SORPTION CAPABILITIES

OF SOILS

FOR PHOSPHATE

REMOVAL

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by

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ABSTRACT

The removal of phosphorus from soils was shown to be the result of three mechanisms: ion exchange, physical adsorption and precipitation. The degree of sorption by the combination of these mechanisms was evaluated by an equilibrium-adsorption procedure. The equilibrium distribution between the soil and liquid phases were correlated using the Langmuir Isotherm Equation. The Langmuir Parameters were incorporated in the expression

$$v_{\omega}/v_c = 1 + (q_{\infty}\, \rho_B / \varepsilon\, C_O)$$

which gave an estimate of the rate of phosphorus movement in the soil. The life-time of a soil-groundwater system was then determined from the groundwater flow rate and the calculated water-to-contaminant velocity ratio.

PROJECT STAFF

The following staff of the Applied Sciences Section were instrumental in the production of this report.

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1.0   INTRODUCTION

The treatment of water by adsorption techniques is an ancient process as indicated by records as far back as the time of Aristotle.[1] At this time, sand filters were used for the purification of sea water and impure drinking waters. According to Bacon in Sylva <u>Sylvarum:</u>

"...... trial hath been made of salt water passed through earth through ten vessels, one within another, and yet it hath not lostsaltiness as to become potable, but when drayned through twenty vessels hath become fresh."

The ability of clays and soils to adsorb components of manure liquors was studied extensively by Sir Humphrey Davy, Lambuschini, Huxtable[2] and others in the early part of the nineteenth century. Credit for the recognition of ion exchange phenomena is generally attributed to two English agricultural chemists, Thompson[3] and Way[2].

Today, purification of septic tank effluent from private waste sources is accomplished chiefly by sand or soil percolation for sites beyond reach of municipal sewage facilities. In this application, the soil acts both as a filter and an ion exchange-adsorption medium. The efficiency of a septic tank tile field system is heavily dependent on the capability of the soil to remove contaminants which may be detrimental to neighbouring sources of natural water. Thus, the movement of these contaminants through the soil poses a major difficulty in the design and planning of septic tank systems.

2.0   ION EXCHANGE AND ADSORPTION

2.1   Structure of Ion Exchangers

The natural materials responsible for the ion-exchange phenomena have been identified as clays, glauconites, zeolites and humic acids. According to Helfferich[4], the most natural ion-exchange minerals are crystalline aluminosilicates with cation exchange properties. Zeolites are typical representatives of this group of materials which include the minerals analcite, $Na(Si_2AlO_6) \bullet H_2O$, chabazite, $(Na, Ca), (Si_2AlO_6)_2 \bullet 6H_2O$, harmotome, $(K, Ba) (Si_5Al_2O_{14}) \bullet H_2O$, heulandite, $Ca(Si_3AlO_8) \bullet 5H_2O$, and natrolite, $Na_2 (Si_3 Al_2 O_{10}) \bullet 2H_2O$. All these minerals have a relatively open three dimensional framework structure with channels and interconnecting cavities in the alumino-silicate lattice. The zeolite lattice consists of SiO_4 and AlO_4 tetrahedra which have their oxygen atoms in common. Since aluminum is trivalent, the lattice carries a negative electric charge (one elementary charge per aluminum atom). This charge is balanced by alkali or alkaline earth cations which do not occupy fixed positions but are free to move in the channels of the lattice framework. These ions act as counter ions and can be replaced by other cations.

Certain aluminosilicates can also act as anion exchangers. The exchange of OH^- for Cl^-, SO_4^{2-}, and PO_4^{3-} has been observed in montmorillonite, [5] kaolinite [6], and in feldspars belonging to the sodalite and cancrinite groups [7].

In general, clays originate as components in residual bodies through weathering of a geological feature or from hydrothermal synthesis at high temperature and pressure. A detailed discussion of their origin can be obtained from the review by Grim[8].

The basic building blocks of the clay minerals, kaolinite, illite, and montmorillonite consist of alternate layers of gibbsite and silica. Kaolinite is a typical two layered clay containing one gibbsite layer and one hydrated silica layer. Montmorillonite is composed of a gibbsite layer between two hydrated silica layers, and is thus designated as a three layer type clay.

2.2   Origin of Ion Exchange Properties

Soil particles are amphoteric as evidenced by their ability to bind both cations and anions, but, generally, they carry a net negative charge which can be measured by the zeta-potential technique. The charge is produced in two ways;, by isomorphous ion substitutions, and by ionization of hydroxyl groups attached to silicon of broken tetrahedron planes; that is,

$$H_2O + Si \bullet OH \rightarrow SiO^- + H_3O^+$$

The amphoteric nature of clay requires the existence of positive charges which may originate from hydrous oxides of iron, aluminum, and manganese and from exposed octahedral groups which react as bases by accepting protons from the surrounding soil solution, thus acquiring a positive electric charge.

Because of the irregular shapes of the clay particles, the charge density is higher on edges, corners, furrows and cavities than on plane surfaces. The charge density also varies with pH and the degree of ionization.

2.3   Exchangeable Ions

The electric charge on soil particles is neutralized by exchangeable counter ions of an opposite charge and these are held to the surface by Coulomb forces and Van der Waals-London forces. Common exchangeable cations are Ca^{2+}, Mg^{2+}, H^+, Al^{3+}, K^+, Na^+, and NH_4^+. Calcium ions are generally predominant although in very acid soils

$Al(OH)_2^+$ constitutes a considerable proportion, increasing with decreasing pH. Sodium is usually very high in alkaline soils.

Exchangeable anions are SO_4^{2-}, Cl^-, NO_3^-, $H_2PO_4^{2-}$, HCO_3^- and anions of humic acids. Some of these ions do lot always function as counter ions but are merely present in the soil solution. In acid saline or sulphate soils the content of SO_4^{2-} is usually very high.

Most studies on soil anion exchange have used PO_4^{3-} and thus the information on the exchange of this anion is more extensive. These investigations have indicated that the anion adsorptive powers of clay soils are associated with the presence of Fe and Al compounds since removal of these substances by various methods tends to either completely destroy or markedly reduce anion adsorption [9]. The mechanism for anion adsorption by pure clay minerals proposes the replacement of OH^- from clay mineral surfaces, especially around the flake edges, and adsorption by anion-exchange sites existing along the basal plane surfaces. Replacement of adsorbed anions which have not been adsorbed via chemisorption is brought about by varying the pH. This reaction favors the theory of deactivation of the Fe and Al compounds present.

Studies on phosphate fixation by soils and clay minerals indicate that the retention of PO_4^{3-} is a result of the reaction with oxides of Fe and Al, the formation of insoluble salts of Fe, Al, Ca as well as fixation by the clay minerals. The fixation by the clay minerals is low, ranging from 0.03 to 0.07 millimoles PO_4^{3-} per gram of clay. Fixed PO_4^{3-} ions can be replaced or released from soil clays by divalent arsenate, silicate, citrate, oxalate, hydroxyl and fluoride ions. Citrate and oxalate operate by dissolving iron compounds, hydroxyl by decomposing clays, and arsenate and silicate by typical exchange reactions [8].

Because no single mechanism is responsible for the uptake of anions in soils and clays, the terms ion exchange, adsorption and chemisorption, which are all applicable, should be replaced by the term "sorption".

2.4   Ion Selectivities of Clays

The selectivity of a clay refers to the preference for one counter ion over another. The valences of the counter ion have a strong effect on the selectivity and thus on equilibria[4]. This effect is purely electrostatic and arises even in ideal systems. *As* a rule [4], the ion exchanger prefers the counter ion of higher valence. The preference increases with dilution of the solution and is strongest with ion exchangers of high internal molality.

For anions, selectivity is in the order:

$$PO_4^{3-} > SO_4^{2-} > Cl^-$$

and, for cations:

$$Th^{4+} > Nd^{3+} > Ca^{2+} > Na^+.$$
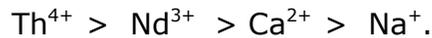
Exceptions to this rule are the anions in order of preference,

$$SO_4^{2-} > I^- > NO_3^- > CrO_4^{2-} > Br^-.$$
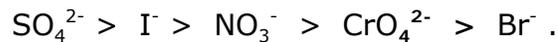
For the case of ions of equal charge, the ion with the smaller hydrated radius is preferred. In the case of the alkali group the order of preference is,

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+,$$

although the crystallographic radius increases down the group;[10] similarly, the alkaline earths display the same trend;

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}$$
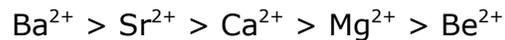
The order for monovalent anions is

$$CNS^- > ClO_4^- > I^- > NO_3^- > Br^- >$$
$$HSO_4^- > NO_2^- > Cl^- > HCO_3^- >$$
$$CH_3COO^- > OH^- > F^-.$$
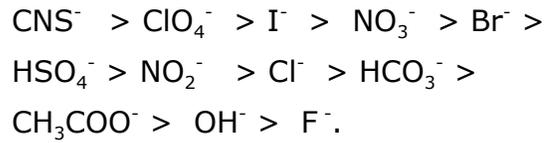
3.0   SORPTION ISOTHERMS

Sorption isotherms describe, in the form of functions or diagrams for a given (constant) temperature, the dependence of the equilibrium concentration of the solute on the sorbent on the concentration in the external solution. It is preferable to relate the concentrations in both phases - ion exchanger and solution - either to unit weight of the solvent in the phase or to unit volume of the phase.[4]

Using this convention, the sorption isotherm is either of two forms:

$$\bar{m} = f(m_i) \tag{1}$$
$$\text{or} \quad \bar{c} = g(c_i) \tag{2}$$

where m_i = concentration of solute i in millimoles per gram solvent (molality); c_i = concentration of solute i in moles per litre (molarity); quantities with bars refer to sorbent phase.

A single point on the sorption isotherm giving the ratio of the ordinate value to the abscissa value is known as the distribution coefficient. It is defined as;

$$\lambda_i = \bar{m}_i / m_i \tag{3}$$

$$\lambda'_i = \bar{c} / c_i \tag{4}$$

where λ_i is the molal distribution coefficient;
             λ'_i is the molar distribution coefficient.

3.1   Sorption Isotherm Models

Early studies on adsorption equilibria were empirical in nature, and attempted to fit empirical or semi-empirical data to experimental results. The first major attempt to give a quantitative formulation to ion exchange equilibria was made by Gans[11] using the mass action law in its simplest form (ie: without activity coefficients). His relation was

$$\overline{m}_A \, m_B / m_A \, \overline{m}_B \;\; = K_B^A \;\; = \;\; const. \tag{5}$$

This equation holds for zeolites with regular behavior. Wiegner and Jenny [12, 13, 14] applied a form of the Freundlich Isotherm, which contained two empirical constants, to ion exchange, namely;

$$x/m = k \, [c/ \, (c_o -c)]^{1/p} \tag{6}$$

where x/m = counter ions sorbed per unit weight of exchanger; c = equilibrium concentration of exchanging ion in solution; c_o = initial concentration of exchanging ion in solution; and k and p are empirical constants.

A more convenient equation suggested by Vageler [15] resembles the Langmuir adsorption isotherm

$$x/m \;\; = \;\; \overline{Q} \bullet Q \, /(Q + c') \tag{7}$$

where Q = amount of exchangeable ion in solution; $\overline{Q}$ = weight capacity of exchanger; c' is an empirical constant.

This equation is used in modified form as

$$x/m \;\; = \;\; \overline{Q} \, [bc \, /(1 + bc)] \tag{8}$$

where $\overline{Q}$ is the weight capacity of the exchanger; c is the equilibrium concentration and b is an empirical constant related to the energy of adsorption.

For multiple ionic species, Boyd, Shubert and Adamson [10] set up the following equation by formal analogy with the Langmuir theory: for species A^+ of an electrolytic solution,

$$(x/m)_{A^+} = \frac{\overline{Q}\, b_A\, c_{A^+}}{1 + b_A\, c_{A^+} + b_B\, c_{B^+}} \tag{9}$$

where $(x/m)_{A^+}$ = amount of A^+ ion adsorbed per unit weight of exchanger; c_A^+, c_B^+ = activities of cations in equilibrium solution; b_A and b_B = constants related to the energy of adsorption of the cations; $\overline{Q}$ is the total exchange capacity.

For the case involving ions of unequal charge,

$$(x/m)\, A^{v+} = \frac{\overline{Q}\, b_A\, (c_A^{v+})^{v_1+}}{1 + b_A\, (c_A^{u+})^{v_1+} + b_B\, (c_B^{u_1+})^{v+}} \tag{10}$$

where v_1 and v_2 are the valence states of the ions involved.

