THE DIFFUSIVE TRANSPORT OF PHOSPHATE AND ASSOCIATED CATION IN SOIL AND SOIL-LIKE SYSTEMS

BY

OLALEKAN OLUWOLE AKINREMI

A Thesis

Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

Department of Soil Science
University of Manitoba
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ABSTRACT

P sorption studies were conducted using the batch technique with calcareous and noncalcareous soils. The calcareous soils had a higher P sorption capacity than the noncalcareous soils. The commonly used adsorption isotherms: Langmuir; Freundlich; Gunary; and Polynomial equation described the sorption data very well, but none of the kinetic equations utilized adequately described P sorption with time.

Column studies were conducted to investigate multi-ionic diffusive transport using a cation exchange resin model system. The objective was to demonstrate the effect of cation exchange on the movement of the phosphate ion. 0.2 g KH_2PO_4 was added to the surface of a Ca-saturated resin-sand mixture packed in a cylindrical wax column to simulate one-dimensional diffusive transport. The ions of interest were Ca^{2+}, K^+, H^+ and phosphate ($H_2PO_4^-$ and $HPO_4^=$).

The pH of the system was low as a result of the added salt and the low buffering capacity of the resin-sand mixture. The higher the CEC of the column, the lower was the pH of the soil column due to the retardation of hydrogen ion movement and hydrogen ion production during precipitation reactions. The movement of K^+ and P was retarded with increased CEC and the K^+ ion moved slightly behind the phosphate ion. There was an accumulation of calcium in the soil solution in the form of a snow-plow as a result of ion exchange with the applied K^+, the level of solution calcium increased with CEC.

In another experiment, $CaCO_3$ was added to the column to act as a buffer and also permit the assessment of the relative contribution of $CaCO_3$ and exchangeable Ca^{2+} to the precipitation and retardation of phosphorus movement. The presence of calcium carbonate as a buffer maintained a pH regime favourable to P precipitation. High levels of precipitation was observed with $CaCO_3$ alone or in combination with Ca^{2+}-saturated exchange resin. The magnitude of P precipitation and retardation was elevated in the presence of exchange resin leading to the conclusion that the exchangeable Ca^{2+} was an important source of the calcium ion involved in the precipitation reaction with the surface applied P.

The ionic distribution obtained in columns packed with calcareous and noncalcareous soils were comparable to those from the resin columns. The calcareous soils had a higher pH than the noncalcareous soils following the addition of 0.2 g KH_2PO_4 even where the initial pH for these soils were similar. Higher levels of precipitated P were obtained in calcareous soils than in noncalcareous soil suggesting that calcium came from both the exchangeable and nonexchangeable sources.

A mathematical model consisting of n equations representing each of the n interacting ionic species was formulated. The model takes into consideration the effect of cation exchange reaction on the mobility of P. Also, the role of H^+ ion was explicitly expressed in the model. Output generated showed a good agreement between the predicted ionic profiles and the observed profiles in the model system. The formulated model is applicable to acid soils where Al^{3+} and Fe^{3+} are the dominant ions on the exchange complex. The model can also be utilized to investigate the influence of salts banded along with phosphate, on the movement and immobilization of phosphate in soils.

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> "Who among the gods is like you O Lord?,
> Who is like you - Majestic in Holiness,
> awesome in Glory working wonders?".
> Exodus 15:11.

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INTRODUCTION

Many aspects of phosphate chemistry have been studied over the years because of the agronomic importance of P and also because of its intensive interaction with the soil matrix. The latter generally results in a low solution concentration of P in the soil even after a generous application of P fertilizer.

Of all the aspects of P chemistry, very few have been studied as extensively as the adsorption of P in the soil. According to Motts (1981), "the impetus to research in this area has largely been the practical necessity to understand the behaviour of applied phosphate fertilizer and it is some indication of the complexity of the problems involved that, even after decades of efforts by soil chemists and agronomists this understanding is far from being complete".

Mathematical modelling of P transport in the soil is often accomplished by combining the continuity equation with the adsorption isotherm (Cho et al., 1970; DeCamargo et al., 1979). The parameters needed for these models are customarily obtained from either the Langmuir or the Freundlich plot of adsorption data. Hence, an experimental measurement of adsorption (or retention) of P in the soil is a prerequisite to the formulation of any model describing its movement.

This study, dealing with the sorption of phosphorus in calcareous and noncalcareous soils is intended to provide sorption parameters which can be incorporated into the transport model for simulating the diffusion of P from the fertilizer band in these soils. As much as possible, a detailed review of the literature on P adsorption will be undertaken. While the controversy surrounding the mechanism for P retention in the soil (the adsorption versus precipitation debate) will be mentioned, its resolution is not intended. This study is thus, pragmatic rather than mechanistic, as such, distinguishing between adsorption and precipitation processes in the soil is beyond the scope of this research.

Interaction of P with the soil can be described in 2 ways: (i) via the equilibrium adsorption isotherm; (ii) through the kinetic approach. Both approaches will be utilized in this study with the aim of generating the equilibrium and kinetic parameters. Also, there are several adsorption isotherms which are known to describe the adsorption of P reasonably well (Barrow, 1978). The choice of an appropriate isotherm can be a daunting exercise for a modeller. It is the aim of this study to generate adsorption parameters using different isotherms. The concentration profile of P obtained with each of these isotherms will then be compared, with the aim of recommending an isotherm. Very seldom are the adsorption isotherms compared with respect to their ability to account for P reactions when incorporated into the transport equation. In this study, the customary Langmuir and Freundlich isotherms will be compared to the Gunary and the polynomial (cubic) equations with respect to the predicted profiles of P when these isotherms are incorporated into the transport equation.

LITERATURE REVIEW

Adsorption Process

The phenomenon of concentration of liquid or gaseous materials on the surface of a solid is known as adsorption (Larsen, 1967). Adsorption is a surface phenomenon, as such, it is a two-dimensional process and this seems to be a distinguishing feature from precipitation that usually involves growth in the three dimension. This distinction is only theoretical, however, as discussion comparing both processes will later reveal.

The soil as a whole is made up of particles that have a net negative charge on their surfaces. Nevertheless, it is still capable of strongly retaining an anion such as P. This process of retention by the soil is referred to as adsorption. Many of the knowledge gained about the adsorption process in the soil has been chiefly from studies involving the fate of P fertilizers in the soil (Motts, 1981). The adsorption process involves two interacting elements, the adsorbate (e.g. P) and the adsorbent (e.g. the soil) thus, the properties of these two govern the adsorption process.

According to Motts (1981), anions can be classified into 2 groups: (1) nonspecifically adsorbed ions; (2) specifically adsorbed ions. The nonspecifically adsorbed ions e.g. Cl^- and NO_3^- are those that are retained on the positive sites by simple electrostatic attraction following anion exchange. These groups of ions are assumed to obey the diffuse layer equilibrium (Arnold, 1978). The second group consists of anions that have a far greater affinity for soil surface than their concentration in solution would suggest. In the adsorption of these ions, simple electrostatic attraction gives way to the formation of chemical bonds with the surface groups. The phosphate ion belongs to this group of specifically adsorbed ions.

Using anion exchange resin, Taylor and Ellis (1978) concluded that at low concentration, P was bonded by two points of attachment (bidentate bonding) after deprotonation of the $H_2PO_4^-$ ion. This was followed by one point attachment (monodentate bonding) at high P concentrations during adsorption on resin surface. This resulted in the deviation of the adsorption plot from that predicted by the Langmuir equation.

Adsorption Isotherms

An adsorption isotherm is defined as the relation between the amount of substance adsorbed by an adsorbent and the equilibrium concentration of the adsorbate at constant temperature. The usefulness of adsorption isotherms in describing phosphorus adsorption is indicated by its utilization in one form or another by virtually all researchers dealing with P adsorption (Griffin and Jurinak, 1975; Taylor and Ellis, 1978; Mead, 1981; Polyzopoulos et al., 1985; Mehadi and Taylor, 1988).

The most widely used adsorption isotherms are the Langmuir, Freundlich, Gunary, Temkin, BET and the polynomial isotherms. For a detailed treatment of adsorption isotherms the reader is referred to a review by Barrow (1978).

(a) The Freundlich Isotherm

The Freundlich adsorption isotherm has been used to characterize phosphorus adsorption in the soil (Olsen and Watanabe, 1957). It is an empirical formulation, as such, it is nonspecific and is applicable to a wide range of equilibrium phosphorus concentration. The Freundlich equation may be written as

$$q = kC^b \qquad [1.1]$$

where q is the amount of P adsorbed per unit mass of adsorbent (μg/g), C is the equilibrium concentration of the adsorbate (μM), k and b are constants. A logarithmic transformation of this equation gives a straight line represented by

$$\log q = \log k + b\log C \qquad [1.2]$$

A plot of log q against log C should give a straight line with log k as the intercept and b as the slope if the sorption data conforms to the Freundlich isotherm. It should be noted that for q = C, a log transformation would similarly give a straight line even though the original equation did not conform to Freundlich isotherm.

(b) The Langmuir Isotherm

In contrast to the Freundlich isotherm, the Langmuir adsorption isotherm was formulated from the kinetic theory of gases and was used extensively to describe gas adsorption on solids. The isotherm has been found to be applicable to phosphorus adsorption under more dilute equilibrium phosphorus concentration. Olsen and Watanabe (1957) reported that the adsorption of phosphorus by soils from dilute solutions showed a closer agreement with the Langmuir isotherm than the Freundlich isotherm.

Apart from the mode of derivation, the popularity of the Langmuir isotherm stems from the ability to generate adsorption parameters which can be of practical significance (Fried and Shapiro, 1956; Olsen and Watanabe, 1957). According to these earlier workers, the major advantage of the Langmuir equation over the Freundlich is that an adsorption maximum can be calculated. This parameter can be related to various soil properties and supply information about the nature of the reaction between the soil and fertilizer phosphorus. In his review, Barrow (1978), was of the opinion that this can hardly be regarded as an advantage, since the maximum calculated at the low concentration is easily exceeded when higher concentrations are used.

The Langmuir equation is written as :

$$q = kbC/(1+kC) \qquad [1.3]$$

where q = amount adsorbed per unit mass of adsorbent ($\mu g\ g^{-1}$)

C = equilibrium concentration of the adsorbate (μM)

b and k are constants

b is the capacity factor referred to as the "adsorption maximum" and k is the "affinity" factor. k reflects the relative rates of adsorption and desorption at equilibrium (Barrow, 1978).

Conformity with the Langmuir isotherm is verified by a plot of the experimental data to the linearized form of equation [1.3]. It is worth noting that equation [1.3] can be linearized in several ways each giving slightly different parameters when applied to the same adsorption data (Dowd and Rigs, 1965). The most common or universal form is given by

$$C/q = 1/kb + C/b \qquad [1.4]$$

If the data conforms with the Langmuir isotherm, a plot of C/q against C will yield a straight line whose slope is $1/b$ and intercept is $1/kb$. A combination of these regression coefficients allows the calculation of b and k.

