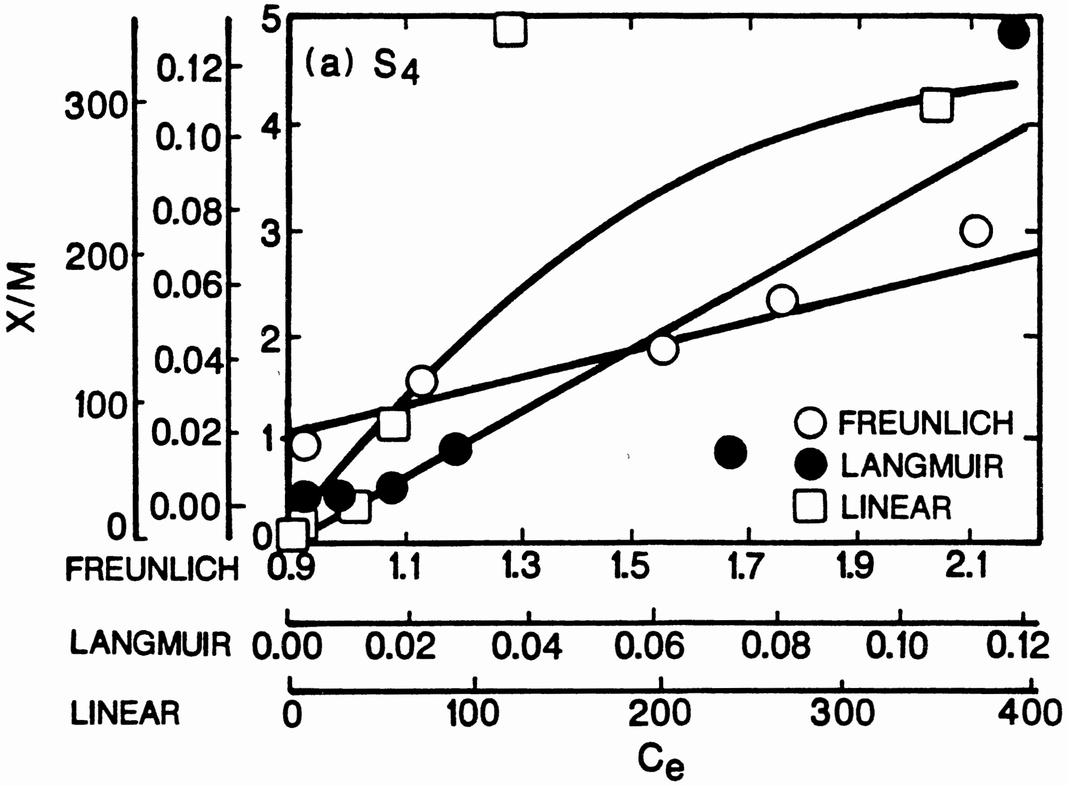
AI-9. Lindane Adsorption Isotherms (Soil 5)
on NRC Soil

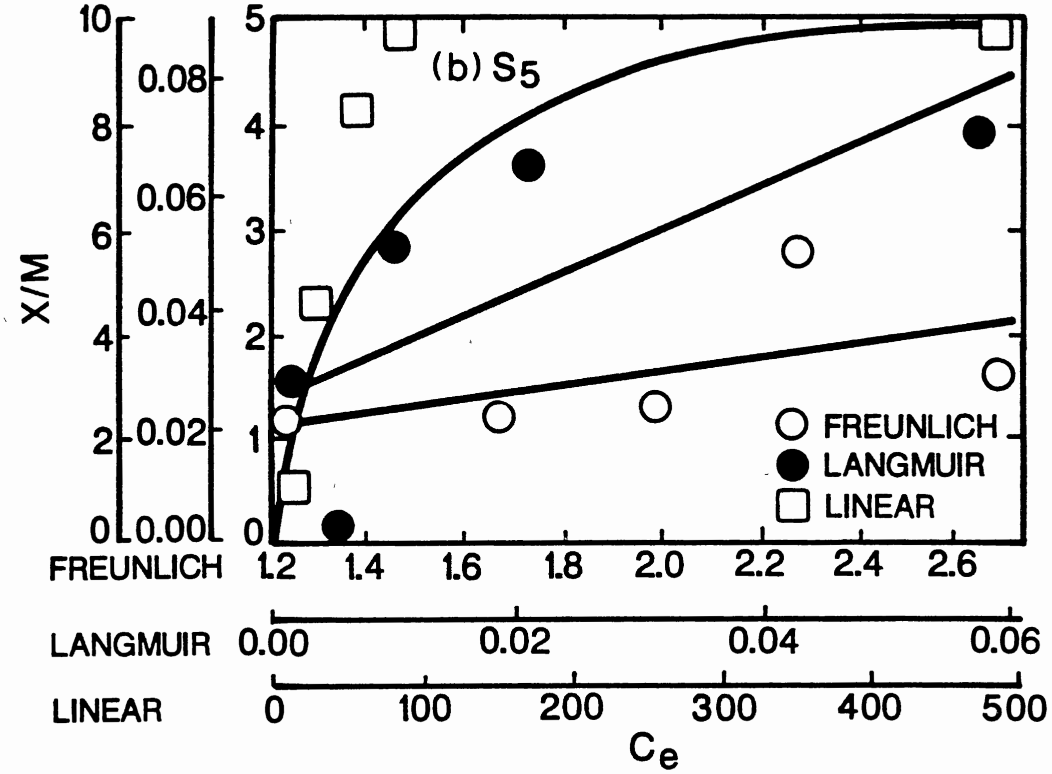


AI-10. Lindane Adsorption Isotherms (a) WS, (b) S1
on Port Soil

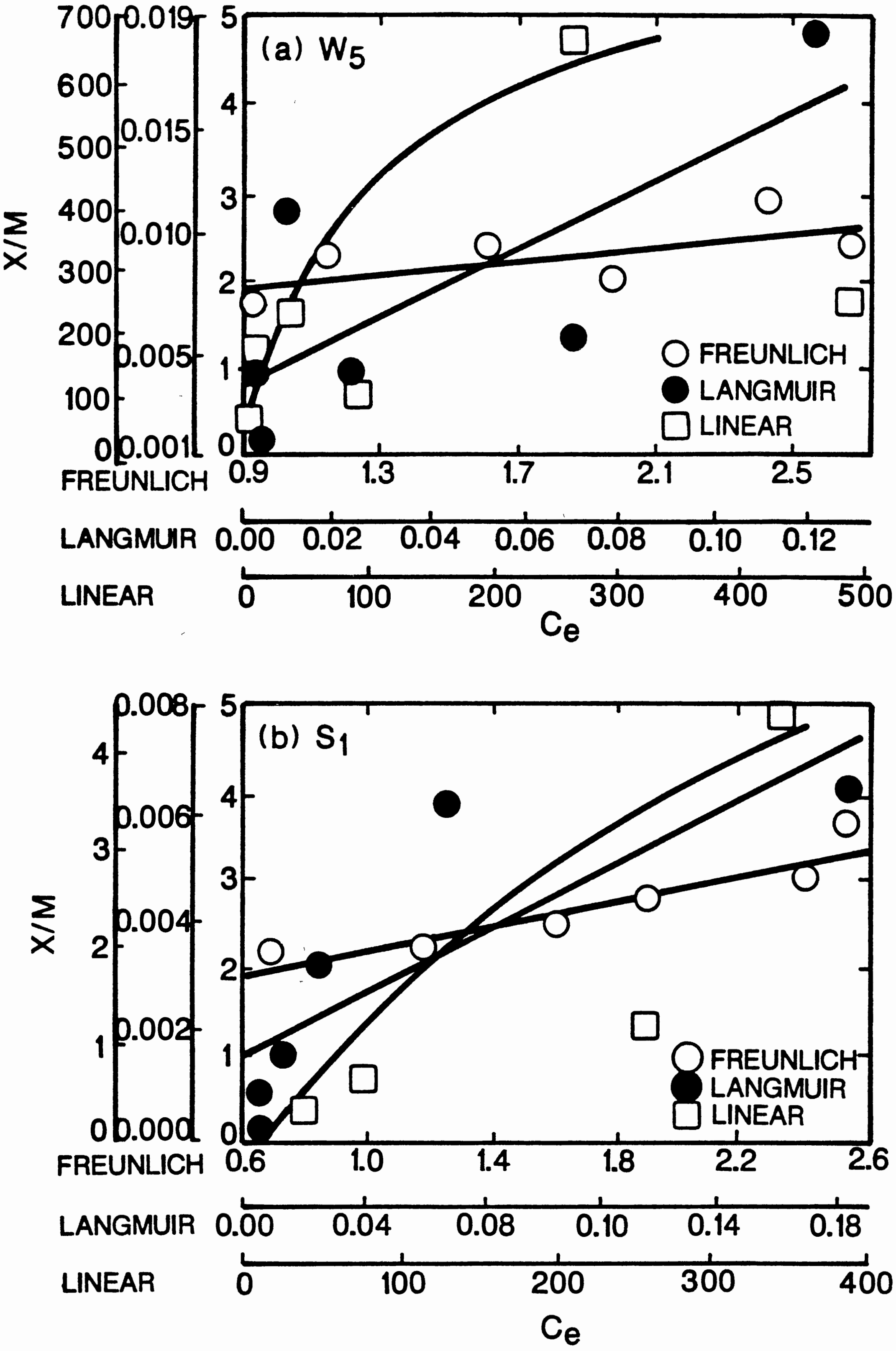


AI-11. Lindane Adsorption Isotherms (a) S2, (b) S3
on Port Soil

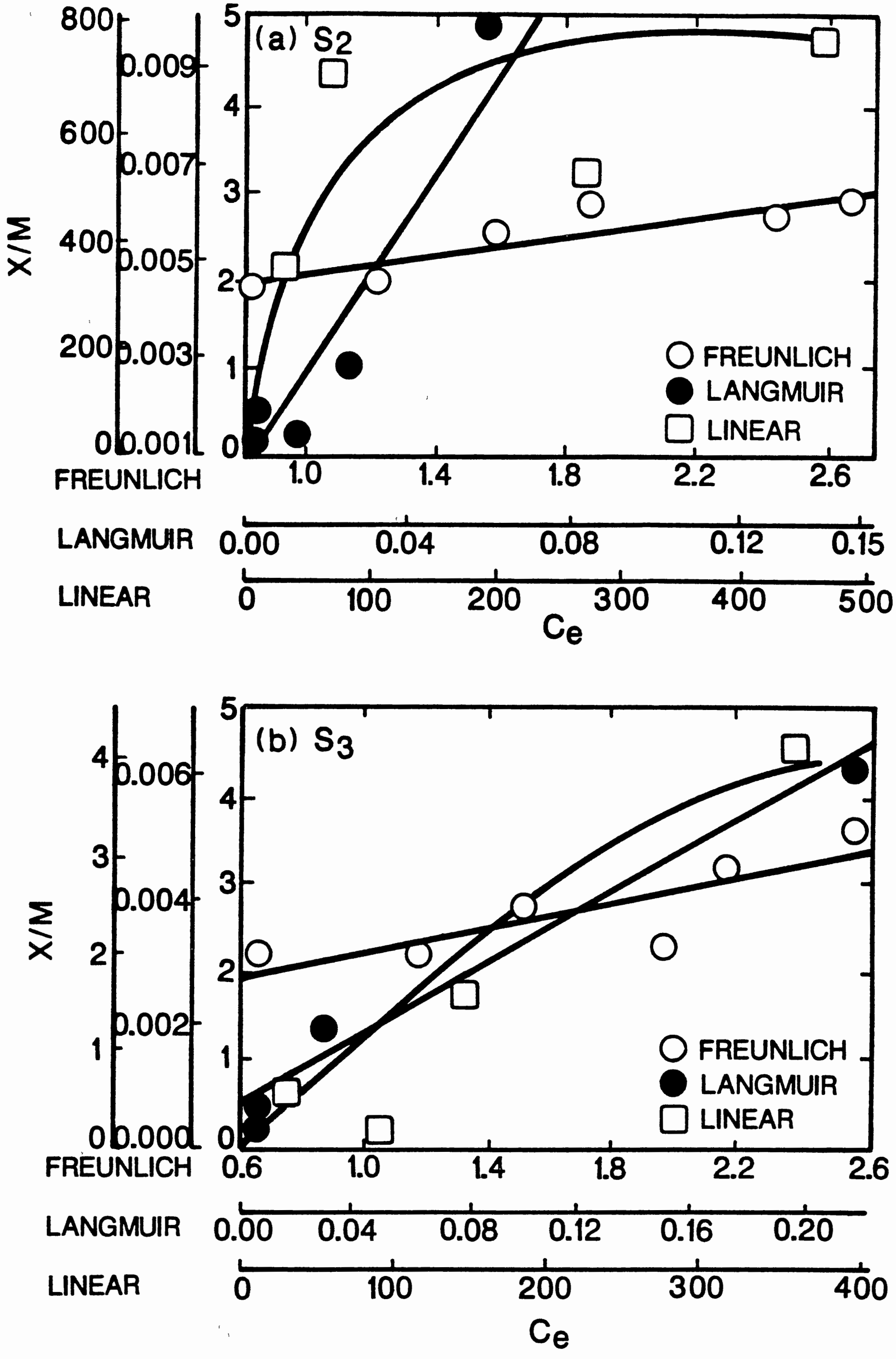




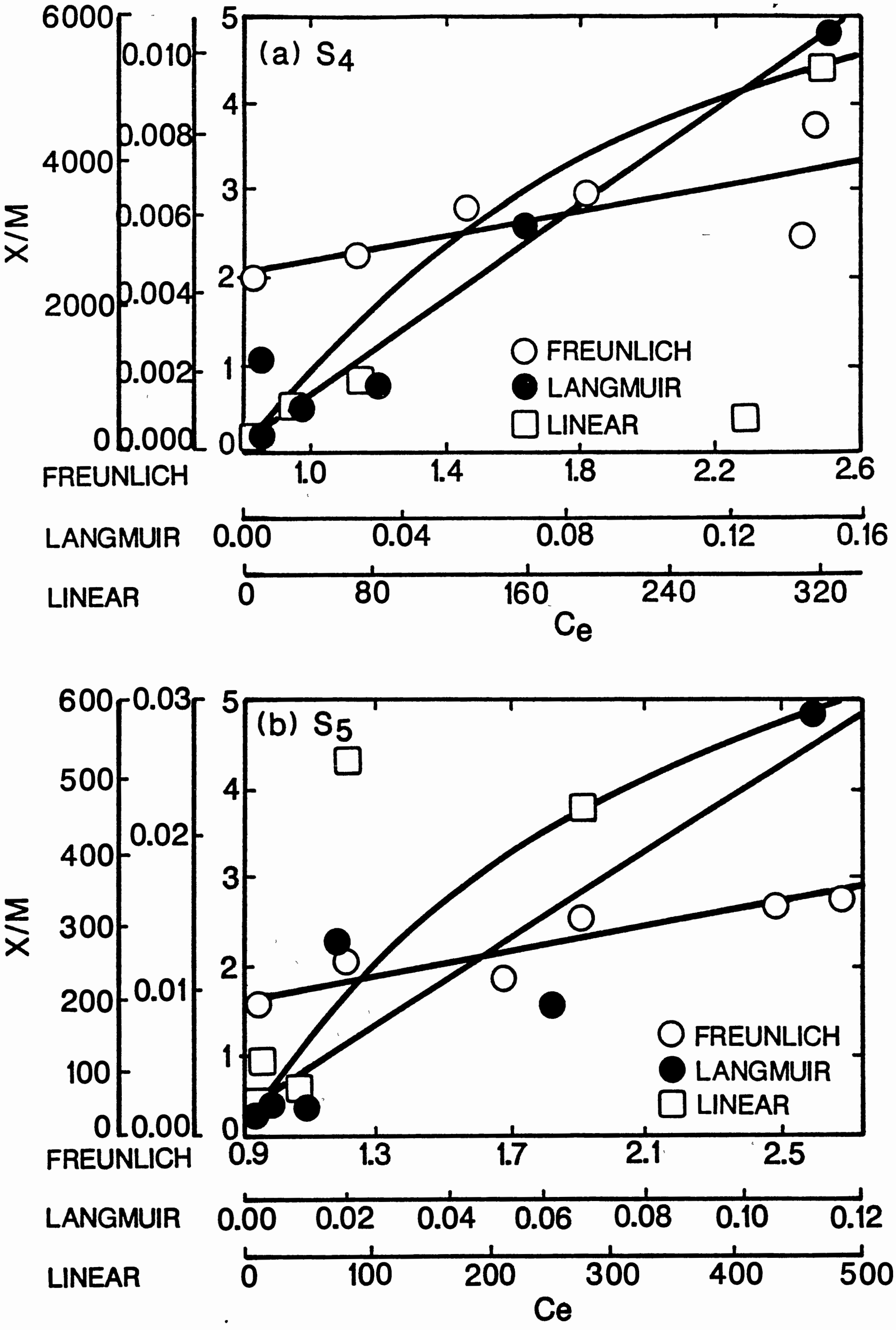
AI-12. Lindane Adsorption Isotherms (a) S4, (b) S5 on Port Soil



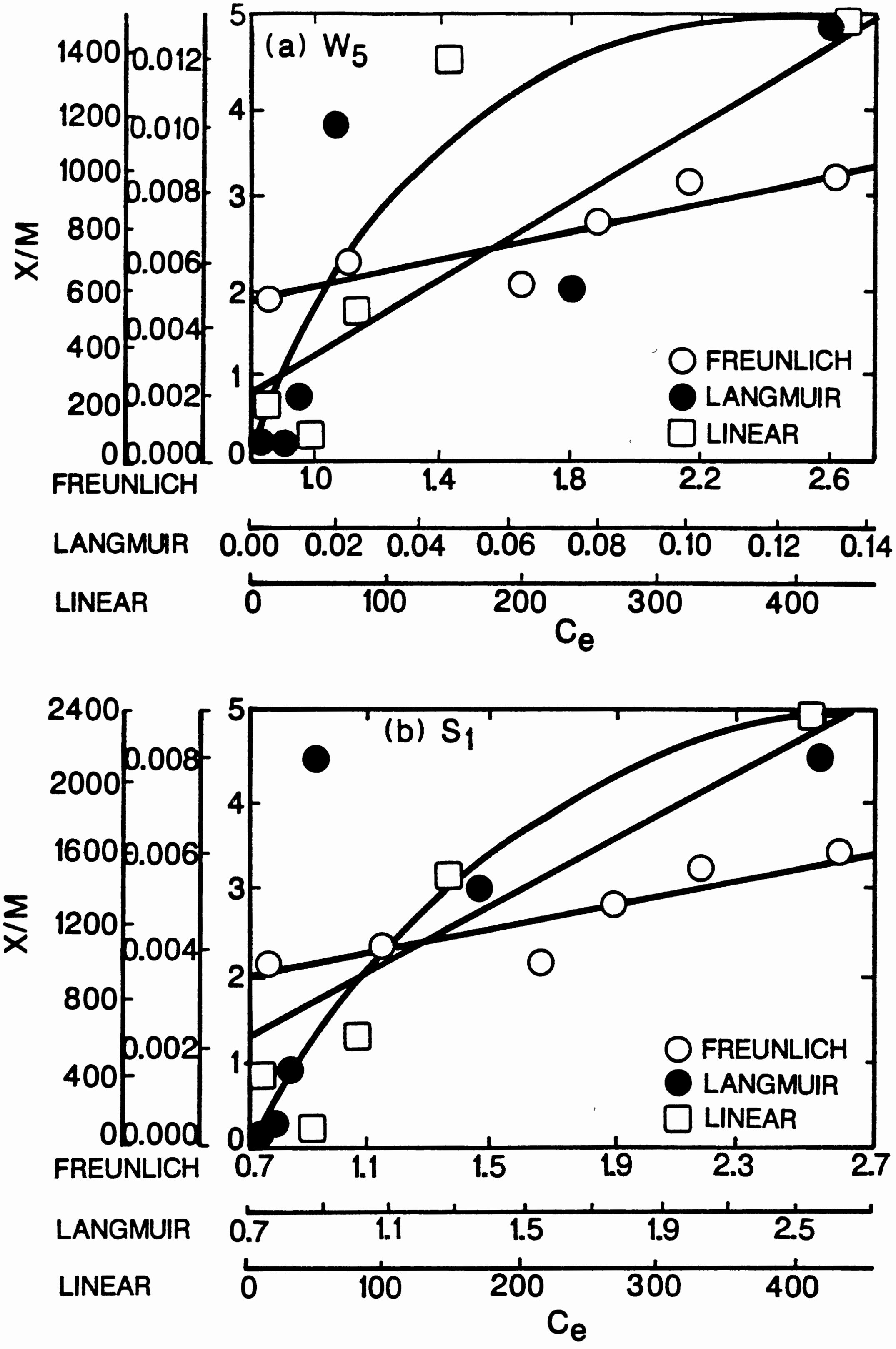
AI-13. Silvex Adsorption Isotherms (a) WS, (b) S1
on NRC Soil



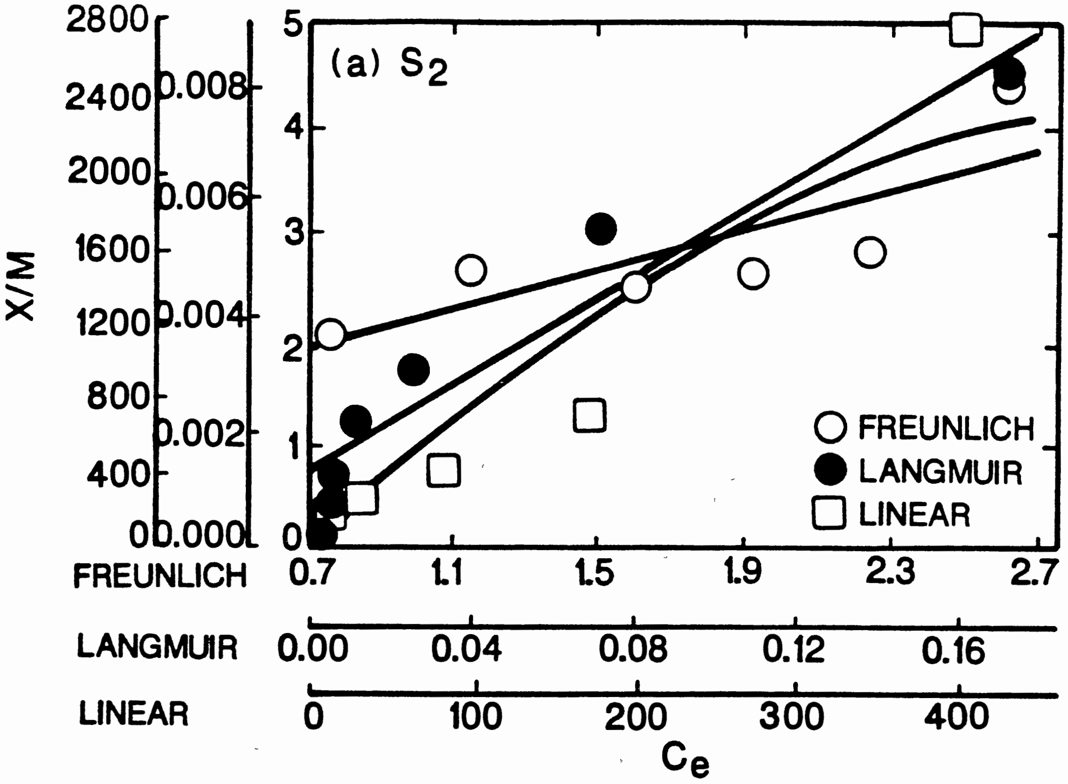
AI-14. Silvex Adsorption Isotherms (a) S2, (b) S3
on NRC Soil

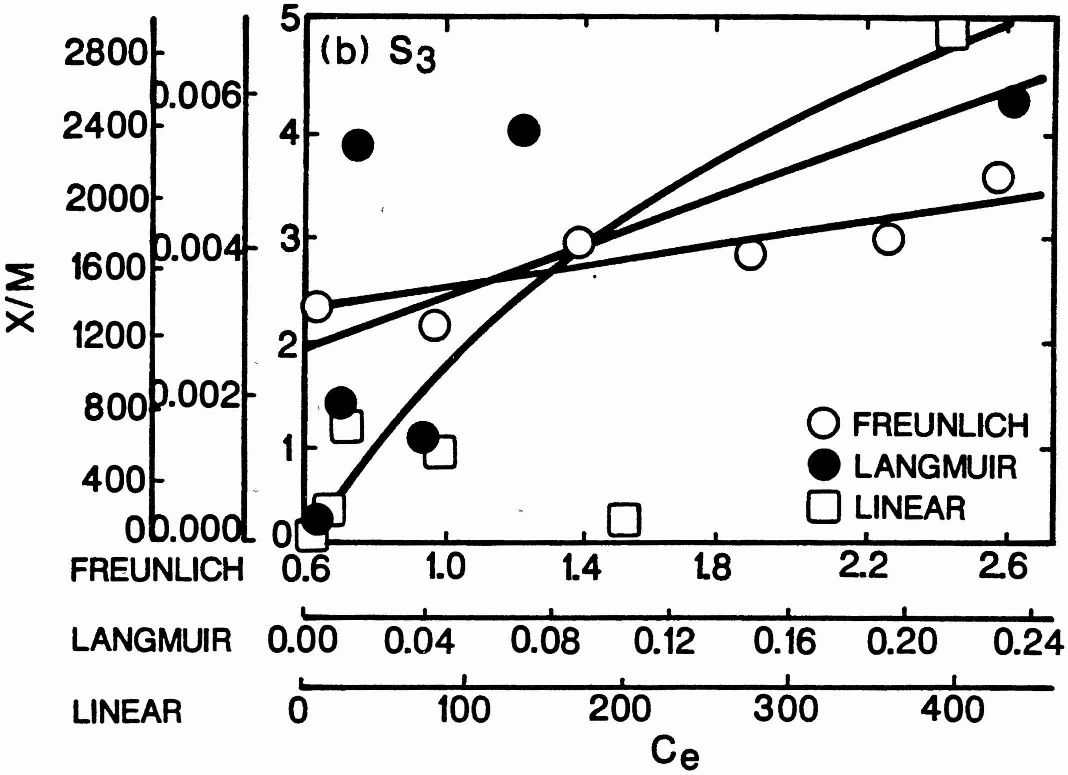


AI-15. Silvex Adsorption Isotherms (a) S4, (b) S5 on NRC Soil

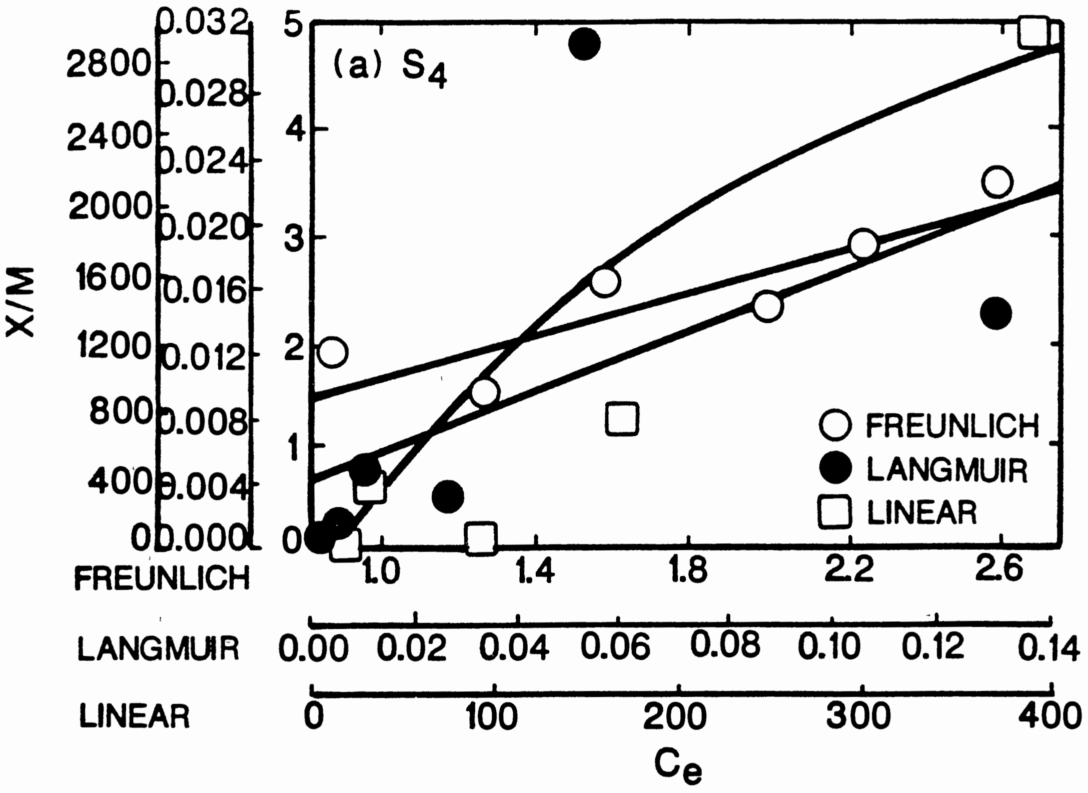


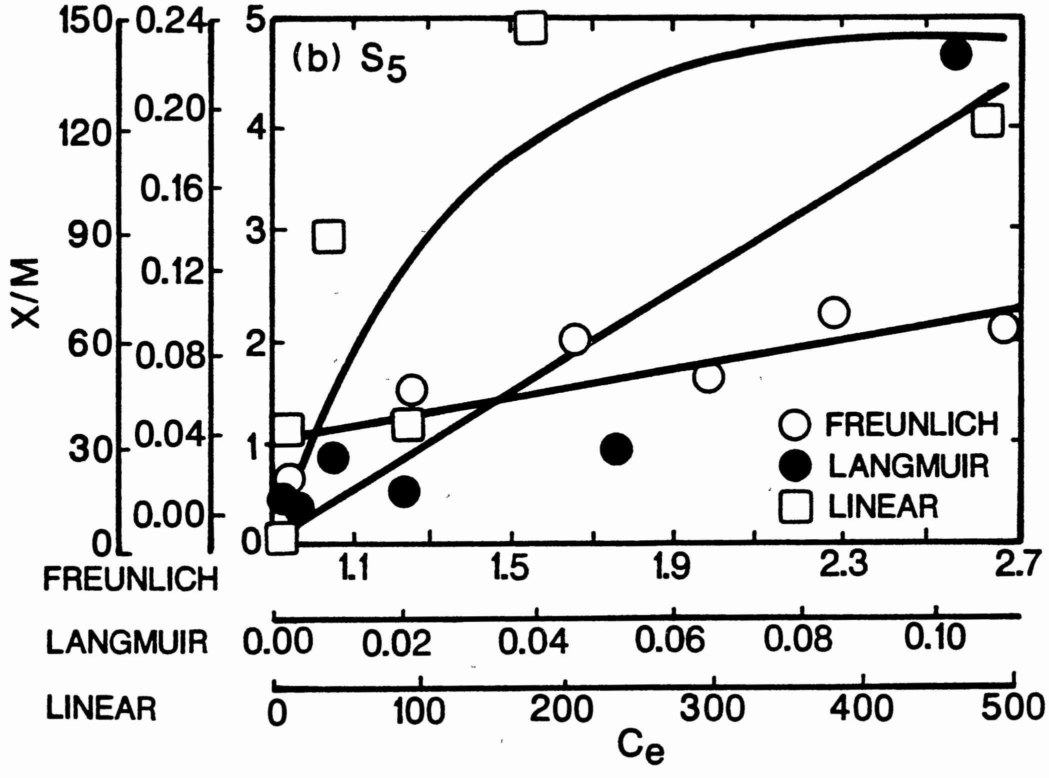
AI-16. Silvex Adsorption Isotherms (a) WS, (b) S1
on Port Soil



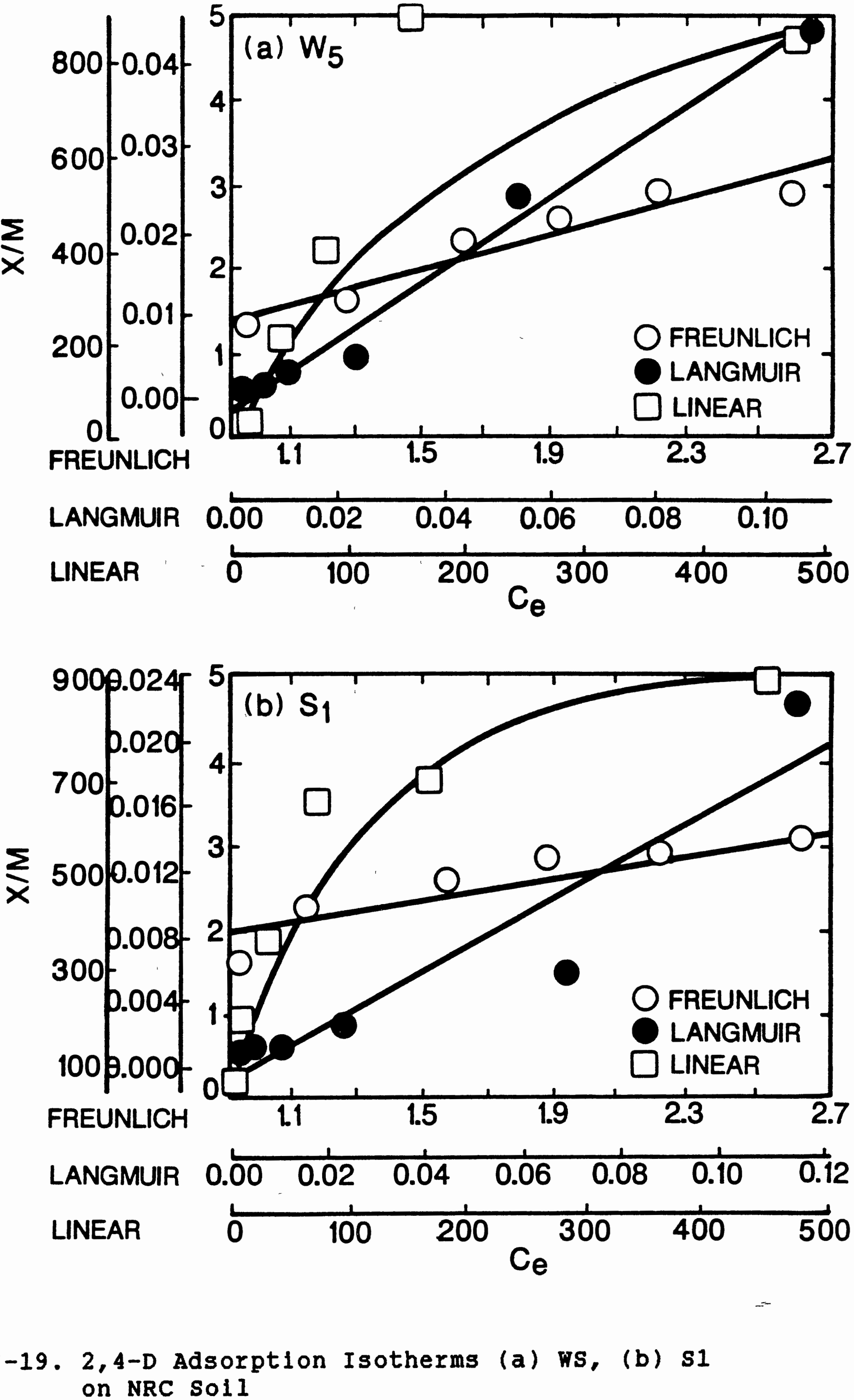


AI-17. Silvex Adsorption Isotherms (a) S2, (b) S3 on Port Soil

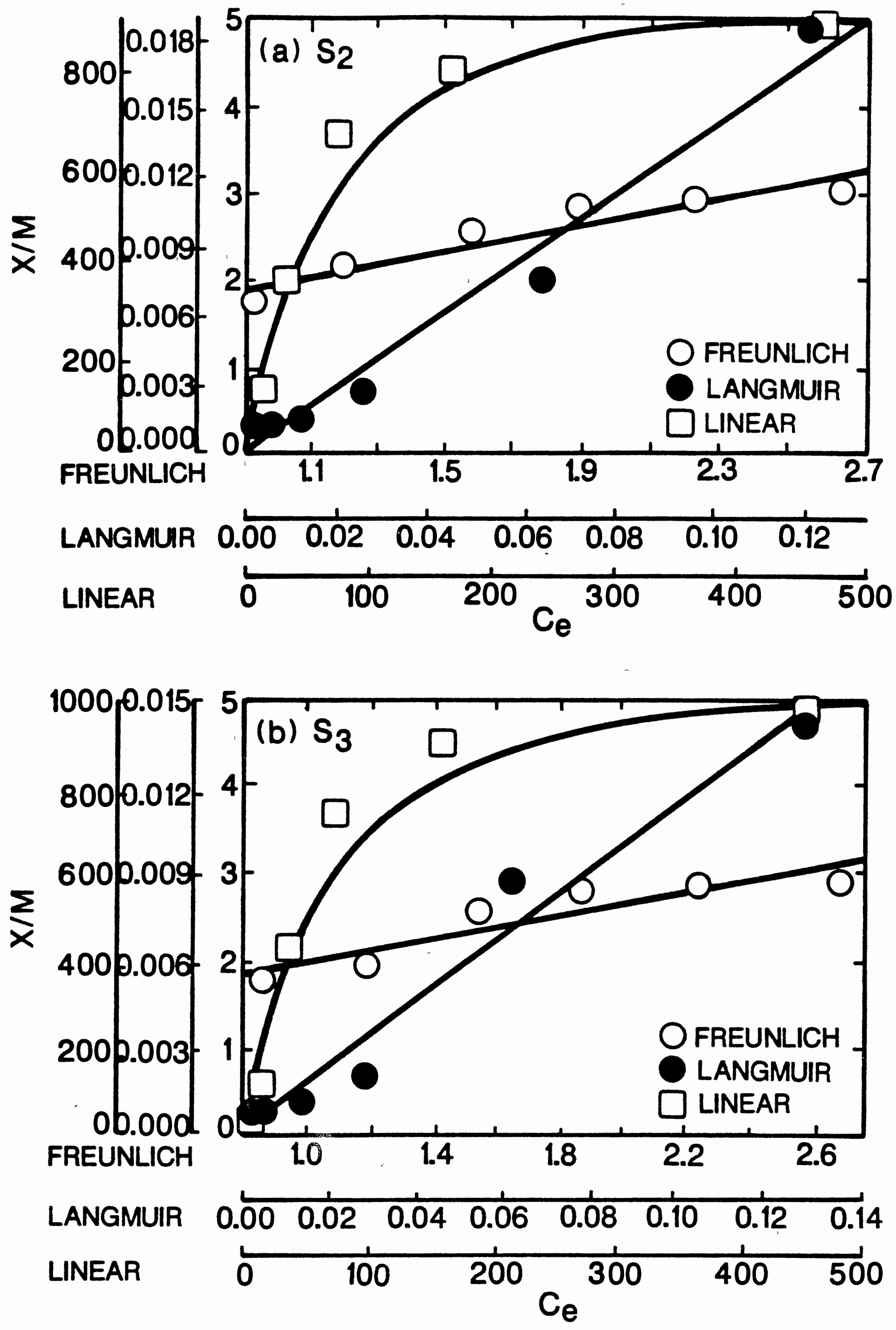




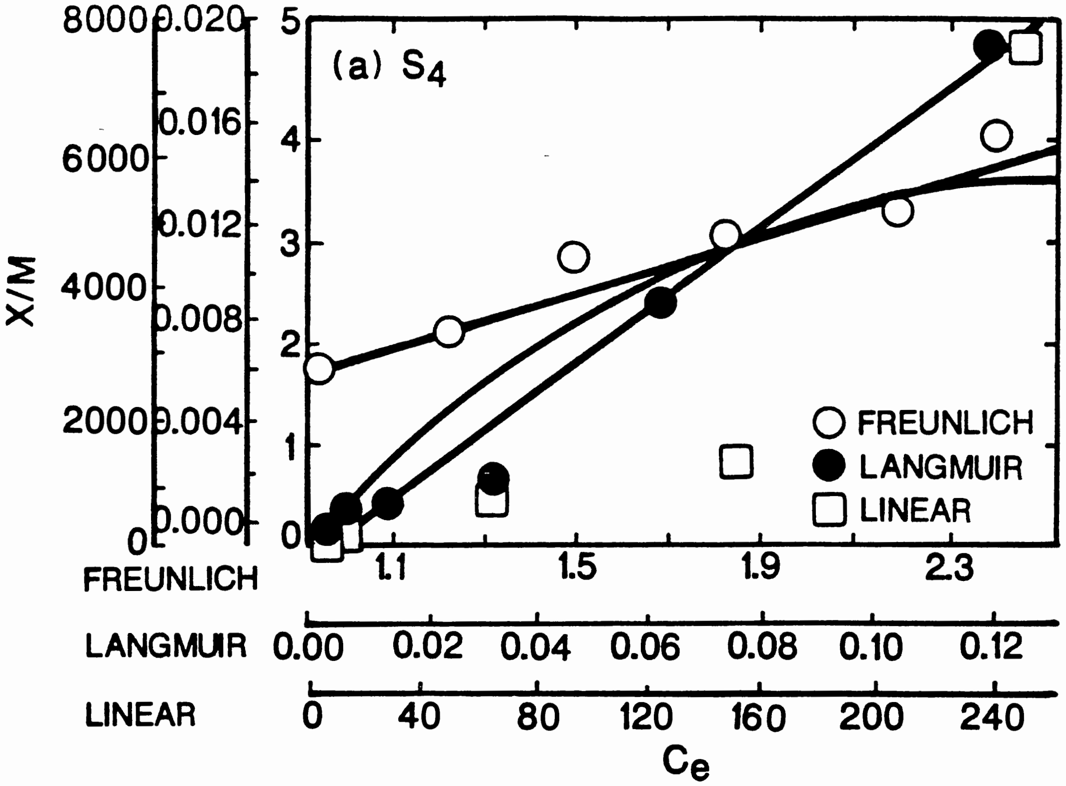
AI-18. Silvex Adsorption Isotherms (a) S4, (b) S5
on Port Soil