3.2   Phosphate Sorption Isotherms

Most studies done on phosphate sorption isotherms have been done from the standpoint of agricultural evaluation. More specifically, their utilization has been directed toward predicting the quantity of fertilizer phosphate required by a soil so that there is sufficient phosphate in the soil to produce a concentration gradient necessary for net movement to the roots.[17, 18, 19]

The applicability of the Langmuir equation has been strengthened by several studies, [18, 19, 20] and a high positive correlation between the maximum value of P adsorbed and the clay content of the soil has been observed.

The approach of the Langmuir analysis to soil adsorption readily allows one to evaluate the effectiveness of soils in limiting discharges from septic tank tile fields. Further applications of soil disposal are in the fields of slow sand filtration and land disposal by spray irrigation. [22]

4.O DYNAMICS OF CONTAMINANT MOVEMENT

To predict the movement of contaminants in soils the effects of dispersion and solution velocity must be evaluated to include the boundary conditions of the system. Many mathematical models have been proposed for analyzing the dynamics of soil systems with various reacting chemical species. [23] The basis for these mathematical descriptions is the equation of continuity for chemical species which is an unsteady state description of the system mass balance. The general form of the equation of change for species "i" is [24]

$$\partial c_i / \partial t + v_s \bullet \nabla c_i = D_i \nabla^2 c_i \pm R_i \tag{11}$$

where c_i is the concentration of species i; v_s is the superficial flow velocity vector; D_i is the dispersion coefficient (replacing the diffusion coefficient to include the mixing phenomena[25]); and R_i is a rate of addition or removal of species.

For dispersion of a single species of ion with no removal, equation (11) becomes:

$$\partial c / \partial t = D \partial^2 c / \partial x^2 - v \partial c / \partial x \tag{12}$$

where c is the concentration of the ion; t is time; D is the longitudinal dispersion coefficient; v is the seepage velocity. For the semi-infinite boundary conditions,

$$
\begin{aligned}
c(x, 0) &= 0, & x &> 0 \\
c(0, t) &= c_o, & t &\geq 0 \\
c(\infty, t) &= 0, & t &\geq 0
\end{aligned}
$$

the analytical solution of the dispersion model [26] is

$$c/c_o = \tfrac{1}{2}\,\text{erfc}\,[(1-\xi)\,/(2\,(\xi\eta)^{1/2})] + \tfrac{1}{2}\,\exp\,(1/\eta)\,\text{erfc}\,[(1+\xi)\,/(2\,(\xi\eta)^{1/2})] \qquad (13)$$

where the two dimensionless groups are

      1.   the Peclet number $Pe = 1/\eta = vL/D$

      2.   the pore volume $\xi = vt/L$

      3.   and L is the length of the model.

If the solute is adsorbed on the medium, then the material balance yields:

$$\partial c\,/\partial t = D\,\partial^2 c/\partial x^2 - v\,\partial c\,/\partial x - 1/\varphi\,\partial F\,/\partial t \qquad (14)$$

where φ is the porosity of the medium; F is a form of the adsorption isotherm.

The three possible adsorption isotherms are as follows:

    1.   Linear equilibrium where $F = k_1 c$ for which equation (14) changes to

$$1 + (k_1/\varphi)\,\partial c/\partial t = D\,\partial^2 c/\partial x^2 - \partial c\,/\partial x \qquad (15)$$

The solution of Lapidus and Amundson [27] is

$$c/c_o = \tfrac{1}{2}\,\text{erfc}\,[(1-\xi')/(2(\xi n)^{1/2})] + \tfrac{1}{2}\,\exp(1/\eta)\,\text{erfc}\,[(1+\xi')\,/(2(\xi n)^{1/2})] \qquad (16)$$

    where the modified pore volume, ξ', is expressed by

$$\xi' = \xi\,/(1 + k_1/\varphi) \qquad (17)$$

    2.   For Freundlich equilibrium adsorption, $F = k_2 c^{n_2}$, a nonlinear parabolic differential equation results;

$$[1 + [(\eta_2 k_2)/\varphi] c^{\eta 2-1}] \partial c/\partial t = \partial^2 c/\partial x - v \partial c/\partial x \qquad (18)$$

A numerical procedure is required for the solution of this equation.[28]

3. Langmuir equilibrium adsorption is given by

$$F = \overline{Q}bc /(1 + bc) = ac /(1 + bc) \qquad (19)$$

where a and b are constants. This produces:

$$[1 + \{a/(\varphi(1 + bc)^2)\}] \partial c/\partial t = D \partial c/\partial t - v \partial c/\partial x \qquad (20)$$

Again, a numerical solution is required.

4.1 Bilinear Adsorption

In addition to Adsorption, there is a continual exchange of ions. To include this case properly, a kinetic model is required to account for the bilinear rate of adsorption. According to Gupta and Greenkorn,[29] this type of model is physically the most appropriate for adsorption in soils and columns of soil. The adsorption reaction for chemical species, A, is represented by:
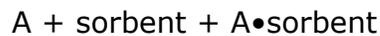
$$A + sorbent + A \bullet sorbent$$

The rate of adsorption at soil surface is

$$\partial (A \bullet sorbent)/\partial t = k_{kin} [(A) \bullet (sorbent) - (1/K_{ad}) (A \bullet sorbent)] \qquad (21)$$

The concentrations are

$$\begin{aligned}
(A) &= c \\
(A \bullet sorbent) &= q \\
(sorbent) &= Q - q \qquad (22)
\end{aligned}$$

Substituting the rate expression in the material balance yields

$$D \left(\partial^2 c / \partial x^2 \right) - v \left(\partial c / \partial x \right) = \left(\rho b / \varphi \right) \left(\partial q / \partial t \right) \tag{23}$$

$$\partial q / \partial t = k_{kin} \left[c(Q-q) - (1/K_{Ad}) q \right] \tag{24}$$

with semi-infinite boundary conditions,

$$c(x, 0) = 0; \qquad x > 0$$
$$q(x, 0) = 0; \qquad x > 0$$
$$c(0, t) = c_o; \qquad t \geq 0$$
$$c(\infty, t) = 0; \qquad t \geq 0$$

and K_{Ad} is the constant b, in the Langmuir equation.

To obtain a solution, these equations must be solved numerically on a computer. The solution [29] of these equations is shown in Figure 1 as plots of c/c_o vs $1/\eta$, the number of pore volumes. These curves show the effect on breakthrough of the kinetic rate constant, the fluid velocity and the dispersion coefficient.

Other mathematical approaches and conditions involving the transport of chemicals in porous media have been published by Lindstrom *et al* [30, 31].

Due to the difficulties in solving these equations, and the fact that a concentration profile is not necessarily required for field conditions, a simpler mathematical technique is required to determine breakthrough.

4.2   Macroscopic Mass Balance

In order to do a total mass balance for determining breakthrough times for a soil-contaminant system, or, in other words, to determine the lifetime of a soil
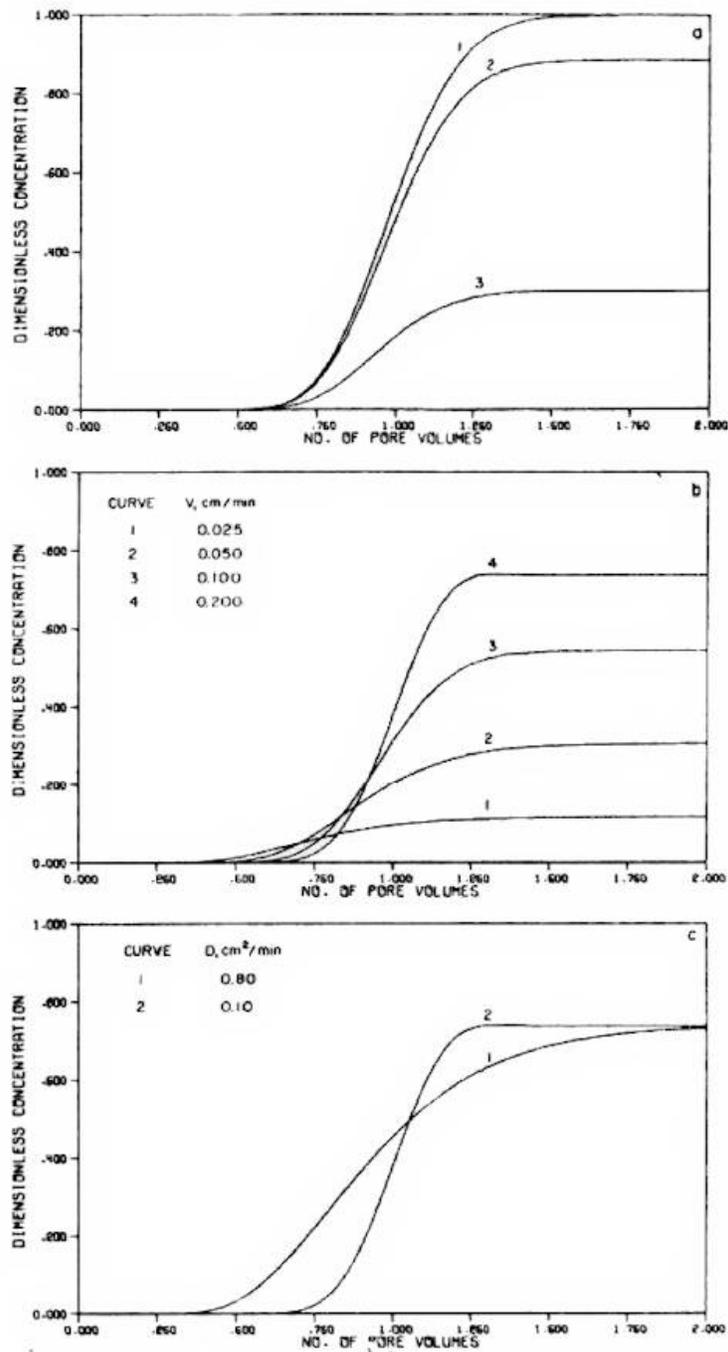
Figure 1. Effect on breakthrough curves of a) kinetic rate constant (V = 0.05 cm/min, D = 0.05 cm^2/min, C$_o$ = 0.00002 g mole/cm^3, K$_{ad}$ = 540,000.0 cm^3/g, and Q = 0.00012 g mole/g adsorbent; for curves 1,2, and 3, K$_{kin}$ is 0.002, and 2.000 cm^3/g mole/min, respectively), (b) fluid velocity (D = 0.1 cm /min, K$_{kin}$ = 2.0 cm^3/ mole/min, C$_o$ = 0.0002 g mole/cm^3, K$_{ad}$ = 540,000.0 cm^3/g mole, and Q = 0.00012 g mole/g adsorbent), and (c) dispersion coefficient (v = 0.20 cm/min, K$_{kin}$ = 2.0 cm^3/ g mole/min, Co = 0.0002 g mole cm^3, K$_{ad}$ = 540,000.0 cm^3/ g mole, and Q = 0.00012 g mole adsorbent).

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adsorption tile field, certain generalizing assumptions must be made based of the behavior of a conventional soil column. Considering Figure 2, a soil column is shown with a plot of the concentration-distance profile. The concentration involved is that of the non-dimensional form $\bar{c}/\bar{c}_o$ where $\bar{c}_o$ is the average input concentration and $\bar{c}$ is the average concentration at a point x from the top of the column. For clarity, the averaging bars will be omitted in further analyses. Thus the following conditions hold:

$$t = 0, x = 0, \qquad c/c_o = 1.0$$
$$t = 0, x = h_{B,} \qquad c/c_o = 0.0$$

where h_B is the bed depth, and

$$t > 0, x = 0, \qquad c/co = 1.0$$
$$t > 0, x = x', \qquad c/c_o = (1.0, 0.0)$$

ie. at some value, x', c/c_o lies in the range from 0 to 1.0 as described by the solution of the differential equations. This range where c/c_o varies from a maximum to its minimum over a bed increment of Δx is known as the reaction zone. This is the region where the actual adsorption and ion exchange processes are taking place. As the soil particles reach equilibrium with the incoming feed, this section of the bed becomes exhausted and the reaction zone moves down the bed as depicted in Figure 2(b). After a period of time, the reaction profile will reach the bottom of the bed and the concentration of the contaminant will rise from zero to a maximum as the concentration profile emerges from the bed indicating a depletion of the active sites in the soil (Figure 2(c)).

To avoid differential equations and reduce the complexity of the breakthrough phenomena, the plug flow assumption must be used. In this case the concentration gradient is a step-function with a non-finite slope, and thus, $\partial c/\partial x$ is non-existent since $\partial c/\partial x \rightarrow \infty$. The soil column behavior, thus, is depicted in Figure 3.