In spite of the popularity of the Langmuir isotherm for describing P sorption in the soil, it has repeatedly been criticized on the basis of its limitations. Barrow (1978) was of the opinion that the Langmuir isotherm is seldom applicable to sorption of P in the soil because it assumed constant energy of adsorption which contradicted observable pattern in the soil. Posner and Bowden (1980), stated that the assumption of no interaction between the adsorbed species is not realistic when the adsorbing species are charged and adsorption changes the charge on the adsorbing surface. They suggested that except under restricted circumstances neither the Langmuir isotherm nor a combination thereof can give a realistic description of the adsorption process.

That conformity with the Langmuir adsorption isotherm is not indicative of an adsorption process was demonstrated by Veith and Sposito (1977). These authors concluded that the Langmuir equation cannot be used statistically to determine whether adsorption or precipitation is occurring during fixation reaction in soils.

(c) Gunary Isotherm

The Gunary adsorption isotherm is a modification of the Langmuir adsorption equation. It was formulated as a result of the failure of the Langmuir equation to adequately describe the data generated in 24 surface soils (Gunary, 1970). The equation is given by:

$$C/q = A + BC + D\sqrt{C} \qquad [1.5]$$

where A, B and D are constant coefficients and C and q are solution P and adsorbed P concentration, respectively.

Though there was no theoretical basis for this modification, the new model gave a better fit in 24 soils accounting for more than 99.8 % of the variation in phosphate sorption (Gunary, 1970). The presence of the square root term was interpreted to imply that the soil will adsorb a little phosphate firmly, a slightly greater amount of P less firmly, and so on until a limiting value is reached.

Other adsorption isotherms have been used to describe P sorption in the soil. The list includes the Temkin (Mead, 1981; Polyzopoulos et al., 1985), the BET (Griffin and Jurinak, 1975; Taylor and Ellis, 1978; Mehadi and Taylor, 1988); and the polynomial equation (Hater and Foster, 1976).

Kinetics of Adsorption

The adsorption isotherms described above were formulated on the implicit assumption that the sorption reactions are instantaneous and the system itself is in equilibrium. Reported sorption studies indicate otherwise, as the influence of equilibration time is commonly observed (Ibrahim and Pat, 1982). Phosphorus sorption is typically rapid during the first few hours or days of incubation, this is then followed by a much slower reaction (Rajan and Fox, 1972; Ryden et al., 1977; Enfield and Ellis, 1983). The initial fast reaction is considered to be primarily due to adsorption while precipitation, to relatively insoluble forms, controls the slow reaction (Rennie and McKercher, 1959; Munns and Fox, 1976; Sawhney, 1977).

Unlike the equilibrium approach, the kinetic aspect of P sorption is not well developed. Several approaches have been utilized in the kinetic study of P sorption, but most of the proposed equations have a limited ability to describe P reaction with the soil (Enfield et al., 1981). The approaches range from empirical descriptions of sorption data (Enfield, 1974; Hater and Foster, 1976) to theoretical approximation (Griffin and Jurinak, 1973).

From the theoretical viewpoint, when the fraction of surface uncoverage was used as the only factor governing the rate of adsorption, then a first order kinetic equation was obtained (Haque et al., 1968). Ignoring the fraction surface uncoverage and considering concentration as the only rate determining factor (or vice versa), leads to a pseudo first-order reaction (Peterson and Kwei, 1961; Sawhney, 1986). Kuo and Lotse (1972) utilized a second order kinetic equation which considered the simultaneous change in phosphate concentration and the change in surface unsaturation due to adsorption. Equilibrium condition was described by a Langmuir isotherm. Griffin and Jurinak (1974) reported that the kinetics of phosphate interaction with calcite could be described by two simultaneous reactions. The first reaction was second order ascribed to the adsorption of phosphate on the calcite surface. The second reaction was first-order and was considered to be associated with the surface arrangement of phosphate clusters into calcium phosphate heteronuclei.

Enfield et al. (1975) made a comparison of 5 kinetic models for describing P sorption in 25 mineral soils. The mean correlation coefficient from the 5 models were 0.81, 0.83, 0.84, 0.86 and 0.86, respectively. Best fit was obtained when a diffusion-limited model was combined with either the Langmuir or Freundlich equation.

Adsorption versus Precipitation

Of all the aspects of phosphorus chemistry, very few are as controversial as the concept of phosphorus fixation. The controversy often boils down to the question of whether the retained P is actually adsorbed, i.e. a surface phenomenon, or a new chemical phase is formed, i.e. precipitation. Uncertainty about the mechanism of P retention has led to the use of the term "sorption" when describing P retention by the soil (Siebsen, 1981). As Enfield and Ellis (1983) pointed out, the problem associated with distinguishing between the twin processes of precipitation and adsorption is reflected in the confusion existing in the literature as to the terminology describing the loss of P from solution. Some choose to describe their data using solubility product theory assuming a precipitation type of process while others attempt to describe the process using sorption isotherms (Enfield and Ellis, 1983).

This problem arises because of the ability of the phosphate ion to participate in adsorption and precipitation reactions (Hsu and Rennie, 1962a; Larsen, 1967; Veith and Sposito, 1977). Sometimes, both reactions occur simultaneously either at different points in the soil or even on the same surface (Sample et al., 1980; Talibudeen, 1981;

Motts, 1981).

Arguments have been made for and against adsorption and precipitation in the literature. The general consensus is that at "low" solution P adsorption will be the dominant process while at "high" P levels precipitation predominates. This distinction has allowed investigators to impose experimental conditions that often guaranteed that the results are best explained as either adsorption or precipitation (Sample et al., 1980). This distinction is however only qualitative as no threshold levels of P has been established in the literature for either of these processes. Such threshold values would be specific to each soil in view of the complexities and difference among soils.

Because the adsorption reaction is presumed to be a rather fast process compared to the precipitation reaction, a kinetic study has been used to experimentally distinguish between these two mechanisms (Olsen and Watanabe, 1957). However, this type of separation has been criticized on the grounds that the chemical bonds formed in both types of reactions are identical in nature (Hsu and Rennie, 1962a; 1962b; Leckie and Stumn, 1969).

In the concentration range at which plants take up P, adsorption may be an important process. However, in the fertilizer band where P concentration may be in the molar range, the role of adsorption can probably be discounted as precipitation will be the dominant process.

Phosphorus Adsorption in the Soil

When the adsorption of phosphorus in the soil is studied, two types of objectives are implicit. There is the agronomic viewpoint, where the retention of P and its control of solution concentration is investigated with the aim of relating the parameters generated to plant availability of fertilizer phosphorus. Secondly, there are those concerned basically with the chemistry of P retention. The latter group concentrates on determining the mechanism of P sorption and the soil constituents responsible for sorption. The use of the adsorption isotherms, some of which have already been discussed, to summarize the sorption data, is a common feature of phosphorus sorption studies.

P adsorption on calcium carbonate has been widely studied, for example, to gain an insight into the P sorption process by calcareous soils (Kuo and Lotse, 1972; Griffin and Jurinak, 1973; Freeman and Rowell, 1981). In their study, Griffin and Jurinak (1973) concluded that the process of adsorption and heterogeneous nucleation are inseparable when describing phosphate interaction with calcite. The adsorption isotherms of phosphate on calcite were shown to be described by a two-region Langmuir isotherm equation. The break in the slope of the Langmuir plot occurred at a concentration level falling between the octocalcium phosphate and the hydroxyapatite line on the solubility diagram.

Phosphorus sorption was studied on kaolinite and montmorillonite by Bar-Yosef et al. (1988). The authors reported that the adsorption of phosphorus by a Ca-clay exceeded that by K-clay. They attributed this to effect of cations on the extent of the diffuse double layer, which determines the accessibility of P to adsorption sites on clay edges.

A phosphorus sorption study of agronomic importance was reported by Kao and Blanchar (1973). These authors investigated P sorption in soil to which phosphate fertilizers had been applied for 82 years. They found that the P sorption capacities of fertilized and unfertilized soils were similar. The soil fertilized with P for 82 years had nearly double the total P content, but the ability to adsorb P was the same.

The Use of Sorption Parameters in P Transport Model

Two groups of researchers are interested in the movement of phosphorus in the soil: the environmentalists; and the agronomists. The environmentalists are concerned with the choice, design and management of waste water land-treatment systems, the object of which is to minimize the potential of future eutrophic reactions and the pollution of underground water when waste water containing P moves through the soil. Mathematical models are formulated to provide information on site selection and the prediction of site longevity, as well as the methods for improving the management of land application systems (Ryden et al., 1981).

On the other hand, the agronomists are interested in the movement of fertilizer P from the point of application to the plant root surfaces where they are taken up. Of importance to this group are the factors controlling the concentration of P in the soil and how this can be manipulated to obtain maximum efficiency of the applied fertilizer.

Several models have been developed to predict P movement in the soil. These range in complexity from the simple, empirical models to more complex, mechanistic multiphasic models. A detail review of some of these models has recently been undertaken (Mansell and Selim, 1981; Ryden et al., 1981; Enfield and Ellis, 1983). A common denominator of these models is the use of a partial differential equation, a generalized form of which is shown below,

$$\partial c/\partial t = D\partial^2 c/\partial x^2 - V\partial c/\partial x - \Phi. \qquad [1.6]$$

Where c is the concentration of P in soil solution, t is time, D is a coefficient combining the diffusion and the hydrodynamic dispersion effects. V is the pore-water velocity, x is the distance and Φ is the reaction term (sink). Φ can be a single process responsible for the removal of P from solution (e.g sorption), or it could be a sum of several processes or pathways of P removal. According to Mansell and Selim (1981) one of the common difficulties with the use of equation [1.6] is the conceptual division of the total concentration, S, of solid phase P into contents for discrete compartments of P compounds. The sum of P in all compartments should provide the total quantity in the solid phase. The simplest mathematical treatment of P interactions in soil has been to define the total concentration (S) in the solid phase as a lumped parameter without any attempt to establish separate compartment of sorbed P.

The main difference between the various models formulated to simulate P convective transport lies in the nature of the sink term Φ. Φ could be a result of sorption-desorption process, precipitation-dissolution, immobilization (chemisorption)-mobilization (mineralization) (Mansell and Selim, 1981). The choice of a particular process depends on individual researchers and the process believed to have predominated. There is no agreement in the literature as to the proper approach for describing the P reaction term.

When the sorption-desorption process is chosen and coupled with the continuity equation, this can be done either using equilibrium or nonequilibrium models. According to Mansell and Selim (1981), models that are formulated for the simulation of phosphorus movement in the soil may be divided into two broad categories. (i) Those approaches that are based on thermodynamics which assume chemical equilibrium and (ii) those that are based on chemical kinetics assuming nonequilibrium.

A basic principle underlying the thermodynamic treatment of P interaction with the soil is that the process must be completely reversible. When P is applied to the soil either in waste water or as fertilizer, it undergoes a complex series of reaction resulting in some degree of irreversibility. As Enfield (1978) concluded, the chemical thermodynamic model for phosphate transport through soil irrigated with waste water is inadequate, since no information is given for P reaction rates. This makes an accurate prediction of the waste water land-treatment systems capacity to react with P over a long time impossible.

