5-1972

Boron Movement in Soil Columns

Joseph William Stucki

Utah State University

Recommended Citation

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BORON MOVEMENT IN SOIL COLUMNS

by

Joseph William Stucki

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Soil Science and Biometeorology

Approved:

Major Professor

Committee Member

Committee Member

Dean of Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah

1972

ACKNOWLEDGMENTS

The completion of this project is the product of much energy on the part of many people. The author was supported as a graduate trainee under the auspices of the Environmental Protection Agency, and as a graduate fellow of the National Defense Education Act. The author wishes to acknowledge with gratitude this assistance as well as that of those who administer these support programs.

Special thanks and gratitude are extended to Dr. J.J. Jurinak, committee chairman and major professor, who has patiently labored to direct this work to its final outcome.

To Dr. E.J. Middlebrooks and Dr. R.L. Smith, committee members, and to Dr. D.W. James, alternate committee member, the author expresses grateful appreciation for extending themselves to offer suggestions and a greater understanding of this work.

A debt of gratitude is felt toward Dr. Sung-ho Lai, Robert A. Griffin, and Javier Santillan, fellow graduate students who have given assistance and orientation to the author.

Recognition must also be given to the support and encouragement of my wife, Penny, who has sacrificed many of her own wants in order to lend assistance to the completion of this project, including typing of manuscripts, proof-reading, as well as supervising the management of our household affairs.

NOTATION

A: cross-sectional area (cm^2)

B_o: saturation solution boron concentration, real or artificial, used in an adsorption function

C: solution phase boron concentration (ppm)

C_o: initial or total solution concentration of any species

c: constant in an adsorption function

D: fluid dispersion coefficient (cm^2/hr)

f: functional symbol

f': derivative of the function f

g: functional symbol

i: general symbol for some species

i: also the subscript for depth increment

j: subscript for time increment

K: a constant parameter

k_1, k_2: rate constants

L: total column length (cm)

N: subscript for the last depth increment where $z = L$

P: general term for gas phase concentration

P_o: general term for saturated vapor concentration

q: adsorbed phase boron concentration (ppm)

Q: cation exchange capacity of a soil (meq/g)

Q_m: monolayer capacity of a soil (μg/g)

S_o: number of surface sites available for adsorption

S_o: also the slope of the breakthrough curve at $C/C_o = 0.50$

t: time (hr)

Δt: time increment (hr)

v: bulk volume of the column (cm^3)

V: volume of the effluent solution at time t (ml)

V_o: effluent volume, or pore volume, when $C/C_o = 0.50$

$\overline{V}$: average interstitial flow velocity (cm/hr)

X: relative solution phase boron concentration (dimensionless)

Y: relative adsorbed phase boron concentration (dimensionless)

z: depth of the column (cm)

Δz: depth increment (cm)

α: pore fraction

θ: fraction of monolayer covered by adsorbate

ρ: bulk density

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ABSTRACT

Boron Movement in Soil Columns

by

Joseph William Stucki, Master of Science

Utah State University, 1972

Major Professor: Dr. J. J. Jurinak
Department: Soil Science and Biometeorology

Three adsorption theories--Langmuir, B.E.T., and Freundlich--were applied to boron interaction with Aiken clay loam and Vernal sandy loam soils to determine which bests describes the system.

Column studies were conducted to obtain constants related to mass fluid flow and fluid dispersion within the column. An inert ion was used to obtain the pore volume and to calculate the fluid dispersion coefficient. These data were used to solve the material balance equation by the explicit numerical method developed by Lai for a digital computer. The output from the computer was a predicted profile boron distribution within the soil column.

The soil columns were undergoing saturated flow and 10 ppm boron solution was introduced at the top and allowed to flow for a specified period of time, at which time the column was segmented and analyzed for boron to obtain the experimental profile boron distribution within the soil column. The experimental and predicted profiles were compared.

(121 pages)

INTRODUCTION

Background

Pollution of the environment has become a topic of extreme concern during recent years and much attention has been directed toward the pollution of waterways and supplies. Water is indeed the one natural resource that is of vital importance to each individual. A great percentage of the world's businesses, industries and agriculture rely heavily upon it for survival. However, none exceed agriculture in their dependence upon it. To the farmer, water with which to irrigate his crops is his life-blood. The growing demand for food supplies depends upon the flourishment of agriculture to meet the increasing needs. The quality of water applied to the soil will to a large extent determine the productivity of the land. Water is the medium by which nutrient elements are transported and in which these, along with the soil and biological material, interact. If the water contains harmful pollutants the land and crops will be directly affected.

One particular nutrient element which may be a pollution hazard to agriculture is boron. Plants require it in trace quantities in order to maintain normal growth (33). Deficiencies of boron will produce definite symptoms (1,4,6,7,8,14,22) and some important diseases such as heart rot and dry rot of sugar beets, top rot of tobacco, brown heart of turnips, cracked stem of celery, drought spot and corky core of apples, and others are associated with a deficiency of boron (8).

However, the tolerance limits of most plants is very low and concentrations of five parts per million or less in the soil solution will be toxic to most species. Little is known as to the actual role of boron in producing toxicity symptoms except that the symptoms are characteristic and an accumulation of the element within the plant occurs (31). As shown by Blair and Brown (3), increased amounts of borax decrease crop yields. It is generally agreed, however, that boron plays a part in converting sugars to pectins and cellulose which are associated with cell-wall structure (32). It is also believed to be involved in the mitotic divisions of cell nuclei (1). With pressure being brought to bear upon industry to reduce the phosphate levels in municipal and industrial effluents, industries such as detergent manufacturers are turning to borax and other boron containing compounds as suitable substitutes. Instead of phosphates we may have borates in the effluents. These could find their way into irrigation waters and the agriculturalist would be faced with boron concentrations above toxic levels in water which must be applied to his fields, thus causing great jeopardy to his crops. Tools and equations that can be successfully applied to predicting boron injury when soils are irrigated with high-boron waters will indeed be a most valuable instrument for determining preventive and correctional procedures in coping with the boron hazard.

Objectives

One primary objective of this study is to determine an adsorption function describing the behavior of boron over a range including concentrations above those normally found in the soil solution of high-boron soils. It has been shown that the Langmuir equation (11) will describe the behavior of boron over the limited range of 0-10 ppm. This study attempts to determine the feasibility of extending the Langmuir to concentrations beyond 10 ppm. Also, two other adsorption theories are considered, the Brunauer, Emmett, and Teller (B.E.T.) and the one proposed by Freundlich.

The other major objective of this study is to describe a predictive model for the profile distribution of boron in a soil column by means of the numerical methods and computer program developed by Lai (19) which he used in a cation exchange system undergoing miscible displacement. The theoretical application of this technique is quite simple since it only requires that an appropriate adsorption function be substituted for the exchange function for the system under study.

Definitions

The adsorbate is the ion in solution which is adsorbed at an interface. In this study the adsorbate is the borate ion, $B(OH)_4^-$ which is the principal form of boron in natural soils (15).

The adsorbent is the soil surface at which the adsorbate becomes concentrated.

The adsorption isotherm is the graphical expression of the amount of adsorbate in solution versus the amount adsorbed while maintaining constant temperature.

The adsorption function is the mathematical equation which best describes the adsorption isotherm and, when written in linear form, produces a straight line from experimental data.

LITERATURE REVIEW

Boron Chemistry

The chemistry of boron has been studied by many workers and its general properties are well known. The principal sources include boron-containing parent materials such as borax, $Na_2B_4O_7 \cdot 10\ H_2O$, colemanite, $Ca_2B_6O_{11} \cdot 5\ H_2O$, tourmaline, $Na(Mg,Fe)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$, kernite $Na_2B_4O_7 \cdot 4\ H_2O$, as well as others not mentioned. All combined they compose but .001 % of the earth's crust (15).

Boron is a non-metal and the first element in Group IIIA of the periodic table. The electronic configuration of the valence shell is $2S^2 2P^1$. However, no singly valent or tervalent cations exist, as with the other elements of Group IIIA--Aluminum, Gallium, Indium, and Thallium. This is due largely to the high ionization and the rather high hydration energies. Strictly covalent bonding is characteristic of boron and SP^2 hybrid bonds are common with three lobes in a typical planar configuration. It is noted that with the promotion of one of the S electrons into one of the P orbitals, forming the SP^2 configuration, the octet of boron remains incomplete as the third P orbital is vacant. This phenomenon is accompanied by smaller than usual electron repulsions and the atoms become electron "acceptors", or Lewis acids, in order to complete the octet by filling the third P orbital. When such a lone pair of electrons from another molecule over-laps the third P orbital, an SP^3 type of hybridization is invoked resulting in the characteristic tetrahedral arrangement of the bonding lobes. This tendency to complete an octet is shown by the existence of tetrahedral compounds of boron such as BH_3CO, in which the lone pair from CO is shared by the third P orbital. Also, boric acid, $B(OH)_3$, tends to convert to the borate ion, $B(OH)_4^-$, in order to complete the octet; thus, boric acid is a Lewis acid (15).

Adsorption in General

The adsorption of gases to solid crystal surfaces was studied in 1918 by I. Langmuir who described this phenomenon in kinetic terms as rates of adsorption-desorption at the solid-gas interface. He defined the rate of adsorption as being a function of the number of empty sites on the surface and the vapor pressure of the gas,

$$\text{Rate of Adsorption} = k_1 P S_o \qquad [1]$$

and the rate of desorption as a function of the number of sites covered by the adsorbate molecules,

$$\text{Rate of Desorption} = k_2 q \qquad [2]$$

where P is the vapor pressure of the gas, S_o is the number of empty sites on the adsorbent, q is the number of occupied sites on the adsorbent, and k_1 and k_2 are the rate constants for the given reactions (20,21).

At equilibrium the rates of adsorption and desorption will be equal; therefore, the rate equations may be equated to produce

$$k_1PS_o = k_2q \qquad [3]$$

If Q_m is defined as the total number of surface sites available for adsorption, then S_o is $(Q_m - q)$. By substitution and rearranging equation [3] gives

$$q = \frac{KQ_mP}{(1 + KP)} \qquad [4]$$

which is the Langmuir equation.

The number of sites on the adsorbent may be expressed in relative terms where θ is the fraction of sites occupied and $(1 - \theta)$ is the fraction not occupied. By making this further substitution, equation [4] becomes

$$\theta = \frac{KP}{(1 + KP)} \qquad [5]$$

K is an apparent equilibrium constant and is related to the heats of adsorption (17).

The Langmuir model predicts a monolayer capacity, Q_m, and embraces chemisorption only. When written in its linear form, equation [4] becomes

$$\frac{P}{q} = \frac{1}{KQ_m} + \frac{P}{Q_m} \qquad [6]$$

giving the slope as $1/Q_m$ and K as the slope/intercept.

Brunauer, Emmett, and Teller (B.E.T) expanded the Langmuir theory from monolayer to multilayer adsorption, and thus derived the equation

$$\frac{V}{V_m} = \frac{c(P/P_o)}{(1 - P/P_o)[1 + (c - 1)P/P_o]} \qquad [7]$$

or, in its more convenient form

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m c} + \frac{c - 1}{V_m c} \cdot \frac{P}{P_o} \qquad [8]$$

where:

P = equilibrium vapor pressure

P_o = saturation vapor pressure

V = volume of gas adsorbed

V_m = volume of gas to form a monolayer

c = parameter related to heats of adsorption

The theory is based on the assumption that each successive layer becomes the template upon which the next layer may adsorb. The heats of adsorption for each layer are uniform and are a function of various factors including the distance from the surface region. This model also predicts a monolayer capacity, V_m, but it also defines adsorption beyond the monolayer region.

Thomas (38) summarizes the bases for various adsorption isotherms by separating them according to the manner in which the heats of adsorption change with surface coverage. According to Figure 1, three possible modes are indicated: constant or uniform heats of adsorption, linear decay of heats of adsorption with surface coverage, and logarithmic decay of heats of adsorption with surface coverage.

The Freundlich adsorption equation is associated with the model of logarithmic decay of the heats of adsorption with increasing coverage. It was originally considered an empirical equation which conveniently represented the Langmuir equation at intermediate surface coverages (38); but Zeldowitch (38) derived an adsorption isotherm for an energetically heterogeneous surface which is synonymous with the

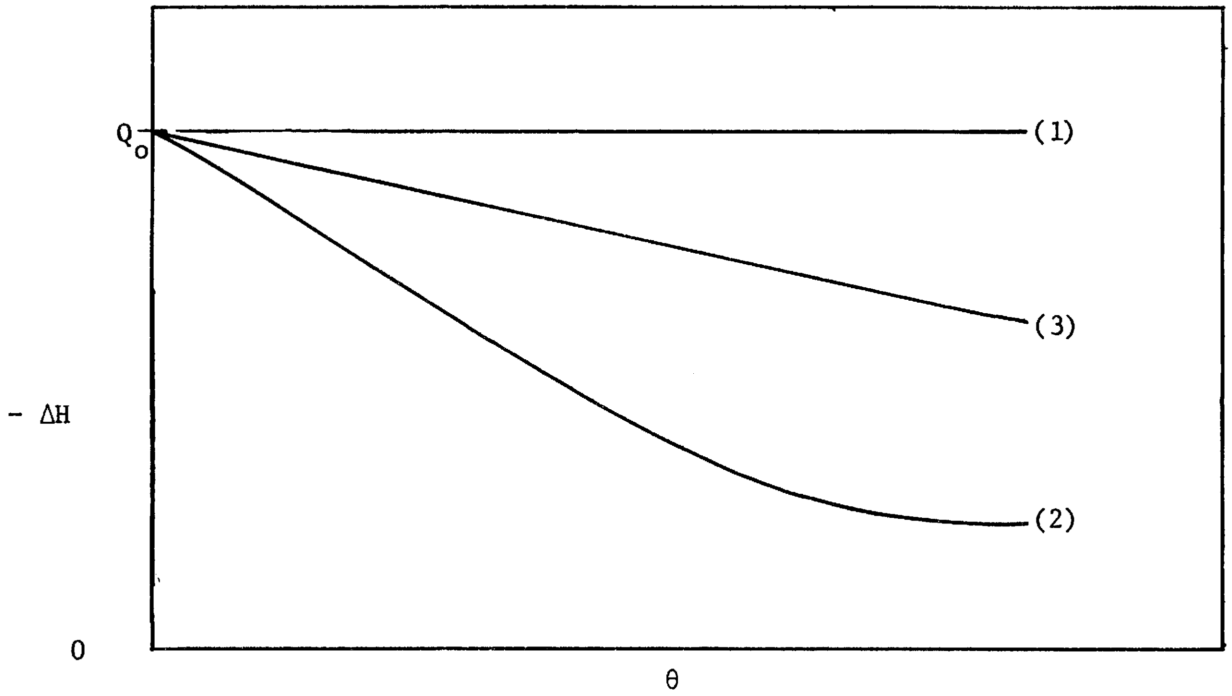

Figure 1. Schematic diagram illustrating (1), constant heats of adsorption (2), logarithmic fall of heat of adsorption; and (3), linear fall of heats of adsorption with increasing coverage. Figure taken from Thomas (38).

Freundlich isotherm, expressed as

$$\theta = kP^{1/n} \qquad [9]$$

The Slygin and Frunkin (Temkin) isotherm describes the system in which a linear rather than logarithmic decay in the heats of adsorption occurs. This condition is found in many systems, especially at low to medium surface coverages (38). This equation will not be applied in this study so no further mention will be made of it.

Boron Adsorption by Soils

In 1958, Hatcher and Bower (11) showed that the Langmuir equation could be applied not only to the solid-gas interface but also to the liquid-solid interface--the soil particles composing the solid surface and the soil solution being the liquid phase. Specifically, they offered evidence that the Langmuir isotherm predicted to a limited extent the behavior of boron in the soil. The data were reasonably accurate in the limit of lower concentrations. Biggar and Fireman (2) confirmed that the isotherm was accurate at lower boron concentrations (below 10 ppm). They observed large deviations at higher concentrations. Singh (36) was thus led to further studies from which he concluded that boron followed a quadratic adsorption isotherm if the entire concentration range is considered. He suggested that the B.E.T. equation, rather than the Langmuir equation, was the proper adsorption function.

Rashid (30) found that there are three distinct regions of boron adsorption, each producing a linear plot according to the Langmuir equation but each of different slope. This suggests that several adsorption sites or mechanisms may be involved and lends supportive evidence to the findings of Singh that boron adsorption is more accurately described by the B.E.T. rather than the Langmuir equation if the whole concentration range is considered.

Factors Influencing Boron Adsorption

Eaton and Wilcox (8) found that one or more of three mechanisms is involved in boron adsorption. These are anion exchange, molecular adsorption, and chemical precipitation. Hingston (16) presented a more detailed break-down of the possible mechanisms as being (a) sorption of borate ions, (b) sorption of molecular boric acid, (c) formation of organic complexes, (d) precipitation of insoluble borates with alumina and silica, and (e) entry of boron into the clay mineral lattice. Observations have shown that liming increases boron fixation within the soil (5,23,24,25,39). Muhr (24) offered convincing evidence that $MgCO_3$ and $CaCO_3$ are effective in fixing borax into forms that are unavailable to soybeans while the sulfates have a much lesser effect. He found also that sodium salts had insignificant effects in fixing borax. Parks and White (29), Gupta (10), and Muhr (22) have shown that organic matter is a most influential factor and contains significant quantities of fixed boron.

The effect of pH on boron fixation has been studied by Cook and Millar (5), Eaton and Wilcox (8), Hingston (16), Kubota, Berger, and Truog (18), Midgely and Dunklee (23), and Olsen and Berger (27). The last reported that fixation increased with increasing pH above 7, but no correlation was seen below pH 7. Kubota, Berger, and Truog (18) reported that the optimum pH is about 6.5-7.0 for boron fixation. In a study of three types of clay minerals, Hingston (16) found that increasing pH causes an increase in the monolayer adsorption and a decrease in the bonding energy of kaolinite and montmorillonite for boron. Illite was observed to have a slight increase in bonding energy with increasing pH. Midgely and Dunklee (23) suggest that pH is only a part of several interacting factors upon which the extent of boron fixation is dependent.

The most recent studies suggest that all of the factors which influence the extent of boron fixation in the soil may be explained by formation of calcium alumino-silicate complexes where the boron substitutes for the aluminum (28). Hatcher, Bower, and Clark (12) conclude that hydroxy-aluminum compounds are responsible for causing boron retention by soils, $Al(OH)_3$ being the major constituent responsible. Sims and Bingham (34,35) concur with Hatcher, Bower, and Clark (12) and suggest further that $Fe(OH)_3$ has a similar effect on boron retention. The common factor being the surface hydroxyl groups which are active in boron retention.

The capacity of one particular soil to retain boron is dependent upon a complex variety of factors which operate separately or together. Griffin (9) summarized most of these factors: pH of the system, type of clay minerals present, amount of clay present, type of exchangeable ions in the soil, amount of organic matter, moisture content of the soil (wetting and drying), time the soil is in contact with the soil solution, temperature, sesquioxides, and salinity of the system.

Predictive Modeling

With the invention of computers and the development of numerical methods it has become possible to develop mathematical models for synthetically predicting solutions to various problems and obtaining results which correspond quite closely to experimental findings. Tanji (37) successfully applied a computer model for predicting the profile distribution of boron within a soil column by combining the principles of chromatography and adsorption. The chromatographic equation used is

$$(C_B)_{i,j} = (C_B)_{i-1,j}(DS/PV) + (C_B)_{i,j-1}(RS/PV) \qquad [10]$$

where:

i = the profile depth

j = the leaching water application increment

C_B = the soil solution boron concentration

DS = the volume of the displacing solution

RS = the volume of the resident solution

PV = the pore volume occupied by the soil during percolation

Thus, the chromatographic equation takes into account both soil depth and the volume of leaching water applied to the soil. DS/PV gives the residual boron concentration for a particular depth increment and RS/PV gives the mobile fraction that is transferred from one depth to the next with the next leaching water increment. Additional parameters were introduced to account for the percent of moisture saturation and for the amount of boron desorbed from the soil surface. The theoretical and experimental data were in good agreement, thus verifying the validity of the model.

The adsorption isotherm or adsorption function used was the Langmuir equation, which produced satisfactory results in the limited concentration range of 0-10 ppm.

A different approach to predictive flow models was taken by Lai (19). Briefly, for the Mg-Ca cation exchange during miscible displacement in the soil solution under steady state flow conditions, he utilized the concepts of material balance, which means that the change in the material flux within a section of the column may be measured as the sum of the rate of change of the solution phase concentration and the rate of change of the exchanger phase concentration within the section, or

$$\begin{matrix}\text{net change}\\ \text{of ion flux}\end{matrix} = \begin{matrix}\text{rate of change}\\ \text{of solution conc.}\end{matrix} + \begin{matrix}\text{rate of cation}\\ \text{exchange}\end{matrix} \qquad [11]$$

where the flux in the flow system is determined by the transport due to both mass fluid flow and fluid dispersion, or

$$\text{Flux} = -D \frac{\partial C_i}{\partial z} + \bar{V} C_i \qquad [12]$$

where the first is the fluid dispersion term and the second represents the mass flow term.

The rates from equation [11] are expressed as

$$\frac{\partial C_i}{\partial t} = \text{rate of change of } C_i$$

$$[13]$$

$$\frac{\partial q_i}{\partial t} = \text{rate of change of } q_i$$

For cation exchange taking place between cations a and b at constant total solution concentration C_o, and cation exchange capacity, Q,

$$C_o = C_a + C_b$$

$$[14]$$

$$Q = q_a + q_b$$

And, if the solution and exchange concentrations are converted to their relative form with their values ranging from 0.0-1.0, the following definition is made for any species i

$$X_i = \frac{C_i}{C_o} \qquad [15]$$

$$Y_i = \frac{q_i}{Q} \qquad [16]$$

Substituting equations [12] and [13] into equation [11] produces the material balance equation in differential form. Further reduction of the equation is made by taking the partial differentials with respect to t and z of equations [15] and [16] and making this substitution to produce the material balance equation in its reduced form

$$D\frac{\partial^2 X}{\partial z^2} - \frac{\partial X}{\partial z} = \left(1 + \frac{\rho Q}{\alpha C_o} f'\right)\frac{\partial X}{\partial t} \qquad [17]$$

Instantaneous equilibrium is a basic assumption which allows Y_i to be expressed in terms of X_i.

The computer model and program used for solving the material balance equation was the explicit method. It employs a finite difference scheme for the evaluation of $X_{i,j+1}$, and involves the values for $X_{i-1,j}$, $X_{i,j}$, and $X_{i+1,j}$, where i represents the depth increment and j represents the time increment. All values in the j+1 row are computed, then used as the initial conditions for the computation of the X values in the next row. The operation is repeated until the desired time and depth increments are reached. A grid illustrating the technique is shown in Figure 2. For more details concerning numerical solutions see Lai (19).

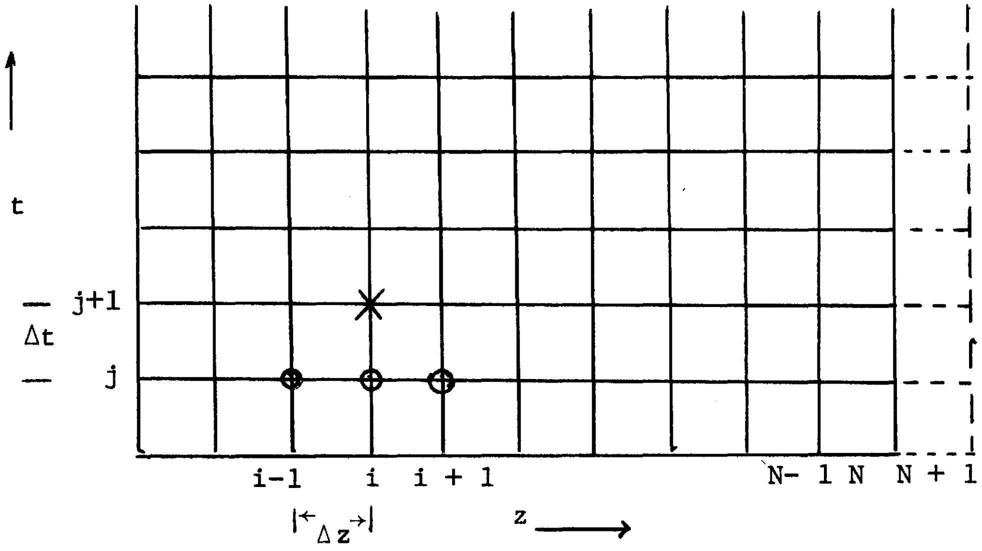

Figure 2. A grid network showing the relationship of the four finite elements of Equation [33]. The three elements encircled are known. The value in the cross is evaluated by the three in the circles.

