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THE EFFECT OF SOIL-PHOSPHATE INTERACTION UPON CONVECTIVE TRANSPORT OF ORTHOPHOSPHATE IN SOIL COLUMNS

by

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ABSTRACT

Three Manitoba soils, Wellwood clay loam, Stockton sandy loam, Lakeland silt loam, varying in pH, were chosen for the purpose of investigating the convective transport of orthophosphate in soil.

The technique chosen for this investigation was the miscible displacement experiment. The method consisted of feeding a known solution of orthophosphate continually onto a soil column and collecting the effluent for the analysis of orthophosphate.

Factors affecting the breakthrough curves were studied by choosing various lengths of soil columns and flow velocities. The breakthrough curves of the three soils were quite different with respect to the soils. The breakthrough curve of the Stockton soil appeared earlier than the other two soils. This indicated that the rate of movement of phosphate was the fastest in the Stockton soil. The slowest rate of movement of phosphate was found in the Lakeland soil. The rates of movement of orthophosphate were approximately 4 to 8 times slower than that of water. The Wellwood and Lakeland soils had a higher fixation capacity than the Stockton soil. Increasing the flow rate modified the breakthrough curves. The breakthrough curves of the Wellwood and Lakeland soils were changed more than the breakthrough curve of the Stockton soil. However, the breakthrough curves remained almost unchanged if the contact time between the solution and the soil was kept constant irrespective of the flow rate and soil length. It seemed that the

contact time of the solution with a soil had a great effect upon controlling the breakthrough curve.

The rate of adsorption of orthophosphate by soil was investigated using a soil column of 0.5 cm in length. Two flow rates were applied to observe the effect of the flow rate upon the rate of adsorption of orthophosphate by using thin sections of a soil column. The rates of the adsorption of orthophosphate by the three soils were all linearly expressible on semilog paper. The magnitude of the slope of the three soils at different flow rates showed that the interaction between soils and phosphate in solution was a rather slow process and was dependent upon the soil characteristics and flow rate. The Stockton sandy loam had the lowest phosphate fixation while the Lakeland had the highest phosphate fixation. The Wellwood had an intermediate phosphate fixation.

The rate of desorption of orthophosphate from the soils was studied by leaching the ^{32}P saturated soils with water. The leaching pattern of phosphate from the Wellwood and Stockton soils showed an initial rapid decrease of phosphate followed by a very slow process. The desorption of phosphate from the Lakeland soil showed only a gradual decrease of phosphate at the slow rate of leaching. The value of the desorption rate was dependent upon the flow rate. The amount of phosphate desorbed seemed independent of the flow velocity and was only the function of the amount adsorbed.

It was concluded that the rate of movement of orthophosphate in soil is the function of the adsorption capacity, flow rate of solution, soil length, and the rate of adsorption of phosphate by soils.

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CHAPTER I

INTRODUCTION

Diffusion of orthophosphate in soil or in a soil like system has received considerable investigation. One reason for this extensive investigation was based on the assumption that the rate of supply of orthophosphate to a plant may be controlled by diffusion. Some contradictory explanations are presented. In some cases the diffusion process seems to limit the rate of supply of orthophosphate to the plant while the opposite is true in other cases.

Another reason for the investigation was to estimate the relative magnitude of possible ground water pollution by orthophosphate. A rough calculation based on the diffusion experiment alone showed that orthophosphate did not seem to contribute much to ground water pollution.

Aside from the diffusive transport, orthophosphate applied to a soil can also be transported by convection. Knowledge on convective transport is very limited and little work on this subject has been reported.

The general theory of convective transport of a non-interacting element and of an element which interacts with soil instantaneously is very much advanced. The theory is known to be successful in predicting the rate of movement of the element. However, the theory of transport of an interacting element with finite rate is still in a primitive stage.

Only a few cases were investigated.

Phosphate and soil interaction is known to be relatively slow but the rate law is not yet fully understood. Also the adsorption isotherm which excludes the rate process is known to be non-linear. These two characteristics make theoretical analysis of the phosphate transport in soil very complicated.

The purpose of this investigation is to observe the effects of soil characteristics, solution flow velocity, and the rate of interaction upon the convective transport of orthophosphate in soil. A miscible displacement technique was chosen to study the transport. Three soil samples from Manitoba which were acid, neutral and alkaline in reaction were chosen to represent a varying degree of the magnitude of soil and phosphate interaction.

Various soil column lengths and flow velocity were chosen to observe the effect of flow velocity and the contact time between the soil and solution on the rate of movement of orthophosphate. To determine the relative magnitude of the empirical rate constants, a soil column of 0.5 cm length was chosen. It is assumed that the soil and the solution were more or less uniformly mixed within 0.5 cm length.

An attempt was made to correlate the relative rate of orthophosphate movement in soil with soil characteristics, flow velocities of the orthophosphate solution and the length of soil column.

CHAPTER II

LITERATURE REVIEW

2.1 MISCIBLE DISPLACEMENT

Transport phenomena of an element through porous material like soil can be grouped depending upon the mode of input. If a solution of different composition is introduced into one end of a soil column continuously, it is generally called miscible displacement. If, however, a finite quantity of some material is introduced into a porous material and it is eluted with another solution, it is called elution development (15). The plot of the solution concentration coming out from a finite length of soil or porous material against the volume of solution passed is called a breakthrough curve for miscible displacement, and an elution curve for elution development.

The subject of miscible displacement in soil research was reviewed by Nielsen and Biggar (26). They have presented five possible types of breakthrough curves for miscible displacement depending upon the following effects.

These are (1) piston flow, (2) longitudinal dispersion, (3) extremely wide range in velocity disbribution, (4) chemical reaction, (5) exclusion of solute by solute-solid interaction or velocity distribution with velocity near zero.

Piston flow would rarely occur in soil because of the diffusion and dispersion due to variation in velocity within the soil pore.

Longitudinal dispersion occurs in soil because of the radial variation in the velocity within a soil pore as well as the variation in pore sizes. The problem for the simplest capillary tube was researched by Taylor (34) and presented by Sheidegger (33). According to Taylor (34), the dispersion coefficient is directly proportional to the velocity and inversely proportional to the diffusion coefficient. Scheidegger (33) presented the velocity dependence of the dispersion coefficient to be v^n where the value of n lies between 1 and 2, and v is the velocity. An extremely wide range in velocity distribution will occur in a soil which is composed of unequal-sized aggregates with a large variation in pore radius.

Chemical reactions in soil can be classified as adsorption, exchange, precipitation and transformation. These affect the breakthrough curve considerably.

Exclusion of solute is caused by electrostatic repulsion by charged soil particles and incomplete mixing throughout the entire soil. For example, anions are repelled from the negatively charged clay surfaces and incomplete mixing occurs due to the nearly stagnant pore solution.

In practice, all effects except piston flow may contribute to the pattern of breakthrough curve. The effect of longitudinal dispersion and variation in velocity distribution tend to cause a general broadening of the breakthrough curve. Separation of these two effects is very difficult. In practice both effects are grouped into one, the dispersion effect.

Any interaction of the solute with a medium directly or indirectly will modify the shape and position of the breakthrough curve. If the displacing fluid or its solutes are retained within the column by any chemical or physical process, such as adsorption and/or exchange, the breakthrough curve will be translated to the right of one pore volume. The breakthrough curve translates to the left of one pore volume when there are increasing effects of solute concentration, the repulsion of anions away from the negatively charged clay surfaces and solution of slightly soluble salts in the soil. At each flow rate, the breakthrough curves are changed, indicating different mixing behavior, when the roles of displaced and displacing liquid are reversed. The contribution of diffusion to the dispersion of the moving front might be expected to increase as the velocity is decreased. As the velocity decreases, the front becomes sharper when the dispersion by velocity distribution decreases.

2.2 FACTORS AFFECTING THE BREAKTHROUGH CURVE.

2.2.1. DENSITY AND VISCOSITY EFFECT

Krupp and Elrick (20) reported that the density difference between theliquids was a much more significant factor than the velocity difference in altering the displacement pattern. Initially the dispersion coefficient decreased when the flow rate was decreased and then greatly increased in a density unstable configuration. Biggar and Nielsen (3) also used the values of density and viscosity of any two solutions in a simple equation to determine whether a displacement will be stable in a vertical column.

2.2.2 VELOCITY EFFECT

Nielsen and Biggar (27) conducted a considerable amount of miscible displacement research by using glass beads to investigate the contribution of diffusion and variations in pore-water velocity to mixing. Sodium chloride and sodium sulphate solution of the same density were allowed to displace each other from the saturated glass beads. Tritium was added to the NaCl at several flow velocities. At the velocity of 56.7 cm per hour, the chloride breakthrough curve was abrupt and $C/C_0=.5$ corresponded to one pore volume. At the velocity of 0.122 cm per hour, the chloride breakthrough curve was shifted to the left at 0.2 pore volume. The chloride breakthrough curve at this low velocity was quite skewed and required 3 pore volumes of the solution before C/C_0 reached 1. At the intermediate velocity of 0.395 cm per hour, the breakthrough curve appeared between the previous two curves. The values for the diffusion coefficient of chloride were 1.74×10^{-4}, 6.21×10^{-5} and 2.82×10^{-5} cm^2 per sec, respectively, for the above experimental velocities. The breakthrough curves of tritium for the three velocities were clearly separated and similar to the chloride breakthrough curves.

The effect of the degree of saturation and the flow velocity upon the rate of movement of chloride was investigated by Corey et al. (11). They used saturated and unsaturated sandstone columns of 30 cm length. It was found that under saturated and unsaturated conditions, different average velocities have entirely different shape and position of breakthrough curves. In a saturated condition, and at a velocity of 5.64 cm per hour, the maximum relative chloride concentration of the elution curve was 0.9 and this occurred at 200 ml of effluent volume. The chloride distribution curve had a smaller dispersion in the saturated condition than in the unsaturated condition, as evidenced from the sharper normal distribution curve. The maximum relative concentration of chloride under the unsaturated condition with velocity of 0.534 cm per hour, was close to one and this occurred at 140 ml effluent volume.

2.2.3 TORTUOSITY EFFECT

Tortuous pathway of a substance in closely packed spheres, which is one of the simplest, is about 1.22 times longer than a linear path (15). Also the average cross-sectional area of a pathway is not constant throughout the path. These effects undoubtedly cause a substance to travel through a soil column in a more tortuous manner than a corresponding capillary tube. Olsen et al.(29) suggest that the tortuous effect is one of the most important factors affecting diffusion in soil. Tortuosity factor has meaning only if an observer chooses the external coordinate as a reference.

2.2.4 MOISTURE CONTENT EFFECT

Lowering the moisture content below water saturation decreased the measured diffusion of Rb (14). A reduction in moisture content of 5-10% gave a 1,000 fold decrease in the measured diffusion of Rb. Some of the effect of lowering the moisture content is due to increased tortuosity. Some effects may be due to net decrease in the quantity of ion in solution as compared to adsorbed ion.

Corey et al.(11) found the dispersion coefficient of chloride and tritium had average values of 0.652 and 0.754 cm^2 per hour for saturated systems respectively. However, under unsaturated conditions, the dispersion coefficient of the chloride and tritium were 0.135 and 0.282 cm^2 per hour, respectively.

Lai and Mortland (21) studied the diffusion of ions in clay minerals under extremely low moisture content where most of the diffusion was assumed to be due to surface diffusion. The diffusion of sodium in expanded Na-vermiculite, which has both internal and external surfaces available for cationic diffusion, decreased with increasing diffusion time. The diffusion coefficient of Na ion for external surface was found to be 3.01×10^{-8} cm^2 sec^{-1} which was 5 times that of the internal surface (0.61×10^{-8} cm^2 sec^{-1}). The diffusion coefficient of Na and Cs ions in collapsed K-vermiculite which has only external surface available for diffusion remained unchanged with diffusion time.

2.2.5 CHEMICAL EFFECT

Chemical reaction is one of the most important factors controlling the position of the breakthrough curve. The previous factors affect mainly the shape of the breakthrough curve. In the case of the diffusion experiment, the chemical reaction contributes variable effects as compared to the above factors. Instead of spreading the diffusion front, the chemical reaction term sometimes contracts and sometimes spreads the diffusion front.

Evans and Barber (13) investigated the factors influencing the diffusion of ^{86}Rb in soil. They found that the rate of diffusion of ^{86}Rb was slower when the ^{86}Rb was more strongly absorbed by soils. In leached dry soils, the correlation coefficient between D_p/b and percent ^{86}Rb fixed gave the value of r of 0.9. When the soil was moist, the correlation coefficient, r, was found to be 0.42. They found the following relationship for the leached dry soil.

$$\frac{D_p}{b} = K_1F + K_2$$

where D_p is the diffusion coefficient, b is the chemical reaction factor, F is the percent fixation of ^{86}Rb against NH_4OAc extraction. K_1 and K_2 are the constants.

Hodgson et al. (16) studied the diffusion of zinc from a $ZnCO_3$ precipitate through an agar-agar to a stream of continuously flowing water. In one treatment, part of the agar-agar was replaced by Ca-polygalacturonate to incorporate a fixed negative charge in the gel in the form of carboxyl groups. In a second treatment, Ca-citrate was introduced into the following stream of water. All phases of these two systems were kept in equilibrium with $CaCO_3$. They found that both Ca-PGA treatment and the mobile complexing agent increased the transport of Zn in the system, but the second treatment was more effective than the first.

Biggar and Nielsen (1) found that the distribution of a tracer some distance from its source, depends upon the geometry of the porous material and the physical and chemical interaction of the tracer solution and media during flow. At flow velocity of 2.11 cm per hour, there was no separation of breakthrough curve between tritium and chloride in saturated glass beads of 200 μ in diameter. The approach of the curves to $C/C_o = 1$ was more gradual. The separation of the tracers occurred in sandstone at a velocity of 0.20 cm per hour and a water content of 0.482 cm^2 per cm^2. The initial breakthrough curves of the tritium was translated to the right of the chloride. As displacement continued the two curves crossed and approached sharply to $C/C_o = 1$. When the water content was decreased by 0.01, both breakthrough curves of tritium and chloride translated to the left of one pore volume and approached $C/C_o = 1$ more gradually than at the higher water content.

The breakthrough curves for saturated clay loam with increasing aggregate size showed the loss of the skewed sigmoid shape and became more concave to the abscisa. The tracers appeared earlier with increasing aggregate size and required a greater volume to reach $C/C_0 = 1$. The breakthrough curves were translated to the left with increasing aggregate size.

Chaudhry and Warkentin (8) studied the exchange of sodium from soils by leaching with calcium sulphate. The exchangeable sodium percentage was rapidly reduced to 5 to 10 percent of the original but required a large amount of leaching solution for further reduction. The process of reduction was slow.

Kay and Elrick (19) studied the adsorption and movement of lindane in soil. They found that the adsorption on different soil types and soil fractions of Honey wood loam were linear. Muck had the greatest relative adsorption rate, while Fox loamy sand had the lowest. The equilibrium adsorption of lindane on the Muck soil had not been reached after 10 hours. The equilibrium was reached less than 2 hours for the other soils. The divergence of the theoretical and observed breakthrough curves for relative concentration value greater than 0.6 was attributed to intra-aggregate diffusion and adsorption.

Davidson et al (12) found that the adsorption isotherm of herbicides fluometuron, and diuron, on porous material were linear for concentration up to 30 ppm. The rate of the movement of fluometuron and diuron in glass beads was not affected by the solution velocity. However, the measured rate of movement of the fluometuron was greater than that calculated from the data of the adsorption isotherm when elution development was carried out. Cho et al.(10) explained the faster rate of movement of an element can be observed for elution development but not for miscible displacement if an irreversible reaction accompanies the transport.

2.3 PHOSPHATE TRANSPORT

Phosphate transport in soil is very complicated and not much is known. The reason lies on the fact that the rate of reaction of phosphate with soil is unknown and supposedly slow. The adsorption isotherm of phosphate is non-linear. The slow rate of reaction excludes the possibility of applying equilibrium dispersion theory for phosphate transport. The non-linear character of the adsorption is restrictive to the extremely low concentration range for the application of linear dispersion theory.

2.3.1 INTERACTION BETWEEN SOIL AND PHOSPHATE

Numerous results were obtained for the phosphorus adsorption by soils (35). The general conclusion is that the phosphorus adsorption followed closely the Langmuir or Freundlich adsorption isotherms.

Experimental results on phosphorus adsorption of some Manitoba soils also shows that the Langmuir isotherm holds for this interaction (35).

The fixation of phosphate in soil is dependant upon the pH of the solution, the concentration of phosphate, and time of contact. Phosphate fixation increased with contact time and concentration (4).

2.3.2 PHOSPHATE DIFFUSION

Bouldin and Black (5) studied one-dimensional diffusion of ^{32}P tagged $Ca(H_2PO_4)_2$ and KH_2PO_4. They used x-ray film and a Geiger tube to estimate the diffused phosphorus. The x-ray film showed many local areas of ^{32}P concentration and there were irregularities in the phosphorus concentration profile in the soil column. In both the Miami silt loam and the Muscotine silt loam with $Ca(H_2PO_4)_2$, peaks in the phosphorus concentration were noted at 4 cm internals. One peak about 1 cm from the source of the phosphorus was found when KH_2PO_4 was added to the Miami silt loam soil.

Olsen et al.(29) applied a diffusion equation to describe the rate of supply of phosphorus to plants by diffusion. They claimed that the phosphate can diffuse fast enough to account for the observed uptake by plants.

Mokady and Zaslavsky (24) and Cho et al (10) described the limitation of the tracer techniques of radio-isotopes in diffusion or transport experiments. Mokady and Zaslavsky pointed out the limitation may be due to different modes of adsorption or immobilization of the tracers and the carrier.

Cho et al (10) reasoned that the different mode of ^{32}P and ^{31}P transport was due to isotopic exchange phenomena.

Phillips et al,(31) studied the effect of phosphorus rate on self-diffusion of phosphorus in clays and soils. The self-diffusion coefficients in clay and soil were linearly related to the amount of phosphorus added. The linear correlation coefficients varied from 0.97 to 0.99.

Place et al.(32) studied the effect of pH on the self-diffusion coefficient of phosphorus -32 in soils. The self-diffusion coefficients of ^{32}P in Kaolinite and Montmorillonite were influenced more by pH than in the other soils. The maximum value of self-diffusion coefficients for Kaolinite and Montmorillonite were in the range of pH 5-6 and 3-4 , respectively. The pH did not influence the diffusion coefficients of Illite and Sharkey clay.

Olsen et al.(30) measured the self-diffusion coefficients of phosphorus in two soils and clays by transient and steady-state methods. The diffusion coefficient of phosphorus for the silty clay loam was less than the sandy loam even though they have corrected for tortuosity effect.

2.3.3 CONVECTIVE TRANSPORT

Lewis and Racz (23) studied phosphorus movement in some calcareous and noncalcareous Manitoba soils. They found that the extent of phosphorus movement from a monoammonium phosphate pellet was greater than a diammonium phosphate pellet.

The extent of phosphorus movement was greater in noncalcareous soils than in calcareous soils in both sources of phosphorus when added as a pellet. The rate of movement of phosphorus was also more rapid in noncalcareous soils than in calcareous soils.

Cho et al (10) investigated the convective transport of ^{31}P and ^{32}P in several Manitoba soils. They found that the mode of the application of phosphate influenced the rate of ^{31}P and ^{32}P movement in soil. The retardation of movement of both ^{31}P and ^{32}P increased with increasing rates of phosphate fixation of the soil.

2.4 GENERAL THEORY OF CONVECTIVE TRANSPORT

The effect of soil-phosphate interaction upon convective transport of phosphate can be analysed by applying the dispersion theory with chemical reactions. The total flux of the phosphate across a fixed plane is assumed to be made up of dispersive and convective fluxes. The dispersive flux is assumed to be proportional to the concentration gradient. Substitution of this relationship into the equation of continuity in one dimensional form with the chemical sink gives

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - V\frac{\partial c}{\partial x} - \alpha\frac{\partial n}{\partial t} \qquad (1)$$

where C is the concentration per ml of soil solution, D the dispersion coefficient, v the linear velocity of water, α the soil to solution ratio, n the concentration per gram of solid, x the distance and t is time. $\partial n/\partial t$ corresponds to the rate of increase of phosphate concentration in solid material.

The solutions of equation [1] at various $\partial n/\partial t$ will be discussed. In every case, the solutions correspond to an infinitely long soil length without phosphate and follows boundary conditions $C = Co$, $x = 0$, $t \geq 0$.

Four cases of $\partial n/\partial t$ will be discussed. 1) without chemical reaction, 2) with extremely fast reversible reactions, 3) with irreversible reactions, and 4) with slow reversible reactions.

Case 1. Without chemical reaction. $\frac{\partial n}{\partial t} = 0$
The solution of equation [1] is

$$\frac{C}{C_o} = \frac{1}{2}\left\{\operatorname{erfc}\left(\frac{x-vt}{\sqrt{4Dt}}\right) + e^{\frac{vx}{D}}\operatorname{erfc}\left(\frac{x+vt}{\sqrt{4Dt}}\right)\right\} \qquad [2]$$

where erf c is the complementary error function.

The second term becomes negligible if t is large. Equation [2] shows that the position of $\frac{C}{Co} = 0.5$ moves with the speed of v, with gradual spreading of the front.

If equation [2] is chosen as an approximate solution for the soil of finite length and time is expressed in terms of the number of pore volumes (N) of solution passed, it becomes (neglecting the second term)

$$\frac{c}{c_o} = \frac{1}{2}\,\mathrm{erfc}\left\{\sqrt{P}\left(\frac{1-N}{\sqrt{N}}\right)\right\} \qquad [3]$$

where $P = \frac{vx}{4D}$ is the Peclet number.