The problem with the use of rate reaction theory to describe P transport and transformation is the general lack of experimental data for reaction rates and rate coefficients. Enfield and Shew (1975), compared two nonequilibrium models of P sorption for their ability to predict phosphorus breakthrough curves. Batch equilibration studies were conducted to measure the kinetics of phosphorus sorption, with the objective of obtaining input data required to evaluate the two models. They reported that the empirical equation $\partial S/\partial t = aC^bS^d$ (a, b and d are empirical constants, C = concentration in solution and S = concentration in the solid phase) produced a better fit of the experimental data than a first order rate equation $\partial S/\partial t = m(kC - S)$, where m and k are constants. On the other hand, DeCamargo et al. (1979), considered two types of sites to be responsible for P sorption. Since P sorption on site 1 occurred instantaneously, it was described by an equilibrium sorption model while site 2 required extensive time to equilibrate and hence necessitated the use of a kinetic equation. The model utilized considered both equilibrium and kinetic reactions. The Freundlich equation was assumed for the equilibrium portion of the model with the model parameters obtained from P sorption isotherms.

Shah et al. (1975) proposed a model assuming sorption-desorption reaction as the reaction term. An equilibrium approach was adopted in their model with the equilibrium relationship between phosphorus in solution and adsorbed P described by the Langmuir isotherm.

The convective transport of orthophosphate in several Manitoba soils was carried out by Cho et al. (1970). The adsorption of P was described as a first-order chemical reaction. These authors found that the rate of phosphate movement was greatly retarded by soil-phosphate interactions. The retardation of phosphate movement was increased with an increase in the rate of phosphate fixation of the various soils. The authors concluded that local equilibrium theory cannot be applied to convective transport of phosphate in soil.

Cameron and Klute (1977) expressed the opinion that "in applying the adsorption-desorption relationships to model chemical transport in the soil, the common trend is to assume that chemical transfer (Φ in equation [1.6]) follows either a kinetic or an equilibrium model but not both". The authors then proposed a combination of equilibrium and kinetic adsorption models to describe the nature of the overall reaction. An analytical solution to the one-dimensional convective-dispersive transport equation with a combination of Freundlich isotherm and first order kinetic adsorption model was developed in their work. Parameters for the P sorption equations were obtained by iteration and the individual and combined effects of model parameters on the breakthrough curves and retention profiles were demonstrated.

Transport models dealing with P from the agronomic point of view are not as highly developed as those existing in the literature for P movement in waste water. As pointed out earlier, many of the models dealing with P movement from fertilizer bands employed, exclusively, the diffusion equation. Some of these models did not study ion transport alone but coupled ion transport from the soil to the plant root surfaces with the absorption of those nutrients by the root (Lewis and Quirk, 1967; Nye and Marriott, 1969; Claasen and Barber, 1976; Cushman, 1979).

The mathematical equation employed is one form or the other of the equation proposed by Nye and Marriott (1969) shown below:

$$\partial Cl/\partial t = (1/r.\partial/\partial r) \times (rD\partial Cl/\partial r + v_o r_o Cl/b) \qquad [1.7]$$

where r is the radial distance from the root axis r_o is the root radius. Cl is ionic concentration in soil solution and v_o is the inward flux of water at the root surfaces, d is the differential diffusion coefficient. b is the differential buffer power, dc/dCl.

With respect to the sorption parameters used with this equation, most of the proposed models adopted the local equilibrium assumption (LEA) while the P isotherm in general is assumed to be linear, hence, the use of such a term as the buffer power.

Hira and Singh (1978) modelled the movement of P from fertilizer assuming diffusion to be the important P movement mechanism. They made a local equilibrium assumption and described the sorption of P by the linear equation

$$S = bC + K \qquad [1.8]$$

b is the slope and is customarily referred to as the buffer power and K is a constant.

The assumptions of local equilibrium and linear adsorption isotherm may not actually describe the situation in the soil as discussed earlier. It is the aim of this study to use sorption models that have been tested and are currently acceptable in the models formulated for P transport in waste water treatment.

MATERIALS AND METHODS

All the six soils that were used in this study were surface soils collected from cultivated fields in the spring of 1987 from a depth of 0 - 15 cm. The soils were air dried, and the fine earth (< 2mm) fractions were collected for study. The six soils were made up of 3 calcareous and 3 noncalcareous soils. The 3 calcareous soils were comprised of the Libau, McCreary and Graysville II series, while the noncalcareous soils consisted of the Portage, Pipestone and Graysville I series. For our purpose, any soil with a $CaCO_3$ content > 1 % was classified as calcareous while noncalcareous soil had a $CaCO_3$ content of < 1 %. The pertinent properties of these soils are shown below in Table 1.1.

In order to generate both the kinetic and equilibrium parameters, varying P concentrations were combined with different incubation times in a 9 x 9 factorial design. The added P concentrations ranged from 5 - 500 μg P ml^{-1} (5, 10, 20, 30, 40, 50, 100, 200, and 500) to permit the generation of a sorption isotherm. At a given P concentration, duplicate samples were incubated for varying periods of time ranging from 1/2 h - 48 h (1/2, 1, 2, 4, 6, 12, 18, 24, 48).

To 2 g of air dried soil in a centrifuge tube was added 20 ml of a solution containing the appropriate concentration of phosphorus (reagent grade KH_2PO_4). The sample was then shaken for the desired period of time on a reciprocating shaker. This was then centrifuged at 10,000 rpm (G force of 4) for 20 minutes and the clear supernatant was collected. The time taken to centrifuge was part of the incubation time. After the appropriate dilution, the phosphorus concentration of the supernatant was determined by the ascorbic acid-molybdate method of Murphy and Riley (1962). The adsorbed P was calculated as the difference between the applied P and the measured P. All experimental treatments were carried out in duplicate. It was assumed that after 24 h of incubation equilibrium had been achieved. The data obtained after 24 h was used for generating the adsorption isotherm.

Table 1.1. Pertinent properties of the soils used.

	SOILS					
Property	Libau	McCreary	†GyvII	PCL	Pipestone	GyvI
$CaCO_3$ (% Eq.)	8	5	2	<1	<1	<1
CEC ($cmol_c\ kg^{-1}$)	18	31	18	41	42	17
[1]MC (%)	33	38	34	42	40	34
pH	7.6	7.6	8.0	7.5	7.4	7.7
[2]Exch Ca^{2+}	18	31	17	30	23	9
Exch Mg^{2+}	5	7	6	8	6	4
Exch K^+	1	2	1	2	4	2
[3]Water-P	1.3	11.0	1.6	5.4	10.1	14.6
[4]$NaHCO_3$-P	48.4	66.8	46.0	51.3	62.6	71.0

[1] moisture content at field capacity weight.

[2] exchangeable calcium, magnesium and potassium in $cmol_c\ kg^{-1}$.

[3] water extractable P at soil to water ratio of 1:10 in $\mu g\ P\ g^{-1}$ soil.

[4] $NaHCO_3$ extraction method (pH 8.5) in $\mu g\ P\ g^{-1}$ soil.

†GYVII stands for calcareous Graysville II series, PCL for Portage clay loam, and GYVI for noncalcareous Graysville I series.

RESULTS AND DISCUSSION

The adsorption of P with time at three initial P concentrations is shown graphically in Figure 1.1. In general the shape of the curves followed a typical sorption-time curve. There was a very rapid rate of P sorption within the first 6 h of incubation, during this time sorption was linearly related to the incubation time. With an increase in time, the curves levelled off and the rate of sorption declined. There was a very little change in the amount of P sorbed between 12 h and the 48 h duration of incubation, an exception to this was the data generated when 500 $\mu g\ g^{-1}$ was the initial P concentration.

There are noticeable differences amongst the soils in the magnitude of P sorbed and the pattern of sorption with increasing initial P concentration. When 20 μg P ml^{-1} was the initial concentration, Figure 1.1a shows a dichotomy in the profile of sorbed P with time amongst the four soils. The two calcareous soils, Libau and McCreary series, had a higher level of sorption than the noncalcareous soils, suggesting that perhaps $CaCO_3$ levels had an influence on the quantity of sorbed P at this concentration level. Libau series with 8 % $CaCO_3$ (Table 1.1) had a higher sorption than the McCreary series with a 5 % $CaCO_3$ content. For the noncalcareous soils, Pipestone and Graysville I series, the soil with the higher CEC and a higher exchangeable Ca, had a higher level of sorbed P.

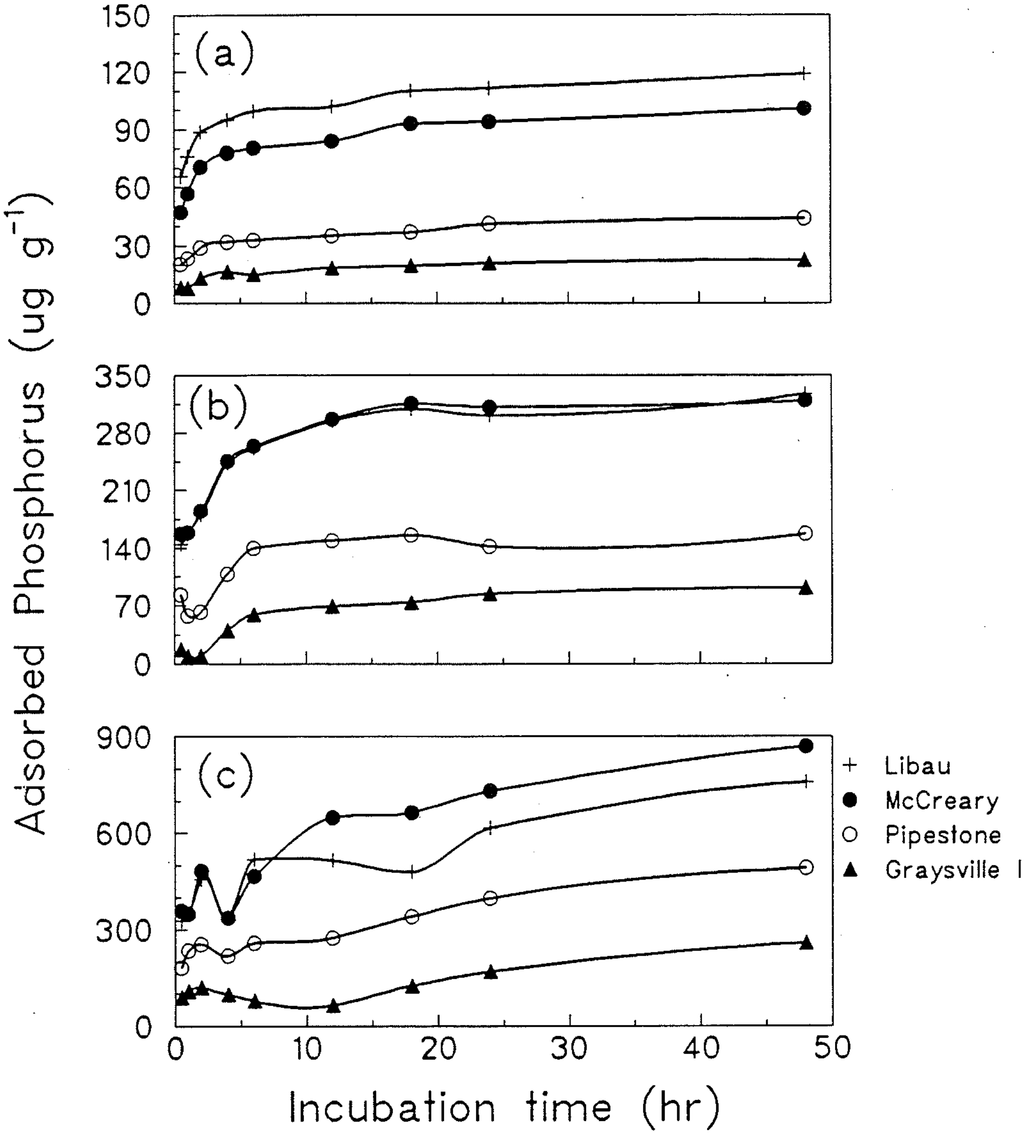

Figure 1.1 - Phosphorus adsorption with time in calcareous and noncalcareous soils; (a) initial P = 20; (b) initial P = 100; (c) initial P = 500 μg P ml^{-1}.