THEORY AND PLAN OF WORK

This study attempts to apply the explicit method as developed by Lai (19) for solving the material balance equation. Because the original system of Lai's involved cation exchange and the present system is concerned with anion adsorption, several modifying assumptions must be made: (a) equilibrium between the solution phase boron and adsorbed phase boron is reached in the column during saturated flow; (b) an adsorption function serves the same purpose in the anion adsorption system as the exchange function serves in the cation exchange system; (c) the value for Q, the cation exchange capacity, must be approximated by the monolayer capacity, Q_m, computed from a given adsorption function (isotherm equation).

The technique and theory of determining the adsorption function is now given.

Adsorption isotherms are determined experimentally by means of batch equilibrium studies. The physical conditions of the soil in the batch studies in no way simulate the conditions found in the column, but at equilibrium the batch method does allow the determination of the quantity of boron adsorbed by the soil at a given boron concentration in solution. The isotherm data are plotted according to three adsorption theories--Langmuir, B.E.T., and Freundlich. Each of the adsorption functions obtained is incorporated into the Fortran IV program and numerical calculations are carried out according to each function with its corresponding parameters for each column studied.

Adsorption Functions

Langmuir

The Langmuir model offers very little difficulty since the equation is simple and the derivative with respect to X (the solution concentration of boron) is straight forward. Equation [4] is the Langmuir equation which may be rewritten

$$q = \frac{KQ_mC}{(1 + KC)} \qquad [18]$$

where C replaces P, the vapor pressure of a gas, as the solution phase concentration of the adsorbate, K and Q_m are evaluated from the linear form of the Langmuir equation [6] with Q_m as 1/slope and K as slope/intercept.

Since X and Y are defined as

$$X = \frac{C}{C_o} \qquad Y = \frac{q}{Q_m} \qquad [19]$$

then equation [18] becomes

$$Y = \frac{KXC_o}{1 + KXC_o} \qquad [20]$$

The derivative with respect to X of equation [20] is

$$\frac{dY}{dX} = \frac{KC_o}{(1 + KXC_o)^2} \qquad [21]$$

Equation [21] then becomes f' in equation [17].

B.E.T.

The B.E.T. model is more difficult to use than the Langmuir model since it is more complex and the saturated concentration value must be determined. The equation is given as equation [8] and is transformed for the purpose of this system to be

$$\frac{C}{q(B_o - C)} = \frac{1}{Q_m c} + \frac{c - 1}{Q_m C} \cdot \frac{C}{C_o} \qquad [22]$$

where C replaces P and B_o replaces P_o.

Substituting equation [19] into equation [22] and expressing it in the form of Y = f(X), gives

$$Y = \frac{B_o C_o c}{(B_o - XC_o)[B_o + (c - 1)XC_o]} \qquad [23]$$

The slope of equation [23]

$$\frac{dY}{dX} = [(B_o - XC_o)[B_o + (c - 1)XC_o]B_oC_oc - XB_oC_oc([B_o - XC_o](c - 1)C_o - C_o[B_o + (c - 1)XC_o])] \; / \; ([B_o - XC_o][B_o + (c - 1)XC_o])^2 \qquad [24]$$

When using the B.E.T. model, equation [24] becomes f' in equation [17].

The choice of the value for B_o is a matter of concern. Theoretically this value should be the saturated solution concentration; however, the solubility of boric acid is so great ($\simeq 10^5$ ppm) that the values for C/B_o become meaningless since the applicable range for the B.E.T. equation is usually in the relative concentration range of 0.05-0.35. If a value for B_o could be chosen which would fit the experimental data in the c/B_o range of 0.05-0.35, then the conclusion is that the B.E.T. equation is valid for the range over which equation [22] has high correlation to the experimental data.

Freundlich

The Freundlich isotherm equation, originally derived empirically, would logically seem to be the most accurate theory to trace the pattern of boron adsorption. The equation is

$$q = KC^{1/n} \qquad [25]$$

where K and n are constants. The linear form is

$$\log q = \log K + \frac{1}{n} \log C \qquad [26]$$

where 1/n is the slope and log K is the intercept. The major difficulty encountered is that its utility is limited because no adsorption maximum can be predicted or calculated. This presents the problem of having no Q value when using it in conjunction with equation [17]. This problem may be avoided by modifying the original derivation of equation [17]. Substituting equations [12] and [13] into equation [11] and performing the appropriate algebra, gives

$$-D \frac{\partial^2 C_i}{\partial z^2} + \bar{V} \frac{\partial C_i}{\partial z} = \frac{\partial C_i}{\partial t} + \frac{\rho q_i}{\alpha \partial t} \qquad [27]$$

Equation [27] may be further modified by expanding the term $\partial q_i/\partial t$ by the chain rule

$$\frac{\partial q_i}{\partial t} = \frac{\partial q_i}{\partial C_i} \frac{\partial C_i}{\partial t}$$

$$\frac{\partial q_i}{\partial C_i} = f' \qquad [28]$$

$$\frac{\partial q_i}{\partial t} = f' \frac{\partial C_i}{\partial t}$$

and, by substitution, equation [27] now is

$$-D \frac{\partial^2 C_i}{\partial z^2} + \bar{V} \frac{\partial C_i}{\partial z} = (1 + \frac{\rho}{\alpha} f') \frac{\partial C_i}{\partial t} \qquad [29]$$

which replaces equation [17] as the mass balance equation to solve by the explicit method. Attention should be drawn to the fact that due to the absence of C_o and Q_m, concentrations are not expressed as X and Y, but as C and q.

In the general case, using the Freundlich adsorption function, equation [29] must be used in place of equation [17] and concentrations are expressed in actual, rather than relative values.

Numerical Computations

The solution to equations [17] and [29] follows the scheme by Lai (19). In short, the finite differences for the mass balance equation are

$$\frac{\partial X}{\partial t} \cong \frac{X_{i,j+1} - X_{i,j}}{\Delta t}$$

$$\frac{\partial^2 X}{\partial z^2} \approx \frac{X_{i+1,j} - 2X_{i,j} + X_{i-1,j}}{\Delta z^2} \qquad [30]$$

$$\frac{\partial X}{\partial z} \approx \frac{X_{i+1,j} - X_{i-1,j}}{2\Delta z}$$

where i is the subscript for the depth increment and j is the subscript for the time increment. Since Y has been expressed as a function of X alone, f'(X) is also a function of X alone, and we let

$$g(X) = \left[1 + \frac{\rho Q}{\alpha C_o} f'(X)\right] \qquad [31]$$

or, for the special case of the Freundlich it is

$$g(X) = \left[1 + \frac{\rho}{\alpha} f'(X)\right] \qquad [32]$$

Substituting equations [30] and [31] into equation [17], and rearranging we obtain

$$X_{i,j+1} = \frac{\Delta t}{g(X_{i,j})}\left[\left(\frac{D}{\Delta z^2} - \frac{\overline{V}}{2\Delta z}\right)X_{i+1,j} - \left(\frac{2D}{\Delta z^2} - \frac{g(X_{i,j})}{\Delta t}\right)X_{i,j} + \left(\frac{D}{\Delta z^2} + \frac{\overline{V}}{2\Delta z}\right)X_{i-1,j}\right. \qquad [33]$$

The initial and boundary conditions are given

$$X_{i,0} = 0$$

$$X_{0,j} = 1.0$$

$$X_{N+1} = X_{N-1}$$

MATERIALS AND METHODS

Materials

Soils

Two different soils were used in this study, Aiken clay loam and Vernal sandy loam. The Aiken clay loam is an iron-rich soil from the Sierra Nevadas of California. The pH is 5.8 and the free iron oxide content is 13 %. The extractable boron content is 0.1 ppm. Vernal sandy loam is a calcareous soil from Eastern Utah with a pH of 7.7 and calcium carbonate content of 10 to 15 %. The extractable boron content is 0.5 ppm (30).

Prior to the study, both soils were air dried, passed through a 2 mesh sieve, and stored in plastic bags.

Chemical Reagents

Boron solutions ranging from 0-50 ppm were prepared by diluting aliquots from a stock solution of 1000 ppm. The stock solution was prepared from oven-dried, granular analytical reagent, H_3BO_3. The 0.10 N $CaCl_2$ solutions were prepared from oven-dried, granular analytical reagent, $CaCl_2 \cdot 2\ H_2o$. The 0.10 N $AgNO_3$ titrating solution was prepared from oven-dried, granular analytical reagent $AgNO_3$. All solutions were stored in plastic bottles.

Laboratory Experiments

Adsorption Isotherm

Kinetics. Plastic erlenmeyer flasks were obtained, into which 10 grams of soil were placed and 25 ml of boron solution were then added. The flasks were stoppered and allowed to shake in a constant temperature water bath at 23.0° C from 5 minutes to two weeks. The contents were centrifuged at 23.0° C and the supernatant liquid decanted and analyzed for boron. The colorimetric method described by Hatcher and Wilcox (13), using carmine dye dissolved in concentrated sulfuric acid, was used in the boron analyses. A Perkin-Elmer Coleman 101 and a Beckman Model B spectrophotometers were used in determining color development. The reaction rates at 20 ppm and 4 ppm of initial solution concentration were determined.

Equilibrium studies. Into plastic 250 ml erlenmeyer flasks, 10 grams of soil was added along with 25 ml of boron solution. The flasks were stoppered and allowed to shake for 24 hours at constant temperature. The temperatures used were 11.5° C, 23.0° C, and 30.0° C ± 0.1° C. Initial boron concentrations from 0-50 ppm were added to the soil. The amount adsorbed versus the amount in solution after equilibrium was obtained and plotted. Three different adsorption theories were tested against the experimental data: Langmuir, B.E.T., and Freundlich.

Column Studies

Column setup. The physical structure of the column used in this study is shown in Figure 3. The column was composed of 11 lucite rings of an inside diameter of 7.65 cm and an outside

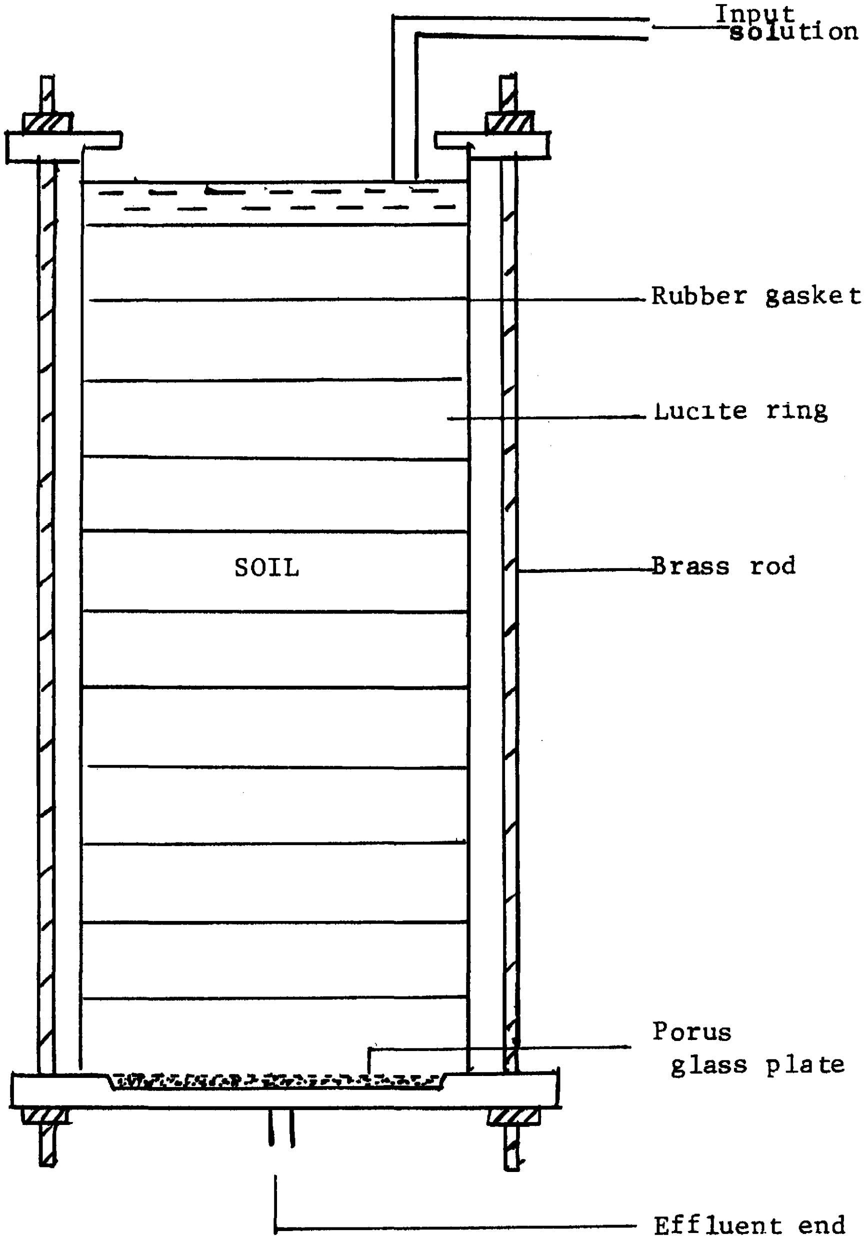

Figure 3. A sideview diagram showing the physical structure of the soil column used in this study.

diameter of 9.00 cm. Ten of the rings were 2 cm in height and the top ring was 4.5 cm high. The column was formed by first imbedding a porous plate in the bottom lucite plate, then be stacking the rings one on top of the other with rubber gaskets between. They were then bound together by three threaded brass rods.

The soil column was packed to a depth of about 21 cm with a given mass of soil using a standardized technique. An ashless Whatman #42 filter disc was placed at the top of the column to prevent disturbance of the column by the input solution.

The bulk density and pore fraction was calculated from the mass and total volume of the soil column.

<u>Determination of flow parameters.</u> The interstitial flow velocity, $\bar{V}$, is calculated from the equation

$$\bar{V} = \frac{V}{A \cdot \alpha \cdot t} \qquad [34]$$

where V is the total effluent volume collected during time, t; A is the cross-sectional area of the column; and α is the pore fraction of the column.

The dispersion coefficient, D, is computed from parameters obtained from the chloride breakthrough curve (BTC). The chloride ion is considered to be a non-reactive ion undergoing interstitial flow through the steady state column as was described by Nielsen and Biggar (26).

The BTC for chloride was obtained by first saturating the column with deionized water, then adding 0.10 N $CaCl_2$ solution utilizing a constant head device. The effluent was collected in test tubes by means of an SMI automatic fraction collector with a 10 ml automatic siphon. The samples were analyzed for chloride by the potentiometric titration technique using 0.10 N $AgNO_3$, a silver billet electrode, and a KNO_3 double-junction reference electrode. Figure 4 shows a typical Cl^- BTC.

The dispersion coefficient was calculated from the equation

$$D = \frac{\bar{V}L}{4\pi S_o^2 V_o^2} \qquad [35]$$

The pore volume, V_o, is obtained graphically from the Cl^- BTC at $C/C_o = 0.50$. The slope at that point on the curve is defined as S_o. L is the height of the entire soil column in cm.

Profile distribution of boron. The Cl^- BTC process described above made the soil column homogeneous in Ca^{++}. The excess salt was flushed out with deionized water until the concentration of Cl^- was below detection by $AgNO_3$ titration. Boron solution of 10 ppm was then introduced at the top of the column until a boron breakthrough curve was obtained. The carmine dye method was again used for the boron analyses.

The column was again flushed with deionized water to remove the initial boron added and the 10 ppm boron solution was reintroduced at the top and allowed to flow for a given time. The flow was terminated, the column was segmented, and the solution extracted under vacuum and analyzed for boron. No method was developed to analyze the adsorbed phase for boron. The Y(z,t) experimental values (adsorbed boron) were theoretically calculated by means of the adsorption isotherm using the solution phase concentrations.

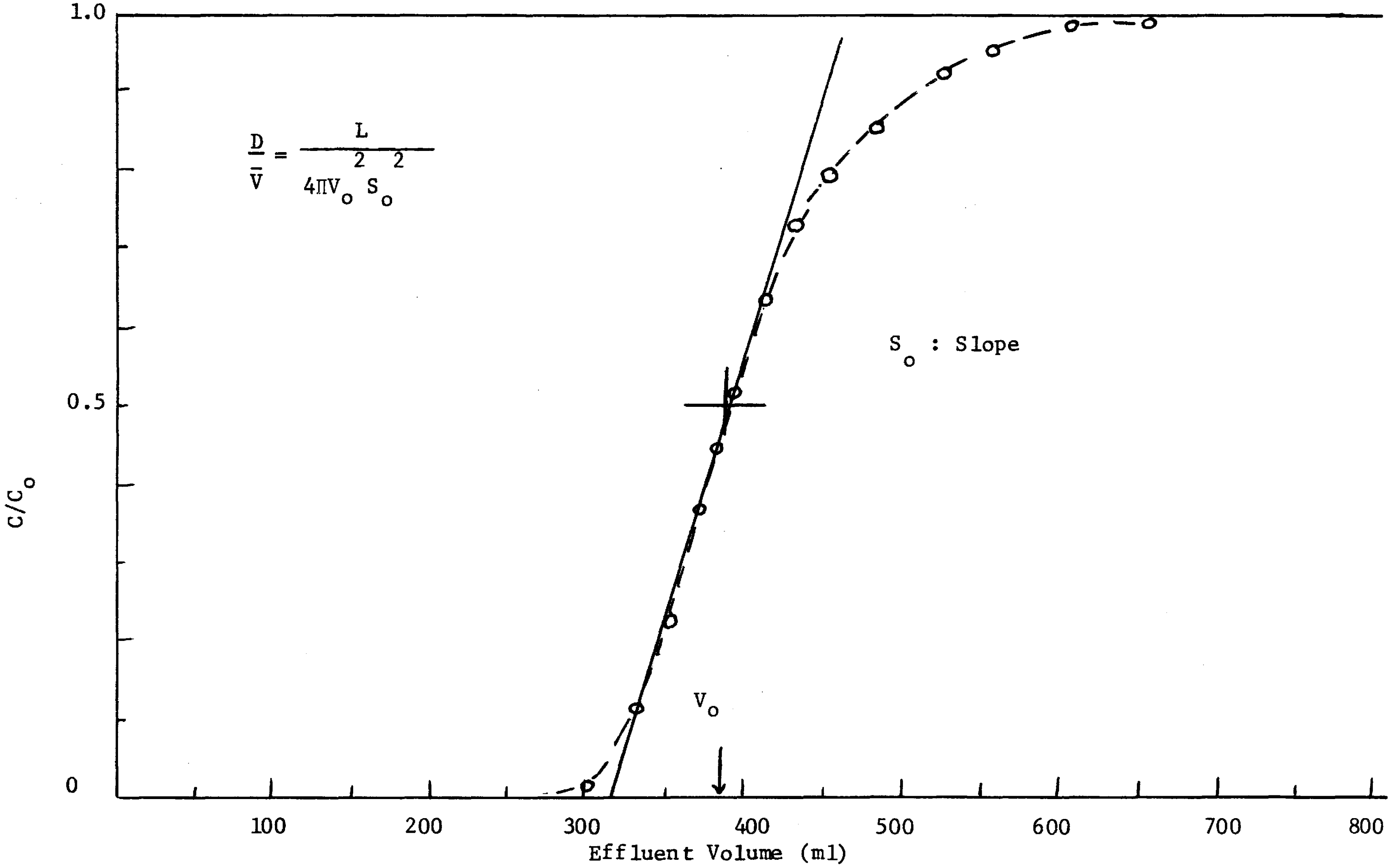

Figure 4. A typical Cl$^-$ breakthrough curve used for calculating dispersion coefficient.

Computer Experiment

The computer used in this experiment was a Univac 1108 located at the University of Utah Computer Center, Salt Lake City, to which a remote terminal is located in the Engineering Building on the campus of Utah State University. The remote terminal consists of a Model 9200 card reader and printer which handles the input and output processes of the program.

The FORTRAN IV Program

1. Input: Read in D, $\overline{V}$, ρ, α, Q_m, and C_o for each column experiment.

2. Set the initial condition $X_{i,0} = 0$ (i = i,n) where n is the last increment.

3. Set the boundary conditions $X_{0,j} = 1.0$ (j = 1,m) where m is the last time increment.

4. Begin the computation of $X_{i,1}$ for the time period 1 using the computation scheme presented in equation [33].

5. Evaluate the bottom boundary value $X_{n+1} = X_{n-1}$ where n is the last depth increment.

6. Output: Print out the values of $X_{i,j}$.

7. Call the Subroutine and compute the corresponding values for $Y_{i,j}$ from the adsorption function.

8. Output: Print out the values for $Y_{i,j}$.

9. Repeat steps 4 to 8 for the next time increment.

10. End the computation.

RESULTS AND DISCUSSION

Adsorption Isotherms

Kinetics

The purpose of this kinetic study was to determine the equilibrium time for the adsorption of boron by Aiken clay loam and Vernal sandy loam soils. The adsorption function was based on equilibrium conditions. If equilibrium is not established, the adsorption function will not describe the behavior of boron in the soil columns. Since the column studies were conducted at one temperature, 23.0° C, the kinetics of adsorption were correspondingly run at the same temperature. The initial boron concentrations used were 4 ppm and 20 ppm.

As shown in Figures 5 and 6, the equilibrium time for both soils was less than 1 hour, and by 30 minutes the greater part of the reaction had been completed. This gives a qualitative evaluation of the time required for equilibrium to be achieved and is not an unrealistic time in terms of the feasibility of equilbirium within the soil column.

Equilibrium Studies

The assumption that equilbrium has been reached allows the amount of boron adsorbed, q, to be plotted against the amount of boron remaining in solution, C. If carried out at constant temperature, the graph is an isotherm. The isotherms for both the Aiken and Vernal soils were obtained and plotted in Figures 7, 8, and 9 for three different temperatures, 11.5° C, 23.0° C,

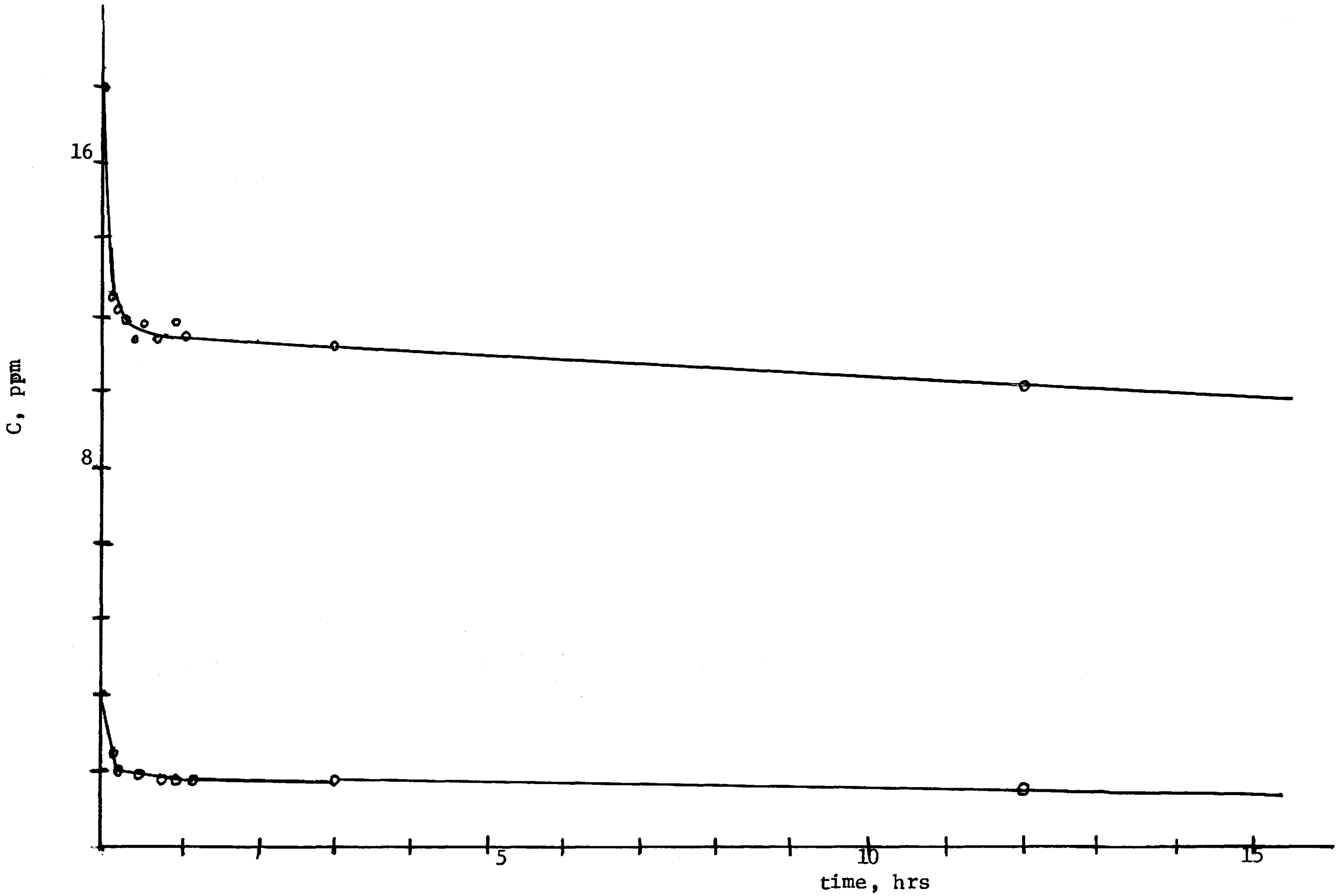

Figure 5. Kinetic plot of Aiken clay loam soil at 23° C.