Figure 2. Adsorption Profiles in Soil Column.

$$t = 0, \; x = 0, \qquad c/c_o = 1.0$$
$$t = 0, \; x = h_B, \qquad c/c_o = 0.0$$

where h_B is the bed depth, and

$$t > 0, \; x = 0, \qquad c/co = 1.0$$
$$t > 0, \; x = x', \qquad c/c_o = (1.0, \; 0.0)$$

ie. at some value, x', c/c_o lies in the range from 0 to 1.0 as described by the solution of the differential equations. This range where c/c_o varies from a maximum to its minimum over a bed increment of tx is known as the reaction zone. This is the region where the actual adsorption and ion exchange processes are taking place. *As* the soil particles reach equilibrium with the incoming feed, this section of the bed becomes exhausted and the reaction zone moves down the bed as depicted in Figure 2(b). After a period of time, the reaction profile will reach the bottom of the bed and the con-centration of the contaminant will rise from zero to a maximum as the concentration profile emerges from the bed indicating a depletion of the active sites in the soil (Figure 2(c)).

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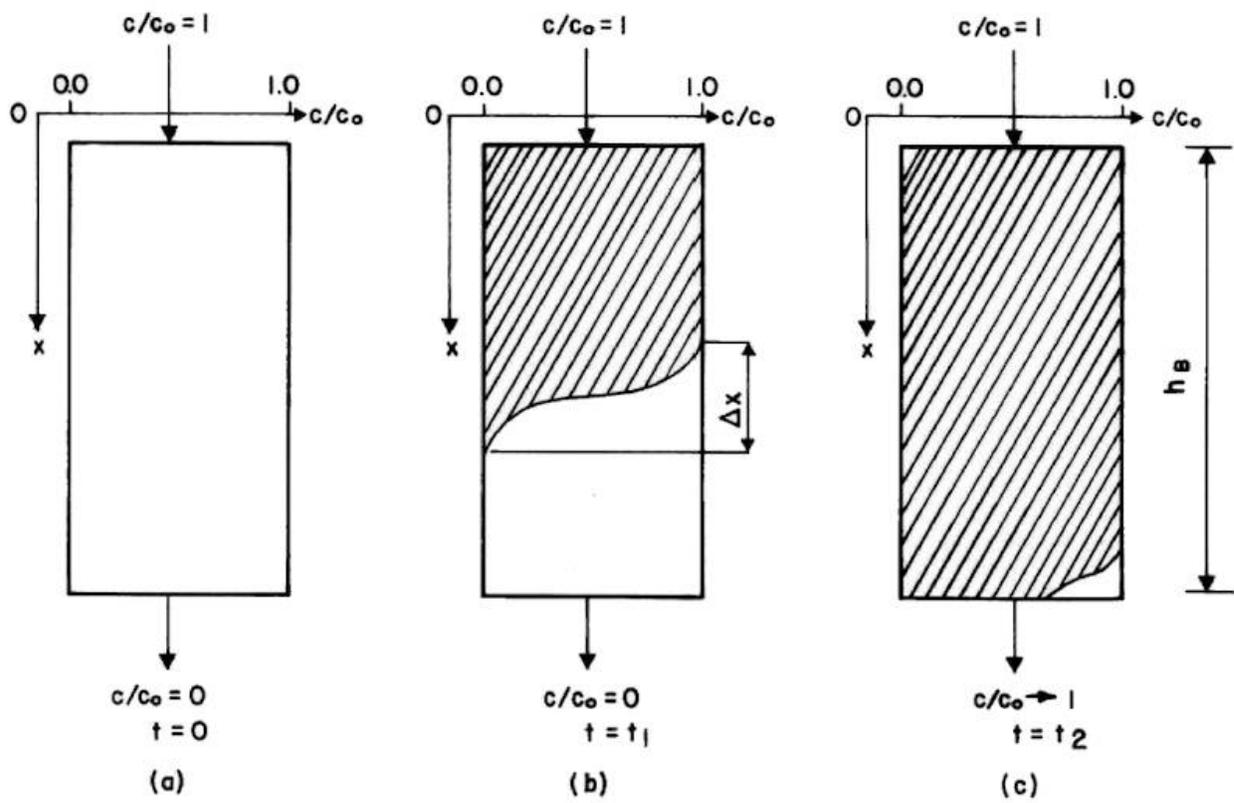
4.3   Derivation of Plug Flow Mass Balance

Consider Figure 3(c) immediately before breakthrough such that the dimensionless concentration at the top of the column is

$$x_1 = c_o/c_o = 1 \qquad\qquad (25)$$
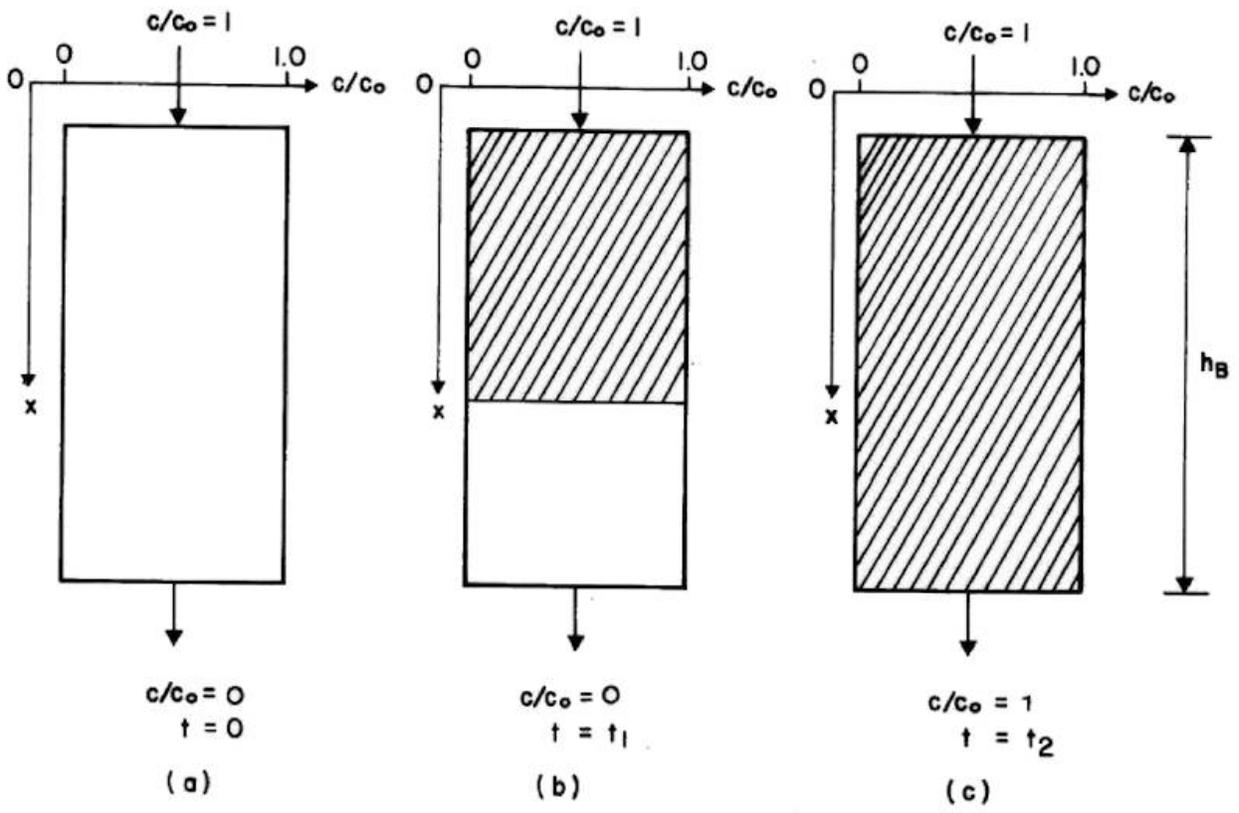
Figure 3.   Plug Flow Sorption Profile.

and at the bottom, the effluent is

$$x_2 = c_f / C_o = 0 \tag{26}$$

i.e. the column is exhausted but breakthrough has not occurred. Therefore, the column mass input is $V_{in} c_o$ over a fixed time period, Δt.

The output is

$$V_{out} c_f = V_{out} \times 0 = 0 \tag{27}$$

where V_{in} and V_{out} are the total volumes in and out of the column over the time Δt; c_o is the input concentration and c_f is the effluent concentration. For plug flow just before breakthrough, $c_f = 0$. Immediately on breakthrough, $c_f = c_o$.

The accumulation in the column is

$$\varepsilon V_B c_o + q_\infty \rho_B V_B$$

where e is the porosity; V_B is the volume of the bed, ρ_B is the density of the bed, q_∞ is the sorption equilibrium value of the contaminant on the soil. The first term of the accumulation is the amount of contaminant contained in the voids of the bed, and the second term is the amount adsorbed on the soil at breakthrough.

Equating, $$V_{in} c_o = \varepsilon V_B c_o + q_\infty \rho_B V_B \tag{28}$$

Or $$V_{in} c_o - \varepsilon V_B c_o = q_\infty \rho_B V_B \tag{29}$$

Thus $$V_{in} - \varepsilon V_B = q_\infty \rho_B V_B / c_o \tag{30}$$

Dividing by εV_B ;

$$(V_{in} / \varepsilon V_B) - 1 = q_\infty \rho_B / \varepsilon c_o \tag{31}$$

or $\qquad V_{in} / \varepsilon \, V_B \;\; = 1 + (q_\infty \, \rho_B / \varepsilon \, c_o)$ (32)

If the cross-sectional area for flow is A over a time period Δt where A is the cross-sectional area of the column, the flow velocity of the aqueous phase is

$$v_\omega \;\; = V_{in} / \varepsilon \, A \, \Delta t \qquad (33)$$

The rate of movement of the breakthrough front is

$$v_c = V_B / A \, \Delta t \;\;\; = h_B / \Delta t \qquad (34)$$

Therefore dividing numerator and denominator of equation (32) by εAΔt, ie. multiplying by unity,

$$\frac{1/ \, \varepsilon A \Delta t}{1/ \, \varepsilon A \Delta t} \;\; = 1$$

yields

$$v_\omega / v_c = 1 + (q_\infty \, \rho_B / \varepsilon \, c_o) \qquad (35)$$

which relates the flow velocity through the bed to the velocity of the moving front.

The quantity, $q_\infty \, \rho_B / c_o$, is a dimensionless coefficient which defines the limiting distribution between the solution and sorbent phases. If q is replaced by the adsorption isotherm in the form

$$q_\infty \;\; = x/m = \overline{Q} \, b c_o \, /(1 + b c_o) \qquad (8)$$

equation (35) becomes

$$v_\omega / \, v_c = 1 + [\overline{Q} \, b c_o \, /(1 + b c_o)] \, \rho_B / \varepsilon \, c_o \qquad (36)$$

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$$v_\omega / v_c = 1 + (\overline{Q} \, b\rho_B / \varepsilon) \, [1 / (1 + bc_o)] \tag{37}$$

Two cases may result depending on the magnitude of bc_o :

    (i) $bc_o \ll 1$

$$v_\omega / v_c = 1 + (\overline{Q} \, b\rho_B / \varepsilon) \tag{38}$$

and, thus the velocity ratio becomes independent of the influent concentration.

    (ii) $bc_o \gg 1$

$$v_\omega / v_c = 1 + (\overline{Q} \, b\rho_B / \varepsilon \, c_o) \tag{39}$$

for which the velocity ratio depends on the maximum adsorptive capacity Q and the influent concentration, and not on the isotherm parameter "b".

5.0   APPLICATION OF CONTAMINANT MOVEMENT EQUATION TO FIELD CONDITIONS

    Experimental data on flow of a contaminant from a source have indicated a dispersion for unconfined flow which is basically linear in nature. The extent of dispersion or the dispersion coefficient has been shown to be a function of the flow Reynolds number. The dispersion and the Reynolds number have been correlated in the form [23]

$$D = a_1 \, v \, Re^{b_1} \tag{40}$$

where D is the dispersion coefficient, a_1 and b_1 are constants, v is the kinematic viscosity and Re is the Reynolds number based on permeability. In most cases b_1 has the value of approximately unity.