Case 2. With extremely fast reversible reactions $\frac{\partial n}{\partial t} = K\frac{\partial c}{\partial t}$. If the reaction is composed of first order reversible reactions and the rate is extremely fast (local equilibrium). $\frac{\partial c}{\partial t}$ and $\frac{\partial n}{\partial t}$ are related as follows.

$$n = Kc \qquad [4]$$

$$\frac{\partial n}{\partial t} = K\frac{\partial c}{\partial t} \qquad [5]$$

where K is the distribution coefficient.
Substituting the relation in equation [5] into equation [1] gives;

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} - \alpha K\frac{\partial c}{\partial t} \qquad [6]$$

$$(1+\alpha K)\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x}$$

$$\frac{\partial c}{\partial t} = D'\frac{\partial^2 c}{\partial x^2} - v'\frac{\partial c}{\partial x} \qquad [7]$$

where D' is the modified diffusion coefficient $(D' = \frac{D}{1+\alpha K})$, and v' is the modified velocity $(v' = \frac{v}{1+\alpha K})$ which is the rate of movement of phosphorus. The solution of equation [7] is

$$\frac{C}{C_0} = \frac{1}{2}\left\{ \operatorname{erfc}\left(\frac{x - v't}{\sqrt{4D't}}\right) + e^{\frac{vx}{D}} \operatorname{erfc}\left(\frac{x + v't}{\sqrt{4D't}}\right) \right. \qquad [8]$$

Equation [8] shows that the position of $\frac{C}{C_0} = 0.5$ moves with the speed of v', with a gradual spreading of the front. The second term becomes negligible if t is large. The values of v' and the modified diffusion coefficient depend on the value of α and K. The greater the value of α and K the slower the speed of v' and the value of D' becomes smaller. If an interaction between soil and an element is great, it will be reflected in the value of K and consequently the element will travel slow as compared to water.

Case 3. with irreversible reaction. For a simple case of first order irreversible reaction $\frac{\partial n}{\partial t} = k_1 C$ [9]

Substituting the relation in equation [9] into equation [1] gives the following equation.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} - \alpha k_1 c \qquad [10]$$

The solution of equation [10] is

$$\frac{C}{C_0} = \frac{1}{2}\left[e^{\frac{vx}{2D} - \sqrt{\frac{v^2}{4D^2} + \frac{\alpha k_1}{D}}\cdot x} \operatorname{erfc}\left(\frac{x - \sqrt{v^2 + 4D\alpha k_1}\cdot t}{\sqrt{4Dt}}\right)\right.$$

$$+ e^{\frac{vx}{2D} + \sqrt{\frac{v^2}{4D^2} + \frac{\alpha k_1}{D}} \cdot x} \quad \operatorname{erfc}\left(\frac{x + \sqrt{v^2 + 4D\alpha k_1} \cdot t}{\sqrt{4Dt}} \right) \Bigg] \qquad [11]$$

The characteristic feature of equation [11] is that it is composed of time independent exponential terms and moving terms. A steady state can be established and the profile decreases exponentially with distance.

Case 4. with slow reversible reactions; $\frac{\partial n}{\partial t} = k_1 C - k_2 n$. Reversible first order reactions with finite rates for $\frac{\partial n}{\partial t}$ will be treated.

$$\frac{\partial n}{\partial t} = k_1 c - k_2 n \qquad [12]$$

k_1 and k_2 are the rate constants.

Substituting equation [12] into equation [1] gives the following equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \alpha k_1 c + \alpha k_2 n \qquad [13]$$

Equation [13] is the simplest non-equilibrium case of solute movement by dispersion and solvent flow through porous material. Equation [13] was solved by Lapidus and Amundson (22). The solution is:

$$\frac{c}{C_0} = e^{\frac{vx}{2D}} \left[e^{-k_2 t} F(t) + k_2 \int_0^t e^{-k_2 \tau} F(\tau)\, d\tau \right. \qquad [14]$$

where

$$F(t) = \int_0^t I_0 \left[2\sqrt{\alpha k_1 k_2 \tau (t-\tau)} \right] \frac{x}{\sqrt{4\pi D \tau^3}} \, e^{-\frac{x}{4D\tau} - \left(\frac{v^2}{4D^2} + \alpha k_1 - k_2 \right)\tau} \cdot d\tau$$

I_0 is the modified Bessel function of zero order.

$$I_0(x) = \sum_{n=0}^{\infty} \frac{\left(\frac{x}{2}\right)^{2n}}{(n!)^2}$$

$$I_0\left[2\sqrt{\alpha k_1 k_2 \tau (t-\tau)}\right] = \sum_{n=0}^{\infty} \frac{\{\alpha k_1 k_2 \tau (t-\tau)\}^n}{(n!)^2}$$

The physical interpretation of equation [14] is not too obvious. However, by carrying out integration for the first term of the infinite series, some understanding of the expression can be deducted.

Equation [14] can be expressed as follows.

$$\frac{C}{C_0} = e^{\frac{vx}{2D}} \int_0^t e^{-k_2 \tau} \frac{dF(\tau)}{d\tau} \, d\tau$$

$$= \frac{1}{2}\left[e^{\frac{vx}{2D} - \sqrt{\frac{v^2}{4D^2} + \frac{\alpha k_1}{D}} \cdot x} \operatorname{erfc}\left(\frac{x - \sqrt{v^2 - 4D\alpha k_1}\, t}{\sqrt{4Dt}} \right) \right.$$

$$\left. + \, e^{\frac{vx}{2D} + \sqrt{\frac{v^2}{4D^2} + \frac{\alpha k_1}{D}} \cdot x} \operatorname{erfc}\left(\frac{x + \sqrt{v^2 + 4D\alpha k_1} \cdot t}{\sqrt{4Dt}} \right) \right]$$

$$+ \, e^{\frac{vx}{2D}} \int_0^t e^{-k_2 \tau} \int_0^{\tau} \frac{\alpha k_1 k_2 x}{\sqrt{4\pi D \xi}} \, e^{-\frac{x^2}{4D\xi} - \left(\frac{v^2}{4D^2} + \alpha k_1 - k_2\right)\xi} \, d\xi \, d\tau$$

$$+ \, ---------- \qquad [15]$$

The first term of the right hand side of equation [15] corresponds to equation [11] , which is the solution for the case of irreversible reaction. The contribution from the subsequent terms may depend upon the values of the parameters. Equation [15] implies that the presence of a reversible reaction manifests itself like an irreversible reaction during short intervals. Divergence of this behavior increases with increasing time.

An equation similar to equation [15] was obtained by Oddson et al.(28). The result of their finding can not be directly applied to the miscible displacement because their finding was based on a type of elution development. General findings, however, are of great importance. They found that the degree of spread of a band increased with decreasing values of rate constants k_1 and k_2. This is conceivable since a slower rate of reaction generally favors the band spread. They also found that the maximum position was only governed by the ratio of k_1 to k_2. Their graphical analysis indicated that the velocity of the maximum position was $k_2 v/k_1$. It is not known whether the value should have been $v/(1 + \frac{k_1}{k_2})$ which is equivalent to v' of equation [7] . Different behavior for the case of miscible displacement could be expected as was noted by Cho et al.(10). This expectation is partially supported by the calculation done by Oddson et al.(28). They found that increasing k_2 while keeping k_1/k_2 constant did not change the maximum position as long as the elution development was fully developed. However, the effect was great before the elution was developed - ie., a type of miscible displacement stage.

Equation [1] to [11] are due to C.M.* Cho.

* Cho, C.M. Lecture note of Soil Physical Chemistry, Department of Soil Science, University of Manitoba, 1969.

CHAPTER III

MATERIALS AND METHODS

SOIL SAMPLES

Three Manitoba soils, Wellwood clay loam, Stockton sandy loam and Lakeland silt loam were chosen for this investigation. The pH of the soil ranged from 5.5 to 7.8. The characteristics of the soil samples were determined by the methods as described by Jackson (17) and they are listed in Table I. The soil samples were air-dried and crushed to pass through a 2.00 mm. sieve.

Phosphate solution, 25 ppm P. Potassium dihydrogen phosphate, KH_2PO_4, was dried at 40°C and 0.1097 gm was dissolved in about 400 ml of distilled water in a 1,000 - ml volumetric flask. The solution was made to 1000 - ml volume and mixed, giving 25 ppm of P.

^{32}P. labelled phosphate solution. 0.0548 gm of dried potassium dihydrogen phosphate was dissolved in 100 ml of distilled water in 500 - ml volumetric flask. Then 25 ml of carrier-free ^{32}P in the form of H_3PO_4 (2.5 uc/ml) was added and the solution made to 500 - ml volume and mixed, giving 25 ppm ^{31}P and 0.125 μc/ml ^{32}P.

TABLE I. EXPERIMENTAL SOIL CHARACTERISTICS.

SOIL	pH	CO_3 (%)	O.M. (%)
Wellwood clay loam	5.5	-	8.06
Stockton sandy loam	7.2	0.7	2.96
Lakeland silt loam	7.8	13.5	8.87

3.1 MISCIBLE DISPLACEMENT EXPERIMENT

Plexiglass tubing of inside diameter 2.5 cm was cut to 15 cm in length. A funnel of identical radius was prepared from a solid plexiglass rod. The funnel and the tube were joined together with plastic tape and a porous circular disc was placed between the tubing and the funnel to retain the experimental soils in the column (Fig. 1). Filter paper was placed on top of the disc and water was filled up to the half-height of the tubing. The tip of the funnel was covered so that the water would not drain. Then air-dried soil was poured into the column slowly to eliminate air trapping. After filling the tubing with desired length of soil excess water was drained by opening the tip of the funnel.

Soil columns of the following lengths, 15, 7.5, 5 and 3 cm were chosen for the study. The dry weights and water contents of these soil columns are in proportion to the soil length. A solution of 25 ppm Phosphorus was fed onto the surface of the soil previously covered with filter paper, with the aid of Masterflex pump (Manufactured by Cole-Parmer Chicago, Illinois) at various average linear speeds The average linear speed was calculated by dividing the flow rates by the effective cross-sectional area. The effluents were collected in test tubes on an automatic fraction collector. The phosphorus content in each effluent fraction was determined by the colorimetric method (17). The volumes of effluent for each fraction were determined in order to calculate the flow rate.

The breakthrough curves were constructed by plotting the ratio of the measured concentration of ^{31}P of any fraction to the initial concentration against the number of pore volume of solution passed. One pore volume is the total volume of water retained within the column.

3.2 ADSORPTION OF PHOSPHATE BY SOIL

The apparatus, method of sampling, and determination of phosphorus in the samples were the same as previously described in miscible displacement. A 0.5 cm-long soil column and a phosphate solution of 25 ppm P were used for this experiment with various average linear velocities The experiment was terminated when the effluent phosphate concentration became almost identical to the input concentration. Total amount of phosphate retained by the soil was calculated. To obtain the rate characterizing the adsorption, the phosphate concentration

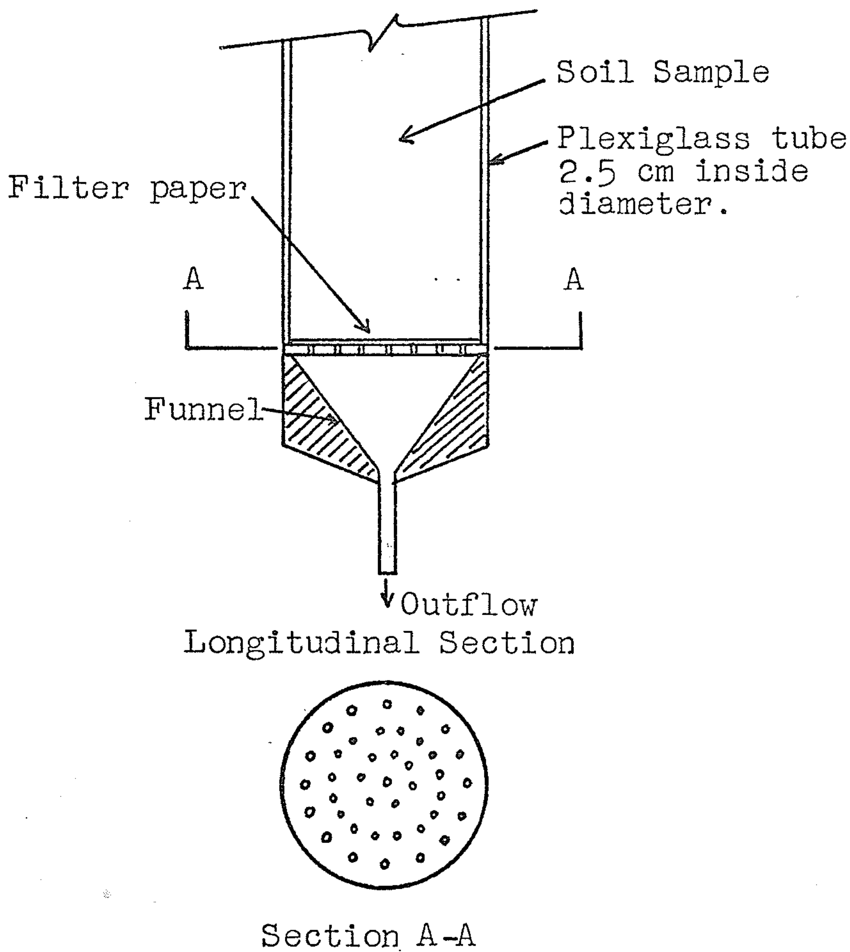


Figure 1. Sketch of Soil Column.

in the effluent was plotted against time in semi-log manner.

3.3 DESORPTION OF ^{32}P - PHOSPHATE FROM SOIL

In order to study the desorption phenomena of the experimental soils, they were first saturated with ^{32}P - labelled phosphate solution. A soil column of 0.5 cm was selected, and 25 ppmP solution labelled with ^{32}P was applied to the surface of the soil column as described in the miscible displacement experiment. The effluent fractions were collected by using an automatic fraction collector until the effluent had the same ^{32}P concentration as the feed solution. The specific activity of the effluent was the same as the specific activity of the feed solution.

The desorption of phosphorus in soils was studied by leaching the column of the P-32 saturated soil with distilled water. The effluent fractions were collected in test tubes. 1 ml from each fraction was transferred to planchet and ^{32}P activity was measured by an end-window G.M. tube and counter.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 MISCIBLE DISPLACEMENT

4.1.1 THE EFFECT OF SOIL LENGTH

The results of miscible displacement of soil solution by orthophosphate solution (25 ppm P) at various soil lengths are shown in Figures 2, 3, 4 and 5.

The breakthrough curve was constructed by plotting C/C_0 against the number of pore volumes (N) of orthophosphate solution passed through the soil.

Figure 2 shows the results of the breakthrough curves of Wellwood clay loam, Stockton sandy loam and Lakeland silt loam all with a 3 cm length at the velocities of 3.5, 6.2 and 6.8 cm per hour, respectively. The breakthrough curves of orthophosphate are quite different depending upon the soils but none of the curves passed $C/C_0 = 0.5$ near one pore volume. This implies that there were interactions between phosphate and the soils. The degree of translation of the breakthrough curve to the right side of one pore volume was the least for the Stockton soil and the greatest for the Lakeland soil. The Wellwood soil had a curve lying in between the other two. Since the degree of the translation was related to the interaction, it was obvious that the Lakeland soil had the highest interaction while the Stockton soil had the least.

It was noticed that the phosphate breakthrough curve of the Stockton soil had the sharpest slope of the three while that of the Lakeland soil was the flatest. It seems probable from the above comparison that the degree of interaction had also affected the sharpness of the breakthrough curve as well as the position of the curve.

The number of pore volumes of solution needed to attain $C/C_o = 0.5$ for the Wellwood, Stockton and Lakeland soils were 5.3, 3.7 and 7.9, respectively. If there is no interaction between soil and solution, such as water, NO_3^-, and Cl^-, the number of pore volumes to attain $C/C_o = 0.5$ should be 1. Since the number of pore volumes to attain $C/C_o = 0.5$ for the experimental soils was 5.3, 3.7 and 7.9, these figures indicate that the movement of phosphate in the three soils was 5.3, 3.7 and 7.9 times slower than water.

The amounts of phosphorus fixed by these soils are shown in Table II. The values were calculated from the difference between the total amount of phosphorus that was added and the total amount of the phosphorus which came out from the soil column up to 10 pore volumes.

The amount of P fixed by soil = $(V_T - V_P)\ C_o - \sum_{n=1} C_n \Delta V_n$.

Where V_T is the total volume of solution collected up to 10 pore volumes, V_p is the number of mls of one pore volume, C_o is the initial concentration, C is the concentration of any fraction, v is the number of mls collected per fraction. Ten pore volumes of solution was abritrarily chosen since the effluent concentration never reached C_o

within the experimental period. The magnitude of the phosphate fixation differed with each soil type. The amount of phosphorus fixation by the three soil was 488, 210 and 1,023 μeq/100 gm, respectively. The Lakeland silt loam with a pH of 7.8 and containing 13.8 % $CaCO_3$, had the highest phosphorus fixation while the Stockton sandy loam with a pH of 7.2 had the lowest fixation. The Wellwood clay loam with a pH of 5.5 had an intermediate fixation. There is a good correlation between the magnitude of phosphate fixation and the degree of the retardation of the phosphate movement.

The probability plots of miscible displacement are shown in Figure 19 of the appendix. They are linear up to $C/C_o = 0.5$. The slopes are listed in Table II. It was noticed that the values of the slopes were independent of the soils. The slopes for Wellwood clay loam, Stockton sandy loam and Lakeland silt loam are -1.75, -1.77 and -1.61, respectively (Figure 19 and Table II). The slope of a theoretical line, $C/C_o = \frac{1}{2}$ erf c (1 - N) also shown in Figure 19 of the appendix is-4.62.

The probability plot of a miscible displacement curve provides information concerning some parameters governing the pattern of miscible displacement. The plot of the equation,

$$\frac{C}{C_o} = \frac{1}{2} \text{ erf c } (1 - N)$$

in a probability plot should be linear with a constant slope.

If a miscible displacement is expressible by the following equation

$$\frac{C}{C_o} = \frac{1}{2} \text{ erf c } \left(\frac{k_1 - N}{k_2}\right)$$

Then the plot of C/C_o in a probability plot should be linear with the value of the slope $\frac{1}{k_2}$ of the slope of the previous plot. The position of N where $C/C_o = 0.5$ corresponds to k_1

If a miscible displacement is expressible by the following equation

$$\frac{C}{C_o} = \frac{1}{2}k \text{ erf c } \left(\frac{k_1 - N}{k_2}\right)$$

then the plot of C/C_o in a probability plot is not linear. If the value of k is not too different from unity, the plot is almost linear below the value of $C/C_o = 0.5$. It was noticed that the slope was independent of the soils. This seems to suggest that the dispersion of the moving front of phosphate was not governed by the soil characteristics. The slope became more gradual with an increasing number of pore volumes of solution. This was particularly noticed for the Wellwood and the Lakeland soils.

The breakthrough curves obtained using a 5 cm length of soil column are shown in Figure 3. Except for minor deviations due to spreading of the breakthrough curves, the general pattern of the curves was identical to that shown in Figure 2. The number of pore volumes of solution needed to attain $C/C_o = 0.5$ and the amount of total phosphorus

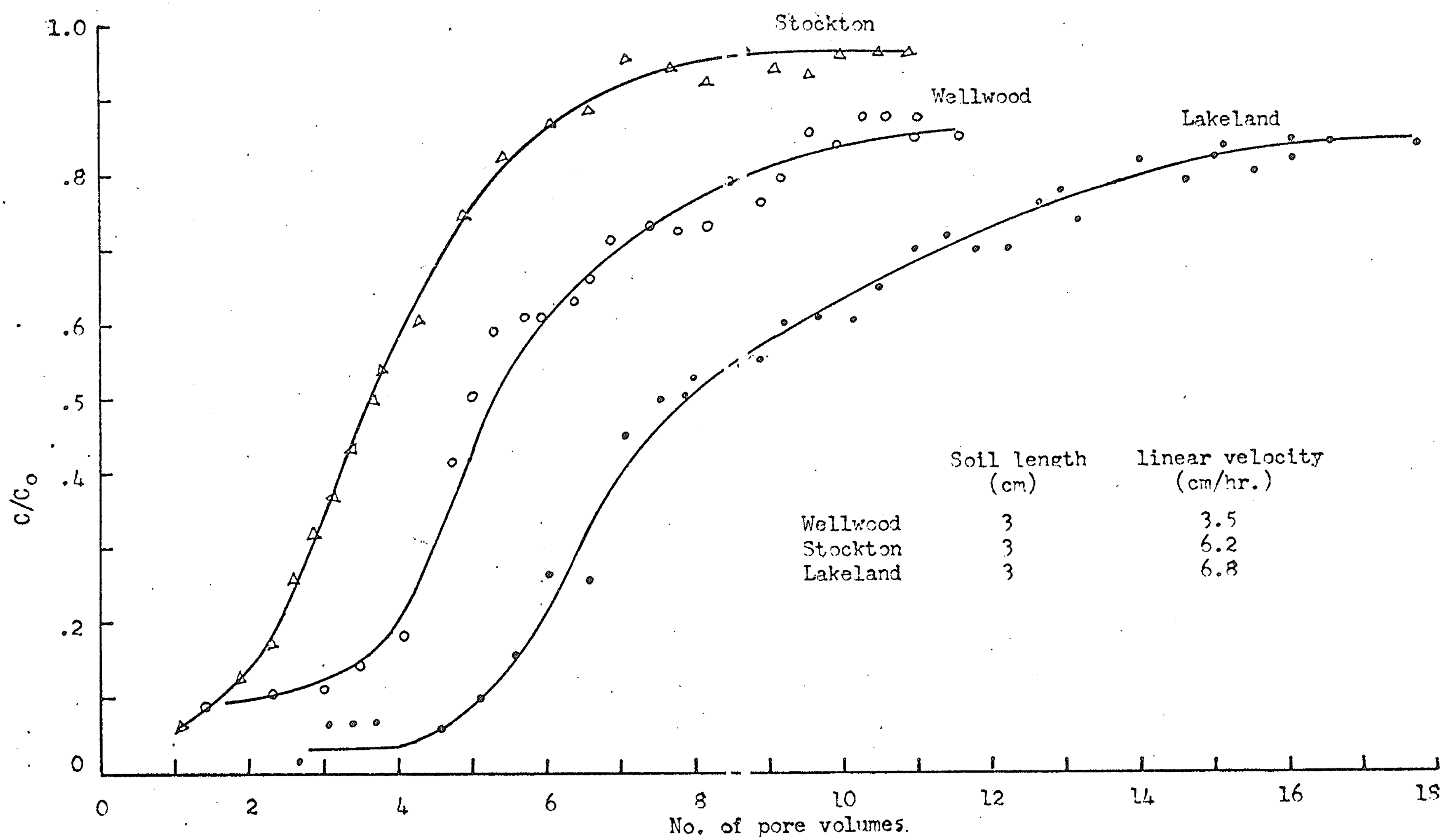


Figure 2. Breakthrough curves for phosphate from the experimental soils.