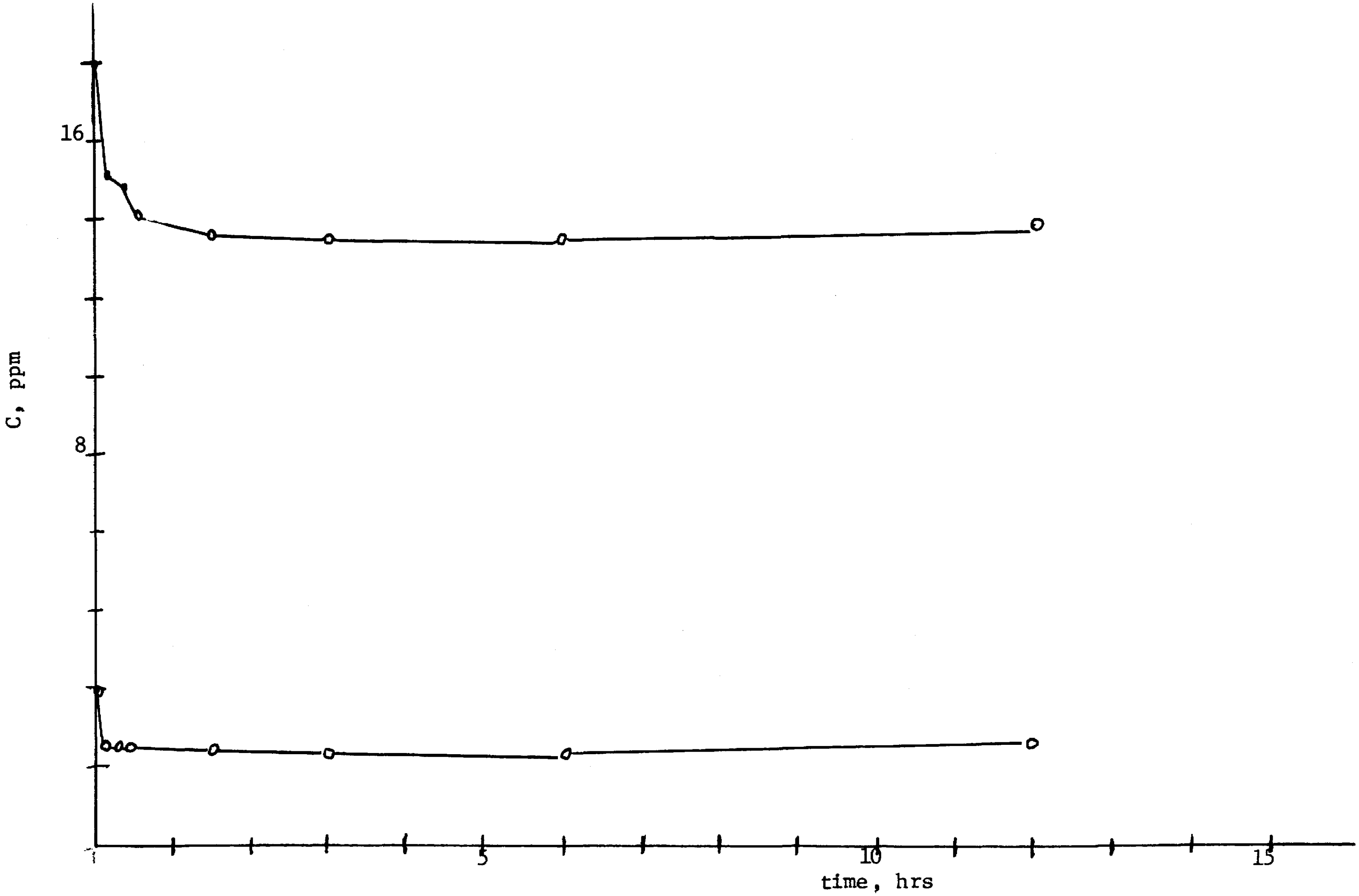

Figure 6. Kinetic plot of Vernal sandy loam soil at 23° C.

and 30.0° C. The comparison of the isotherms in Figures 7, 8, and 9 reveals distinct depressions or steps in the curves. The consistency of the depressions in the curves suggests that the curve may not be uniform and indicates a trend that points to a non-homogeneous adsorption surface of some unknown description. Several hypotheses are mentioned as possible explanations: (a) the depressed region of the curve represents a transition phase from one mechanism of adsorption to another; (b) the depressed region reflects a transition from one group of uniform sites with lower energies to another group of sites with higher energies; or (c) the non-uniform curve indicates heterogeneous adsorption surface with energies of adsorption that change continuously with amount of surface area covered by the adsorbate. While the actual discovery of the mechanism that describes this phenomenon is not the purpose of this study, it is of interest to obtain an adsorption function which in the mathematical computations, accounts for the non-uniformity of the curve. The experimental datawere plotted in linear form according to the Langmuir, B.E.T., and Freundlich models for the purpose of obtaining a descriptive adsorption function of boron in a soil system. A linear regression analysis was conducted of the plot resulting from each model. The experimental data, isotherm constants, and linear regression data are listed in Appendix A.

Langmuir. The experimental data were plotted in Figures 10, 11, and 12 according to the linear form of Equation [18]

$$\frac{C}{q} = \frac{1}{Q_m K} + \frac{C}{Q_m}$$

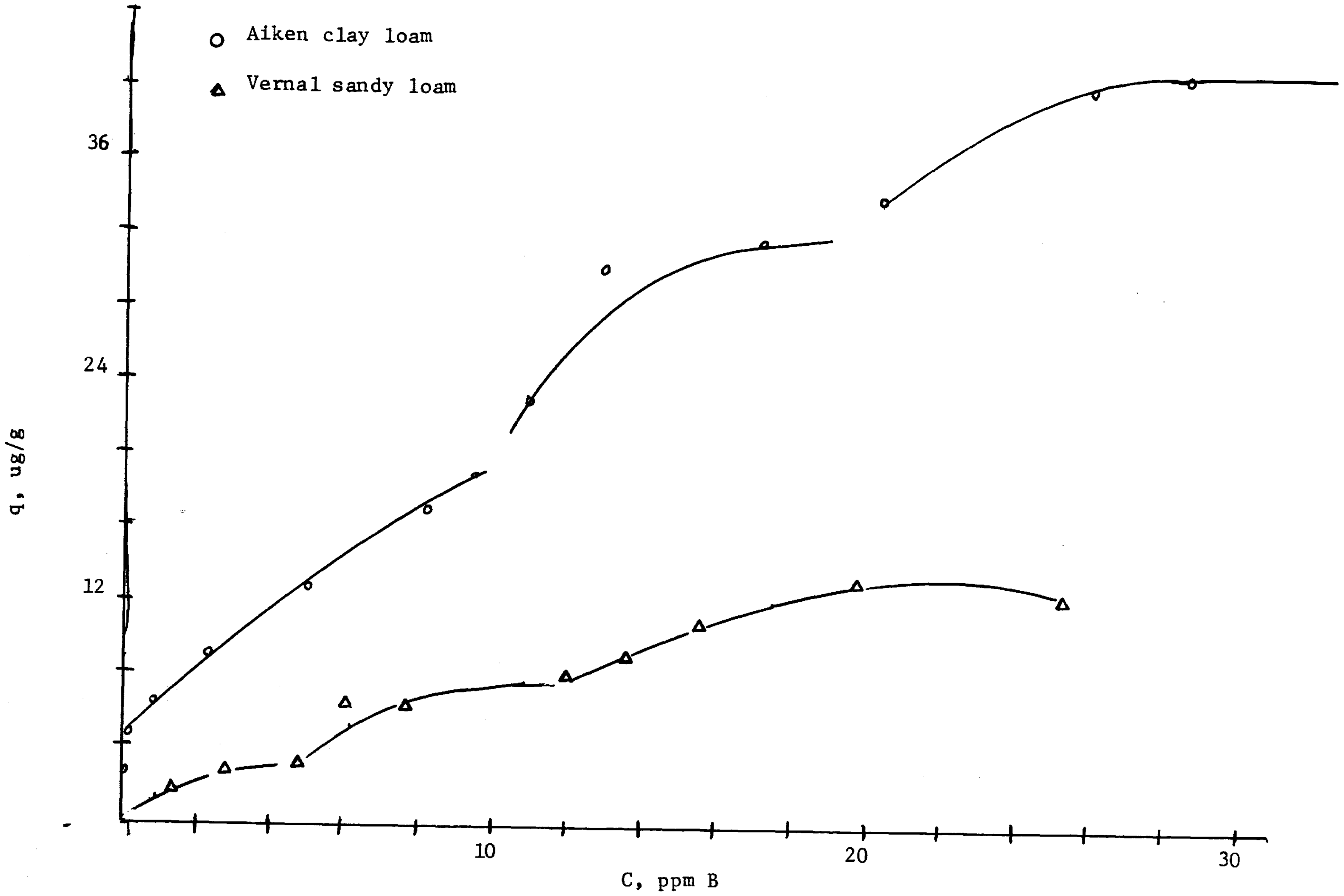

Figure 7. Equilibrium isotherm for Aiken clay loam soil and Vernal sandy loam soil at 11.5° C.

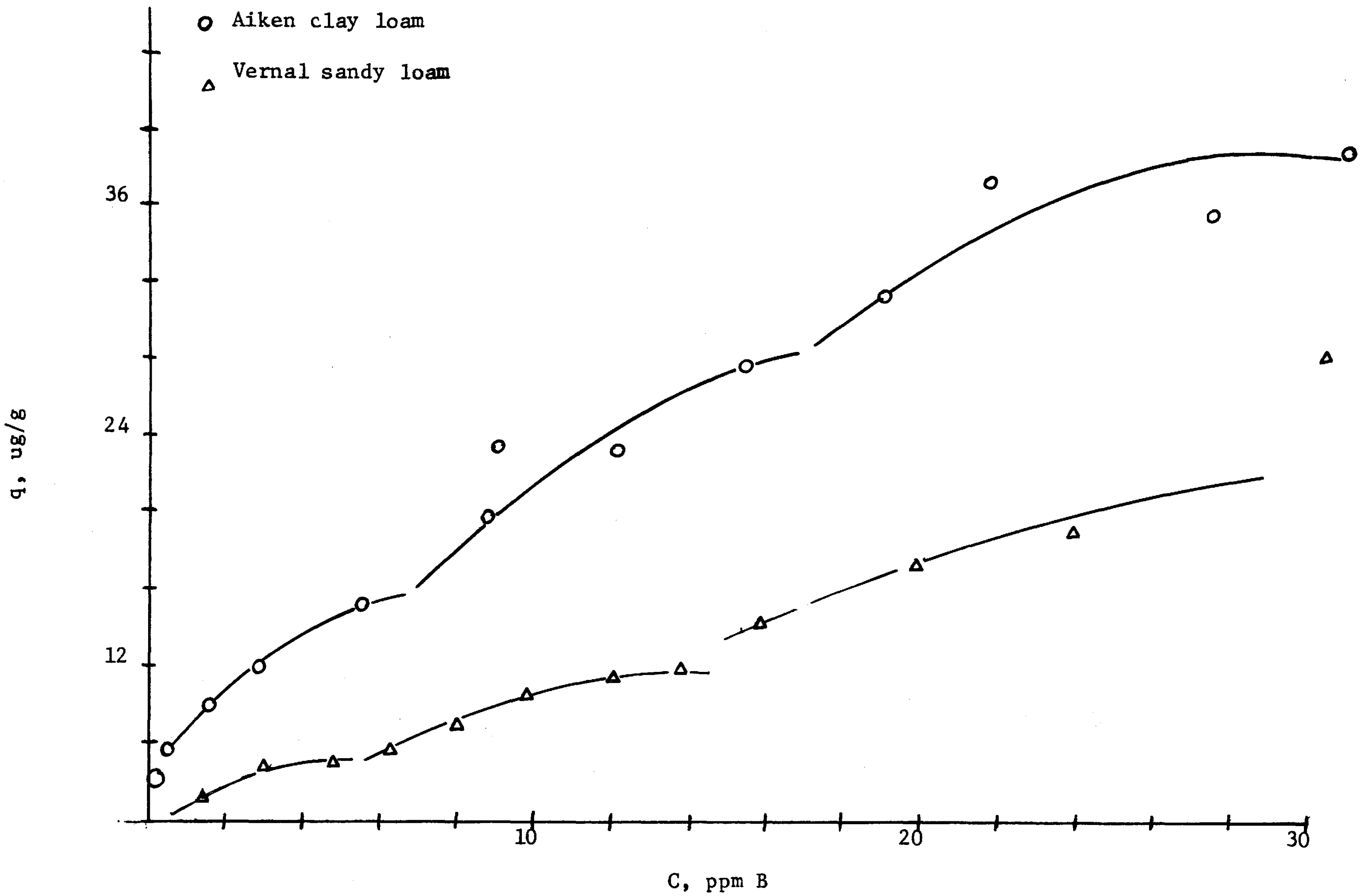

Figure 8. Equilibrium isotherm for Aiken clay loam soil and Vernal sandy loam soil at 23.0° C.

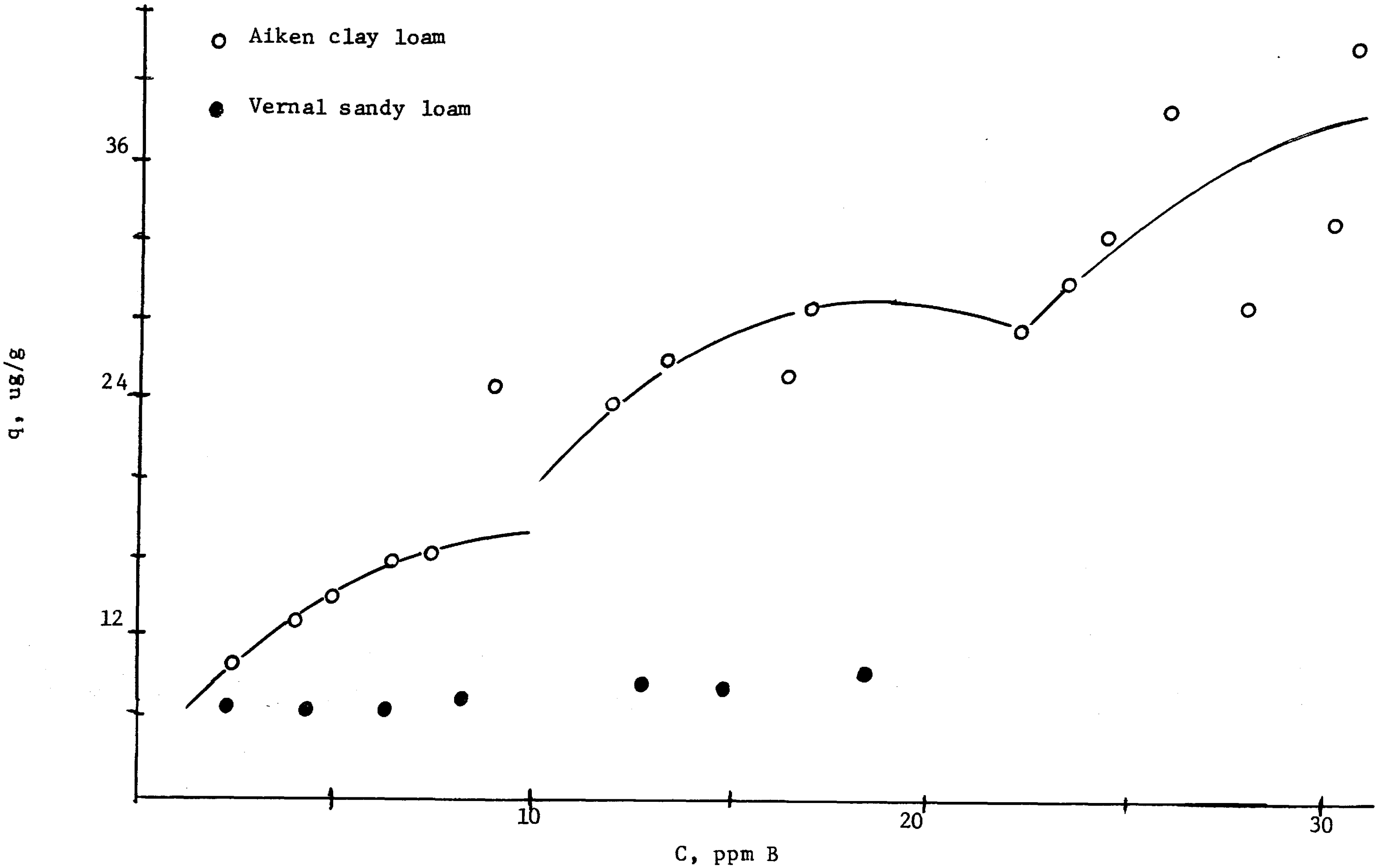

Figure 9. Equilibrium isotherm for Aiken clay loam soil and Vernal sandy loam soil at 30.0° C.

A linear regression analysis was conducted and produced the linear relationships illustrated in Figures 10, 11, and 12. The boron solution concentration regions of interest were: 0-40 ppm, 0-12 ppm, and 12-40 ppm. Tables 24 and 25 or Appendix A give the linear correlation of the respective regions for each soil and temperature. It is noted that the correlation coefficients, r, vary quite broadly for all three regions and the general correlation of the two regions, 0-12 and 12-40 ppm, are related to the overall correlation of the 0-40 ppm region. That is, any situation which justifies one or both of these regions as being satisfactory with respect to linear regression analysis will just as well accept the overall region as being satisfactory. The average values for the correlation coefficients using the Langmuir isotherm are .787, .742, and .835 for the 0-40, 0-12, and 12-40 ppm regions, respectively. The averages for the individual soils vary slightly from these values. Perfect correlation or complete linearity is represented by 1.000. Considering the linear regression analyses, the Langmuir model proves to be unsatisfactory for describing the behavior of boron in the Aiken and Vernal soils.

B.E.T. The multilayer adsorption model, advanced by Brunauer, Emmett, and Teller, attempts to describe the non-uniform isotherm with one equation (equation [22]). The choice for the value of B_o was made by inspection of the experimental values of C. It is desirable that the ratio of C to B_o be approximately within the interval 0.05-0.35. The value of 50 ppm was chosen which gives the range of C to be 2.5-17.5 ppm. This range expands the limits of the Langmuir equation. Equation [22] is plotted in Figures 13, 14, and 15 and fits the linear regression line with a correlation of .9959

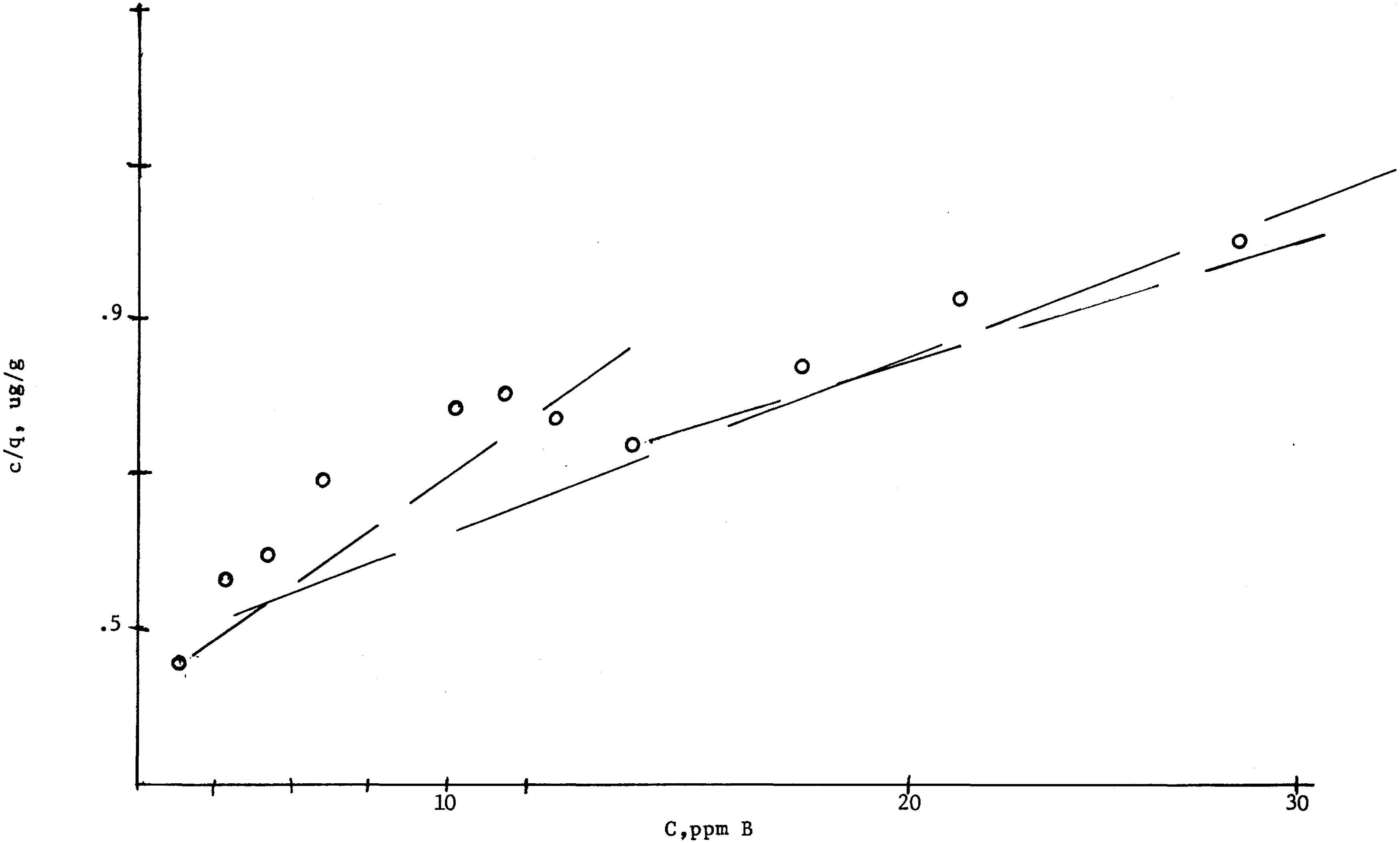

Figure 10. Langmuir isotherm for Aiken clay loam soil at 11.5° C.