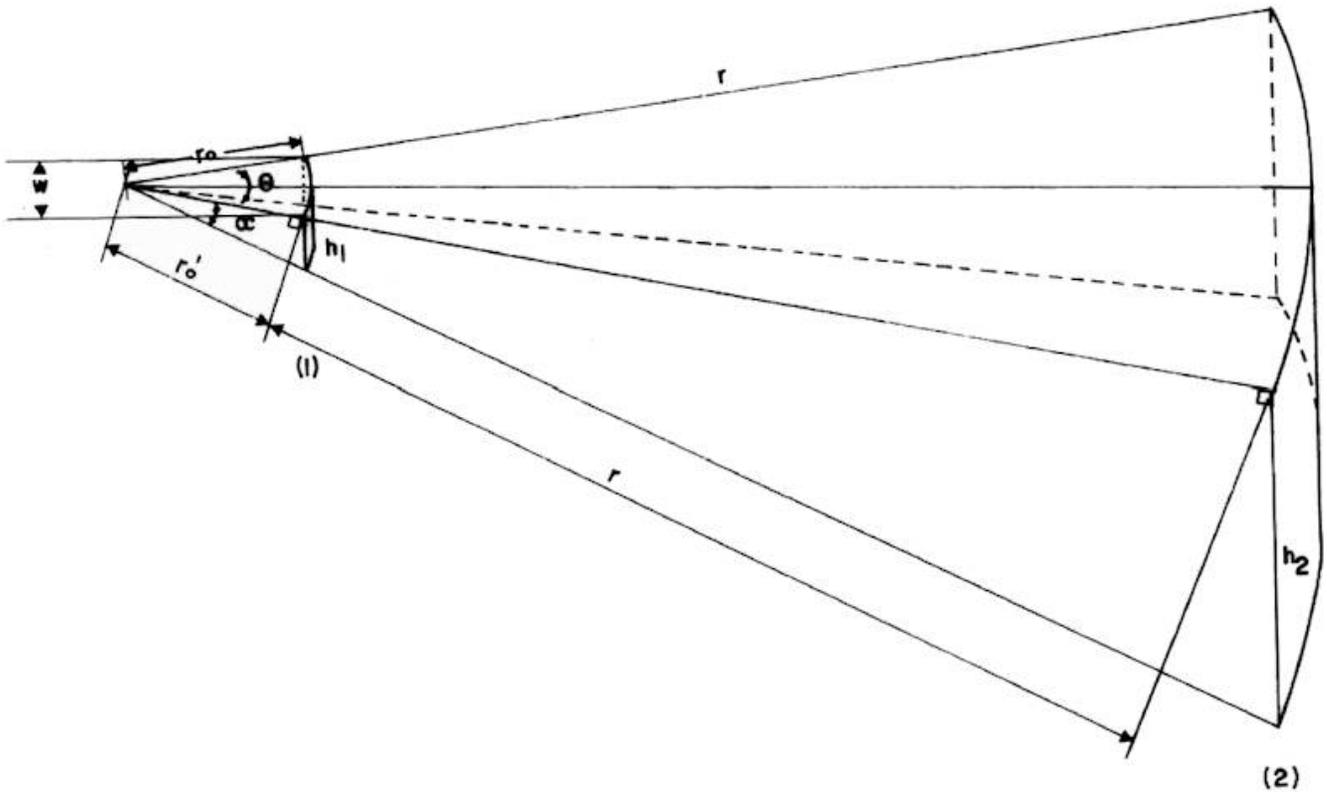   Consider Figure 4 in which a source of pollution is entering the soil at a

Figure 4.   Contaminant Dispersion Model.

concentration c_0 through a cylindrical area at point 1 and then disperses so that at some point at a distance, r, from the source, the flow area has expanded as shown by point 2. These areas subtend angles 0 and a whose vertices are located at a distances, r_0 and $r_{0,}$ back from the source. At point 1 the arc length and depth are

$$a_1 = r_0 \theta ; \qquad h_1 = r'_0 \tan \alpha \qquad (41)$$

and at point 2

$$a_2 = (r_0 + r)\theta ; \qquad h_2 = (r'_0 + r)\theta \tan \alpha \qquad (42)$$

Therefore, the flow areas are:

point (1): $\quad A_1 = a_1 h_1 \quad = \quad r_0 r'_0 \tan \alpha \qquad (43)$

point (2): $\quad A_2 = a_2 h_2 \quad = \quad (r_0 + r)(r'_0 + r)\,\theta \tan \alpha \qquad (44)$

The relationship between concentration and flow areas is given by the integrated continuity equation:

$$c_1 A_1 v_1 \quad = \quad c_2 A_2 v_2 \qquad (45)$$

for two positions, 1 and 2.

Thus $\quad c_2 \;=\; c_1 A_1 v_1 / A_2 v_2 \qquad (46)$

For simplification purposes, it must be assumed that

$$v_1 = v_2 \qquad (47)$$

neglecting differences in velocity resulting from lateral dispersion; therefore,

$$c_2 = c_1 \; A_1/A_2 \qquad (48)$$

26

Substituting values for A_1 and A_2 from equations (43) and (44)

$$c_2 = \frac{c_1 \, r_o \, r'_o \; \theta \tan \alpha}{(r_o + r)(r'_o + r) \, \theta \tan \alpha} \qquad (49)$$

Or

$$c_2 = \frac{c_1 \, r_o \, r'_o}{(r_o + r)(r' + r)} \qquad (50)$$

which gives the concentration at a distance r from the source. Applying this result to equation (39), the following is obtained:

$$\frac{v_\omega}{v_c} = 1 + \frac{\overline{Q} \, \rho_B \, b}{\varepsilon} \; \frac{1}{1 + bc_o \, [r_o /(r_o + r)][(r'_o /(r'_o + r)]} \qquad (51)$$

This equation includes the effect of distance on the rate of contaminant movement. The values of r_o and r'_o are given by

$$r_o = \frac{W/2}{\sin\theta/2} \, , \qquad r'_o = \frac{h_1}{\tan \alpha} \qquad (52)$$

and h_1 is usually equal to the tile diameter as a first approximation, α is an experimentally determined angle, W is the width of the tile bed and θ is the plan view angle dependent on dispersion.

If dispersion depth values h_1 and h_2 are known.

$$\frac{v_\omega}{v_c} = \frac{1 + \overline{Q} \, \rho_B \, b}{\varepsilon} \; \frac{1}{1 + bc_o \, [r_o /(r_o + r)] \, h_1/h_2} \qquad (53)$$

For a constant depth above an impermeable layer, $h_1 = h_2$, then

$$\frac{v_\omega}{v_c} = \frac{1 + \overline{Q} \, \rho_B \, b}{\varepsilon} \; \frac{1}{1 + bc_o \, [r_o /(r_o + r)]} \qquad (54)$$

27

In any rase, some approximation to the contaminant flow profile is required to be made based on the flow hydrology.

6.0   EXPERIMENTAL

6.1   Determination of Phosphorus Existing in Soil

The concentration of phosphorus existing on the soil of a tile field varies with distance from the point where it initially leaves the tile to enter the soil. To observe the gradation in phosphorus concentration with distance, soil samples taken at several points away from the source of contamination must be analyzed to determine the amount of inorganic P present on the soil.

Most soil phosphate determinations involve two distinct steps; extraction of the soil to obtain the phosphorus in solution, and then a quantitative analysis of the phosphorus content. Colorimetric methods forming the molydenum blue complex appear to be the most sensitive technique for soil extracts containing small amounts of PO_4 - P.

6.1.1   Principles of the Extraction Technique

Soil extraction using a strong acid such as 1M sulphuric acid gives an approximation of the total inorganic phosphorus in a soil.[32] Parton[33] suggested that the solubility of inorganic phosphorus is a function of pH and the total amount can be brought into solution provided the pH is made sufficiently low. At pH 1.0 all the inorganic phosphorus will be mobilized but not necessarily in solution as some re-adsorption of phosphorus will occur.[33] Parton overcame this problem using a radioactive tracer to determine the degree of re-adsorption. Because the time to reach equilibrium may be in the order of three weeks, the effects of re-adsorption have been neglected in this study.

The phosphates in solution are generally considered to be in the form of aluminum phosphate, iron phosphate, and calcium and dicalcium phosphate. These phosphates may be fractionated separately with different extractants although there is a general degree of overlap of each phosphate form. [32]

6.1.2   Reagents

1M H_2SO_4 (56.6 ml 18M H_2SO_4 (conc) in 1 litre).   Reagents according to "Standard Methods" [34] for PO_4^{3-} - P analysis.

6.1.3   Procedure

Weigh out accurately 1.0 gm of soil passing a 60 mesh sieve into a 250 ml Erlenmeyer flask. Add 50 ml of 1M H_2SO_4 solution, seal the flask and shake for ½ hour. Because of the presence of sewage on the soil, H_2S may form, and must be released before pressure builds up. Filter the solution completely through a 0.45 μ millipore filter. Wash the soil residue twice with 10 ml of distilled water. Dilute the entire sample to exactly 100 ml in a volumetric flask. Analyze an aliquot for inorganic P using the stannous chloride technique described in "Standard Methods". [34]

6.2   Phosphate Isotherm Determination

The previously described phosphate analysis measures the amount of phosphorus or phosphate already held in the soil. The isotherm test measures the amount of phosphorus a soil will rapidly take up.

It is also worthwhile to note that the maximum capacity for phosphate adsorption is not equivalent to the soil anion exchange capacity. It is possible that the sum of the phosphate ions present on the soil and the adsorption capacity may approach the value of the anion exchange capacity provided that the amount of adsorbed chloride, sulphate and nitrate is low.

6.2.1 <u>Reagents</u>

Standardized P solutions of concentrations 1.63 mg P/L (5 mg/L PO_4^{3-}) made with deionized water, and deionized water containing 0.01M NaCl or 0.01M $CaCl_2$. Reagents for the stannous chloride technique are listed in "Standard Methods". [34]

6.2.2 <u>Procedure</u>

Weigh out accurately, approximately 1, 3, 5, 7 and 10 gm samples of soil passing 200 mesh (or 60 mesh in the case of sand), into 250 ml Erlenmeyer flasks. Add 150 ml of standardized phosphorus reagent, seal the flasks, and shake for 24 hours (as a standard shaking time) or longer if desired. Allow to stand 1 hour, then centrifuge the supernatant to obtain 100 ml of solution. Filter the centrate and analyze an aliquot for PO_4 - P using the stannous chloride method.

As mentioned in section 6.2.1 standards containing 0.01 M Na Cl or $CaCl_2$ were used because they simulate soil solutions, stabilize pH, and aid in the coagulation of soil colloids which could interfere with phosphate measurements.[35] However it has been observed by several authors[36, 37] that calcium contacting solutions gave higher adsorption values than sodium chloride contacting solutions, especially at pH values greater than 5.5. Thus, the NaCl solutions are usually favoured.

7.0   RESULTS AND DISCUSSION

7.1   <u>Phosphorus Analysis of Soils</u>

To test the analytical technique of determining soil phosphorus, soil samples were removed from nine points in a 43.2 cm column of sand through which sewage had been flowing for one year. The phosphorus in the feed varied from 1.5 to 35 m/L.

The samples were analyzed for total inorganic phosphorus as described in

section 1.4, and the results plotted vs. distance as in Figure 5. The curve drawn through the points shows the approximate phosphorus profile in the column. The shape of the sorbed phase concentration curve is similar to that predicted by Lindstrom and Stone (30) in their mathematical analysis of this type of problem. Their curves for various exchange coefficients are reproduced in Figure 6 for comparison.

The existing background concentration on the soil may be considered to be 105 µg/gm which is the bottom point of Figure 5.

In a similar manner, samples from a septic tank tile field may be analyzed to determine PO_4 -P profiles and thus determine the extent of utilization of the soil by the septic tank effluent.

A study of this nature carried out over a long period on a specific tile field will also give information on the rate of movement of the contaminant front, and thus predictions as to the life of the tile field may be made.