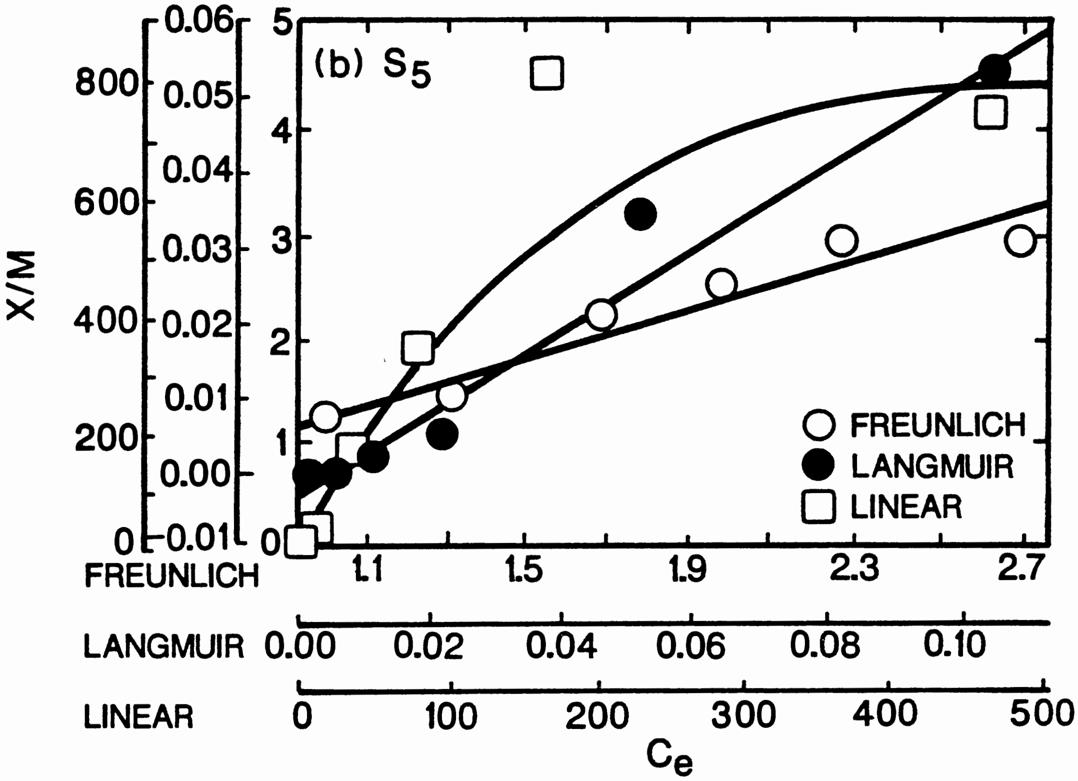


AI-19. 2,4-D Adsorption Isotherms (a) WS, (b) S1 on NRC Soil

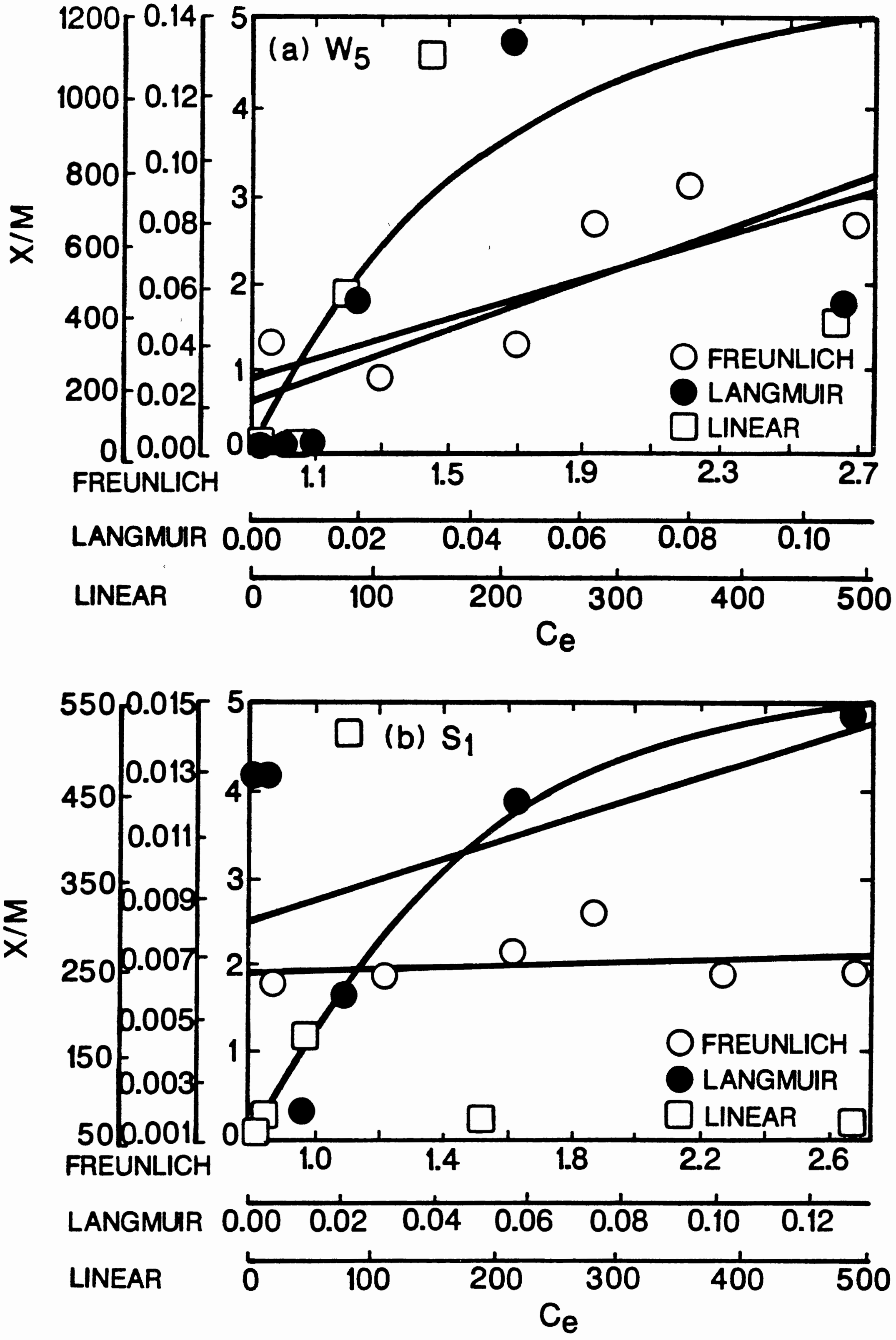


AI-20. 2,4-D Adsorption Isotherms (a) S2, (b) S3 on NRC Soil

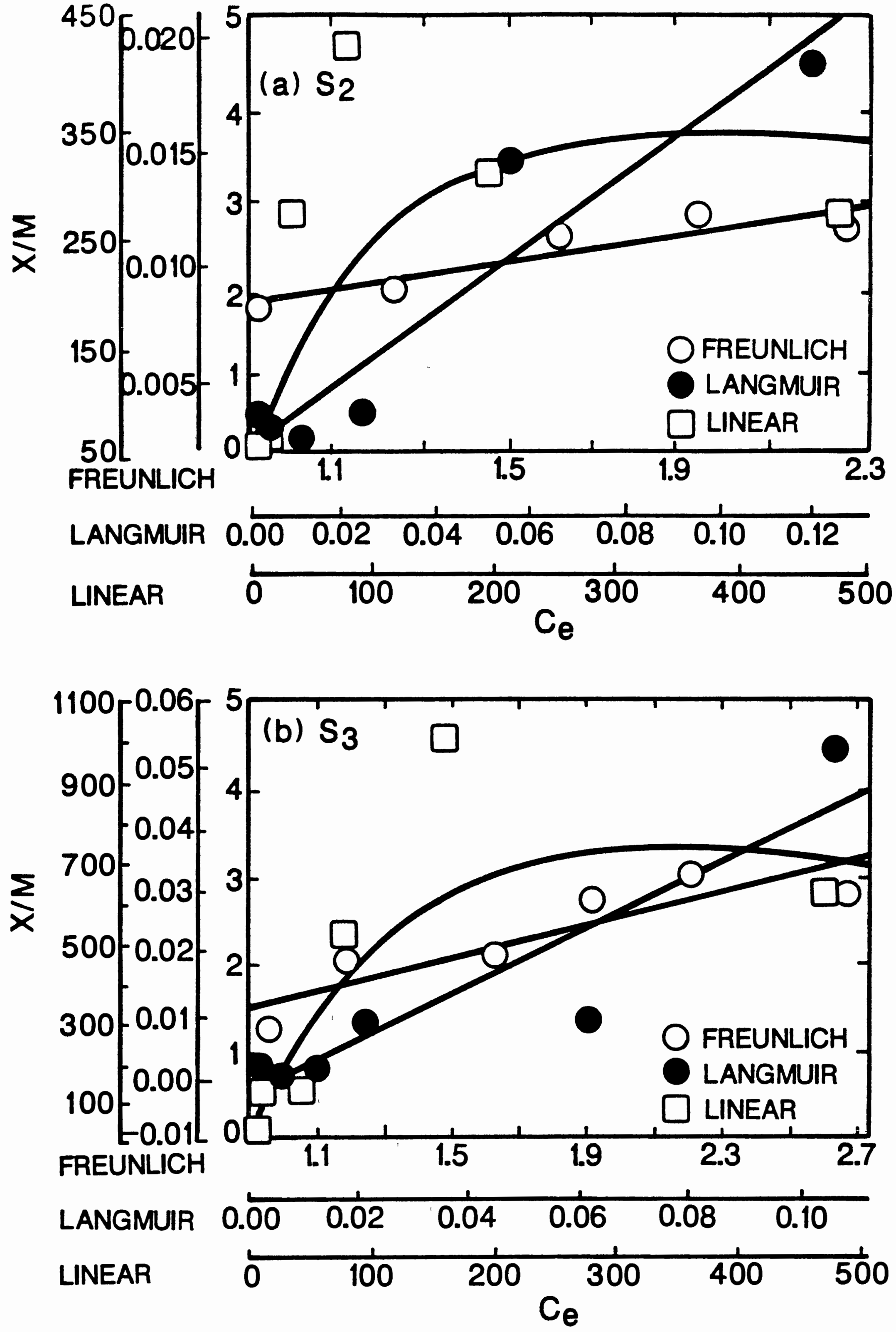




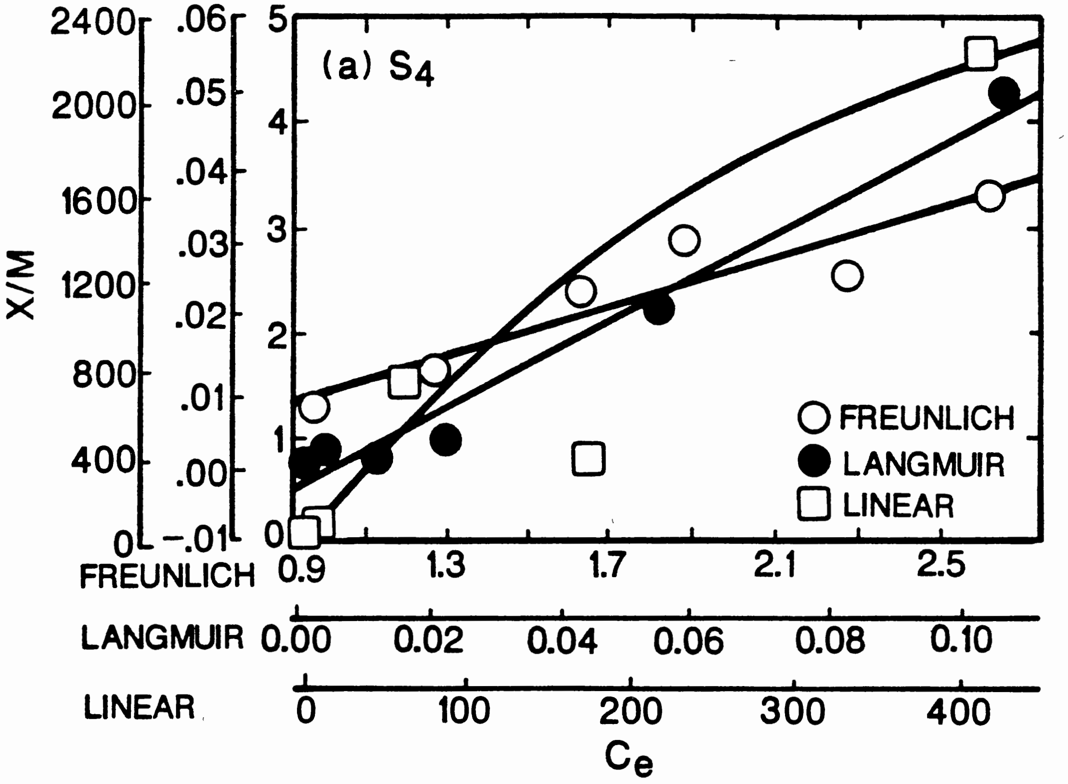
AI-21. 2,4-D Adsorption Isotherms (a) S4, (b) S5 on NRC Soil

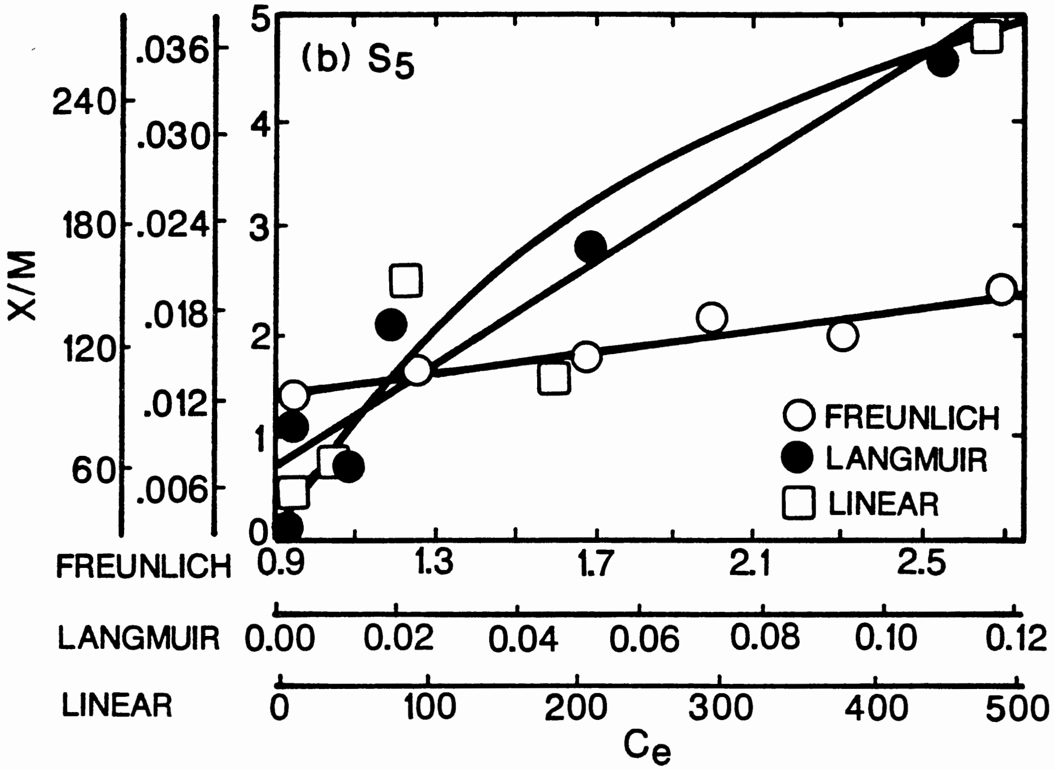


AI-22. 2,4-D Adsorption Isotherms (a) WS, (b) S1 on Port Soil



AI-23. 2,4-D Adsorption Isotherms (a) S2, (b) S3 on Port Soil

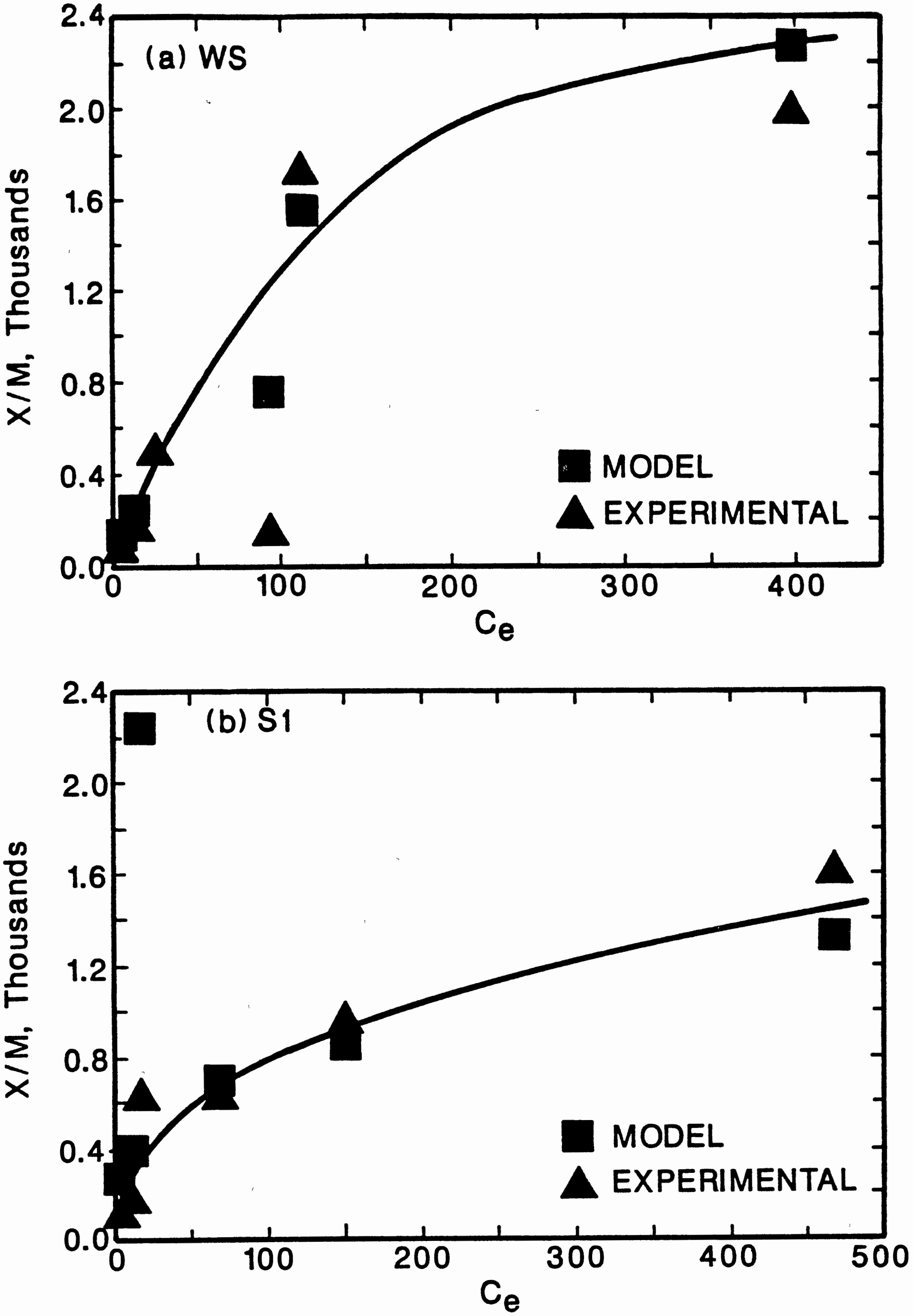




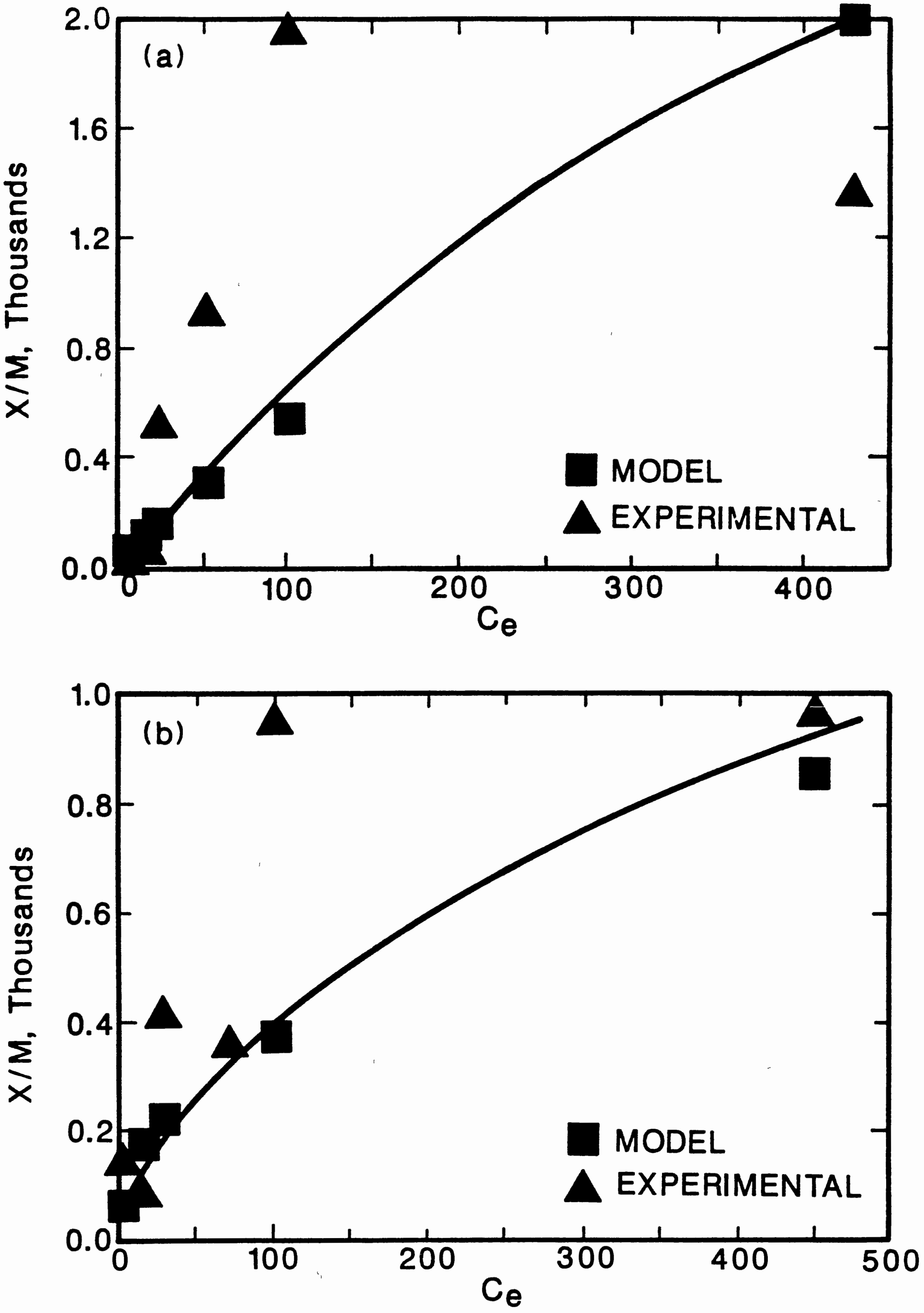
AI-24. 2,4-D Adsorption Isotherms (a) S4, (b) S5 on Port Soil

APPENDIX B

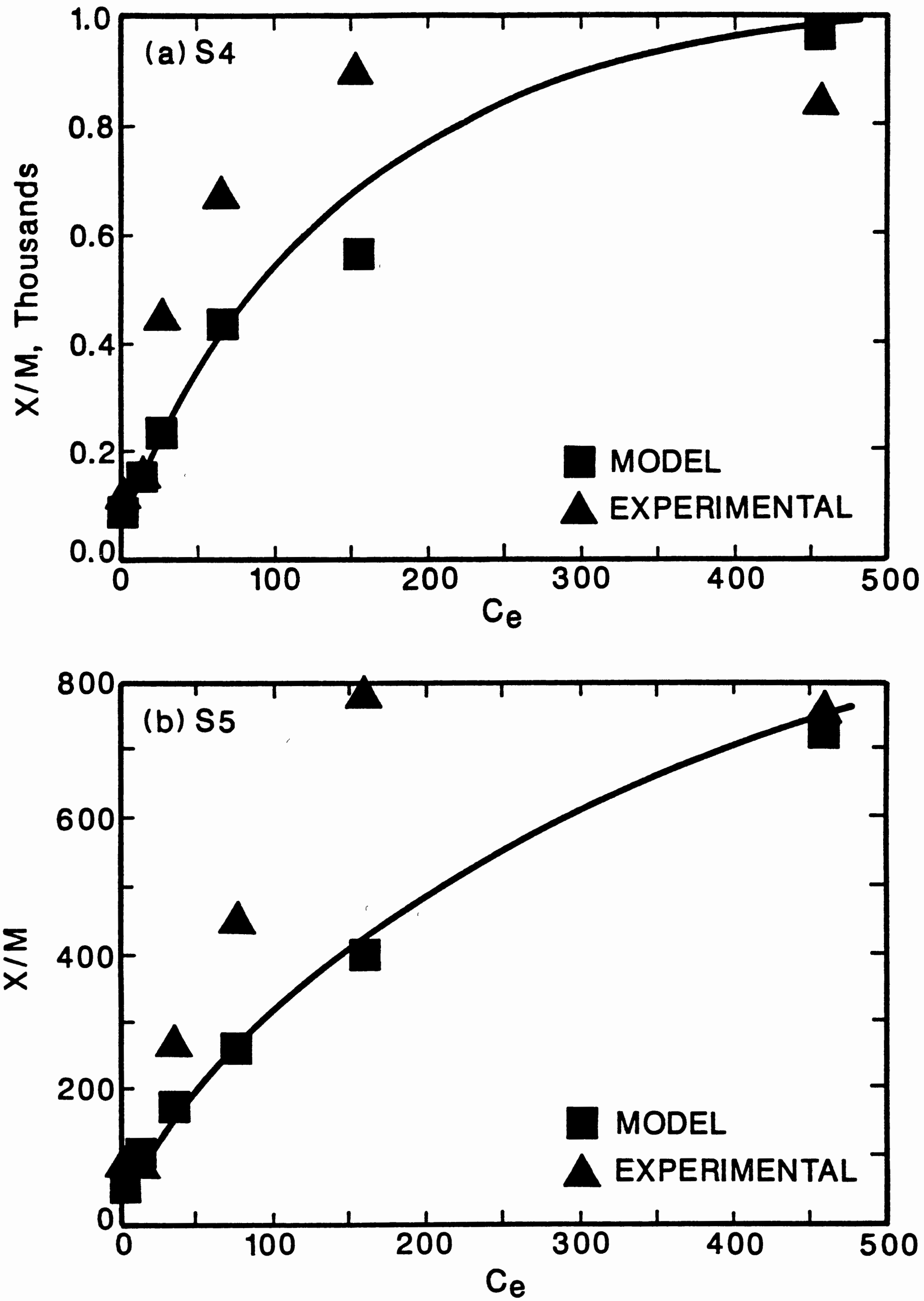
SRS MULTIPLE FREUNDLICH-TYPE ISOTHERMS FOR LINDANE, SILVEX AND 2,4-D IN BINARY SYSTEMS ON PORT SOIL AND SOIL FRACTIONS



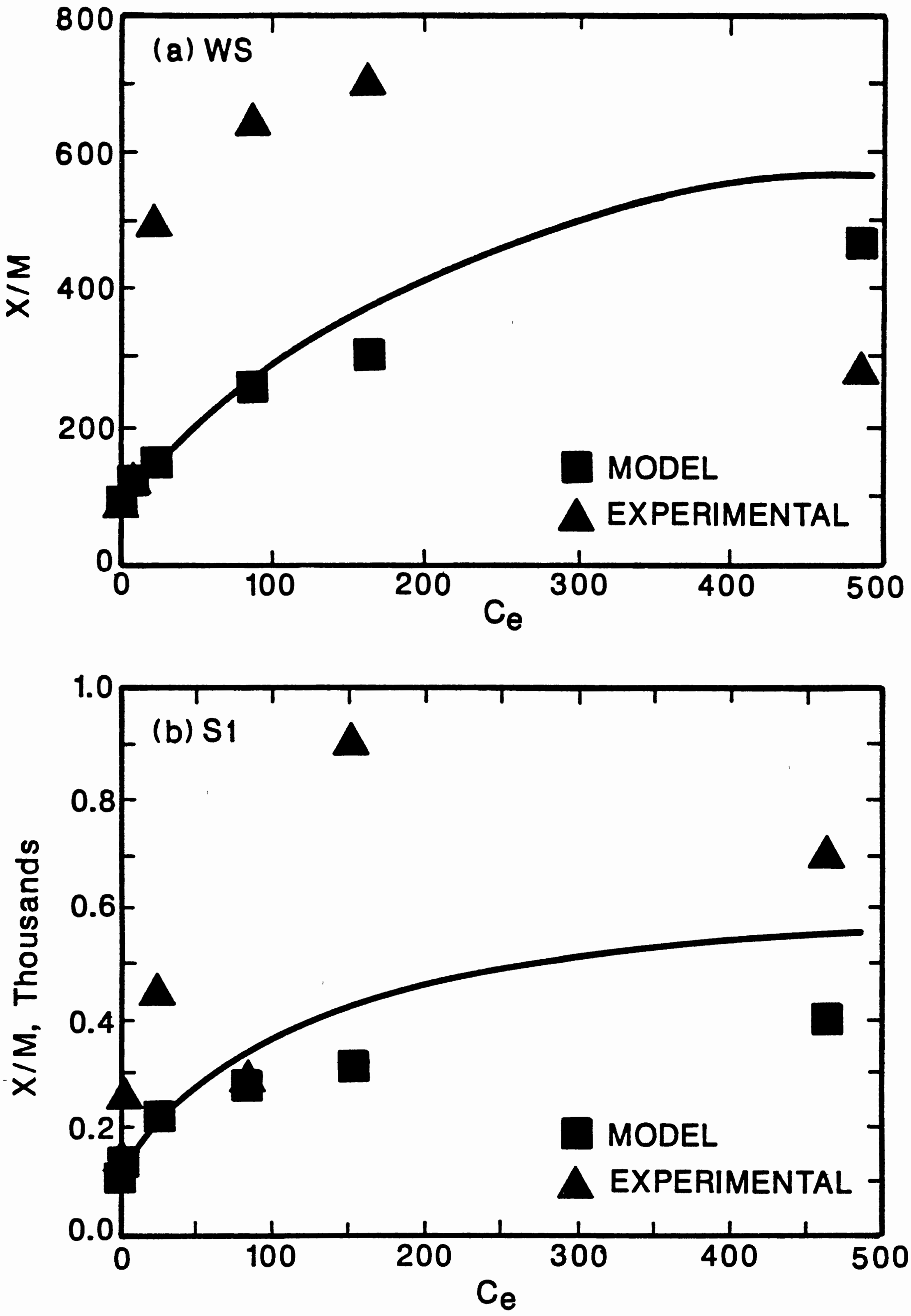
AII-1. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) WS, (b) S1 at 25°C



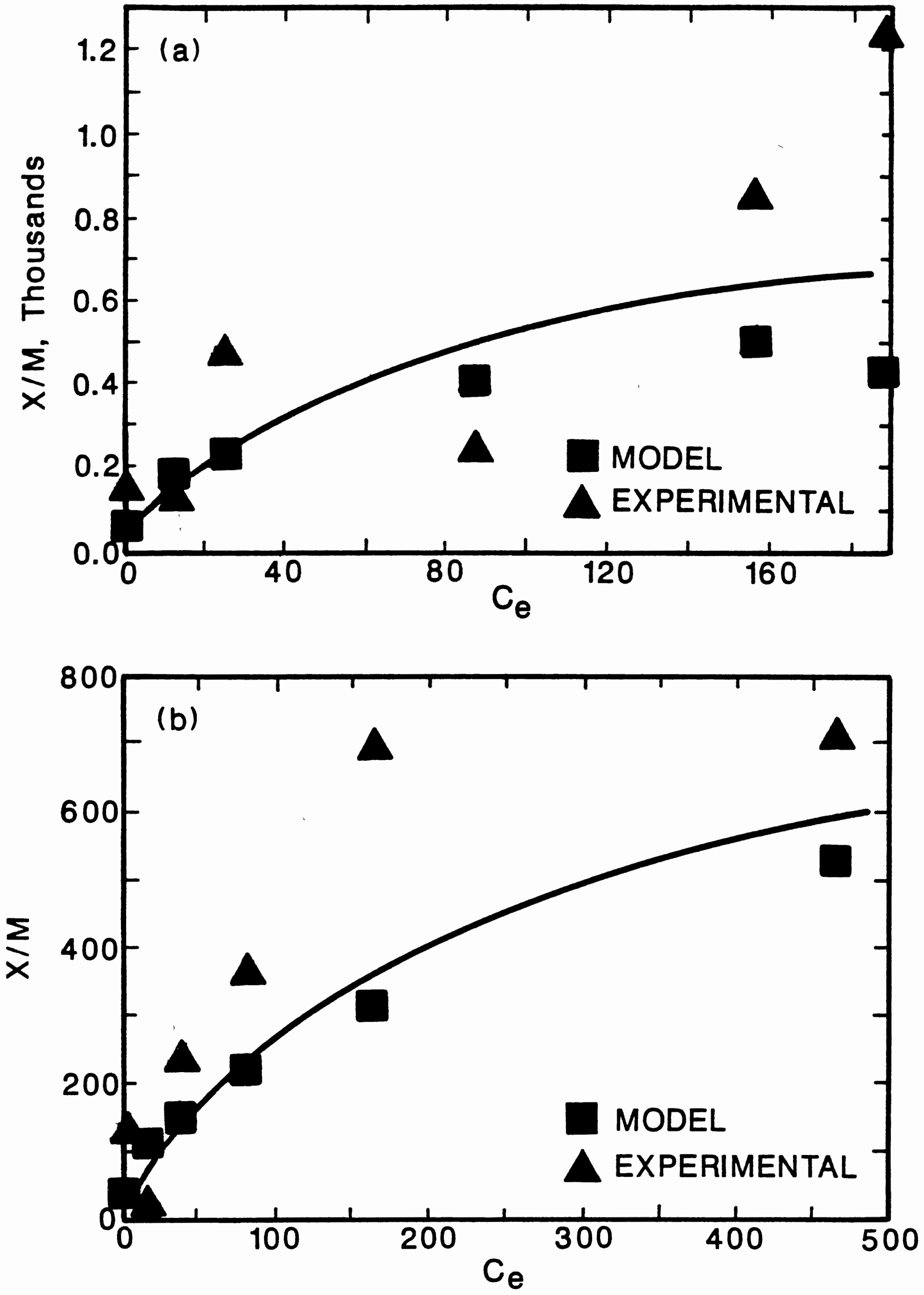
AII-2. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) S2, (b) S3 at 25°C



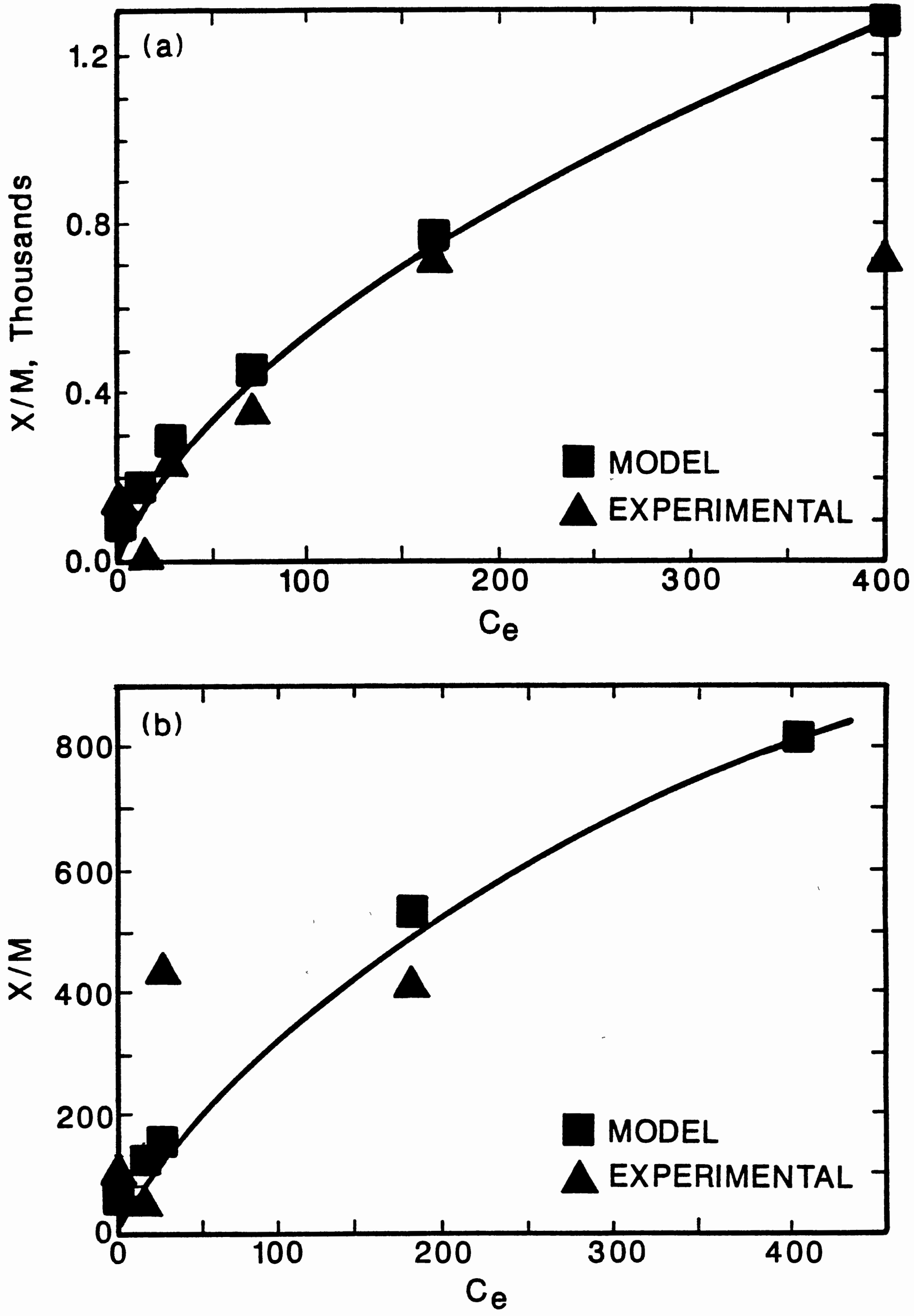
AII-3. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) S4, (b) S5 at 25°C



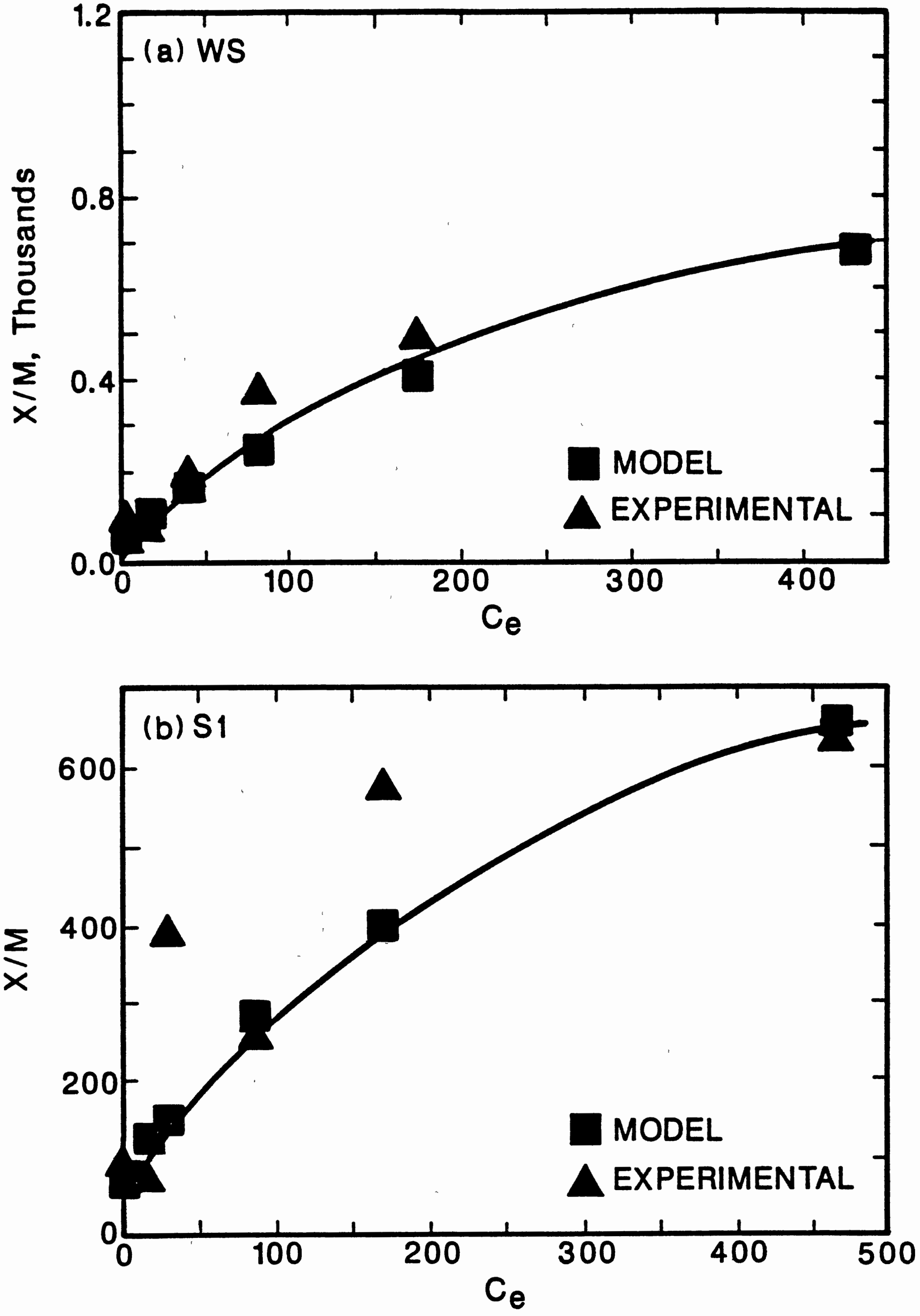
AII-4. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) WS, (b) S1 at 30°C