TABLE II

SUMMARY OF THE MISCIBLE DISPLACEMENT FOR THE
THREE EXPERIMENTAL SOILS WITH 3 CM LENGTH

Soil	Soil length (cm)	Dry wt. of soil (gm.)	Water content in soil (gm.)	Average linear Velocity (cm/hr.)	p-fixed (μeq/100gm)	Miscible displacement		Probability plots of miscible displacement	
						Figure	no. of pore volumes at $C/C_0 = 0.5$	Figure (appendix)	slope
Wellwood	3	10.1	8.5	3.5	488	2	5.3	19	-1.75
Stockton	3	15.1	6.6	6.2	210	2	3.7	19	-1.77
Lakeland	3	8.2	8.1	6.8	1,023	2	7.9	19	-1.61

fixation are almost identical (Figure 3 and Table III). The results indicate that the soil length, which determines the contact time between the solution and soil, did not affect the relative rate of movement of phosphate at these contact times.

The breakthrough curves obtained using a 7.5 cm length of a soil column are shown in Figure 4. The shape and position of the breakthrough curve from the Stockton soil is almost identical to the breakthrough curves obtained using 3 and 5 cm (Figure 2 and Figure 3). This implies that the contact time of the phosphate solution with the Stockton soil did not affect the rate of movement of phosphate.

The breakthrough curves obtained using the Wellwood and the Lakeland soils with 7.5 cm length, however, are quite different from the previous two figures. The fronts of the breakthrough curve up to $C/C_o = 0.5$ obtained with the 7.5 cm length are almost identical to the two previous curves. The ends of the curves are quite different, and both curves seemed to have reached a plateau within the experimental period. Thus it is quite obvious that there might be some time dependent reactions occuring within the two soils.

Table III, which summarized these results indicates that the number of pore volumes to attain $C/C_o = 0.5$, however is independent of the soil length. Also the slope of the probability plots showed that the value was independent of the soil length up to $C/C_o = 0.5$. From $C/C_o = 0.5$ on the slopes seem to change to new values.

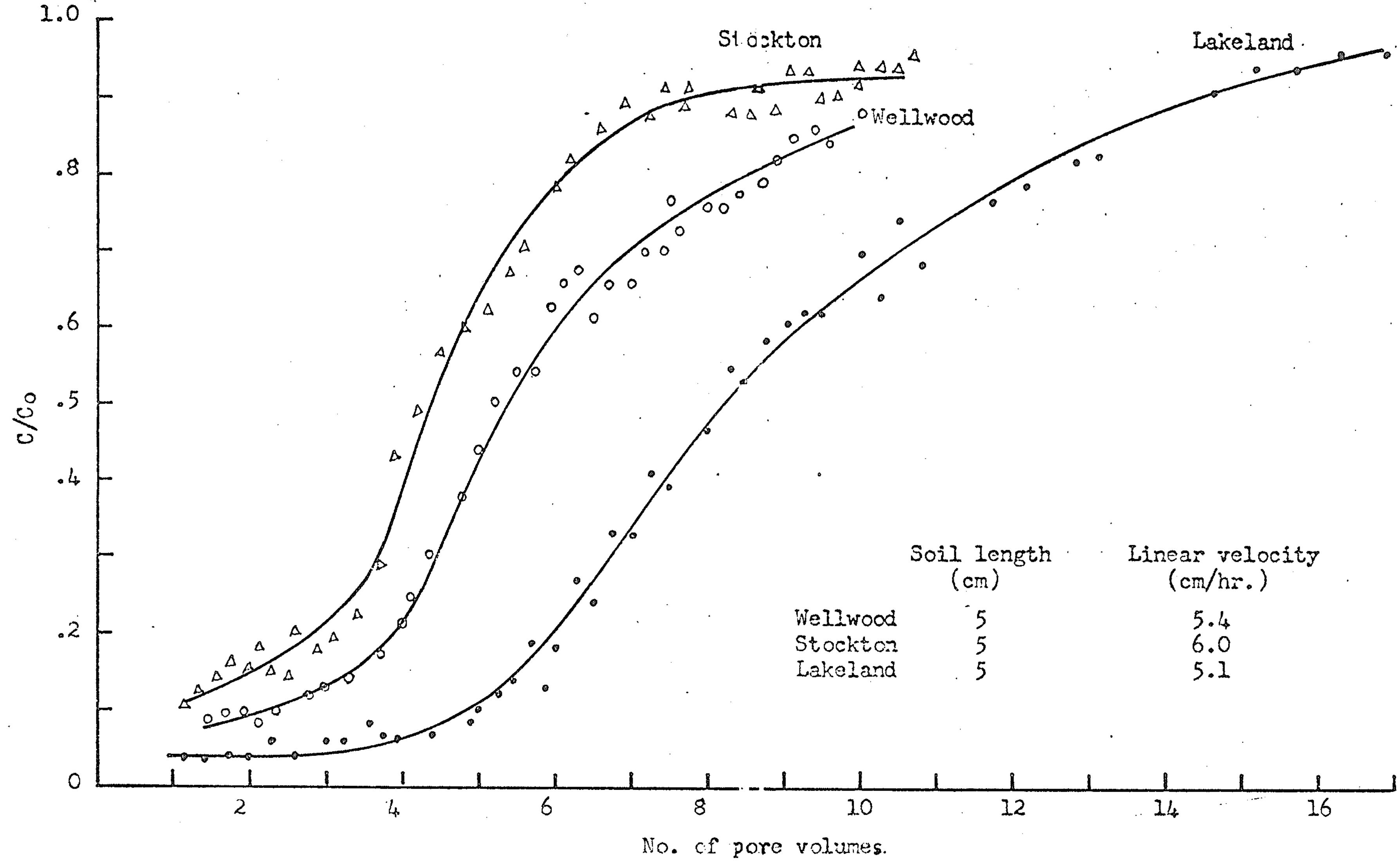
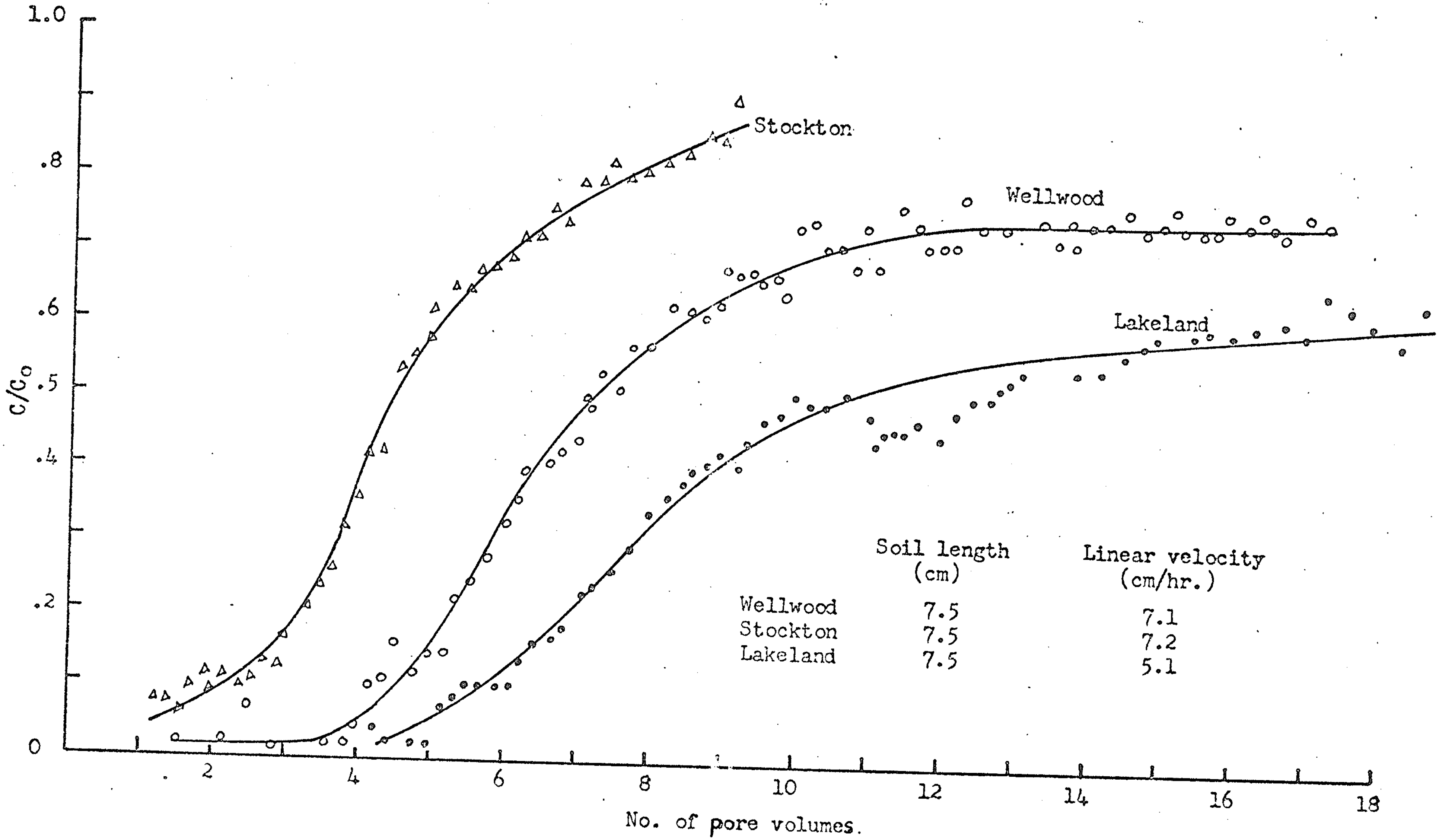


Figure 3. Breakthrough curves for phosphate from the experimental soils.

The amount of phosphate fixed shown in Table III also indicates that the phosphate fixed by the soils up to 10 pore volumes is independent of the soil length. If, however, a graphical interpretation is carried out, it is obvious that the total amount of phosphate retained by the soils is a function of the soil length. This dependency seems to be least for the Stockton soil and the highest for the Lakeland.

In Figure 5, the breakthrough curves of the phosphate solution using a soil column of 15 cm length are shown. The shape and position of the breakthrough curve for the Stockton soil is almost identical to those obtained using 3, 5 and 7.5 cm (Figure 2, 3 and 4). This shows that the contact time of the phosphate solution with the Stockton soil did not affect the rate of movement of phosphate.

The Wellwood clay loam seemed to disperse with the addition of a large quantity of KH_2PO_4 solution and the solutions permeability decreased with time. Consequently a 11.5 cm length was chosen for the Wellwood clay loam. The breakthough curve obtained from the Wellwood soil was quite different from the previous figures. The fronts of the breakthrough curve up to $C/C_o = 0.5$ obtained with 11.5 cm are almost identical to the 3 cm length of the Wellwood soil in Figure 2. The ends of the curve (Figure 5) are quite different and the curve did not reach $C/C_o = 1$ within the experimental period. Therefore, it is quite probable that there might be some time dependent reactions accuring within



	Soil length (cm)	Linear velocity (cm/hr.)
Wellwood	7.5	7.1
Stockton	7.5	7.2
Lakeland	7.5	5.1

Figure 4. Breakthrough curves for phosphate from the experimental soils.

the soil. The Lakeland soil also displayed similar characteristics as those exhibited by the Wellwood soil. The front of the breakthrough curve seems to be independent of the soil length. The ends of the curve, however, seems dependent upon the soil length, and it only reached $C/C_0 = 0.7$, with a very gradual slope, within the experimental period.

Table III indicates the number of pore volumes to attain $C/C_0 = 0.5$. It was observed that the value was independent of the soil length in the Stockton and the Lakeland soils. The number of pore volumes to attain $C/C_0 = 0.5$ for the Wellwood soil was 6 for a 11.5 cm length and was 7.1 for a 7.5 cm length. It is not known why this phenomena is observed for the Wellwood soil.

The slope of the probability plots showed the value to be almost constant for the Stockton soil irrespective of the soil length. This, however, was not the case for the Wellwood and the Lakeland soils. The amount of phosphate fixed, as shown in Table III was calculated by taking the value up to 10 pore volumes as previously discussed. The values for the respective soils were almost constant irrespective of the soil length.

4.1.2 THE EFFECT OF FLOW VELOCITY

4.1.2.1 5 CM LENGTH OF SOIL COLUMN

To observe the effect of varying flow velocity upon the miscible displacement, soil lengths of 5 and 15 cm

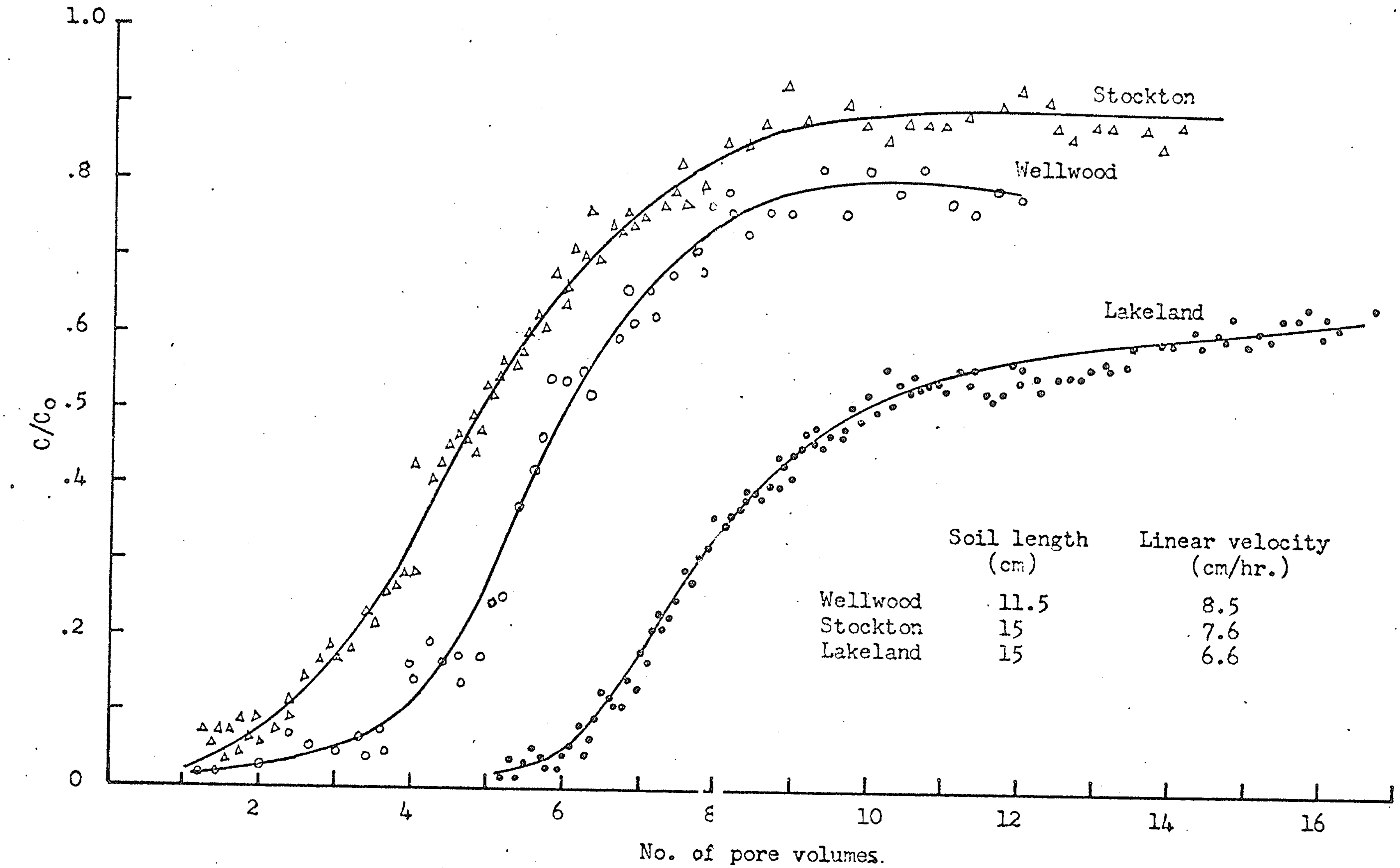


Figure 5. Breakthrough curves for phosphate from the experimental soils.

TABLE III

SUMMARY OF THE MISCIBLE DISPLACEMENT FOR THE THREE EXPERIMENTAL SOILS WITH 5, 7.5 AND 15 CM LENGTH

Soil	Soil length (cm)	Dry wt. of soil (gm.)	Water content in soil (gm.)	Average linear Velocity (cm/hr.)	p-fixed (μeq/100gm)	Miscible displacement		Probability plots of miscible displacement	
						Figure	no. of pore volumes at $C/C_0 = 0.5$	Figure (appendix)	slope
Well-wood	5	19.1	15.5	5.4	515	3	5.4	20	-1.47
Stock-ton	5	30.1	12.8	6.0	210	3	4.4	20	-1.57
Lake-land	5	16.4	16.9	5.1	1,040	3	8.2	20	-1.47
Well-wood	7.5	29.4	19.1	7.1	570	4	7.1	21	-1.59
Stock-ton	7.5	44.8	19.6	7.2	251	4	4.4	21	-1.77
Lake-land	7.5	26.2	23.9	5.1	1,064	4	10.4	21	-1.53
Well-wood	11.5	39.5	28.7	8.5	507	5	6.0	22	-1.94
Stock-ton	15	87.5	37.5	7.6	198	5	4.9	22	-1.65
Lake-land	15	53.8	48.2	6.6	1,078	5	9.9	22	-2.26

were chosen and the rate of flow of solution was varied.

Figure 6 shows the breakthrough curve obtained using a 5 cm length with twice as fast a flow rate as was presented in Figure 3.

The general characteristics of the breakthrough curves in Figure 6 and Figure 3 are almost the same except for one notable difference. The difference between the two figures is that the curves in Figure 6 are all shifted to the left. The magnitude of the shift of the breakthrough curve to the left as compared to those shown in Figure 3 is approximately 0.5 pore volume. This shifting is reflected in the values of P - fixed as shown in Table IV. The experimental results indicate that the average rate of movement of phosphate will increase with an increasing flow rate of solution.

The results obtained using a still faster flow rate with the same length of soil columns are shown in Figure 7.

The Wellwood clay loam seemed to disperse with the addition of KH_2PO_4 solution and the solution permeability decreased with time. The solution was trapped on the upper part of the soil column and it was unable to control the flow rate. Thus, the experiment on a 5 cm length of the Wellwood soil at this velocity was not carried out.