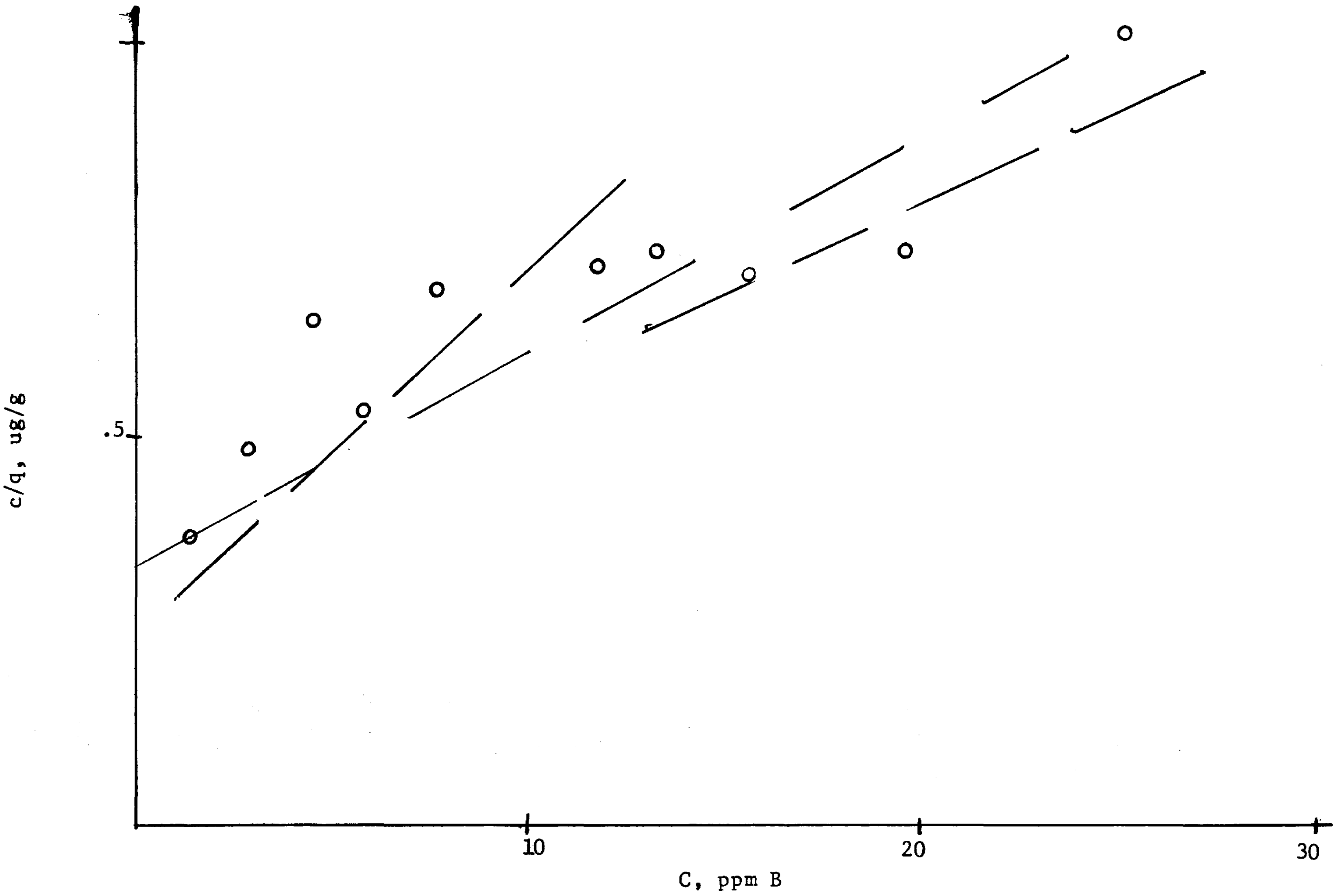

Figure 11. Langmuir isotherm for Vernal sandy loam soil at 11.5° C.

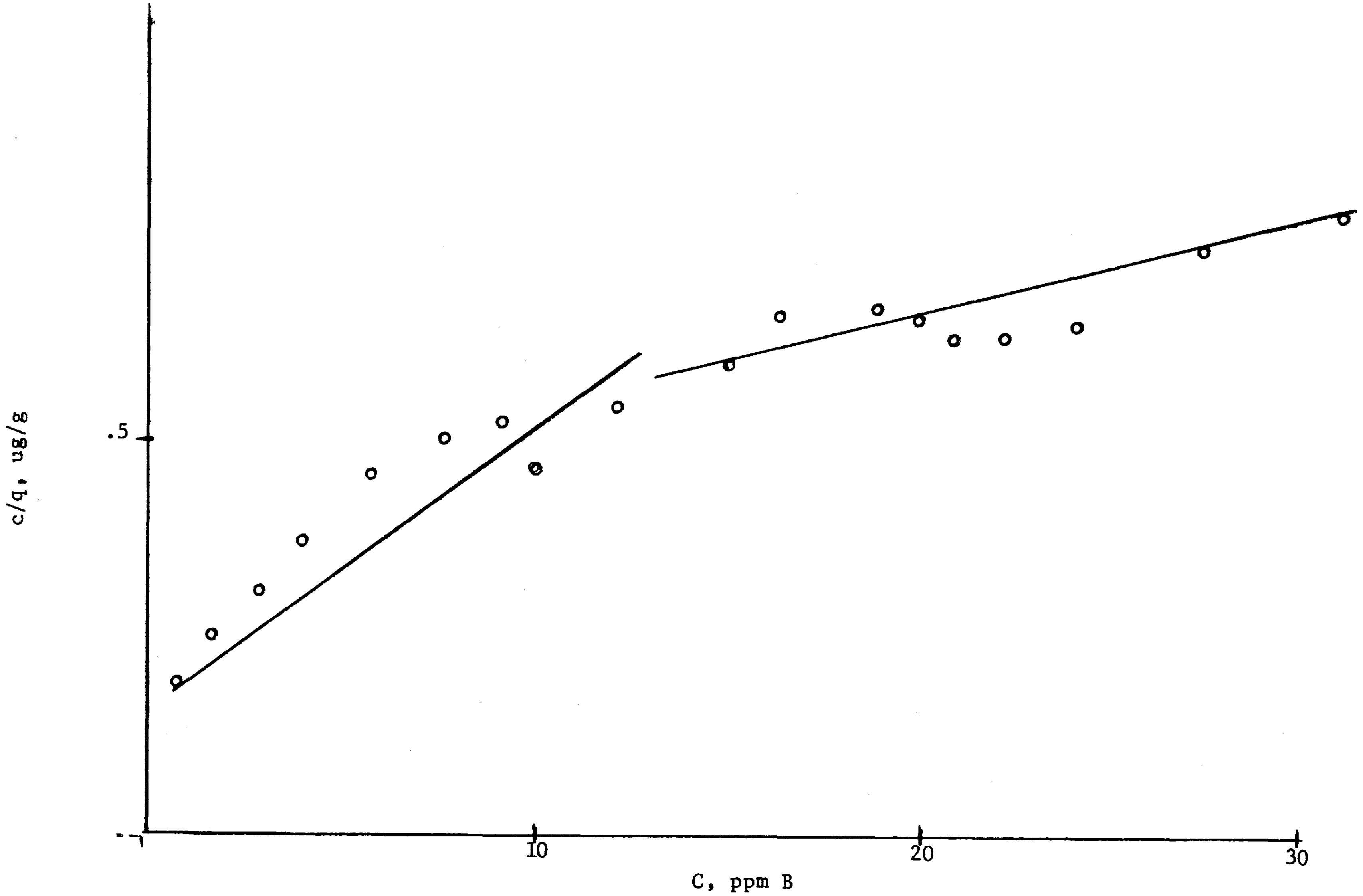

Figure 12. Langmuir isotherm for Aiken clay loam soil at 23.0° C.

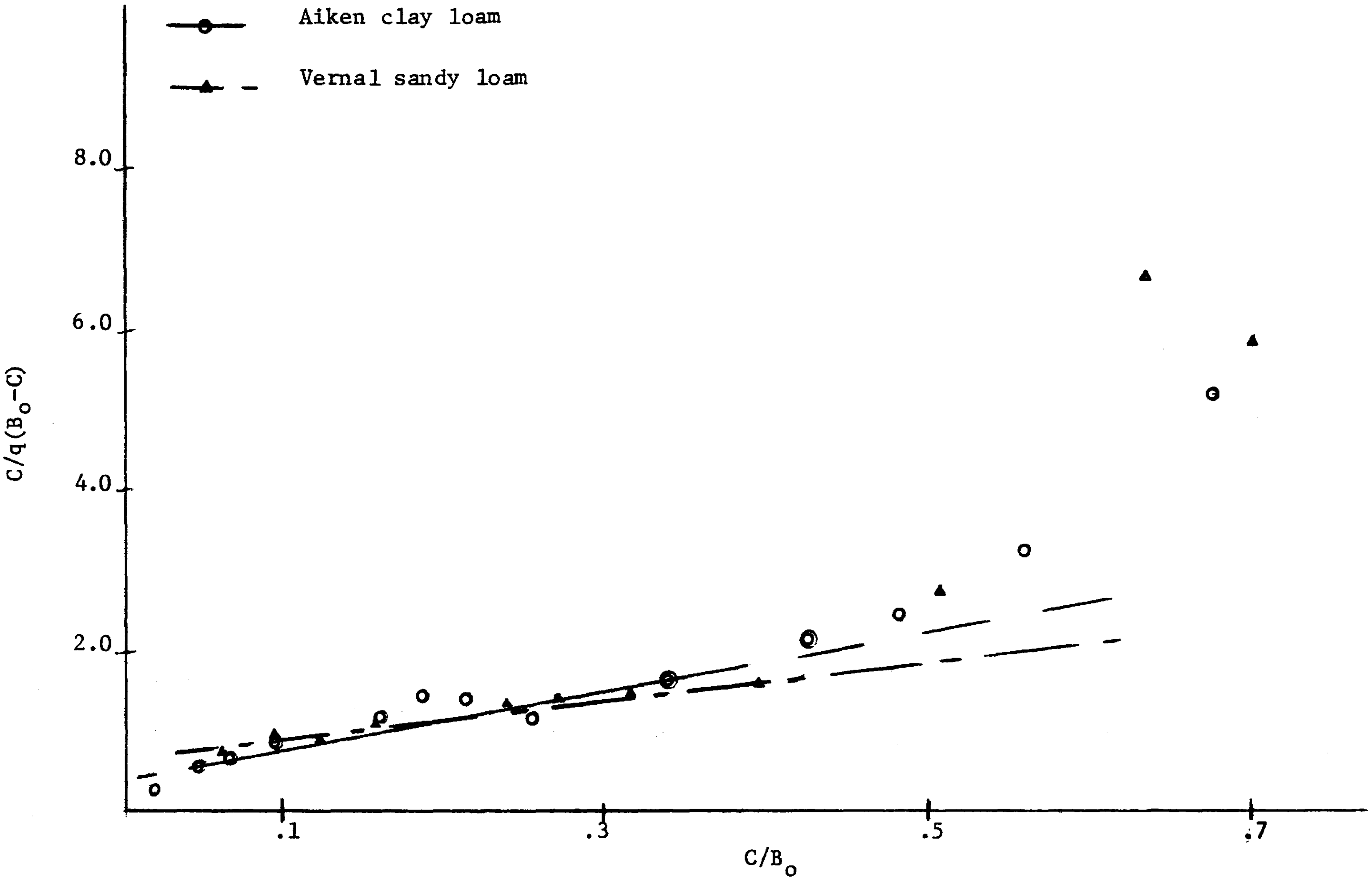

Figure 13. B.E.T. isotherm for Aiken clay loam and Vernal sandy loam soils at 11.5° C.

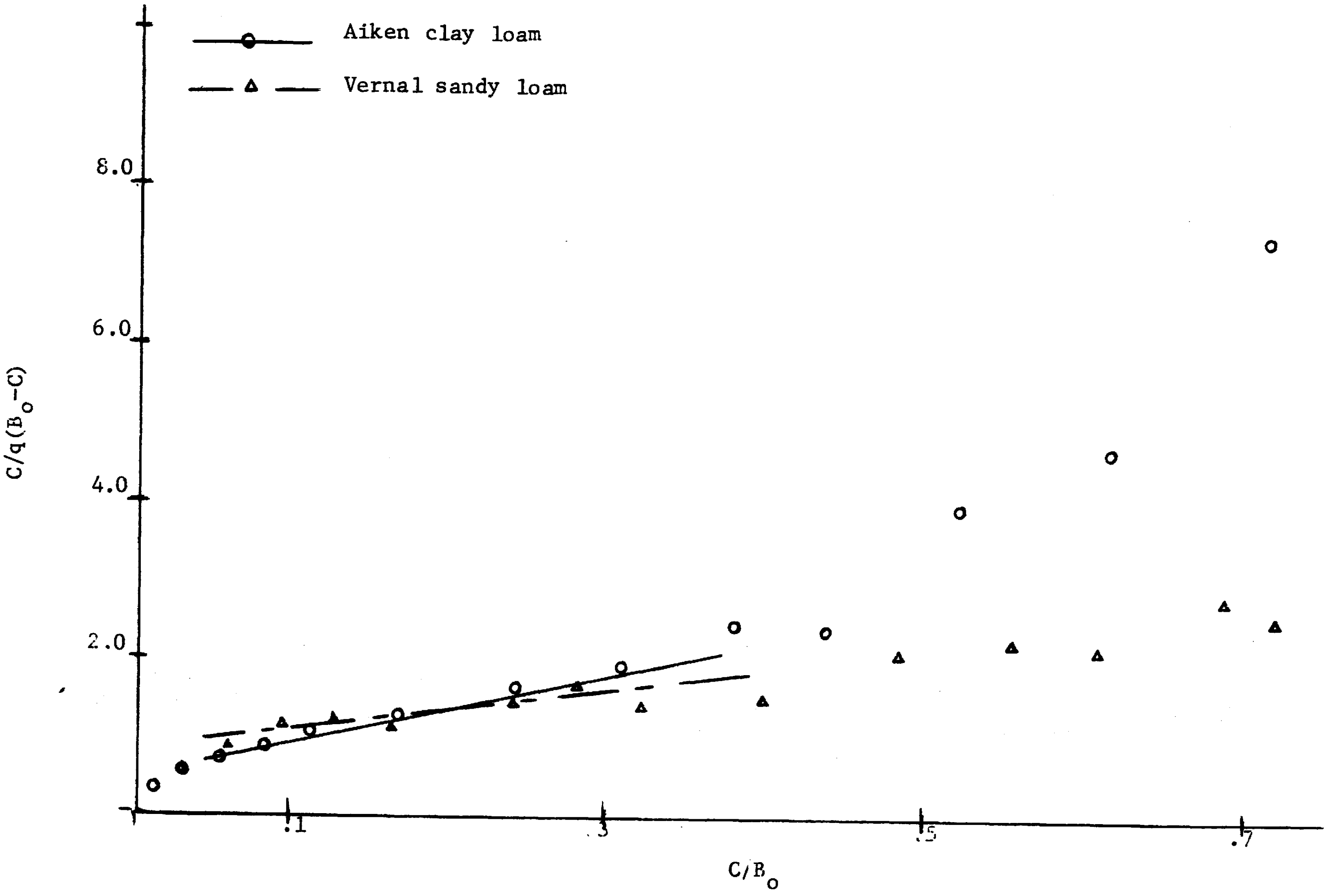

Figure 14. B.E.T. isotherm for Aiken clay loam and Vernal sandy loam soils at 23.0° C.

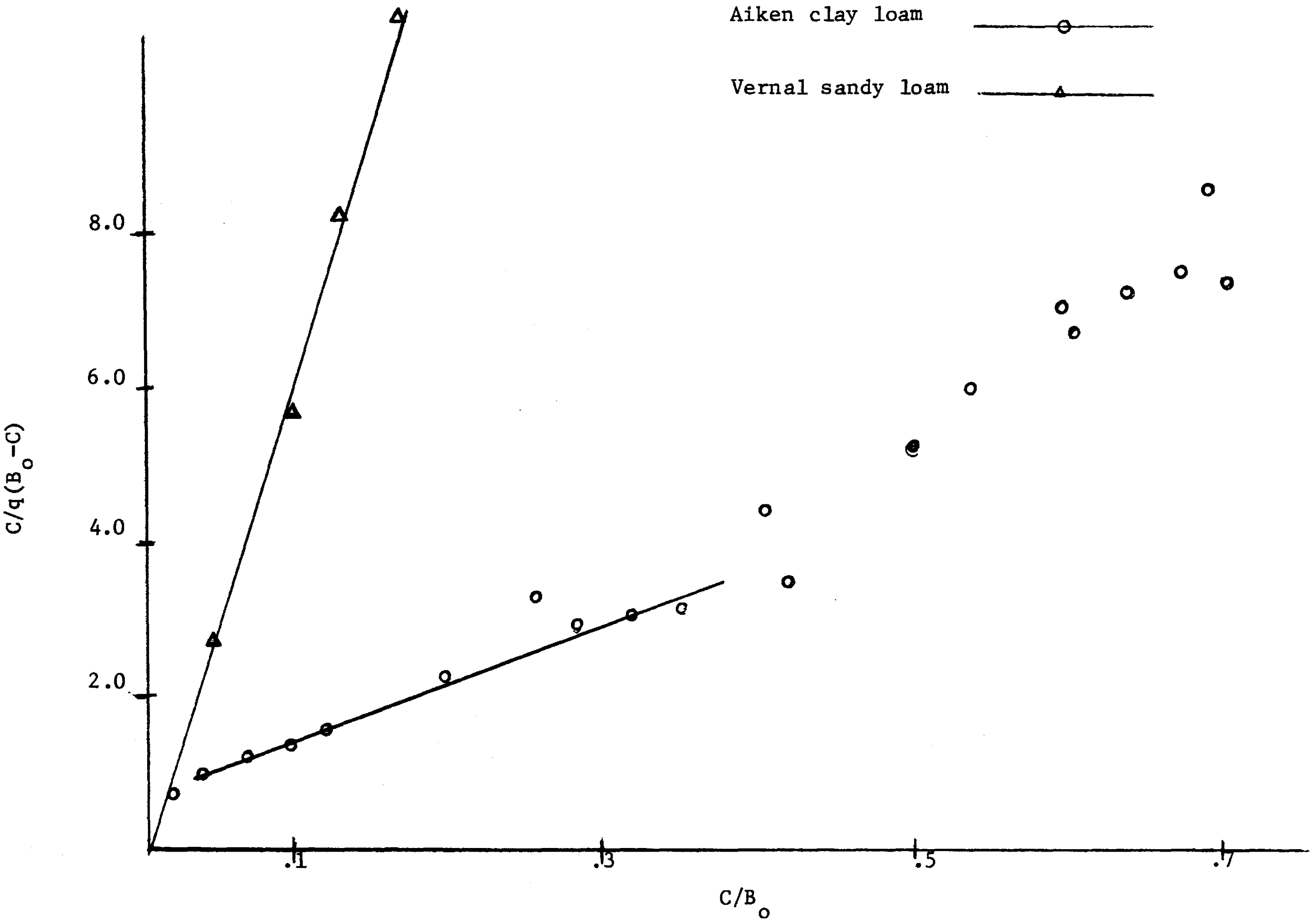

Figure 15. B.E.T. isotherm for Aiken clay loam and Vernal sandy loam soils at 30° C.

for the Aiken soil and .9568 for the Vernal soil. Both values are considerably better than those obtained by the Langmuir model. Adsorption at all temperatures for both soils give similarly high correlation. The overall average of correlation coefficients for the two soils at all three temperatures is .976; and for each individual soil the averages are .978 and .973 for the Aiken and Vernal soils respectively. It is noted that the correlation coefficients are high, but, in addition, the deviations about the line are not large. The statistical treatment lacks rigorous treatment, but the qualitative results indicate a definite distinction between the B.E.T. and the Langmuir models in describing B adsorption.

Freundlich. The parameters associated with equation [25], the Freundlich equation, have not been correlated with any useful property of the soil system. Nevertheless, the equation accurately describes many systems and has potential theoretical merit. The isotherm is given by plotting log C versus log q. The linearity indicates the degree of accuracy with which it describes the system. Figures 16, 17, and 18 for the Aiken soil show the linear regression line for the experimental data and the correlation coefficient is .984. The Vernal soil, Figures 19, 20, and 21, give similar results. The average value for r is .975 for the Aiken soil, .928 for the Vernal soil, and .951 overall. These values are slightly less than those obtained for the B.E.T. model but are acceptable and probably reflect no significance between the two. The application and validity of the model will become more apparent in the predictive model results.

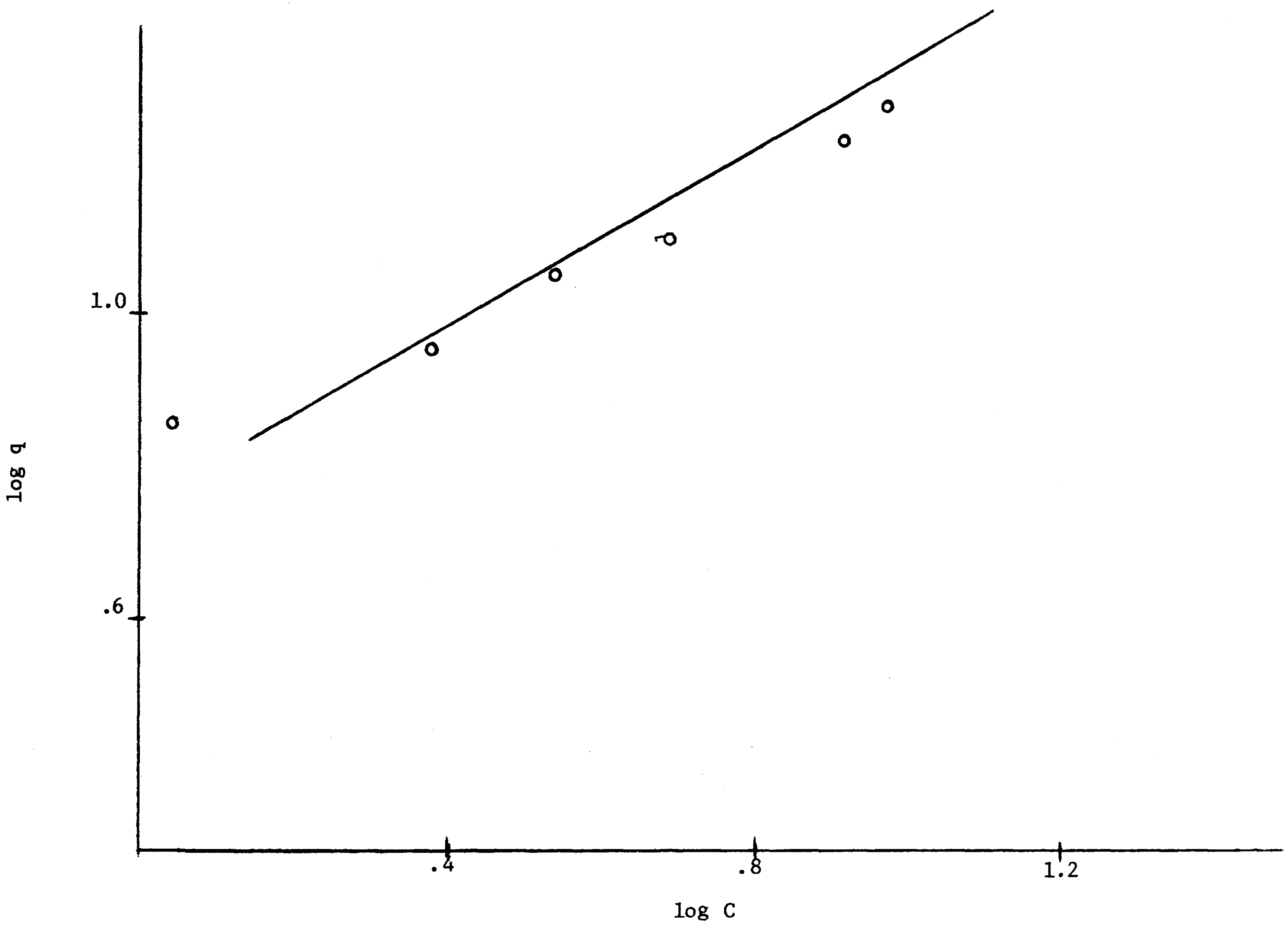

Figure 16. Freundlich for Aiken clay loam soil at 11.5° C.