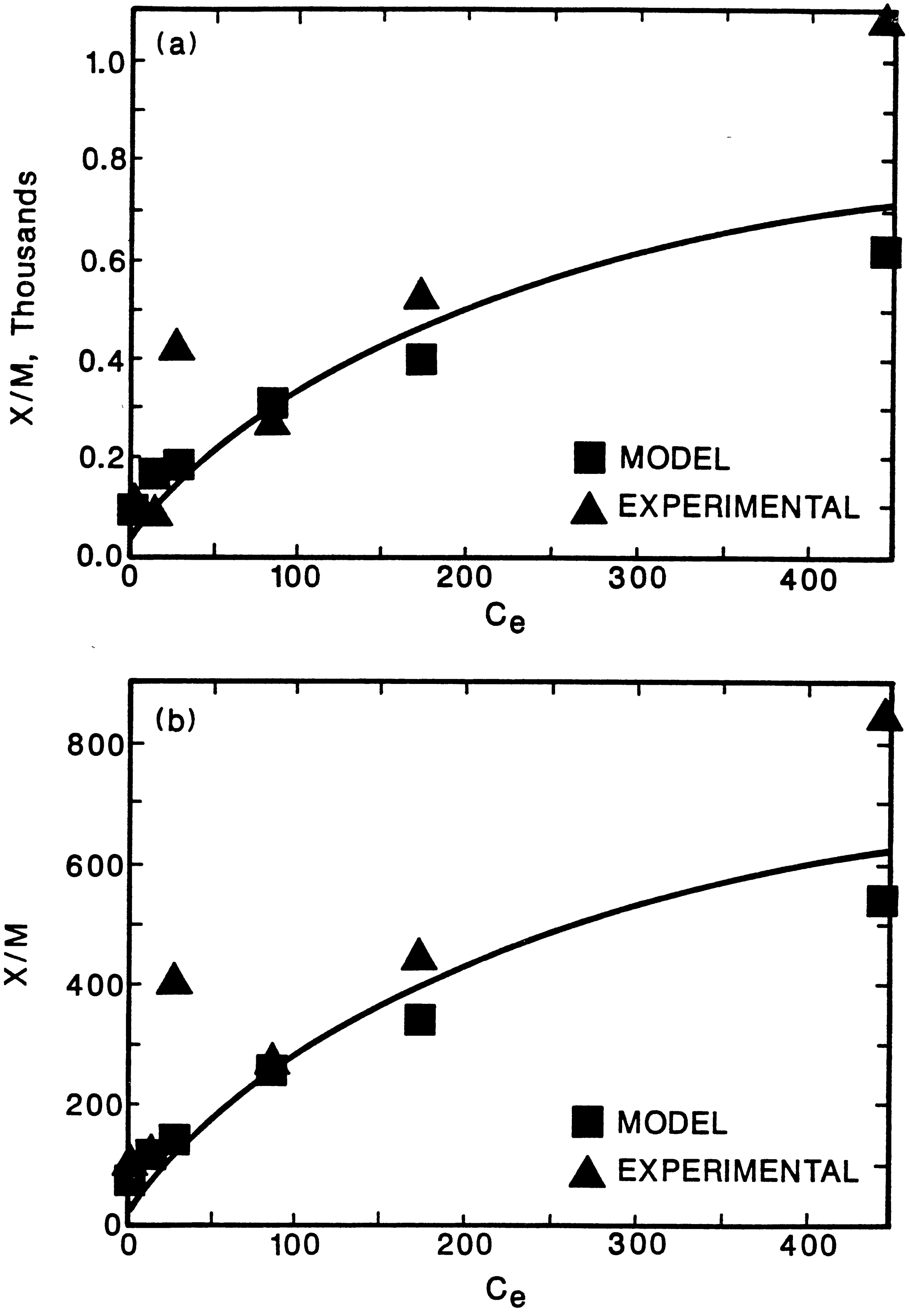
AII-5. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) S2, (b) S3 at 30°C



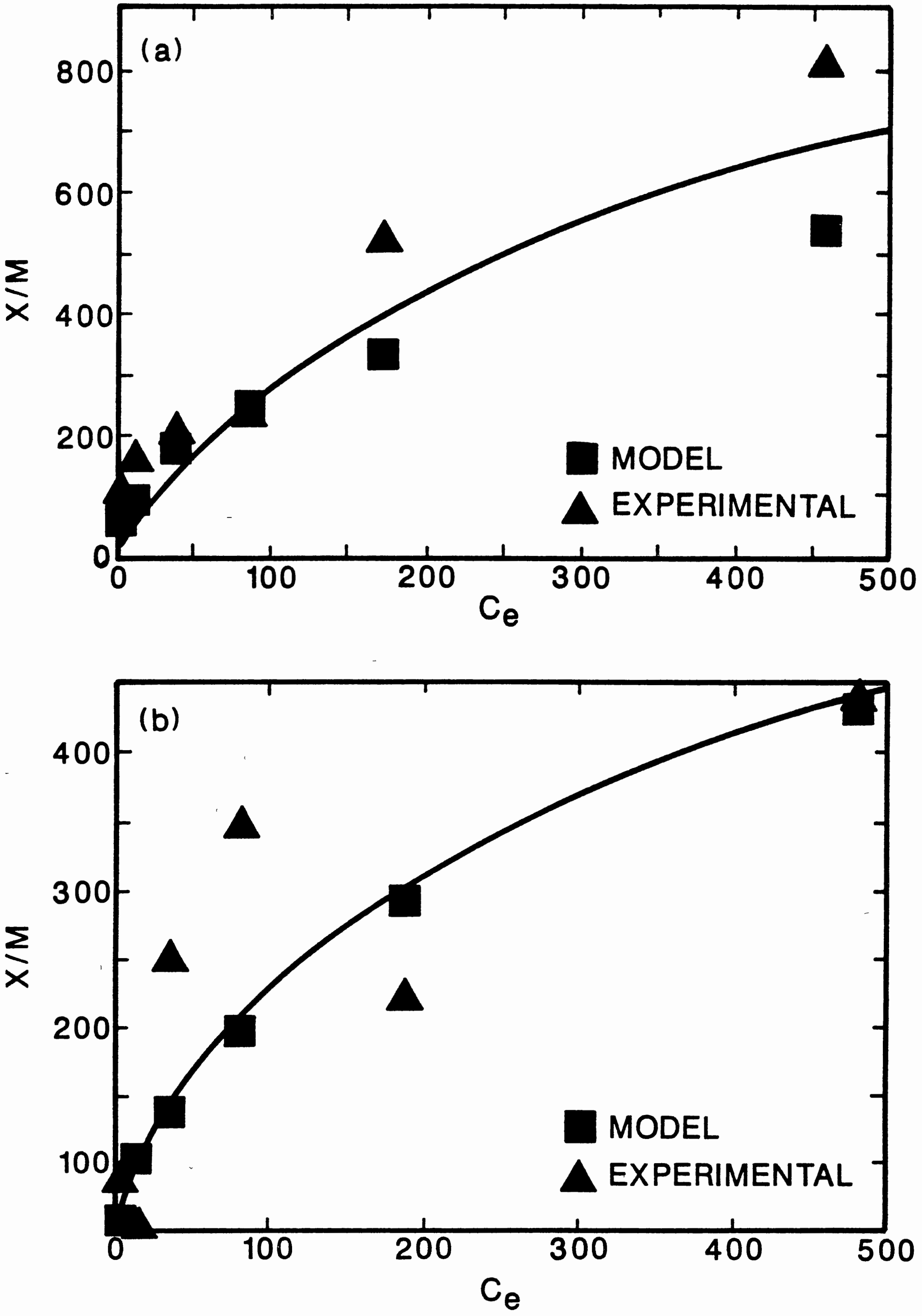
AII-6. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) S4, (b) S5 at 30°C



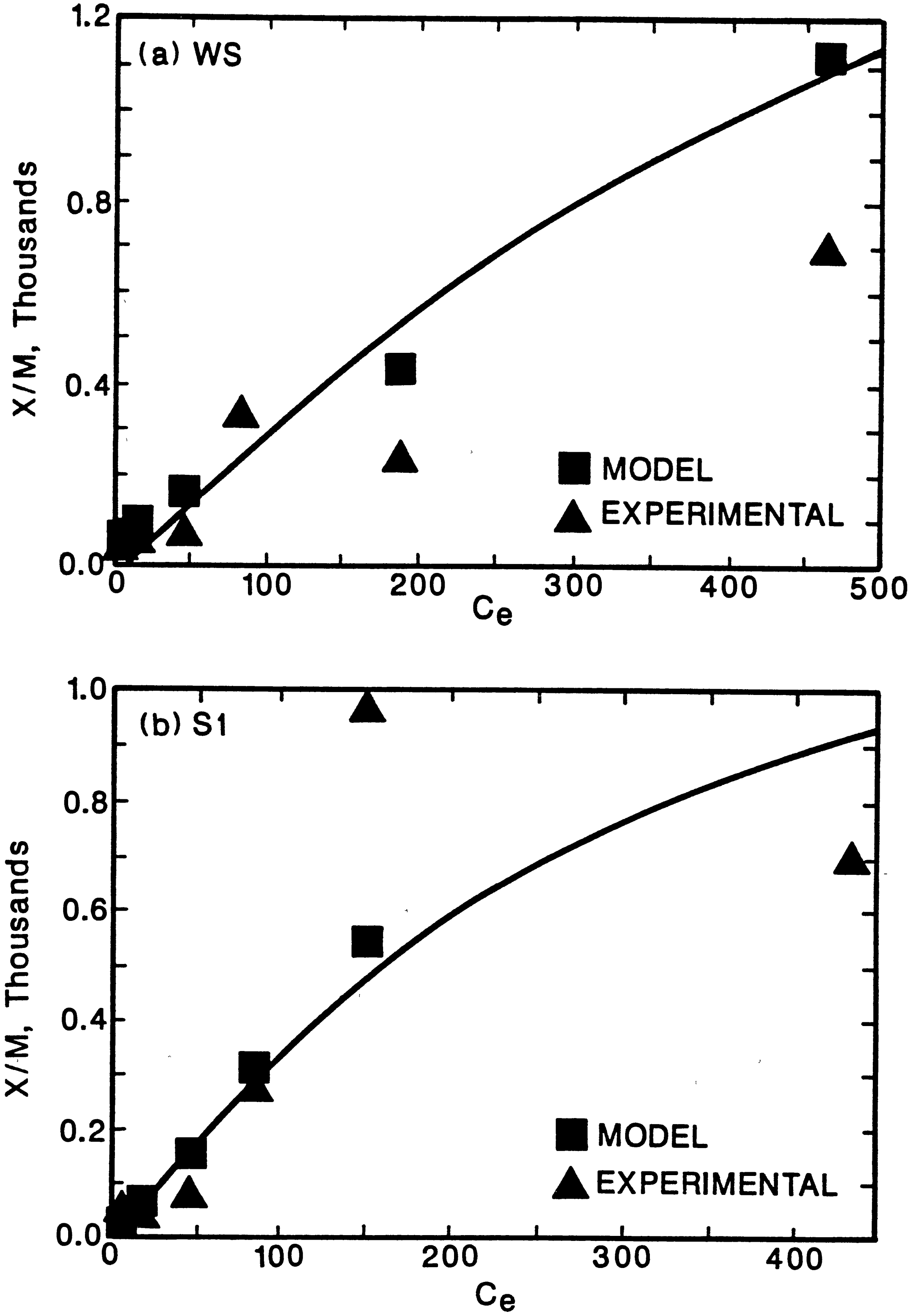
AII-7. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) WS, (b) S1 at 35°C



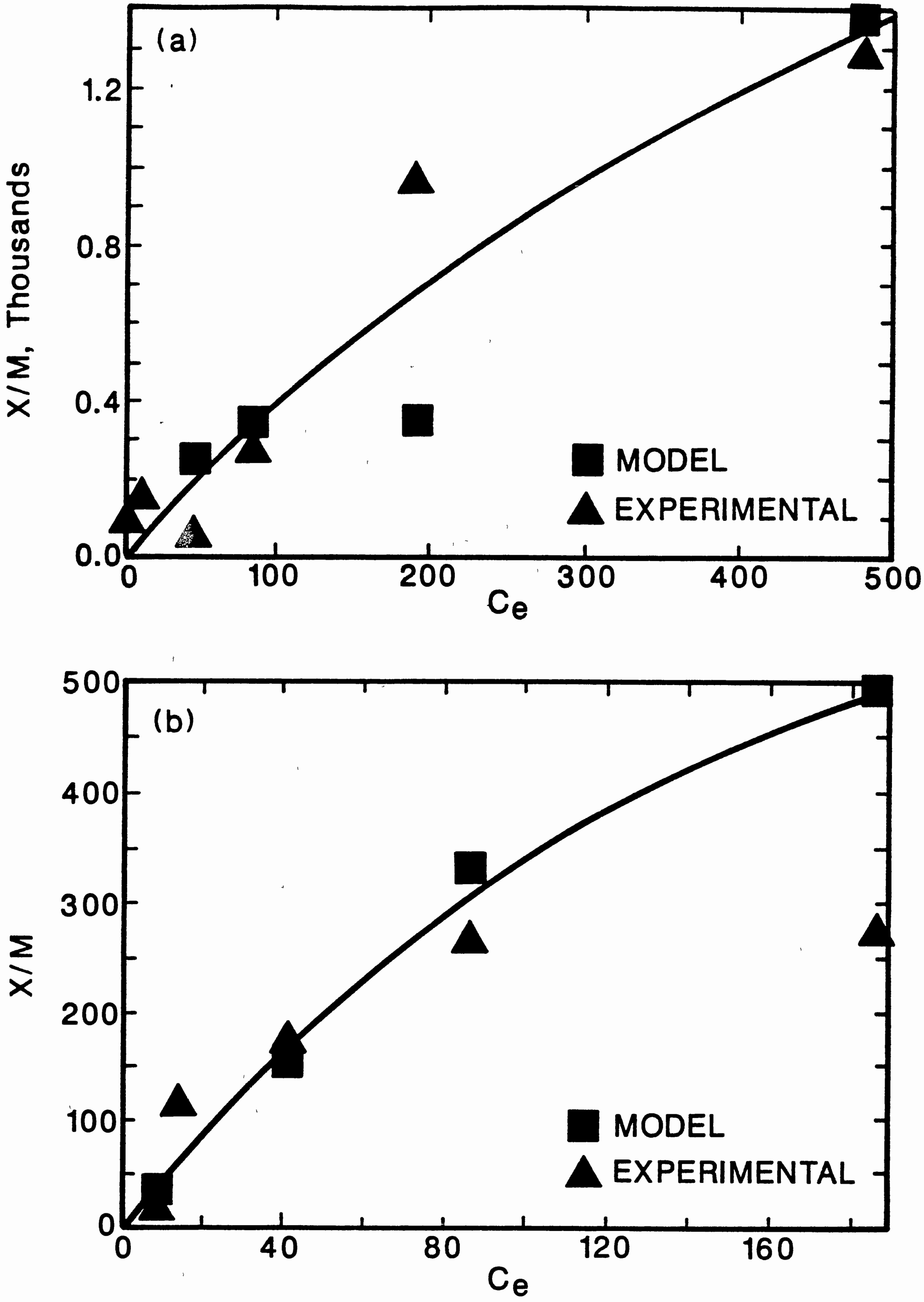
AII-8. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) S2, (b) S3 at 35°C



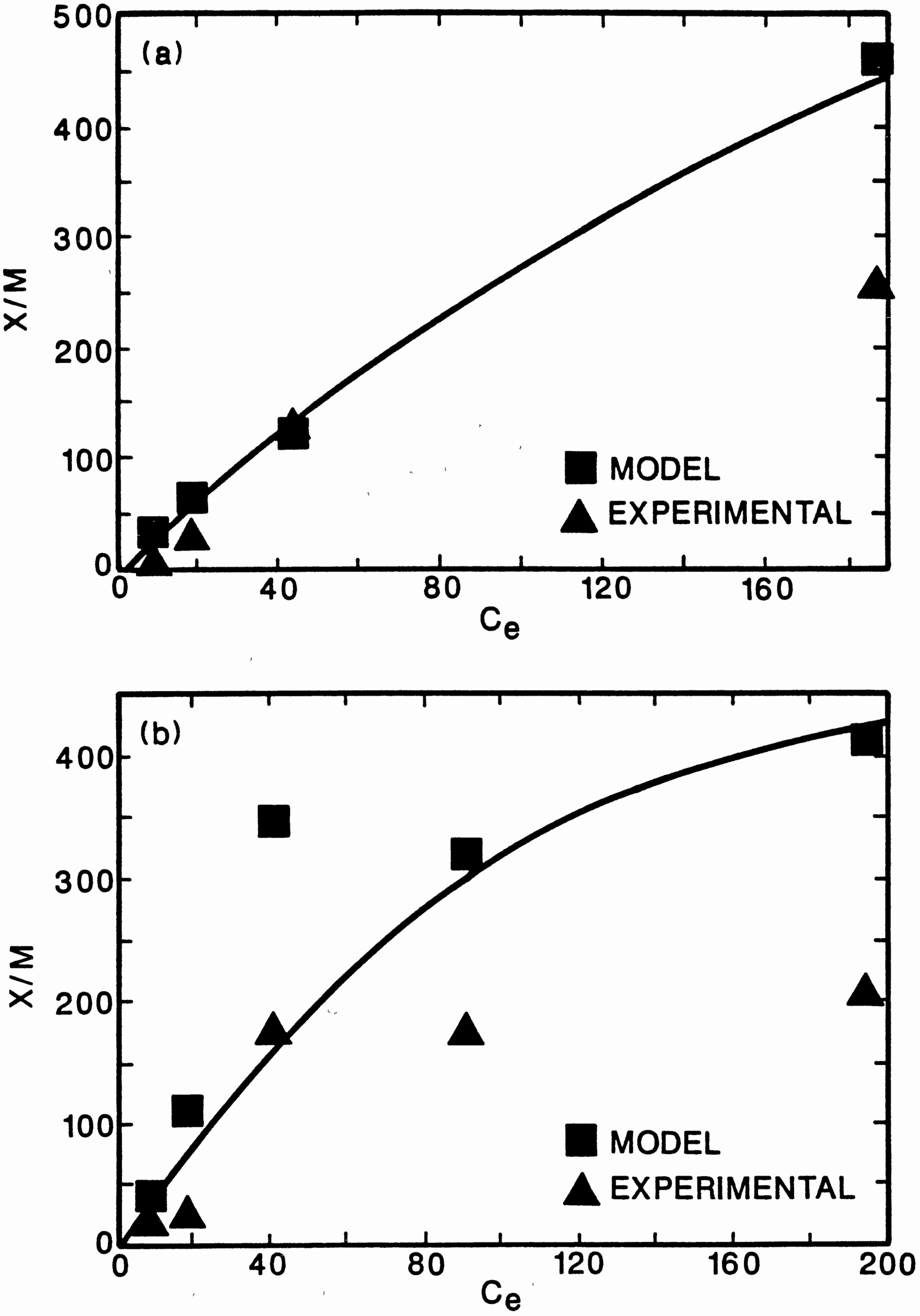
AII-9. SRS Multiple Freundlich-Type Isotherms of Lindane with Silvex present on (a) S4, (b) S5 at 35°C



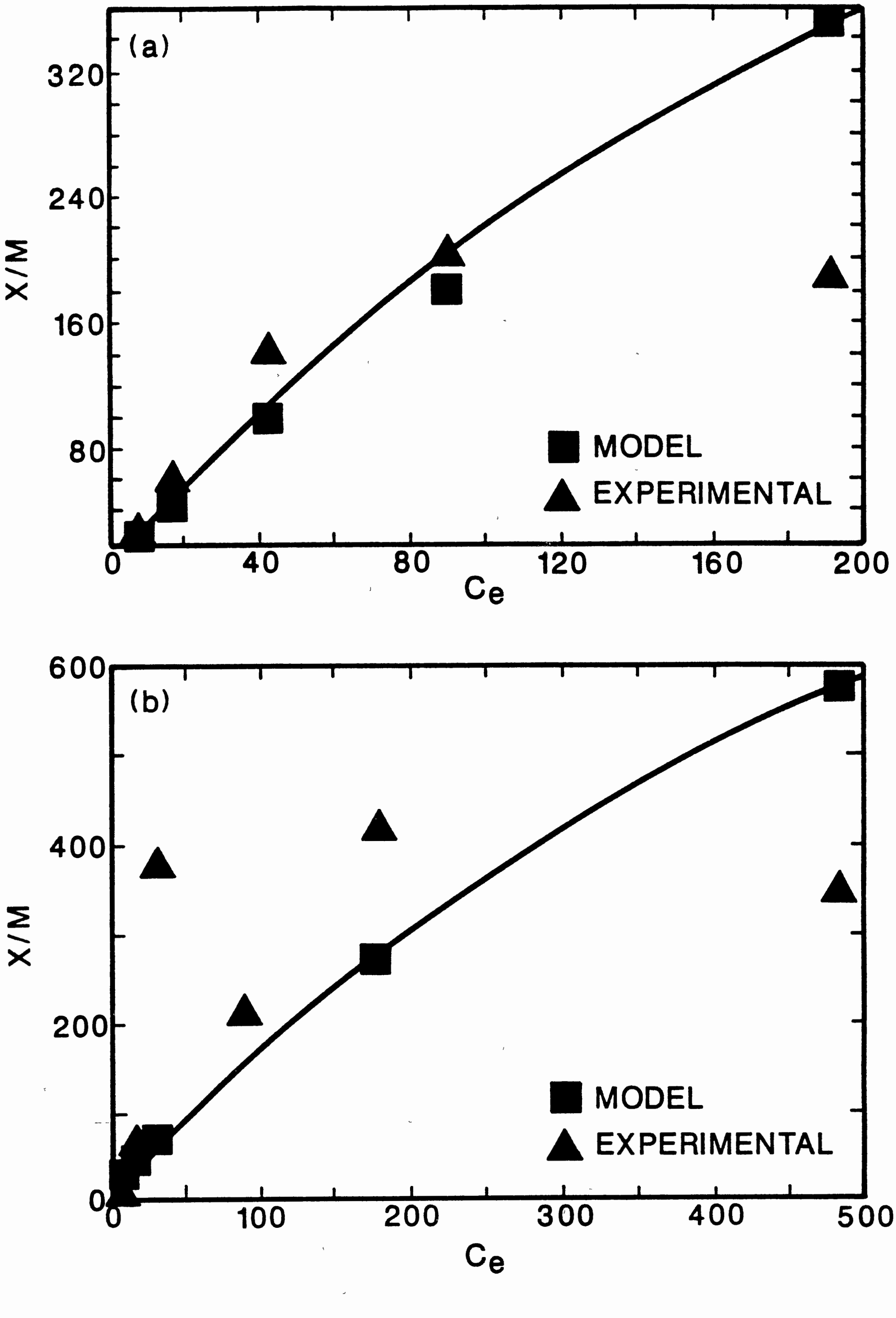
AII-10. SRS Multiple Freundlich-Type Isotherms
of Silvex with Lindane present on
(a) WS, (b) S1 at 25°C



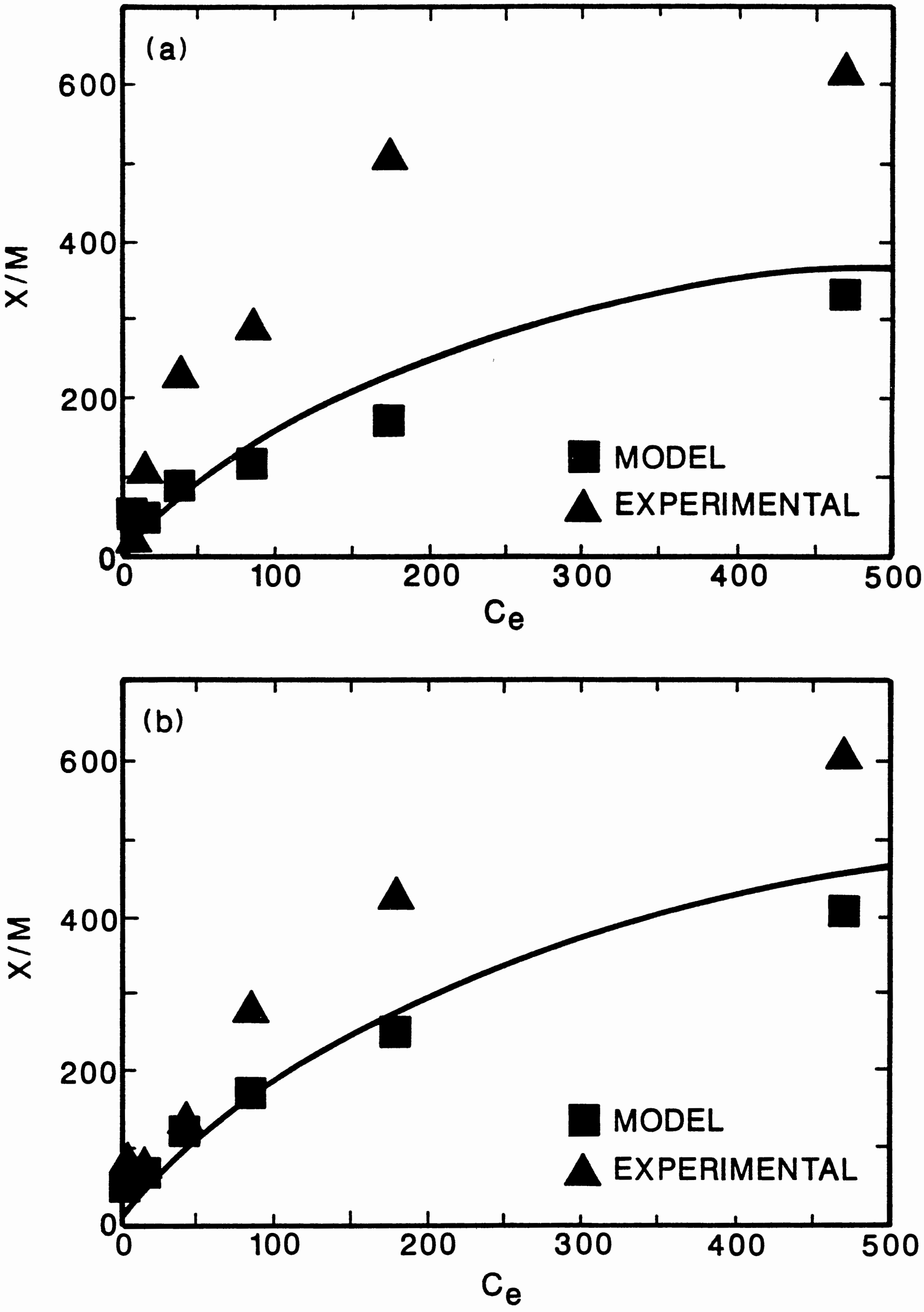
AII-11 SRS Multiple Freundlich-Type Isotherms of Silvex with lindane present on (a) S2, (b) S3 at 25°C



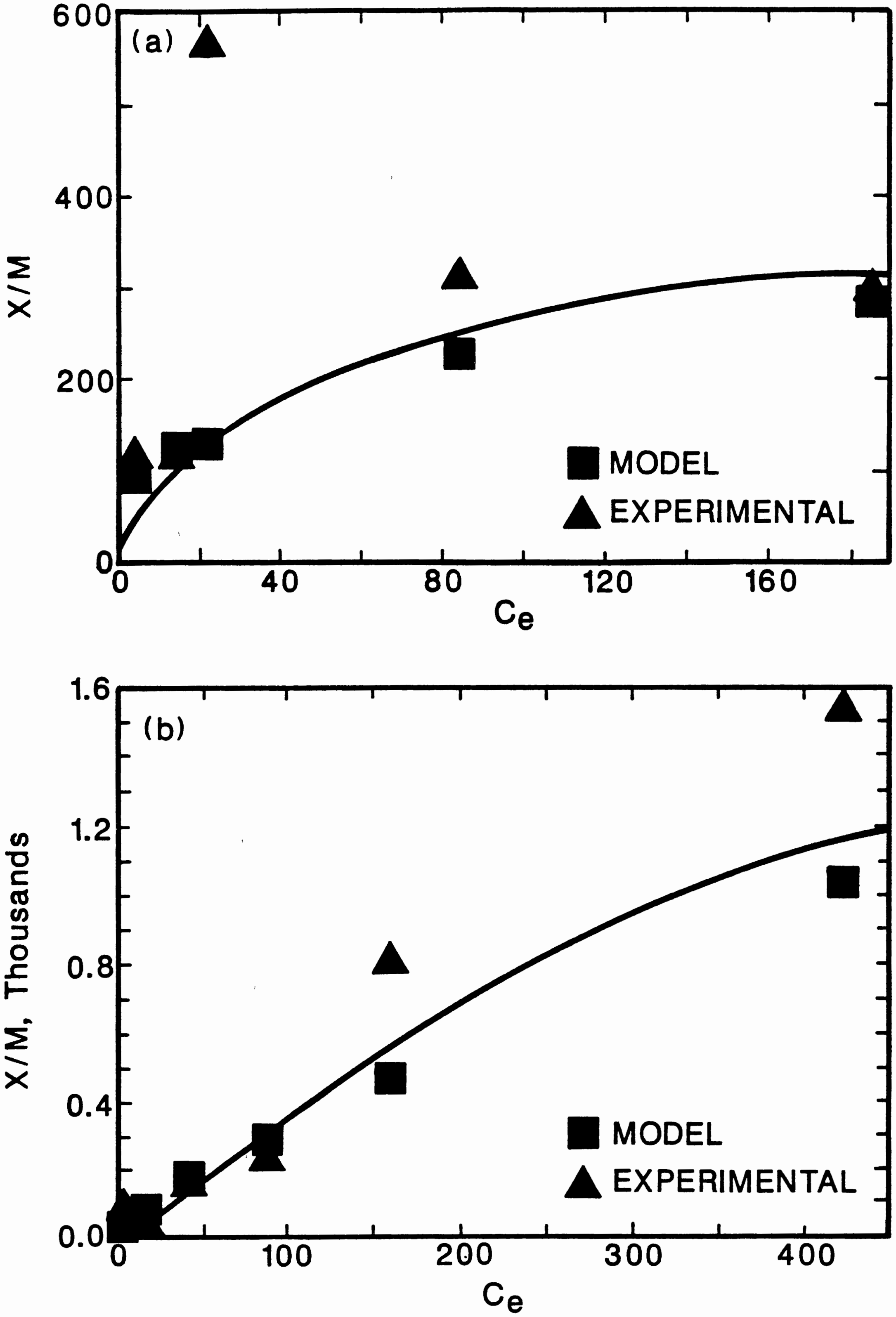
AII-12 SRS Multiple Freundlich-Type Isotherms of Silvex with lindane present on (a) S4, (b) S5 at 25°C



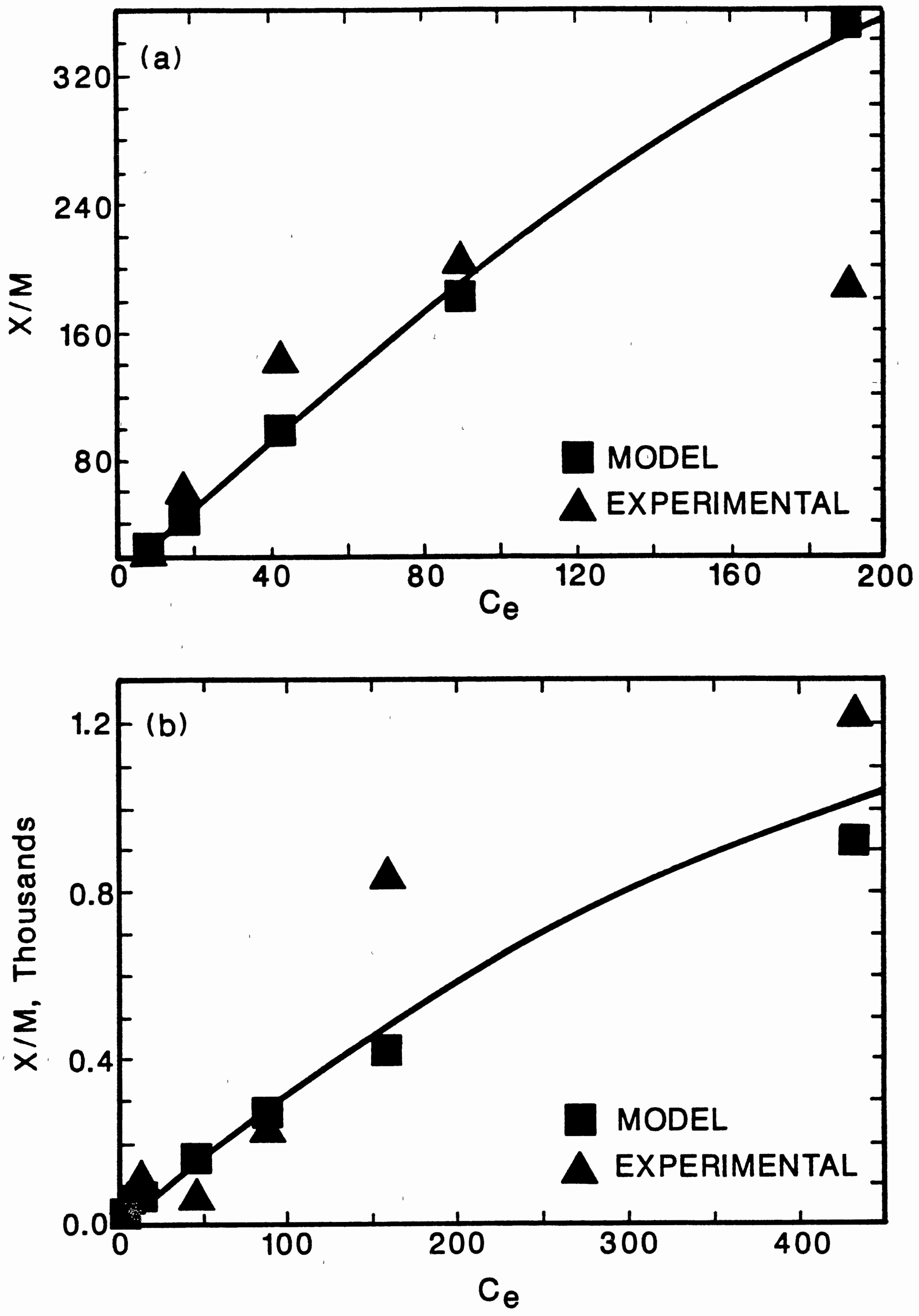
AII-13 SRS Multiple Freundlich-Type Isotherms of Silvex with lindane present on (a) WS, (b) S1 at 30°C



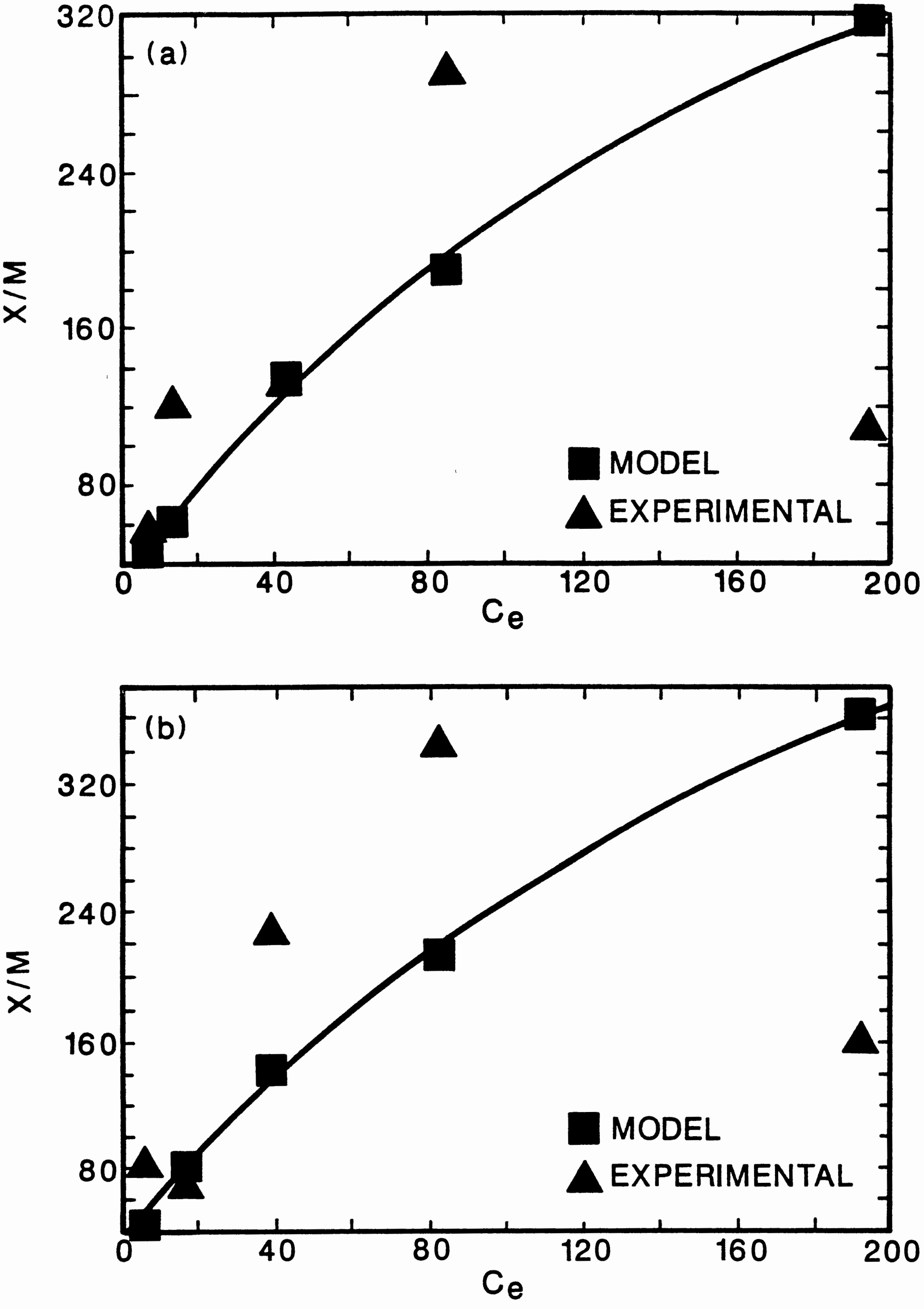
AII-14. SRS Multiple Freundlich-Type Isotherms of Silvex with Lindane present on (a) S2, (b) S3 at 30°C



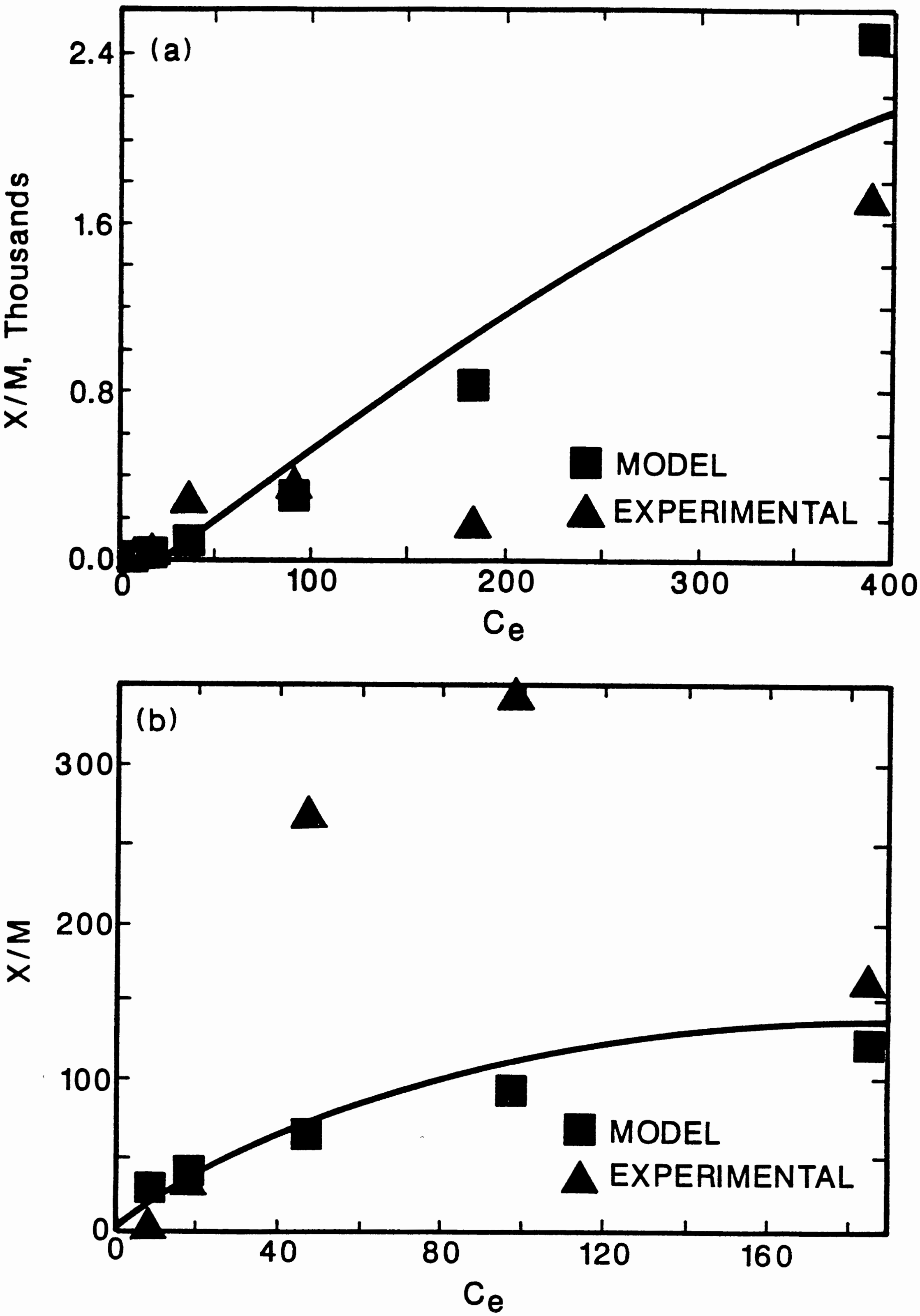
AII-15. SRS Multiple Freundlich-Type Isotherms of Silvex with Lindane present on (a) S4, (b) S5 at 30°C