When the initial concentration was increased to 100 μg P ml^{-1}, (Figure 1.1b), the difference between the calcareous and noncalcareous soils was maintained similar to what was previously observed. However, there was virtually no difference in the magnitude of P sorbed by the two calcareous soils. Since these soils contained different amounts of $CaCO_3$, the similarity in their sorption capacity at this concentration level indicates that, perhaps, solid phases other than calcite was involved in the sorption. Also, processes other than adsorption may be involved.

It is possible that, at this concentration level, there was a contribution to the overall P retention from the precipitation of P by the exchangeable cation (Ca^{2+}) displaced by the added potassium. This presumption is supported by the data obtained at the maximum P concentration of 500 μg P ml^{-1} shown in Figure 1.1c. Here the McCreary soil had a higher quantity of sorbed P though with a lower $CaCO_3$ content than the Libau series.

Weir and Soper (1962) found that noncalcareous soils sorbed more P than calcareous soils and attributed this to the difference in the clay content of these soils. In this experiment, the McCreary soil with lower carbonate content, had a higher CEC and exchangeable Ca^{++} than the Libau series. This could partly explain the reversal in their relative sorption level with an increase in P concentration.

The adsorption isotherm for all the soils are shown in Figures 1.2 and 1.3. These plots represent the adsorption data obtained after 24 h of incubation. The shape of the isotherm resembles that of the L

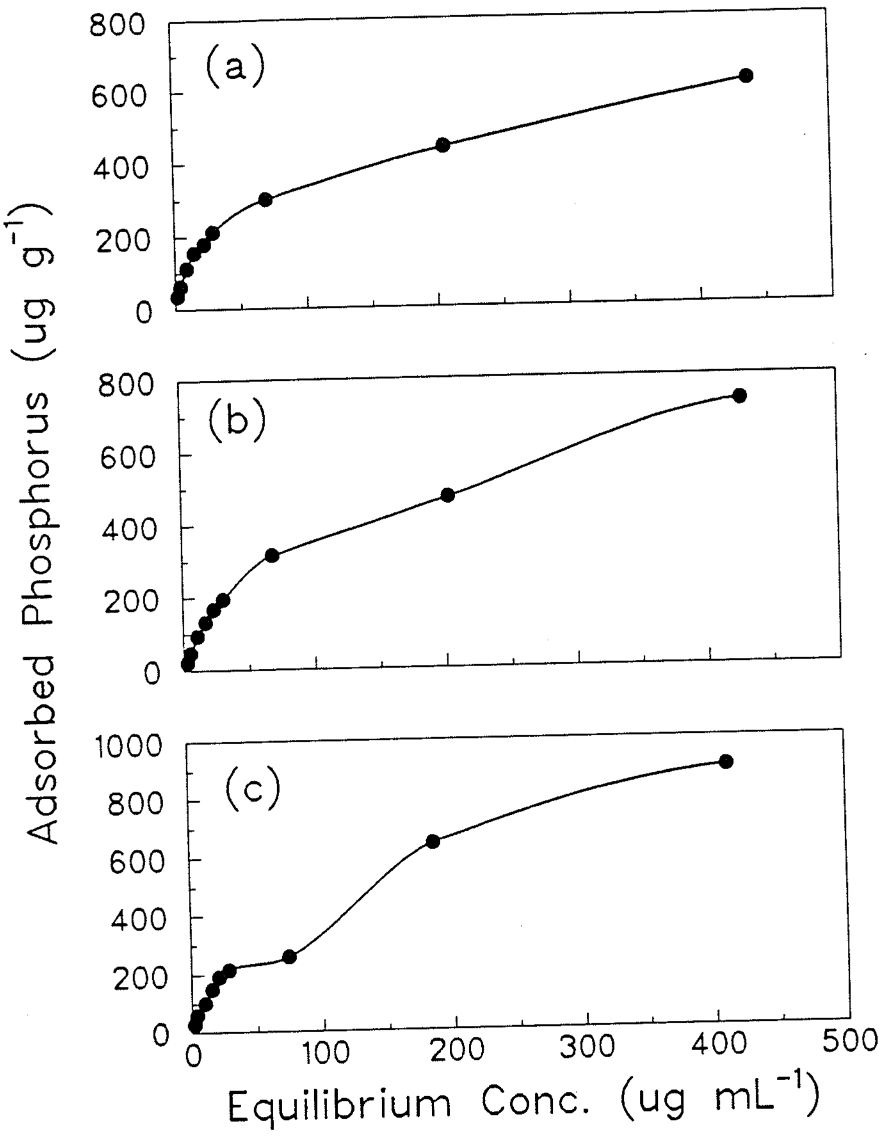

Figure 1.2 - Phosphorus adsorption isotherms in calcareous soils; (a) Libau; (b) McCreary; (c) Graysville II.

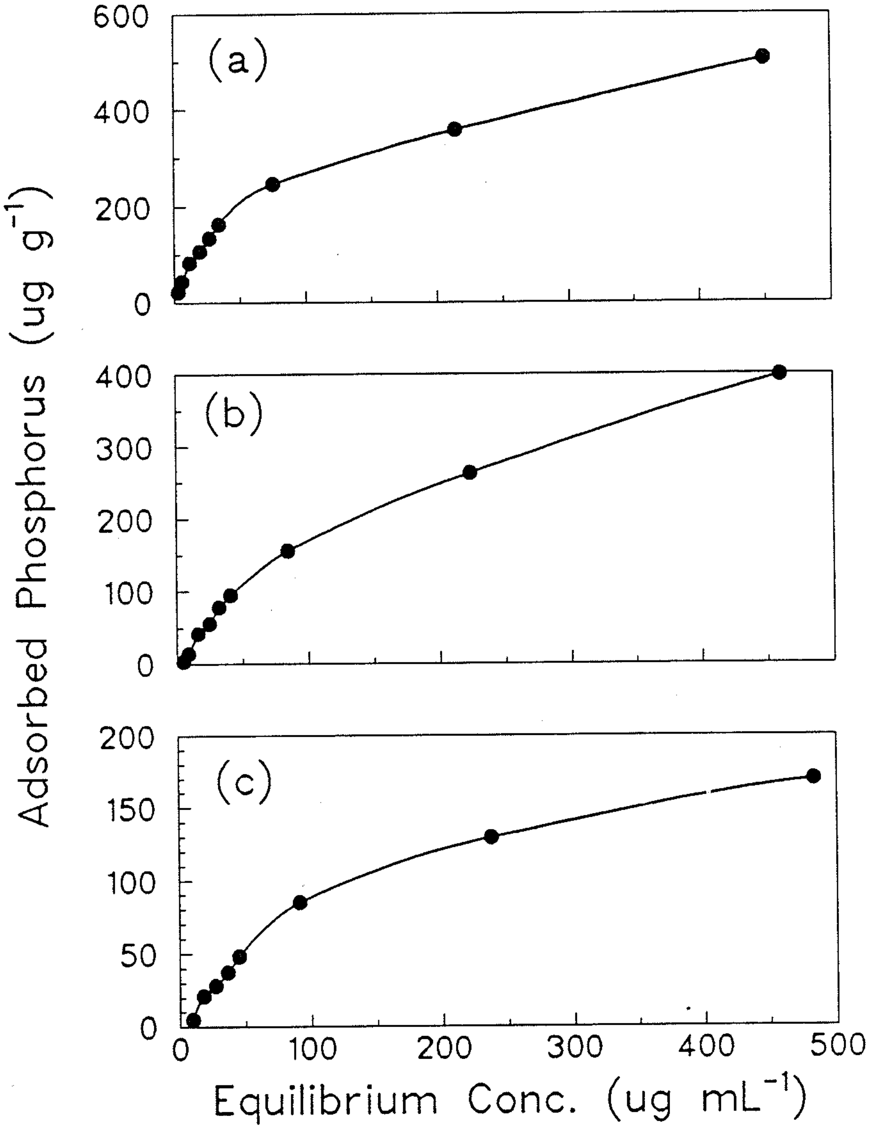

Figure 1.3 - Phosphorus adsorption isotherms in noncalcareous soils; (a) Portage CL; (b) Pipestone; (c) Graysville I.

type ("Langmuir") class of isotherm according to the classification of Giles et al. (1960). These data will be used to obtain sorption parameters through regression analysis according to the various adsorption equations listed below.

(1) Langmuir Isotherm $C/q = 1/kb + C/b$

(2) Freundlich Isotherm $\log q = \log k + b \log C$.

(3) Gunary Isotherm $C/q = A + BC + D\sqrt{C}$

(4) Cubic Adsorption Isotherm (Polynomial equation)

$$q = A + bC + dC^2 + gC^3$$

where A, b, d, and g are regression coefficients for the cubic equation. The parameters obtained after performing the appropriate regression analysis are listed for all the soils in Table 1.2.

In general, the four equations described the sorption data obtained reasonably well as the regression coefficients (r^2) indicate. The highest r^2 was obtained in all the six soils with the Gunary and Cubic isotherms both of which appeared superior to the remaining adsorption isotherms in describing the obtained data. Barrow (1978) suggested that the fewer the parameters to be estimated by a regression equation the better is the equation when comparing isotherms with similar r^2. The Freundlich and the Langmuir isotherms were about equally effective in fitting the adsorption data.

Table 1.2 P sorption parameters in calcareous and non-calcareous soils.

	INTERCEPT	S1*	S2	S3	ADS-MAX	k	r^2
Libau series							
LANG	0.08023	0.00153			653.6	0.01907	0.971
FREUND	3.60009	0.48479					0.982
GUNARY	0.00059	0.01411	0.02036		1694.9		0.999
POLY	58.06309	5.35099	-0.02391	3.3×10^{-5}			0.989
McCreary series							
LANG	0.12114	0.00117			854.7	0.00966	0.966
FREUND	2.82079	0.66101					0.952
GUNARY	0.00305	0.15829	-0.02224		327.9		0.996
POLY	22.97712	6.26848	-0.02843	4.1×10^{-5}			0.997
Carbonated Graysville II							
LANG	0.09933	0.00093			1076.4	0.00935	0.910
FREUND	3.17432	0.62025					0.980
GUNARY	0.00147	0.06107	0.00389		682.1		0.990
POLY	65.04000	3.94880	-0.00484	4.0×10^{-7}			0.990
Portage Clay Loam							
LANG	0.14437	0.00175			571.4	0.01212	0.980
FREUND	2.83239	0.58885					0.969
GUNARY	0.00137	0.09269	0.01230		729.9		0.999
POLY	24.71366	4.37242	-0.01850	2.5×10^{-5}			0.996
Pipestone							
LANG	0.37850	0.00177			564.9	0.00468	0.982
FREUND	1.98488	0.66548					0.986
GUNARY	0.00154	0.33339	0.00792		651.0		0.994
POLY	6.41525	2.37138	-0.00753	9.2×10^{-6}			0.999
Non-carbonated Graysville I							
LANG	0.78021	0.00429			233.1	0.00550	0.994
FREUND	1.30209	0.64532					0.969
GUNARY	0.00363	0.77345	0.00764		275.6		0.993
POLY	-2.96927	1.30678	-0.00430	4.8×10^{-6}			0.999

*S1, S2, and S3 stand for slope of the first, second and third term, respectively.