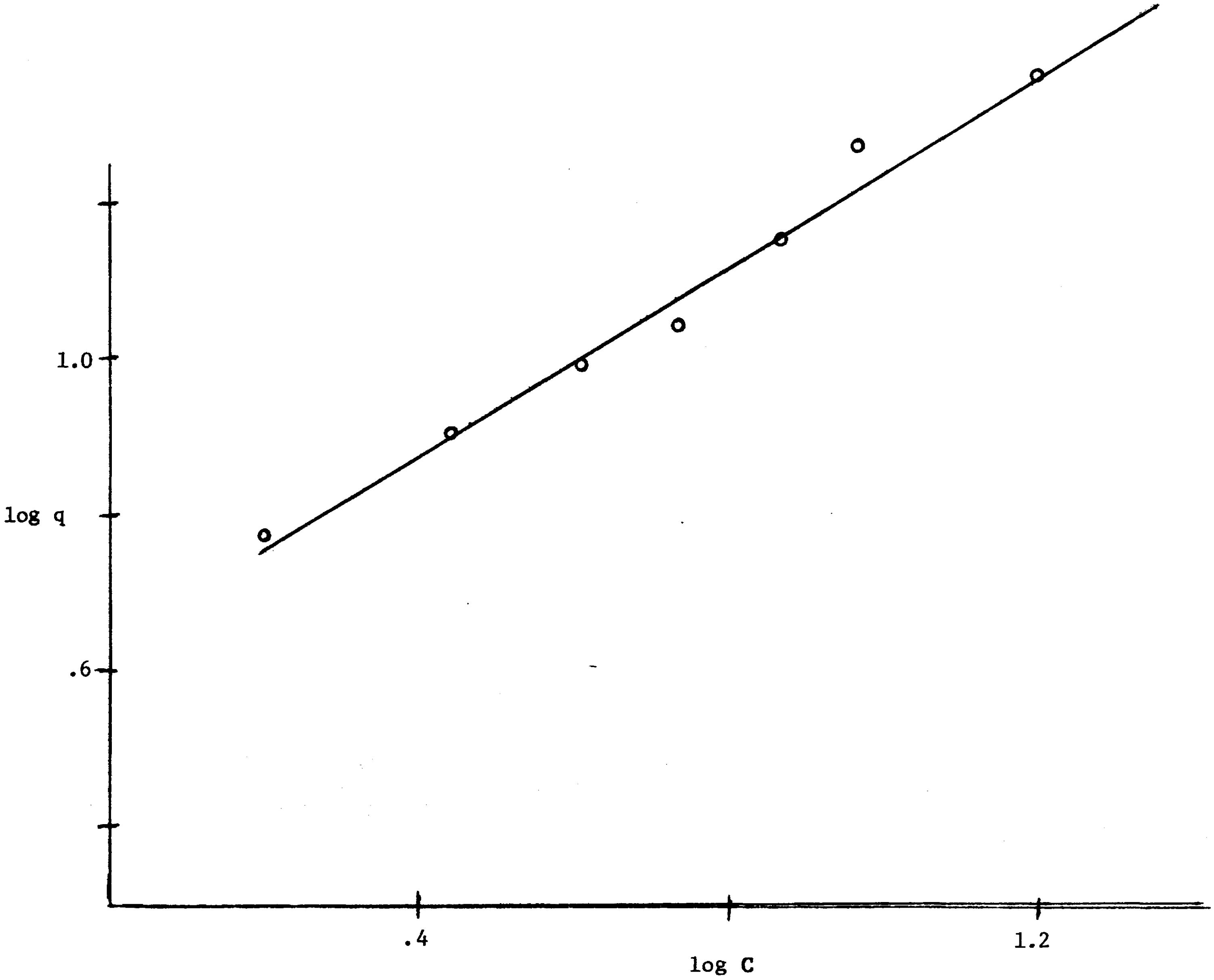

Figure 17. Freundlich for Aiken clay loam soil at 23.0° C.

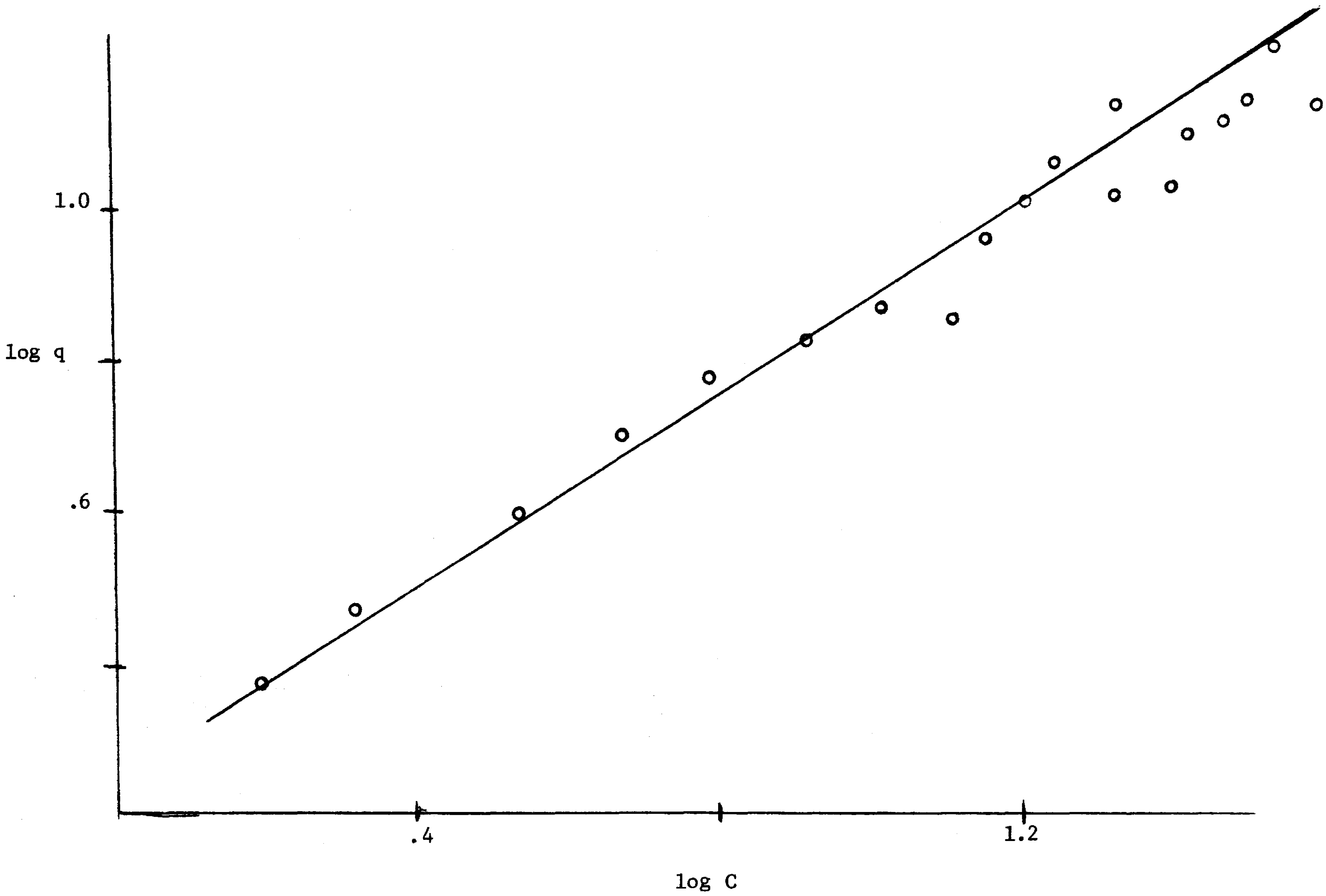

Figure 18. Freundlich for Aiken clay loam soil at 30.0° C.

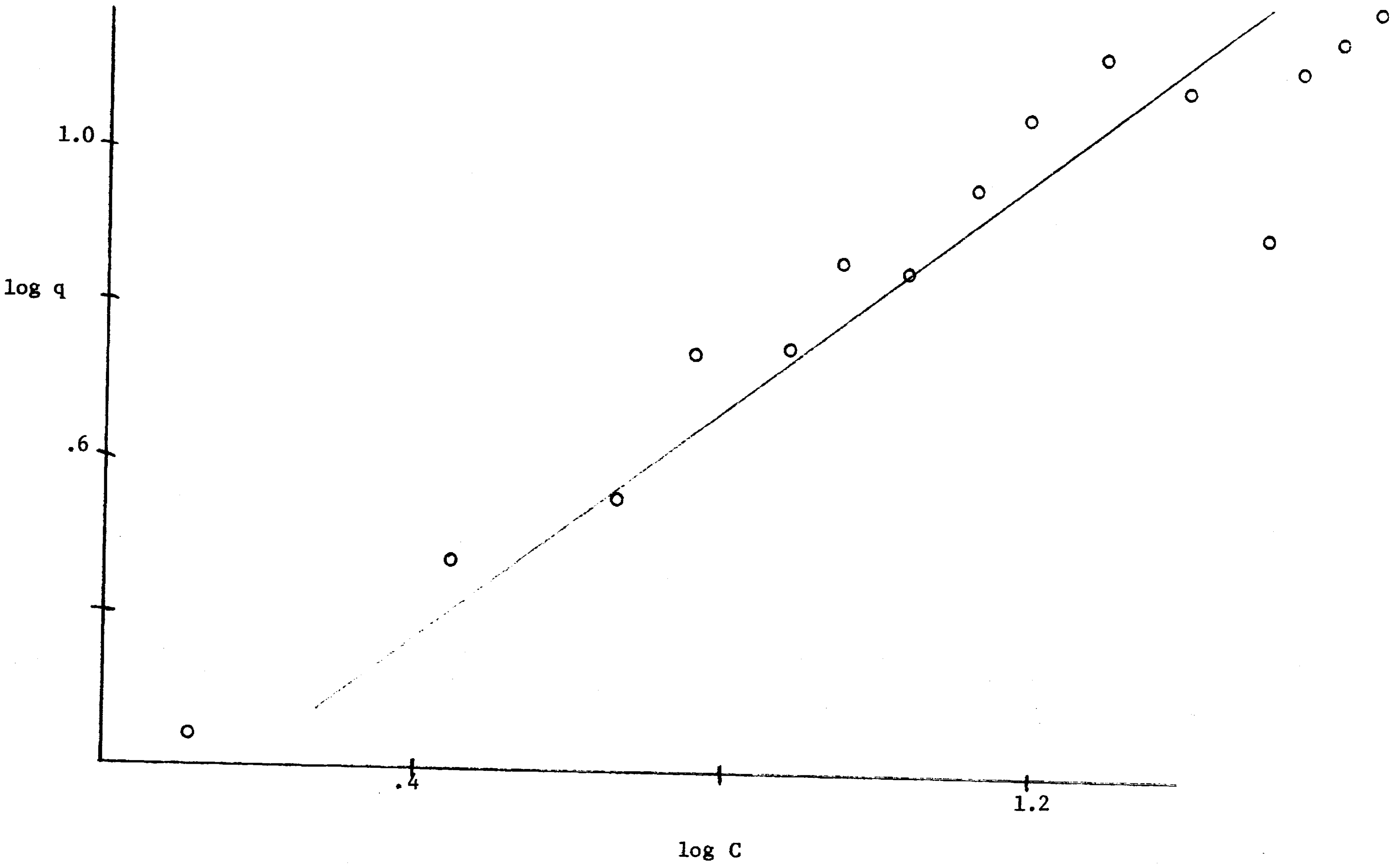

Figure 19. Freundlich for Aiken clay loam soil at 11.5° C.

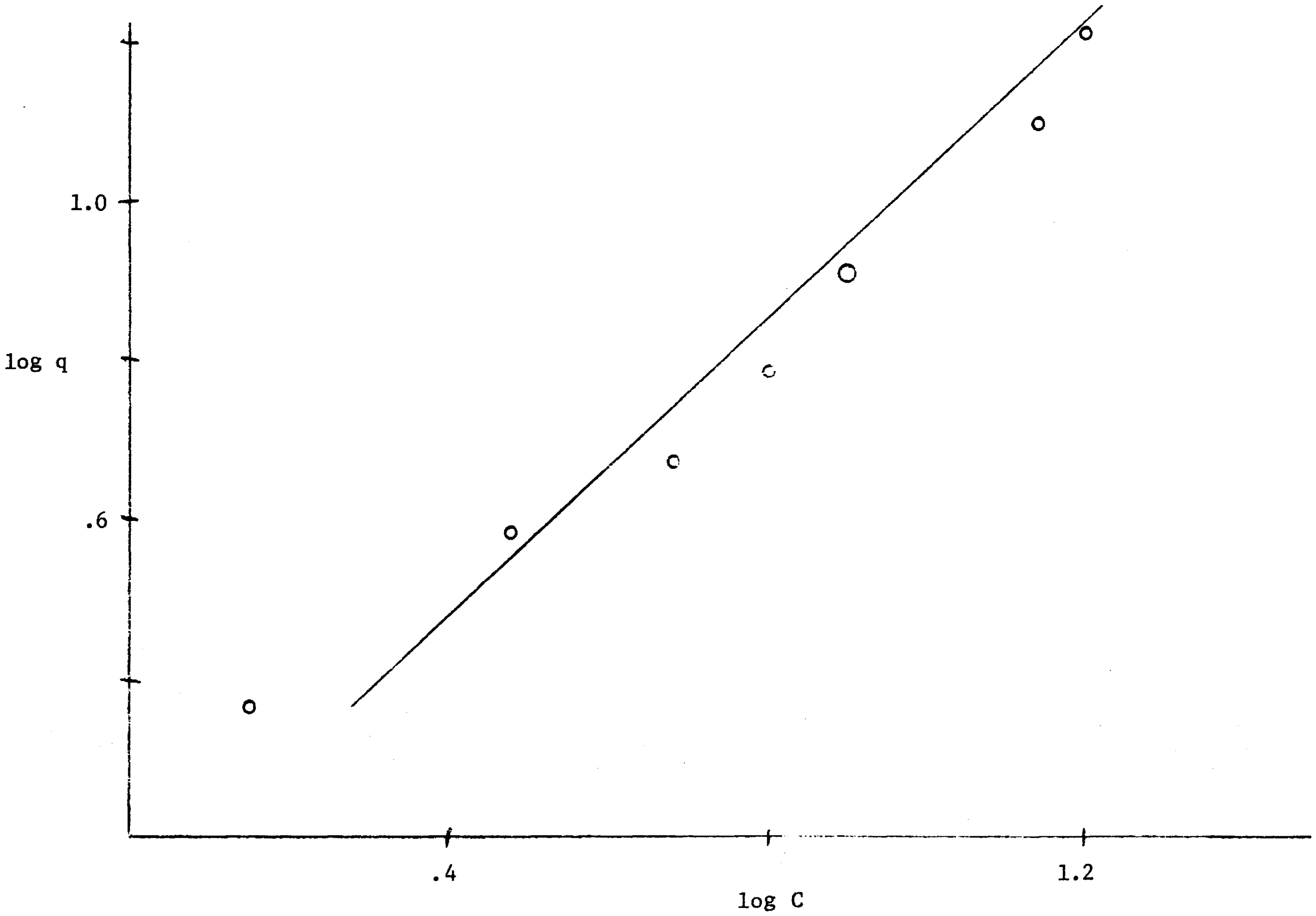

Figure 20. Freundlich for Vernal sandy loam soil at 23.0° C.

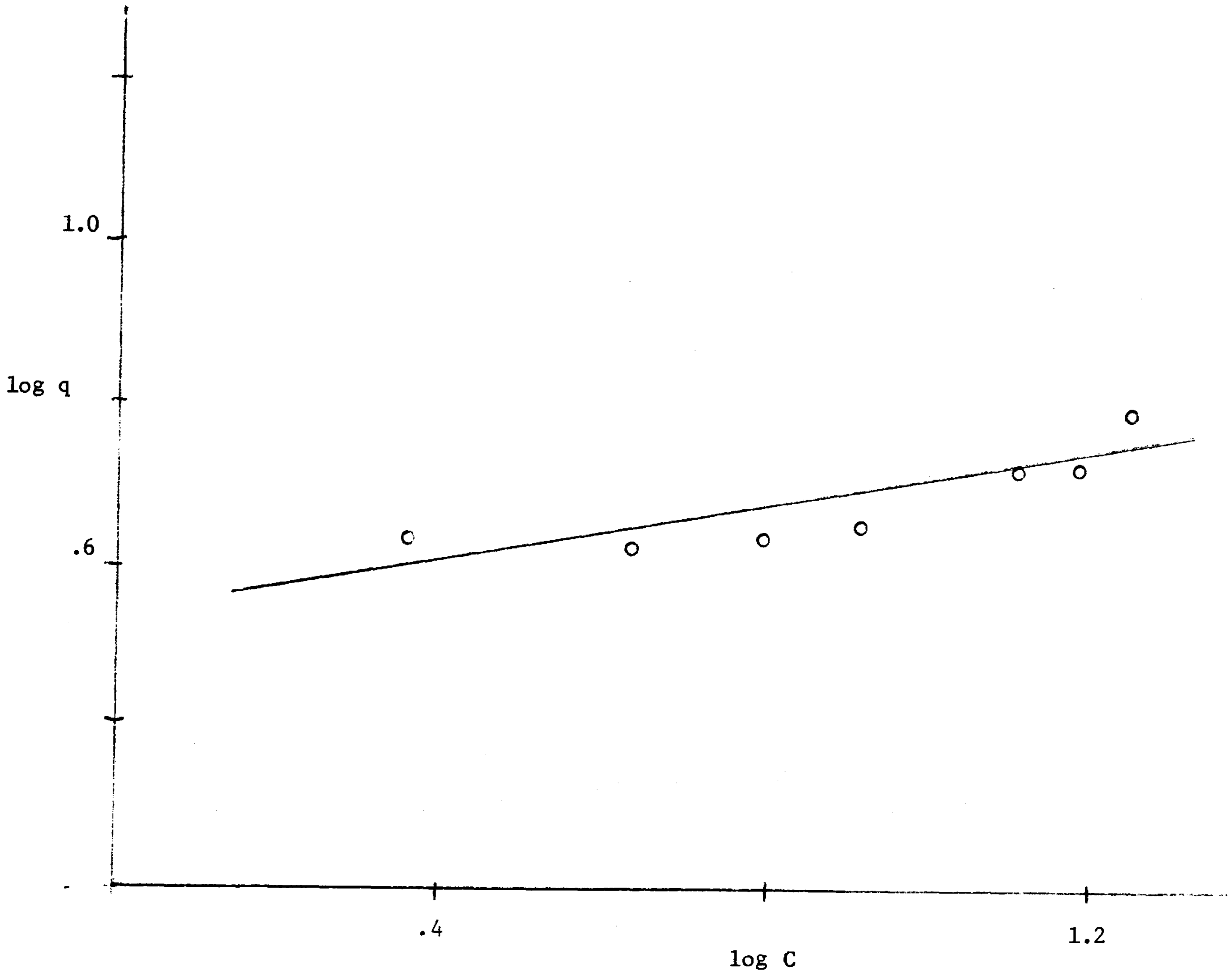

Figure 21. Freundlich for Vernal sandy loam at 30.0° C.

The overall conclusions that can be drawn from the evidence presented by the experimental data is that the B.E.T. equation describes the behavior of boron in Aiken and Vernal soils. The Freundlich equation, however, has equal merit and a choice between B.E.T. and Freundlich models must be based on individual situations. The primary advantage of the Freundlich over the B.E.T. model is the greater range of values for C for which the equation can be applied. The Langmuir equation is unsatisfactory as the descriptive isotherm for any region of the curve. Generally, the acceptance of a particular equation for describing the system does not infer that the theoretical model used in its derivation applies equally well to the system. Speculation, however, leads one to the conclusion that, generally speaking, adsorption at the soil mineral interface involves more than a simple homogeneous monolayer and that the theories involving more complex interactions are perhaps more realistic.

Soil Column Studies

Determination of Column Parameters

Chloride BTC. The chloride breakthrough curves were obtained for each column to determine the pore volume of the column, the average interstitial flow velocity, and the fluid dispersion coefficient. Figures 22, 23, and 24 show the BTC for columns IA, IIA, and IIB. The tabular values for these are found in Appendix B. The BTC produces a slope, S_o, at the point where C/C_o is 0.50. The pore volume, V_o, at that point is assumed to be the effluent volume. The fluid dispersion coefficient is computed using these two parameters along with flow velocity and column length and varies inversely with the squares of the pore volume and S_o. The sensitivity

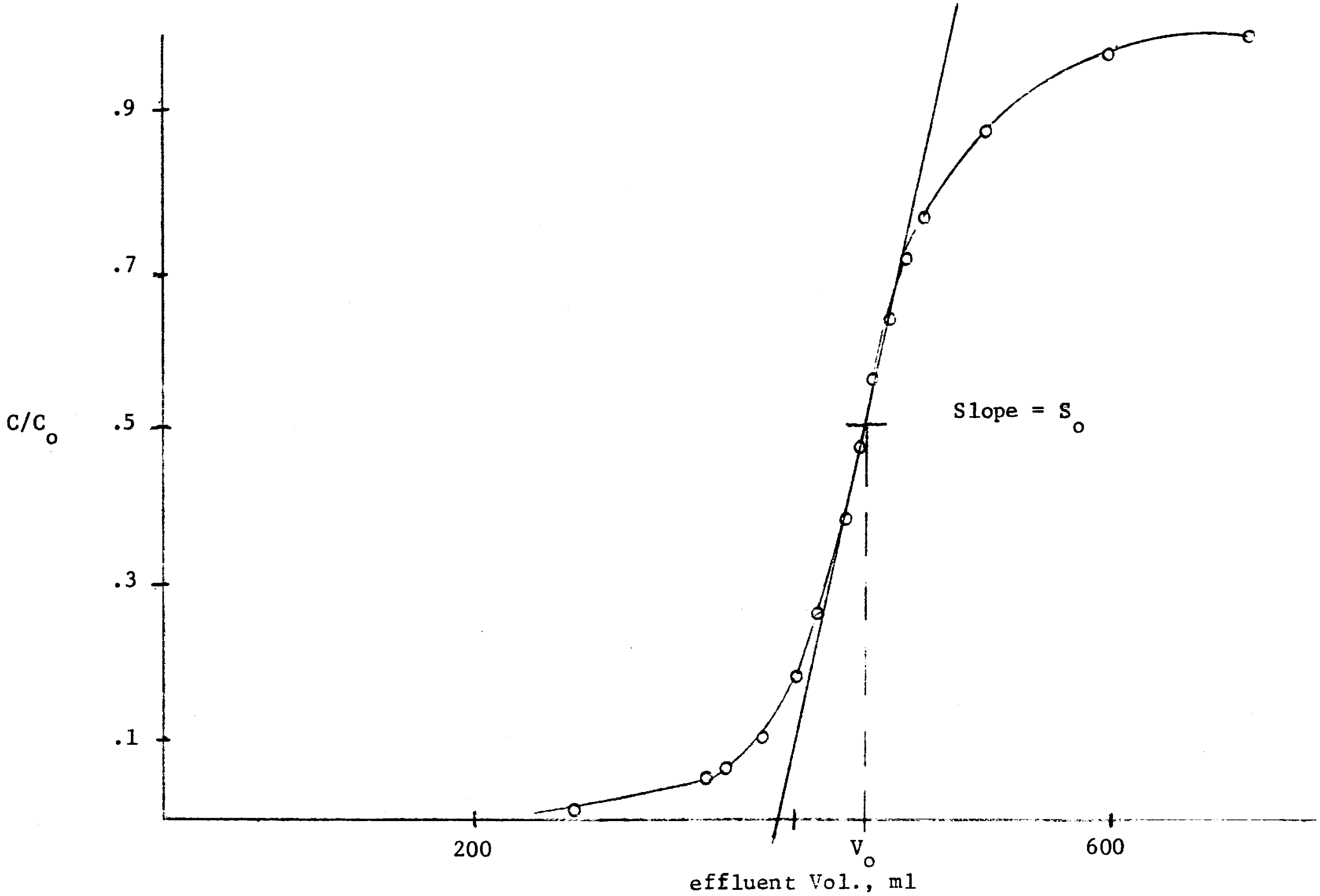

Figure 22. Chloride BTC for Column I.