The shape and position of the breakthrough curve from the Stockton soil at the flow velocity of 39.8 cm per hour was identical to the breakthrough curve at the flow velocity of 13.6 cm per hour (Figure 6) but it was different from the breakthrough curve at a velocity of 6 cm per hour

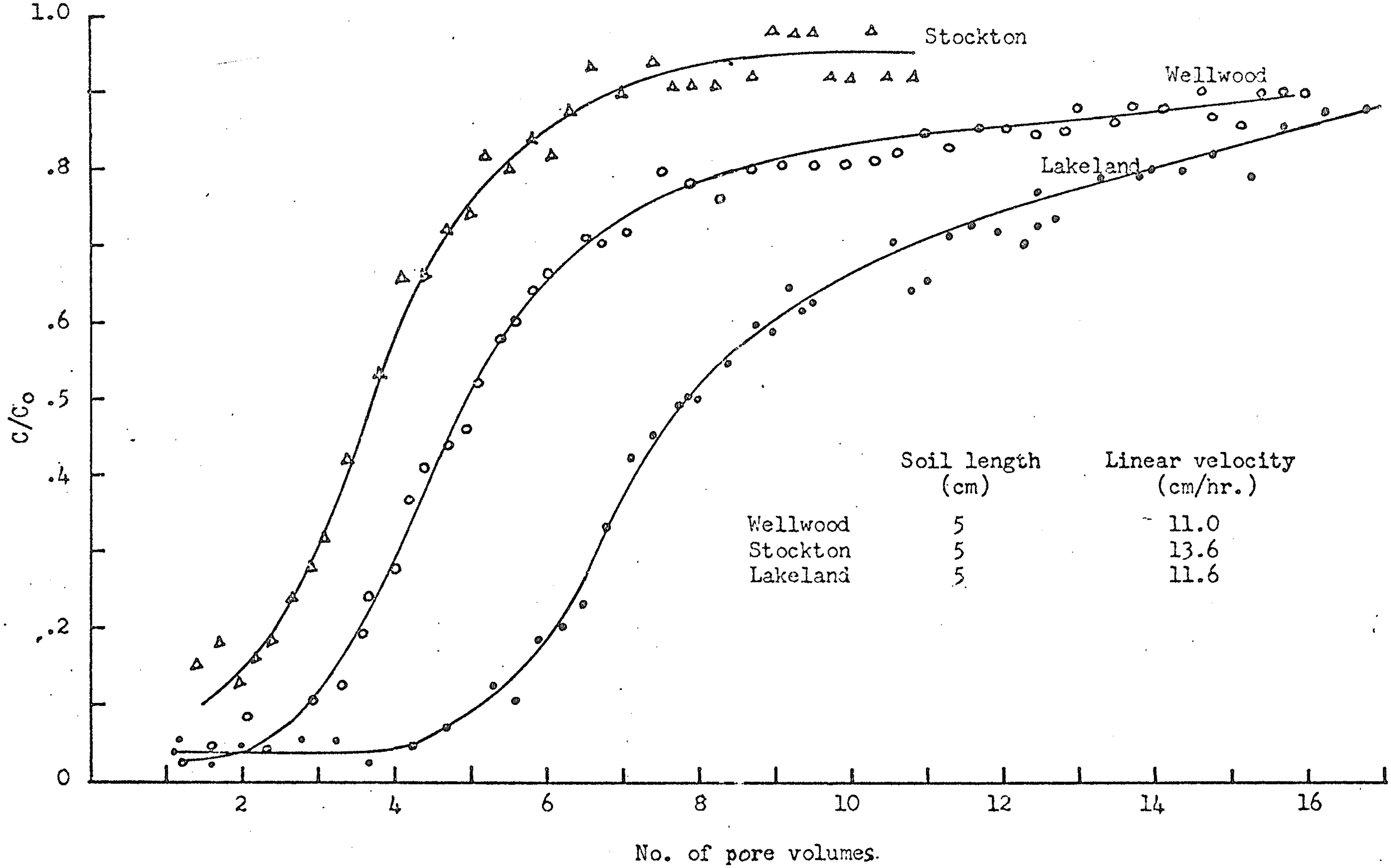


Figure 6. Breakthrough curves for phosphate for the experimental soils.

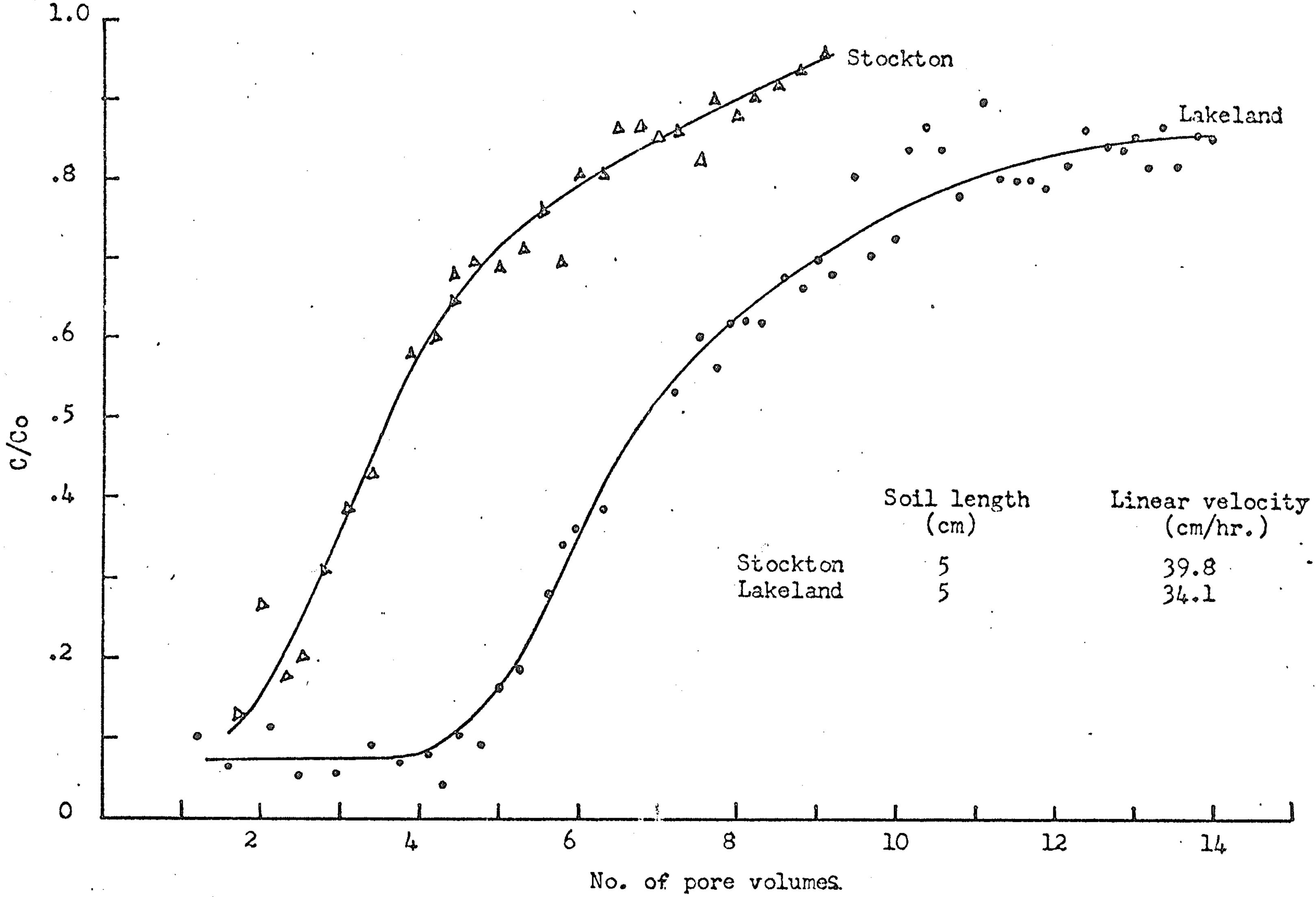


Figure 7. Breakthrough curves for phosphate from the experimental soils.

(Figure 3). This implies that the contact time of the phosphate solution with the Stockton soil did not affect the rate of movement of phosphate at the fast flow rate, but did indeed affect the rate of movement at the slow flow rate.

The breakthrough curve obtained using the Lakeland soil was quite different from the previous 2 figures (Figure 3 and 6). The front of the breakthrough curve up to $C/C_o =$ 0.5, obtained with a 5 cm length at the faster flow velocity (Figure 7) had a sharper slope than the slow flow velocity in Figure 3 and Figure 6. The ends of the curve (Figure 7) are quite different from Figure 3 and Figure 6 and the curve did not reach $C/C_o = 1$ within the experimental period. The curve was shifted to the left as compared to that of Figure 6 and its magnitude was close to 1 pore volume.

4.1.2.2 15 CM LENGTH OF SOIL COLUMN

The breakthrough curves obtained using a 15 cm length of the soil column with a fast flow rate are shown in Figure 8. The flow rate applied to obtain Figure 8 was 2 times greater than in Figure 5. The shape and position of the breakthrough curve from the Lakeland soil at the faster velocity (Figure 8) is identical to the breakthrough curve at the slower velocity (Figure 5). This may indicate that the contact time of the phosphate solution with the Lakeland soil did not affect the rate of movement of phosphate within this time duration.

TABLE IV

SUMMARY OF MISCIBLE DISPLACEMENT FOR THE THREE EXPERIMENTAL SOILS WITH 5 CM LENGTH

Soil	Soil length (cm)	Dry wt. of soil (gm)	Water content in soil (gm.)	Average linear Velocity (cm/hr.)	p-fixed (μeq/100gm)	Miscible displacement		Probability plots of miscible displacement	
						Figure	No. of pore volumes at $C/C_o = 0.5$	Figure (appendix)	slope
Well-wood	5	19.5	15.9	11.0	473	6	5.0	23	-1.68
Stock-ton	5	27.9	12.9	13.6	181	6	3.7	23	-1.80
Lake-land	5	17.6	16.9	11.6	973	6	7.9	23	-1.60
Stock-ton	5	32.1	13.9	39.8	164	7	3.6	24	-2.06
Lake-land	5	17.2	16.4	34.1	790	7	6.8	24	-1.82

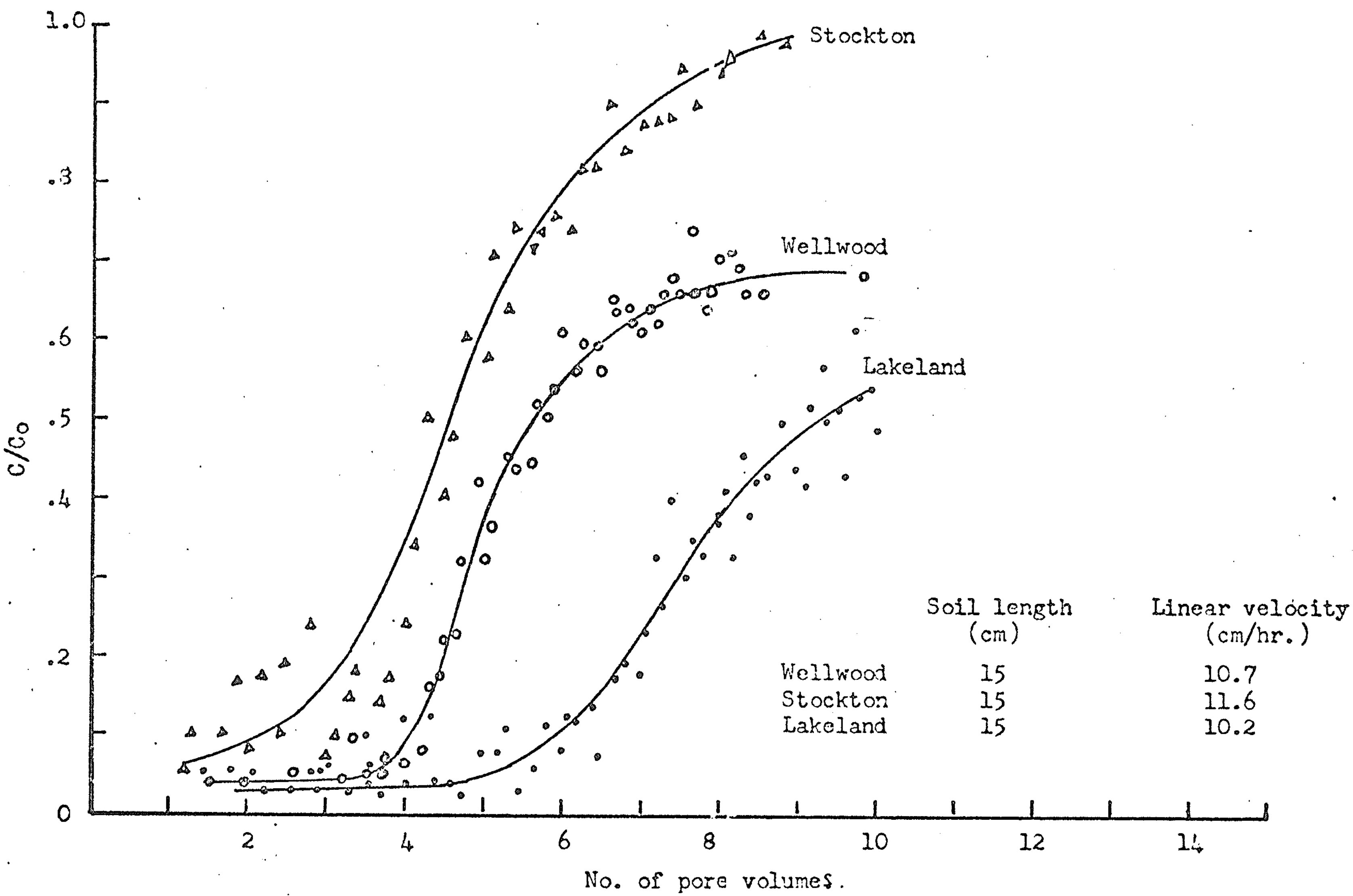


Figure 8. Breakthrough curves for phosphate from the experimental soils.

The breakthrough curves obtained using the Wellwood and the Stockton soils with a 15 cm length with the faster velocity are quite different from the previous figure obtained with the slower flow velocity. The fronts of the breakthrough curves up to $C/C_o = 0.5$ obtained with the faster flow rate are slightly steeper than those with the slower velocity. The ends of the curves are quite different, and both curves did not reach $C/C_o = 1$ within the experimental period. Thus it is quite obvious that there might be some time dependent reaction occuring within the two soils.

The number of pore volumes to attain $C/C_o = 0.5$ is dependent upon the flow velocity. Also the slope of the probability plots showed the value to be dependent upon the flow velocity. From $C/C_o = 0.5$ on the slopes there seems to be a change to new values.

The amount of phosphate fixed shown in Table V was calculated by taking the value up to 10 pore volume.

A still faster flow rate was applied to a 15 cm. soil column. The flow rate was approximately 3 times faster than the previous experiment. The results are shown in Figure 9.

The Wellwood clay loam seem to disperse with the addition of KH_2PO_4 solution and the solution permeability decreased with time and it was not possible to control the flow velocity from the soil column. Therefore the experiment using a 15 cm length of the Wellwood soil at this velocity was discarded in Figure 9.

The breakthrough curves obtained using the Stockton and Lakeland soils at the flow velocity of 31.9 and 30.3 cm per hour are quite different from the two previous figures (Figure 5 and 8). The shape of the curves at the greater velocity (Figure 9) had the sharpest slope of them all while it was flatter for the slower velocity (Figure 5 and 8.) the shape of the front of the breakthrough of the Lakeland soil (Figure 9) up to $C/C_o = 0.5$ was very similar to the previous curve in Figure 5 but it was different from the previous curve in Figure 8. The front of the curve in Figure 9 was sharper than that in Figure 5. The ends of the curves are quite different from the previous figures (Figure 5 and 8) and both curves did not reach $C/C_o = 1$ within the experimental period as discussed in Figure 4.

The number of pore volumes to attain $C/C_o = 0.5$ in Table V is dependent upon the flow velocity. Also the slope of the probability plots showed the value to be dependent upon the flow velocity.

The amount of phosphate fixed, shown in Table V was calculated by taking the values up to 10 pore volumes.

4.1.3 THE EFFECT OF CONTACT TIME

The effect of contact time can be visualized by comparing the results shown in Figure 6 and in Figure 9. The results in Figure 6 obtained using a 5 cm. length with a flow rate of approximately 12 cm per hour and the results in Figure 9 obtained using a 15 cm length with a flow rate of 31 cm per

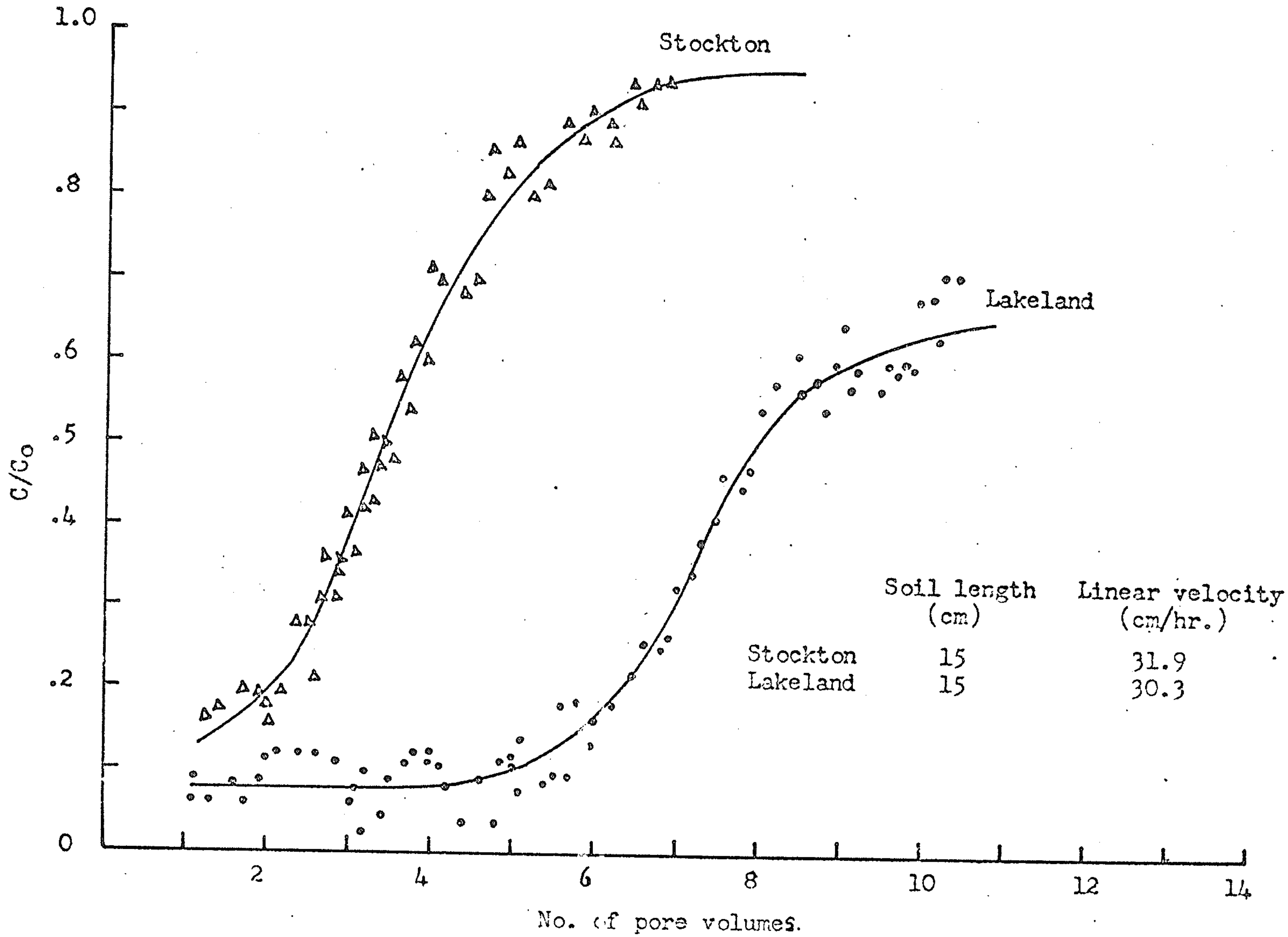


Figure 9. Breakthrough curves for phosphate from the experimental soils.

TABLE V

SUMMARY OF THE MISCIBLE DISPLACEMENT FOR THE THREE EXPERIMENTAL SOILS WITH 15 CM LENGTH

Soil	Soil Length (cm)	Dry wt. of soil (gm.)	Water content in soil (gm.)	Average linear Velocity (cm/hr.)	p-fixed (µeq/100gm)	Miscible displacement		Probability plots of miscible displacement	
						Figure	No. of pore volumes at $C/C_o = 0.5$	Figure (appendix)	slope
Well-wood	15	57.4	46.5	10.7	371	8	5.6	25	-2.81
Stock-ton	15	68.6	40.5	11.6	319	8	4.6	25	-3.0
Lake-land	15	49.5	47.0	10.2	1,054	8	9.2	25	-1.77
Stock-ton	15	83.6	39.4	31.9	160	9	3.4	26	-1.93
Lake-land	15	47.9	46.3	30.3	958	9	8.0	26	-1.54

hour both had approximately 30 minutes of contact time between solution and the soils. The shape and position of the breakthrough curves from both the Stockton and the Lakeland soils with a 5 cm length of soil column are almost identical to the breakthrough curves with a 15 cm length of soil column.

The numbers of pore volumes of solution to attain $C/C_o = 0.5$ of the 5 and 15 cm length of soil columns in Figure 6 and Figure 9 are the same. Also the slope of the probability plots showed the value to be the same. From $C/C_o = 0.5$ on the slopes there seems to be a change to new values. It seems that the contact time of the solution with the soils has a great effect upon controlling the breakthrough curve.

4.2 THE RATE OF ADSORPTION OF ORTHOPHOSPHATE BY SOILS

The results of the rate study of adsorption of phosphate by the experimental soils at various velocities are presented in Table VI and VII. The soil length of 0.5 cm was chosen for the soils. It was assumed that there was negligible effect of dispersion during passage of phosphate through the column of the 0.5 cm soil length. Also it was assumed that the rate of increase in the phosphate concentration in the effluent was of the first order reaction. The difference in the concentration between the initial and any fraction, $(C_o - C)$, were plotted against time on semilog paper. The summary in Table VI and VII are the averages of the two experiments. Complete results are shown in Figure 10 and 11.