7.2   Phosphorus Isotherms

   7.2.1   Langmuir Isotherm Model

A plot of phosphorus adsorbed and equilibrium concentration of phosphorus in the supernatant, in units of mg P/100 gm soil and mg P/L, respectively, is shown in Figure 7. It may be observed that this plot of x/m vs c_e produces a curve that approaches a horizontal asymptote. Considering the Langmuir equation,

$$x/m = \overline{Q}\, bc_e /(1 + bc_e) \qquad\qquad (8)$$

it is obvious that as c_e becomes large,
   ie $bc_e \gg 1$,
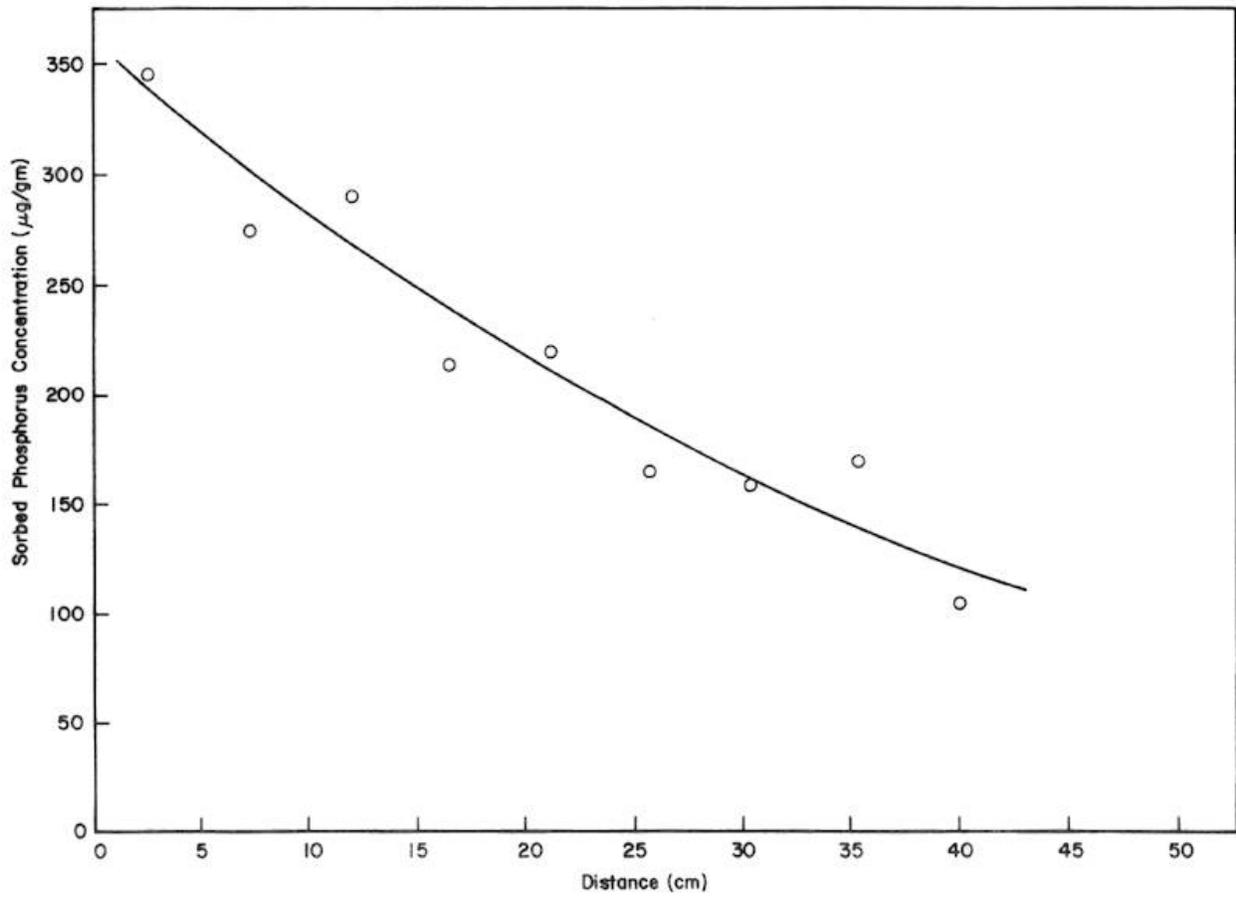 $X/m = \overline{Q}$

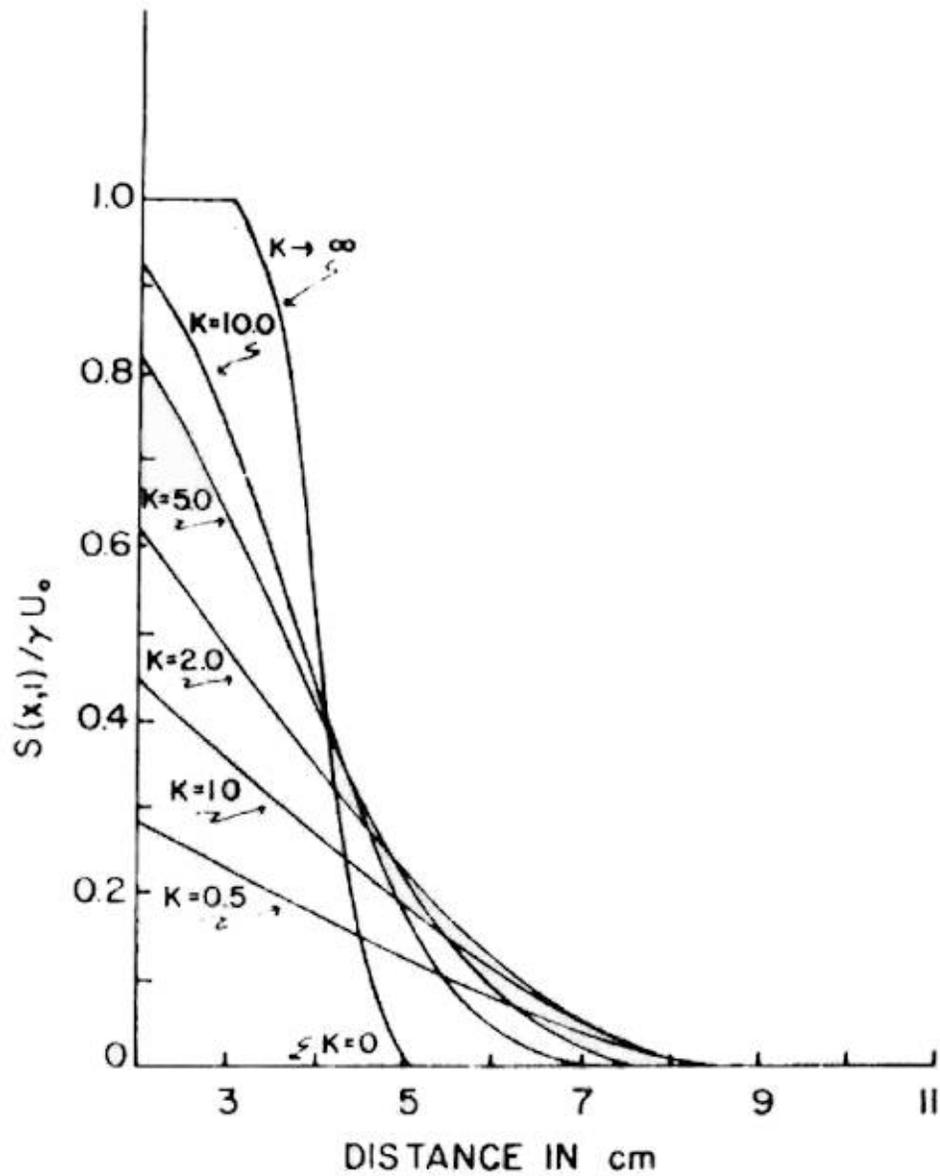**Figure 5**. Phosphorus Concentrations in a 43.2 cm Laboratory Column.

Figure 6. Relative sorbed phase concentration $S(x,1)/\tau\, U_o$ distributions for some values of K (rate of exchange coefficient) as a function of distance x (cm) from the top boundary (x = 0 plane).

indicating that the isotherm curve will approach the value of $\overline{Q}$ which is the maximum sorptive capacity.

To determine $\overline{Q}$ more readily, the Langmuir equation may be expressed as

$$\frac{1}{x/m} = \frac{1 + bc_e}{\overline{Q}\, bc_e} \tag{55}$$

$$= 1/\overline{Q}\, b \bullet 1/c_e + 1/\overline{Q} \tag{56}$$

Plotting $1/(x/m)$ vs $1/c_e$ generally generally produces a straight line, the c_e intercept of which on the $1/(x/m)$ axis gives $1/\overline{Q}$, allowing one to obtain a value for the maximum adsorption capacity, $\overline{Q}$, (Figure 8). The $\overline{Q}_{max}$ value is frequently cited in the soils literature as a characteristic of the soil; however, the x/m value of most practical interest is the one that occurs at the concentration of the wastewater to be applied in the field.

Other examples of isotherm plots are shown in Figure 9 for various soils from the Kingston Ontario area. The variation in $\overline{Q}_{max}$ is due to the different compositions of the adsorbing fractions, which consist mainly of clay and silt, and the amount of phosphorus previously adsorbed and occupies active adsorption or exchange sites.

7.2.2   <u>Active Adsorbing Fraction of Soil</u>

According to Bear[38] it is well known from numerous investigations that the ion exchange property of soil is due almost entirely to the clay and silt fractions (<20 µm) and the organic matter; the colloidal material of soil being most important.