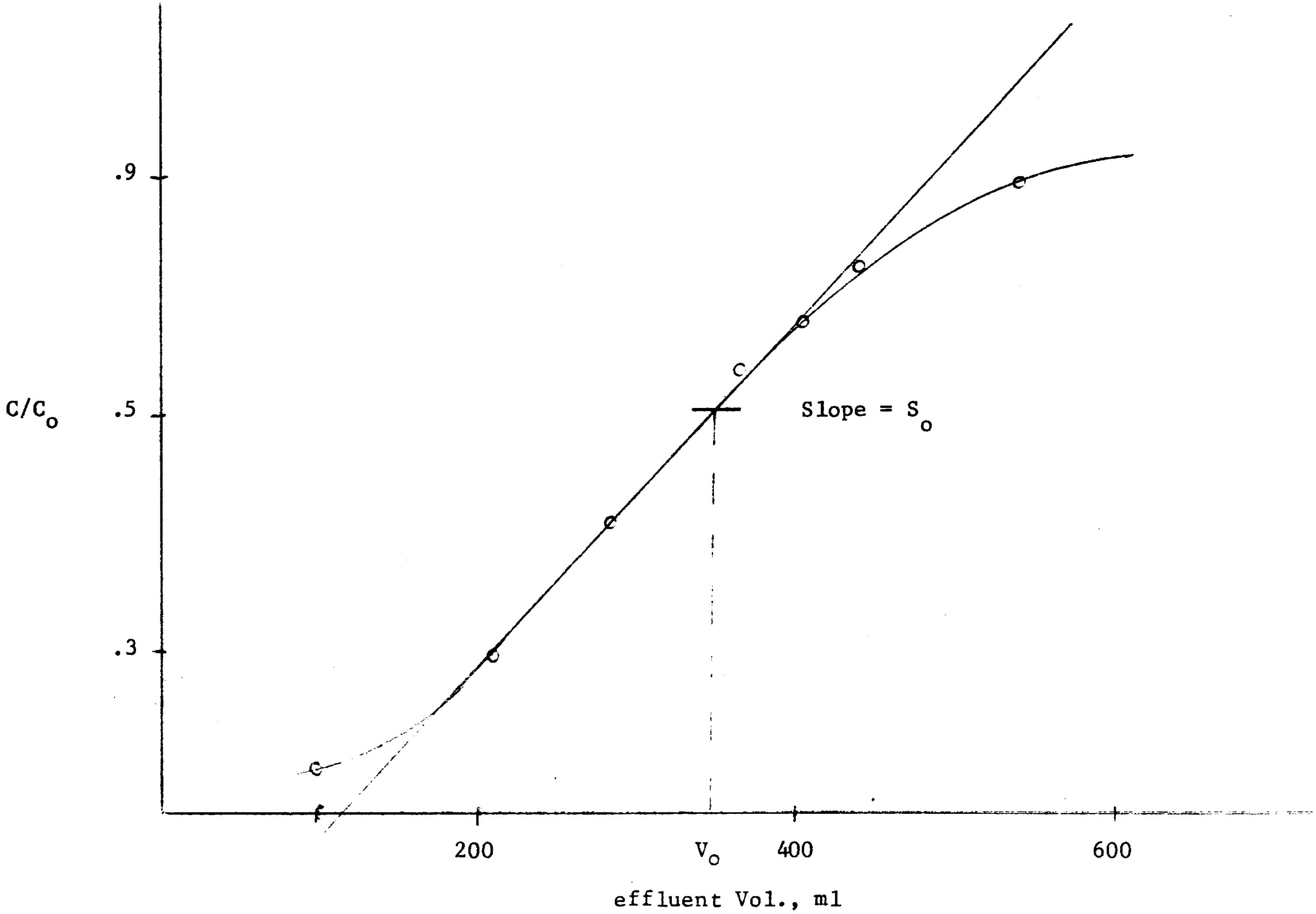

Figure 23. Chloride BTC for Column II.

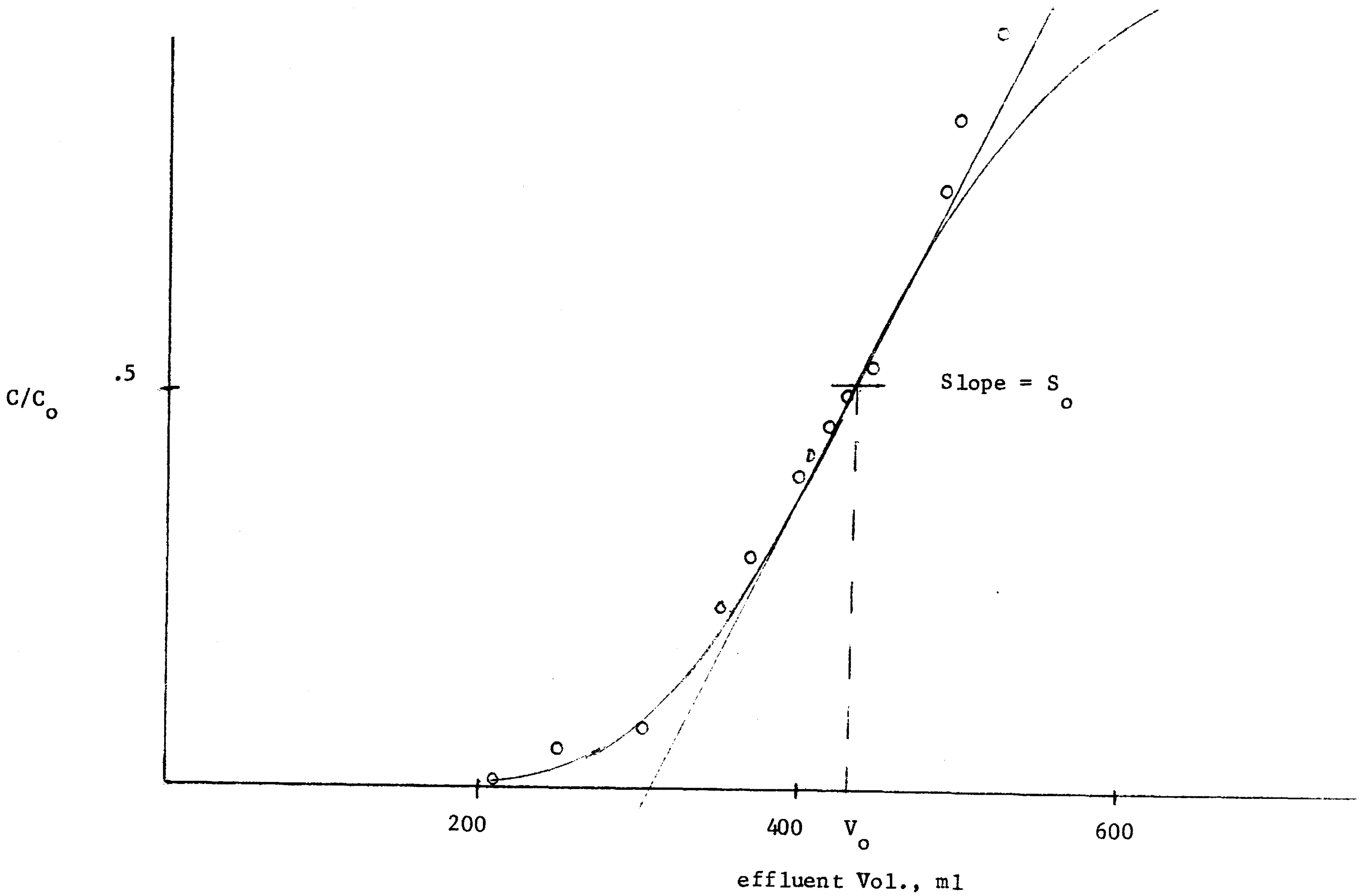

Figure 24. Chloride BTC for Column III.

to these parameters is further illustrated by the variation between the fluid dispersion coefficients of the Aiken and Vernal soils. For the Aiken soil, the order of magnitude of the dispersion coefficient is on the order of 10^{-2}. For the Vernal soil, the dispersion coefficient is on the order of 1-10. This difference may be reduced slightly be decreasing the rate of effluent flow from the Vernal columns. This, however, will not alter the BTC and the resulting values of S_o and V_o.

Boron profile distribution. The boron BTC was only obtained for the purpose of determining the time it took for boron to move through the column. Since the relative concentration $C/C_o = 0.50$ was a qualitative measure of the rate of movement of boron through the column, the total boron BTC data was not obtained. One particular column can be used for either breakthrough studies or profile distribution studies. The profile distribution of boron was of major interest so the boron BTC data was only incidental to accomplishing that end.

The column was segmented at a given time interval and the solution analyzed for boron. The adsorbed phase boron was calculated by using the appropriate adsorption function. The profile distributions with depth are shown in Figures 25, 26, and 27.

The Predictive Model

The Fortran IV program used in this study is given in Appendix C. The adsorption functions of Langmuir, B.E.T., and Freundlich models were used in the program to predict the profile distributions of boron in soil columns I, II, and III. The slopes of the functions,

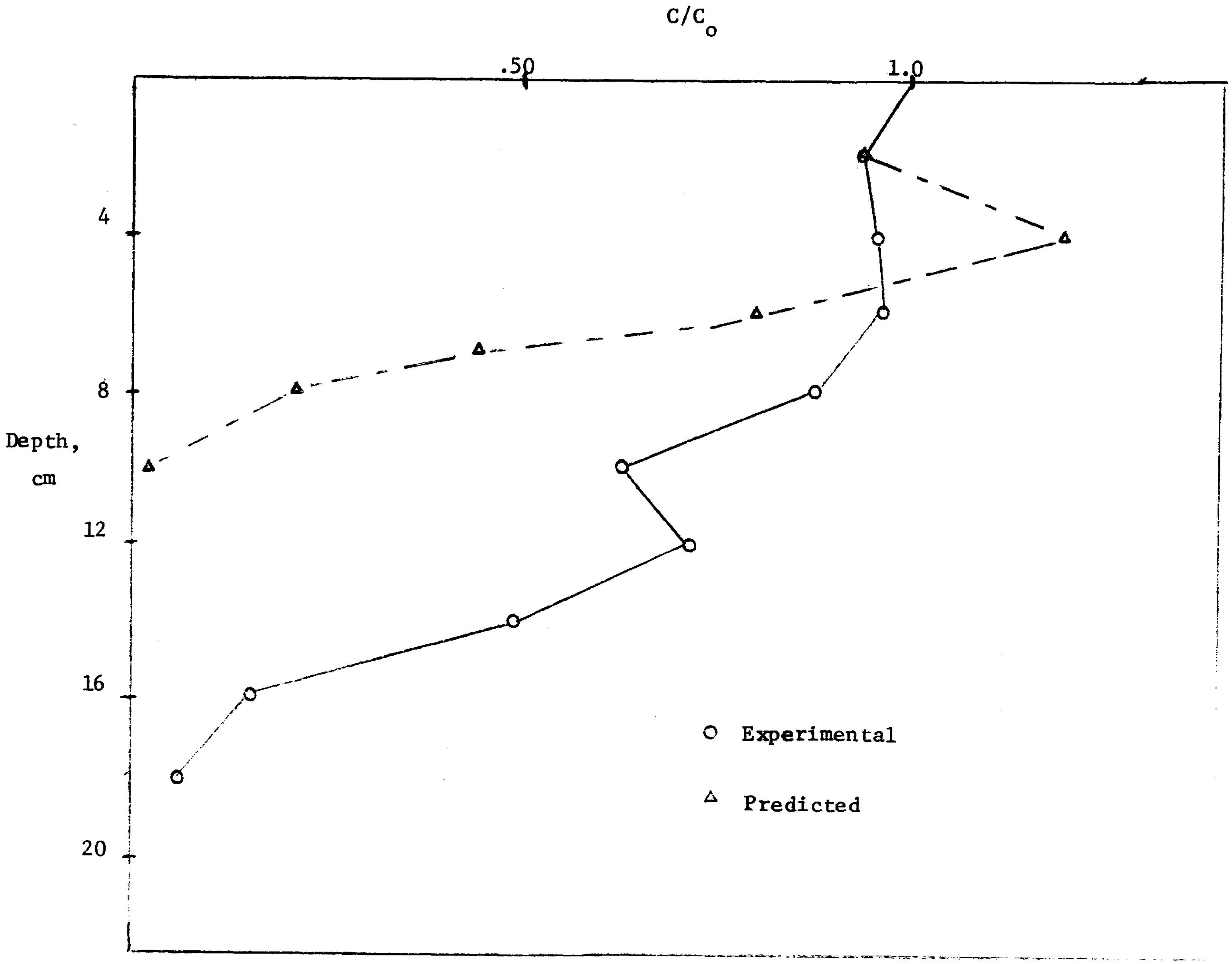

Figure 25. Profile boron distribution by Langmuir. Column I.

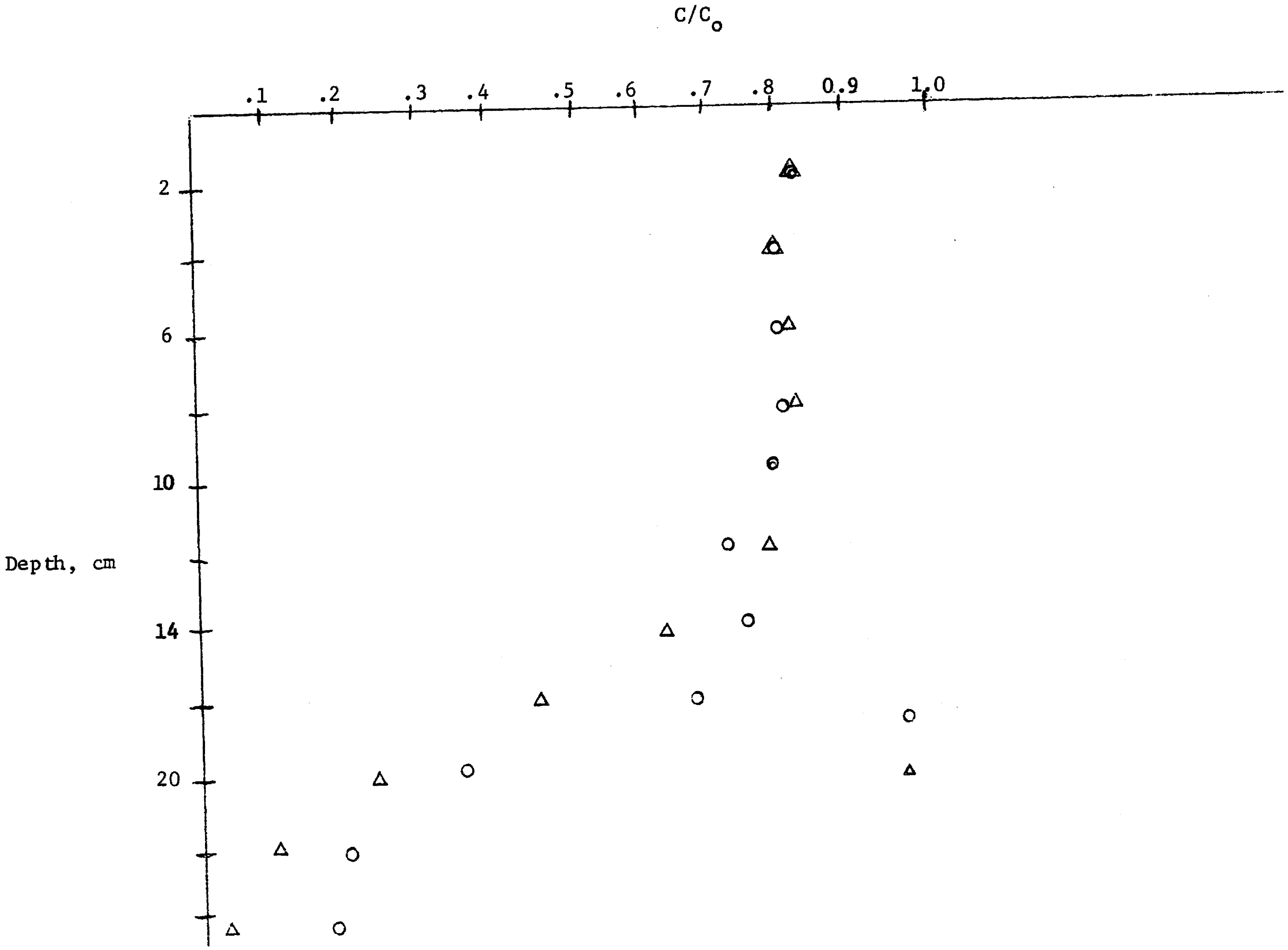

Figure 26. Adsorbed phase profile distribution of boron by Langmuir theory. Column I

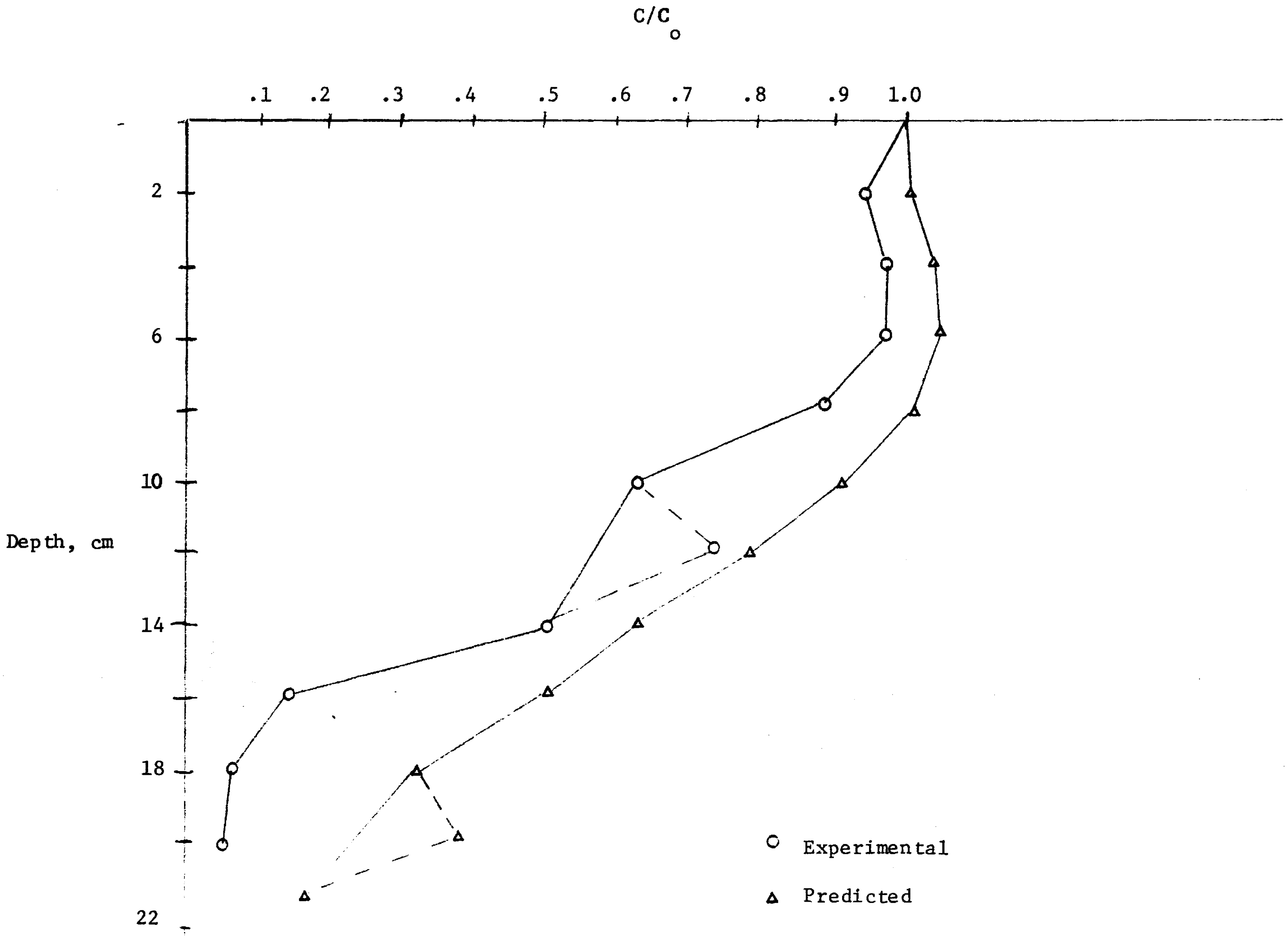

Figure 27. Profile boron distribution by B.E.T. Column I.

as derived in the Materials and Methods section, were used to solve the material balance equation.

Langmuir Model

The predicted profile distribution of boron for column I is shown in Figure 25, along with the experimentally determined profile distribution for boron from the same column. The predicted data approximate the shape of the curve for the experimental data, but the position of the curve shows that the model predicted the boron adsorption to be greater than that actually observed. These data suggest that equilibrium may not have been reached in the column. However, since the Langmuir model did not generally fit the experimental equilibrium adsorption data, its use in the present predictive model may not be valid.

The adsorbed phase concentrations are plotted in Figure 26, but only reflect the findings in Figure 25, since the predicted and experimental values are computed by the adsorption function from the solution phase boron concentrations. Figure 26 represents a sample of the adsorbed phase profile distributions of boron and none of the corresponding figures for columns II and III will be shown.

No Langmuir function was obtained for the Vernal soil since the low value of the regression coefficient (r + 0.133) precluded extensive analysis by the model.

B.E.T. Model

The boron concentration profiles predicted by the B.E.T. equation for column I are plotted in Figure 27. The prediction of boron transport in Aiken clay loam soil is considered reasonable. The shape of the profile is in accord, but the experimental data are slightly displaced. The high linear correlation of the isotherm studies suggests that the prediction should be good if the model has considered all other factors which determine the boron profile distribution. The predictive values indicate less adsorption than actually occurred so the closeness of the data indicate the solution of the material balance equation is qualitatively correct.

Figures 28 and 29 show the boron concentration profiles predicted by the B.E.T. equation for columns II and III. The profile distribution of the predictive data indicate more adsorption than actually occurred; however, the general shape of the curve is reasonably close to a certain depth. One factor which may contribute to the discrepancies is the high flow velocities with which the boron flows through the column. This could possibly be corrected by reducing the flow velocity.

The sensitivities of the predicted profile with respect to the dispersion coefficient, the time interval, and the depth interval were tested. Figures 27, 28, and 29 represent converged solutions to the predictive model. High values ($D > 1.0$) of the dispersion coefficient give a converged solution to the predictive model only when further manipulation of the depth and time increments is made. As a general rule, the greater the dispersion coefficient, the smaller the depth and time increments must be in order to obtain convergence. The limits of the values for Δt and Δz are: (a) the ratio of $\Delta t/\Delta z^2$ must be greater than 0.0 and less than or equal to 0.5, and (b) the smaller the time increment, the greater is the number of iterations the computer must make.

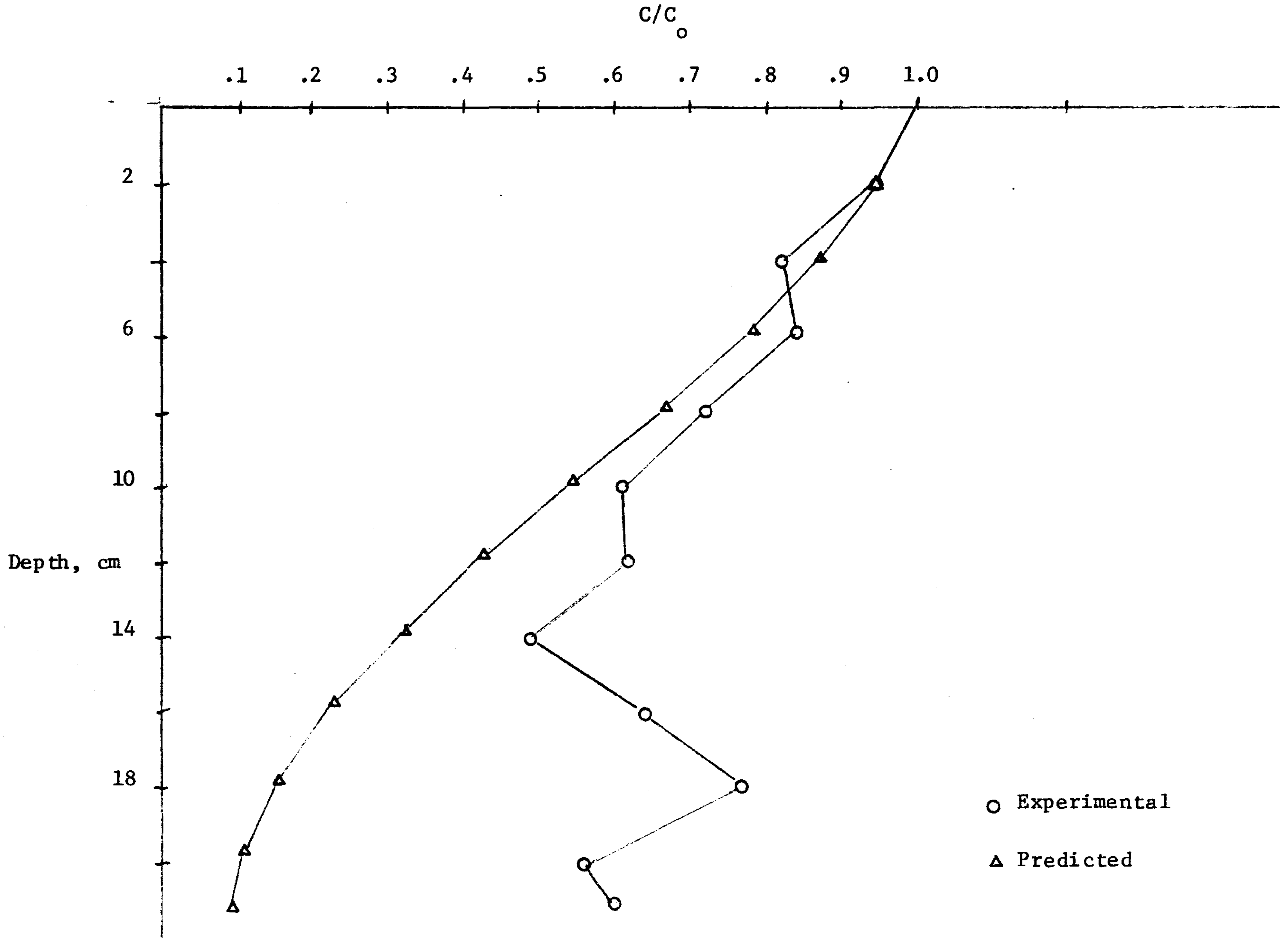

Figure 28. Profile boron distribution by B.E.T. Column II.