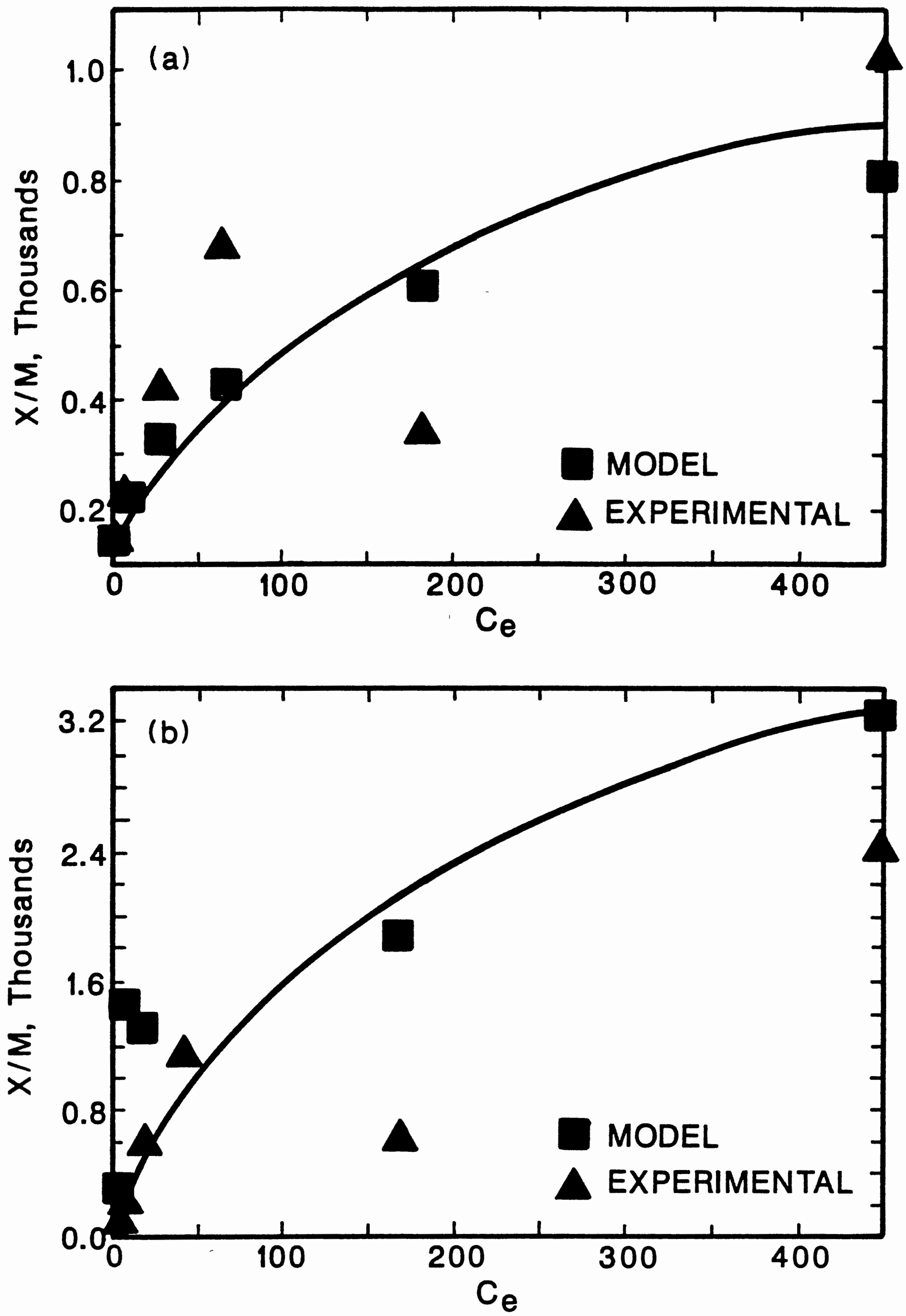
AII-16. SRS Multiple Freundlich-Type Isotherms of Silvex with Lindane present on (a) WS, (b) S1 at 35°C



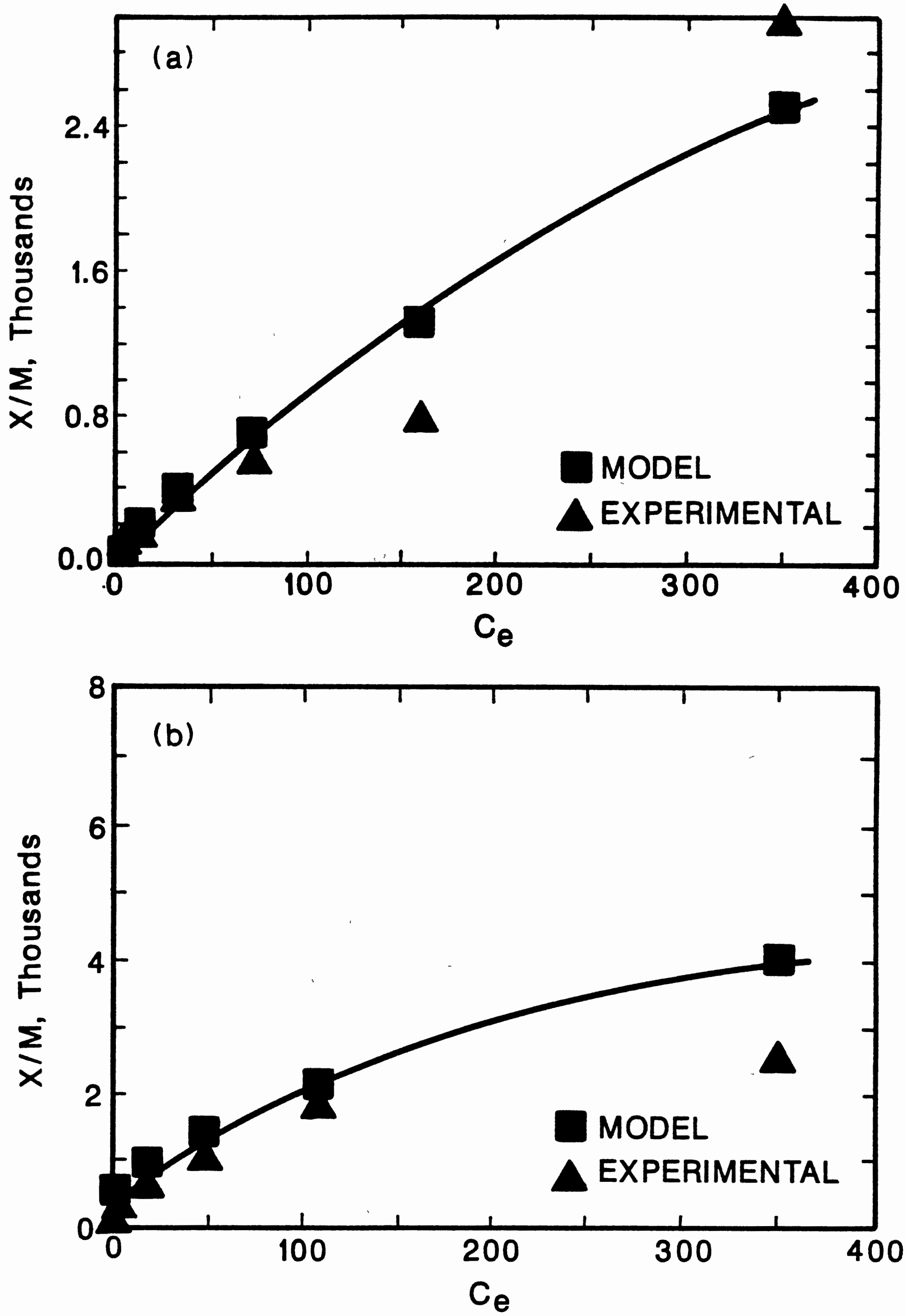
AII-17. SRS Multiple Freundlich-Type Isotherms of Silvex with Lindane present on (a) S2, (b) S3 at 35°C



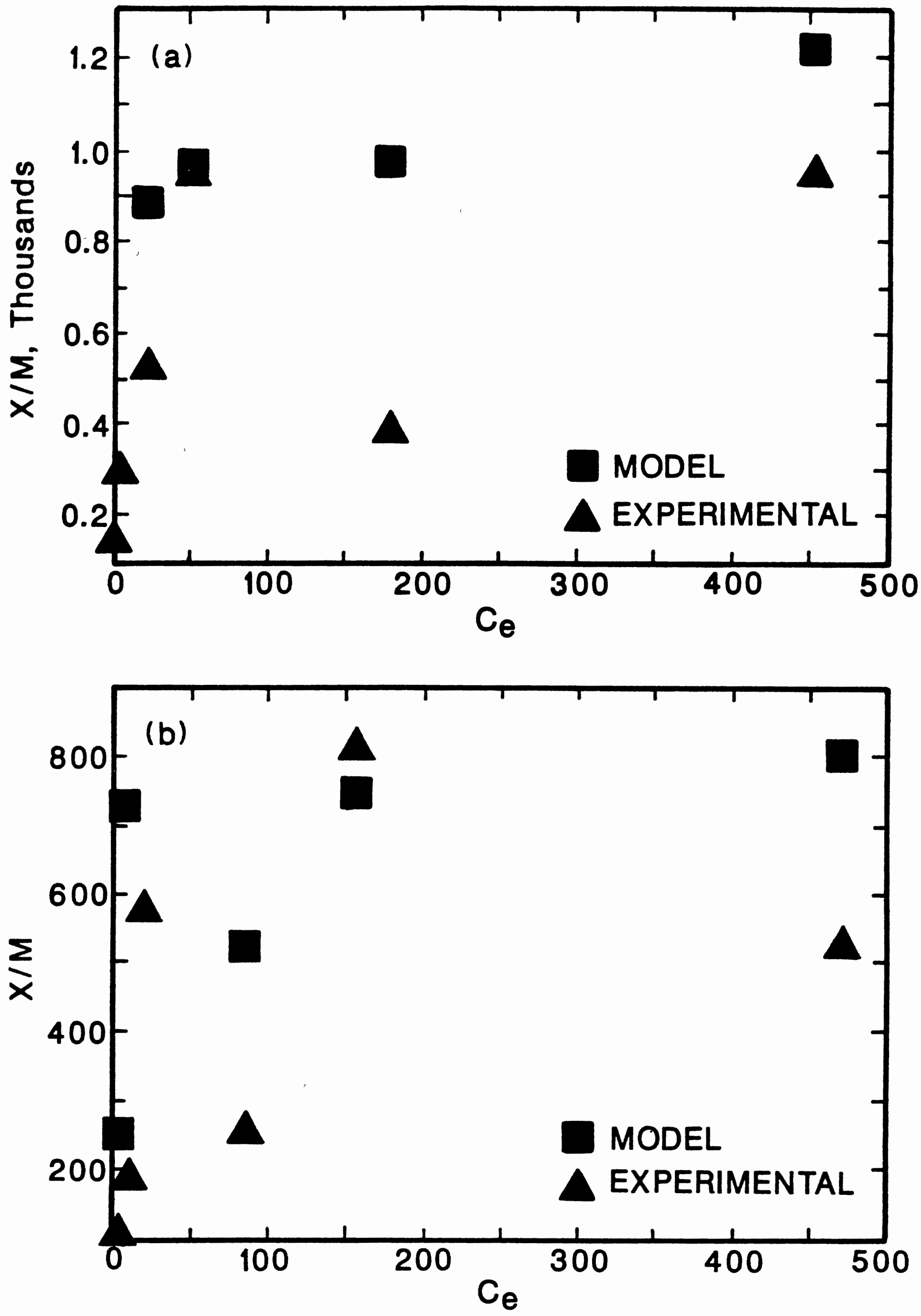
AII-18. SRS Multiple Freundlich-Type Isotherms of Silvex with Lindane present on (a) S4, (b) S5 at 35°C



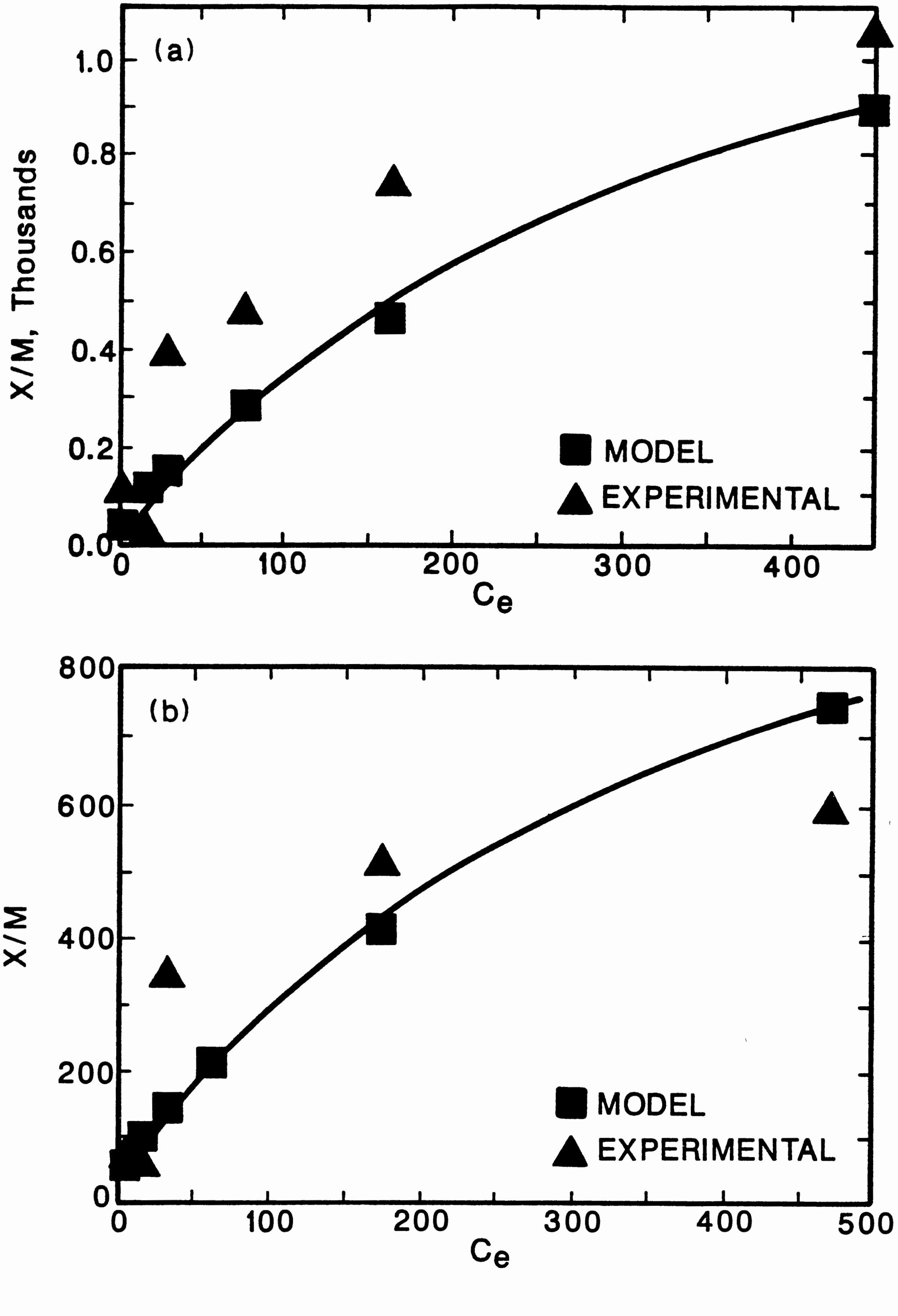
AII-19. SRS Multiple Freundlich-Type Isotherms of Lindane with 2,4-D present on (a) WS, (b) S1 at 25°C



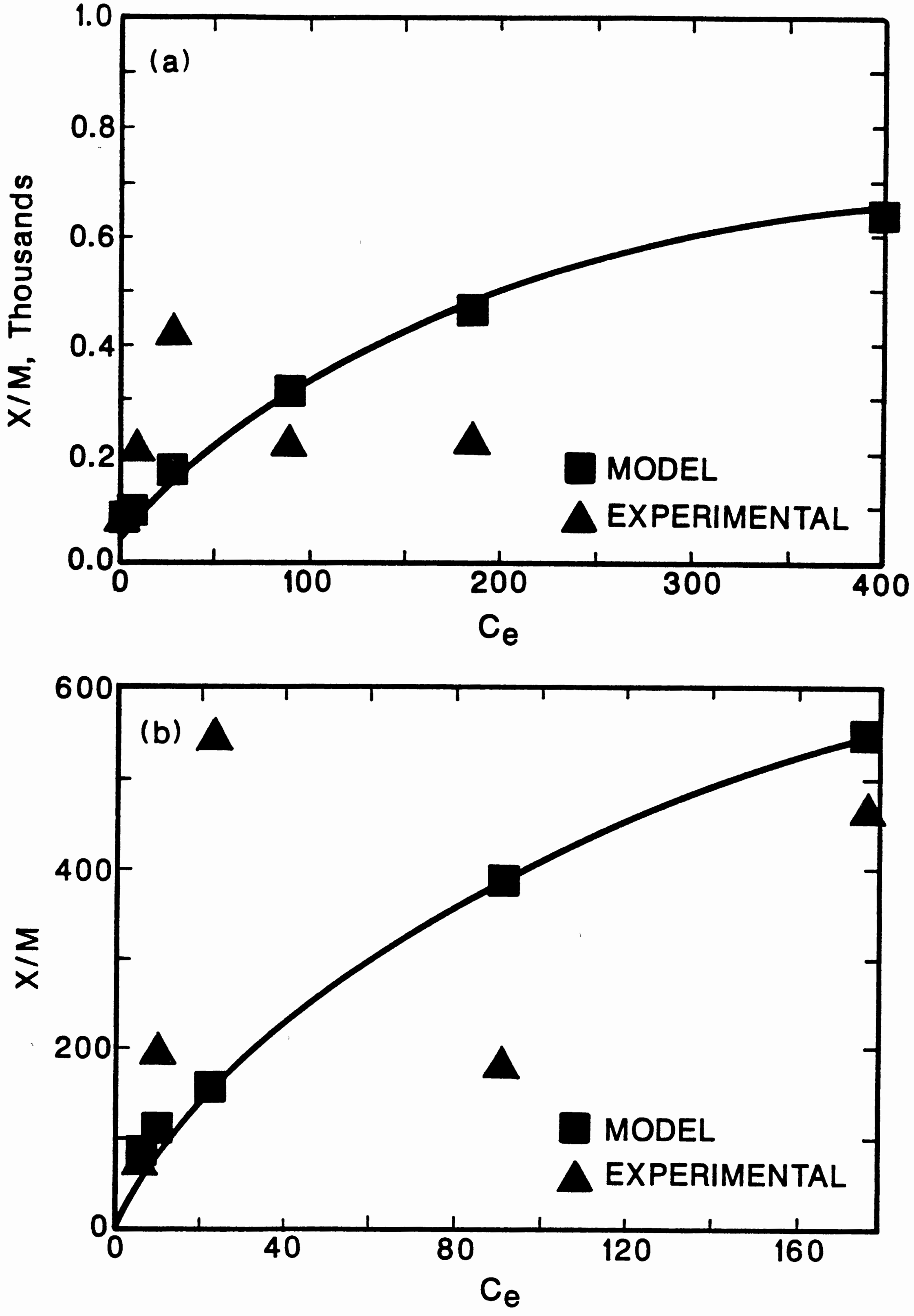
AII-20. SRS Multiple Freundlich-Type Isotherms of Lindane with 2,4-D present on (a) S2, (b) S3 at 25°C



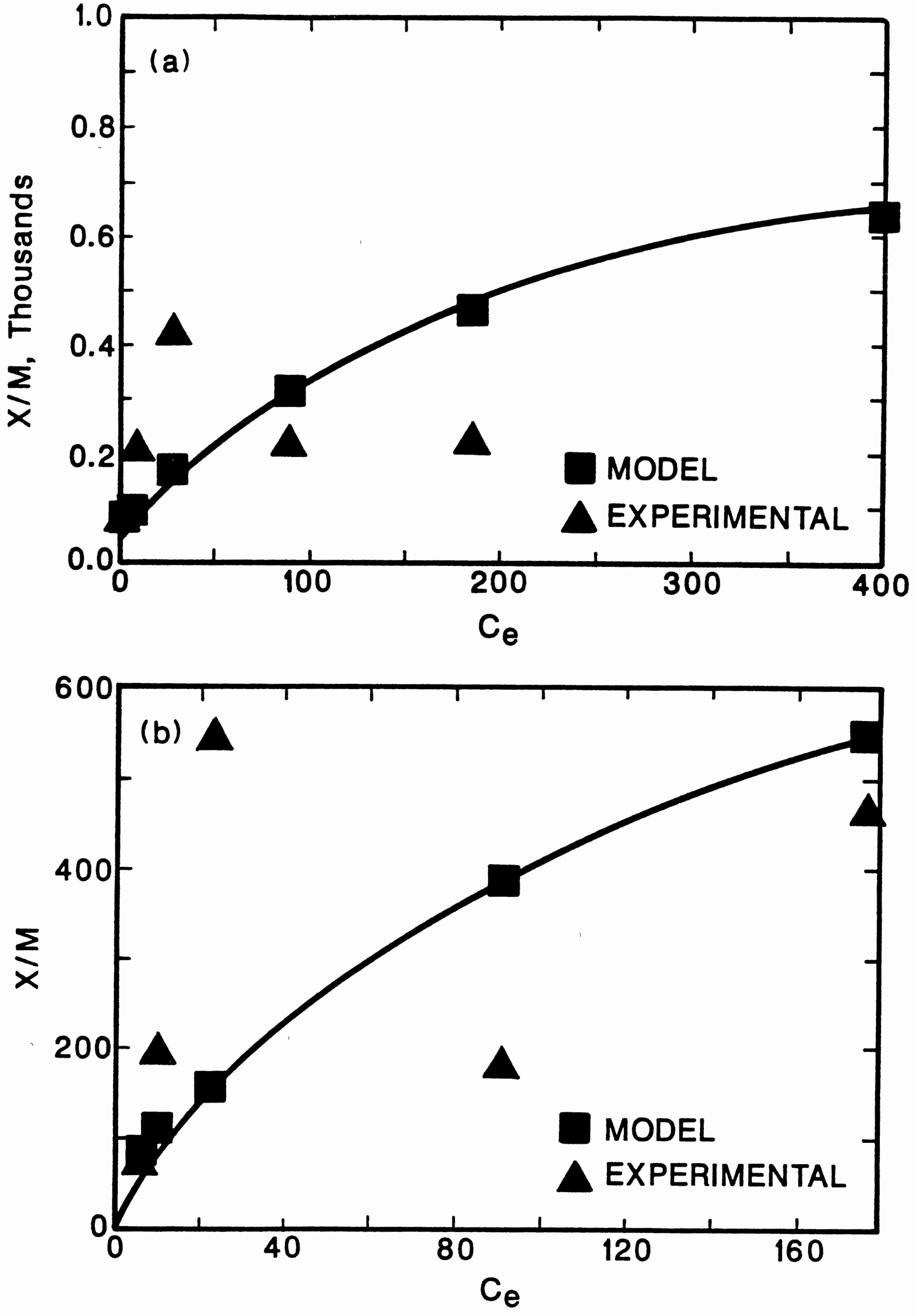
AII-21. SRS Multiple Freundlich-Type Isotherms of Lindane with 2,4-D present on (a) S4, (b) S5 at 25°C



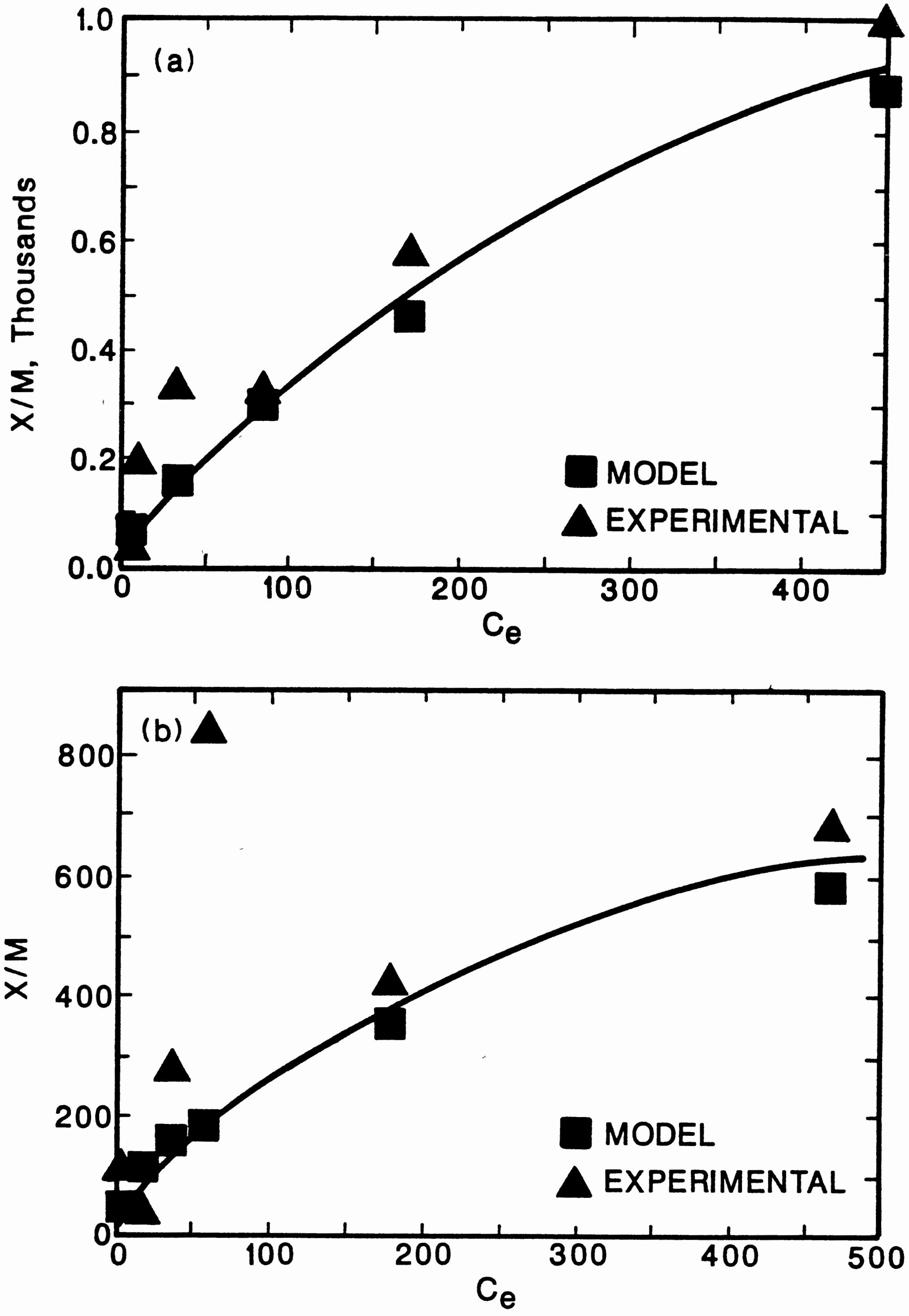
AII-22 SRS Multiple Freundlich-Type Isotherms
of Lindane with 2,4-D present on
(a) WS, (b) S1 at 30°C



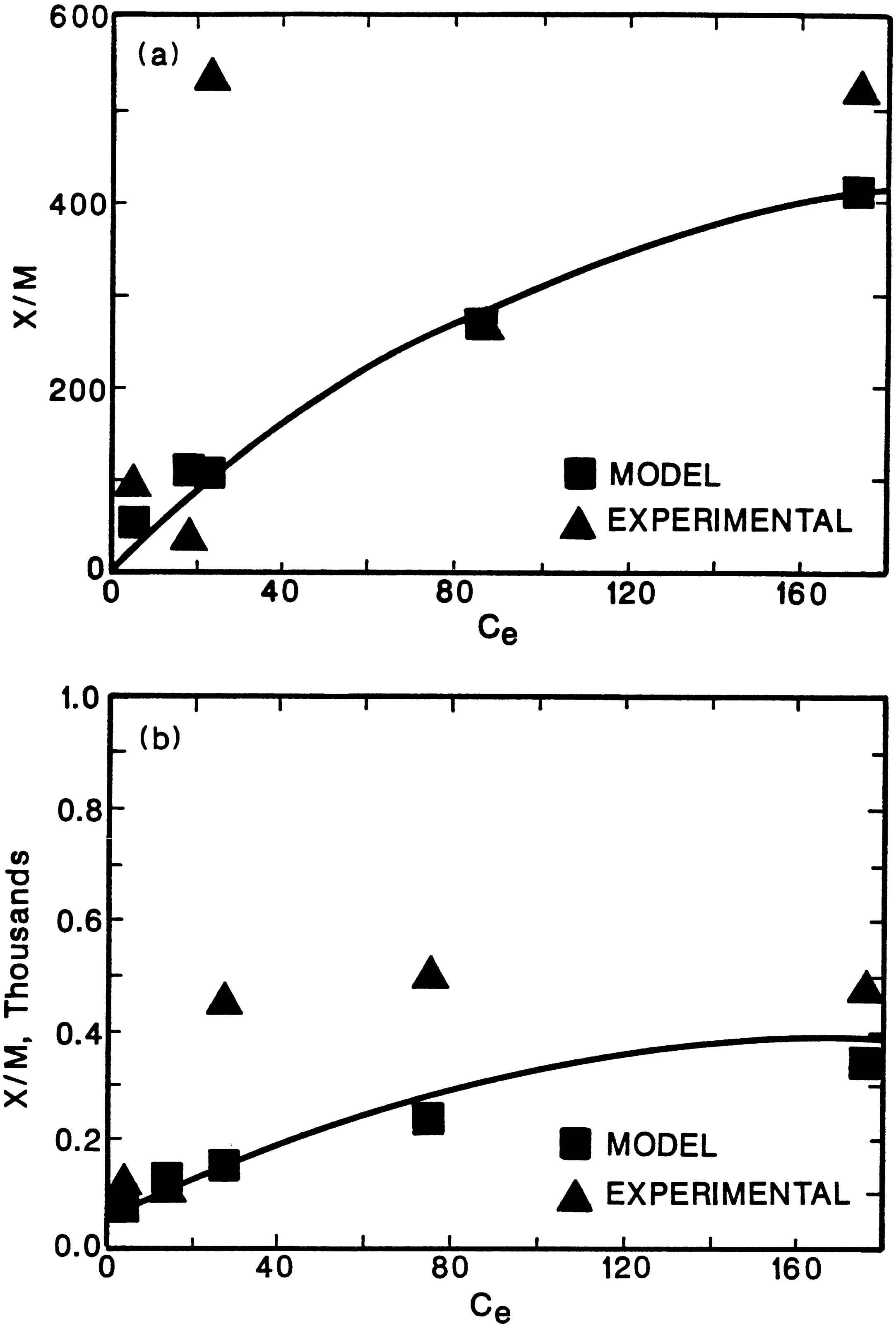
AII-23. SRS Multiple Freundlich-Type Isotherms of Lindane with 2,4-D present on (a) S2, (b) S3 at 30°C



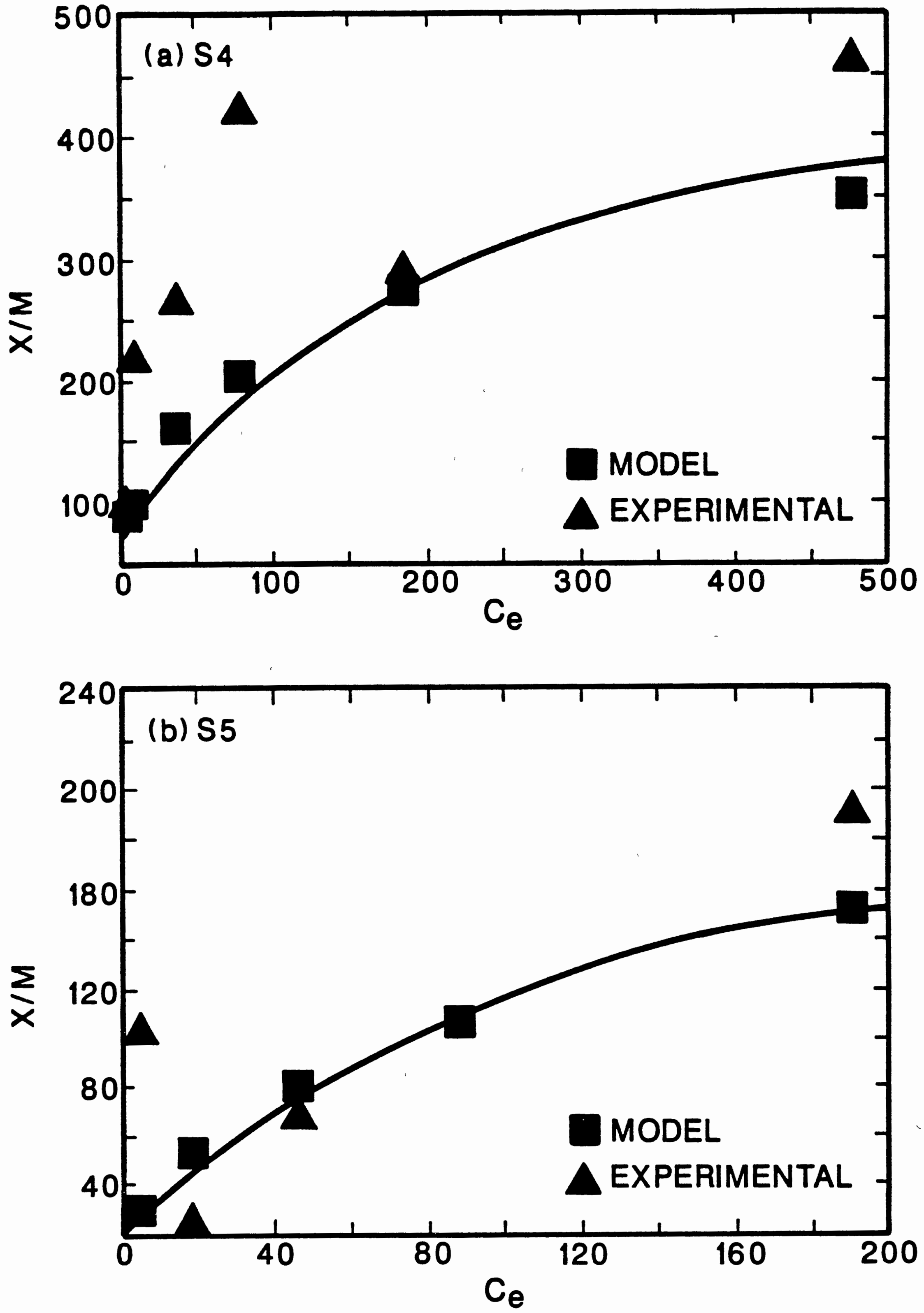
AII-23. SRS Multiple Freundlich-Type Isotherms of Lindane with 2,4-D present on (a) S2, (b) S3 at 30°C



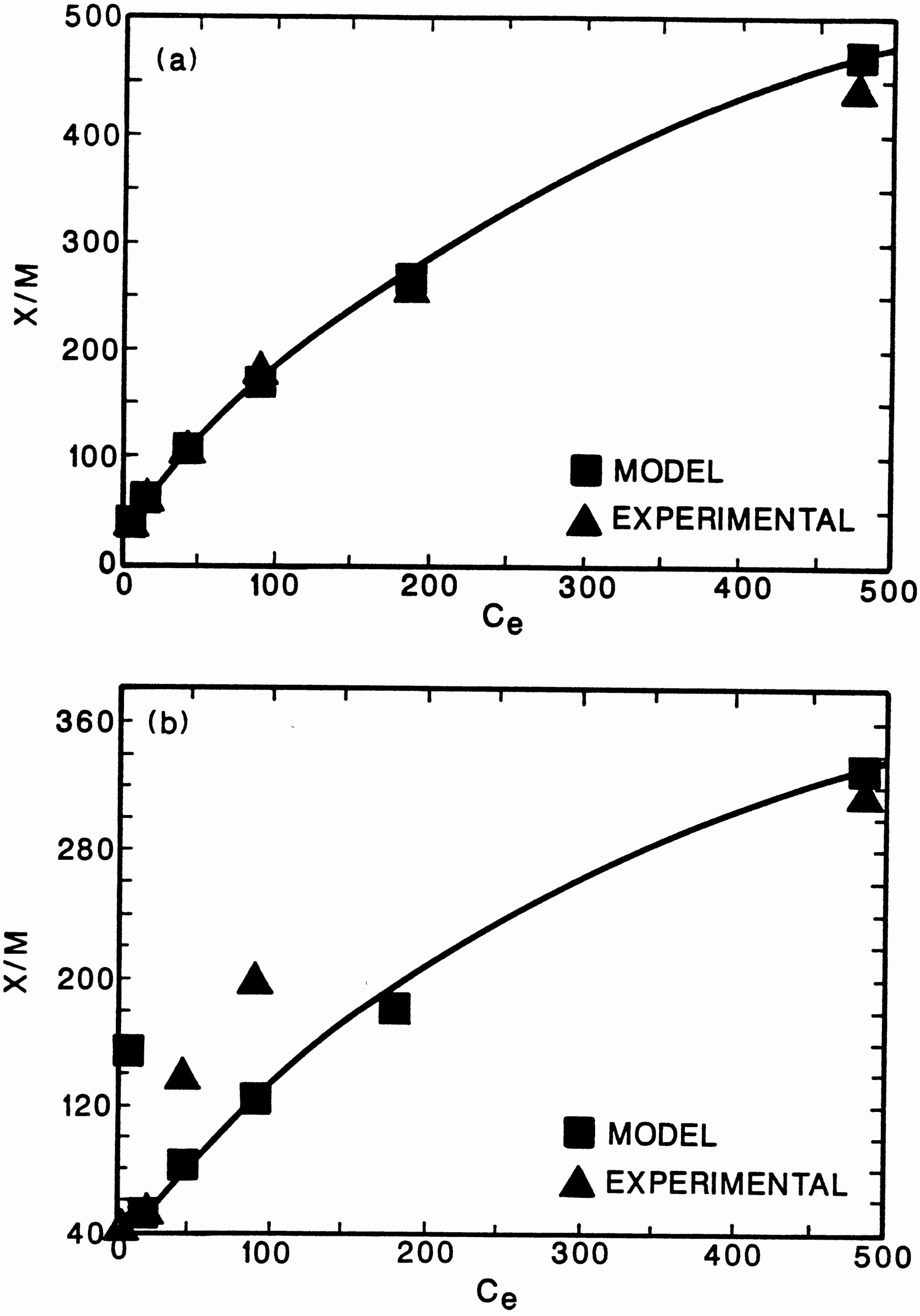
AII-25. SRS Multiple Freundlich-Type Isotherms of Lindane with 2,4-D present on (a) WS, (b) S1 at 35°C



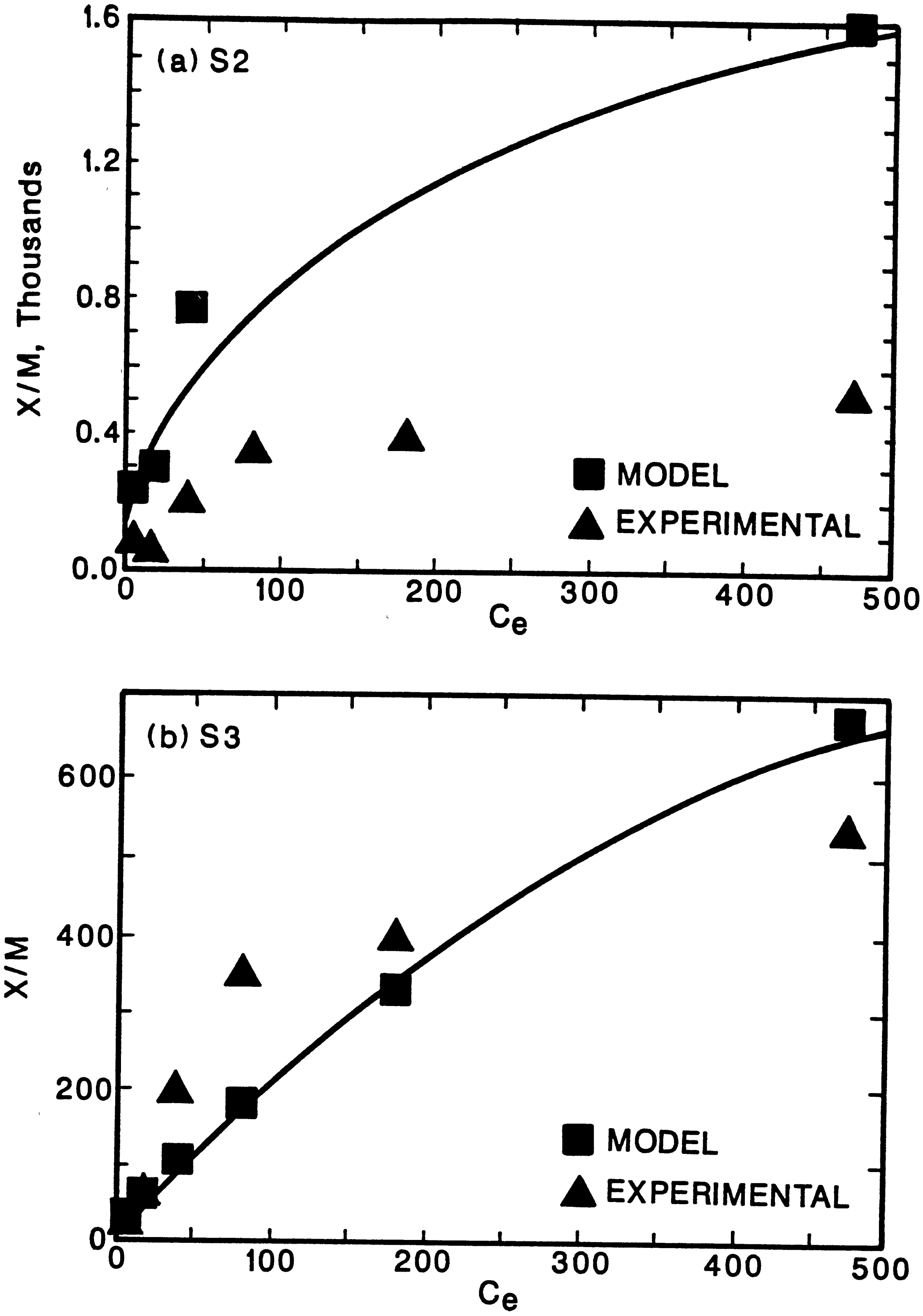
AII-26 SRS Multiple Freundlich-Type Isotherms of Lindane with 2,4-D present on (a) S2, (b) S3 at 35°C