4.2.1 SLOW FLOW RATE

Figure 10 shows that the rates of adsorption of orthophosphate by the soils are linearly expressible in a semilog manner and are quite different depending upon the soils. The slope of the curve represents the experimental rate constant of adsorption and indicates how fast the interaction process occures in the soil. The slope of the lines are -.048, -.059 and -.019 for the Wellwood, Stockton and Lakeland soils, respectively. They indicate that the interaction between soil and phosphate in solution was a rather slow process.

The exponential decay equations for the three soils are listed in Table VI. The equation was calculated by using the least square method.

The magnitude of the phosphate fixation of the three soils are 407,293, 682 μeq/100 gm., respectively. The Stockton sandy loam with pH of 7.2 had the lowest phosphate fixation, while the Lakeland silt loam with pH of 7.8 and containing 13.5 % $CaCO_3$ had the highest phosphate fixation. The Wellwood clay loam with pH of 5.5 had an intermediate phosphate fixation. The results showed that the amounts of phosphate fixation vary inversely as the magnitude of the slope. The Lakeland soil had the highest phosphate fixation and the lowest value of the slope while the Stockton soil had

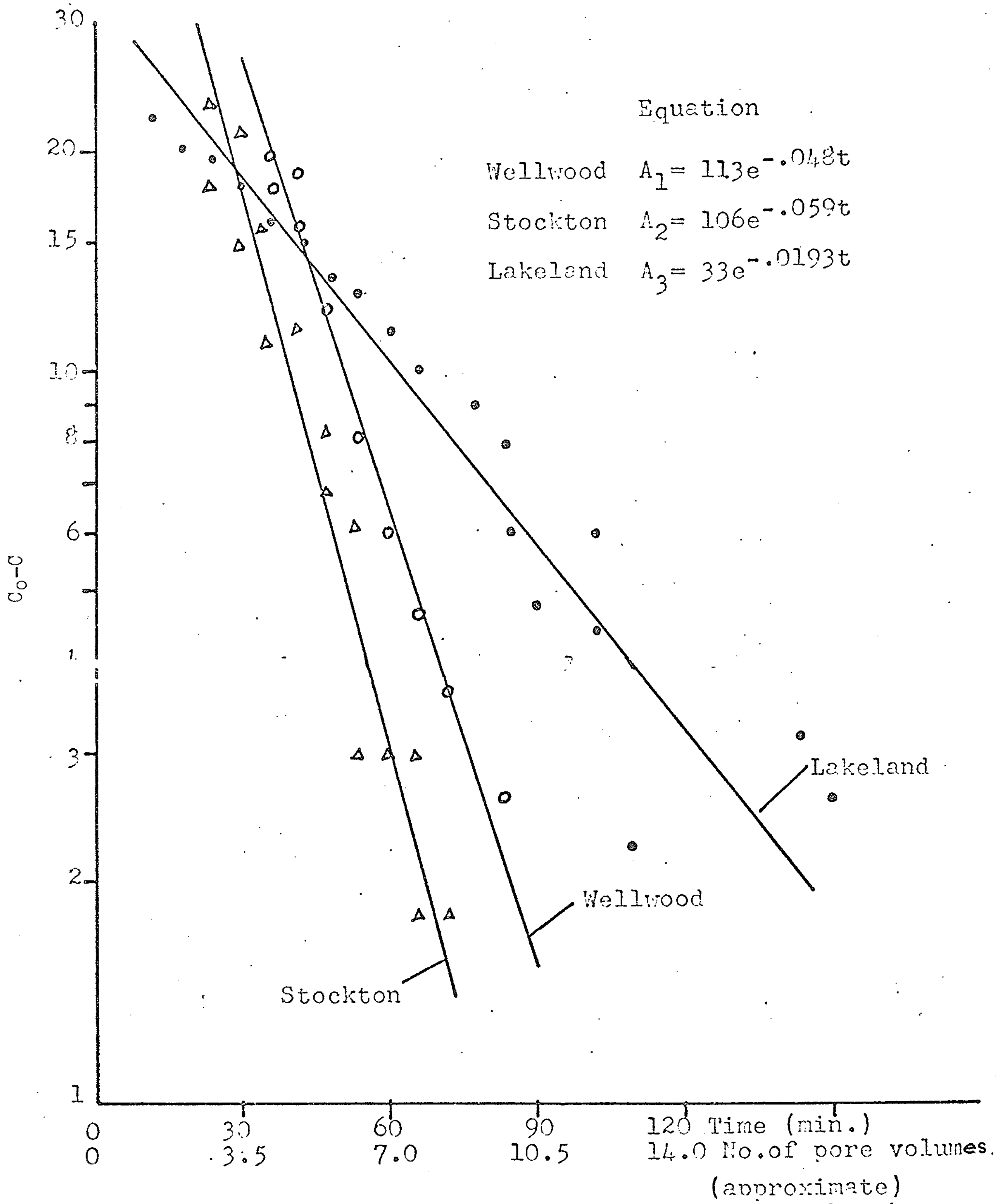


Figure 10. Semi-log plots of the rate of orthophosphate adsorption by the three soils with the slow flow rate.

the lowest phosphate fixation and the highest value of the slope. The Wellwood had an intermediate phosphate fixation and an intermediate value of the slope.

4.2.2 FAST FLOW RATE

Figure 11 shows the rate of adsorption of orthophosphate by the 0.5 cm length of the Wellwood clay loam, Stockton sandy loam and Lakeland silt loam with the fast flow velocity. The flow velocity applied in Figure 11 was two times greater than the flow velocity in Figure 10. The slopes of the three soil are -.091, -.055 and -.037, respectively. The rate of phosphate adsorption by the Wellwood rapidly decreased with time while the Stockton and Lakeland soils were gradually decreased with time (Figure 11).

The rate of phosphate adsorption of the Stockton soil with slow and fast flow velocities were .059 and .055 per min., respectively (Table VI and VII). Comparing the results with those listed in the tables it was noticed that the flow velocity did not affect the rate of phosphate adsorption in the Stockton soil. The rate of phosphate adsorption of the Wellwood and Lakeland soils were affected by the flow velocity. The adsorption rate of the Wellwood and Lakeland soils at the slow velocity were .048 and .019 per min. while at the fast flow velocity they were .091 and .037 per min. respectively. The rate of phosphate adsorption of the Wellwood and Lakeland soils at the flow velocities of 3.6 and 3.7 cm per hour were two times less than that at the flow velocities

TABLE VI

SUMMARY OF THE ADSORPTION BY THE
THREE EXPERIMENTAL SOILS WITH THE SLOW FLOW RATE

Soil	Dry wt. of soil (gm.)	Water content in soil (gm.)	Linear Velocity (cm/hr)	P-fixed (μeq/100gm)	Slope	Equation
Wellwood	3.3	2.25	3.6	407	-.048	$A_1 = 113e^{-.048t}$
Stockton	4.5	2.4	3.6	293	-.059	$A_2 = 106e^{-.059t}$
Lakeland	3.5	2.5	3.7	682	-.019	$A_3 = 33e^{-.0193t}$

of 7.7 and 6.9 cm per hour. This indicates that the rates for the two soils are dependent upon the flow velocity almost in a linear manner. This may mean that there are at least two distinct reaction rates in the Wellwood and the Lakeland soils with different magnitudes, one fast and the other slow.

The magnitudes of phosphate fixation of the three soils are 350, 184 and 412 μeq/100 gm, respectively. The Stockton soil had the lowest phosphate fixation while the Lakeland silt loam had the highest phosphate fixation. The Wellwood clay loam had an intermediate phosphate fixation.

The relationship between the rate constant and the magnitude of the phosphate fixation does not seem to hold at this fast flow rate. This inconsistency lies on the fact that the Wellwood soil with the fast flow rate had a relatively slow rate at the very early period of the adsorption experiment. The amount of phosphate fixation which was summarized in Table VI, and VII were calculated by taking the value of C/C_o up to 1. Theoretically, the phosphate fixation in soil at different flow velocities, which was based on equal weight of soil samples, should have had the same value. The results from this study as presented in Table VI, VII and VIII indicate different fixation. It is not known why these inconsistent results were obtained. One of the probable reasons is that the determination of C near C_o can never be determined very accurately and the experiment was terminated before C reached to C_o.

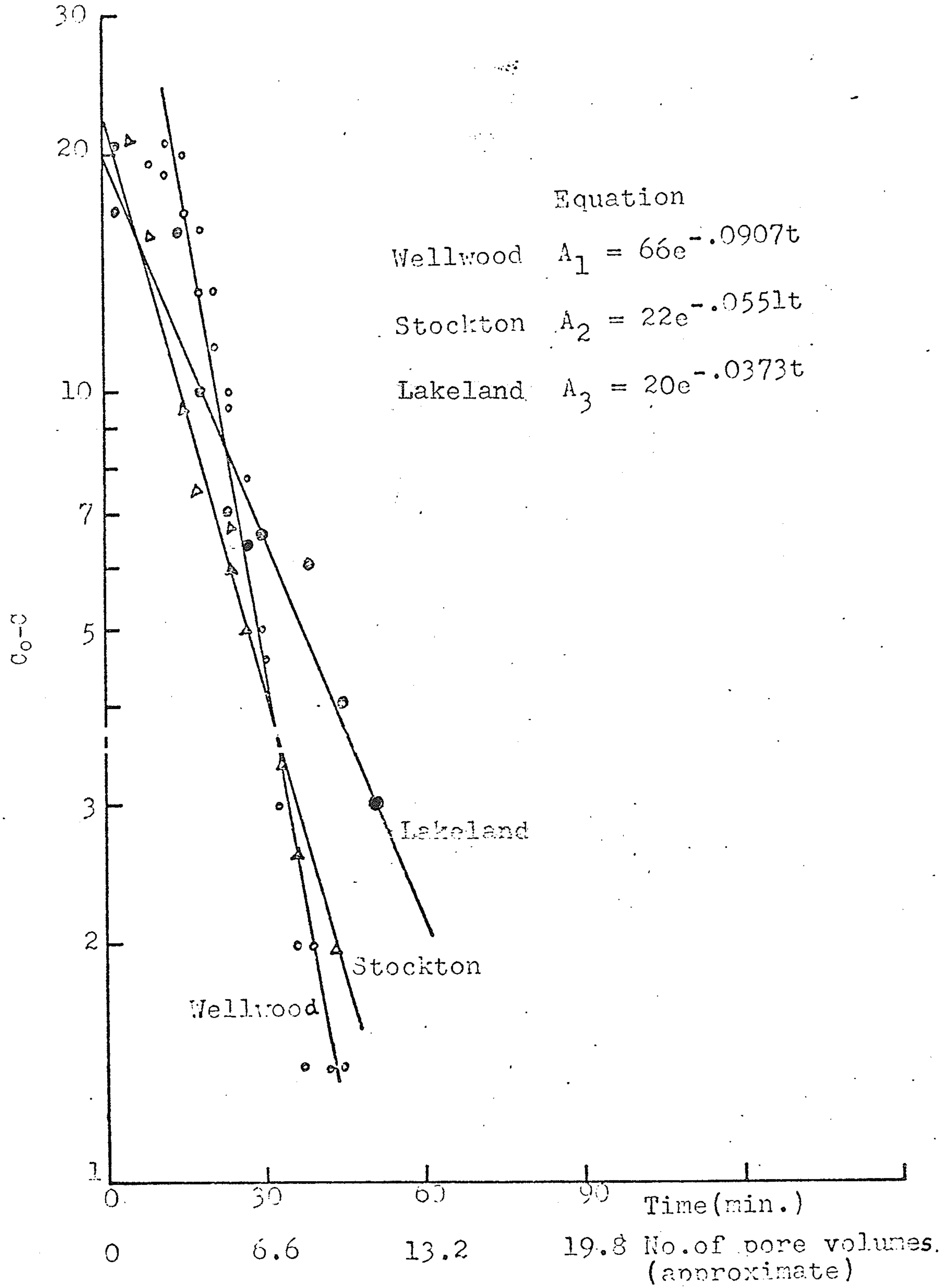


Fig. 11 Semi-log plots of the rate of orthophosphate adsorption by the three soils with the fast rate.

TABLE VII

SUMMARY OF THE ADSORPTION EXPERIMENT BY THE THREE SOILS WITH THE FAST FLOW RATE

Soil	Dry wt. of soil (gm)	Water content in soil (gm)	Linear velocity (cm/hr.)	P-fixed (μeq/100gm)	Slope	Equation
Wellwood	3.3	2.2	7.7	350	-.0907	$A = 66e^{-.0907t}$
Stockton	4.5	2.3	7.0	184	-.0551	$A = 22e^{-.0551t}$
Lakeland	3.5	2.7	6.9	412	-.0373	$A = 20e^{-.0373t}$

4.3 THE RATE OF DESORPTION OF ORTHOPHOSPHATE BY SOILS

The results of the experimentally measured phosphate desorption from the 0.5 cm length of the three experimental soils at various velocities are given in Figure 13 to Figure 18 and summarized in Table VIII and IX. The desorption of phosphate from soil was studied by using a ^{32}P labelled phosphate solution, 25 ppm P, to saturate the soil column and then leaching the column with distilled water. At the low concentration of P, the ^{32}P measurement had less error than the ^{31}P determination. It was assumed that there was negligible effects of dispersion during the leaching of the 0.5 cm soil with distilled water. The rate of decrease in the phosphate concentration in the effluent was assumed to be a first order reaction. The activities of the effluent fractions from the soil column were plotted against time on semilog paper as shown in Figure 13 to Figure 18. The summarized results in Table XIII and IX are the averages of duplicate runs.

4.3.1 SLOW FLOW RATE

Figure 13 shows the rates of desorption of orthophosphate from the Wellwood soil in a semilog manner. The slope of the curve represents the experimental rate constant of desorption and indicates how fast the phosphate is leached out from the soils. The leaching pattern of phosphate of the Wellwood soil showed an initial rapid decrease of phosphate followed by a very slow process.

The exponential decay equation for the Wellwood soil is listed in Table VIII. The exponential decay equation was calculated by plotting the activity of ^{32}P in the effluent fraction against time on a semilog graph. A typical curve was shown in Figure 12.

From the curve, the phosphorus concentration decreased rapidly at the first but then decreased gradually as time increased. A graphical resolution of the multi-exponential curve into an individual exponential term was carried out.

First, the linear portion of the gradual decrease in the curve was determined by using the simple regression technique. The equation corresponds to

$$\ln A_2 = \ln B_2 - k_2 t$$

where: A_2 = ^{32}P activity per unit volume of effluent

B_2 = constant

k_2 = slope of regression line, rate constant

t = time as dependent variable

After the values of B_2 and k_2 were obtained, A_2 was calculated using the equation:

$$A_2 = B_2 e^{-k_2 t}$$

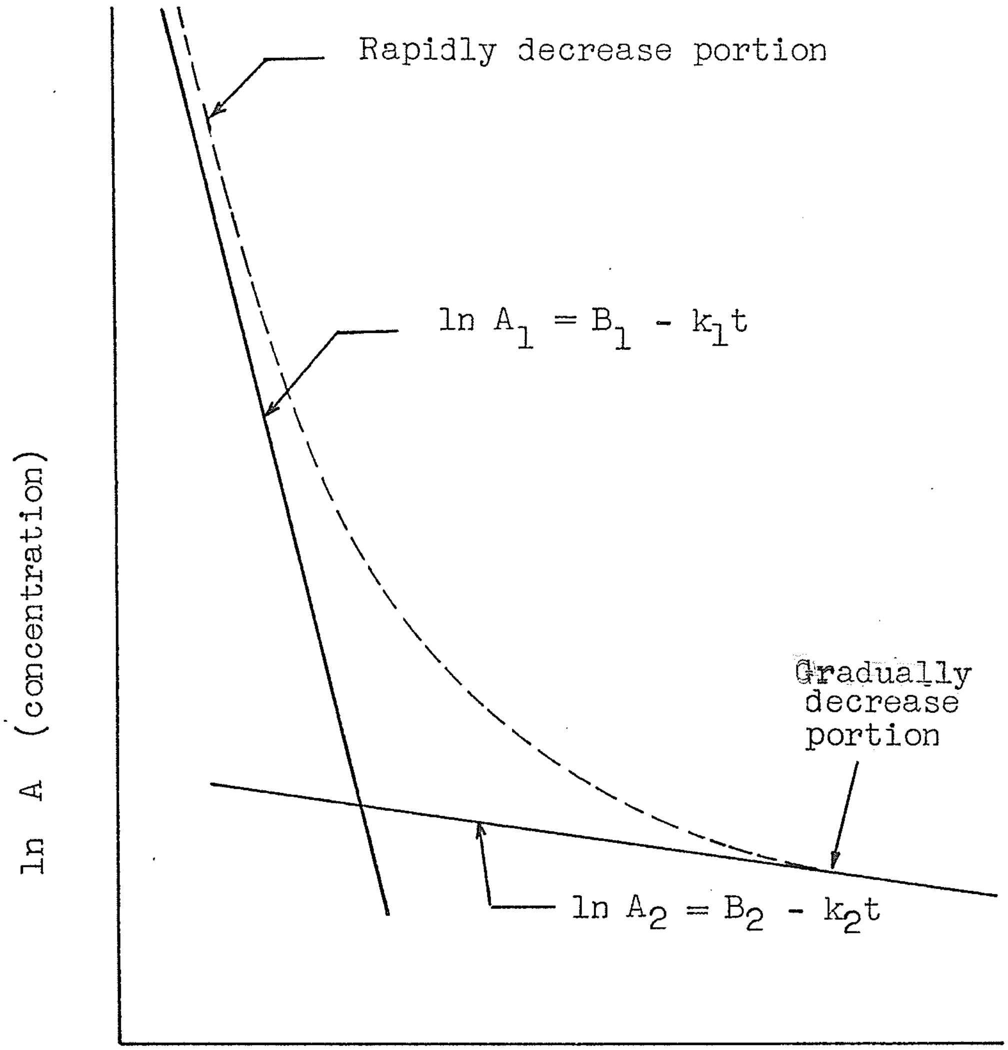


Figure 12. Semilog plots of the activity of ^{32}P against time.

and was subtracted from the experimentally obtained A. From the newly obtained values another regression line corresponding to

$$A_1 = B_1 e^{-k_1 t} \qquad \text{was obtained}$$

The approximate linear curves of the two required equations are shown in Figure 12. A combination of the two equations will form the exponential decay equation, which is

$$A = B_1 e^{-k_1 t} + B_2 e^{-k_2 t}$$

The average initial slope of the exponential decay equation of the soils was calculated by differentiation of the exponential decay equation.

$$\frac{d\ln A}{dt} = -\frac{k_1 B_1 e^{-k_1 t} - k_2 B_2 e^{-k_2 t}}{B_1 e^{-k_1 t} + B_2 e^{-k_2 t}}$$

when t is small, $\frac{d\ln A}{dt}$ is:

$$\frac{d\ln A}{dt} \quad -\frac{(k_1 B_1 + k_2 B_2)}{B_1 + B_2}$$

The initial slope of the exponential decay equation is, therefore, $-\frac{(k_1 B_1 + k_2 B_2)}{B_1 + B_2}$ at the early stage, and is k_2 at the latter stage.

The initial slope of the desorption rate curve of the Wellwood soil is -.0431. It showed that the rate of phosphate desorption from the soil was a rather slow process. The slopes of the exponential decay equation of phosphate desorption at the initial rapid and final slow process are -.0488 and -.0092, respectively.

The amount of phosphorus adsorbed by the Wellwood soil was 854 μeq/100 gm. The values were calculated from the difference between the total activity of phosphorus added and the total activity of the phosphorus leached out from the soil column up to $C/C_o = 1$. The amount of activity of

$$^{32}P \text{ adsorbed, by soil} = \left(\frac{cpm}{ml}\right) V_T \text{ standard} - \sum_{n=1}^{n} \left(\frac{cpm}{ml}\right)_n \cdot V_n$$

where V_T is the total volume of solution collected until $C/C_o = 1$ was reached, V is the mls collected per fraction, and cpm is the count per min. To obtain the value of the total amount of P fixed, the total activity of ^{32}P retained by the soil was divided by the specific activity.

The amounts of phosphate adsorbed and phosphate desorbed of the Wellwood soil were 854, 687 μeq/100 gm. respectively. Not all of the 32P adsorbed by the soil was desorbed during the experiment.

Figure 14 shows the desorption rate of phosphate from the Stockton soil. The desorption pattern showed an initial rapid decrease of phosphate, followed by a very slow decrease.