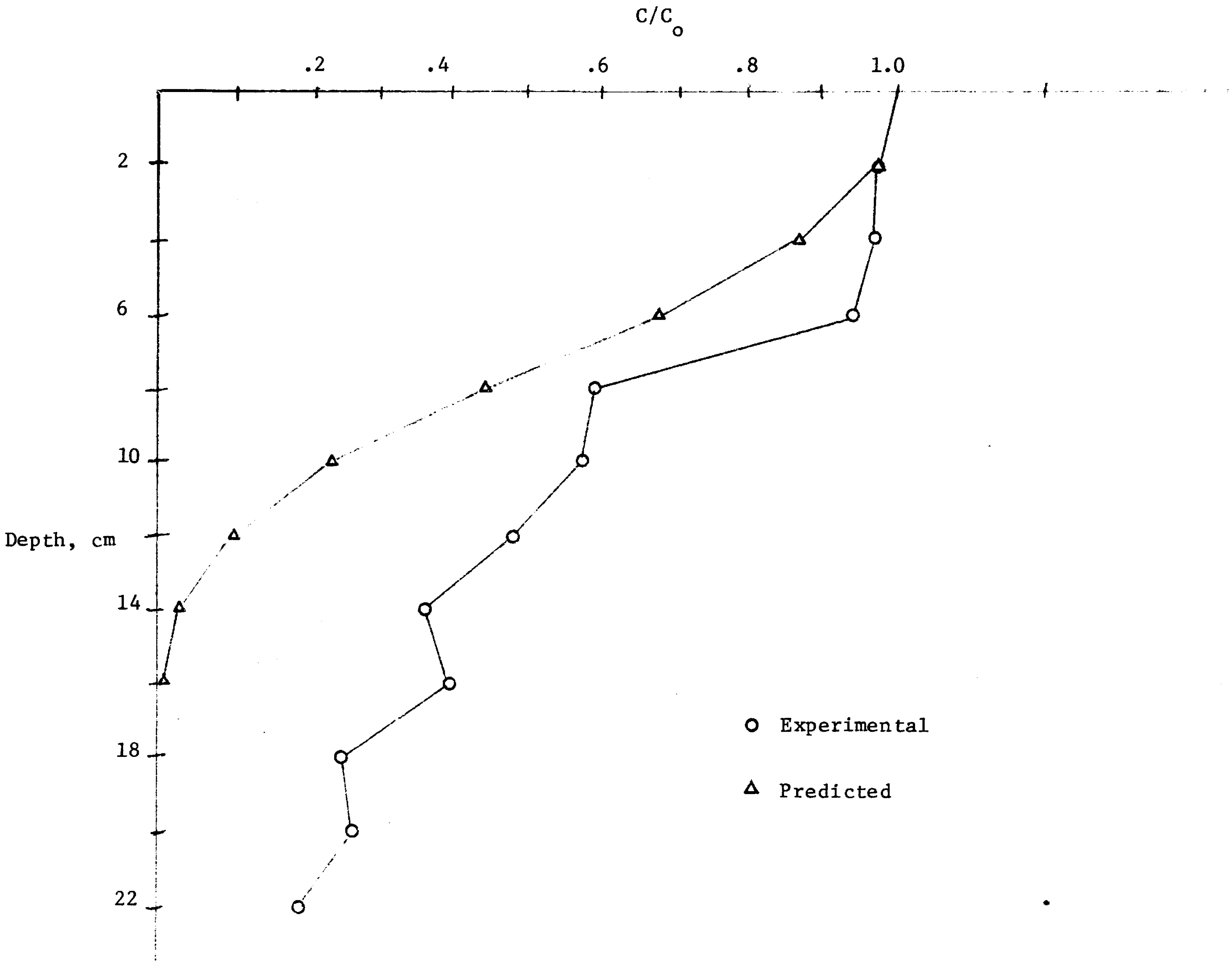

Figure 29. Profile boron distribution by B.E.T. Column III.

Freundlich Model

The comparative results of experimental boron distributions in soil columns I, II, and III are shown in Figure 30, 31, and 32. As the Figures show, the Freundlich function does not predict well. As in the case of the Langmuir model, the model predicts much more adsorption than was measured experimentally. The Freundlich adsorption function, in contrast to the Langmuir function, is capable of describing the experimentally determined equilibrium concentrations with high linear correlation. It is not obvious why the Freundlich equation did not yield better prediction. However, it is believed that the major source of error is associated with the manner in which the adsorption function was applied in the predictive model.

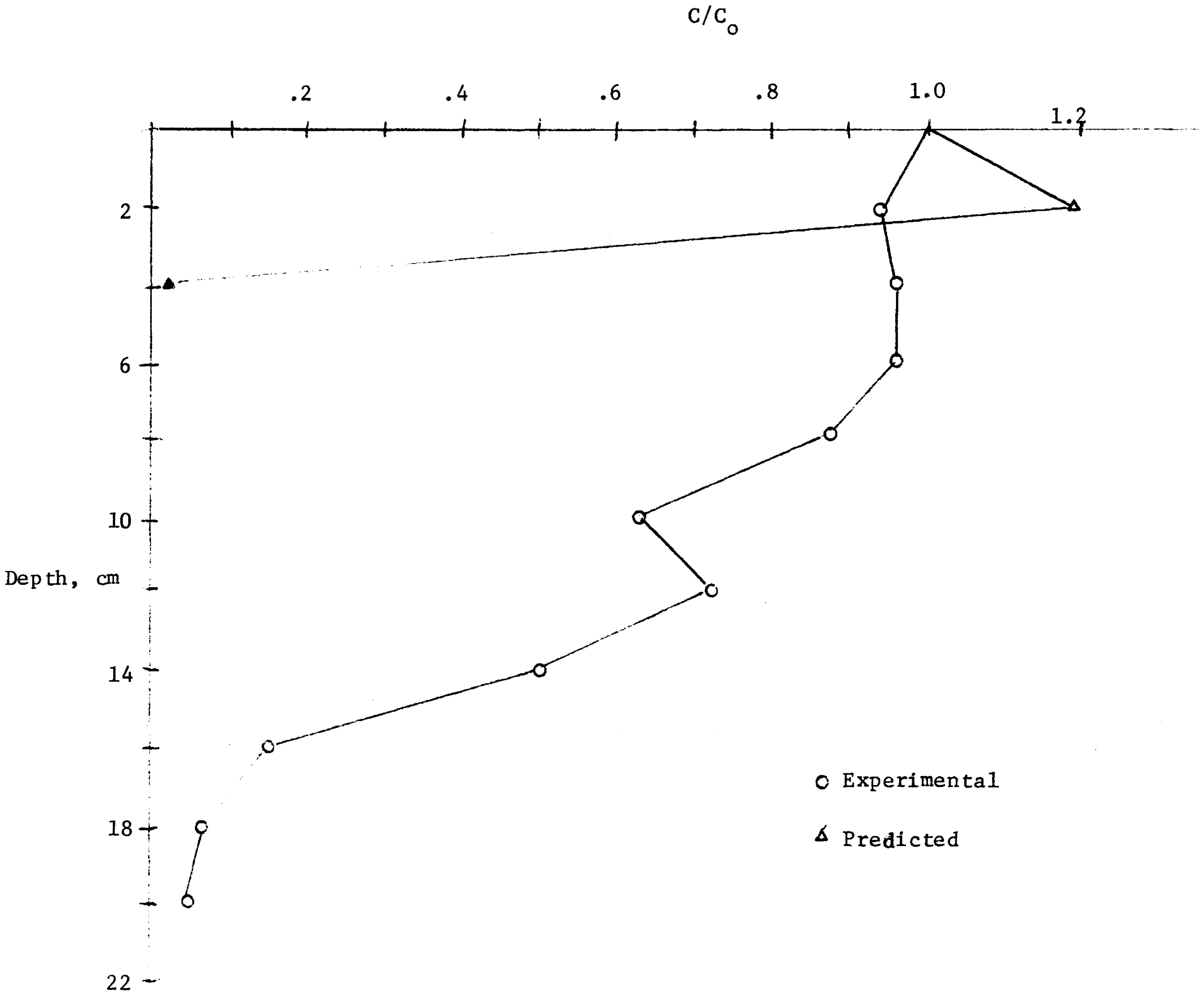

Figure 30. Profile boron distribution by Freundlich. Column I.

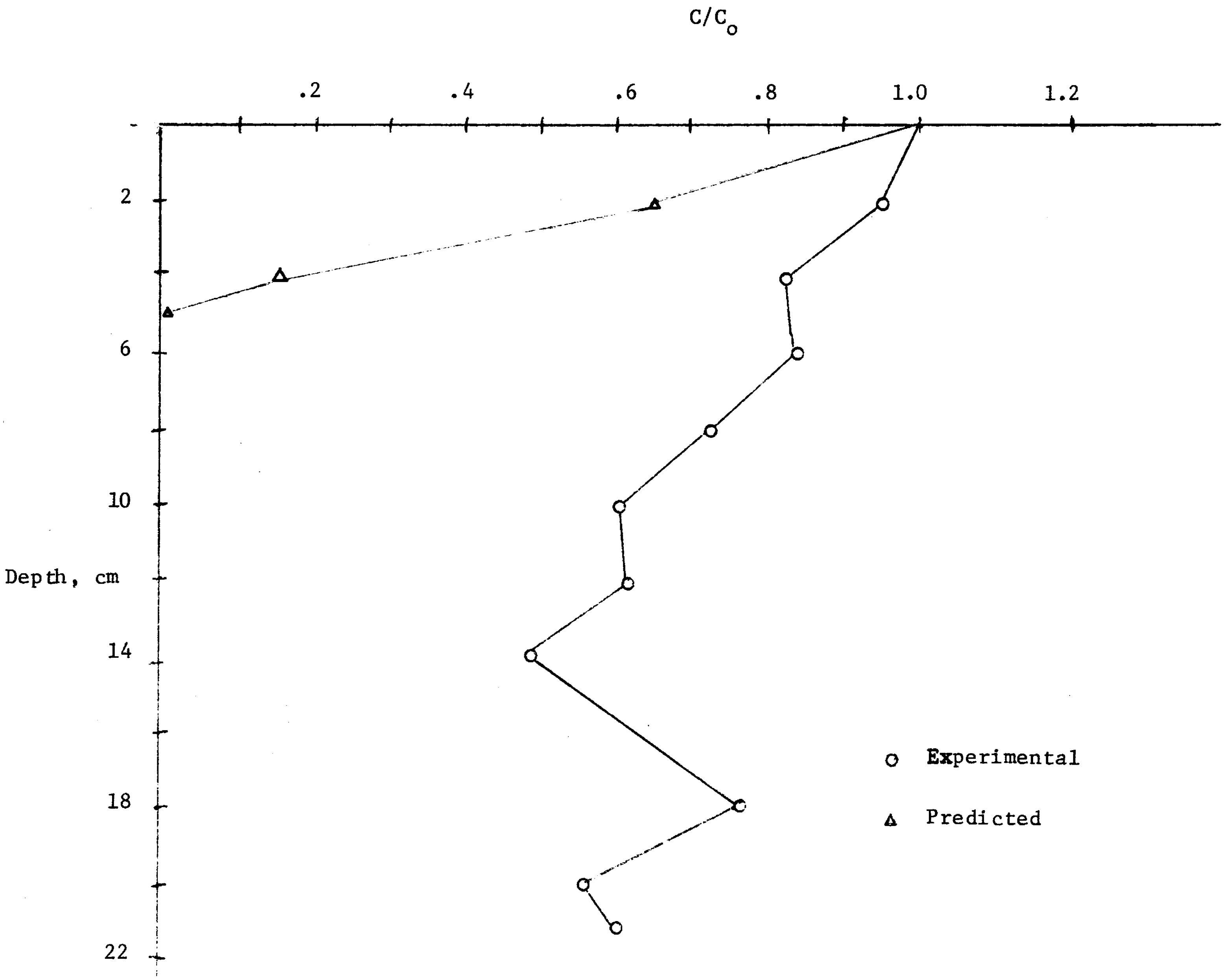

Figure 31. Profile boron distribution by Freundlich. Column II.

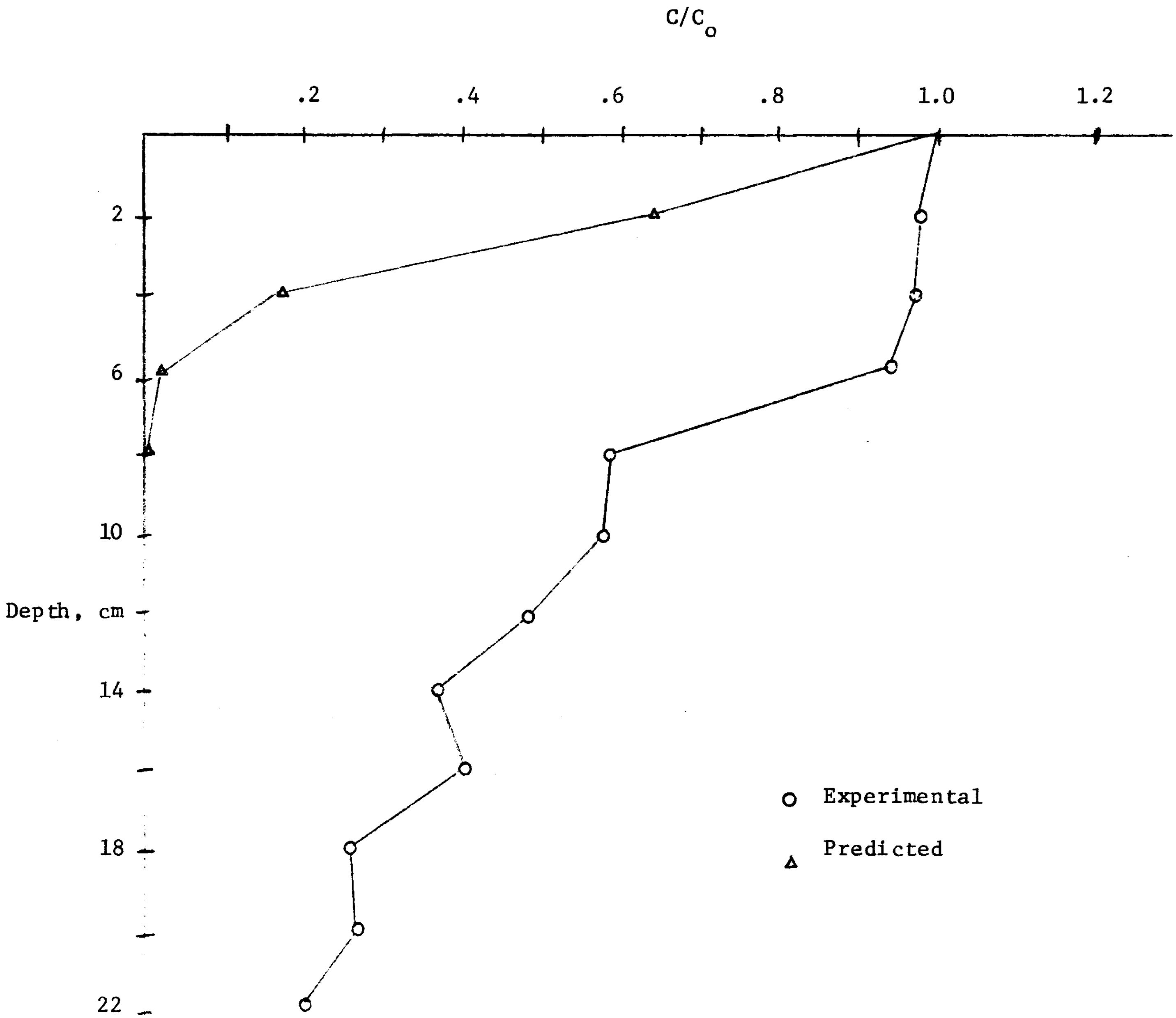

Figure 32. Profile boron distribution by Freundlich. Column III.

SUMMARY AND CONCLUSIONS

Three adsorption models were considered and tested with the experimental data to determine which best describes the behavior of boron in Aiken clay loam and Vernal sandy loam soils. The Langmuir, B.E.T., and Freundlich adsorption equations were obtained at three different temperatures (11.5° C, 23.0° C, and 30.0° C). Linear regression analyses were conducted to obtain the relative linear correlation values for the three adsorption equations at the three given temperatures.

The isotherms displayed consistent depressions or steps at regular intervals. This phenomenon was observed for both soils at all three temperatures.

Soil column studies were conducted on Aiken clay loam soil and Vernal sandy loam soil at 23.0° C to determine the profile boron distribution. The initial boron concentration introduced at the tops of the columns was 10 ppm. The boron solution was allowed to flow under saturated soil moisture conditions for a specified time interval, at which time the column was segmented and the profile solution boron concentration was determined.

The adsorption functions were applied to the mathematical model developed by Lai to determine (a) the feasibility of applying his model to an anion adsorption system rather than to a cation exchange system, and (b) which adsorption function produces the best predictive model of boron movement in soil columns.

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APPENDIXES

Appendix A

Equilibrium Data

Table 1. Kinetic data for Aiken clay loam soil at 23° C. for 4 ppm boron.

Reaction Time, hrs.	Boron Solution Concentration, ppm
.083	2.3
.167	2.2
.250	1.9
.333	1.9
.500	1.9
.667	1.8
.833	1.8
1.000	1.8
3.000	1.7
12.000	1.4
24.000	1.2
(2 weeks)	1.1

Table 2. Kinetic data for Aiken clay loam soil at 23° C. for 20 ppm boron.

Reaction Time, hrs.	Boron Solution Concentration, ppm
.083	14.4
.167	14.0
.250	13.8
.333	13.3
.500	13.7
.667	13.3
.833	13.7
1.000	13.3
3.000	13.0
12.000	12.0
24.000	12.0
(2 weeks)	11.0

Table 3. Kinetic data for Vernal sandy loam soil at 23° C for 4 ppm boron.

Reaction Time, hrs.	Boron Solution Concentration, ppm
.167	2.47
.333	2.47
.500	2.47
1.500	2.47
3.000	2.28
6.000	2.33
12.000	2.71
24.000	2.71

Table 4. Kinetic data for Vernal sandy loam soil at 23° C for 20 ppm boron.

Reaction Time, hrs.	Boron Solution Concentration, ppm
.167	17.11
.333	16.87
.500	16.16
1.500	15.55
3.000	15.50
6.000	15.55
12.000	15.93
24.000	16.26

Table 5. Equilibrium solution and adsorbed phase boron concentrations for Aiken clay loam soil at 11.5° C. Soil-liquid ratio is 1:2.5.

Initial Concentration of Boron, ppm	B Solution Concentration at Equilibrium, ppm	B Adsorbed (μg)/g Soil
0.00	0.00	0.00
1.00	0.01	2.49
2.00	0.02	4.95
4.00	1.10	7.23
6.00	2.40	8.99
8.00	3.47	11.29
10.00	4.90	12.59
15.00	8.20	16.98
17.00	9.45	18.80
20.00	10.81	22.92
25.00	12.80	30.26
30.00	17.20	31.72
35.00	21.30	34.05
40.00	24.20	39.44
45.00	28.50	40.74
50.00	33.80	40.24

Table 6. Variables for the Langmuir and B.E.T. equations computed from Table 5 for Aiken clay loam soil at 11.5° C.

Langmuir		B.E.T.	
C	C/q	C/B_o	$C/q(B_o-C)$
0.00	.00	--	--
0.01	.00	.000	.0000
0.02	.00	.001	.0001
1.10	.15	.022	.0030
2.40	.27	.048	.0056
3,47	.31	.069	.0066
4.90	.39	.098	.0086
8.20	.48	.164	.0115
9.45	.50	.189	.0124
10.81	.47	.216	.0120
12.80	.42	.256	.0114
17.20	.54	.344	.0165
21.30	.63	.426	.0218
24.20	.61	.484	.0238
28.50	.70	.570	.0325
33.80	.84	.676	.0519

Table 7. Freundlich equation variables computed from Table 5 for Aiken clay loam soil at 11.5° C.

C,ppm	q,ug/g	log C	log q
1.10	7.23	.041	.859
2.40	8.93	.380	.951
3.47	11.29	.540	1.053
4.90	12.59	.690	1.100
8.20	16.98	.914	1.230
9.45	18.80	.975	1.274
10.81	22.92	1.034	1.360
12.80	30.26	1.107	1.481
17.20	31.72	1.236	1.501
21.30	34.05	1.328	1.532
24.20	39.44	1.384	1.596
28.50	40.74	1.455	1.610
33.80	40.24	1.529	1.605

Table 8. Equilibrium solution and adsorbed phase boron concentrations for Aiken clay loam soil at 23.0° C. Soil-liquid ratio is 1:2.5.

Initial Concentration of Boron, ppm	B Solution Concentration at Equilibrium, ppm	B Adsorbed (μg)/g Soil
0.00	0.00	0.00
1.00	0.13	2.17
2.00	0.59	3.52
4.00	1.60	5.99
6.00	2.75	8.12
8.00	4.05	9.85
10.00	5.48	11.28
15.00	8.66	15.83
20.00	9.00	19.45
25.00	15.50	]3.70
30.00	19.00	27.37
35.00	21.80	32.96
40.00	27.50	31.14
45.00	31.00	34.80
50.00	36.00	34.86

Table 9. Variables for the Langmuir and B.E.T. equations computed from Table 8 for Aiken clay loam soil at 23.0° C.

Langmuir		B.E.T.	
C	C/q	C/B_o	$C/q(B_o-C)$
0.00	.00	--	--
0.13	.06	.003	.0012
0.59	.17	.012	.0034
1.60	.27	.032	.0055
2.75	.34	.055	.0072
4.05	.41	.081	.0089
5.48	.49	.110	.0109
8.66	.55	.169	.0128
9.00	.63	.244	.0166
15.50	.65	.310	.0189
19.00	.69	.380	.0223
21.80	.66	.436	.0234
27.50	.88	.550	.0391
31.00	.89	.620	.0466
36.00	1.03	.720	.0735

Table 10. Freundlich equation variables computed from Table 8 for Aiken clay loam soil at 23.0° C.

C,ppm	q,ug/g	log C	log q
.00	0.00	--	.334
.13	2.17	.886	.334
.59	3.52	.229	.775
1.60	5.99	.202	.775
2.75	8.12	.437	.908
4.05	9.85	.605	.992
5.48	11.28	.736	1.050
9.00	19.45	.953	1.286
9.00	19.45	.953	1.286
15.50	23.70	1.189	1.373
19.00	27.37	1.275	1.435
21.80	32.96	1.336	1.516
27.50	31.19	1.437	1.492
31.00	34.80	1.489	1.539
36.00	34.86	1.553	1.539

Table 11. Equilibrium solution and adsorbed phase boron concentrations for Aiken clay loam soil at 30.0° C. Soil-liquid ratio is 1:2.5.