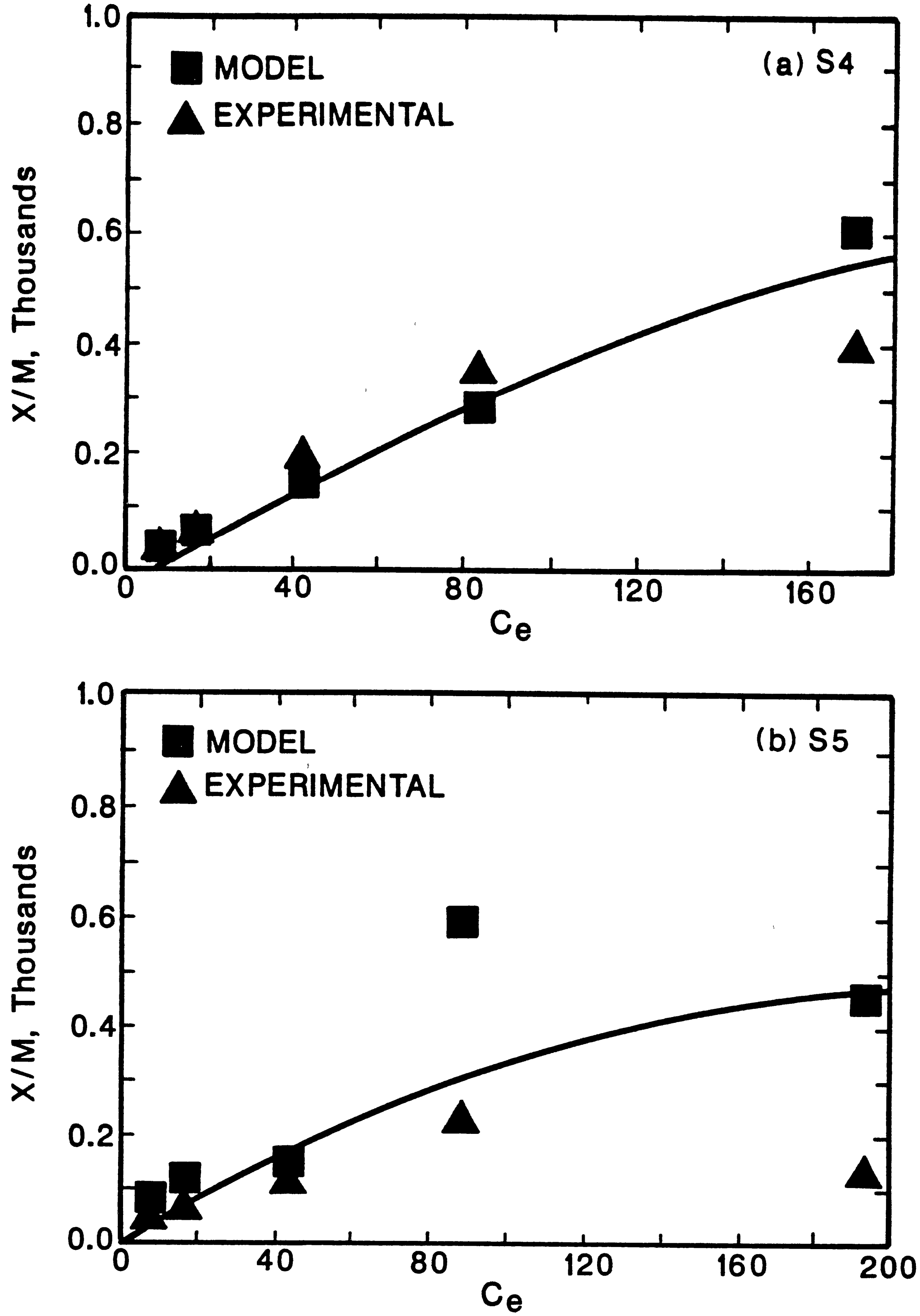
AII-27. SRS Multiple Freundlich-Type Isotherms of Lindane with 2,4-D present on (a) S4, (b) S5 at 35°C



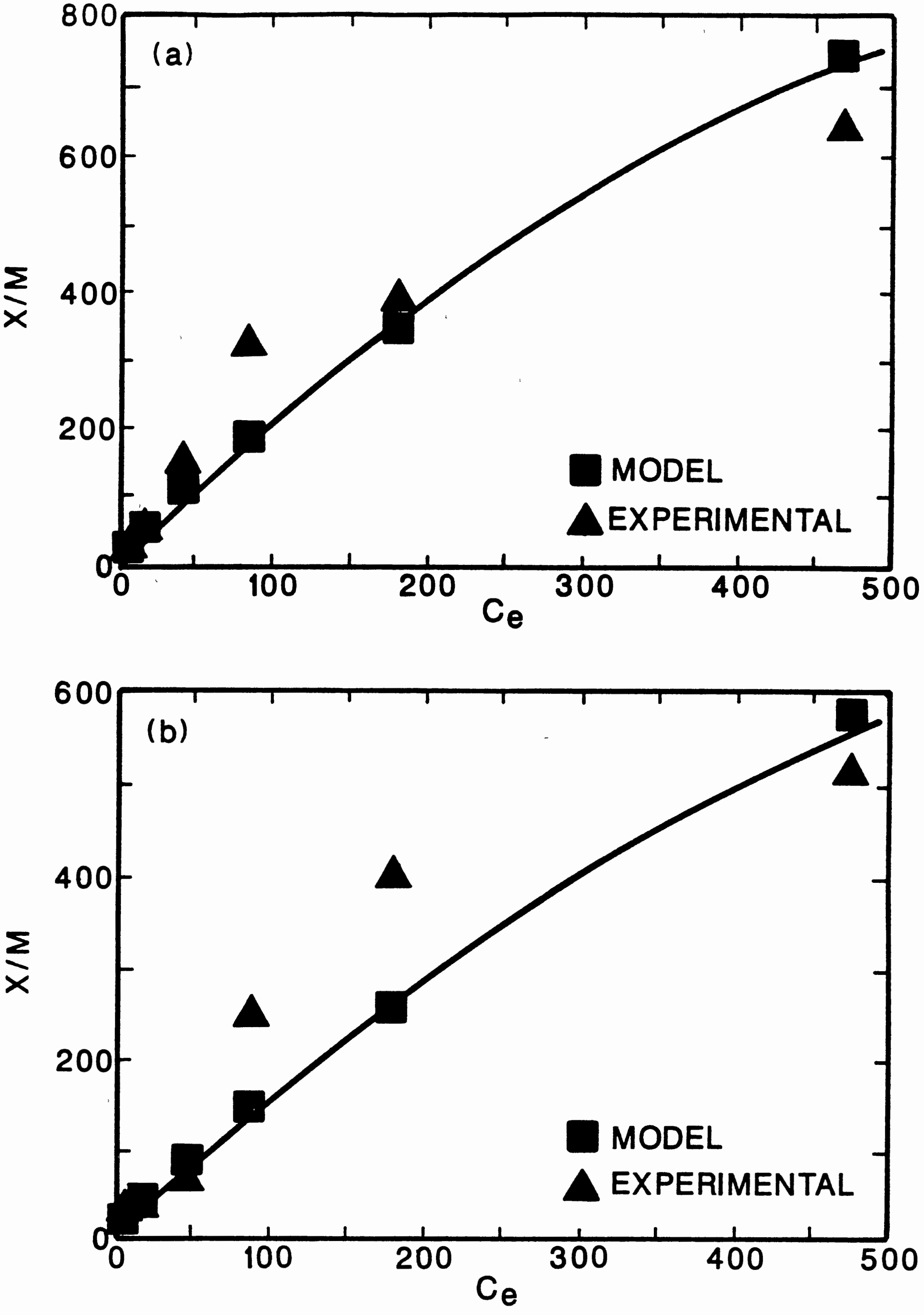
AII-28. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Lindane present on (a) WS, (b) S1 at 25°C



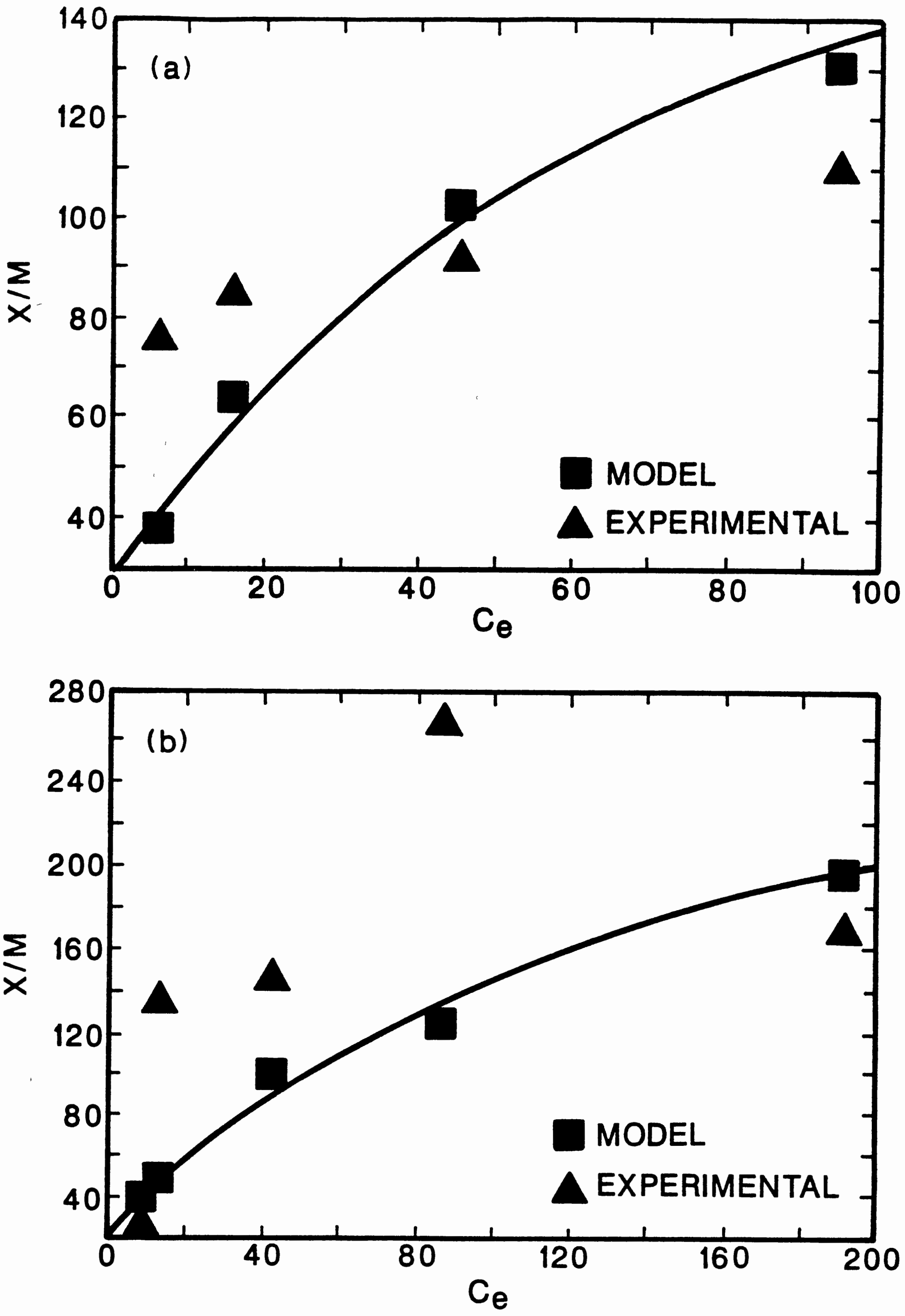
AII-29. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Lindane present on (a) S2, (b) S3 at 25°C



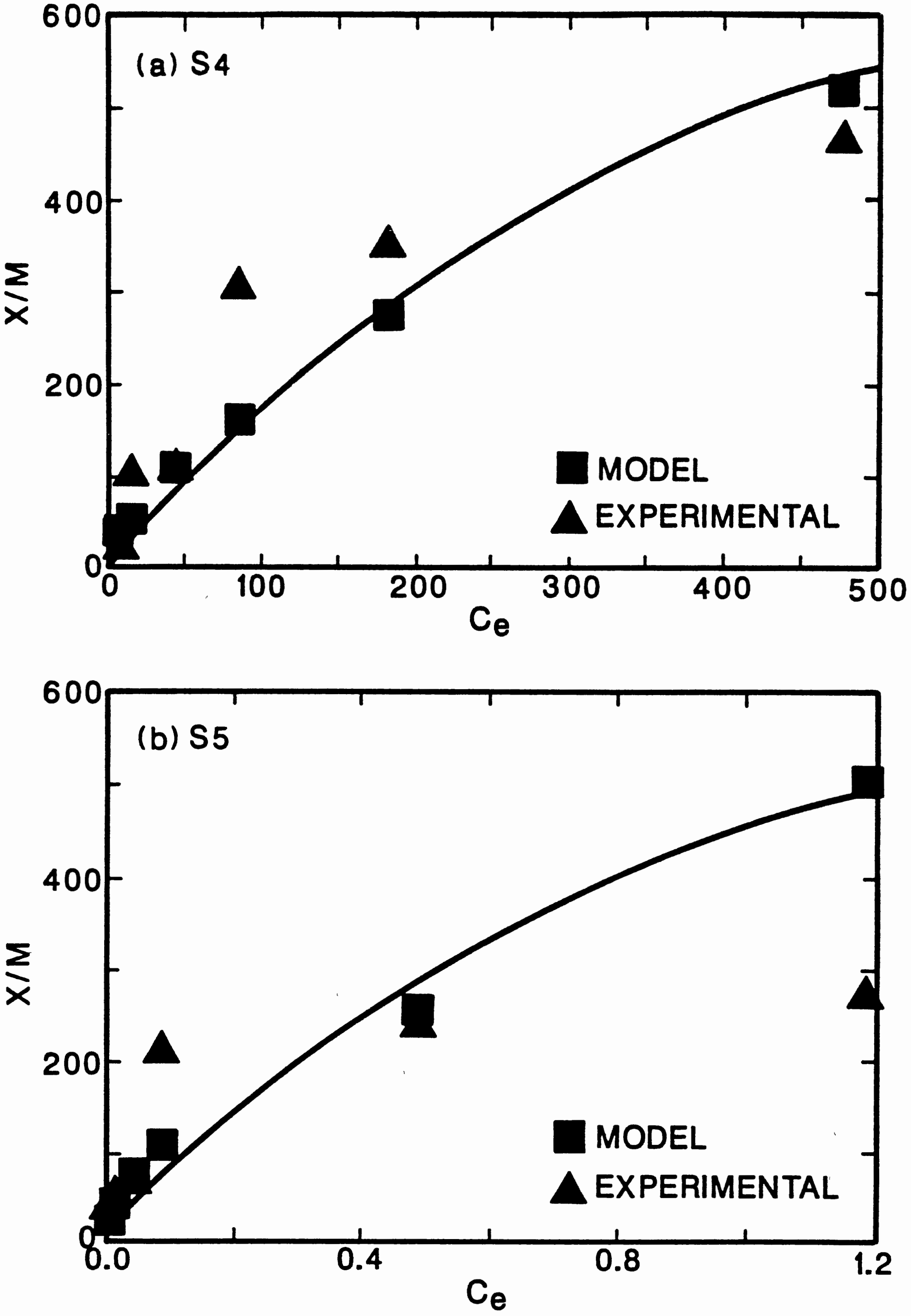
AII-30. SRS Multiple Freundlich-Type Isotherms
of 2,4-D with Lindane present on
(a) S4, (b) S5 at 25°C



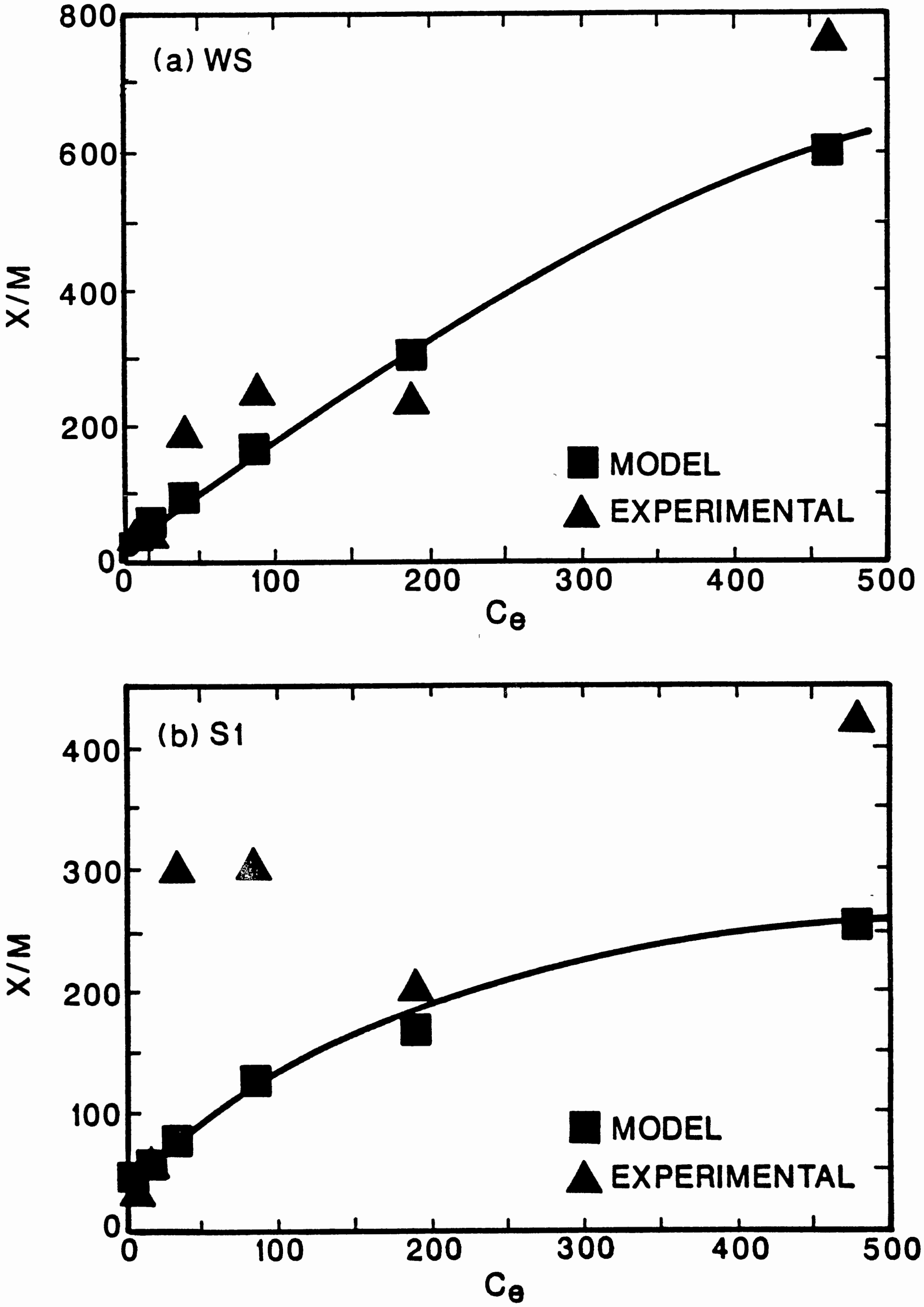
AII-31. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Lindane present on (a) WS, (b) S1 at 30°C



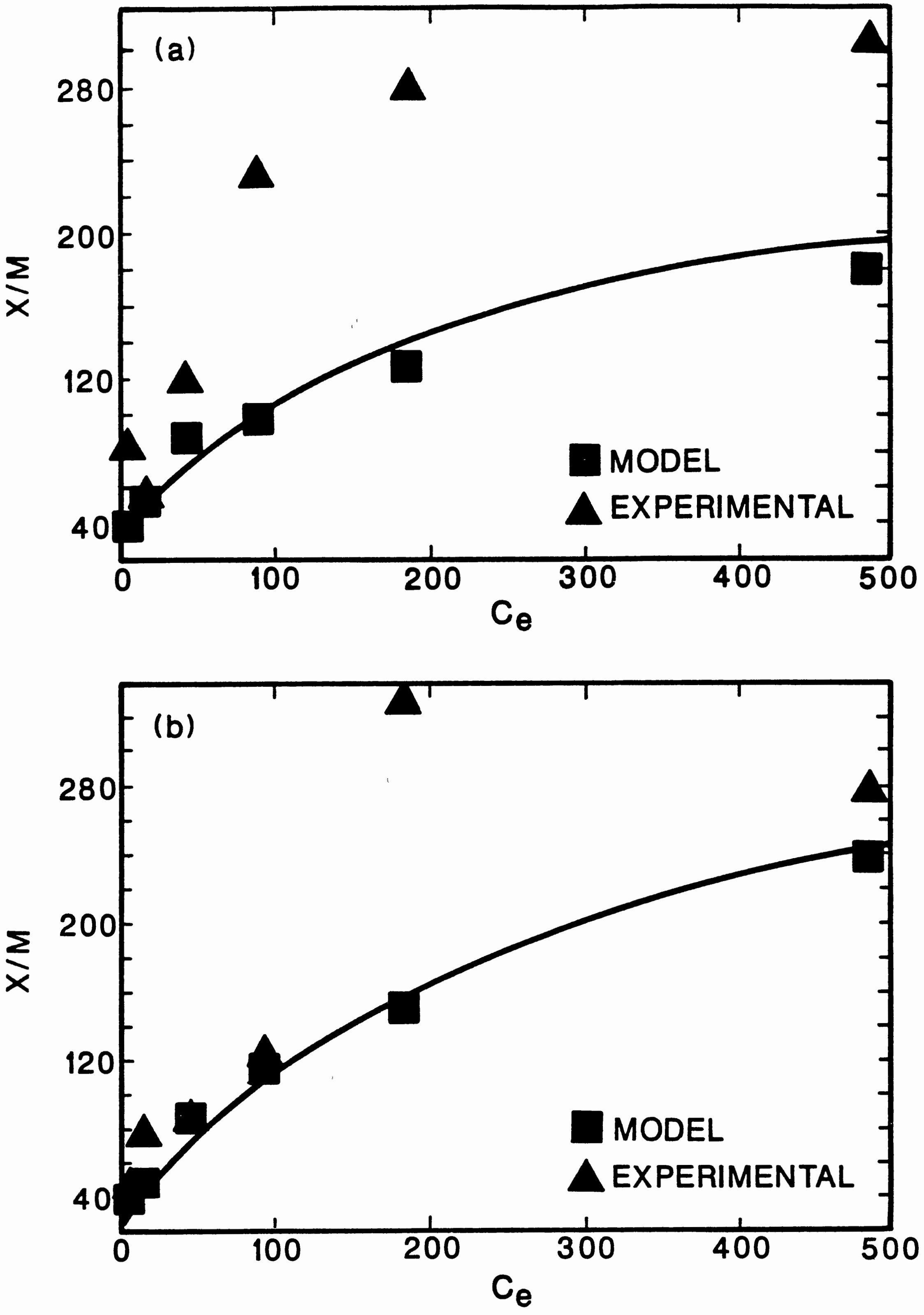
AII-32. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Lindane present on (a) S2, (b) S3 at 30°C



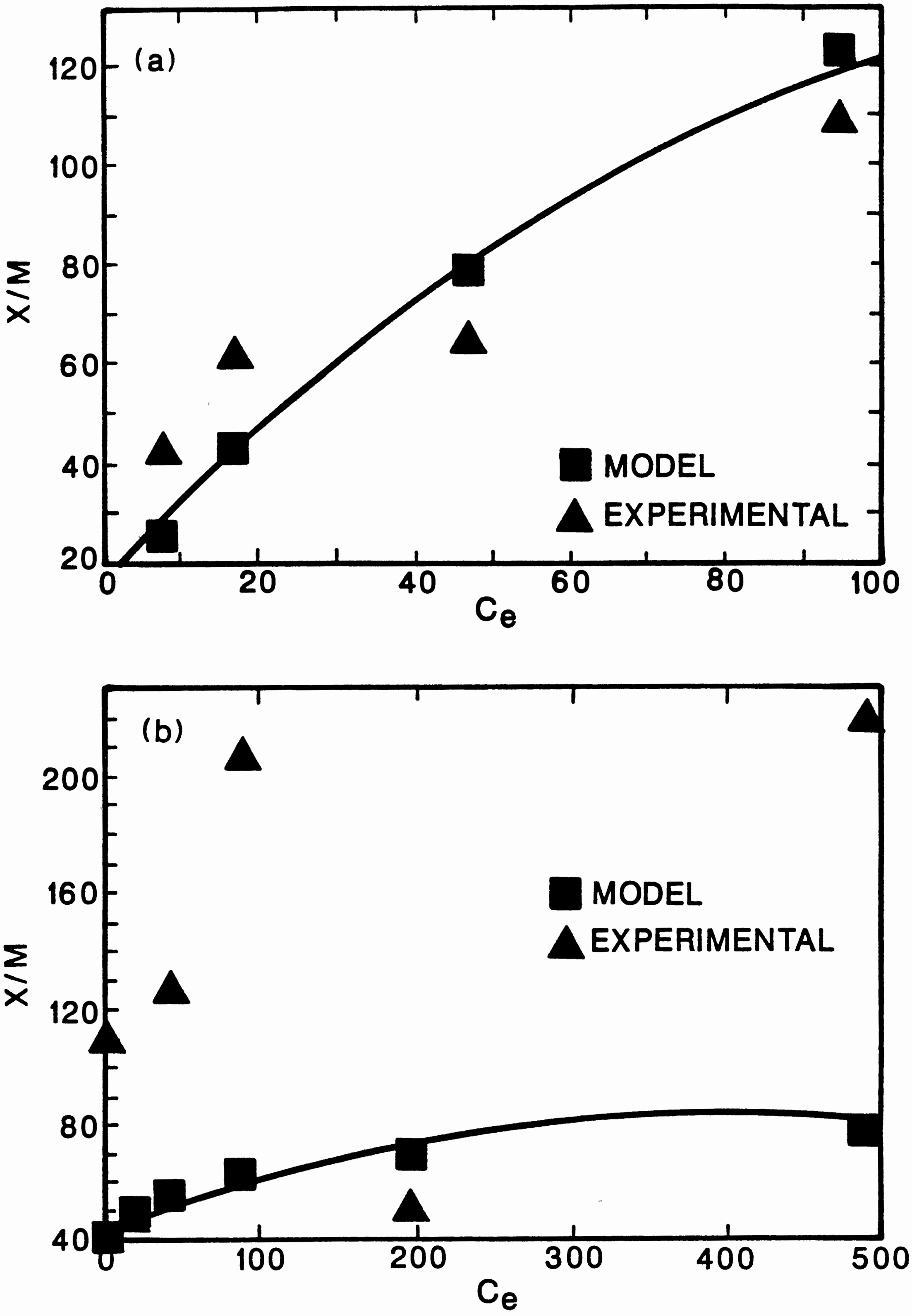
AII-33. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Lindane present on (a) S4, (b) S5 at 30°C



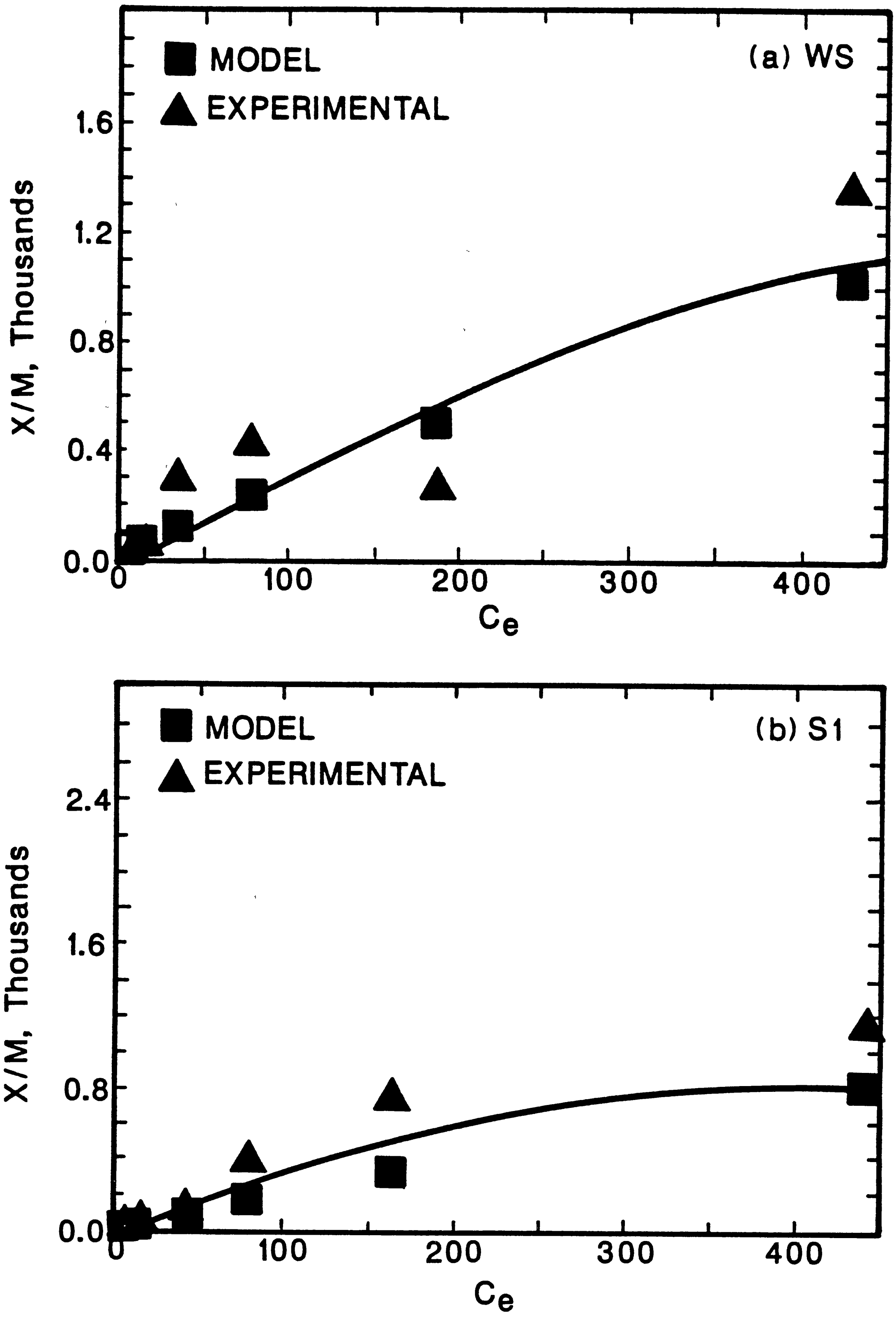
AII-34. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Lindane present on (a) WS, (b) S1 at 35°C



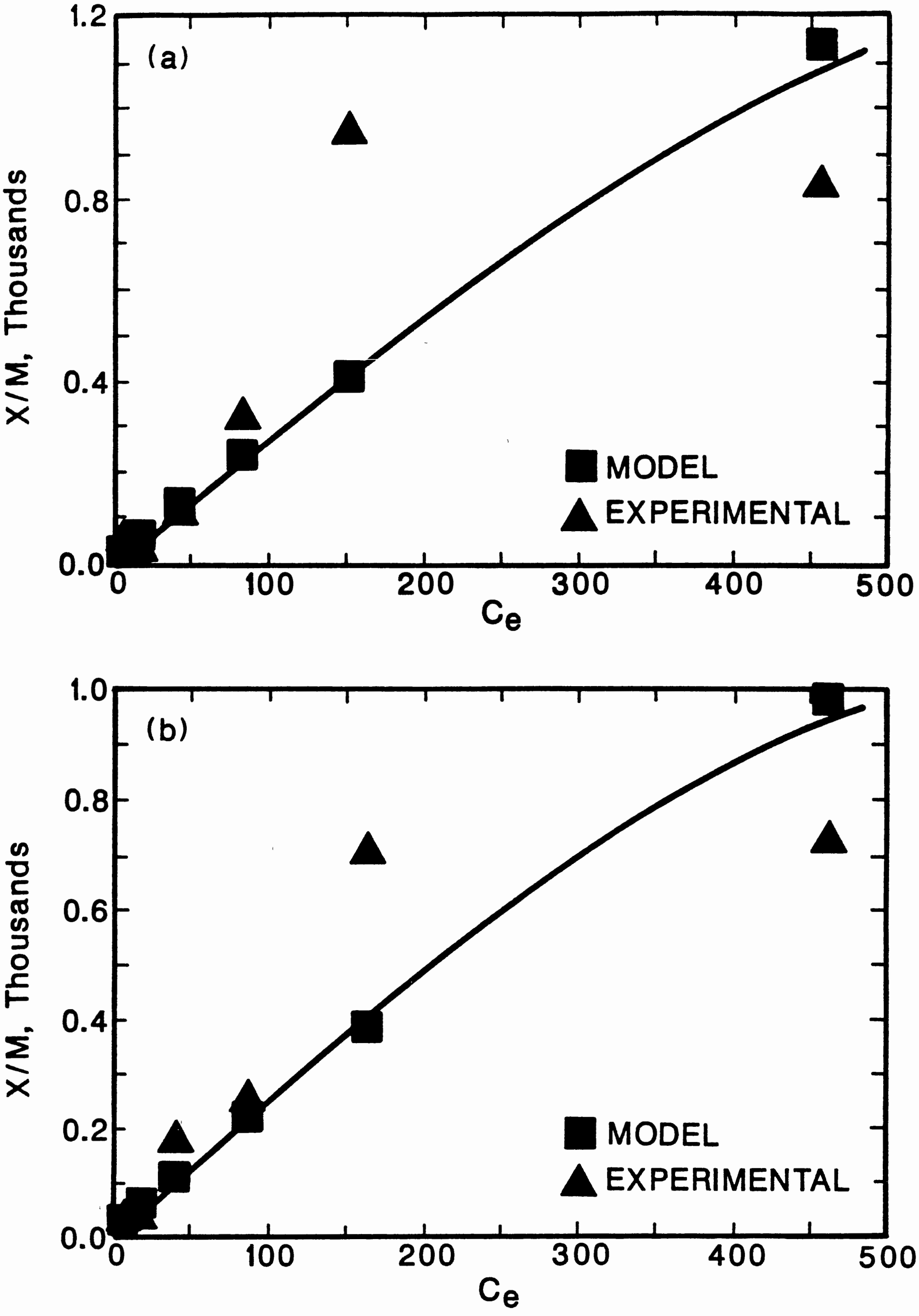
AII-35. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Lindane present on (a) S2, (b) S3 at 35°C



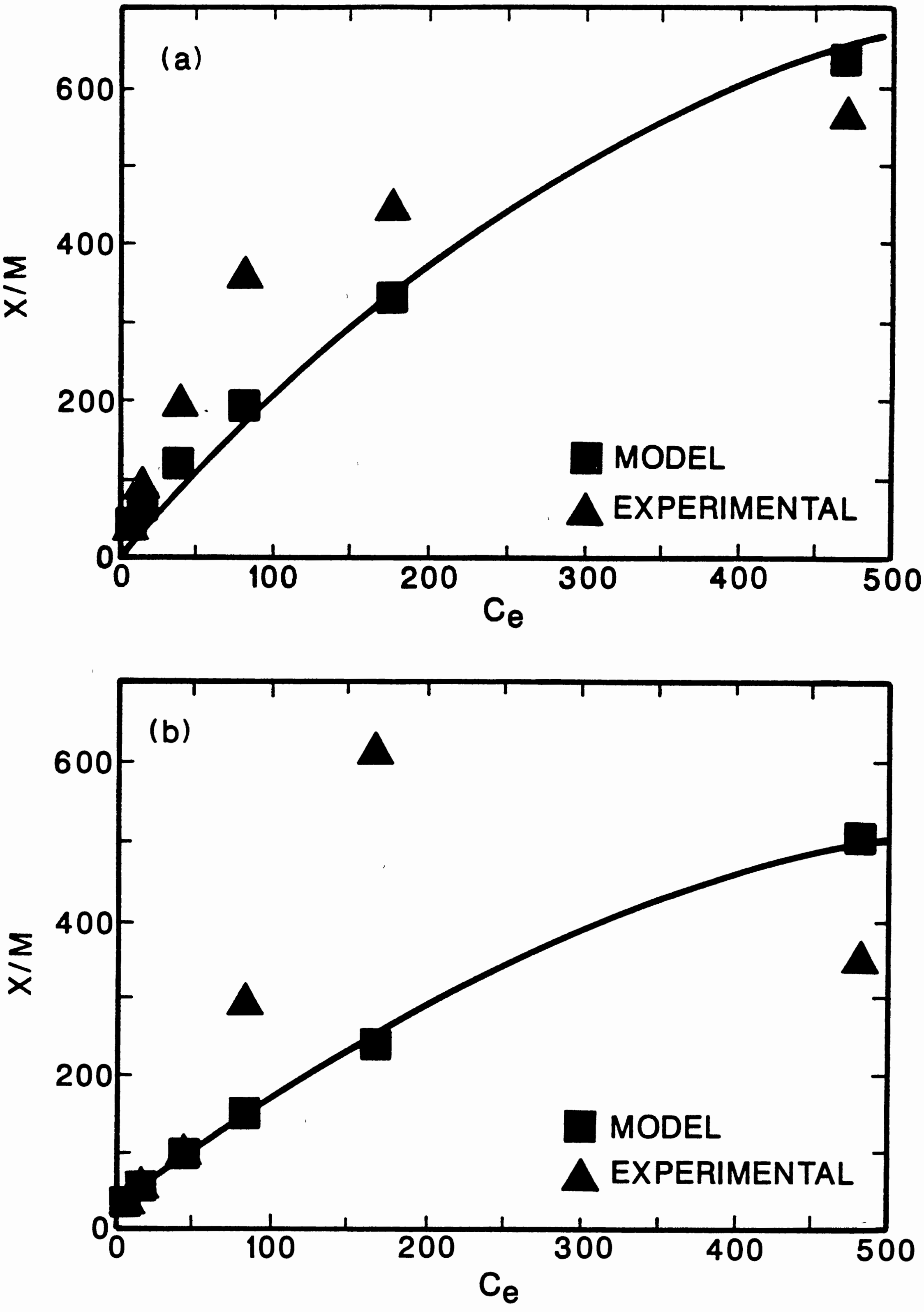
AII-36. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Lindane present on (a) S4, (b) S5 at 35°C



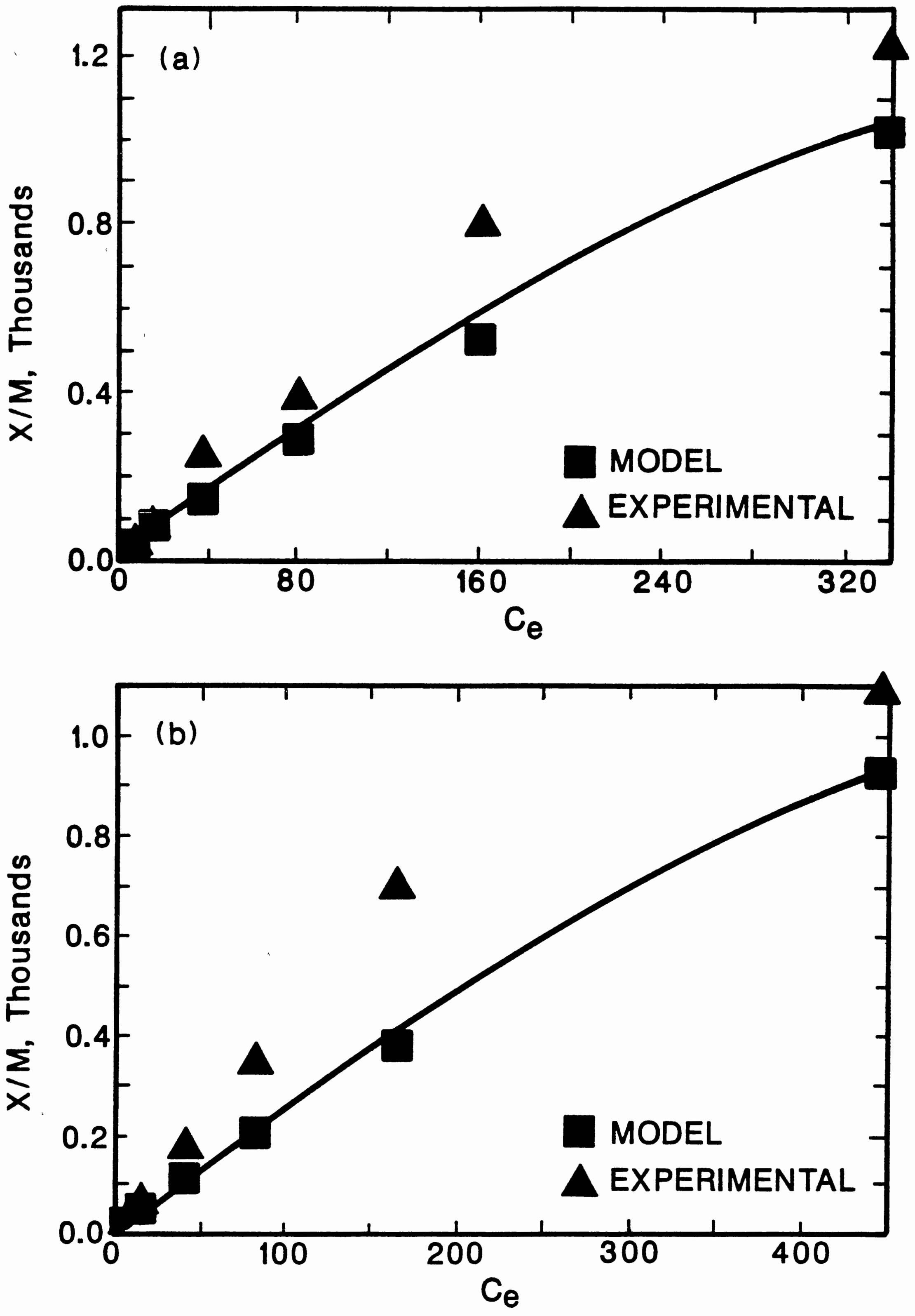
AII-37. SRS Multiple Freundlich-Type Isotherms of Silvex with 2,4-D present on (a) WS, (b) S1 at 25°C