The exponential decay equation of the Stockton soil is shown in Table VIII. The slopes of the initial rapid decrease of phosphate and the gradual decrease of phosphate

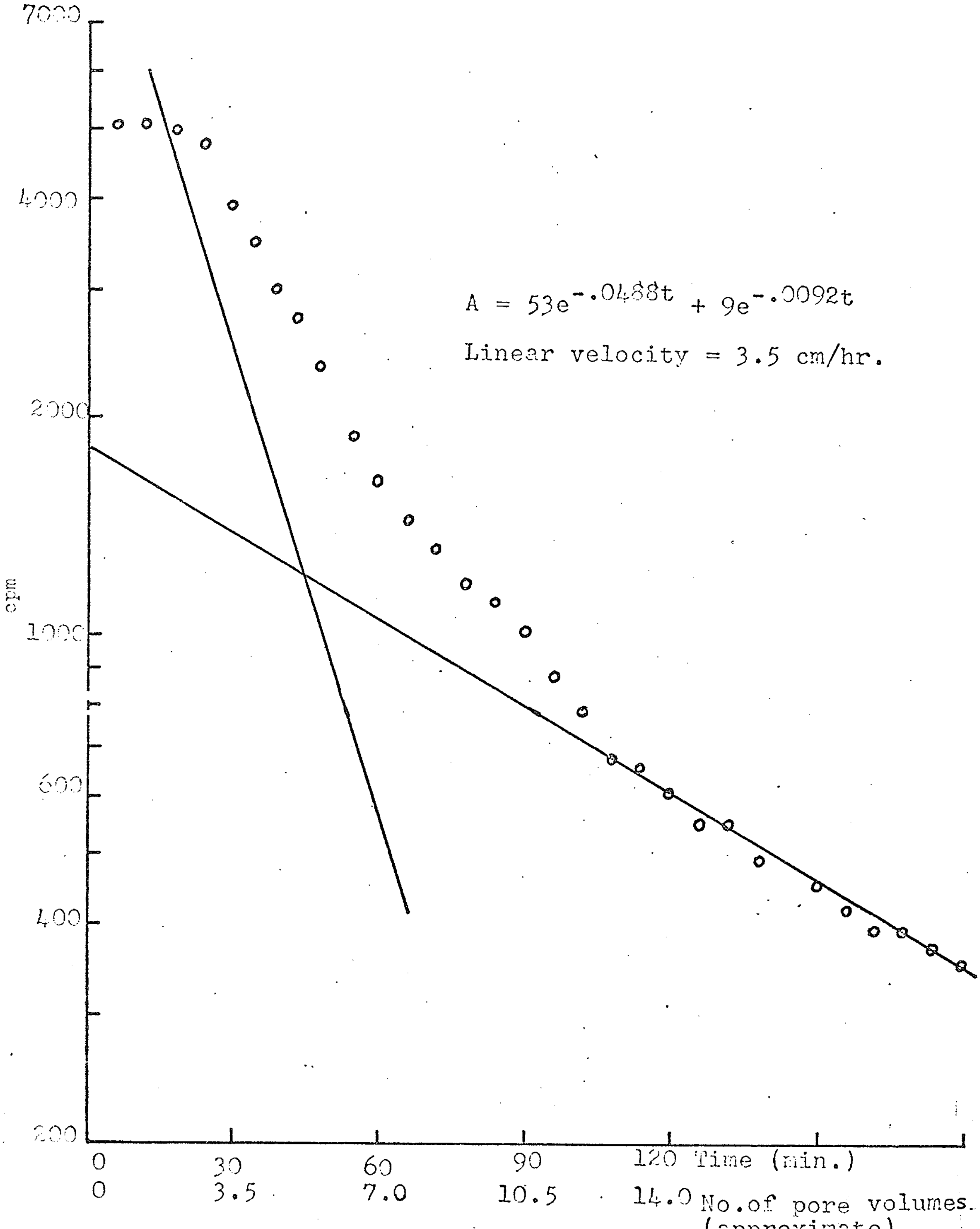


Figure 13. Semi-log plots of the desorption from the Wellwood soil against time.

in the exponential equation were -.0616 and -.0089, respectively. The initial slope of the desorption curve of the Stockton soil was -.0553 while the Wellwood soil was -.0431. This showed that the desorption rate of phosphate from the Stockton soil was faster than that of the Wellwood soil.

The amounts of phosphate adsorbed and phosphate desorbed of the Stockton soil were 600 and 428 ueq/100 gm, respectively. The magnitude of phosphate adsorbed and phosphate desorption of the Stockton soil was less than those of the Wellwood soil.

Figure 15 shows the desorption rate of phosphate from the Lakeland soil. The desorption pattern of the Lakeland soil was quite different from the Stockton and the Wellwood soils. The desorption of phosphate from the Lakeland showed only a gradual decrease of phosphate.

The exponential decay equation was calculated using the least square method and is listed in Table VIII. The slope of the desorption rate curve of the soil was -.0111. This indicated that the rate of phosphate desorption from the Lakeland soil was a rather slow process.

The initial slope of the Wellwood, Stockton and Lakeland soils are -.0431, -.0553 and -.0111, respectively. This showed that the Stockton sandy loam had the fastest rate of phosphate desorption while the Lakeland clay loam had the slowest rate of phosphate desorption. The Wellwood silt loam had an intermediate rate of phosphate desorption.

The magnitude of phosphate adsorbed and phosphate

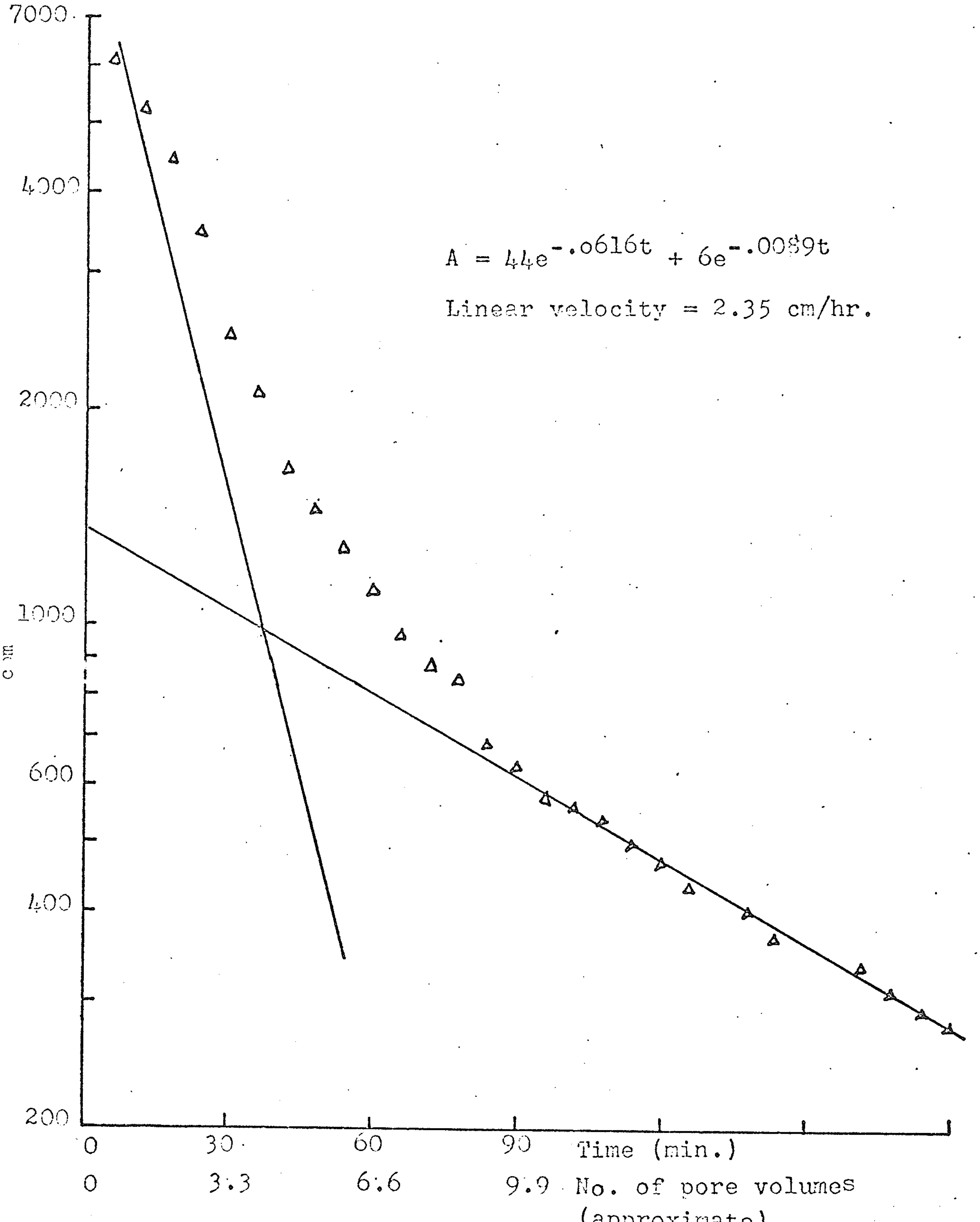


Figure 14. Semi-log plots of the desorption from the Stockton soil against time.

desorbed from the Lakeland soil was 1,506 and 1,018 μeq/100 gm, respectively. The results of the magnitude of phosphate adsorbed and phosphate desorbed of the three soils (Table VIII) showed that the Lakeland soil had the highest value of phosphate adsorbed and phosphate desorbed while the Stockton soil had the lowest phosphate adsorbed and phosphate desorbed. The Wellwood soil had an intermediate magnitude of phosphate adsorbed and phosphate desorbed. The results showed that the magnitude of phosphate adsorbed and phosphate desorbed vary inversely as the value of the slope as shown in Table VIII. Theoretically, the labelled phosphate and the phosphate adsorption of the three soils at different flow velocities, based on equal weight of soil samples, should have the same value. The results from this study as presented in Table VIII indicated different values of adsorption from those listed in the Table VI and VII. The magnitude of phosphate adsorption in Table VIII was calculated using the difference in activities (cpm) between the total activity added and the total activity leaving the soil column. Then the activity (cpm) was converted for the weight by dividing with the specific activity of the standard solution. Undoubtedly there could have been more ^{32}P adsorbed than ^{31}P adsorbed by the soils due to isotopic exchange.

It is interesting to note that the values of k_2 which corresponds to the slower rate of desorption for the three soils are almost identical. The physical meaning of the value was not investigated in this experiment.

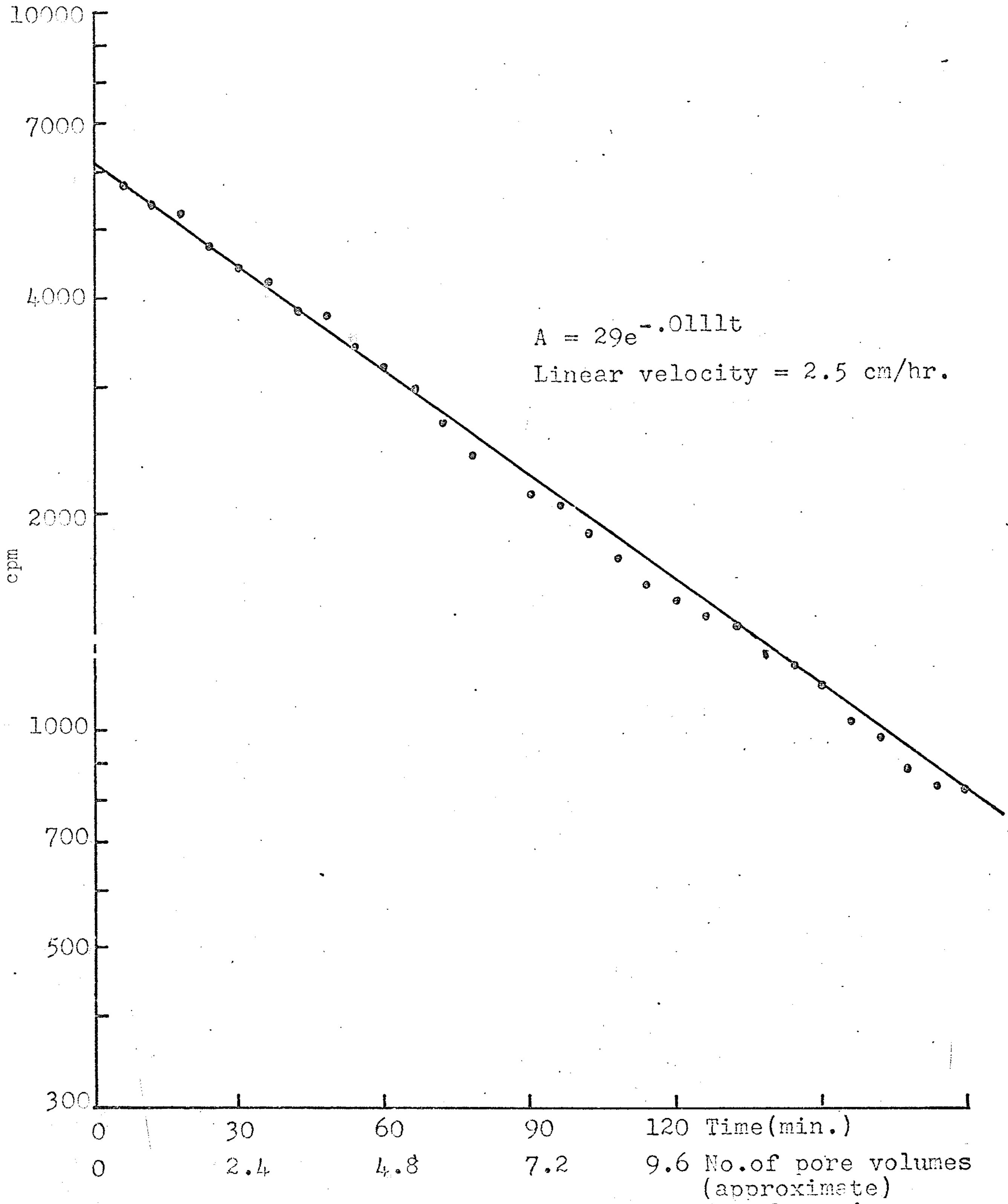


Figure 15. Semi-log plots of the desorption from the Lakeland soil against time

TABLE VIII

SUMMARY OF THE DESORPTION EXPERIMENT FROM THE THREE SOILS WITH THE SLOW FLOW RATE

Soil	Dry wt. of soil (gm)	Water content in soil (gm.)	Linear velocity (cm/hr.)	P-adsorbed (μeq/100gm)	P-desorbed (μeq/100gm)	Initial slope	Equation	Figure
Wellwood	3.3	2.1	3.5	854	687	-.0431	$A = 53e^{-.0488t} + 9e^{-.0092t}$	13
Stockton	4.5	2.35	2.35	600	428	-.0553	$A = 44e^{-.0616t} + 6e^{-.0089t}$	14
Lakeland	3.5	3.3	2.5	1,506	1,018	-.0111	$A = 29e^{-.0111t}$	15

4.3.2 FAST FLOW RATE

Figure 16 shows the desorption rate curve obtained using a 0.5 cm length of the Wellwood soil with twice as fast a flow rate as was presented in Figure 13.

The general characteristics of the desorption patterns of the Wellwood soil at the velocity of 7.7 cm per hour (Figure 16) was quite different from that at the velocity of 3.5 cm per hour (Figure 13). The leaching pattern of the soil with the fast flow velocity was steeper than that with the slow flow velocity. This implies that the shape of the desorption curve is a function of velocity of the leaching solution.

The exponential decay equation of the Wellwood soil with the slow and fast flow velocity was quite different as shown in Table VIII and IX.

The average slope of the Wellwood soil with the slow and fast flow velocity are -.0431, -.0604, respectively. This shows that the phosphate in the Wellwood soil is leached out faster at the faster flow velocity than that at the slow flow velocity.

The phosphorus desorption of the Wellwood soil at the slow and fast flow velocities are 687 and 671, respectively. The result indicates that the amount of phosphate that can be desorbed is not a function of the flow velocity.

The result of the desorption pattern of the Stockton soil obtained using a faster flow velocity, 6.9 cm per hour is

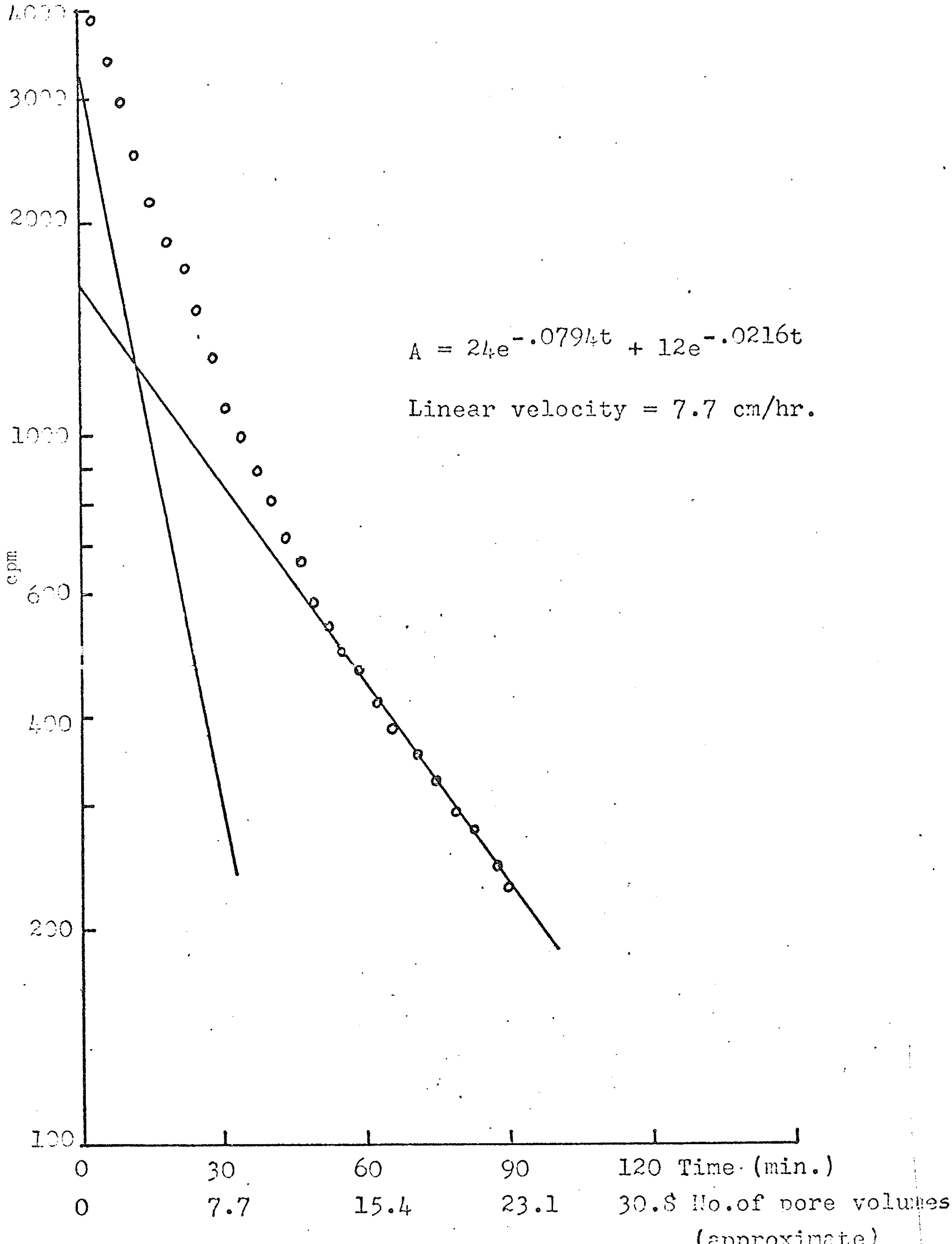


Figure 16. Semi-log plots of the desorption from the Wellwood soil against time.

shown in Figure 17.

The desorption pattern of the Stockton soil at the flow velocity of 6.9 cm per hour was quite different from that at the flow velocity of 2.35 cm per hour (Figure 14). The desorption pattern of the Stockton soil at the faster flow velocity was steeper than that at the slow flow velocity.

The exponential decay equation of the Stockton soil at the slow and fast flow velocities are shown in Table VIII and IX.

The initial slope of the Stockton soil at the fast flow velocity, 6.9 cm/hr. is approximately two times the value corresponding to the slow flow velocity, 2.35 cm/hr. (Table VIII and IX). At the fast flow velocity, the phosphate in the Stockton soil was desorbed faster than at the low flow velocity.

The magnitudes of the phosphorus desorbed of the Stockton soil at the slow and fast flow velocities are 428, and 402 ueq/100 gm, respectively.

Figure 18 shows the desorption of phosphate from the Lakeland at the fast flow velocity was two times greater than that in Figure 15.