Figure 10 shows a plot of $\overline{Q}_{max}$ vs the percent silt for various samples taken from two different areas. In both cases thee is a correlation between % silt and clay and the value of $\overline{Q}_{max}$ for phosphorus. Studies done on sand of high silica content showed no phosphorus retention. Also soil fractions larger than 100 mesh containing no organics exhibited negligible phosphorus removal.
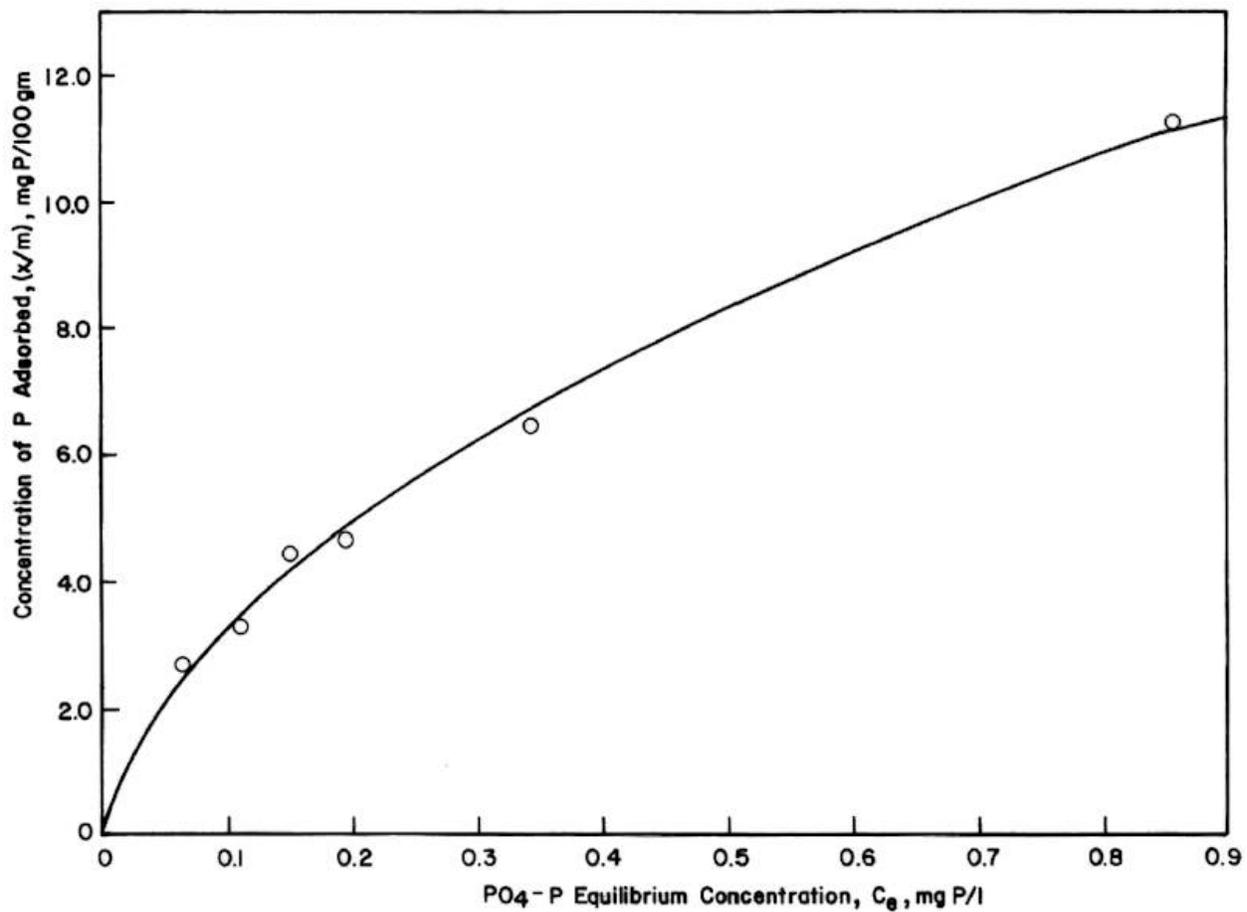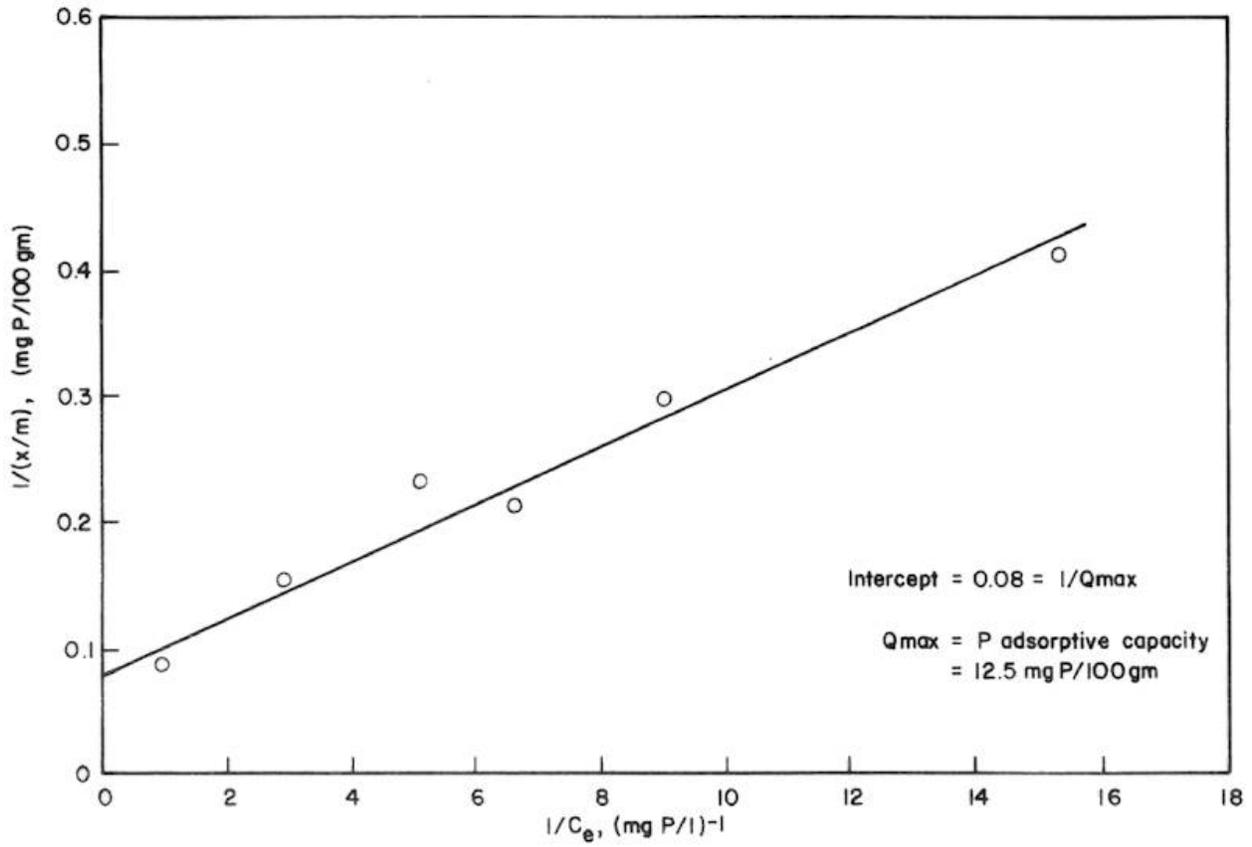
Figure 7. Phosphorus Adsorption Isotherm for Soil.
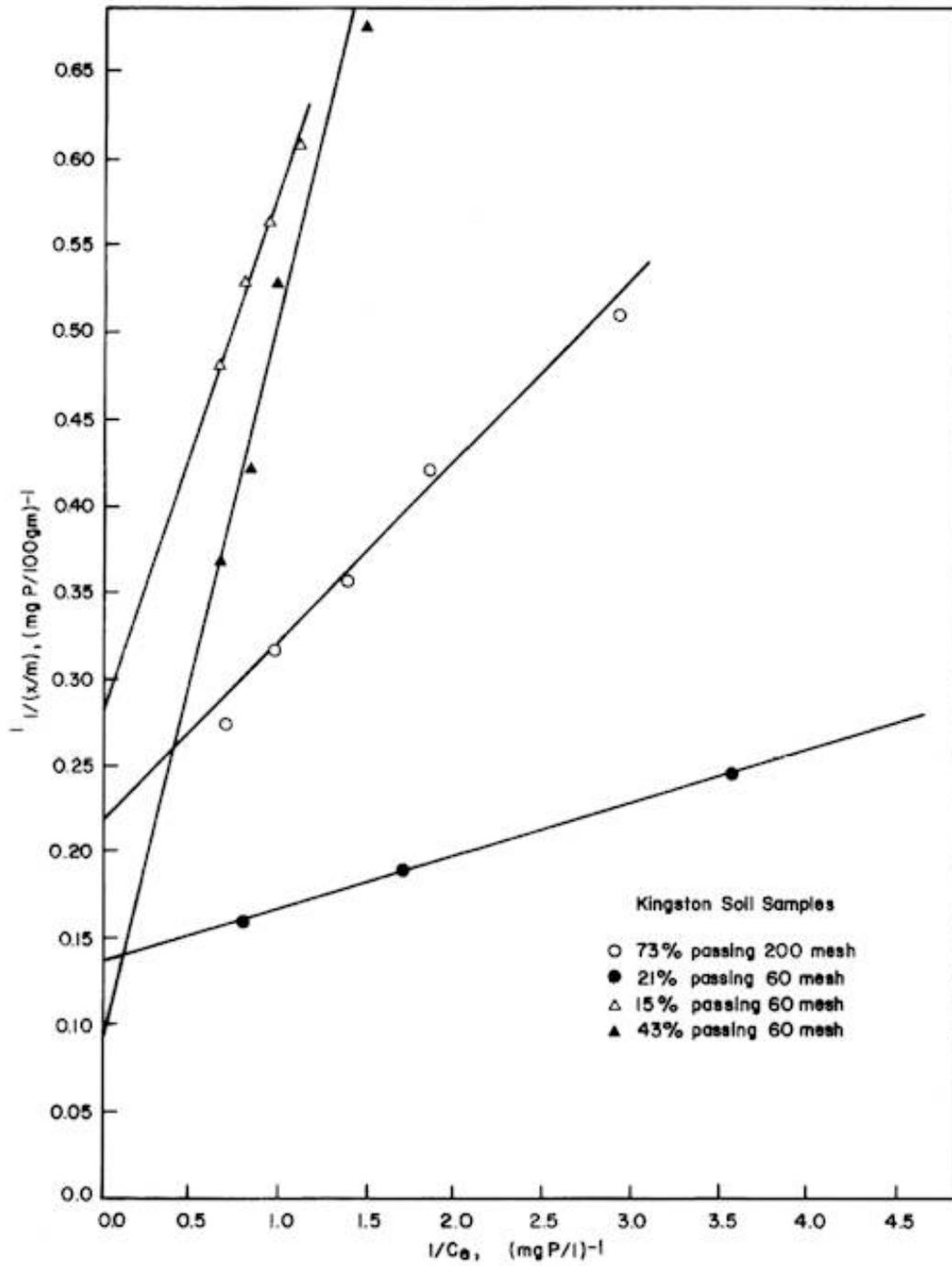
Figure 8. Plot of $1/(x/m)$ vs $1/C_e$.

Figure 9. Plots of $1/(x/m)$ vs $1/C_e$ for several Kingston, Ontario soils.

7.2.3   Phosphorus Desorption

If physical adsorption were the dominant mechanism, adsorbed phosphorus would be rapidly desorbed when the concentration in the applied solution is low. Samples which had undergone the adsorption process were subject to desorption using distilled water and shaking over period of one week. These samples did not release phosphorus of an equivalent amount as adsorbed but retained a significant quantity. This is the criterion which indicates that the removal phenomenon is not solely the result of physical adsorption but other mechanisms also remove or insolublize the phosphate.

Rainfall leaching will tend to remove a fraction of the sorbed P, but this effect is usually minimal since rainfall percolation rates are usually quite small relative to the wastewater application rate, and, with the long time involved in ground water travel, considerable retention and slow mineralization of phosphate ion occur.

7.2.4   pH Effects

The overall effects of soil pH on adsorption are well known and have been thoroughly discussed.[38, 21] In general, the removal of phosphate decreases with increasing pH except for the conditions involving a $CaCl_2$ solution at high pH. The literature confirms this fiend for acid soils in which iron and aluminum are responsible for the removal.[39, 40] However for alkaline soils in which calcium is responsible for removals, the reverse is true of pH.[39, 40]

The data from the Kingston soil samples are plotted in Figure 11 showing the trend of x/m with soil supernatant pH. As anticipated with these acid soils, the amount adsorbed decreased with increasing pH. In general, no prediction of this variation could be made since the independent variables such as initial soil pH, initial phosphorus concentration, and the nature of the soil counter ions and co-ions are dependent on the nature of the clay and silt mineral content.
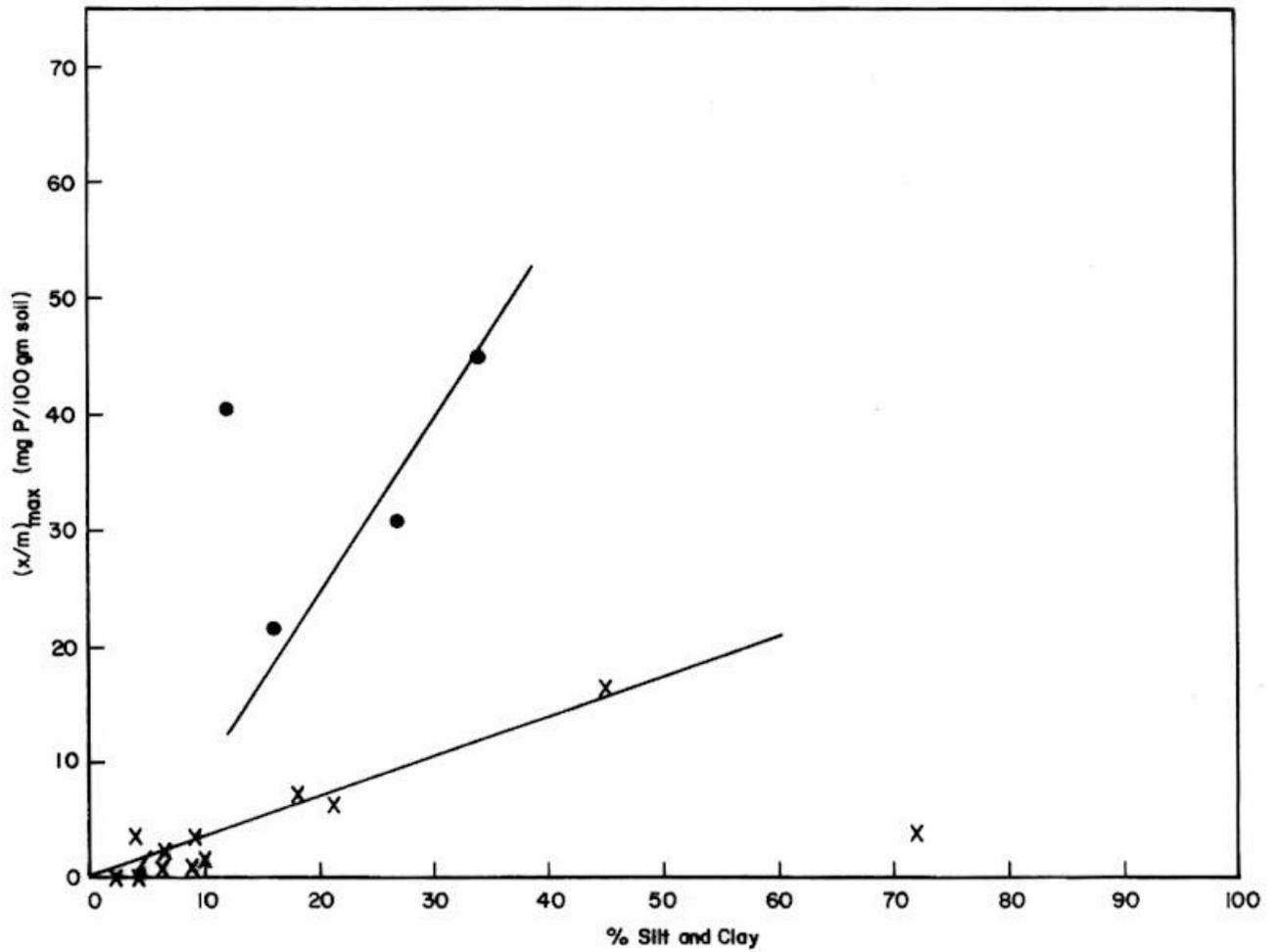
Figure 10. Plot of P vs % Silt and Clay for Two Kingston Locations.