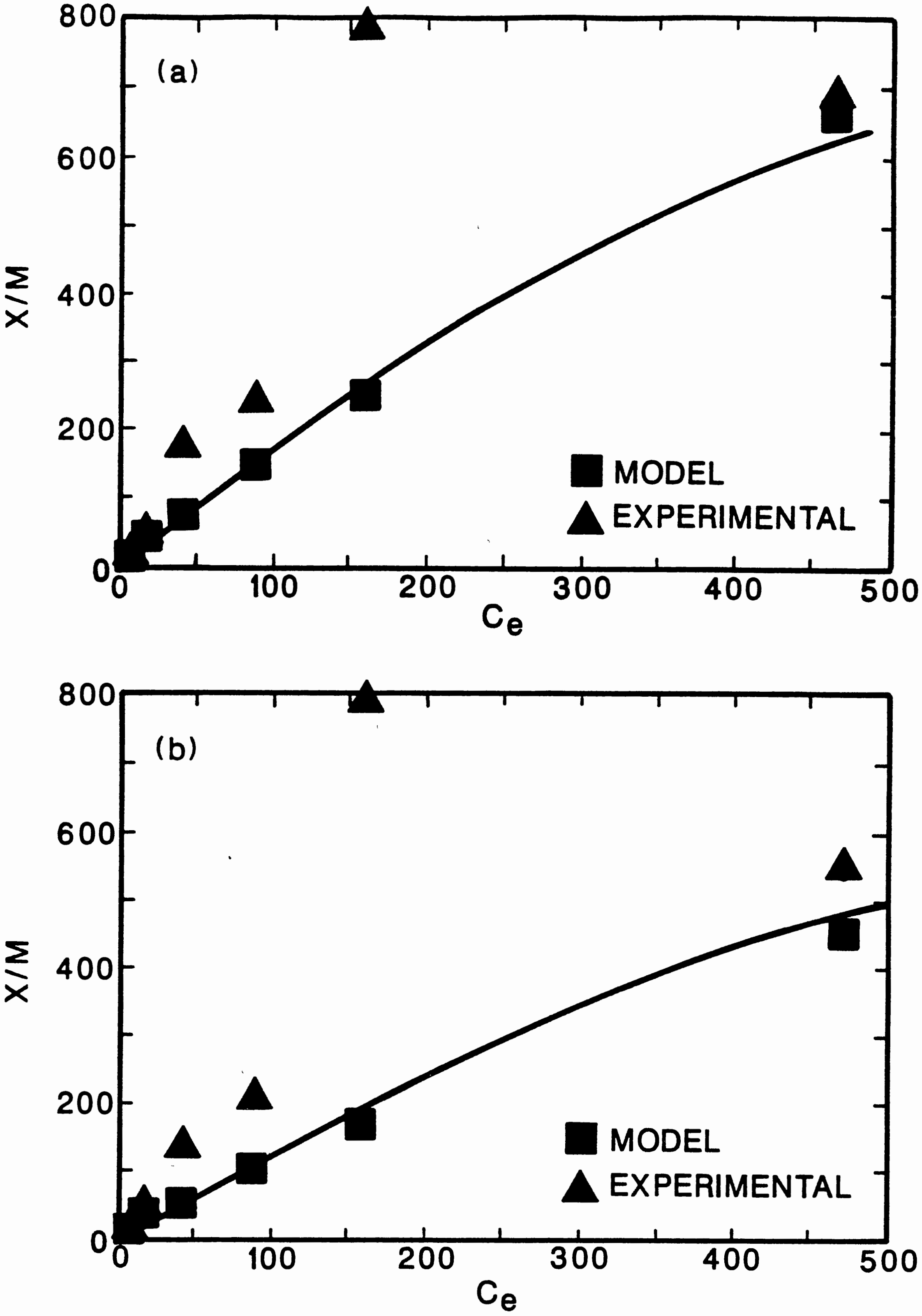
AII-38. SRS Multiple Freundlich-Type Isotherms of Silvex with 2,4-D present on (a) S2, (b) S3 at 25°C



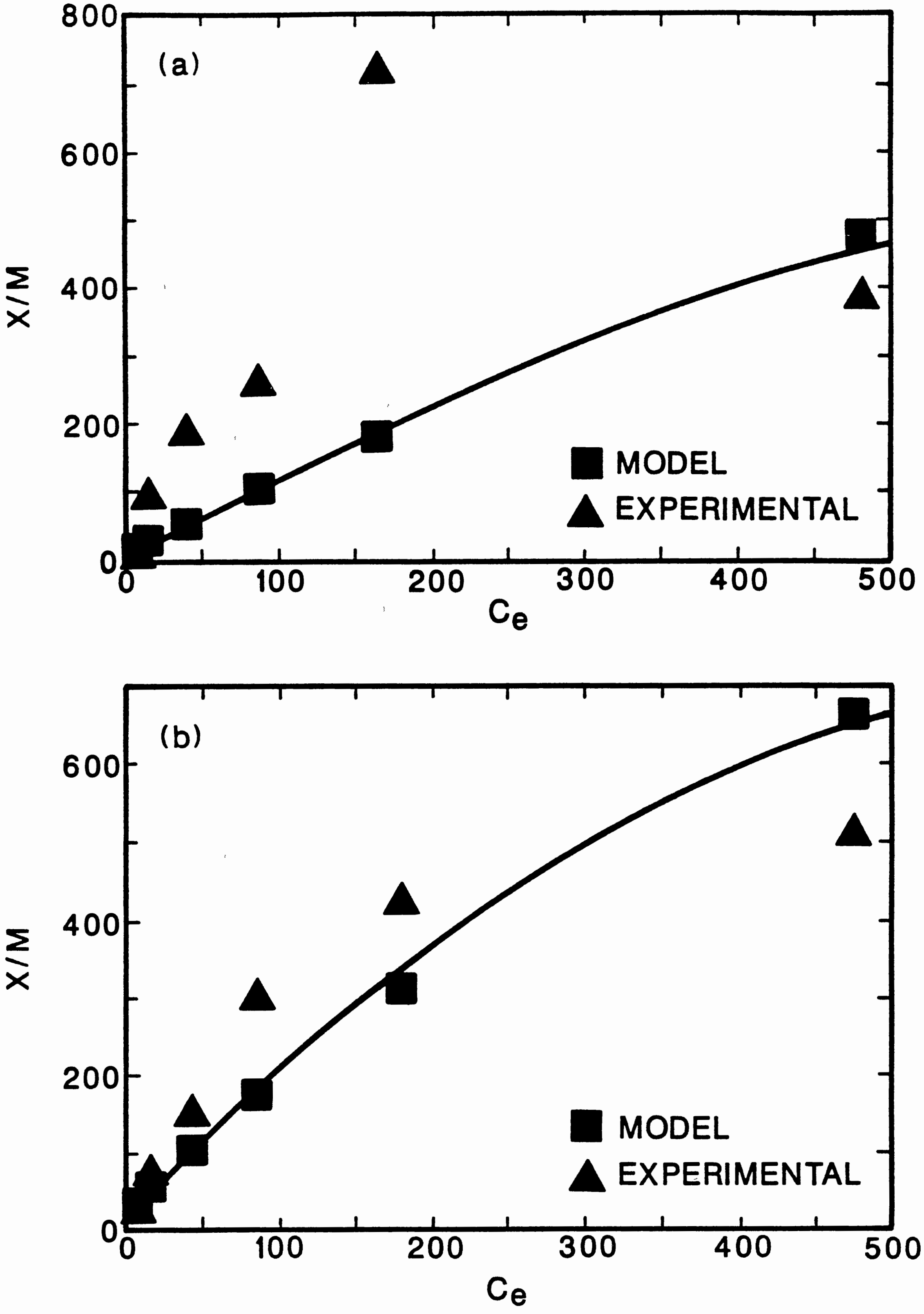
AII-39. SRS Multiple Freundlich-Type Isotherms of Silvex with 2,4-D present on (a) S4, (b) S5 at 25°C



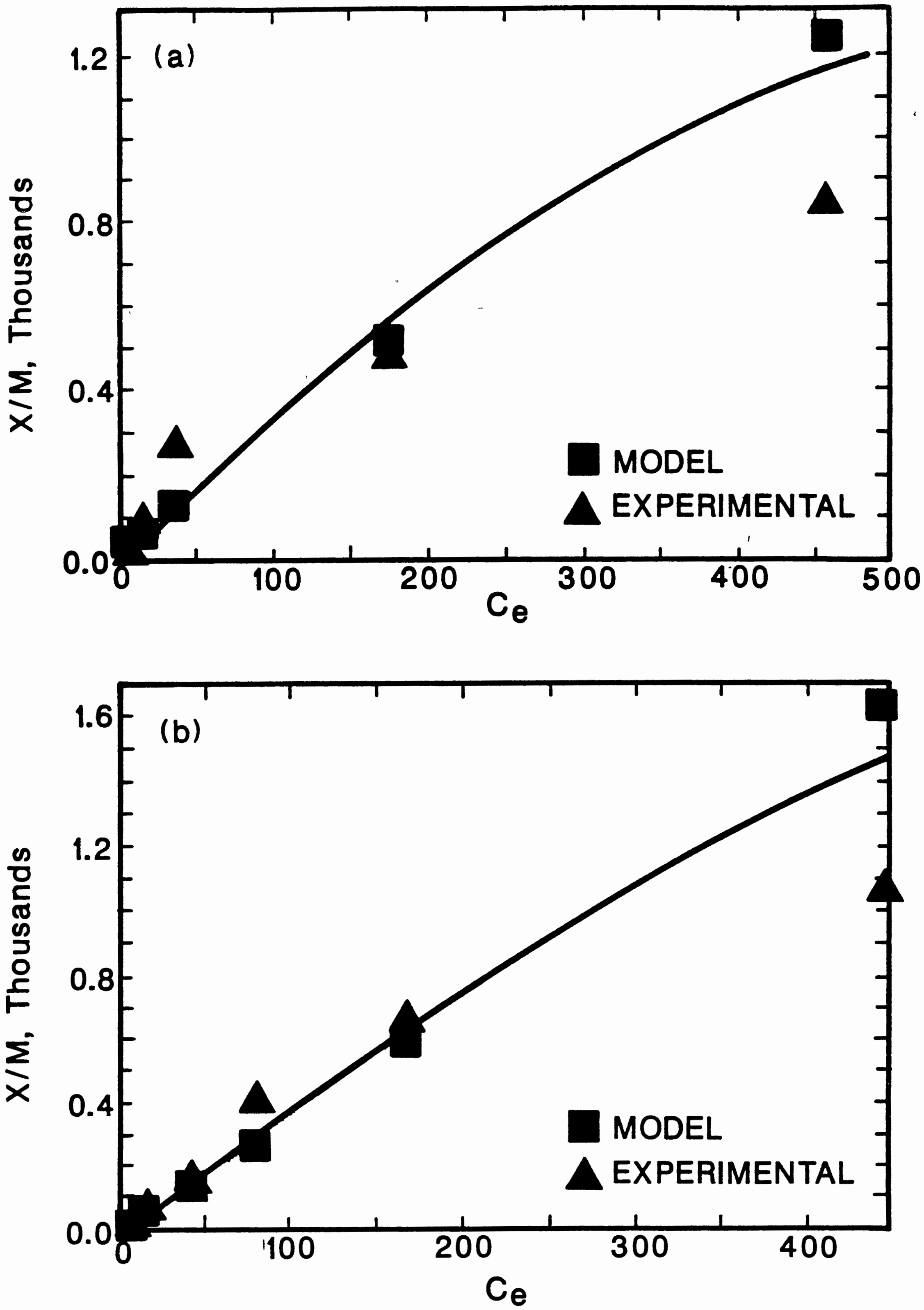
AII-40. SRS Multiple Freundlich-Type Isotherms of Silvex with 2,4-D present on (a) WS, (b) S1 at 30°C



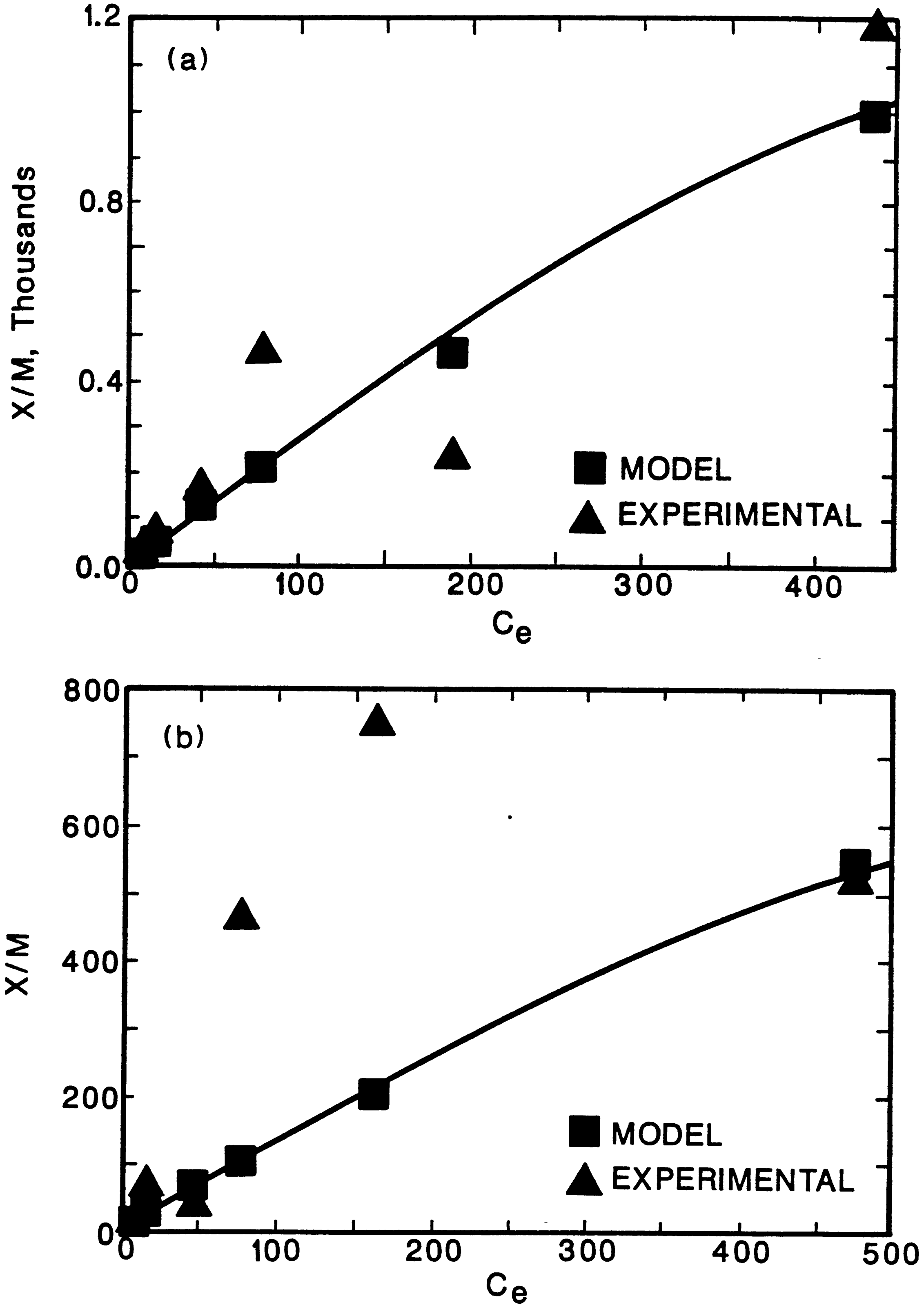
AII-41. SRS Multiple Freundlich-Type Isotherms of Silvex with 2,4-D present on (a) S2, (b) S3 at 30°C



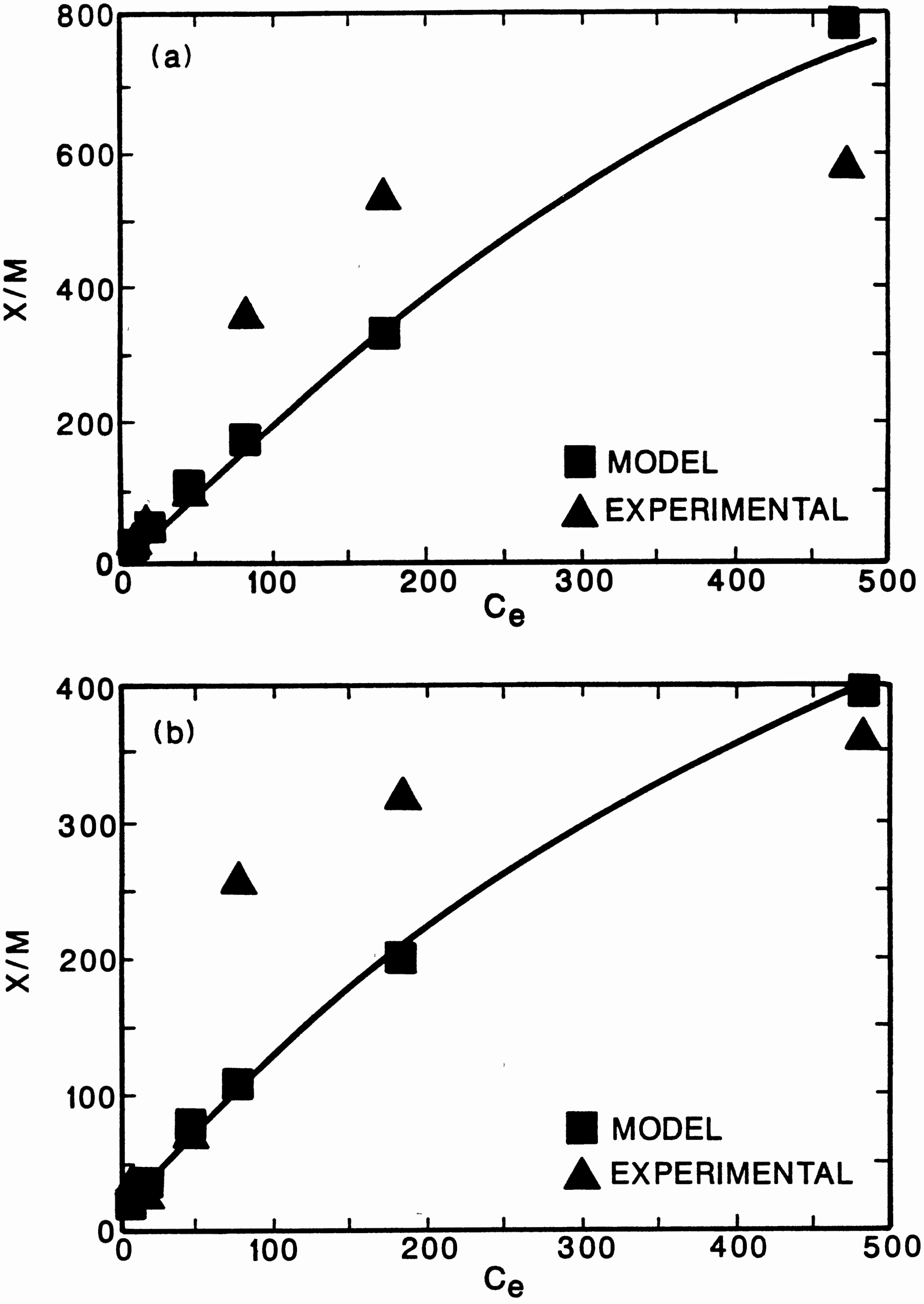
AII-42. SRS Multiple Freundlich-Type Isotherms of Silvex with 2,4-D present on (a) S4, (b) S5 at 30°C



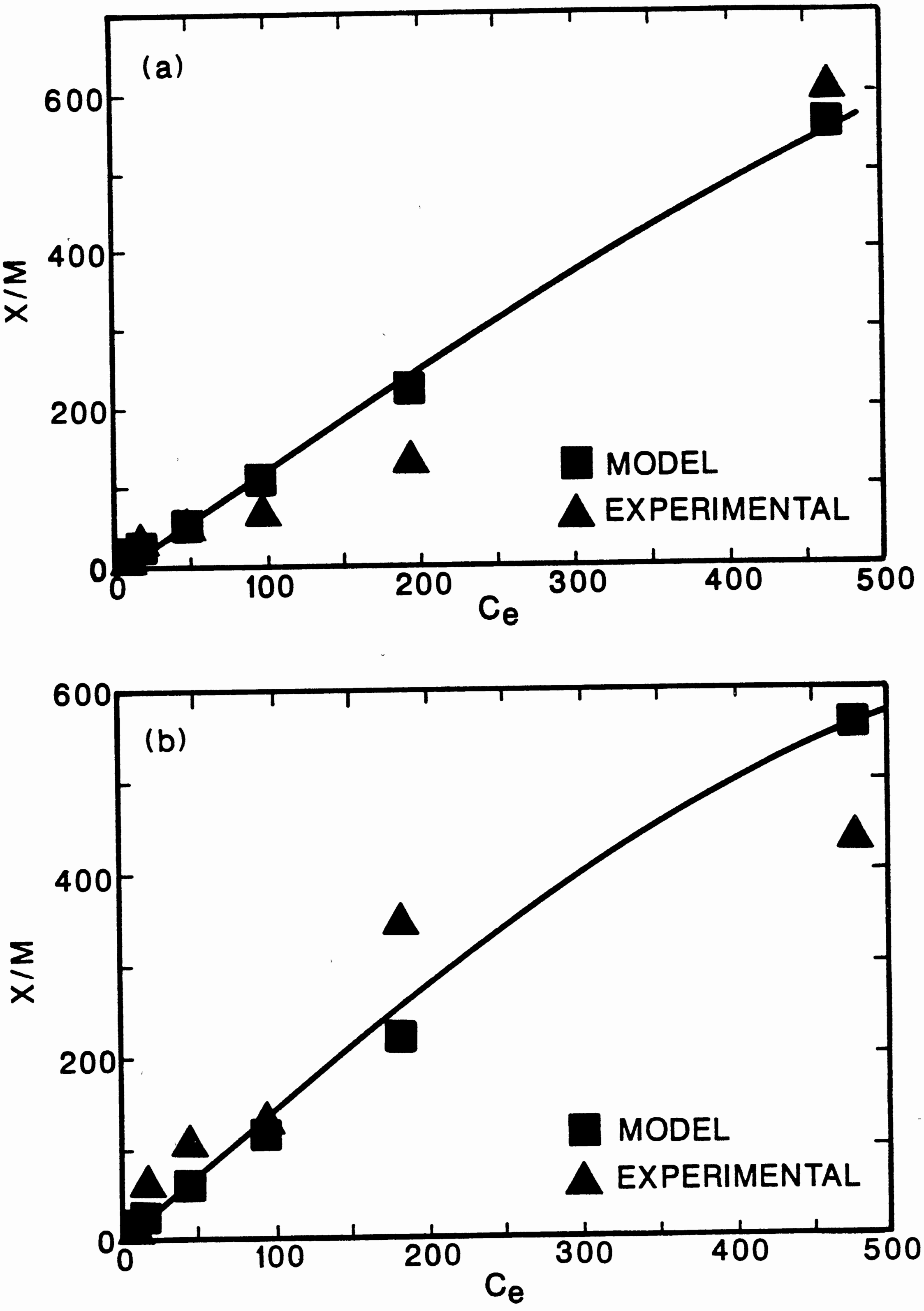
AII-43. SRS Multiple Freundlich-Type Isotherms of Silvex with 2,4-D present on (a) WS, (b) S1 at 35°C



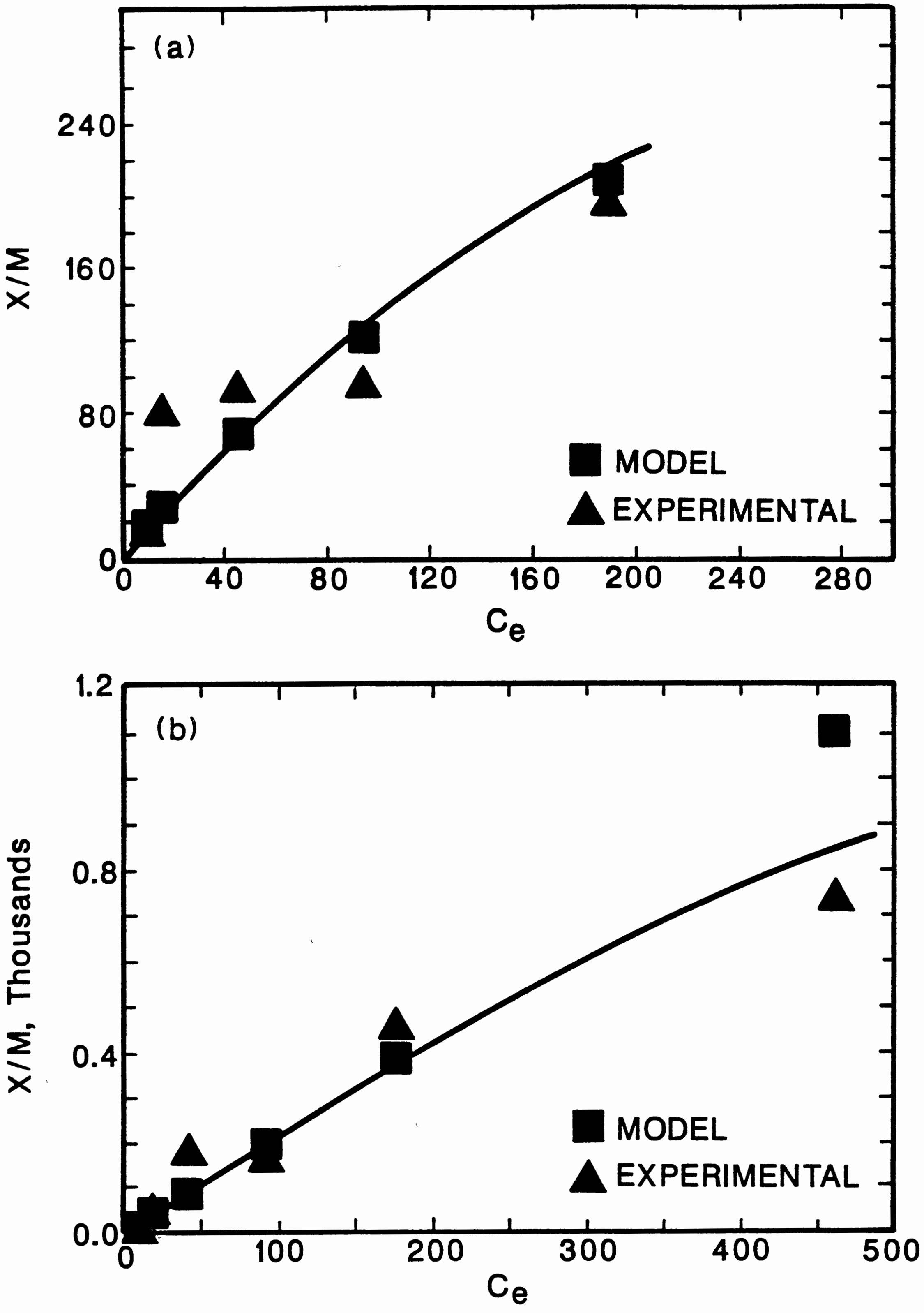
AII-44. SRS Multiple Freundlich-Type Isotherms of Silvex with 2,4-D present on (a) S2, (b) S3 at 35°C



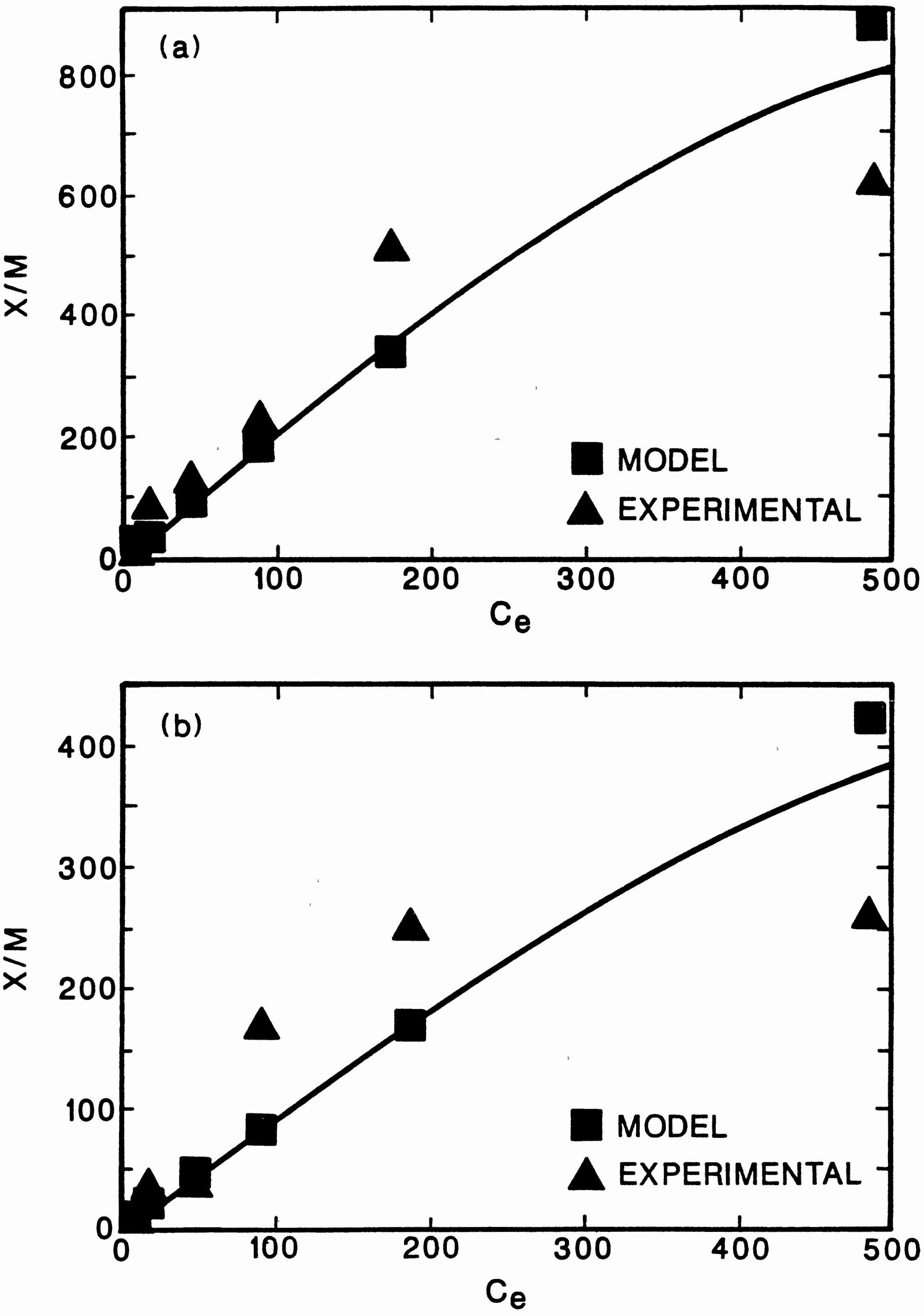
AII-45. SRS Multiple Freundlich-Type Isotherms of Silvex with 2,4-D present on (a) S4, (b) S5 at 35°C



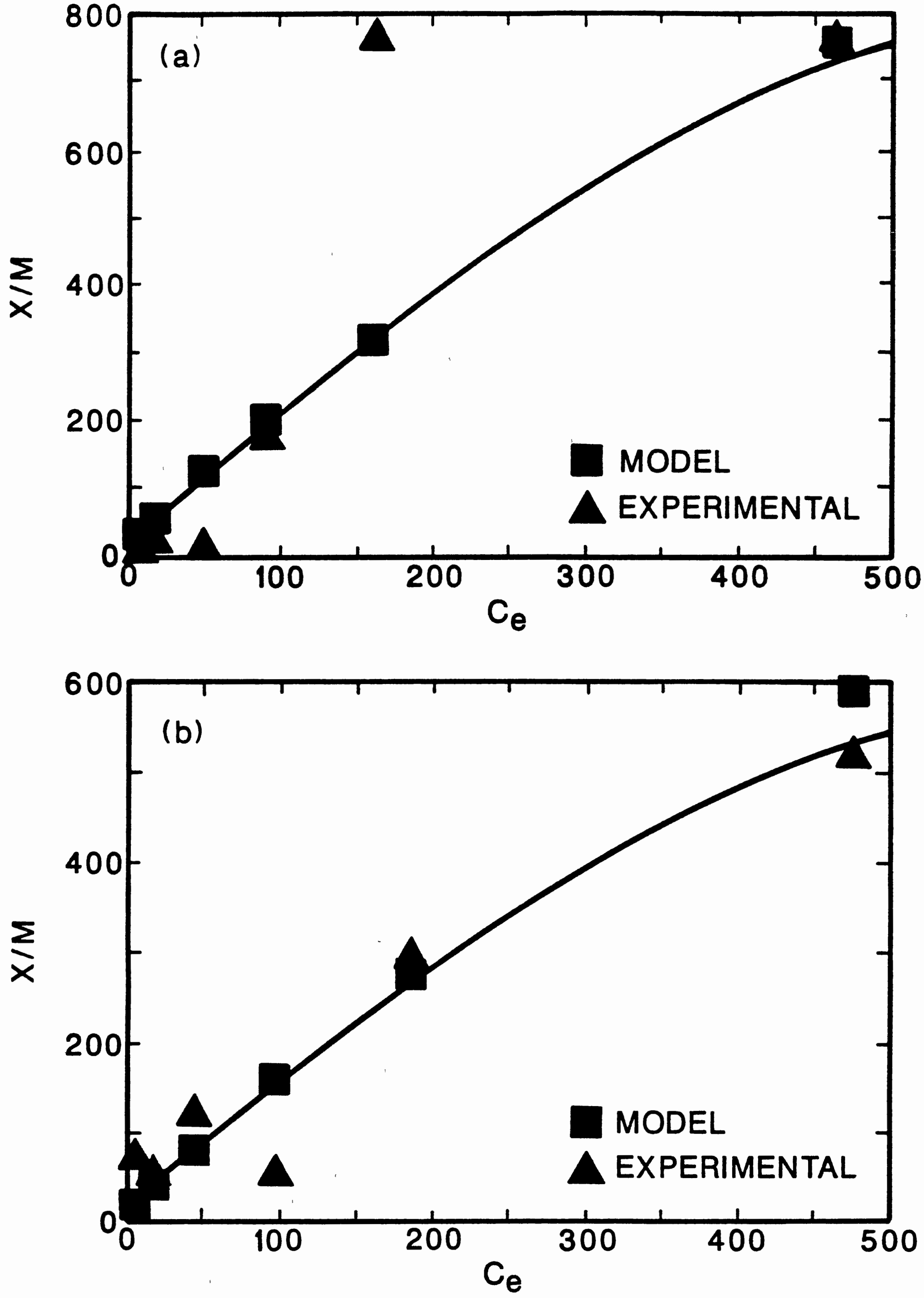
AII-46. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Silvex present on (a) WS, (b) S1 at 25°C



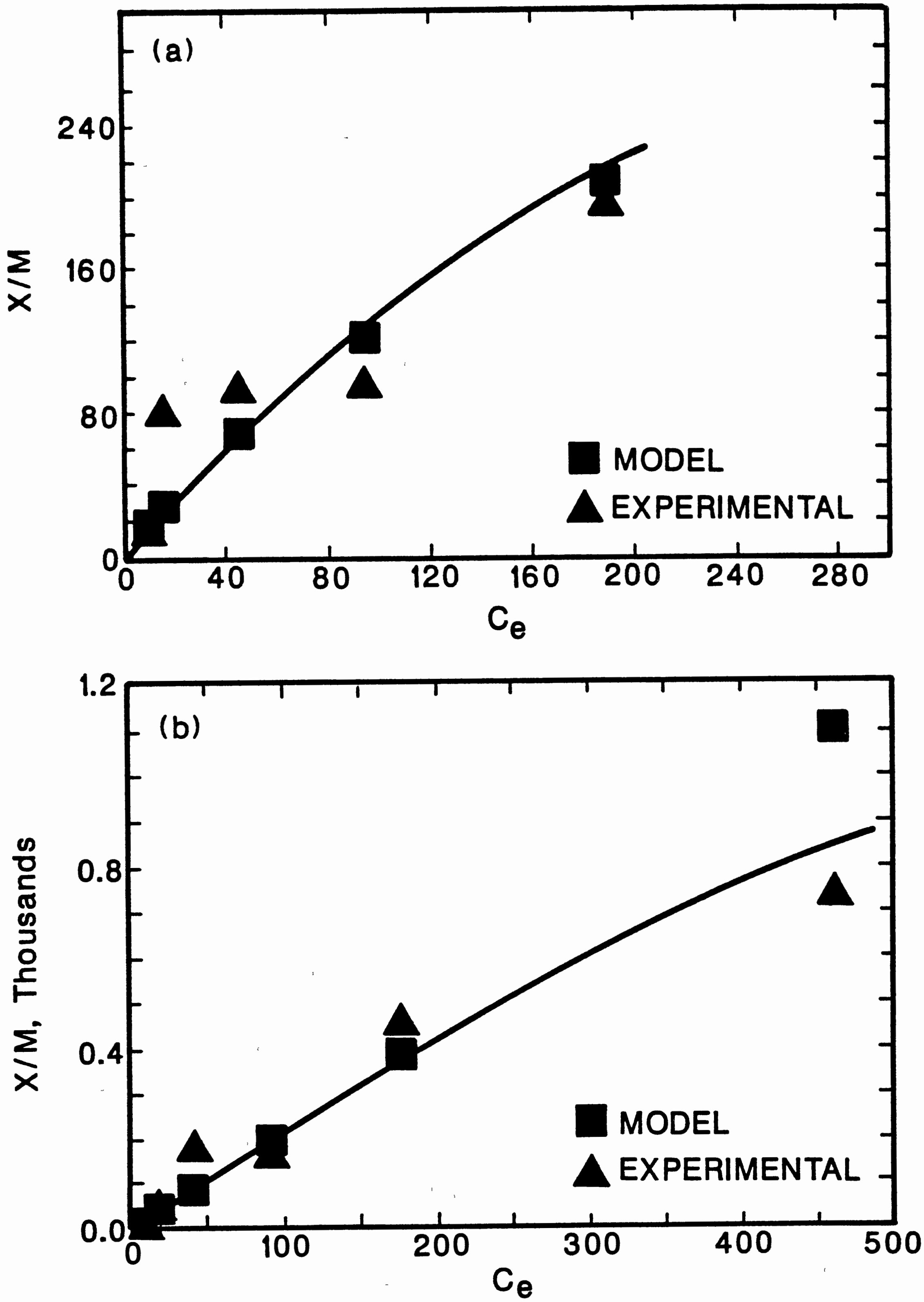
AII-47. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Silvex present on (a) S2, (b) S3 at 25°C