The shape of the desorption curve from the Lakeland soil at the flow velocity of 5 cm per hour (Figure 18) was quite different from the desorption curve at the flow velocity of 2.5 cm per hour (Figure 15). The desorption curve from the Lakeland soil at the flow velocity of 5 cm per hour showed an initial rapid decrease of phosphate; followed by a very

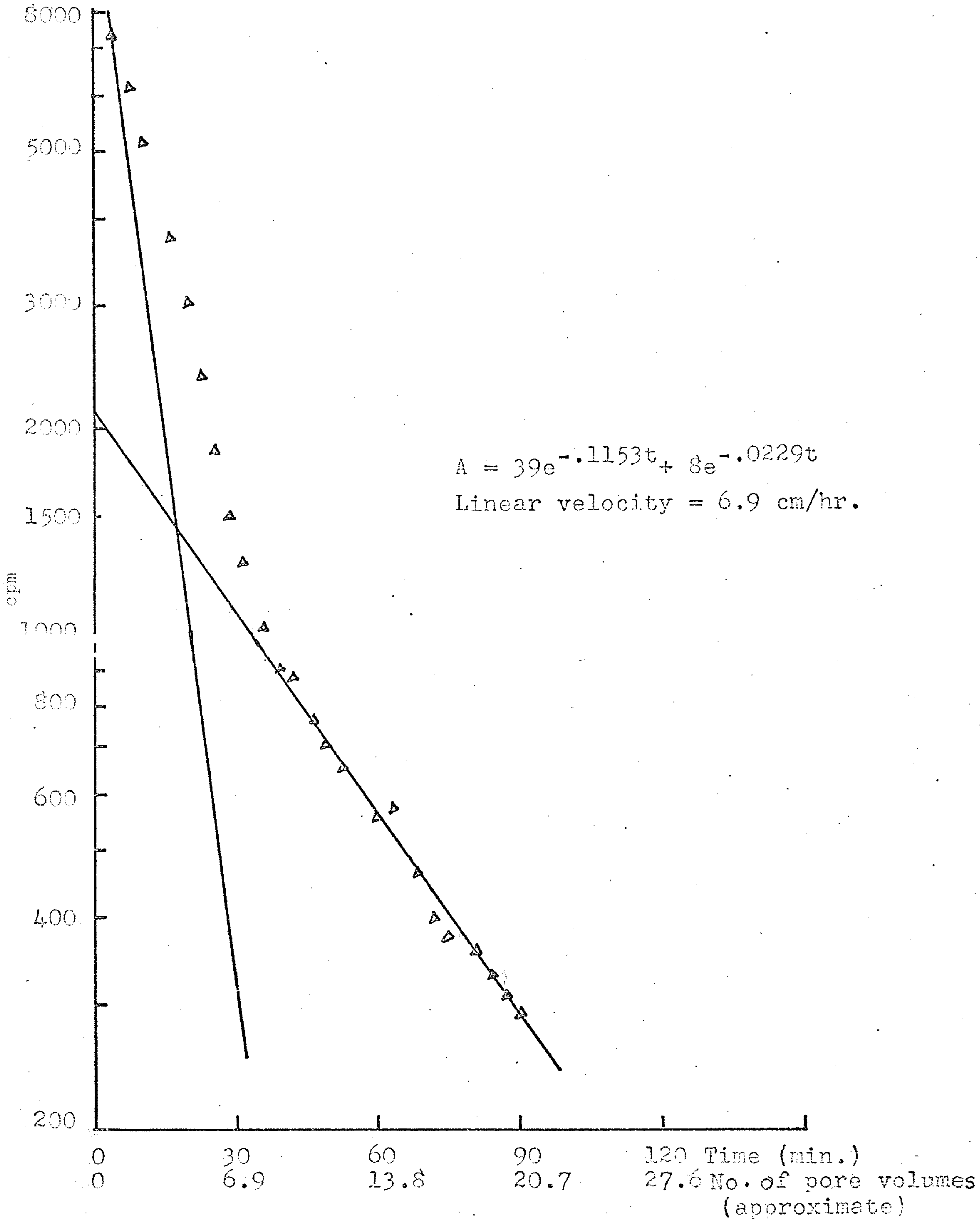


Figure 17. Semi-log plots of the desorption from the Stockton soil against time.

slow decrease in phosphate. At the flow velocity of 2.5 cm per hour, the curve was almost linear.

The exponential decay equation of the Lakeland soil at the fast flow velocity was quite different from the equation at the slow flow velocity as shown in Table VIII and IX. The equation of the Lakeland soil at the slow flow velocity had only one term of the exponential equation while the equation at the fast flow velocity had two terms of the exponential equation.

The average slope of the Lakeland soil at the slow and fast flow velocities are -.0111 and -0.555, respectively. This showed that the value of the slope was dependent of the flow velocity.

The amounts of phosphorus desorbed from the Lakeland soil at the slow and fast flow velocity are 1,018 and 999 μeq/100 gm., respectively. The magnitudes of the phosphate desorption of the three soils are 671, 402 and 999 μeq/100 gm, respectively. The amount of ^{32}P desorbed seems independent of the flow velocity and is only the function of the amount adsorbed. The fractional of ^{32}P desorbed as compared to the amount adsorbed is approximately 70 ~ 75%. The slope of the desorption should be dependent upon the amount adsorbed if there is one exponential decay curve for the desorption. A similar problem was analysed by Cho et al (9). However, paying attention to k_2, which describes the slower rate of desorption, the value seems independent of the soil characteristics. The values as listed in Tables

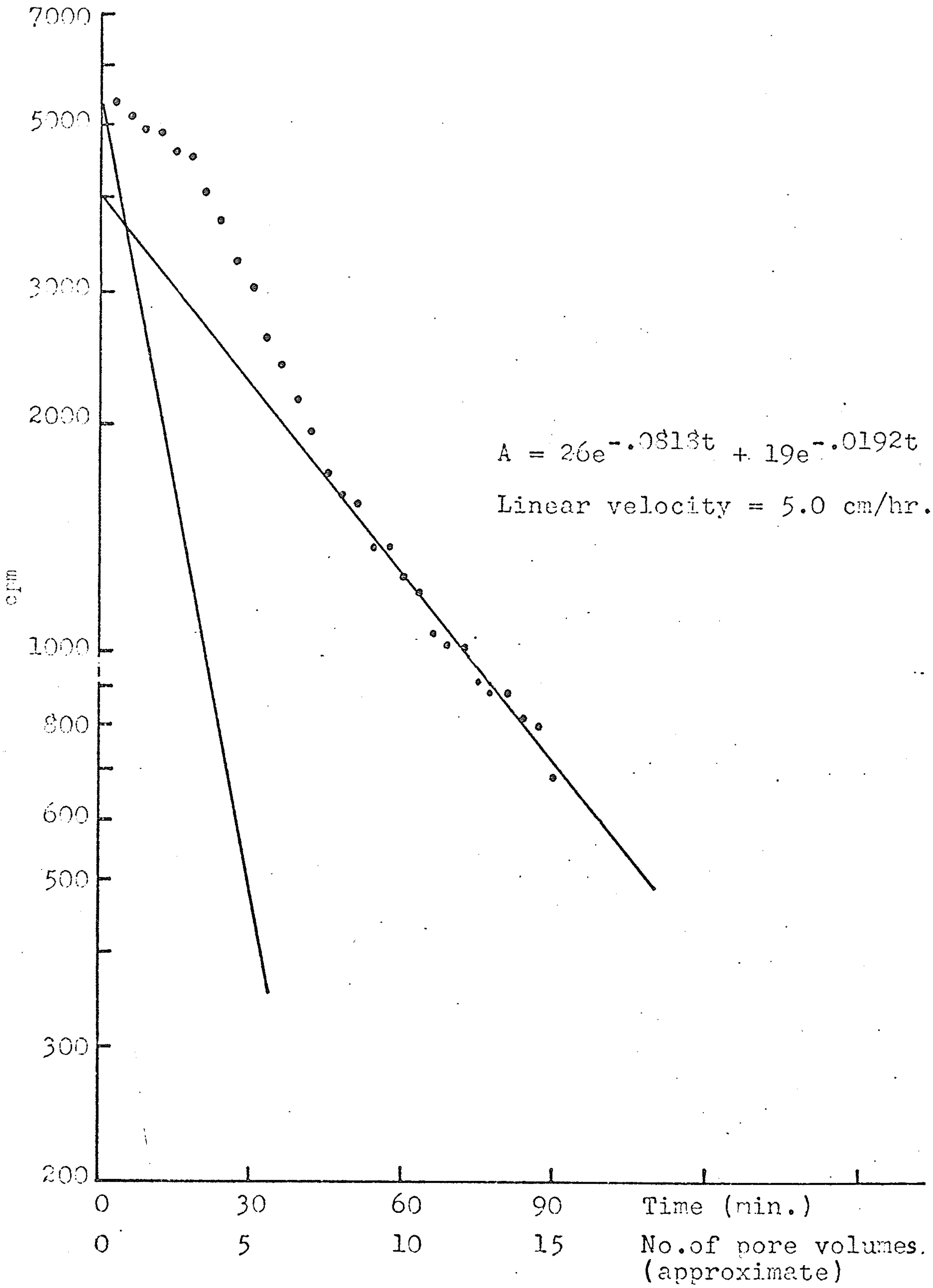


Figure 18. Semi-log plots of the desorption from the Lakeland soil against time.

VIII and IX, even though they are different, if they are divided by the corresponding flow velocities, they become almost identical. The value is close to between .003 ~ .004. The physical meaning of this value should require further investigation.

TABLE IX

SUMMARY OF THE DESORPTION FROM THE THREE EXPERIMENTAL SOILS WITH THE FAST FLOW RATE

Soil	Dry wt. of soil (gm)	Water content in soil (gm)	Linear velocity (cm/hr.)	P-desorbed (ueq/100gm)	Initial slope	Equation	Figure
Wellwood	3.3	2.1	7.7	671	-.0604	$A = 24e^{-.0794t} + 12e^{-.0216t}$	16
Stockton	4.5	2.35	6.9	402	-.0998	$A = 39e^{-.1153t} + 8e^{-.0229t}$	17
Lakeland	3.5	3.3	5.0	999	-.0555	$A = 26e^{-.0818t} + 19e^{-.0192t}$	18

CHAPTER V

CONCLUSIONS AND SUMMARY

The effects of soil-phosphate interaction upon convective transport of orthophosphate in the three soils, Wellwood clay loam, Stockton sandy loam and Lakeland clay loam were studied.

The following results were obtained:

A.) Miscible displacement

Soil columns of the following lengths 15, 7.5, 5 and 3 cm were chosen for the study. A solution of 25 ppm P was fed onto the surface of the soil with various flow velocities.

I The effect of soil length

The breakthrough curves of the soils were quite different among the soils. The breakthrough curve appeared earlier indicating a faster rate of movement of phosphate in the Stockton soil than in the other soils. The Lakeland soil which had 13.8% free lime exhibited the maximum retardation of the phosphate movement.

In general, the breakthrough curves were independent of the soil length for the Stockton soil. However, the curves became flatter with increasing soil length for the other soils. The front of the breakthrough curves and the number of pore volumes to attain $C/C_o = 0.5$, however, were almost independent of the soil length. This was clearly indicated by the probability plots of the breakthrough curves. The slopes of the probability plots were the same for all the soils.

The amount of phosphate fixed by the three soils up to 10 pore volumes was almost constant but the total quantity increased with increasing soil length.

II The effect of flow velocity

Two soil lengths (5 and 15 cm.) of the three soils and various flow velocities were chosen for this study. The slope of the probability plot as well as the number of pore volumes to attain $C/C_0 = 0.5$ changed with the flow velocity. The degree of change was more pronounced on the Wellwood and the Lakeland soils which had higher fixation capacity than the Stockton soil.

III The effect of contact time

Both the 5 cm column with the flow rate of 12 cm per hour and the 15 cm column with flow rate of 31 cm per hour had thirty minutes contact time between the solution and the soils. The shape and position of the breakthrough curves from both the Stockton and the Lakeland soils with a 5 and 15 cm length of soil column are almost identical. The number of pore volumes and slopes of the probability plots show the value to be the same. It seems that the contact time of the solution with the soils has a great effect upon controlling the breakthrough curve.

B.) Rate of adsorption of orthophosphate by soil

A soil column of 0.5 cm was selected for this study. A phosphate solution was applied at the different flow rates.

The rates of the adsorption of orthophosphate by the Wellwood, Stockton and Lakeland soils are linearly expressible in a semilog manner. The slopes of the linear plot were quite different depending upon the soils.

The slopes of the line were -.048, -.059 and -.019 per min. for the slow flow rate and were -.091, -.055 and -.037 per min for the fast flow rate for the Wellwood, Stockton and Lakeland soils, respectively. This indicated that the interaction between soil and phosphate in solution was a rather slow process and was dependent upon the soil characteristics and flow rate.

The Stockton sandy loam with pH of 7.2 had the lowest phosphate fixation, while the Lakeland silt loam with pH of 7.8 and containing 13.8 % $CaCO_3$ had the highest phosphate fixation. The Wellwood clay loam had an intermediate phosphate fixation.

The amounts of phosphate fixation varied inversely with the magnitude of the slope for the three soils at a slow flow velocity but it did not seem to hold at a fast flow velocity.

C.) Rate of desorption of orthophosphate from soil

The leaching pattern of phosphate from the Wellwood and Stockton soils showed an initial rapid decrease of phosphate followed by a very slow process. The desorption of phosphate from the Lakeland soil showed only a gradual decrease of phosphate at the slow rate of leaching.

The slopes of the three soils at the slow flow rate were -.0431, -.0553 and -.0111 per min respectively. At the fast flow rate the corresponding values of the slope were -.0604, -.0998 and -.0555, respectively. This showed that the value of the slope was dependent on the flow velocity and the rate of phosphate desorption from the soil was a rather slow process.

The value of the rate constant, k_2 which described the slower rate of desorption seemed independent of the soil characteristics.

The amount of ^{32}P desorbed seemed independent of the flow velocity and was only the function of the amount adsorbed. About 70 – 75% of the adsorbed ^{32}P was desorbed by the leaching process.

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APPENDICES

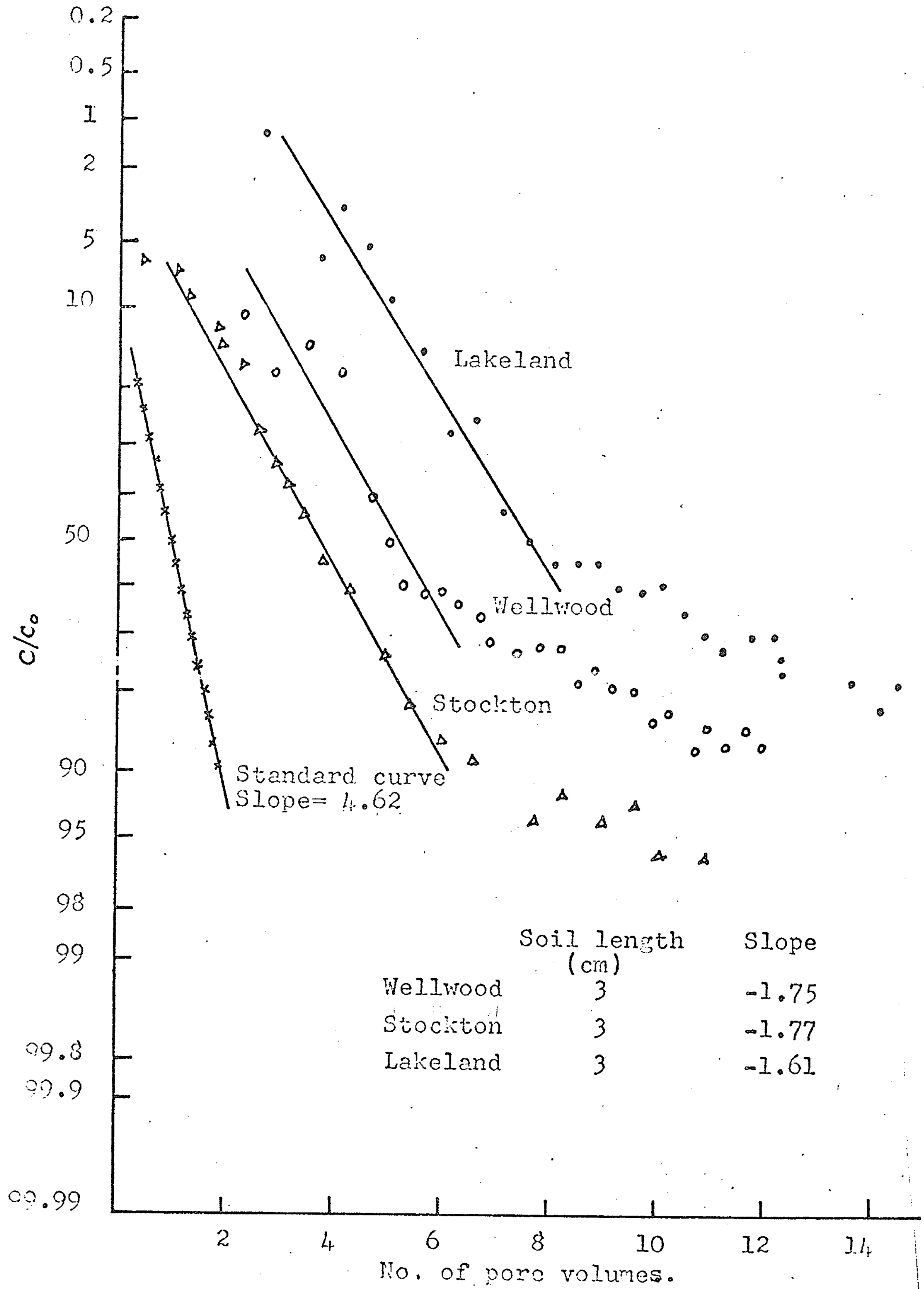


Figure 19. Probability plots of miscible displacement for the three soils.

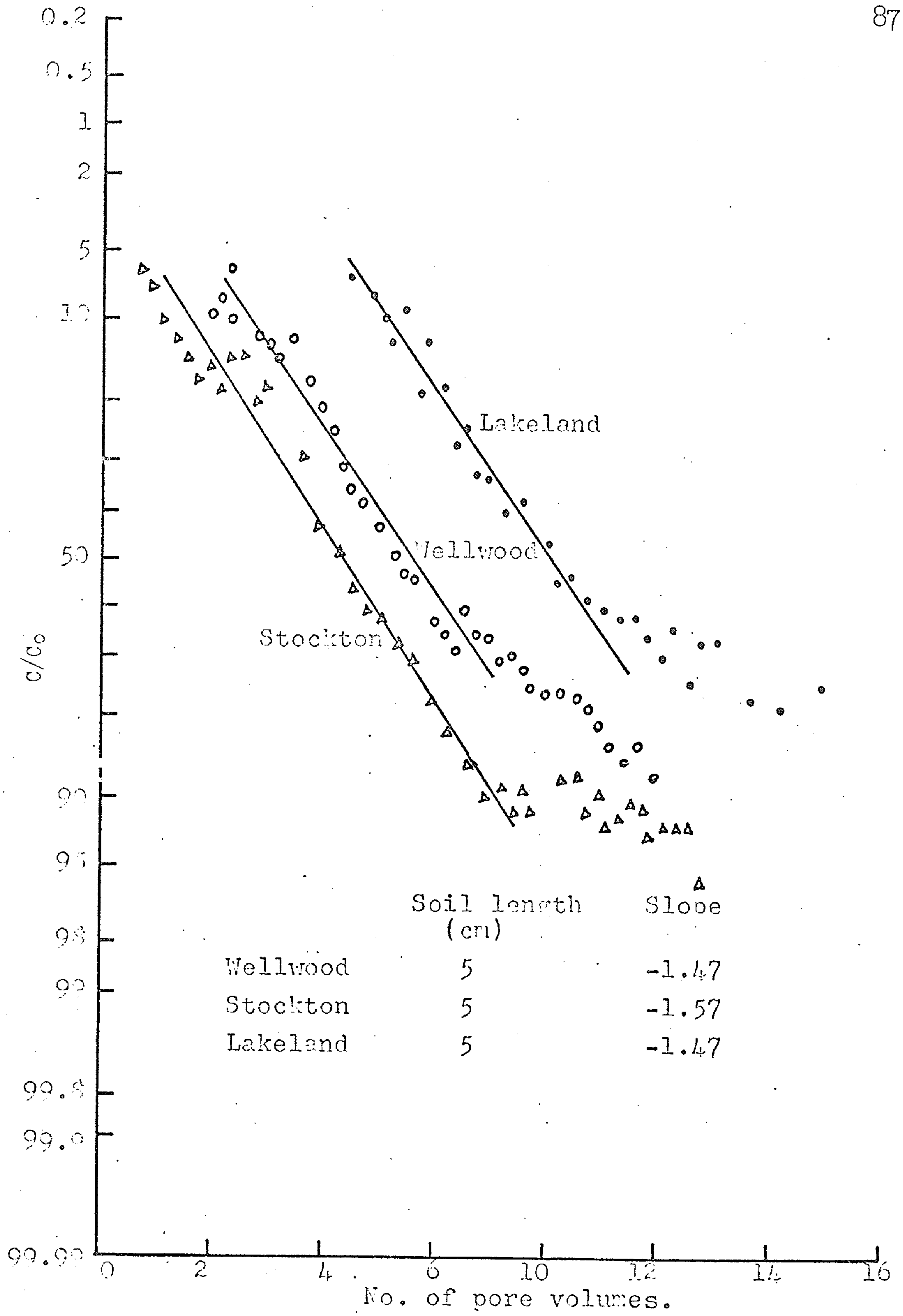


Figure 20. Probability plots of miscible displacement of the three soils.