From the Langmuir and Gunary equations, it was possible to calculate the adsorption maximum for each of the soils. There was no agreement between the adsorption maxima obtained from the two isotherms. A similar observation was made by Holford et al., (1974) who reported that the Gunary empirical equation predicted maxima as large as 240 per cent of the Langmuir adsorption maxima.

The relative magnitudes of the adsorption maxima obtained closely followed the sorption curves described earlier with the calcareous soil having adsorption maxima higher than the noncalcareous soils. The adsorption maxima ranged from 653 to 1076 μg P g^{-1} soil for the 3 calcareous soils while the corresponding figures for noncalcareous soils ranged from 233 to 571 μg P g^{-1} soil. The problem, however, with these values is that they are not constant as Barrow (1978) mentioned, but will vary with the maximum concentration of P utilized. There is no doubt that these values would change if sorption data for a concentration range higher than 500 μg g^{-1} were included in the regression analysis. This is a limitation of the isotherms as already discussed, especially from the view point of using the parameters to describe P movement in the soil.

The Langmuir isotherm also yields another parameter which in Table 1.2 is described as the k-factor generally known as the affinity factor. The k-factor is a measure of the equilibrium constant between phosphate ion and the soil. This value ranged from 0.005 - 0.02 for the six soils and a higher k factor was obtained in the calcareous soils than in the noncalcareous soils except for the portage clay loam.

The high correlation coefficients obtained when the various isotherms were applied to the sorption data are not sufficient conditions to deduce the mechanism of sorption. That is, the fitting of the sorption data to the adsorption isotherms does not on its own confirm that the adsorption process was the dominant mechanism of P retention by the soils. Since this study however is not mechanistic, but rather, is a means of summarizing the sorption data, the good agreement will enable one to proceed to the next stage, that of using these parameters in the transport equation.

General Theory of Diffusive Transport

The effect of phosphate sorption on the diffusive transport of phosphorus can be analyzed through the application of a diffusion equation with chemical reaction. For this analysis, a simple model of diffusion with an interaction term described by P sorption will be utilized. The total flux of phosphate across a fixed plane will be assumed to be due to diffusive flux which is proportional to the concentration gradient.

Theory

A formal statement of this is represented by Ficks' first law of diffusion which is stated as:

$$J = - DdC/dx \qquad [1.8]$$

where J is the flux of solute in g (or mol) $cm^{-2}\ s^{-1}$ across a plane of 1 cm^2 perpendicular to the direction of flow, x is the distance, C is the concentration in g (or mol) cm^{-3}, and D is the diffusion coefficient in units of $cm^2\ s^{-1}$.

The negative sign is needed to give diffusion from high to low concentration, dC/dx being negative (Wild, 1981). For the purpose of this analysis, it is assumed that sorption process is the only process controlling the loss of P from the solution. The main focus of this analysis is to make comparisons between the profile of P obtained when the four adsorption isotherms are incorporated into the diffusion equation.

The equation of continuity without a sink or source term states that the rate of change in concentration is due to net influx.

$$\partial c/\partial t = -\nabla.J \qquad [1.9]$$

$$\partial c/\partial t = -\partial J/\partial x$$

If the continuity equation is applied to Ficks' first law, Ficks' second law, commonly called the diffusion equation is obtained, that is:

$$\partial c/\partial t = \partial/\partial x(D\partial c/\partial x) \qquad [1.10]$$

$$\partial c/\partial t = D\partial^2 c/\partial x^2$$

It is assumed that the Diffusion coefficient is a constant.

When there is a sink or source, the diffusion equation expressed by [1.10] can be combined with a chemical term, which for the analysis will be P sorption, to obtain

$$\partial C/\partial t = D\partial^2 C/\partial x^2 - \Phi. \qquad [1.11]$$

Φ is a chemical term representing P sorption and the negative sign implies that the sorption process leads to the disappearance of P (sink term).

$$\Phi = \partial S/\partial t$$

where S = adsorbed P concentration (expressed as g^{-1} soil) and t is time. To express S and C in the same unit, the sorption term was multiplied by the dilution factor ρ/Θ. ρ is the bulk density and Θ is the volumetric moisture content

Equation [1.11] then becomes:

$$\partial C/\partial t = D\partial^2 C/\partial x^2 - \rho/\Theta\ \partial S/\partial t \qquad [1.12]$$

The final form of equation [1.12] depends on the type of adsorption isotherm used to express the rate of change.

The Equilibrium Approach

In combining the various adsorption isotherms with the diffusion equation a final obstacle becomes apparent. The sorption isotherms are equations expressing the state of the system at equilibrium while the expression in equation [1.12] is of the kinetic form. To overcome this problem, the Local Equilibrium Assumption (LEA) was made. This assumption implies that the rate of sorption is a linear function of the rate of change in solution concentration. For example, with the Langmuir isotherm, the mathematical relation given by $\partial S/\partial t = \partial S/\partial C \times \partial C/\partial t$ was used to obtain the following:

$$S = kbC/(1 + kC)$$

$$\partial S/\partial C = kb/(1 + kC)^2$$

$$\partial S/\partial t = kb/(1 + kC)^2 \times \partial C/\partial t \qquad [1.13a]$$

Similar calculations were performed for the other isotherms with the final equation shown below in 1.13b to 1.13d for Freundlich, Gunary and the cubic equations, respectively.

$$\partial S/\partial t = abC^{b-1} \times \partial C/\partial t \tag{1.13b}$$

$$\partial S/\partial t = \frac{(BC + A + \sqrt{C}) - B(BC + \sqrt{C}/2)}{(BC + A + \sqrt{C})^2} \times \partial C/\partial t \tag{1.13c}$$

$$\partial S/\partial t = (b + 2dC + 3gC^2) \times \partial C/\partial t \tag{1.13d}$$

The validity of the local equilibrium assumption for modelling sorbing solute transport has been previously analyzed (Jennings et al., 1984; Valochi, 1985). According to Valochi (1985), criteria for local equilibrium to be valid are derived by comparing the time moment formula for the non-equilibrium and equilibrium models. While such analysis may be necessary for convective transport where the seepage velocity may be high enough to invalidate LEA, it is safe to assume the validity of the LEA for the diffusive transport.

These adsorption isotherms are non-linear and their incorporation into equation [1.12] leads to a non-linear differential equation for which the analytical solution is not available. The solution was obtained by numerical approximation. The initial and boundary condition chosen for the analyses were:

$$C = C_o \text{ at } x = 0 \qquad t >= 0;$$

$$dC/dx = 0 \text{ at } x = 1 \qquad t >= 0. \tag{1.14}$$

This initial and boundary conditions correspond to the situation where a P salt is uniformly placed on the surface of a soil and yields a constant P concentration (C_o) during the diffusion process. The numerical approximation was achieved by using the method of Crank-Nicholson and the Thomas algorithm. A similar method has been successfully utilized (Cho, 1985; 1990). The finite difference form of the transport equation containing one of the sorption isotherms is presented in detail in Appendix A.

Results from Numerical Solution.

The aim of performing this numerical analysis was to compare the P profile obtained without an adsorption isotherm to those obtained when the various isotherms were incorporated in the transport equation. Since several isotherms exist for describing P sorption, there is no criteria established in the literature for the choice of any particular isotherm. This type of comparison could establish the basis for selecting one isotherm over the other.

The results of numerical approximation are represented by plots of P concentration against distance as shown in Figure 1.4. Figure 1.4a shows the P profile obtained after t = 200 h in the Libau soil series. The diffusion coefficient chosen for this calculation was 0.03 $cm^2 h^{-1}$. The initial concentration was chosen to be 200 mmol L^{-1}. The sorption parameters used in this calculation are those listed in Table 1.2. When the diffusion equation was solved without any adsorption term (NOAD), rapid movement of P occurred as indicated by the extent of P movement. After 200 h P moved to a distance of 8 cm from the top of the column. The inclusion of the sorption term resulted in an entirely different profile of P. Not only was P retarded, moving only 1.5 cm down the column after 200 h, but the concentration at any portion of the column was much smaller than in the case of diffusion without an interaction term. The resultant effect of sorption, as indicated by this model, was to reduce the distance of P movement and concentration of P throughout the column.

An important result also shown in Figure 1.4a was that the concentration profile obtained from all the different isotherms were virtually identical. Such knowledge permits the freedom of choice of any of the various isotherms. This eliminates the confusion one faces regarding which of the several isotherms should be used to describe P sorption in the transport model.

The stability of the numerical solution and the model was tested by increasing time to 1000 h while maintaining the same initial concentration at 200 mmol L^{-1}. As Figure 1.4b shows, the same relationship was maintained with an increased time. The effect of time on P diffusion is obtained by a comparison of Figures 1.4a and 1.4b. The maximum depth of P penetration was increased from 1.5 cm to 3.2 cm when incubation time was increased from 200 to 1000 h.

The above results are for the Libau series, a calcareous soil with a high P sorption capacity. A similar sets of calculation was performed using the sorption data for the Graysville I series, a noncalcareous soil with the lowest P sorption capacity amongst the soils studied (Table 1.2). The results of the calculations are shown in Figure 1.5. The profile of P obtained for the Graysville I soil is similar to that for the calcareous Libau series. The effect of P sorption on the phosphate transport is apparent when calculated P solution profiles in the two soils are compared (Figs 1.4 and 1.5). After 200 hr P moved to a distance of 1.5 cm in Libau series while in the Graysville I it moved to a distance of 3.5 cm during the same period. The low sorption capacity of the Graysville I series is thus reflected by the greater distance of P penetration.