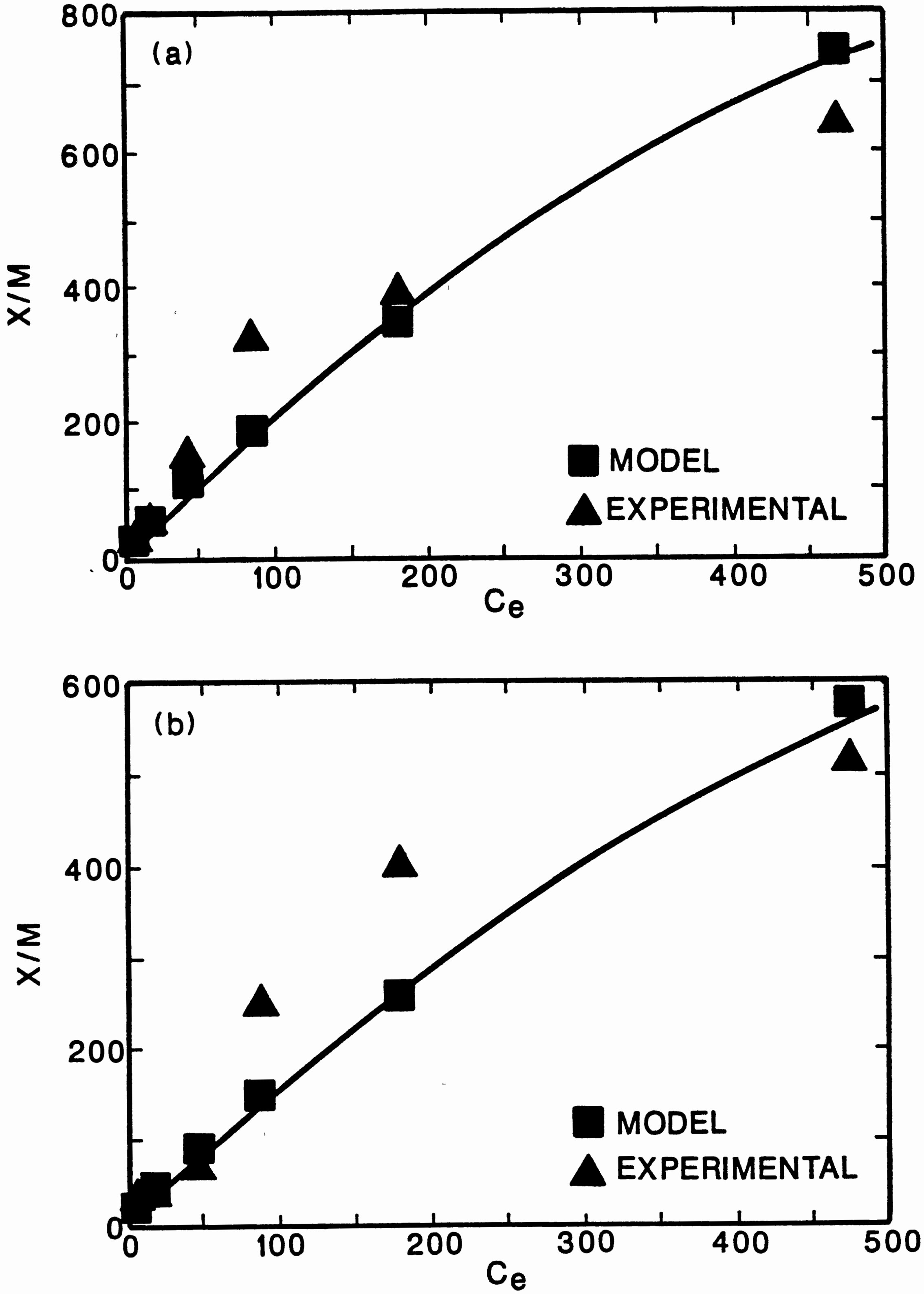
AII-48. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Silvex present on (a) S4, (b) S5 at 25°C



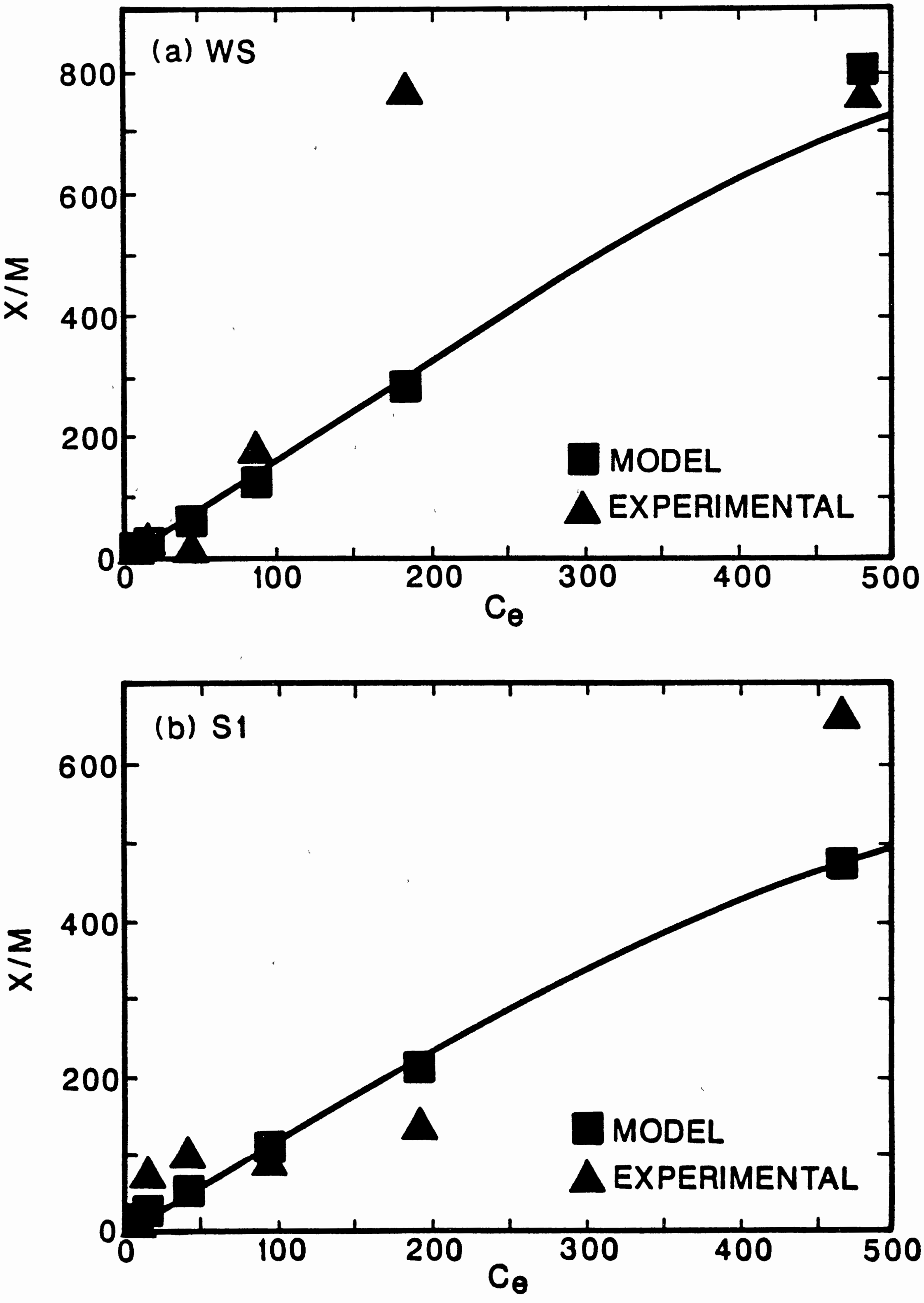
AII-49. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Silvex present on (a) WS, (b) S1 at 30°C



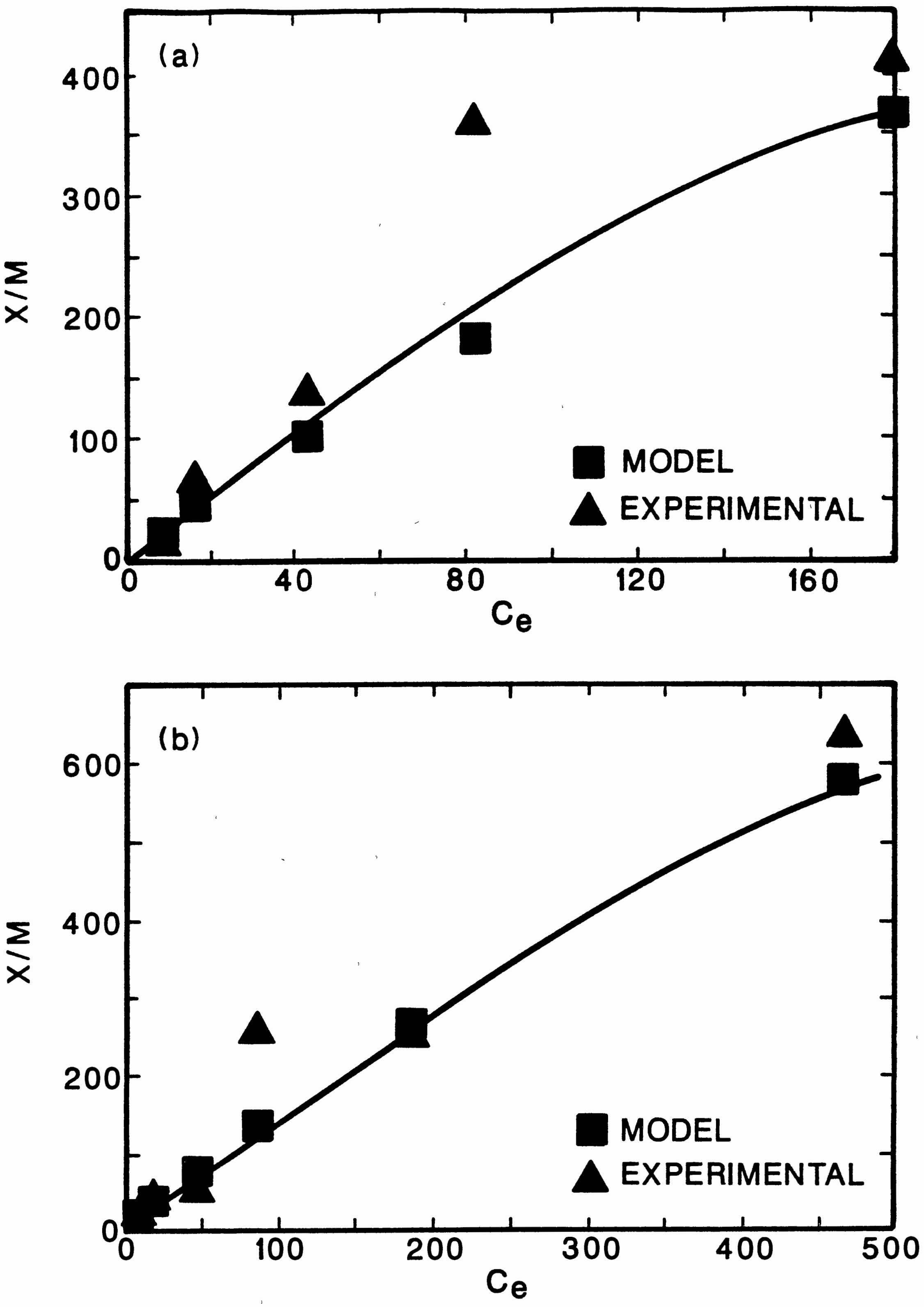
AII-50. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Silvex present on (a) S2, (b) S3 at 25°C



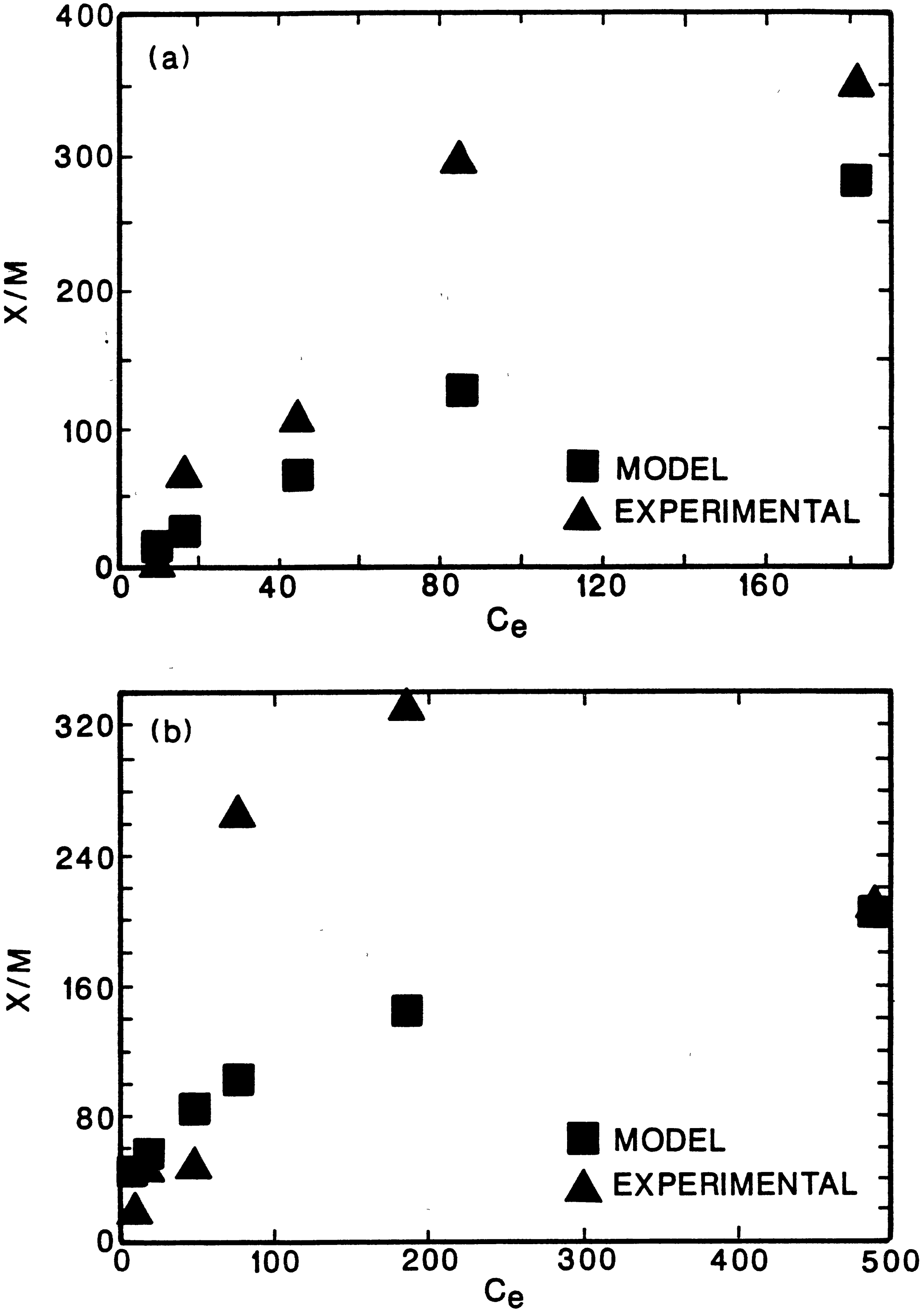
AII-51. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Silvex present on (a) S4, (b) S5 at 30°C



AII-52. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Silvex present on (a) WS, (b) S1 at 35°C



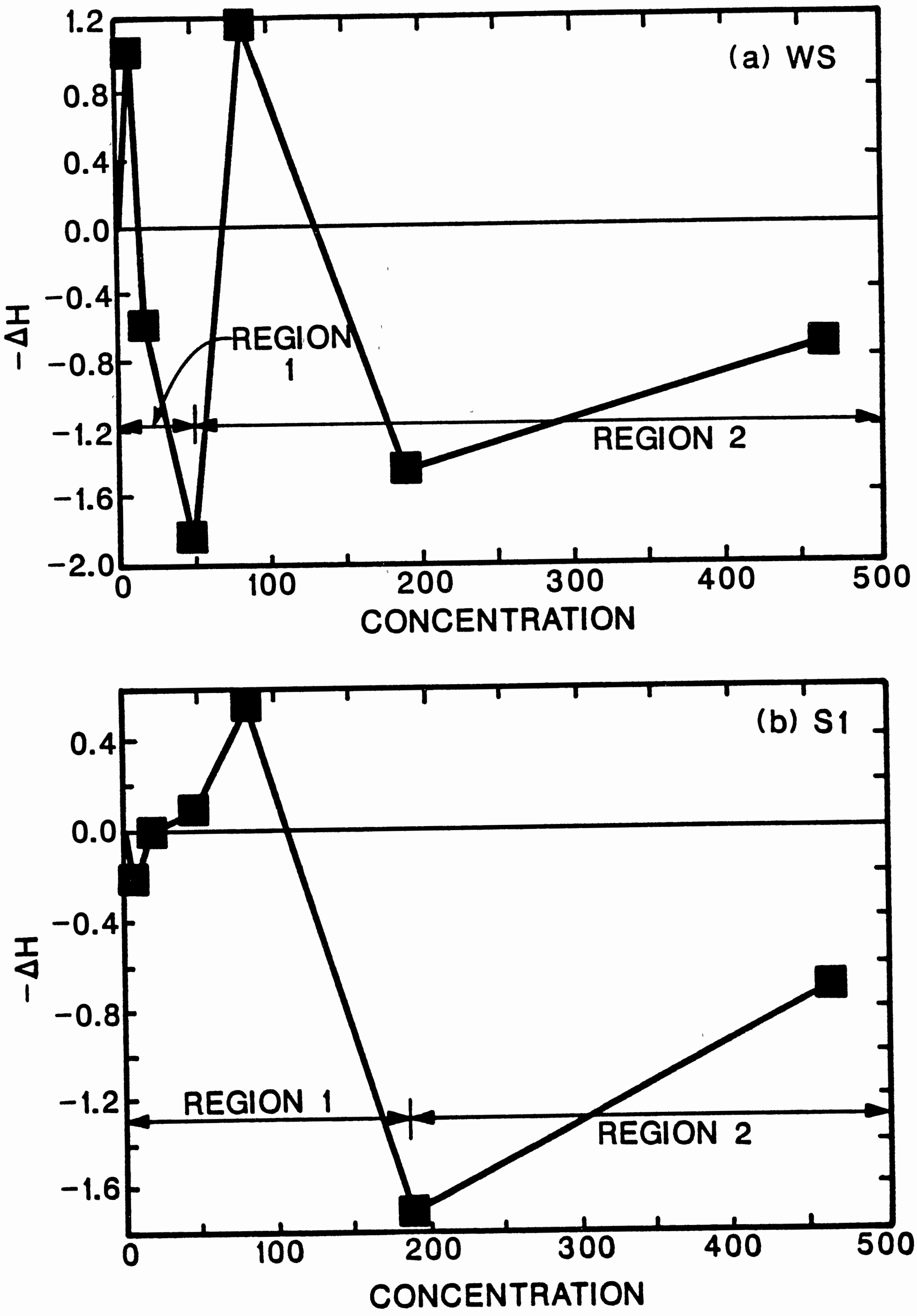
AII-53. SRS Multiple Freundlich-Type Isotherms of 2,4-D with Silvex present on (a) S2, (b) S3 at 35°C



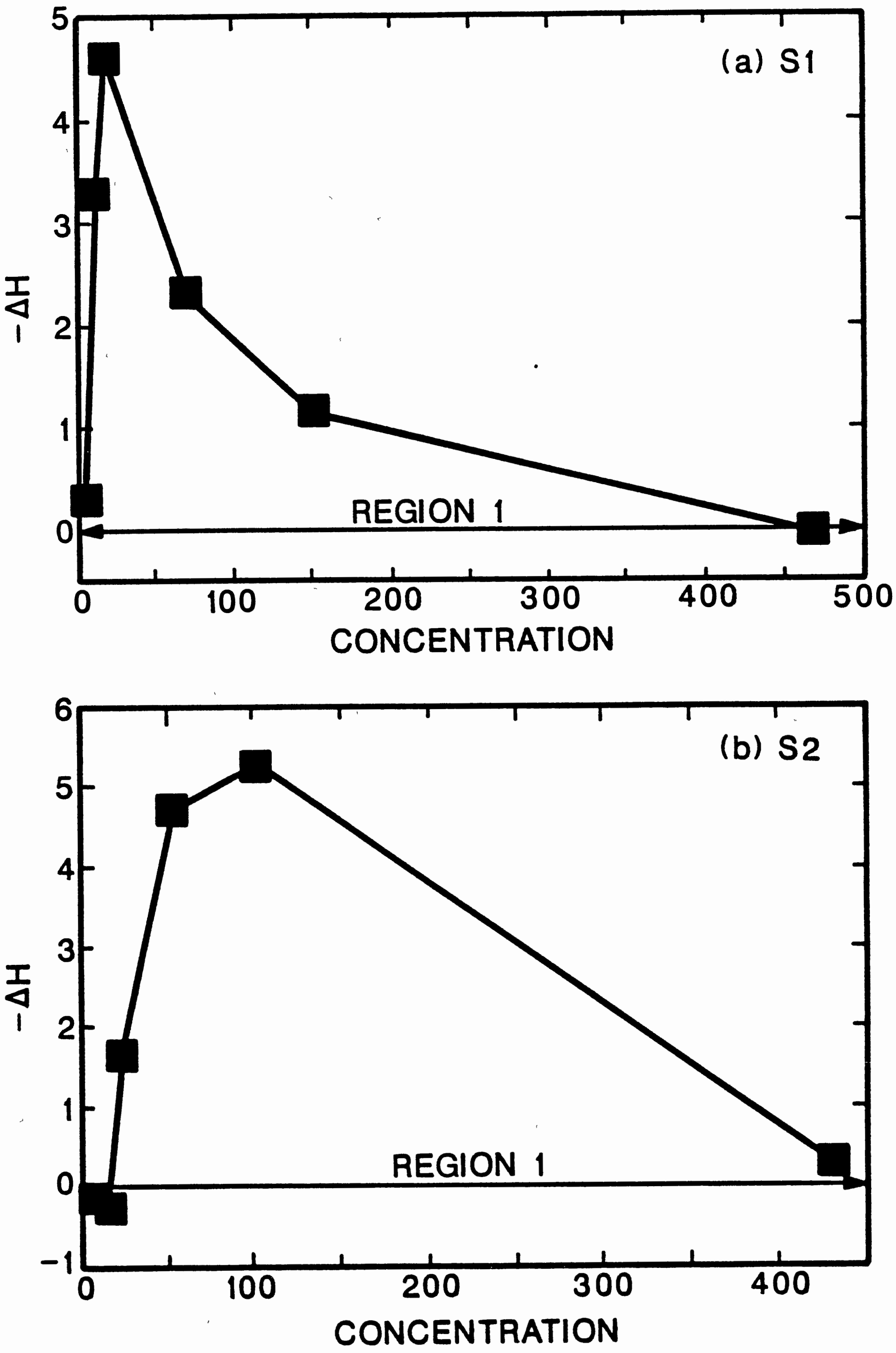
AII-54. SRS Multiple Freundlich-Type Isotherms
of 2,4-D with Silvex present on
(a) S4, (b) S5 at 35°C

APPENDIX C

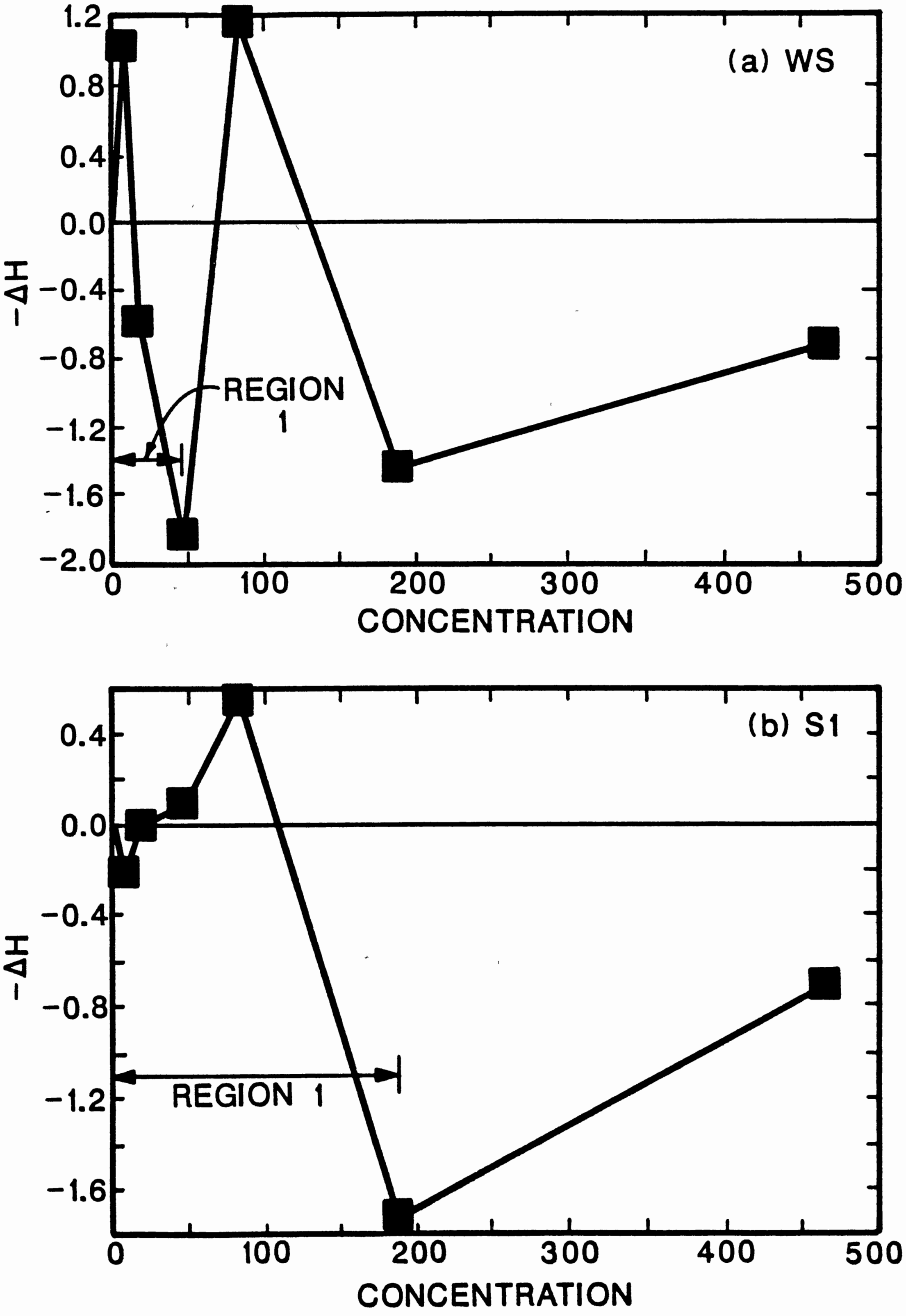
ISOSTERIC HEATS OF ADSORPTION PLOTS FOR LINDANE, SILVEX AND 2,4-D ON PORT SOIL AND SOIL FRACITONS



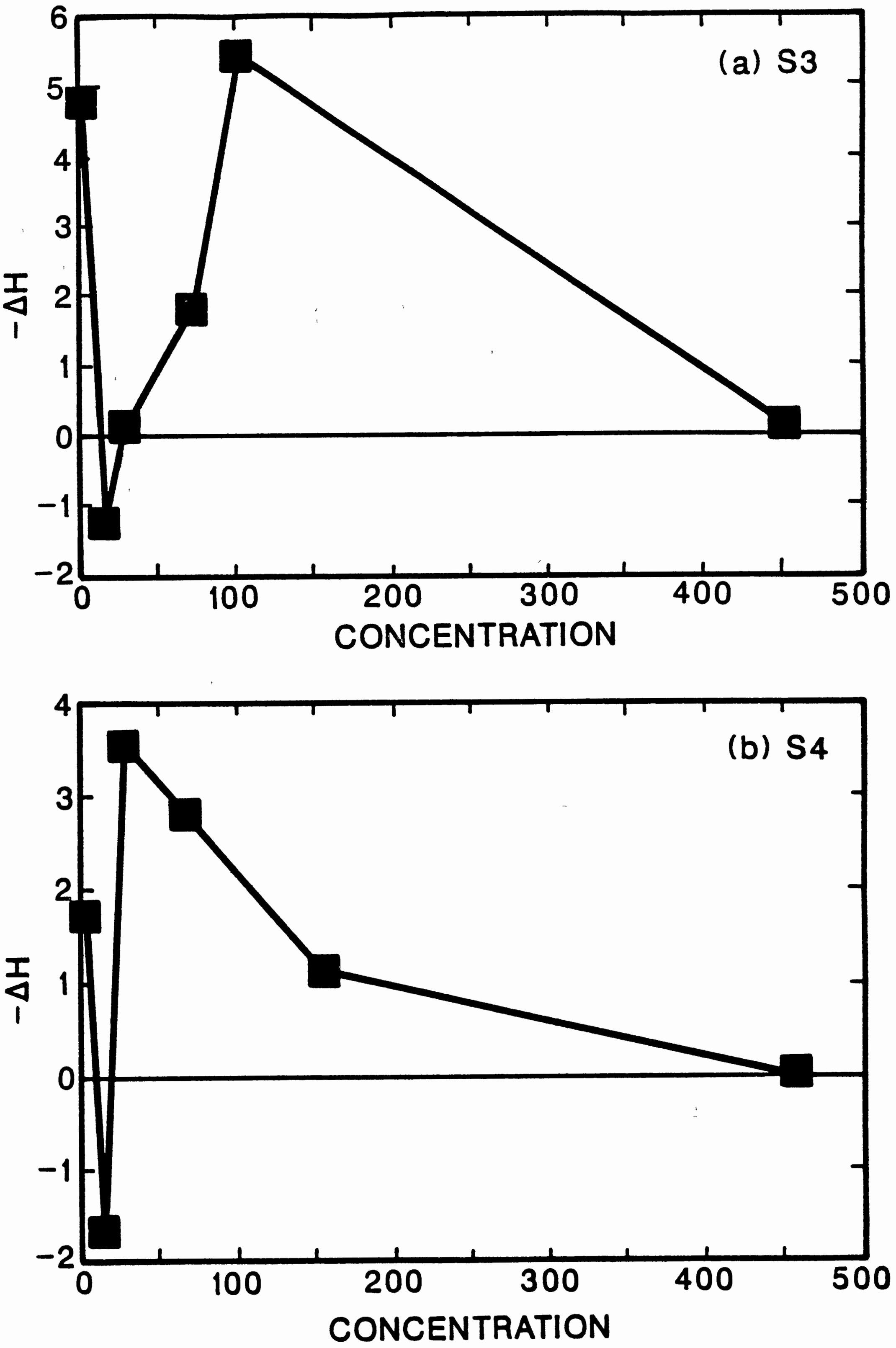
AIII-1. Isosteric Heats of Adsorption of Silvex with Lindane present on (a) WS, (b) S1



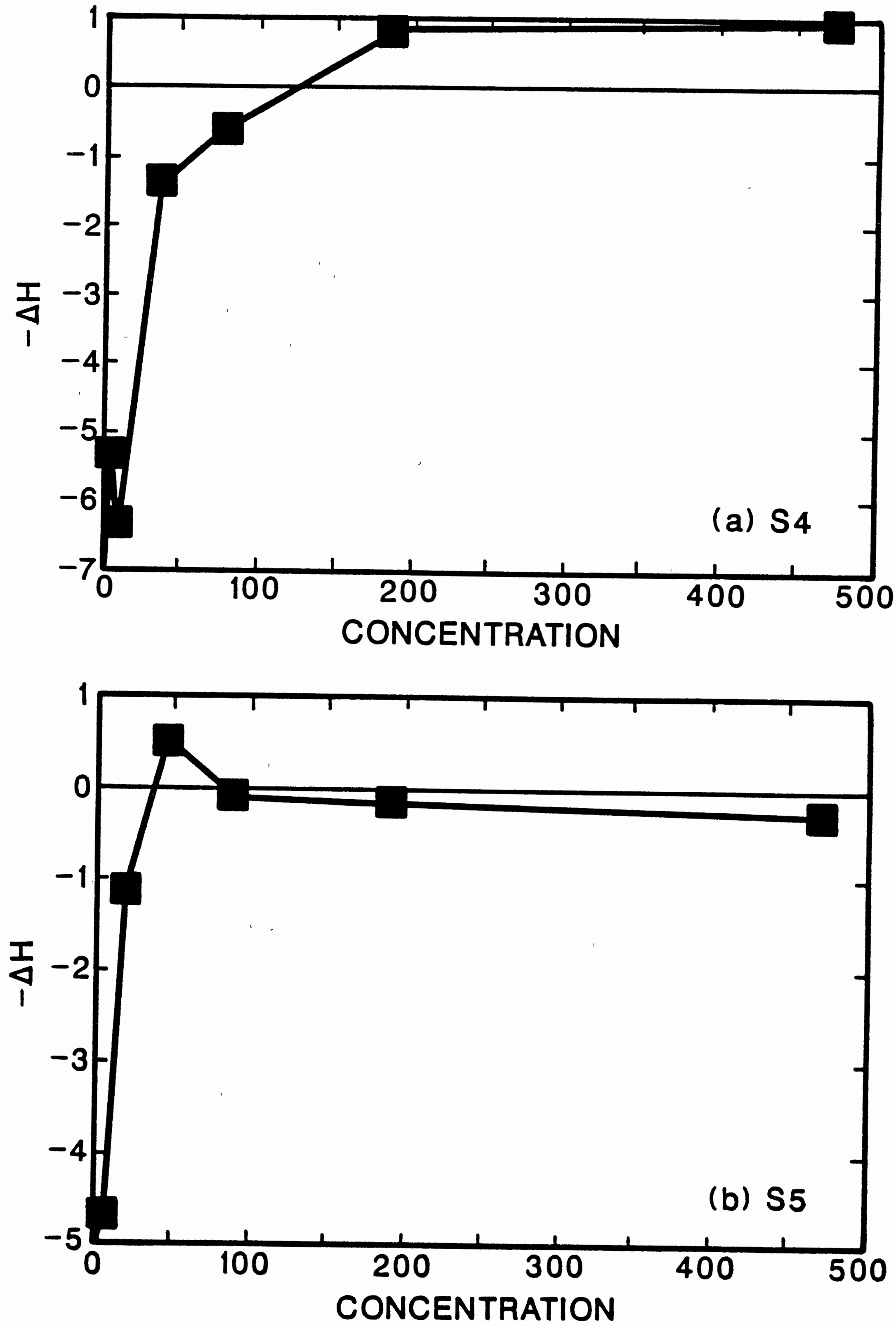
AIII-2. Isosteric Heats of Adsorption of Lindane with Silvex present on (a) S1, (b) S2



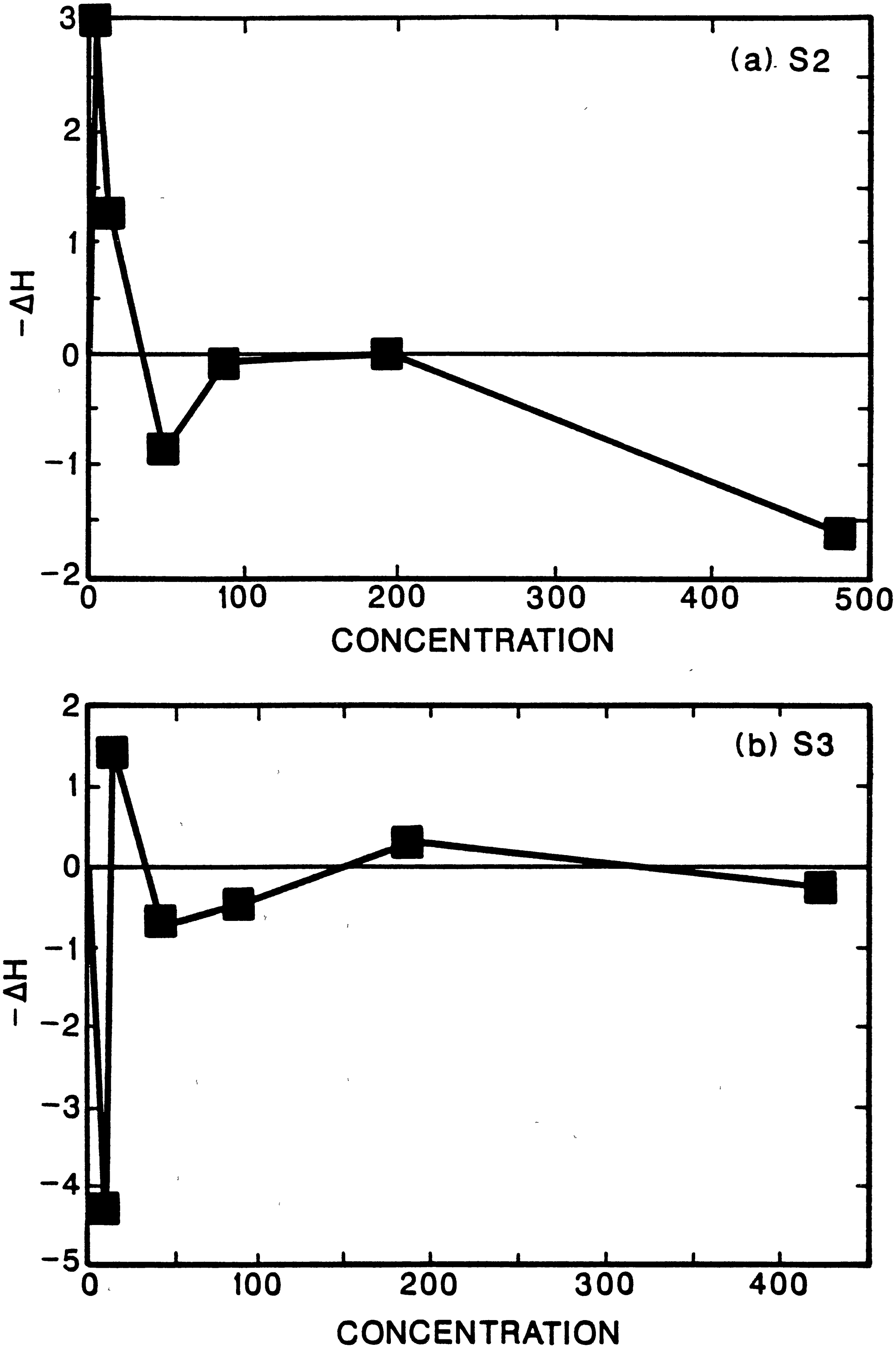
AIII-3. Isosteric Heats of Adsorption of Silvex with Lindane present on (a) WS, (b) S1



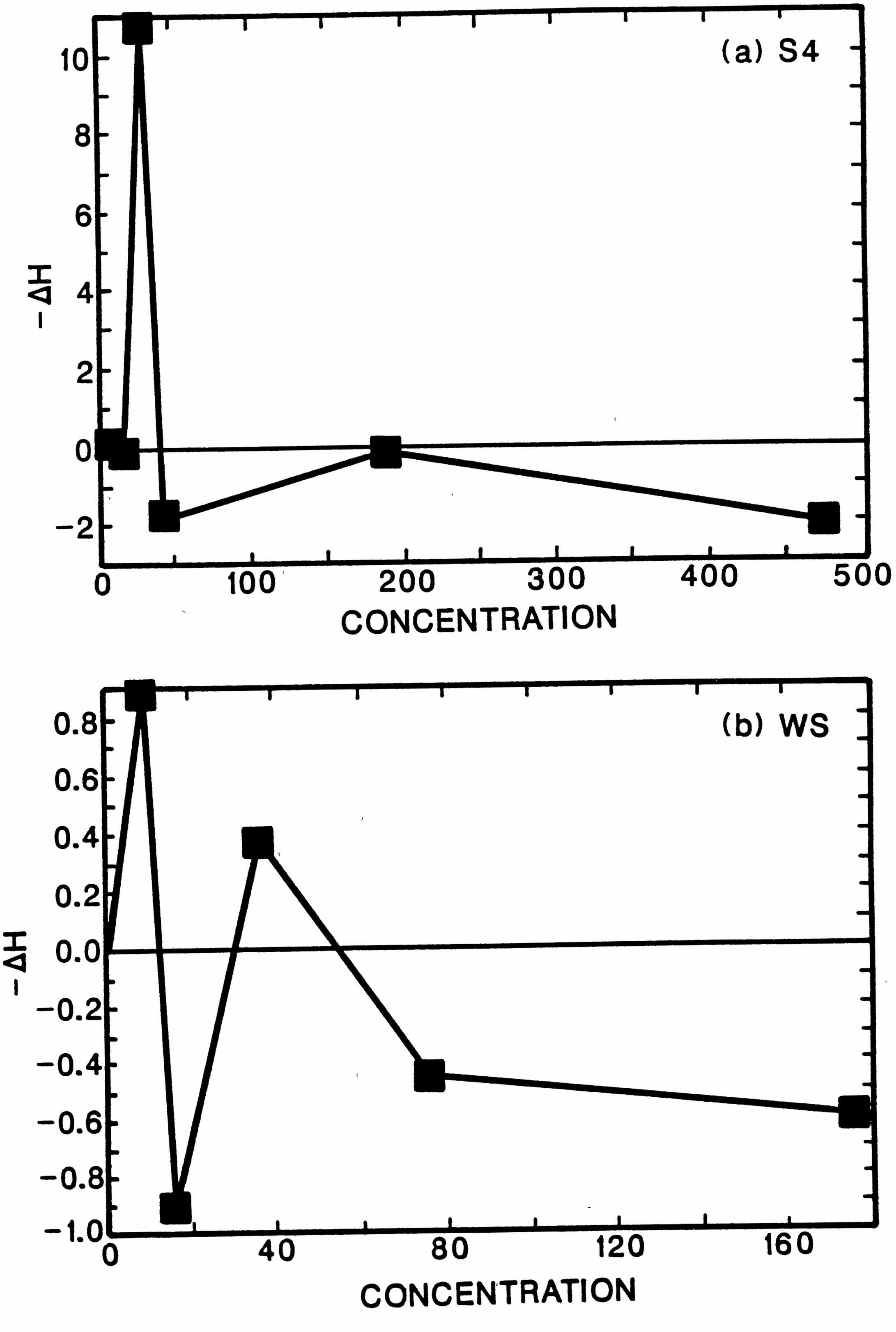
AIII-4. Isosteric Heats of Adsorption of Lindane with Silvex present on (a) S3, (b) S4