7.2.5   Effects of Contacting Solutions

Isotherm analyses were performed on a Toronto soil of pH 6.8 and passing 200 mesh, using different contacting solutions of phosphorus. The solutions used were:

1.   phosphorus in distilled water
2.   phosphorus in 0.01M NaCl
3.   phosphorus in 0.01M $CaCl_2$

As mentioned before, some investigators favour using 0.01M NaCl or 0.01M $CaCl_2$ because it may simulate soil solutions, stabilize pH, and aid in coagulation of soil colloids which could interfere with phosphorus measurements.

The isotherms for the three contacting solutions are plotted in Figure12. The values for this soil are shown in Table 1.

Table 1.   Effect of Contacting Solutions.

	Solution	$\overline{Q}_{max}$
1	P in distilled water	10.3
2	P in 0.01M NaCl	26.1
3	P in 0.01M $CaCl_2$	28.2

The results show that $\overline{Q}_{max}$ is increased by the use of NaCl and $CaCl_2$. The question of which solution should be used must be based on the nature of the effluent entering the soil and the concentration of Ca^{2+} and Na^+ already present in the ground water. In the large, Na^+ is preferred over Ca because of the precipitating effect of Ca^{2+} in producing higher $\overline{Q}_{max}$ values. In this investigation, only phosphorus and distilled water solutions were used in order to minimize effects which were not native to the soil sample being analyzed.
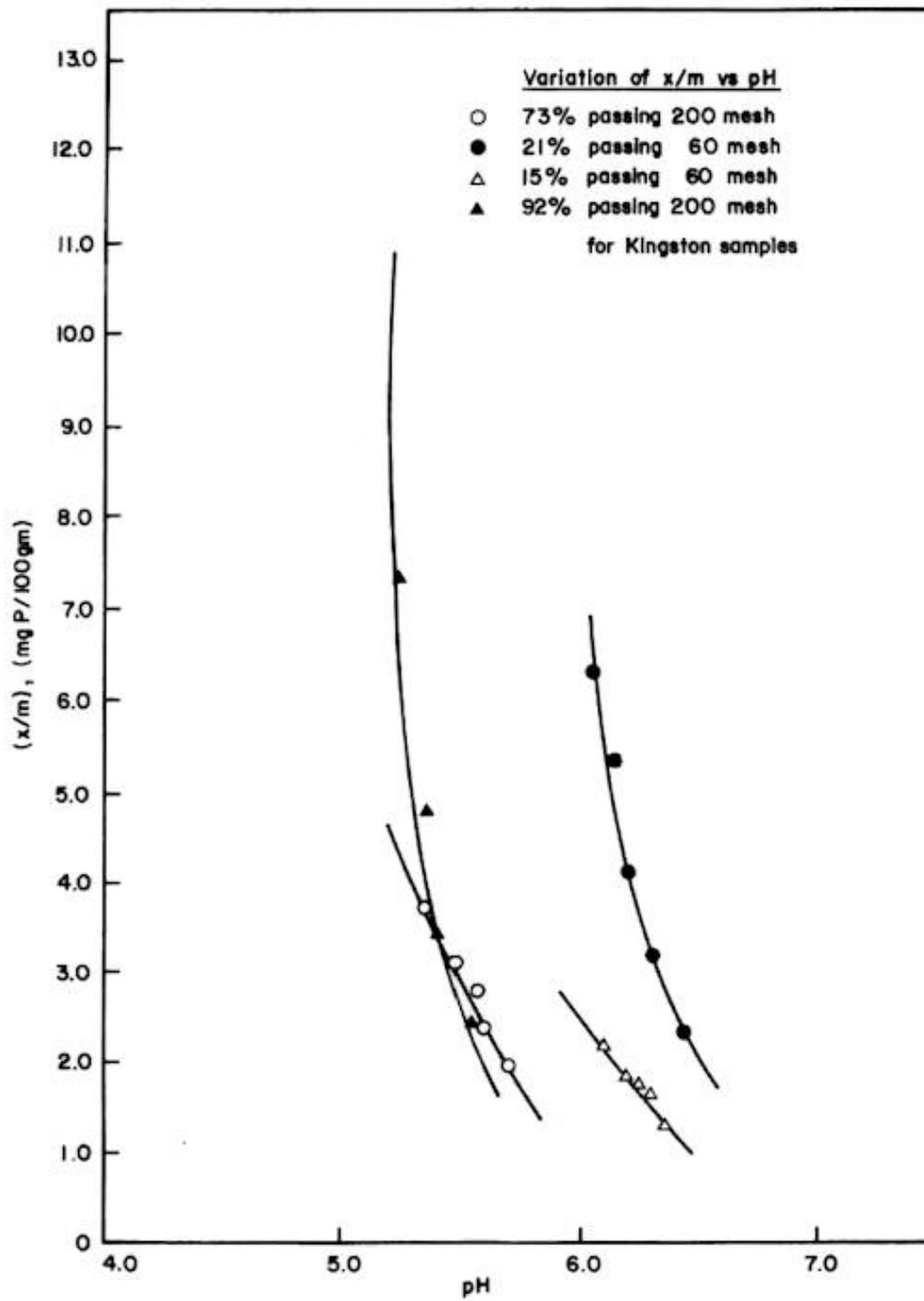
Figure 11. Variation of (x/m) with pH.

7.2.6   Approach to Equilibrium

To test the approach to equilibrium, two sets of samples were weighed out and shaken for five days with one sample from each set removed and analyzed after 4 hrs, 24 hrs, 72 hrs and 120 hrs. One set of samples contained 1.0 gram quantities of Toronto soil, pH 6.8, and the other set contained 5.0 gram samples of the same soil. The phosphorus solutions contained 1.63 mg/L P (5 mg/L PO_4^{3-}) for both sets. The values for x/m and time are plotted in Figure 13 for each set of samples.

From the curves it is apparent that equilibrium was reached in 30 hr for the 5 gm sample, and almost approached at 120 hours for the 1 gram sample. One reason for the differences in approach to equilibrium is the variation in relative initial ratios of phosphorus to soil weights as shown in Table 2.

Table 2.   Phosphorus to Soil Ratios.

Sample Size	Solution Concentration (mg P/L)	Initial ratio P to Soil (mg P/100 gm)
1.000	1.63	22.3
5.000	1.63	4.84

The difference in the rate of approach to equilibrium is governed by Fick's First Law which is expressed as

$$dS/dt = k_m (S^* - S) \tag{57}$$

where S is the amount of P adsorbed per unit weight of soil, S^* is the equilibrium amount adsorbed and k_m is the mass transfer coefficient for a particular batchwise shaking process. If we consider the low range of the equilibrium isotherm which is approximately linear, the relationship between the solution concentration and the adsorbed concentration is
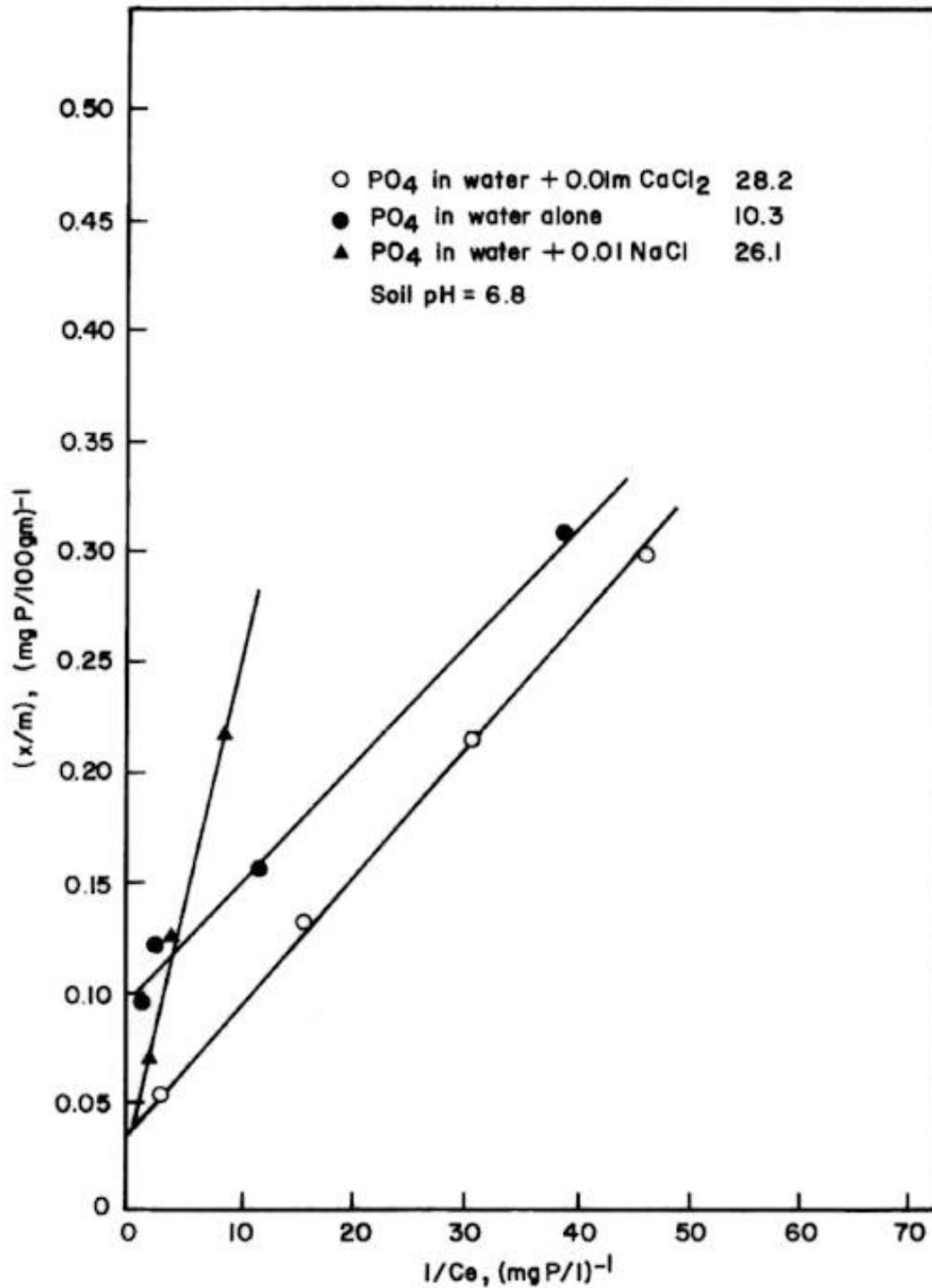
$$S^* = \lambda c \tag{58}$$