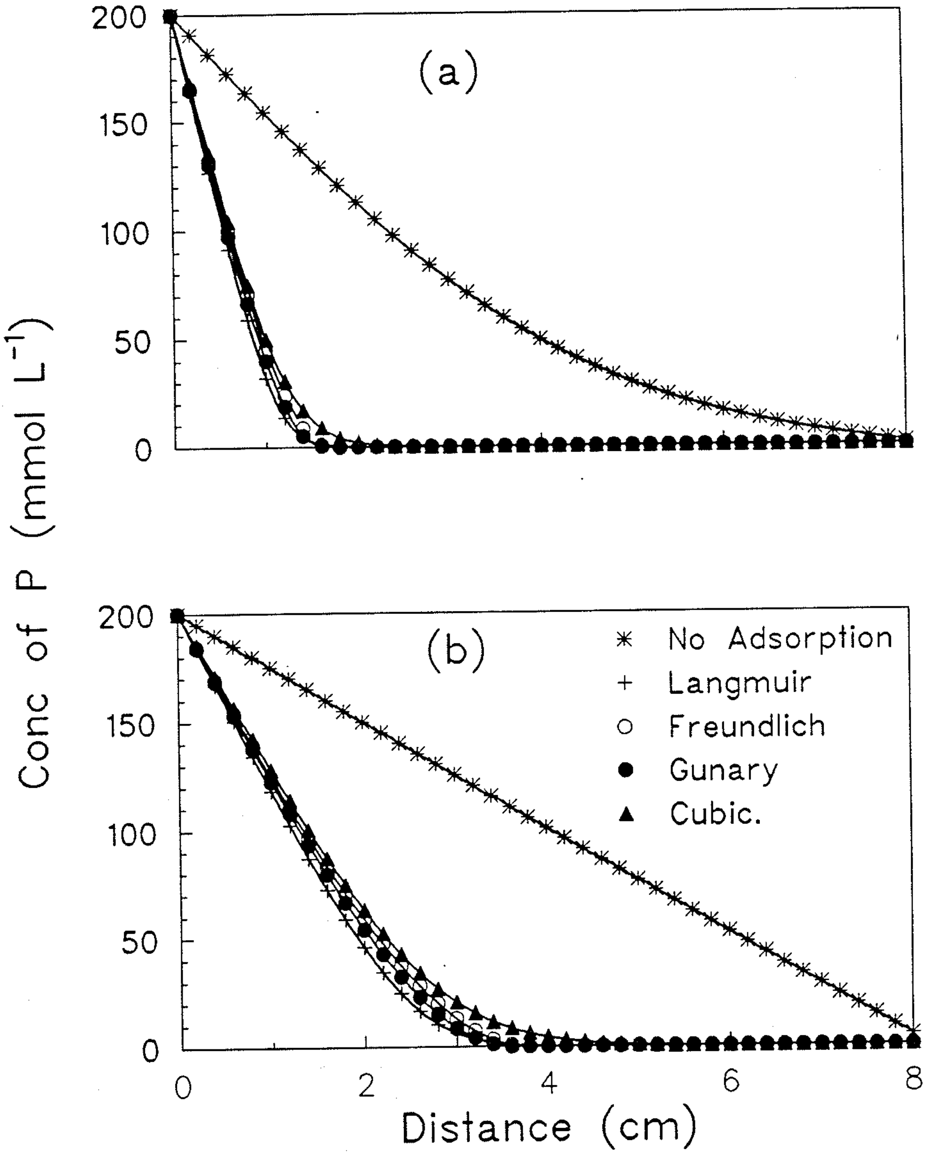

Figure 1.4 - Calculated P concentration in Libau soil with the various sorption isotherms; (a) t=200, (b) t=1000 h.

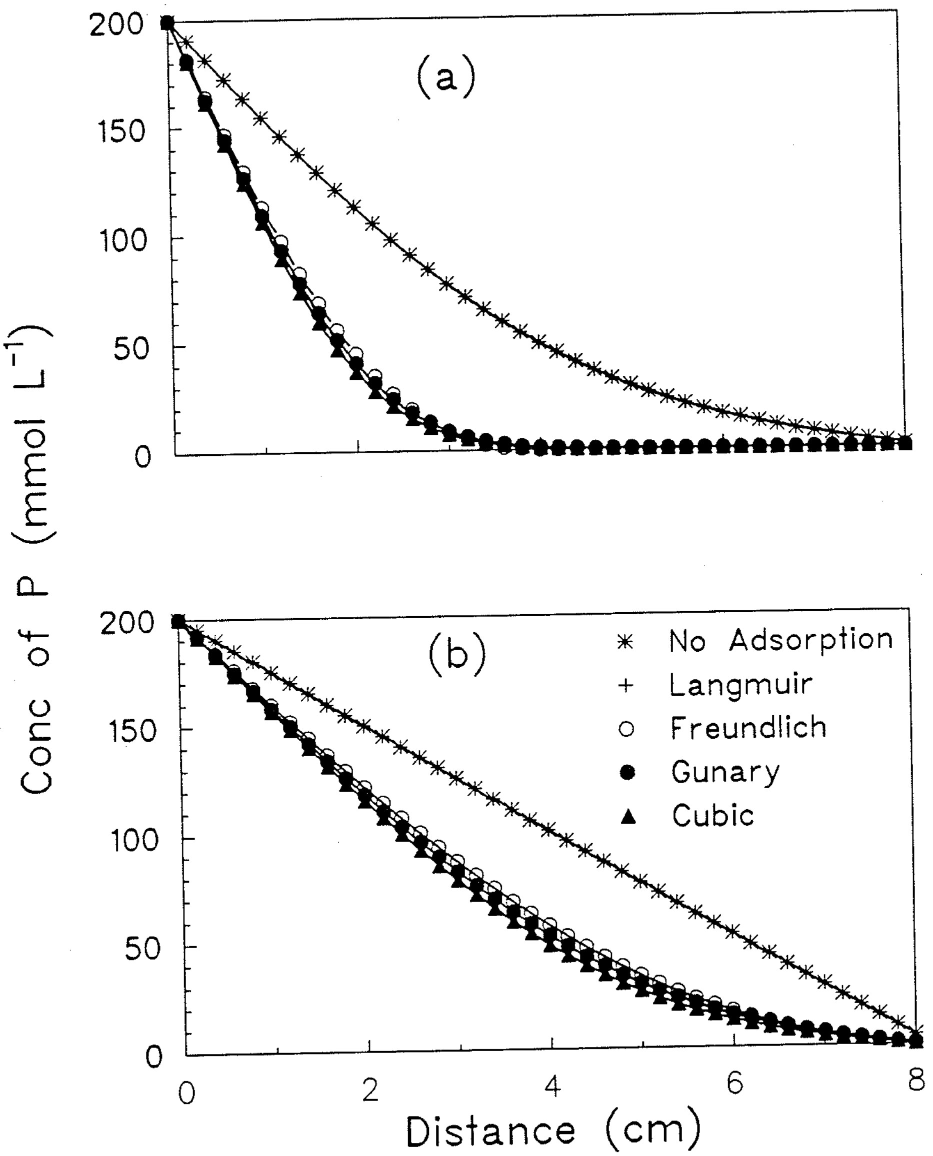

Figure 1.5 - Calculated P concentration in Graysville I soil with the various sorption isotherms; (a) t=200, (b) t=1000 h.

Kinetics of P Sorption

The data generated on the P sorption with time in all the six soils is presented in Appendix B. The kinetic equations that were applied through regression analyses to the sorption data and the results obtained from the analyses are shown in Table 1.3.

Table 1.3. Parameters of P Sorption Kinetics in the Soils.

Kinetic equation		Libau	[†]MCR	PCL	PIPE	GYV
$\partial s/\partial t = aC^bS^d$	a	1.4×10^8	1778	6.3×10^4	1.5	2.7
	b	3.41	2.83	3.43	0.93	1.54
	d	-5.75	-3.16	-4.61	-0.47	-1.76
	r^2	0.67	0.52	0.68	0.18	0.42
$\partial s/\partial t = f(kC-S)$	f	0.14	0.70	0.19	0.79	0.86
	K	15.1	5.0	3.3	0.8	0.3
	r^2	0.2	0.31	0.24	0.25	0.33
$\partial s/\partial t = B(mC^n-S)$	m	32	21	18	7	0.4
	n	0.45	0.5	0.51	0.6	0.9
	B	2.63	2.65	2.74	2.92	1
	r^2	0.55	0.4	0.76	0.73	0.36

[†]MCR stands for McCreary series, PCL for Portage clay loam, Pipe for Pipestone and GYV for noncalcareous Graysville I series.

Included in this table are the correlation coefficients (r^2) for the regression analyses. None of these equations described the kinetics of sorption satisfactorily in these soils as indicated by the low correlation coefficients. The values obtained for the equation parameters are comparable in magnitude to those reported for 25 mineral soils by Enfield et al. (1975). The very low correlation coefficients in this analyses support the assertion that the kinetic approach of P sorption is not as developed as the equilibrium approach. The lack of an equation to satisfactorily describe the kinetic data obtained will preclude further analysis, such as was conducted using the equilibrium parameters.

SUMMARY AND CONCLUSION

P sorption studies were conducted with calcareous and noncalcareous soils using KH_2PO_4. The calcareous soils had higher P sorption capacities than the noncalcareous soils. Amongst the calcareous soils, sorption maxima were not related to the carbonate content. The commonly used adsorption isotherms i.e. Freundlich, Langmuir, Gunary, etc. described the sorption data very well. None of the kinetic equations described P sorption with time adequately. The various isotherms yielded identical P profiles when incorporated into the diffusion equation. It is thus concluded that as long as an isotherm describes the sorption data fairly well, such an isotherm can be utilized to model P transport in the soil where sorption is the dominant retention mechanism.

CHAPTER II

The Diffusive Transport Of Phosphorus In a Model System: a Multi-Ionic Approach

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GENERAL LITERATURE REVIEW

Mode of P Transport in the Soil

When fertilizer P is applied to the soil surface or placed in a band, its availability to the plant roots depends upon its rate of movement from the source into the surrounding soil. Three mechanisms are widely recognized through which a nutrient can reach the root surface. These are: root interception or root extension; mass flow; and diffusion. The importance of each mode of movement depends upon the ion of interest and its concentration in the soil solution.

It has been argued (Barber, 1961; Barber et al., 1963; Barber, 1980), that, for the phosphate ion, diffusion is the most important pathway. Such arguments are based on the consideration of the concentration of P in the soil solution which is usually less than 1 $\mu g\ g^{-1}$, (Barber, 1963), plant content of P, approximately 0.2% and plant transpiration ratio of about 400. Using the average figures reported in the literature for these parameters, Barber (1980) concluded that mass flow would supply on the average only 1% of P used by the plant and that in many soils, diffusion is the mechanism for the supply of 90 to 98% of the P absorbed by the root.

Some evidence indicating the importance of diffusion in the supply of P to plant root growing in the soil was obtained by autoradiographs (Lewis and Quirk, 1967; Bhat and Nye, 1973). These showed the depletion of ^{32}P about the root and the formation of a P concentration gradient extending perpendicular to the root.

The realization of the importance of this transport mechanism has concentrated research efforts on the diffusive movement when the transport of P is studied in the soil (Black and Bouldin, 1954; Bouldin, 1960; Lewis and Quirk, 1967; Khasawneh, 1974; Hira and Singh, 1978; Sample et al., 1979).

Diffusion Process

Diffusion is defined as the spreading out of a solute within the solution phase from a region of high concentration to a region of low concentration. It is caused by a random thermal motion similar to the Brownian movement of colloidal particles. As a result of this motion, which occurs randomly in all directions, any irregularities in the concentration of a solution eventually disappear.

Several factors govern the rate of P diffusion in the soil. These include: chemical reaction with the soil (Lehr et al., 1959; Lewis and Racz, 1969; Williams, 1971); soil bulk density (Hira and Singh, 1977b); and the amount of P present at the source (Rennie and Bole, 1968; Olsen and Kemper, 1968; Hira and Singh, 1978).