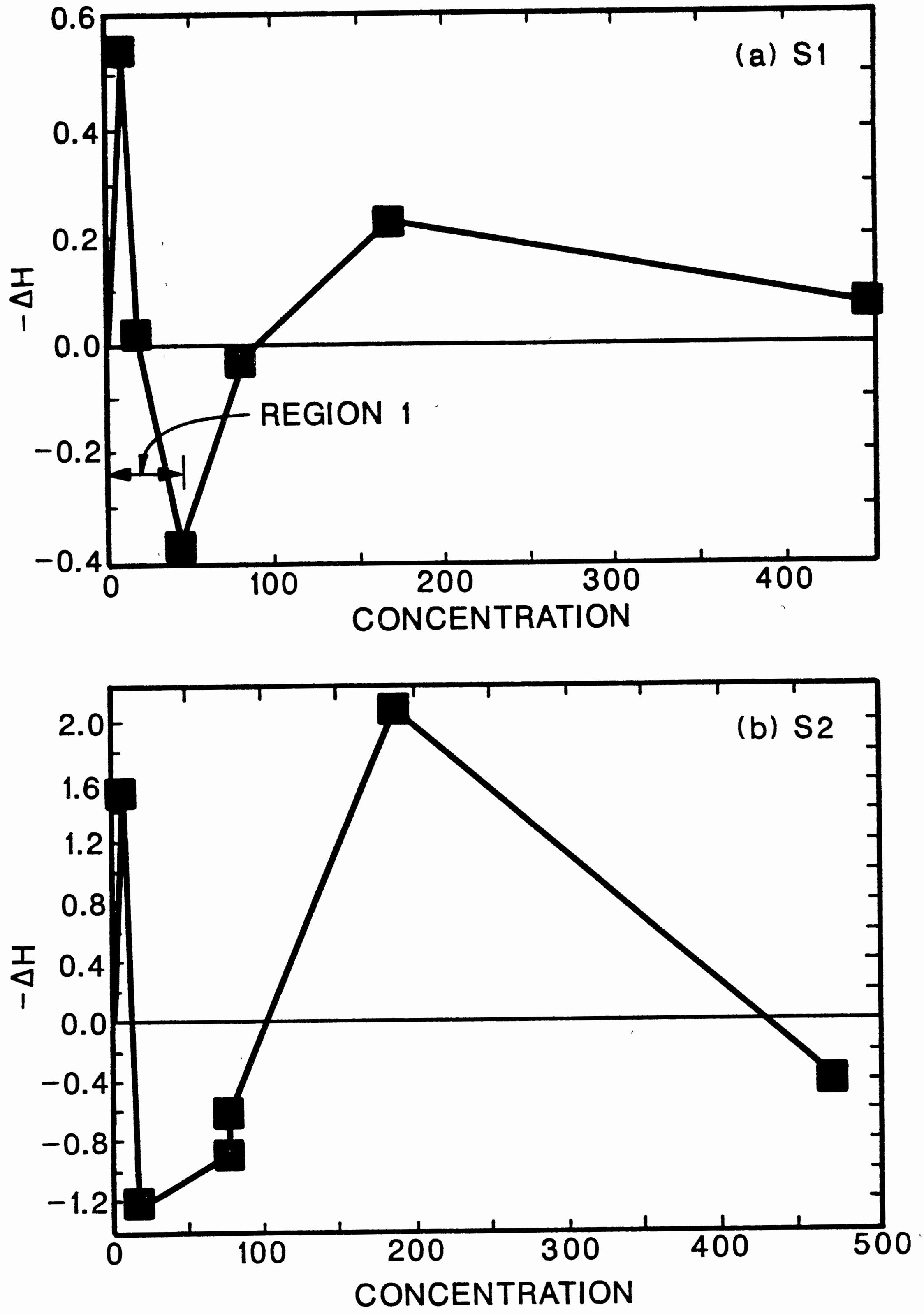
AIII-5. Isosteric Heats of Adsorption of 2,4-D with Lindane present on (a) S4, (b) S5



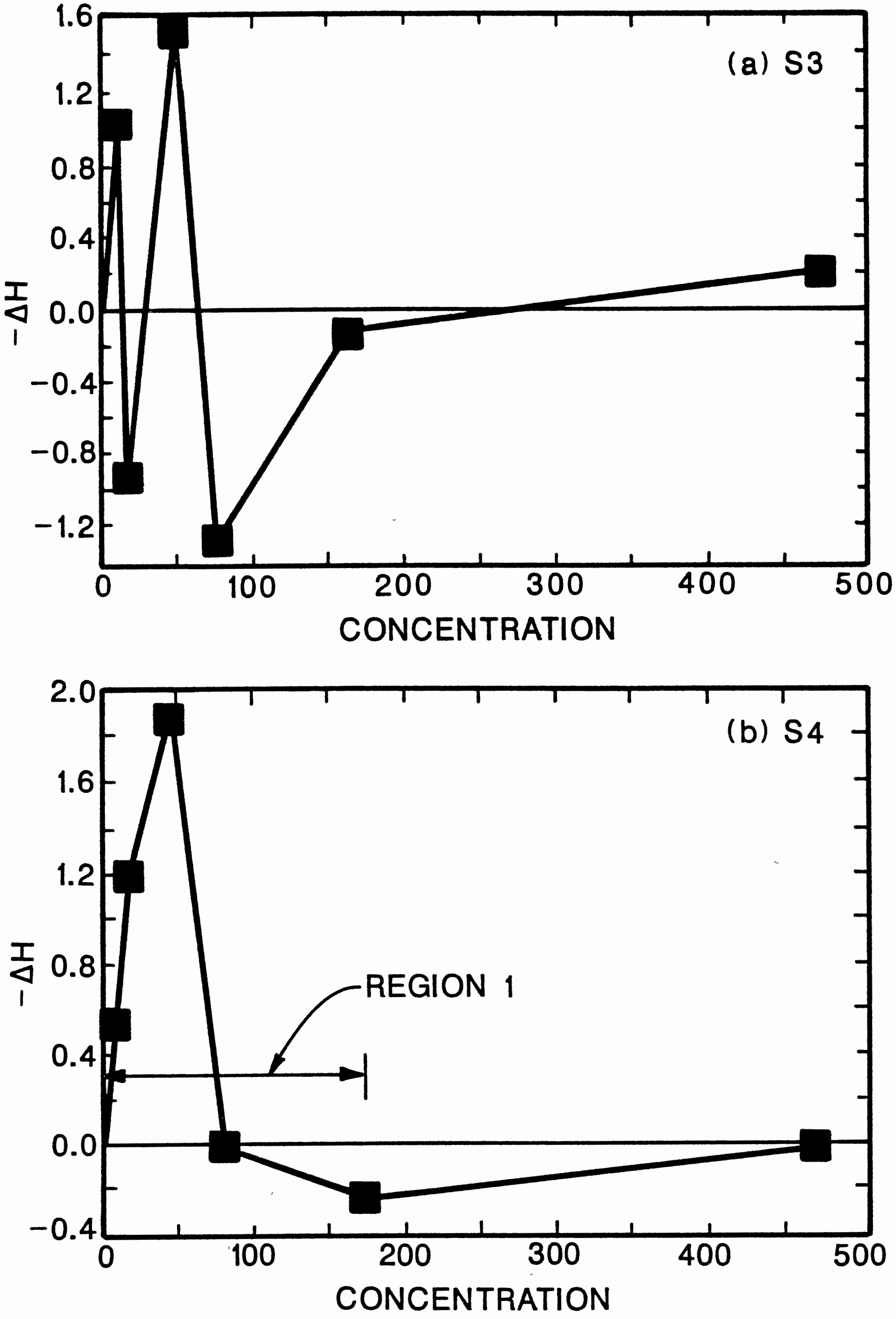
AIII-6. Isosteric Heats of Adsorption of Silvex with Lindane present on (a) S2, (b) S3



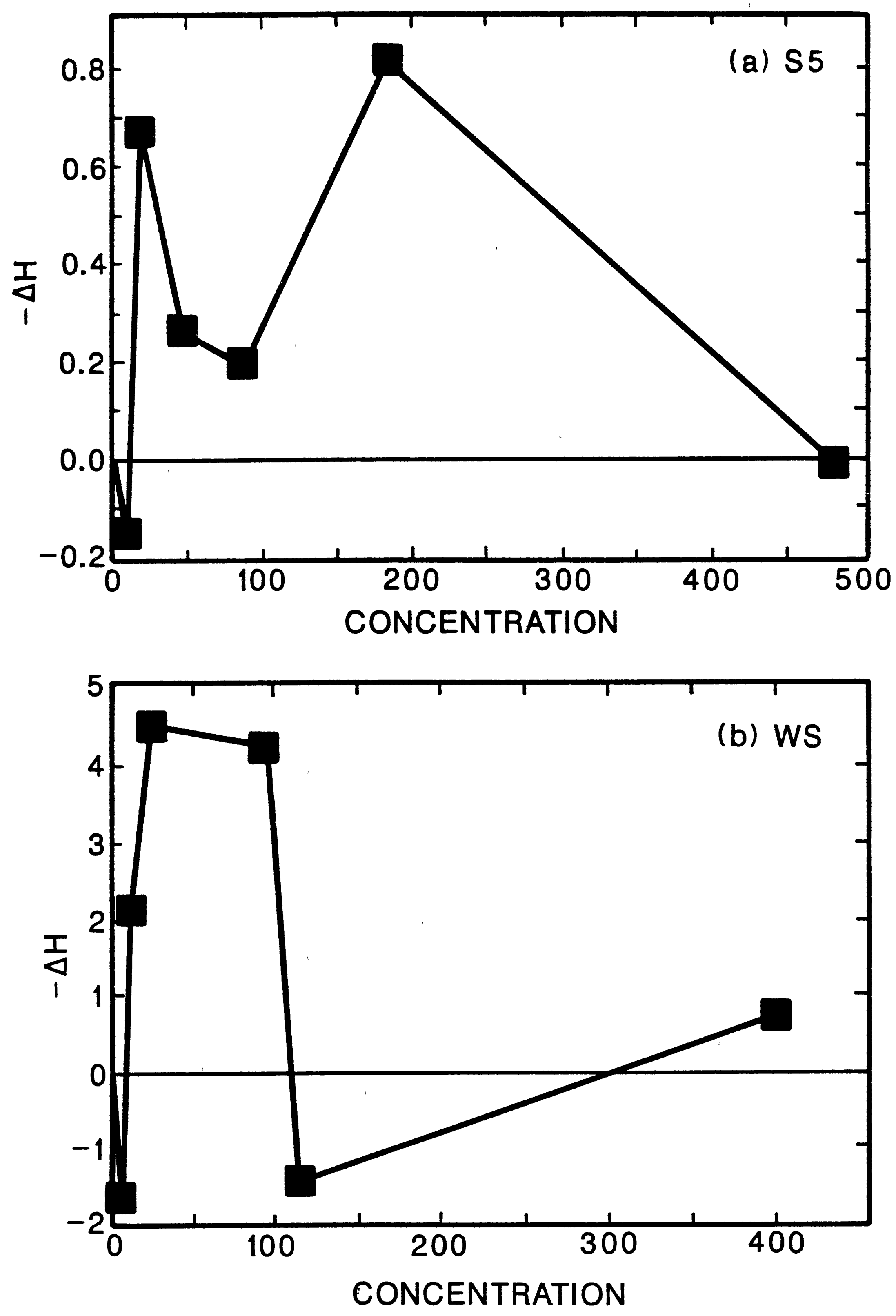
AIII-7. Isosteric Heats of Adsorption of Silvex with Lindane and with 2,4-D present on (a) S4, (b) WS respectively



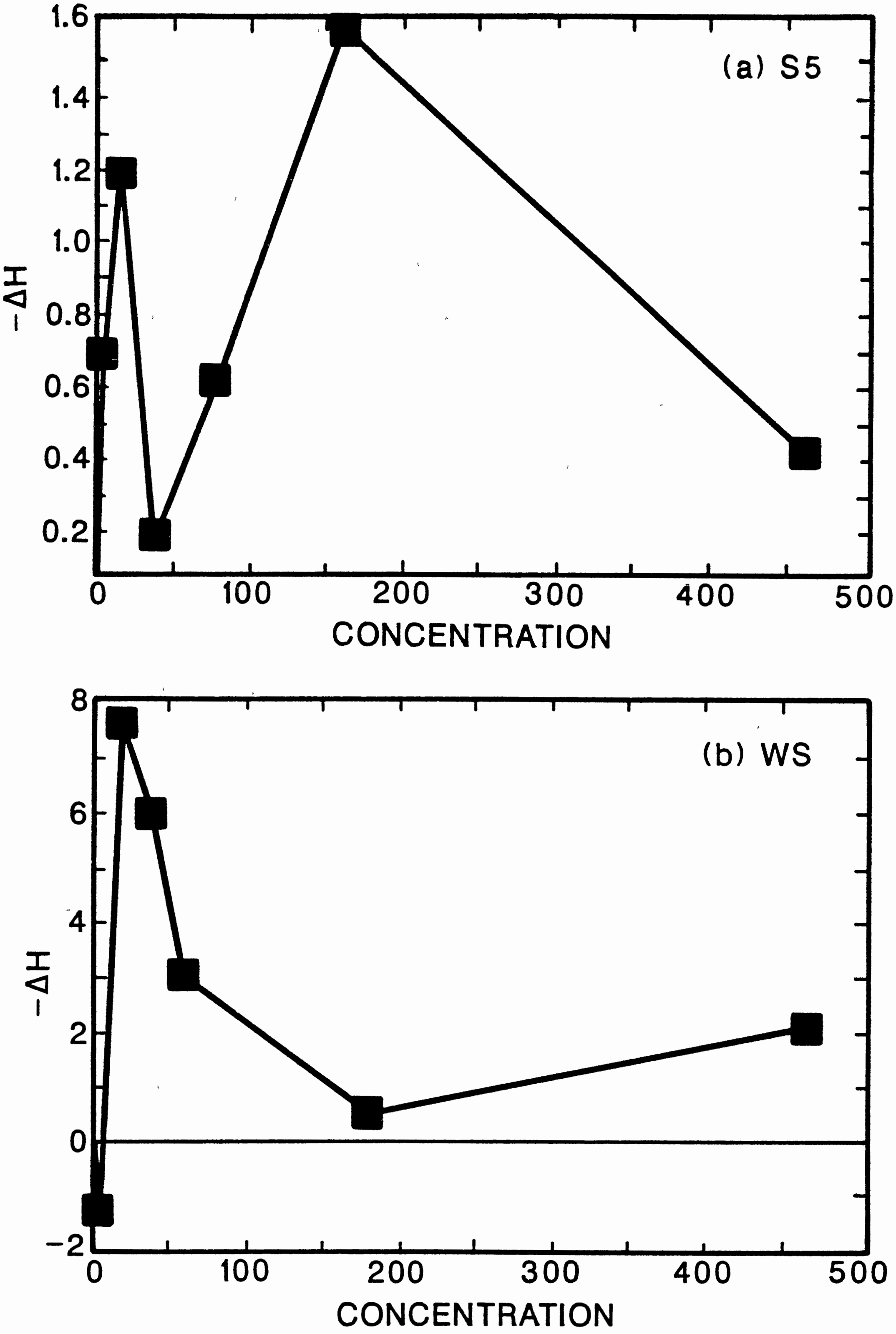
AIII-8. Isosteric heats Adsorption of Silvex with 2,4-D present on (a) S1, (b) S2



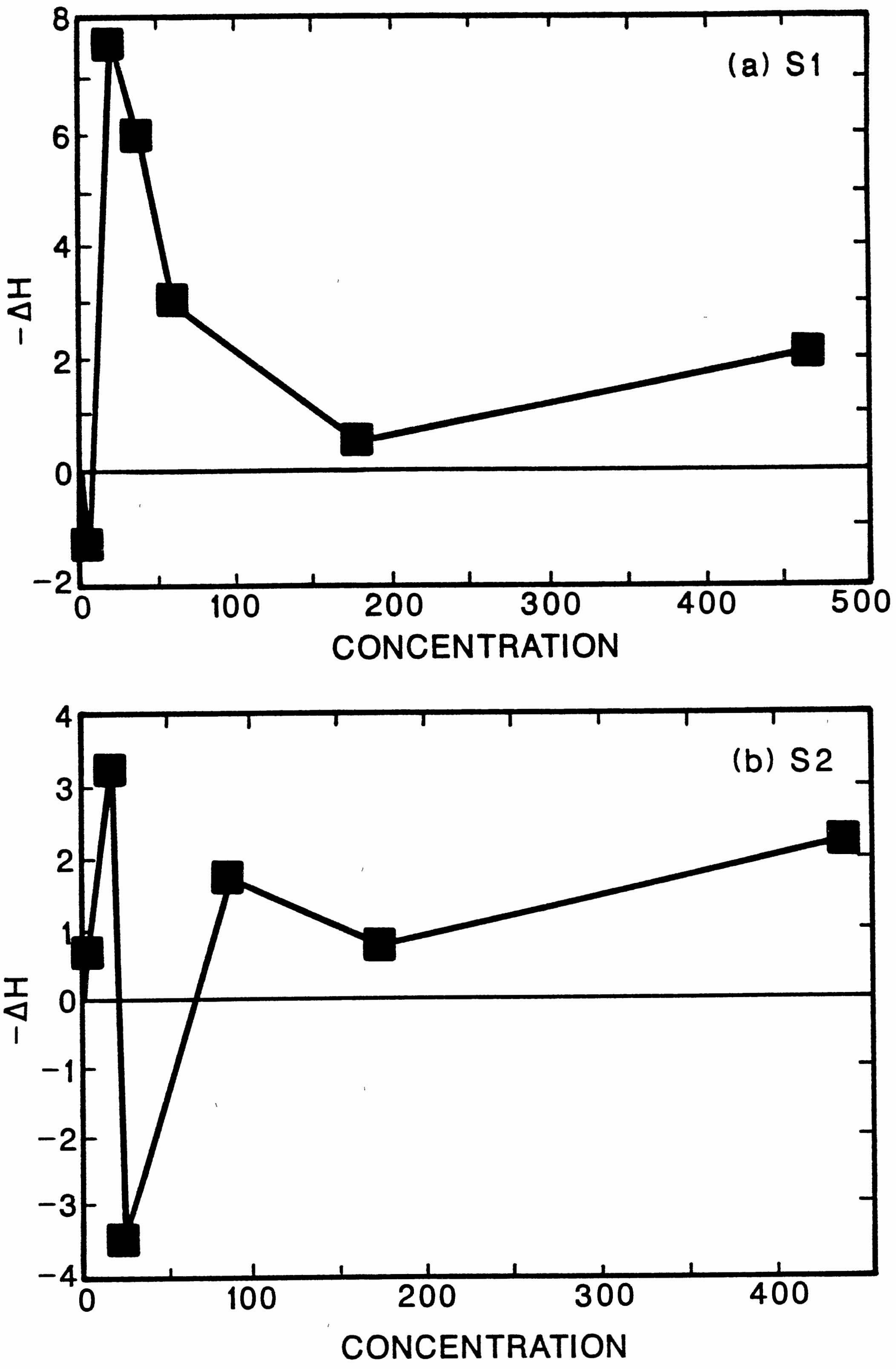
AIII-9. Isosteric heats Adsorption of Silvex with 2,4-D present on (a) S3, (b) S4



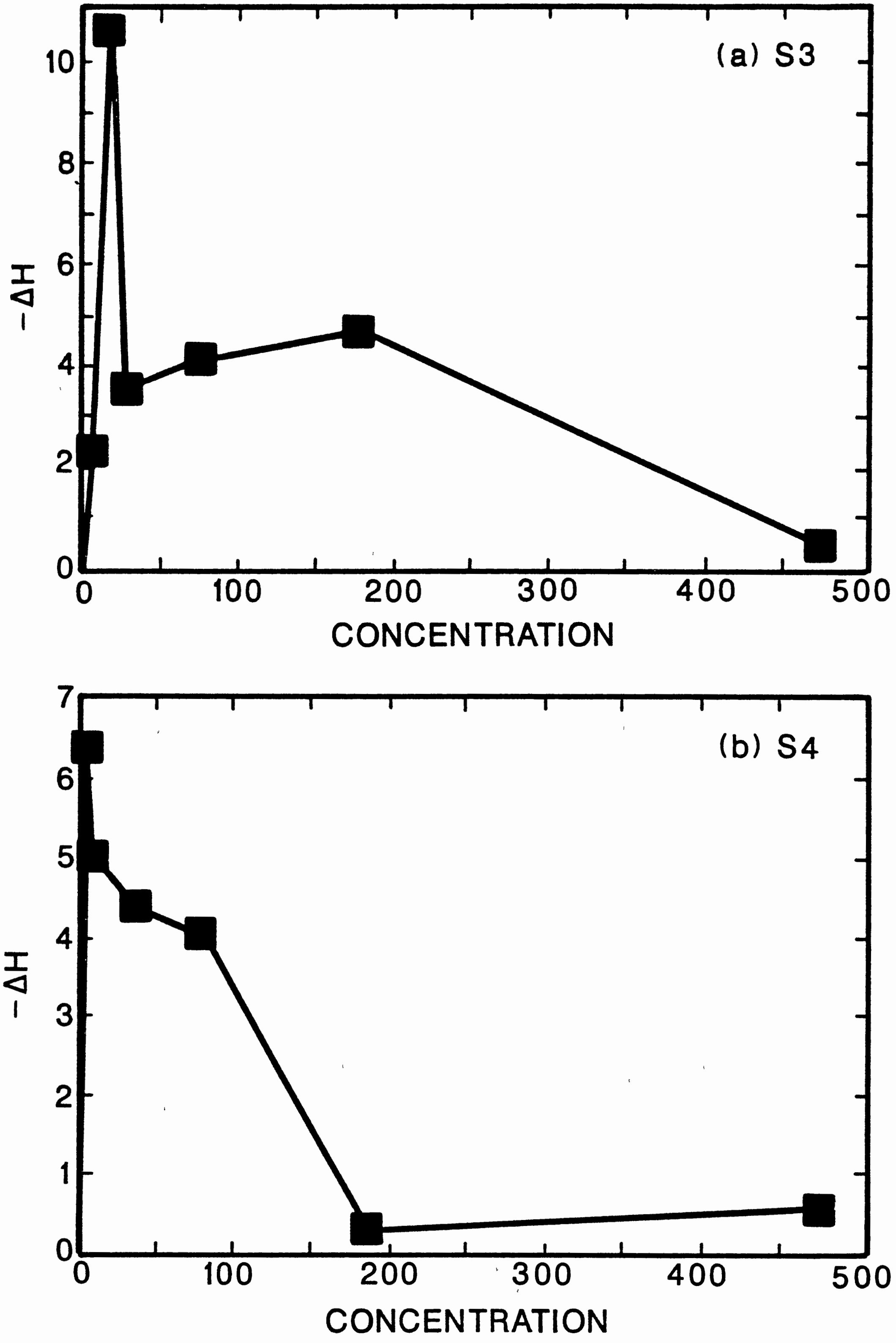
AIII-10. Isosteric heats Adsorption of Silvex and Lindane with 2,4-D and Silvex present respectively on (a) S5, (b) WS



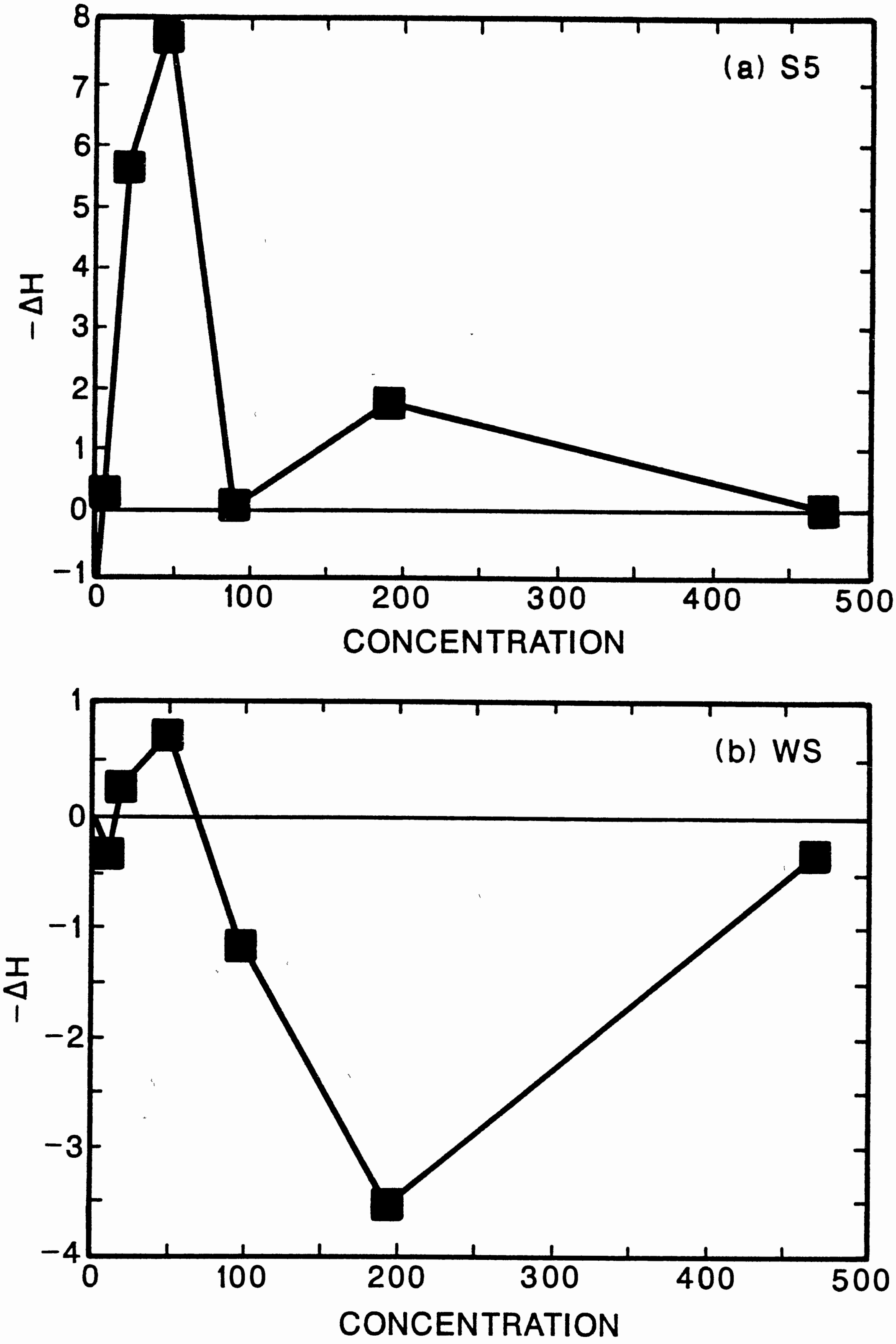
AIII-11. Isosteric heats Adsorption of Lindane with Silvex and 2,4-D present respectively on (a) S5, (b) WS



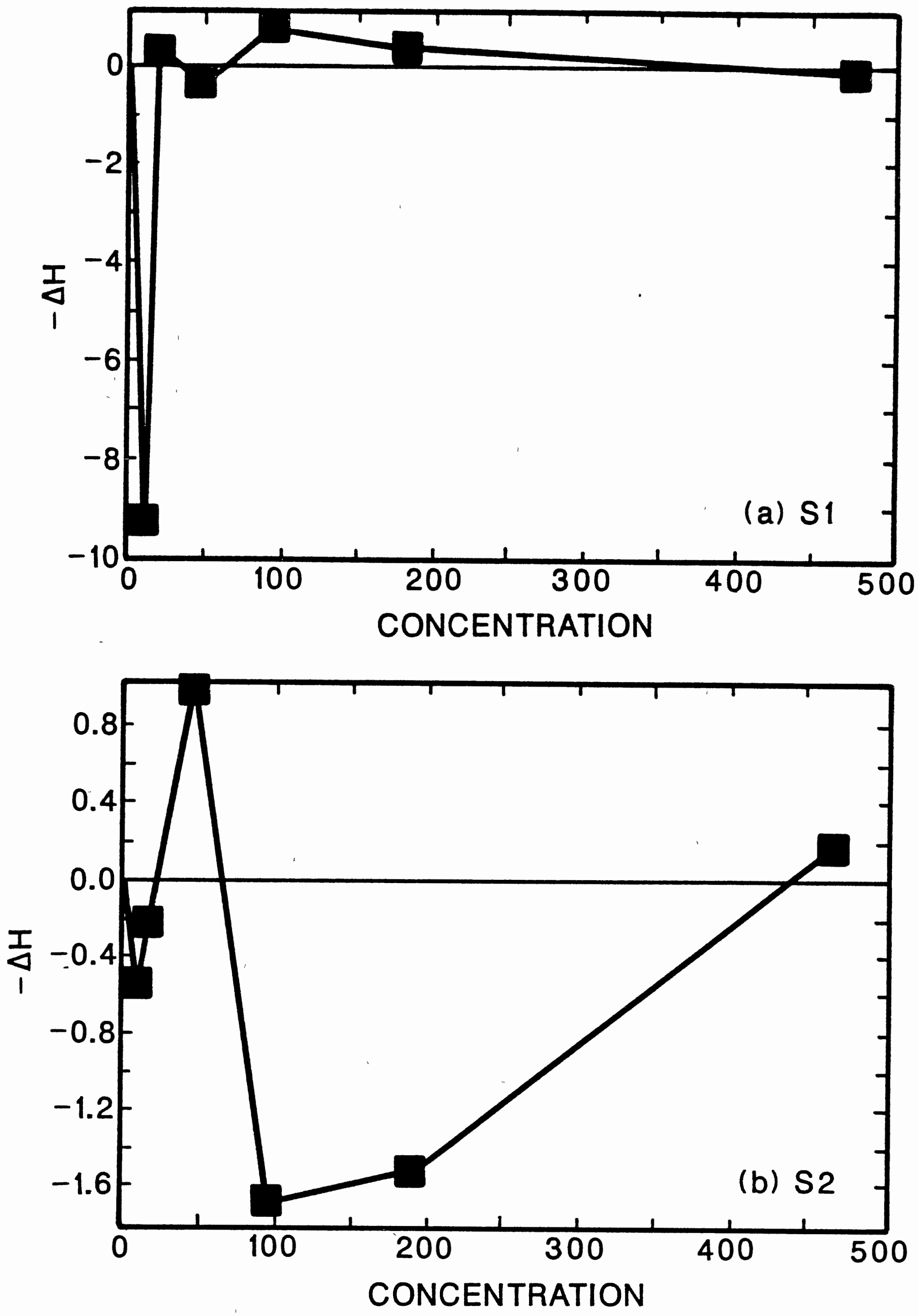
AIII-12. Isosteric heats Adsorption of Lindane with 2,4-D present on (a) S1, (b) S2



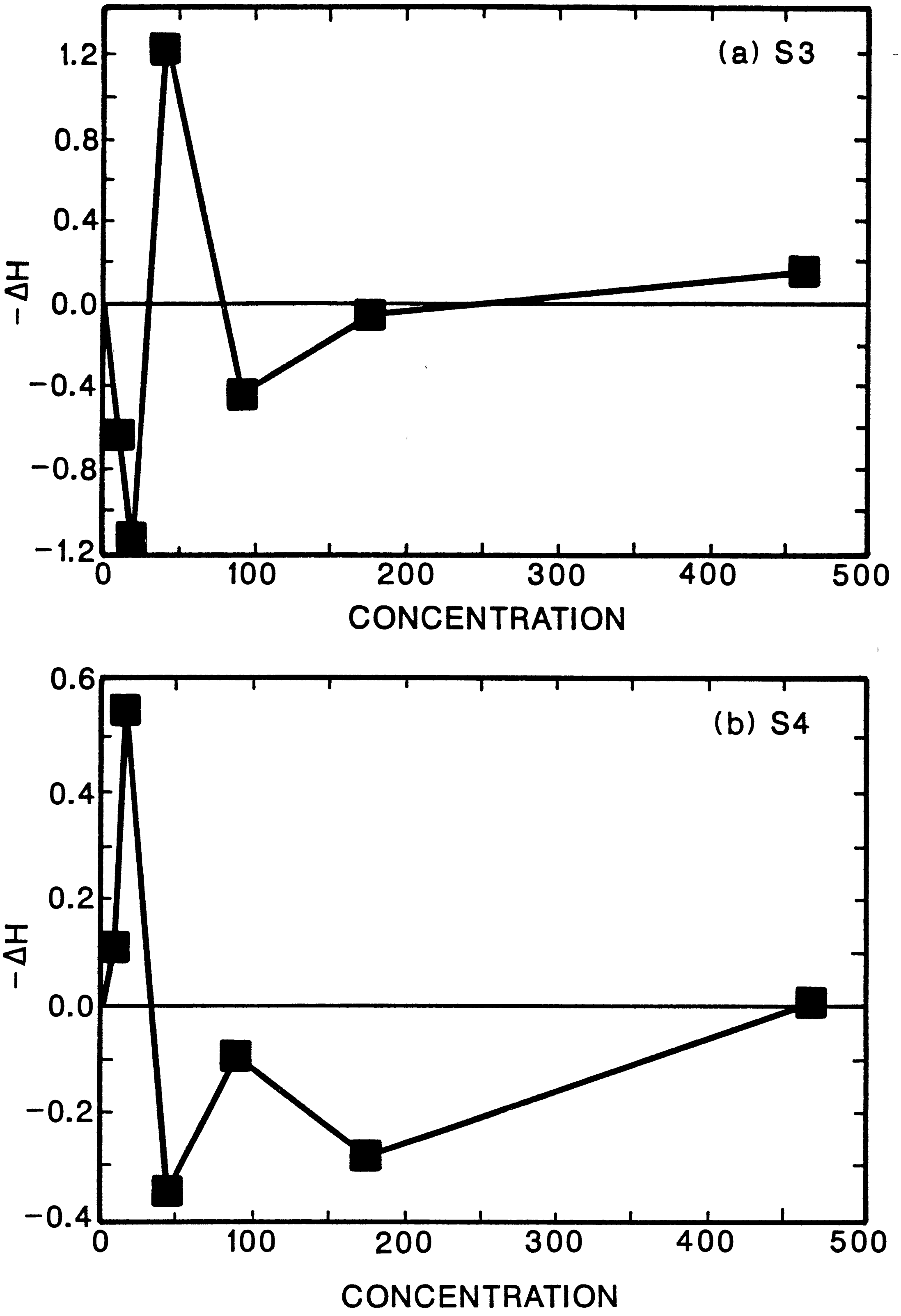
AIII-13. Isosteric heats Adsorption of Lindane with 2,4-D present on (a) S3, (b) S4



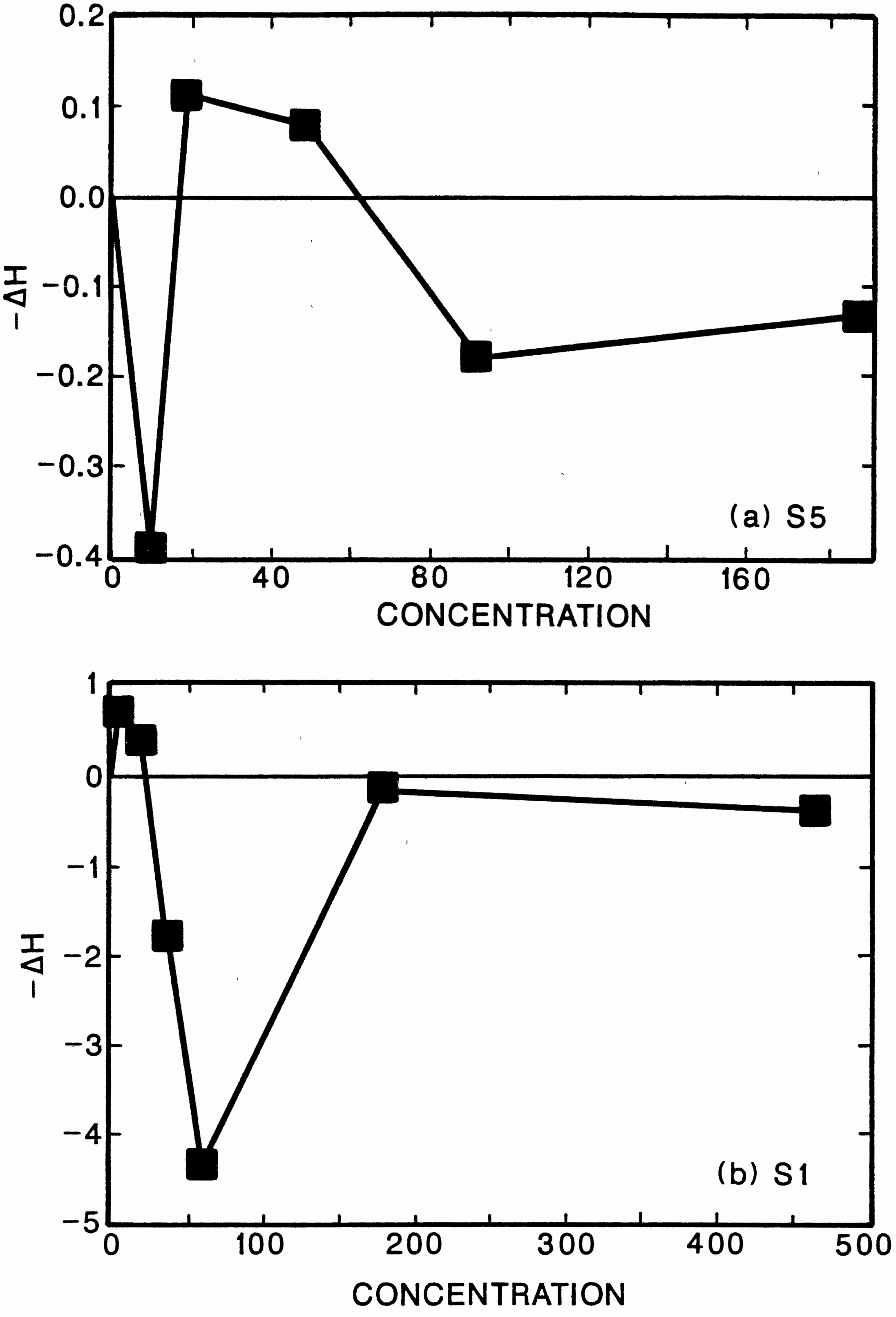
AIII-14. Isosteric heats Adsorption of Lindane and 2,4-D with 2,4-D and Silvex present respectively on (a) S5, (b) WS



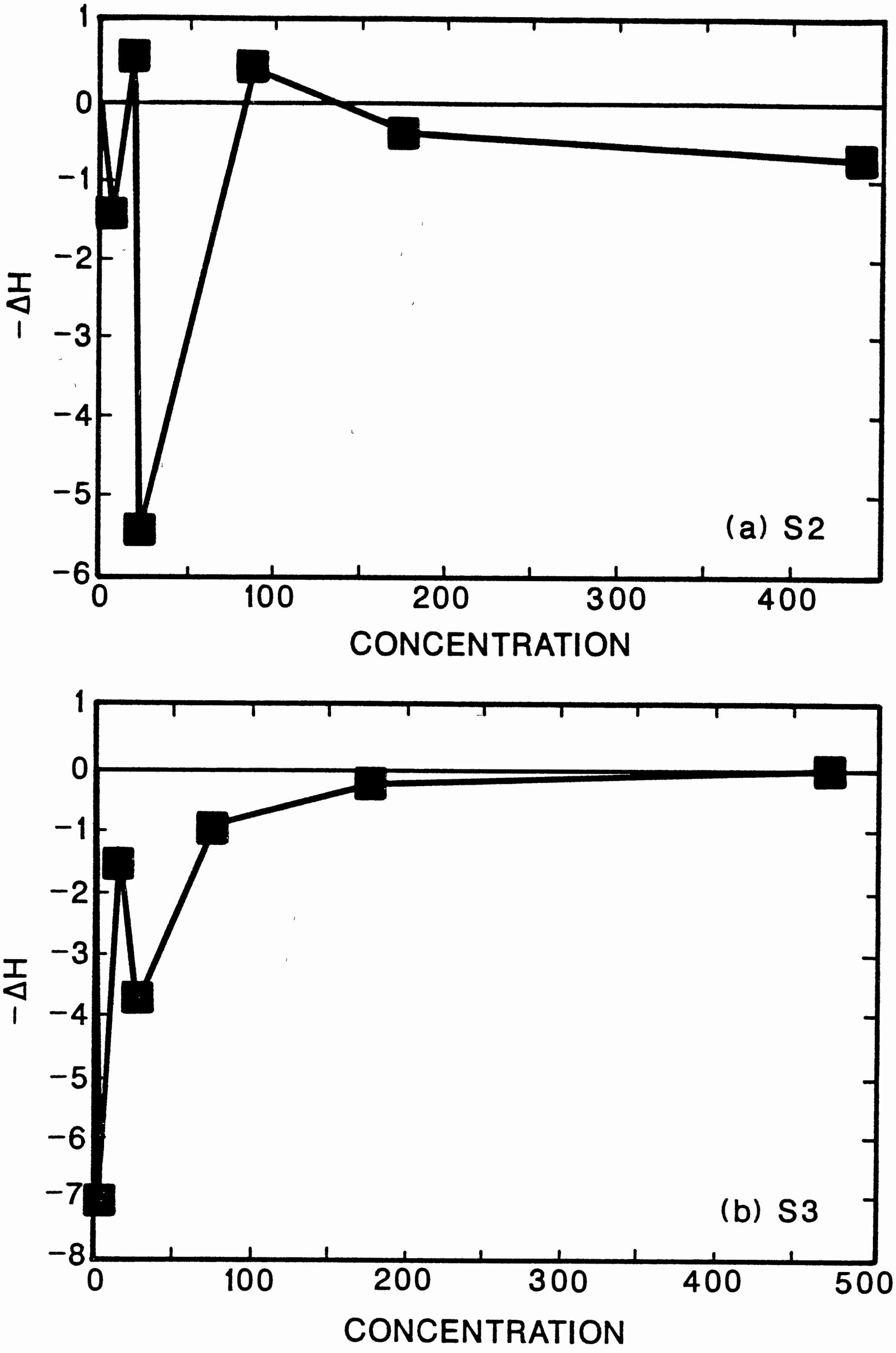
AIII-15. Isosteric heats Adsorption of 2,4-D with Silvex present on (a) S1, (b) S2



AIII-16. Isosteric heats Adsorption of 2,4-D with Silvex present on (a) S3, (b) S4



AIII-17. Isosteric heats Adsorption of 2,4-D with Silvex and Lindane present respectively on (a) S5, (b) S1



AIII-18. Isosteric heats Adsorption of 2,4-D with Lindane present on (a) S2, (b) S3

VITA

Polycarp Soo Ho

Candidate for the Degree of

Doctor of Philosophy

Thesis: ADSORPTION OF LINDANE, SILVEX, AND 2,4-D ONTO WHOLE SOIL AND SOIL ORGANIC FRACTIONS IN SINGLE AND MULTI-SOLUTE SYSTEMS

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