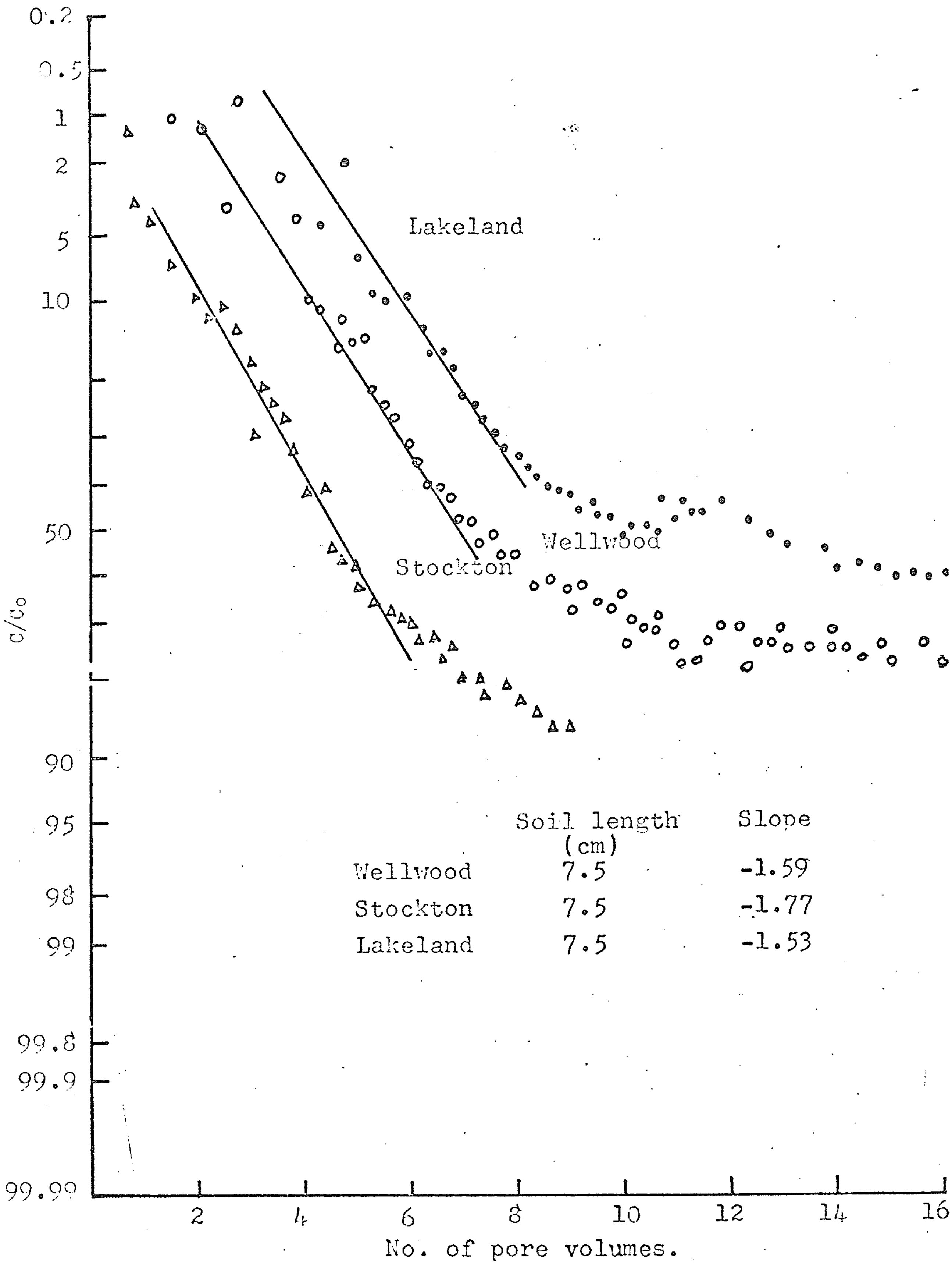


Figure 21. Probability plots of miscible displacement of the three soils.

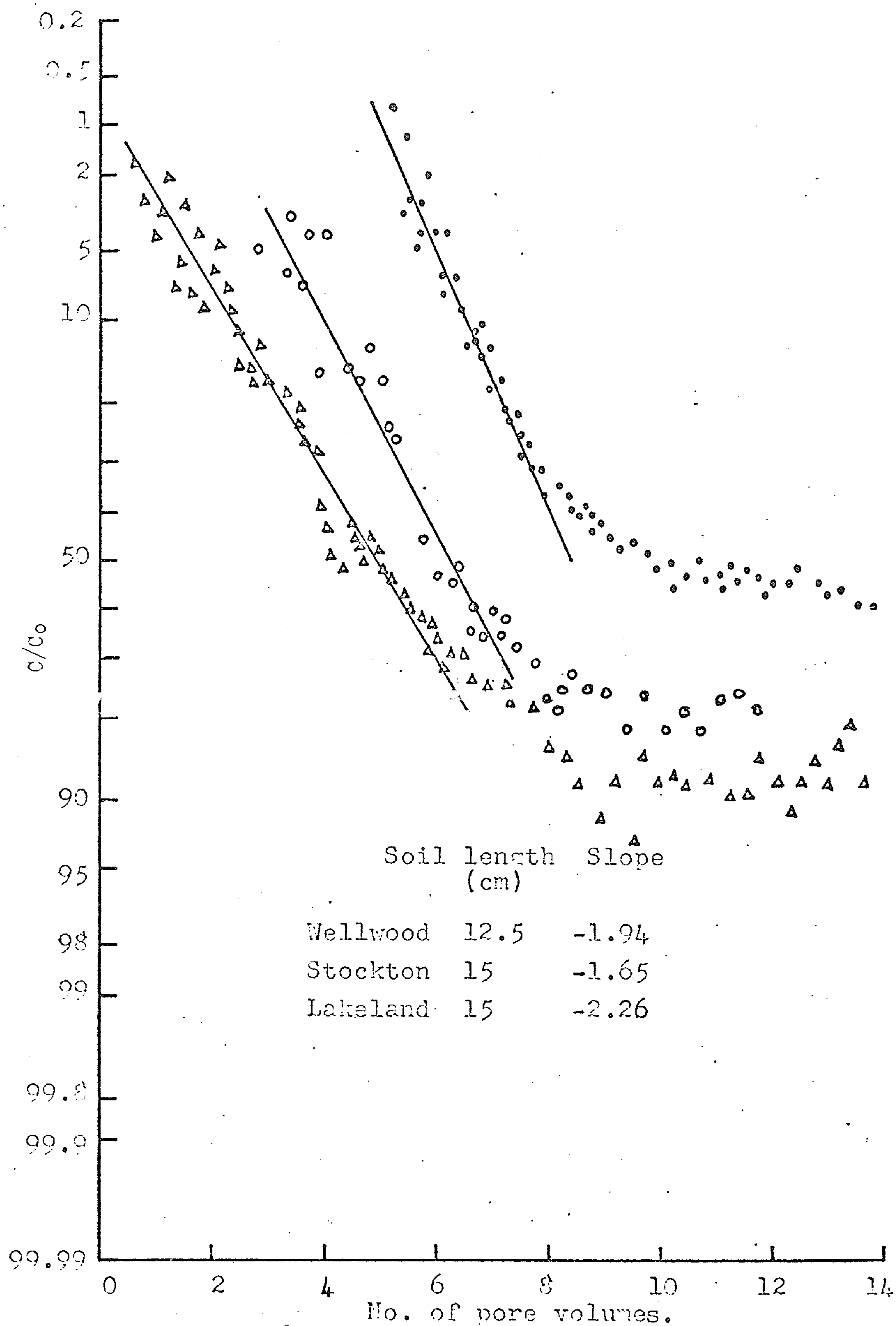


Figure 22. Probability plots of miscible displacement of the three soils.

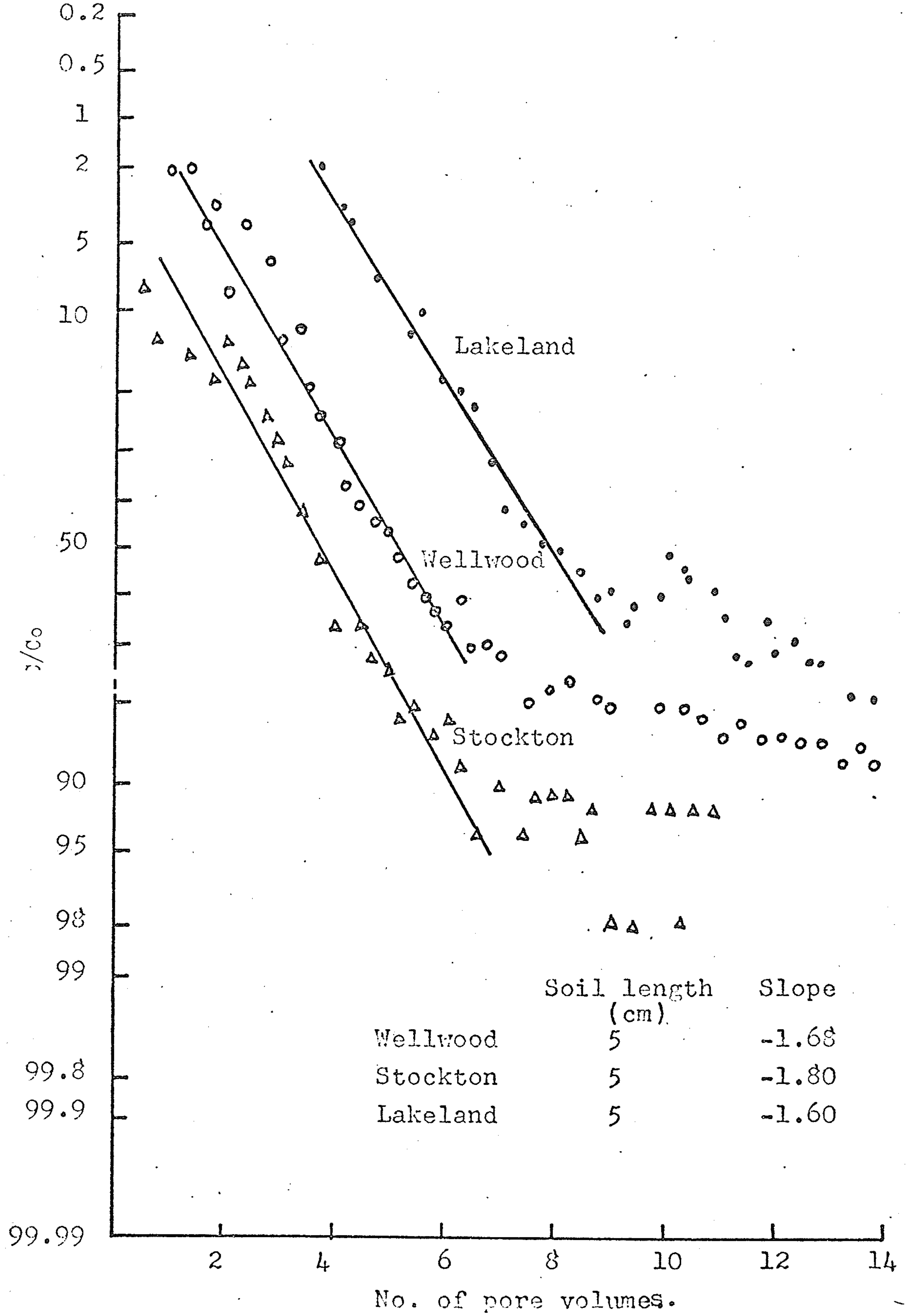


Figure 23. Probability plots of miscible displacement of the three soils.

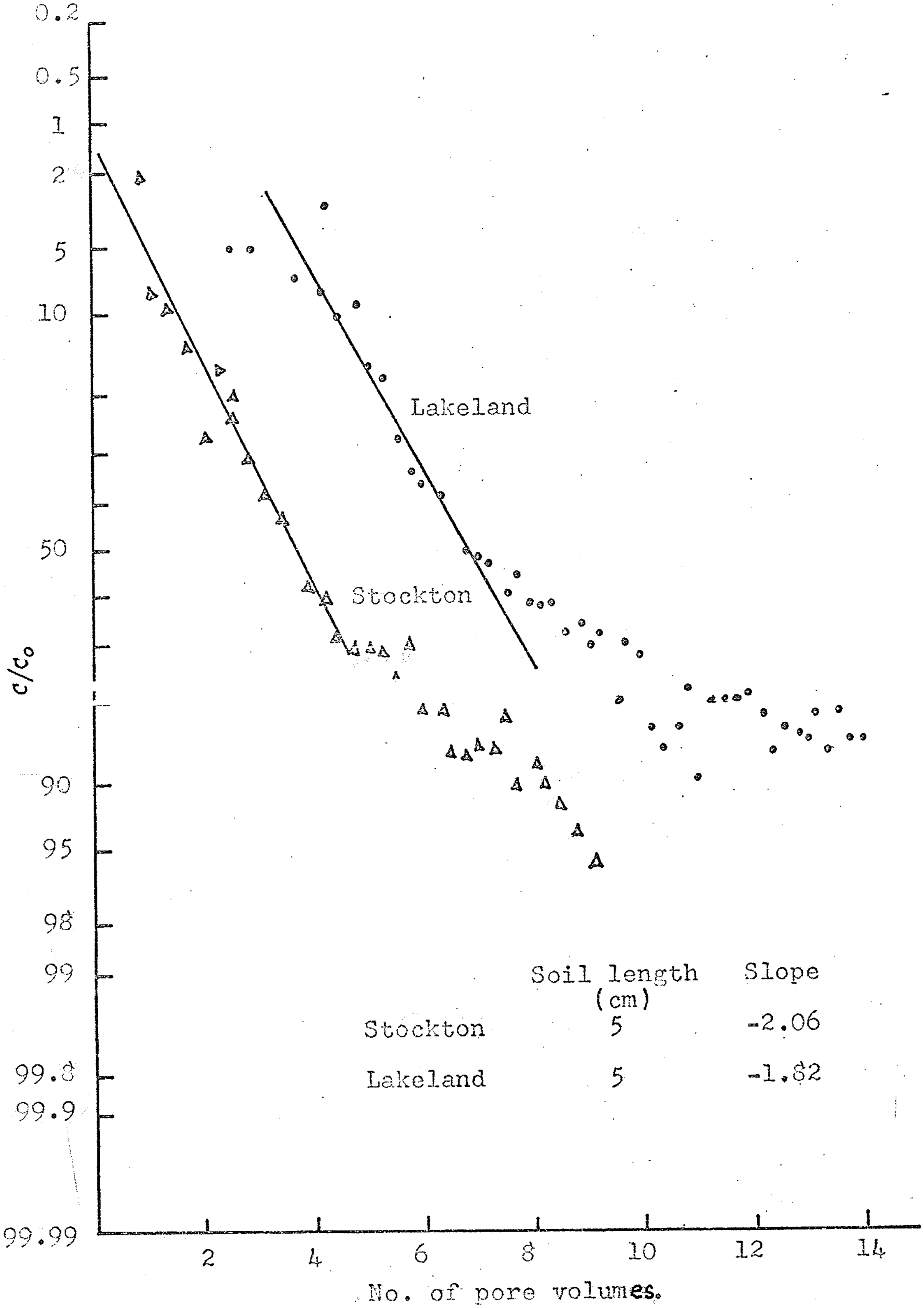
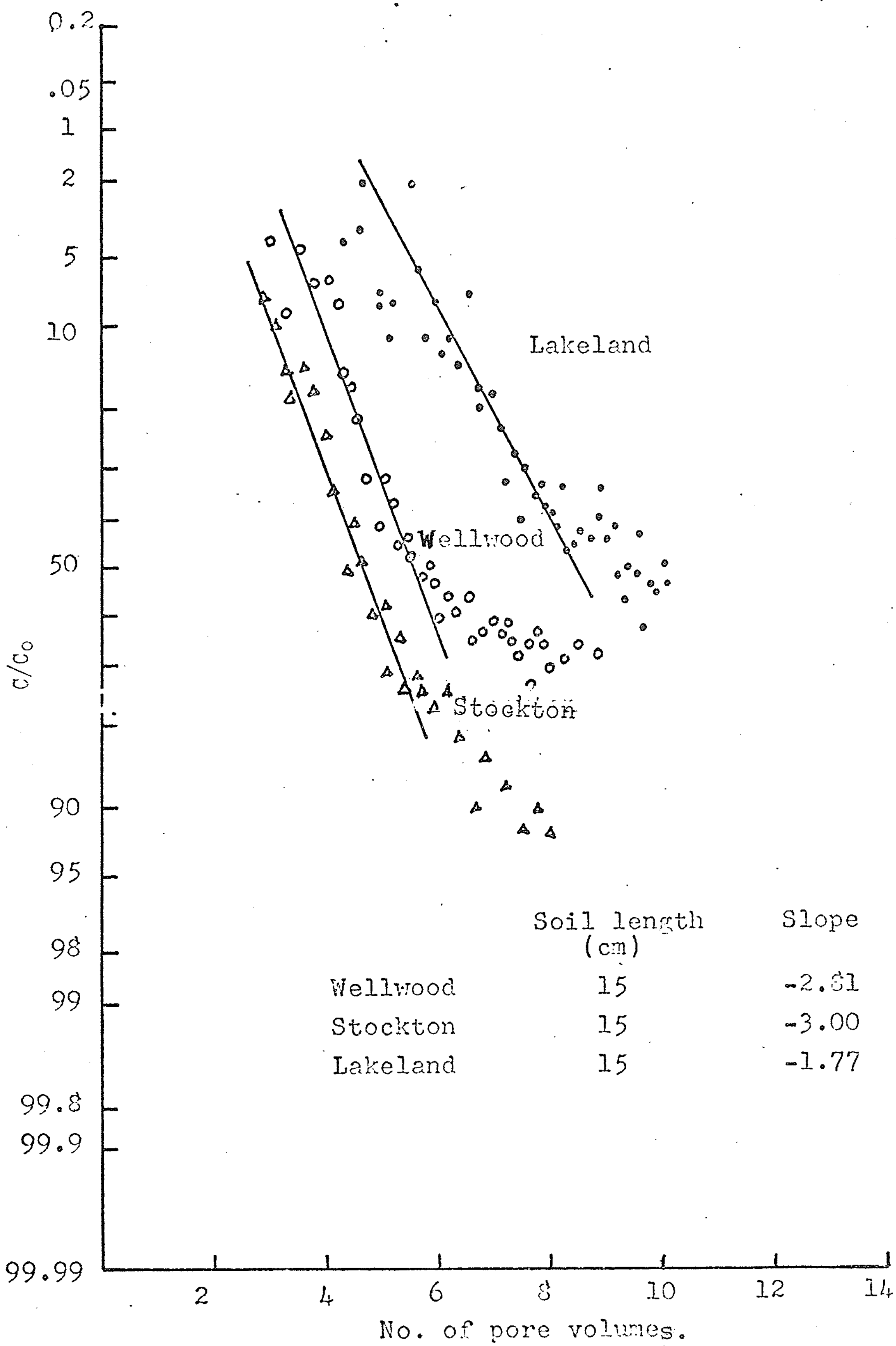


Figure 24. Probability plots of miscible displacement of the two soils.



	Soil length (cm)	Slope
Wellwood	15	-2.81
Stockton	15	-3.00
Lakeland	15	-1.77

Figure 25. Probability plots of miscible displacement of the three soils.

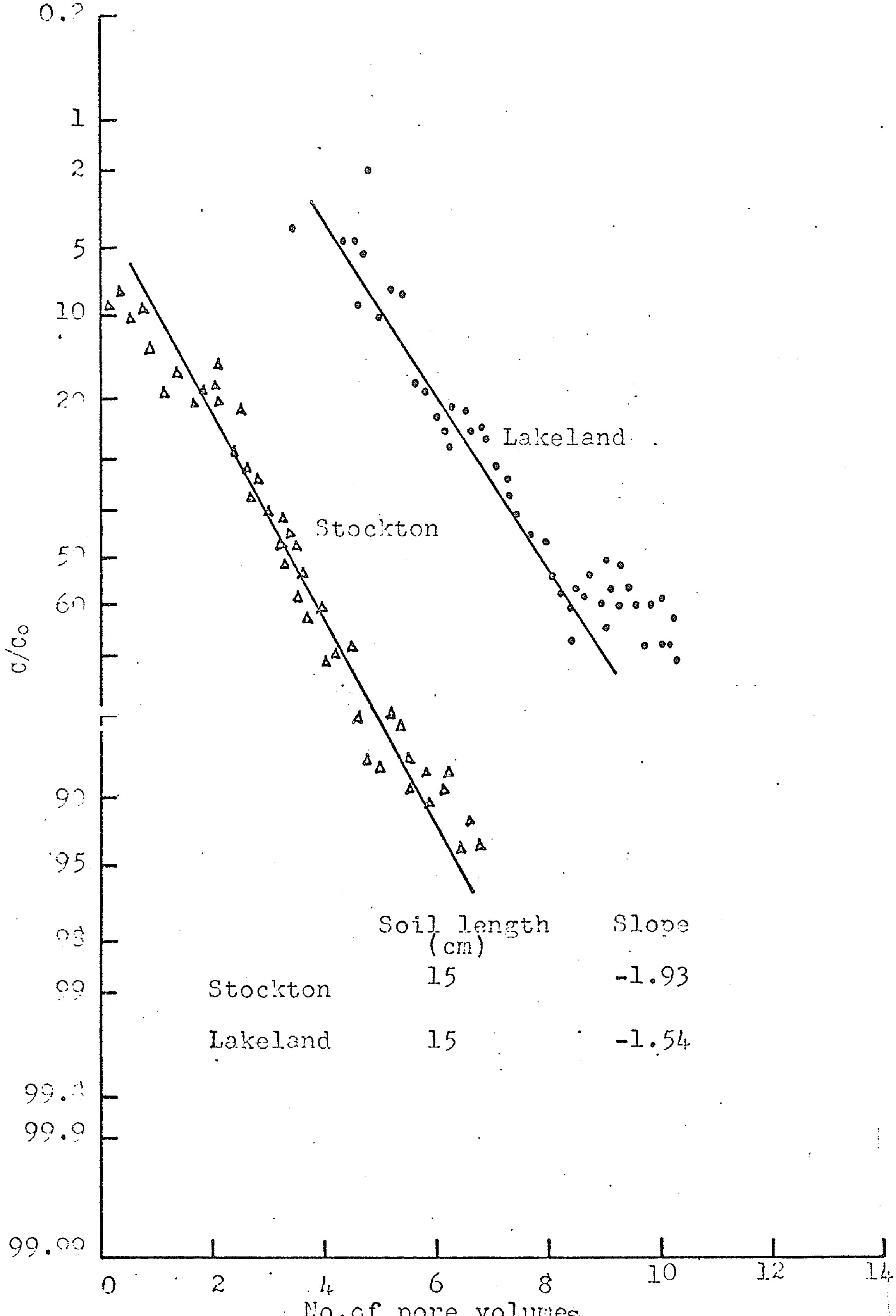


Figure 26. Probability plots of miscible displacement of the two soils.