Nye (1968) proposed equation [2.1] for calculating the effective diffusion coefficient (De) of an ion in the soil.

$$De = Di\theta f \, dC_1/dC \qquad [2.1]$$

De = effective diffusion coefficient in soil ($cm^2 \; s^{-1}$)

Di = the diffusion coefficient of P in free solution

= ($8.9 \times 10^{-6} \; cm^2 \; s^{-1}$)

f = tortuosity factor , θ = the volumetric water content,

$dC_1/dC = 1/b$, the reciprocal of the slope of the linear adsorption isotherm which is also known as the buffer capacity. C_1 and C are the concentrations of P in solution and adsorbed phase, respectively. For the influence of these factors on De the reader is referred to Barber (1980).

Hira and Singh (1978) applied equation [2.1] to the diffusion of P in soil and found that it did not take into consideration the effect of applied concentration. These authors then proposed an empirical equation of the form:

$$D = Di\theta f/b \ (Q)^{1/2} \qquad [2.2]$$

Q = QA/Qi and QA is the P concentration applied at the surface while Qi is the unit concentration of P at which the experimental value of D approaches the value obtained from equation [2.1].

P Diffusion Studies

As early as 1954, Bouldin and Black published results of research work that investigated phosphorus diffusion in the soil with the aid of ^{32}P. Their objective was to investigate the existence and magnitude of irregularities in the distribution of phosphorus when diffusing through the soil. The validity of ^{32}P measurements as estimates of total diffused P distribution in the soil was also verified. These authors reported that irregularities in the P profile occurred in some soils when KH_2PO_4 or $CaHPO_4$ was added but not in others. Phosphorus concentration peaks were found at 4 cm intervals when $CaHPO_4$ was applied while with KH_2PO_4 the interval was 1 cm in the soils exhibiting these irregularities.

The study also showed that the overall picture of P diffusion obtained from ^{32}P measurement was not substantially different from that obtained by total P analysis. No explanation was given in this study as to why soils differ in their ability to have irregular P profiles or the differences existing between the applied salts. It is possible that the CEC of the soil, the cation composition on the exchange complex coupled with the effect of pH of the applied salt, have a bearing on the observation reported in this study.

The movement of phosphorus from fertilizer pellets of monoammonium phosphate (MAP) and diammonium phosphate (DAP) has been studied (Racz and Lewis, 1969). They reported that P from MAP moved to a greater extent and at a faster rate than that from DAP. The difference between the salts was more noticeable in calcareous soils than in noncalcareous soils. Irrespective of the applied salt, the extent of P movement was greater in noncalcareous soils than in calcareous soils. This was explained by the higher pH, and higher Ca and Mg levels in calcareous soil both favouring P precipitation and consequently its retardation. Of all the soil parameters examined, it was found that the $CaCO_3$ content had a very large effect on the movement of applied phosphorus. There was no relationship between P distribution and the soil texture. It is possible that the large carbonate content of their soils masked any effect of exchangeable Ca^{2+} on P transport.

Khasawneh et al. (1974) investigated the diffusive movement of ortho- and polyphosphate in an acidic soil limed to a pH of 6. They reported that the extent of P movement was similar between the 3 sources of P (diammonium phosphate - DAP, triammonium pyrophosphate - TPP and ammonium polyphosphate - APP), but the distribution patterns were different. Higher fraction of added P was precipitated with the polyphosphate than with orthophosphate. A significant effect of the initial moisture content of the soil on the extent of movement was observed. For example, when TPP was applied, P moved to a distance of 18 mm after 7 d at a moisture content of 6.7%, this increased to 25 mm and 34 mm as the moisture content was increased to 9.6% and 19%, respectively. The effect of moisture content on the extent of P movement was likely due to the influence of tortuosity and volumetric moisture content on the diffusion coefficient. In this study, the effects of exchangeable cations and the carbonates added on the subsequent movement and retardation of P was not analyzed.

In a subsequent paper, Khasawneh et al. (1978) concluded that the reactions of all forms of phosphate was due to precipitation rather than to reversible sorption. This conclusion was reached because of their observation that the alkali-soluble P was increasing with time even in that portion of the soil column where the water-soluble P declined. Such observation did not agree with sorption-desorption theory. From the results of this study, it is reasonable to assume that high concentrations of an anion such as P, and a cationic species like Ca^{2+} in the fertilizer band would favour precipitation reactions rather than P adsorption.

A third paper in this series (Sample et al., 1979) looked at the effect of the cation associated with phosphate on the movement of phosphate in the soil. They reported that the exchangeable Ca^{2+} in the first 6 mm of the soil contacted by fertilizer solution from DAP was replaced by NH_4^+, the displaced Ca^{2+} was precipitated in situ by phosphate. This observation is very important for it suggests the possibility of the added cation influencing phosphate ion movement, precipitation and retardation through the ion exchange interactions.

A drop in pH following precipitation reaction was observed by these authors and this was attributed to a depletion of exchangeable cation in the zone just beyond the fertilizer solution front. An alternative explanation is that the lowered pH probably resulted from the precipitation process itself as predicted by the mathematical model of Cho (1990).

A study similar to the ones reviewed above was conducted by Hashimoto and Lehr (1972). These authors reported that the distribution pattern of P was established within the first week of their study with minor changes thereafter. They were of the opinion that long incubation periods, particularly under conditions simulating band placement are not necessary to compare the agronomic effectiveness of different phosphates. The research results indicated that the immobilization reactions of P restricted the movement of P markedly. After 4 weeks of incubation the movement was much less than would be expected of a nonreactive species in the same period. They observed that the diffusion and immobilization of P appears to be continuous processes that should proceed until all the P has been immobilized. Though their data suggested that there was more P in the immobilized form than in the water-soluble form, the authors did not discuss the mechanism of such reactions.

Effect of Added Salt on P Diffusion in Soil

Some studies that investigated the salt effect (dual banding) on the solubility and plant availability of phosphate will be reviewed.

These studies, in general, have some relevance to P movement from the fertilizer band, especially as affected by added cationic species. When N fertilizer, particularly NH_4^+, is applied together with P fertilizer, increased uptake of P by the plant has been observed. This effect is generally known as the ammonium ion effect. A detail review of this phenomenon has been undertaken by various researchers (Miller, 1974; Miller and Ohlrogge, 1977; Sheppard and Racz, 1980).

To clarify the mechanisms involved in this phenomenon, various researchers have added ammonium and other salts to P fertilizers, usually monocalcium phosphate (MCP), and observed the solubility, mobility and plant uptake of P from such bands.

Bouldin et al. (1960), studied the effects of associated salts on the transformation of MCP at the site of application. They reported that the fraction of the applied P that remained at the granule site (in situ precipitation) varied from 92% when MCP was mixed with $CaCO_3$ to only 2% when $(NH_4)_2SO_4$ was mixed with MCP. An important result from this study indicated that the rate at which water was transported to a fertilizer granule is slower than the rates of dissolution and crystallization of the solid phases. Such an observation makes the assumption of a constant boundary condition for one-dimensional diffusive transport with surface application of P fertilizer reasonable. This assumption will be made in the model formulated to simulate P diffusive transport to be presented in Chapter 4.

Blanchar and Caldwell (1966) studied ion concentration in static fertilizer zones and the effects on plants. They observed that when MCP was used as the fertilizer, there was no decrease in soil pH beyond a distance of 3 cm from the pellet. Addition of NH_4Cl or KCl however resulted in a lower pH compared to MCP alone. The reduction of pH in the region farther away from the band with salt addition was attributed to either diffusion of hydrogen ion from acidic MCP or the salt effect on measured soil pH. Since there probably was higher precipitation, it may also be due to the production of H^+ from increased precipitation of P with the addition of KCl and NH_4Cl. These authors reported that the ammonium concentration was higher than K in all fertilizer zones when NH_4Cl and KCl, respectively, were added to MCP. This was an indication of a greater NH_4^+ ion diffusion than K^+ according to these authors. Other possible causes include the difference in the selectivity coefficient of K-Ca versus NH_4-Ca exchange. If K^+ is more efficient than NH_4^+ in replacing Ca^{2+}, then the concentration of K^+ will be lowered and its movement will be retarded more than that of NH_4^+. Also, NH_4^+ ion exists in equilibrium with NH_3. The diffusion coefficient of NH_3 in water is probably higher than NH_4^+ and hence allowed NH_4^+ to apparently move farther in the soil than K. Differences in the magnitude of fixed potassium and ammonium could also be responsible for the result obtained.

The same study also showed that the movement of Ca^{2+} away from the MCP band was enhanced by the addition of NH_4Cl or KCl. While Ca^{2+} moved only 3 cm with MCP alone, it moved to at least 7 cm from the band on addition of either NH_4Cl or KCl. This observation was attributed to the competition of the added cation for the exchange sites with Ca^{2+} leading to more solution Ca^{2+}. Unlike the effect of added salt on the movement of Ca^{2+} from the MCP band, Blanchar and Caldwell (1966) observed that the distance of P movement was not substantially influenced by the salt addition. Very high concentration of P existed in the areas adjacent to the pellet regardless of the salt added.

Isensee and Walsh (1972) studied the influence of banded fertilizer on the chemical environment of the band. They reported that when 5 salts (MCP, KCl, NH_4NO_3, $(NH_4)_2HPO_4$ and urea) were added in various combinations, the highest Ca^{2+} solution concentration was obtained with either NH_4NO_3 or KCl added separately. This was due to exchange reaction of the added cation with soil Ca^{2+}.

When urea was combined with $(NH_4)_2HPO_4$ (DAP) or MCP, solution P was drastically reduced. A combination of high pH due to urea and high P (from MCP) favoured the formation of relatively insoluble P. In an earlier paper, Isensee and Walsh (1971) had shown that the pH near banded fertilizer can be changed substantially. The pH of the soil solution 0.9 - 2.5 cm from the band was as low as 4.2 from a treatment of NH_4NO_3 + MCP + KCl and as high as 8.15 from urea + KCl treatment.

Isensee and Walsh (1972) found that when DAP was applied in a band, solution Ca^{2+} and Mg^{2+} were generally diminished. Also, they reported that the exchangeable calcium was lowered to 3.3 $cmol_c\ kg^{-1}$ compared to 6.7 for the control. They inferred that the formation of $CaHPO_4$ probably accounted for the low solution and exchangeable Ca level, According to these authors, calcium was displaced from the exchange sites by the NH_4^+ ion and was rapidly removed from solution as various Ca-phosphate compounds formed. This result is very similar to that obtained by Blanchar and Caldwell (1966) where the displacement of exchangeable Ca^{2+} was highest with the addition of NH_4Cl or KCl.

These studies demonstrate clearly the role that cation exchange reactions play on the build-up of soil cation such as Ca^{2+} which have the potential to form a precipitate with the added P. Since P fertilizers cannot be applied without an associated cation, the interaction of such cation with the exchangeable cations in the soil can influence the movement and immobilization of P especially if the cation resident in the soil is capable of undergoing precipitation reactions with P. Such consideration was not encountered in the literature dealing with phosphorus transport.

The Use of Exchange Resin to Simulate Soil

The soil, because of its complexity and variability is often not an ideal medium for analyzing the influence of cation exchange on ion transport. Some of the problems with using the soil as the transport medium include: heterogeneity of the exchange system; variation in CEC of the soil with depth plus the presence of solid phases capable of interfering with P transport through adsorption and precipitation. Some of these problems have led various researchers to utilize exchange resins as model systems which permit conclusions to be drawn about a particular process without undue interferences.