Initial Concentration of Boron, ppm	B Solution Concentration at Equilibrium, ppm	B Adsorbed (μg)/g Soil
0.00	0.00	0.00
1.00	0.46	1.35
2.00	0.90	2.75
4.00	2.10	4.72
6.00	3.45	6.36
8.00	4.78	8.03
10.00	6.20	9.48
15.00	10.30	11.73
17.50	13.00	11.23
20.00	14.25	14.35
22.50	16.00	16.22
25.00	17.65	18.34
27.00	20.50	16.19
30.00	21.20	21.93
32.00	25.20	16.88
35.00	27.00	19.94
38.00	29.70	20.69
40.00	30.50	23.70
42.00	32.00	24.90
45.00	34.50	26.09
48.00	35.10	32.15
50.00	39.00	27.45

Table 12. Variables for the Langmuir and B.E.T. equations computed from Table 11 for Aiken clay loam soil at 30.0°C.

Langmuir		B.E.T.	
C	C/q	C/B_o	$C/q(B_o-C)$
0.00	.00	.009	.0069
0.46	.34	.009	.0069
0.90	.33	.018	.0067
2.10	.45	.042	.0093
3.45	.54	.069	.0117
4.78	.60	.096	.0132
6.20	.65	.200	.0213
10.30	.88	.200	.0213
13.00	1.16	.260	.0313
14.25	.99	.285	.0278
16.00	.99	.320	.0290
17.65	.96	.353	.0298
20.50	1.27	.410	.0429
21.20	.97	.424	.0336
25.20	1.49	.504	.0511
27.00	1.35	.540	.0589
29.70	1.44	.594	.0707
30.50	1.29	.610	.0660
32.00	1.28	.640	.0714
34.50	1.32	.690	.0853
35.10	1.09	.702	.0733
39.00	1.42	.780	.1292

Table 13. Freundlich equation variables computed from Table 11 for Aiken clay loam soil at 23.0° C.

C,ppm	q,ug/g	log C	log q
2.0	4.72	.322	.674
3.45	6.36	.538	.804
4.78	8.03	.679	.904
6.20	9.48	.792	.976
10.30	11.73	1.013	1.069
13.00	11.23	1.114	1.050
14.25	14.35	1.154	1.157
16.00	16.22	1.204	1.210
17.65	18.34	1.247	1.263
20.50	16.19	1.318	1.209
21.20	21.93	1.326	1.341
25.20	16.88	1.401	1.227
27.00	19.94	1.431	1.300
29.70	20.69	1.473	1.316
30.50	23.70	1.484	1.375
32.00	24.90	1.505	1.396
34.50	26.09	1.538	1.417
35.10	32.15	1.545	1.507
39.00	27.45	1.591	1.438

Table 14. Equilibrium solution and adsorbed phase boron concentrations for Vernal sandy loam soil at 11.5° C. Soil-liquid ratio is 1:2.5.

Initial Concentration of Boron, ppm	B Solution Concentration at Equilibrium, ppm	B Adsorbed (μg)/g Soil
0.00	0.00	0.00
1.00	0.00	--
2.00	1.30	1.75
4.00	2.82	2.95
6.00	4.58	3.56
8.00	5.79	5.54
10.00	7.75	5.62
15.00	11.72	8.21
17.00	13.37	9.07
20.00	15.51	11.23
25.00	19.58	13.55
30.00	25.09	12.28
35.00	31.64	8.39
40.00	34.75	13.14
45.00	39.23	14.44
50.00	43.71	15.72

Table 15. Variables for the Langmuir and B.E.T. equations computed from Table 14 for Vernal sandy loam soil at 11.5° C.

Langmuir		B.E.T.	
C	C/q	C/B_o	$C/q(B_o-C)$
1.30	.74	.026	.0153
2.82	.95	.056	.0202
4.58	1.29	.092	.0284
5.79	1.04	.116	.0236
7.75	1.38	.155	.0326
11.72	1.43	.234	.0373
13.37	1.47	.267	.0403
15.51	1.38	.310	.0401
19.58	1.44	.392	.0476
25.09	2.04	.502	.0821
31.64	3.77	.633	.2054
34.75	2.65	.695	.1734
39.23	2.72	.784	.2520
43.71	2.78	.874	.4420

Table 16. Freundlich equation variables computed from Table 14 for Vernal sandy loam soil at 11.5° C.

C,ppm	q,ug/g	log C	log q
1.30	1.75	.119	.241
2.82	2.95	.450	.470
4.58	3.56	.660	.550
5.79	5.54	.762	.743
7.75	5.62	.889	.749
11.72	8.21	1.068	.914
13.37	9.07	1.126	.957
15.51	11.23	1.190	1.050
19.58	13.55	1.290	1.132
25.09	12.28	1.291	1.089
31.64	8.39	1.399	.923
34.75	13.14	1.500	1.118
39.23	14.44	1.540	1.159
43.71	15.72	1.593	1.196

Table 17. Equilibrium solution and adsorbed phase boron concentrations for Vernal sandy loam soil at 23° C. Soil-liquid ratio is 1:2.5.

Initial Concentration of Boron, ppm	B Solution Concentration at Equilibrium, ppm	B Adsorbed (μg)/g Soil
0.00	0.20	--
1.00	0.86	0.35
2.00	1.42	1.46
4.00	3.03	2.44
6.00	4.80	3.00
8.00	6.44	3.90
10.00	7.95	5.13
15.00	12.02	7.45
17.00	13.86	7.85
20.00	15.86	10.35
25.00	19.77	13.08
30.00	24.04	14.91
35.00	27.65	18.38
40.00	30.44	23.91
45.00	34.54	26.15
50.00	36.18	34.55

Table 18. Variables for the Langmuir and B.E.T. equations computed from Table 17 for Vernal sandy loam soil at 23.0° C.

Langmuir		B.E.T.	
C	C/q	C/B_o	$C/q(B_o-C)$
0.20	--	--	--
0.86	2.46	.017	.0500
1.42	.97	.028	.0201
3.03	1.24	.061	.0265
4.80	1.60	.096	.0354
6.44	1.65	.129	.0379
7.95	1.55	.159	.0369
12.02	1.61	.240	.0425
13.86	1.76	.277	.0488
15.86	1.53	.317	.0449
19.77	1.51	.395	.0500
24.04	1.61	.481	.0621
27.65	1.50	.553	.0673
30.44	1.27	.609	.0651
34.54	1.32	.691	.0855
36.18	1.05	.724	.0758

Table 19. Freundlich equation viables computed from Table 17 for Vernal sandy loam soil at 23.0° C.

C,ppm	q,ug/g	log C	log q
.20	--	--	--
.86	.35	--	--
1.42	1.46	.150	.161
3.03	2.44	.479	.385
4.80	3.00	.679	.476
6.44	3.90	.807	.589
7.95	5.13	.899	.707
12.02	7.45	1.078	.870
13.86	7.85	1.139	.893
15.86	10.35	1.199	1.013
19.77	13.08	1.293	1.114
24.04	14.91	1.378	1.172
27.65	18.38	1.439	1.263
30.44	23.91	1.482	1.372
34.54	26.15	1.537	1.416
36.18	34.55	1.556	1.537

Table 20. Equilibrium solution and adsorbed phase boron concentrations for Vernal sandy loam soil at 30.0° C. Soil-liquid ratio is 1:2.5.

Initial Concentration of Boron, ppm	B Solution Concentration at Equilibrium, ppm	B Adsorbed (μg)/g Soil
0.00	--	--
1.00	--	--
2.00	--	--
4.00	2.26	4.34
6.00	4.33	4.18
8.00	6.26	4.34
10.00	8.20	4.51
15.00	12.87	5.32
17.00	14.87	5.32
20.00	17.52	6.21
25.00	9.42	--
30.00	13.94	--
35.00	20.06	--
40.00	26.84	--
45.00	30.71	--
50.00	35.87	--

Table 21. Variables for the Langmuir and B.E.T. equations computed from Table 20 for Vernal sandy loam soil at 30.0° C.

Langmuir		B.E.T.	
C	C/q	C/B_o	$C/q(B_o-C)$
2.26	.52	.045	.0109
4.33	1.04	.087	.0227
6.26	1.44	.125	.0330
8.20	1.82	.164	.0435
12.87	2.42	.257	.0652
14.87	2.80	.297	.0796
17.52	2.82	.350	.0869
9.42	--	--	--
13.94	--	--	--
20.06	--	--	--
26.84	--	--	--
30.71	--	--	--
35.87	--	--	--

Table 22. Freundlich equation variables computed from Table 20 for Vernal sandy loam soil at 30.0° C.

C,ppm	q,ug/g	log C	log q
2.26	4.34	.355	.637
4.33	4.18	.636	.621
6.26	4.34	.797	.638
8.20	4.51	.914	.654
12.87	5.32	1.110	.725
14.87	5.32	1.172	.726
17.52	6.21	1.243	.793

Table 23. Linear regression analyses of adsorption functions for Aiken clay loam soil.

Model	Range of C,ppm	Regression Equation	r
Temperature: 11.5° C			
Langmuir	0-34	$y = .179 + .024x$	.916
Langmuir	0-13	$y = .110 + .036x$	.877
Langmuir	13-34	$y = .239 + .017x$	.967
B.E.T.	2-20	$y = .0036 + .040x$	.973
Freundlich	0-34	$y = .762 + .575x$	.984
Temperature: 23.0° C			
Langmuir	0-36	$y = .254 + .022x$	.951
Langmuir	0-9	$y = .173 + .043x$	.935
Langmuir	9-36	$y = .318 + .019x$	.959
B.E.T.	2-20	$y = .0056 + .043$	.996
Freundlich	0-36	$y = .646 + .605x$	.991
Temperature: 30.0° C			
Langmuir	0-39	$y = .433 + .029x$	.891
Langmuir	0-13	$y = .349 + .019x$	.332
Langmuir	13-39	$y = .808 + .016x$	.639
B.E.T.	2-20	$y = .0067 + .073x$	.966
Freundlich	0-39	$y = .457 + .626x$	.949

Table 24. Linear regression analyses of adsorption functions for Vernal sandy loam soil.

Model	Range of C,ppm	Regression Equation	r
		Temperature: 11.5° C	
Langmuir	1-44	y = .668 + .059x	.890
Langmuir	1-12	y = .485 + .102x	.824
Langmuir	12-44	y = .657 + .058x	.774
B.E.T.	1-20	y = .018 + .076x	.964
Freundlich	1-44	y = .0004 + .750x	.950
		Temperature: 23.0° C	
Langmuir	0-36	y = 1.478 + .0027x	.133
Langmuir	0-12	-----	--
Langmuir	12-36	-----	--
B.E.T.	1-20	y = .026 + .069x	.957
Freundlich	0-36	y = .114 + .964x	.984
		Temperature: 30.0° C	
Langmuir	2-18	y = 3.711 + .124x	.942
B.E.T.	2-18	y = .001 + .249x	.999
Freundlich	2-18	y = .534 + .170x	.850

Table 25. Average values for correlation coefficients from Tables 23 and 24.

Soil	Adsorption Function	Range	Average
Aiken	Langmuir	0-40	.919
		0-12	.715
		12-40	.855
	B.E.T.	2-20	.978
	Freundlich	0-40	.975
Vernal	Langmuir	0-40	.655
		0-12	.824
		12-40	.774
	B.E.T.	2-20	.973
	Freundlich	0-40	.928
Aiken + Vernal	Langmuir	0-40	.787
		0-12	.742
		12-40	.835
	B.E.T.	2-20	.976
	Freundlich	0-40	.951

Appendix B

Column Data

Table 26. The basic column and soil parameters for the computer experiments.

Item	Unit	Column		
		I	II	III
Dispersion coefficient	CM^2/hr	.088	16.110	4.824
Flow velocity	CM/hr	1.552	5.126	6.540
Flow rate	CM^3/hr	45.91	118.64	153.74
Bulk density	g/CM^3	1.23	1.32	1.30
Pore fraction		.54	.50	.51
Monolayer capacity	μg/g	18.50	10.46	10.46
Tital concentration	ppm	10.00	10.46	10.82
Column length	cm	21.30	21.50	21.00
Total time	hr	22.00	10.28	10.83
Pore volume	ml	646	343	430
Total input volume	ml	1010	1220	1320
Total input volume	(pore volume)	1.56	3.55	3.06

Table 27. Chloride BTC for Column I.

Effluent Volume, ml	Chloride Conc. meq/ml	C/C_o
100	.0000	.000
600	.0085	.169
610	.0117	.232
620	.0153	.304
630	.0193	.383
640	.0236	.468
650	.0280	.555
660	.0319	.633
670	.0357	.708
680	.0385	.764
750	.0470	.933
760	.0470	.933
770	.0478	.948
800	.0485	.962
1010	.0504	1.000

C_0 = .0504 meq/ml

Table 28. Chloride BTC for Column II.

Effluent Volume, ml	Chloride Conc. meq/ml	C/C_o
150	.010	.098
200	.017	.173
210	.020	.198
300	.040	.400
310	.043	.430
320	.045	.450
330	.047	.470
340	.050	.499
350	.052	.523
360	.055	.552
400	.061	.610
420	.065	.650
430	.067	.666
600	.082	.816

C_o = 0.10 meq/ml

Table 29. Chloride BTC for Column III.

Effluent Volume, ml	Chloride Conc. meq/ml	C/C_o
200	.000	.00
250	.001	.005
300	.007	.074
350	.023	.230
400	.039	.398
410	.043	.430
420	.046	.462
430	.050	.501
440	.054	.541
450	.058	.587
480	.075	.756
500	.084	.853
1000	.099	1.000

C_o = .099 meq/ml

Table 30. Experimental profile boron distribution.

Depth, cm	Solution Phase Boron, ppm	Depth, cm	Solution Phase Boron, ppm
Column I: C_o = 10.00 ppm			
0	10.00	12	7.36
2	9.41	14	5.09
4	9.77	16	1.31
6	9.71	18	.63
8	8.84	20	.57
10	6.22	22	--
Column II: C_0 = 10.46 ppm			
0	10.46	12	6.41
2	9.89	14	5.06
4	8.57	16	6.75
6	8.71	18	8.13
8	7.53	20	5.77
10	6.34	22	6.24
Column III: C_o = 10.82 ppm			
0	10.82	12	4.99
2	10.30	14	3.71
4	10.17	16	4.15
6	9.82	18	2.56
8	6.10	20	2.78
10	6.00	22	--

Table 31. Predicted profile boron distribution for Column I. Langmuir model

Depth	Relative Concentrations	
	Solution Phase	Adsorbed Phase
0	1.00	.80
1	0.97	.80
2	0.94	.79
3	1.06	.81
4	1.20	.83
5	1.12	.76
6	0.80	.64
7	0.45	.45
8	0.21	.24
9	0.08	.11
10	0.03	.04
11	0.01	.00
12	0.00	.00

Table 32. Predicted profile boron distribution. B.E.T. model

Depth, cm	Relative Solution conc.	Depth, cm	Relative Solution conc.
Column I			
0	1.00	12	0.79
2	1.00	14	0.62
4	1.00	16	0.47
6	0.99	18	0.35
8	1.02	20	0.26
10	0.96	22	0.17
Column II			
0	1.00	12	0.42
2	0.95	14	0.31
4	0.87	16	0.22
6	0.77	18	0.15
8	0.66	20	0.11
10	0.54	22	0.09
Column III			
0	1.00	12	0.10
2	0.97	14	0.03
4	0.87	16	0.01
6	0.67	18	0.00
8	0.44	20	0.00
10	0.23	22	0.00

Table 33. Predicted profile boron distribution. Freundlich model

Depth, cm	Relative Solution Conc.	Depth, cm	Relative Solution Conc.
	Column I		
0	1.00	12	--
2	1.29	14	--
4	0.00	16	--
6	--	18	--
8	--	20	--
10	--	22	--
	Column II		
0	1.00	12	--
2	0.64	14	--
4	0.16	16	--
6	0.01	18	--
8	0.00	20	--
10	--	22	--
	Column III		
0	1.00	12	--
2	0.64	14	--
4	0.16	16	--
6	0.01	18	--
8	0.00	20	--
10	--	22	--

Appendix C

FORTRAN Programs

1. The FORTRAN program to solve Equation [17] using the explicit method developed by Lai with a Langmuir adsorption function.

```
C.......................................................................
C
C    PURPOSE
C      TO SOLVE THE MATERIAL BALANCE EQUATION, WHICH IS THE INITIAL
C      BOUNDARY VALUE PROBLEM THAT GOVERNS ANION TRANSPORT IN STEADY
C      STATE SATURATED FLOW.
C
C
C    DESCRIPTION OF PARAMETERS
C      IDSET     NUMBER OF DATA SETS
C      SIGN      DATA SET IDENTIFICATION, AN ALPHANUMERIC
C                ARRAY
C      D         DISPERSION COEFFICIENT
C      V         INTERSTITIAL FLOW VELOCITY
C      RO        BULK DENSITY
C      ALF       PORE FRACTION
C      QM        ADSORPTION CAPACITY OF THE ADSORBENT
C      CO        TOTAL SOLUTION CONCENTRATION
C      BO        SATURATED SOLUTION CONCENTRATION
C      HZ        DEPTH INCREMENT
C      HT        TIME INCREMENT
C      IZ        OUTPUT CONTROL NUMBER
C      IT        OUTPUT CONTROL NUMBER
C      N         TOTAL NUMBER OF DEPTH INCREMENTS
C      MT        TOTAL NUMBER OF TIME INCREMENTS
C      C         CONSTANT IN THE ADSORPTION FUNCTION
C      T         TIME
C      X         SOLUTION PHASE CONCENTRATION, AN ARRAY
C      YOX       ADSORBED PHASE CONCENTRATION, AN ARRAY
C
C    INPUT
C      SIGN
C      D,V,RO, ALF,QM,CO
C      HZ,HT,MT,N,IT,IZ
C      C
C
C    OUTPUT
C      SIGN
C      D,V,RO,ALF,QM,CO
C      HZ,HT
```

```
C       C
C       T,X(I)
C       YOX(I)
C
C     SUBROUTINE REQUIRED
C       ADFCN
C
C     METHOD
C       AN EXPLICIT METHOD DESCRIBED BY LAI
C
C.....................................................................
C     MAIN PROGRAM
C
        DIMENSION X(100), Y(100), YOX(100), SIGN(11)
        IDSET = 3
        DO 10 ID = 1, IDSET
C
C     INPUT OF BASIC DATA
C
        READ 99, (SIGN(I), I = 1, 11)
        PRINT 199, (SIGN(I), I = 1, 11)
        READ 100, D,V,RO,ALF,QM,CO
        READ 101, HZ,HT,MT,N,IT,IZ
        PRINT 200, D,V,RO,ALF,QM,CO
        PRINT 201, HZ,HT
        NP1 = H + 1
        NM1 = N - 1
        DZ2 = D/(HZ*HZ)
        VZ = V/(2.*HZ)
        RQAC = (RO*QM)/(ALF*CO)
        READ 102,C
        PRINT 202, C
C
C     SET THE TOP BOUNDARY AND INITIAL CONDITIONS
C
        X(1) = 1.0
        DO 1 I = 2, NP1
      1 X(I) = 0.0
        KN + 0
        T = 0.0
C
C     BEGIN THE COMPUTATION OF X(I)
C
        DO 20 IIT = 1, MT
        DO 30 I = 2, N
        EOX = (C*X(I)*CO)/(1. + C*X(I)*CO)
        FOX = (C*CO)/((1. + C*X(I)*CO)**2)
        FT = (1. + RQAC*FOX)/HT
        Y(I) = ((DZ2 - VZ)*X(I + 1) - (2.*DZ2 - FT)*X(I) +
       &(DZ2 + VZ)*X(I - 1))/FT
     30 CONTINUE
```

```
C
C    EVALUATE THE BOTTOM BOUNDARY
C
      Y(NP1) = Y(NM1)
      DO 40 J = 2, NP1
   40 X(J) = Y(J)
      KN = KN + 1
      T = T + HT
      IF(KN.NE.IT) GO TO 20
C
C    OUTPUT X(I)
C
      PRINT 203, T, (X(I), I = 1, N, IZ)
C
C    COMPUTE YOX(I) IN SUBROUTINE ADFCN
C
      CALL ADFCN(X,C,N,QM,YOX)
C
C    OUTPUT YOX(I)
C
      PRINT 204, (YOX(I), I = 1, N)
      KN = 0
   20 CONTINUE
   10 CONTINUE
C
   99 FORMAT(11A4)
  100 FORMAT(6F10.4)
  101 FORMAT(2F10.4, 4I5)
  102 FORMAT(1F10.5)
  199 FORMAT(1H1,10X,11A4)
  200 FORMAT(1H1,a4X,'DISPERSION COEFFICIENT',F15.6/15X,
     &'FLOW VELOCITY',F15.6/15X,'BULK DENSITY',F15.6/15X,
     &'MAXIMUM ADSORPTION LIMIT FOR THIS CONCENTRATION',F15.6/15X,
     &'PORE FRACTION',F15.6/15X,'FLOW RATE',F15.6/15X,
     &'SLOPE OF FUNCTION'F15.6)
  201 FORMAT(//14X,'DEPTH INTERVAL',F15.6,10X,"TIME INTERVAL',F15.6)
  202 FORMAT(//13X,"CONSTANT C IS', F15.6)
  203 FORMAT(1H ,14X,'TIME IS',F10.2,10X,'EFFLUENT VOLUME IS ',F10.2//
     &(8F13.7))
   204 FORMAT(//(9F13.7))
      STOP
     END

      SUBROUTINE ADFCN(X,C,N,QM,YOX)
C....................................................................
C
C    SUBROUTINE ADFCN
C
C    PURPOSE
C      TO EVALUATE Y(I) AS A FUNCTION OF X(I)
C
C    USAGE
C      CALL ADFCN X,C,N,QM,YOX
C
C....................................................................
```

```
C
      DIMENSION X(100), YOX(100)
      Do 1 I = 1, N
    1 YOX(I) = (C*X(I)*CO)/(1. + C*X(I)*CO)
      RETURN
      END
```

II. The FORTRAN program to solve Equation [17] using the explicit method developed by Lai with a B.E.T. adsorption function.

```
C...............................................................
C    THE FORTRAN PROGRAM USING THE B.E.T. ADSORPTION FUNCTION IS PROGRAM
C      I WITH SUBSTITUTION MADE FOR THE FUNCTIONS FOX AND YOX.
C
C      THE FUNCTION FOR FOX IS
C
C        FOX = [(BO - X(I)*CO)*[BO + (C - 1)*X(I)*BO]*BO*CO*C -
C              X(I)*BO*CO*C*([BO - X(I)*CO]*(C - 1)*CO - CO*[BO + (C - 1)
C              *X(I)*CO])]/([BO - X(I)*CO)*[BO + (C - 1)*X(I)*CO)
C
C      THE FUNCTION FOR YOX IS
C
C        YOX(I) = (BO*CO*C)/[BO - X(I)*CO)*(BO + [C - 1]*X(I)*CO)]
C...............................................................
```

III. The FORTRAN program to solve Equation [29] using the explicit method developed by Lai with a Freundlich adsorption function.

```
C...................................................................
C    THE FORTRAN PROGRAM USING THE FREUNDLICH ADSORPTION FUNCTION IS
C      PROGRAM I WITH SUBSTITUTION MADE FOR THE FUNCTIONS FOX, YOX,
C      AND ROAC.
C
C      THE FUNCTION FOR FOX IS
C
C        FOX = (C/S)*(X(I)**(1./S - 1))
C
C      THE FUNCTION FOR YOX IS
C
C        YOX(I) = C*(X(I)**(1./S))
C
C      THE FUNCTION FOR ROAC IS
C
C        ROAC = RO/ALF
C...................................................................
```

VITA

Joseph William Stucki

Candidate for the Degree of

Master of Science

Thesis: Boron Movement in Soil Columns

Major Field: Soil Science and Biometeorology

Biographical Information:

Personal Data: Born at Rexburg, Idaho, February 4, 1946, son of J. Wendell and Lasca A. Stucki; married Penny Jo Nickel August 9, 1968; Two children--Tawnya Joy and Julia Ann.

Education: Attended elementary and junior high school in Sugar City, Idaho; graduated from Madison High School in 1964; received a junior college diploma from Ricks College in 1968; the Bachelor of Science degree from Brigham Young University with a major in Chemistry in 1970; Master of Science in Soil Science and Biometeorology from Utah State University in 1972.