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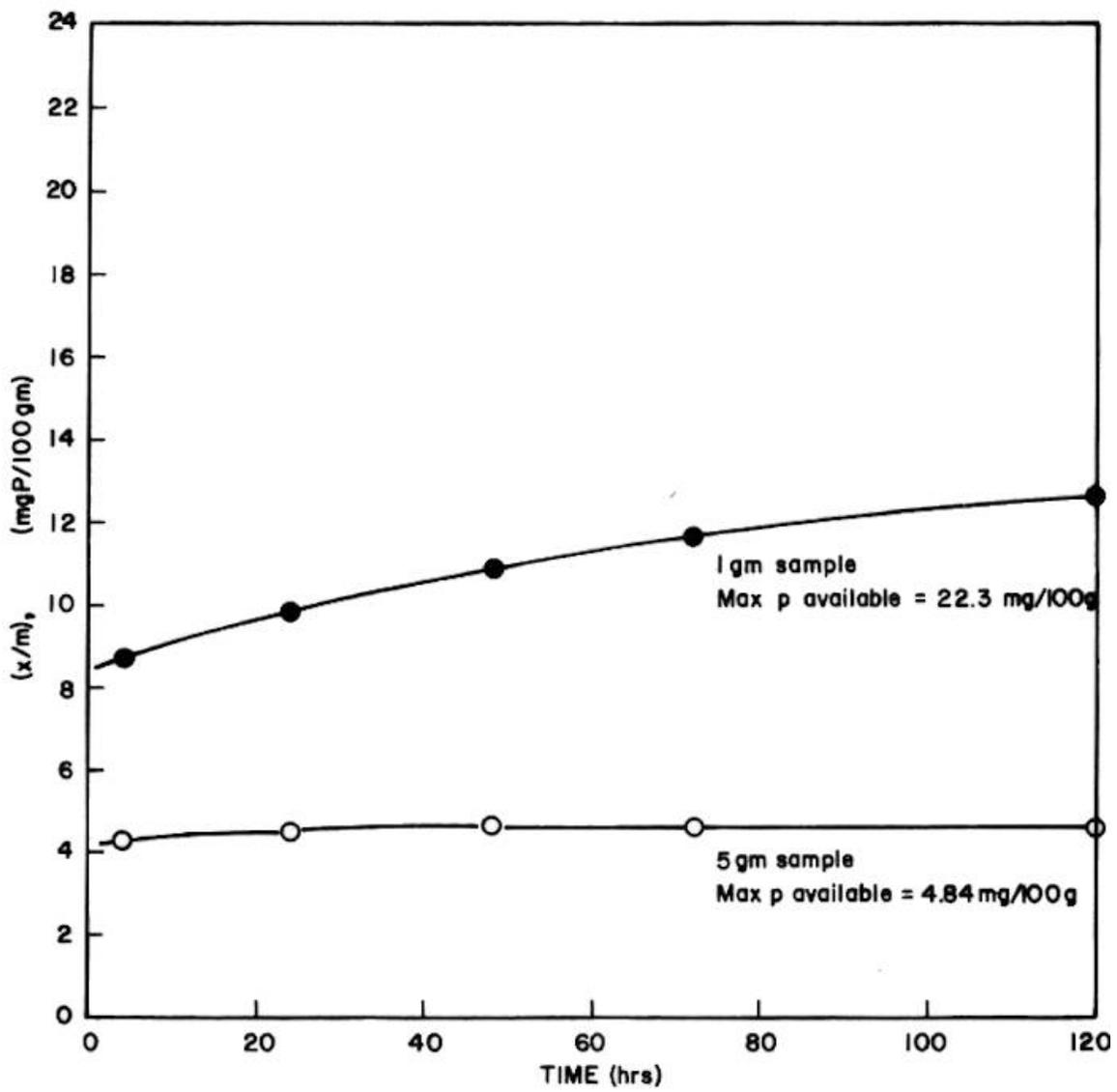**Figure12.**   Effect of Stabilizing Solutions on PO$_4$ -P Adsorption.

Figure 13. Approach to Equilibrium.

where λ is a partition coefficient and c is the solution concentration referred to the unit weight of sample. Therefore Fick's law becomes

$$dS/dt = k_m (\lambda c - S) \tag{59}$$

The value of c is 22.3 mg P/100 gm for the 1 gm sample and 4.84 mg P/100 gm for the 5 gm sample. If the initial amount of P on the soil is S_o, the concentration driving forces for the two samples are (λ x 22.3 - S_o) and (λ x 4.84 - S_o), respectively. The 1 gram sample has a greater slope, dS/dt, and thus, the time to reach equilibrium will be greater.

This result then implies that the equilibrium time for each sample weight or concentration will be different, and attainment of equilibrium is only reached after 120 hours for all cases covered in this concentration range.

For the range of concentrations involved in this study, 78% approach to equilibrium can be attained within 24 hours. The rate of water travel through soil is often less than several meters per day so adequate contact time per day is available for P removal.

7.3   Example Calculation of Contaminant Movement in Soil

The application of the contaminant movement equation derived in Section 5.0 is illustrated below using a hypothetical example. Data for an actual situation are in the collection phase and are not yet available.

Consider the case shown in Figure 14 for a septic tank tile field with 4 laterals 15.24 m in length and 1.829 m apart. The following physical parameters would be obtained by measurement:

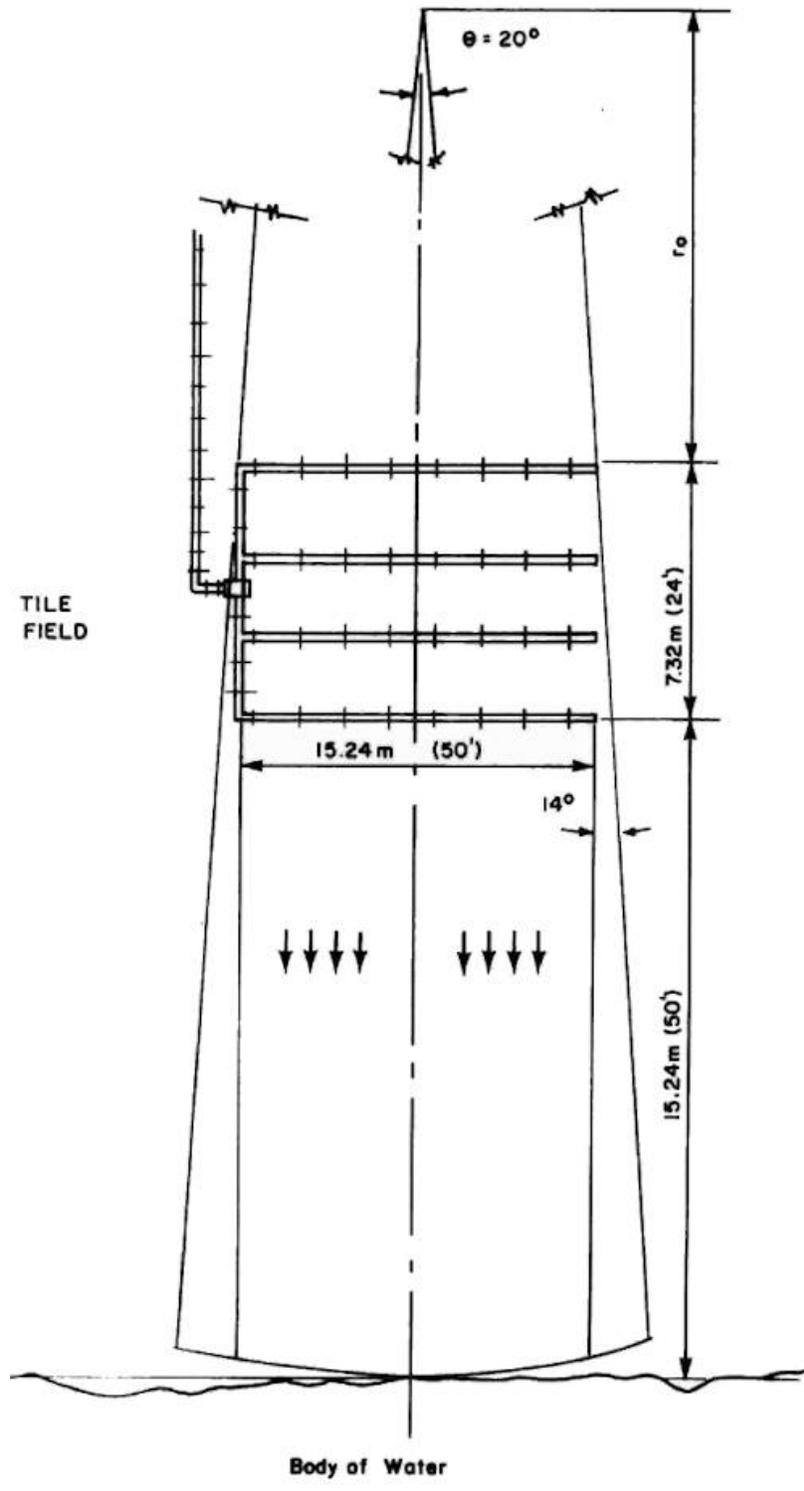$$v_\omega \; = \; \text{water movement rate} = 0.1 \text{ m/day}$$

Figure 14. Tile Field Configuration.

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ρ_B = soil density = 2.7 gm/cm^3 or 2.7 x 10^3 gm/L

ε = soil porosity = 0.2

r   = movement distance to body of water

          = 7.32 + 15.24 = 22.56 m

The chemical parameters are:

c_o = the septic tank phosphorus effluent concentration

          = 20 mg/L P, obtained by chemical analysis,

$\overline{Q}_{max}$ = 4.52 mg P/100 gm or 4.52 x 10^{-2} mg P/gm soil

b   = 2.193 L/mg

and $\overline{Q}_{max}$ and b are obtained from a Langmuir isotherm analysis.

A further assumption to be made is that the phosphorus penetrates to a depth of 61.0 cm at the lateral farthest from the lake, and increases linearly to a depth of 183.0 cm at the bank.

ie: h_1 = 0.61 m

       h_2 = 1.83 m

and the angle of dispersion, 0, is 28°.

From the appropriate equation for the relative rates of movement,
the value of v_c may be obtained,

$$\frac{v_\omega}{v_c} = 1 + \frac{\overline{Q}_{max}\, \rho_B\, b}{\varepsilon} \cdot \frac{1}{1 + bc_o\, [r_o/(r_o + r)]\, h_1/h_2} \tag{53}$$

and r_o = W/2 / sinθ/2

therefore r_o = 15.24/2 /sin 14°   = 31.5 m

$$\frac{v_{\omega}}{v_c} = 1 + \frac{4.52 \times 10^{-2} \times 2.7 \times 10^3 \times 2.193}{0.2} \quad \frac{1}{1+2.193 \times 20.0 \, (31.5/54.1)(0.61/1.63)}$$

$$= 1 + 1338.2 \ (0.1051)$$

$$= 141.7$$

Therefore   for v_{ω} = 0.1 m/day,

v_c = 0.1/141.7 = 7.058 x 10^{-4} m/day

To move 22.56 m, the time required is

$$t = \frac{22.56 \text{ m}}{7.058 \times 10^{-4}} = 3.196 \times 10^4 \text{ days}$$

or 87.6 years.

If the rate of water movement were 0.3 m/day, the time for the soil to be exhausted would be 29.2 years.

8.0   Conclusions

1.   Phosphorus removal from effluents passing through soil is caused by a combination of three mechanisms: ion exchange, physical adsorption and precipitation.

2.   The ability to remove anions from solution is related to the structure and mineral content of the clays.

3.   Clays act in the ion exchange mode as compared to the adsorption mode, prefer the counter ion of higher valence, and selectivity increases with decreasing hydrated radius.

4.   Phosphate isotherms can be determined by a 24 hour batch equilibration with a solution of a known phosphorus concentration.

5.   The Langmuir isotherm provides a convenient method for modelling the sorption variation with concentration.

6.   The Langmuir model can be readily extended to multi-species solutions to estimate sorption properties.

7.   The rate of movement of a contaminant in groundwater flow can be estimated using a form of the equation

$$v_\omega / v_c = 1 + q_\infty \rho_B / \varepsilon c_o$$

and the required parameters are the maximum adsorption capacity, the soil density and porosity, and the concentration of the contaminant.

Nomenclature

a	empirical constant = $\overline{Q}\, b$
a_1	empirical constant
A_i	cross-sectional area at position, i, m^2
b	empirical constant related to energy of adsorption, L/mg
b_i	value of b for species i
b_1	empirical constant
c	concentration, mg/L or moles/L
c_i	concentration of species i, mg/L, moles/L
c_e	equilibrium concentration, mg/L, moles/L
c_β	final concentration, mg/L, moles/L
$\overline{c}_o$	initial concentration, mg/L, moles/L
c'	empirical constant
D	dispersion coefficient, cm/sec
h_B	height of bed, m
k	empirical constant
k_l	linear equilibrium constant, L/mg
k_{km}	kinetic rate constant
k_m	mass transfer coefficient, sec^{-1}
K_B^A	equilibrium coefficient based on the mass action law.
L	length of bed, m
m	weight of soil sample, gm
m_i	molality of species, i, m mol/gm solvent
$\overline{m}_i$	molality of species, i, on exchanger, m mol/gm solvent
n_i	depth of dispersion at point i,
n_2	constant for Freundlich Isotherm
p	empirical constant
Pe	Peclet Number = vL/d
q	adsorbed concentration = x/m, mg/gm; or $(x/m)_{100}$, mg/100 gm
$\overline{Q}$	weight capacity of exchanger mg/gm or mg/100 gm
r	radial distance, m
Re	Reynolds' Number = $vd\rho/\mu$

R_i	rate of addition or removal of species i, mg/L sec
S	amount of adsorption on soil, mg/gm
S*	amount of adsorption on soil at equilibrium, mg/gm
t	time, sec
v	velocity, m/sec
V	volume, m^3
W	width of initial dispersion, m
n	amount of solute adsorbed, mg

Greek Letters

α	angle, rad
ε	porosity
θ	angle, rad
η	1/Pe
n_i	molal distribution coefficient
$n!_i$	molar distribution coefficient
μ	viscosity, cp
v	valence state
ξ	pore volume = vt/L
ξ'	modified pore volume
ρ	density
ρ_B	soil density
φ	porosity

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