Van Beek and Pal (1977) utilized cation exchange resin to study the influence of cation exchange and gypsum solubility on the transport of sodium, calcium and sulphate through soils. The rationale of these authors for using exchange resin instead of soil was that the disturbing interferences, such as swelling of the soil, dissolution of the soil solid phase, and the variation in cation exchange capacity, had to be eliminated as much as possible to make correct analysis of the system being investigated. They obtained a good agreement between the breakthrough curves of ions determined experimentally with those predicted by the continuous simulation modelling programme (CSMP). The deviation existing between the two was attributed to dispersion/diffusion processes not taken into account in the computer programme.

Veith and Sposito (1977) used Al-, Fe- and Ag-saturated cation exchange resin in their study to test the hypothesis that the Langmuir adsorption isotherm could as well be used to describe a precipitation reaction. The silver saturated resin was reacted with KCl such that the silver liberated from the exchange sites by K^+ was precipitated as AgCl. The experiment demonstrated that the cation resident on the exchanger could participate in solution reaction if liberated through ion exchange reactions.

The overall reaction of the system used by Veith and Sposito (1977) was given as:

$$\text{Ag-Resin} + \text{KCl} \rightleftharpoons \text{AgCl}_{(ppt)} + \text{K-Resin}.$$

The authors also reported that even though secondary precipitation of Cl^- occurred, the data conformed perfectly with the Langmuir adsorption isotherm. This led to the conclusion that this isotherm cannot be used to ascertain the nature of the anion-soil interaction.

Hsu and Rennie (1962b) investigated the precipitation of phosphate by exchangeable aluminium on a cation exchange resin. These authors made use of the synthetic resin to avoid the complexity of the soil system, and because of the similarity in the exchange behaviour between cation exchange resin and the soil clay minerals.

The equations describing the processes occurring in their system were given by:

$$AlR_3 + 3M^+ \rightleftharpoons 3MR + Al^{3+}$$

$$Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2^+ + 2H^+$$

$$Al(OH)_2^+ + H_2PO_4^- \rightleftharpoons Al(OH)_2H_2PO_4$$

where "R" represents the exchange complex, and M^+ any monovalent cation in solution.

The authors obtained experimental data which showed that the exchangeable aluminum on resin precipitated phosphate from solutions. They observed that when Al-saturated resin was incubated with NaH_2PO_4 solution, the pH of the solution decreased with increasing fixation of phosphate in the presence or absence of a buffer. The removal of $Al(OH)_2^+$ from solution as a result of precipitation reaction with P, caused more hydrolysis of Al^{3+} and was responsible for the pH decline.

Kim et al. (1983a, 1983b) used Al- and Fe-saturated exchange resin, to study the fixation kinetics of potassium and phosphate in aluminum and iron systems. They reported that when KH_2PO_4 solution was reacted with the Al-saturated cation exchange resin, the phosphate and K concentrations in the solution always decreased rapidly at first and approached an equilibrium value very slowly. The Al concentration in solution increased from zero to a maximum and gradually declined with time. They suggested that Al was liberated into solution by ion exchange with K^+ and then precipitated as taranakite. A reduction in pH following precipitation similar to that reported by Hsu and Rennie (1962b) was also observed by these authors. The system of equations describing the reaction was given as:

$$Al.R_3 + 3K^+ \rightleftharpoons Al^{3+} + 3K\text{-}R$$

$$Al + 2H_2O \rightleftharpoons Al(OH)_2 + 2H^+$$

$$5Al(OH)_2^+ + 3K + 3H_2PO_4^- + 8H_2O \rightleftharpoons K_3[(Al(OH)_2]_5(H_2PO_4)_8.8H_2O$$

(taranakite)

A similar result was obtained with Fe-impregnated resin (Kim et al., 1983b).

The various studies reviewed above, though performed using a batch-type technique, are quite relevant for the following reasons: they all clearly demonstrated the release of exchange cation into solution by ion exchange reaction. With the appropriate anion in the soil solution, such liberated cation participated in precipitation reaction. Evidence seems to support the possibility of such reactions in a soil system especially in a base saturated soil, with Ca^{2+} dominating the exchange sites, and in acid soils with Fe^{3+} and Al^{3+} as the exchangeable cations. These cations are known to form insoluble precipitates with phosphate when present in the soil solution.

Experiment I: Multi-Ionic Diffusive Transport in a Model System of Calcium Impregnated Resin

INTRODUCTION

The extensive interaction of phosphorus with the soil matrix reduces its concentration in the soil solution considerably following the application of phosphatic fertilizers. This knowledge has given rise to the agronomic practice of fertilizer banding as opposed to broadcasting when phosphorus is concerned.

One way of generating information on the fate of P applied in a band is through the use of soil column to study one-dimensional diffusive transport of P (Bouldin and Black, 1954; Lewis and Racz, 1969; Hashimoto and Lehr, 1973; Khasawneh et al., 1974). Also, mathematical models have been formulated to describe the movement of P to plant root surfaces (Bouldin, 1961). Many of these studies have concentrated solely on the ion of interest, phosphate, with little or no attention paid to the cation that is associated with the applied P or the cation resident in the soil prior to P application.

This study attempts to clarify the role that the cation accompanying P has on the movement and the retardation of P when applied to the soil. It is known that cations applied to the soil interact with the native exchangeable cation in the form of exchange reactions. This causes a build-up of exchangeable cations in the soil solution. For convective transport, this phenomenon was termed the snow-plow effect and mathematical models have been formulated for its analysis (Starr and Parlange, 1979; Bary et al., 1983; Cho, 1985).

The hypothesis is that the exchange reaction of an incoming cation with the resident cation not only affects the movement of the cations, but also has an influence on the transport of the anionic species. When a salt such as KH_2PO_4, is applied to a soil whose exchange sites is dominated by Ca^{2+}, the K^+ ion (because of its high concentration) will flush out a considerable amount of exchangeable calcium during the cation exchange reaction. The calcium in solution can combine with the phosphate ion ($HPO_4^=$) to form an insoluble salt, presumably dicalcium phosphate dihydrate (DCPD). This precipitation reaction then impedes or retards the movement of phosphorus. The degree of retardation depends, among other things, on the cation exchange capacity (CEC) of the soil which determines the amount of soil Ca^{2+} liberated into solution. Retardation also depends on the pH of the soil which governs the relative abundance of the $H_2PO_4^-/HPO_4^=$ ions. The above hypothesis is a departure from the classical theory of phosphate transport where adsorption rather than precipitation is presumed to be the dominant process.

This study was performed to test the above hypothesis in a model system of cation exchange resin. Since cation exchange resin is not suppose to adsorb P, precipitation reaction is emphasised as the dominant interaction process. It is the first of a set of experiments designed to provide some information on what might happen in a soil system during multi-ionic (K^+, P ($H_2PO_4^-$ and $HPO_4^=$), Ca^{2+} and H^+) diffusive transport. Particular attention was paid to the exchange reaction between the applied cation, K^+, and the exchangeable cation, Ca^{2+}, and how this affects the transport of P. A knowledge of the role that the exchangeable cations play in P movement, could help clarify the dominant process responsible for P sorption in the soil.

MATERIALS AND METHODS

The wide variation in the chemical composition of soil makes it difficult to draw a generalized model based on the results from a specific soil. Not only are the properties unique for a given soil, but they are also fixed (e.g. the CEC). In addition, the composition of ions on the exchange sites complicates the nature of their interaction with phosphate thereby confounding observed results.

To overcome some of these problems, a model system of cation exchange resin (Amberlite CG 120) was chosen. The resin had a mesh size of 100-200 and a cation exchange capacity of 430 $\text{cmol}_c\ \text{kg}^{-1}$. The high CEC of the resin made dilution with acid-washed sand necessary to bring the CEC to a level comparable to that of the soil. In this system, one is able to modify seemingly fixed soil properties such as the CEC and the cation suite, thus defining the nature of the interaction with the phosphate ion.

To simulate conditions similar to that prevailing in a calcareous soil (or a base saturated soil), the resin was saturated with Ca^{2+}. A known amount of resin (40 g) was placed in a Buchner funnel, and 500 mL of 0.5 mol L^{-1} $CaCl_2$ solution was added in aliquots of 25 mL. This was followed by leaching with an additional 500 mL of 0.025 mol L^{-1} $CaCl_2$ solution in aliquots of 25 mL. The resin was then washed with water until the silver nitrate test was negative for the chloride ion. About 1500 mL of water in 50 mL portions was necessary to achieve this.

The resin was then air dried and the air-dry moisture content determined. A sample of the air-dry resin was extracted with either 1.0 mol L^{-1} neutral NH_4OAc or 1 mol L^{-1} HCl, and the chemical analysis of the extract revealed complete saturation of the exchange sites with Ca^{2+}.

Washed quartz sand was crushed with a shatter box to provide materials with a mesh size comparable with the resin. Sand particles that passed through a 150 mesh sieve were eliminated because of the possibility of this fraction exhibiting cation exchange characteristics. The resin was thoroughly mixed with the sand in varying proportions to produce resin-sand mixture with CEC of 0, 21.5 and 43 $cmol_c\ kg^{-1}$. The 0 $cmol_c\ kg^{-1}$ mixture (i.e sand with no resin) was termed the control treatment.

The mixture was packed into a wax column prepared using the method of Khasawneh and Soileau (1969). The wax column was 10 cm in height with an internal diameter of 4.5 cm. The "soil" was packed to a bulk density of 1.6 Mg m^{-3} and wetted to a moisture content of 15 % (by weight) by adding the appropriate quantity of water to the soil surface. The column was then allowed to equilibrate for 24 h before applying the salt.

The salt used in all columns was 0.2 g of KH_2PO_4. This was applied as uniformly as possible to the soil surface to simulate a one-dimensional diffusive transport. The columns were then placed on a porcelain plate perforated with holes which was then set in a glass jar with water and were incubated for periods of time ranging from 3 d to 2 wk. All experiments were carried out in duplicate.

After the desired period of incubation the wax columns were sectioned at 2 mm interval using a meat cutter. Samples were then taken from each section for both moisture content and chemical analyses. Approximately 1 g of the resin-sand mixture in each section was weighed into a centrifuge tube. One mL of water was applied and the pH of the mixture was measured. Nine mL of water was then added for extraction at a soil to solution ratio of 1:10. This was termed "the water extractable fraction". After water extraction, the same sample was extracted with 1 mol L^{-1} HCl in 2 successions. The two acid extracts were composited and termed "the acid extractable fraction". The water extractable fraction approximates what is in soil solution i.e the mobile phase, while the acid extractable fraction approximates what is on the solid i.e. the immobile phase.

The pH of the "soil" (1:1 in water) was determined using a glass electrode. The extractable P was determined by the ascorbic acid-ammonium molybdate method of Murphy and Riley (1962), while the extractable K^+ and Ca^{2+} were determined using an atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

The soil pH

The resin-sand mixture is a weakly buffered system, hence, it assumed the pH imposed by the salt, as a result of this, the pH of the columns was depressed below the initial pH 7 (Fig. 2.1). The pH of a solution in equilibrium with KH_2PO_4 was given as 4 by Lindsay et al. (1962). As Figure 2.1 reveals, the pH at the top of the column was

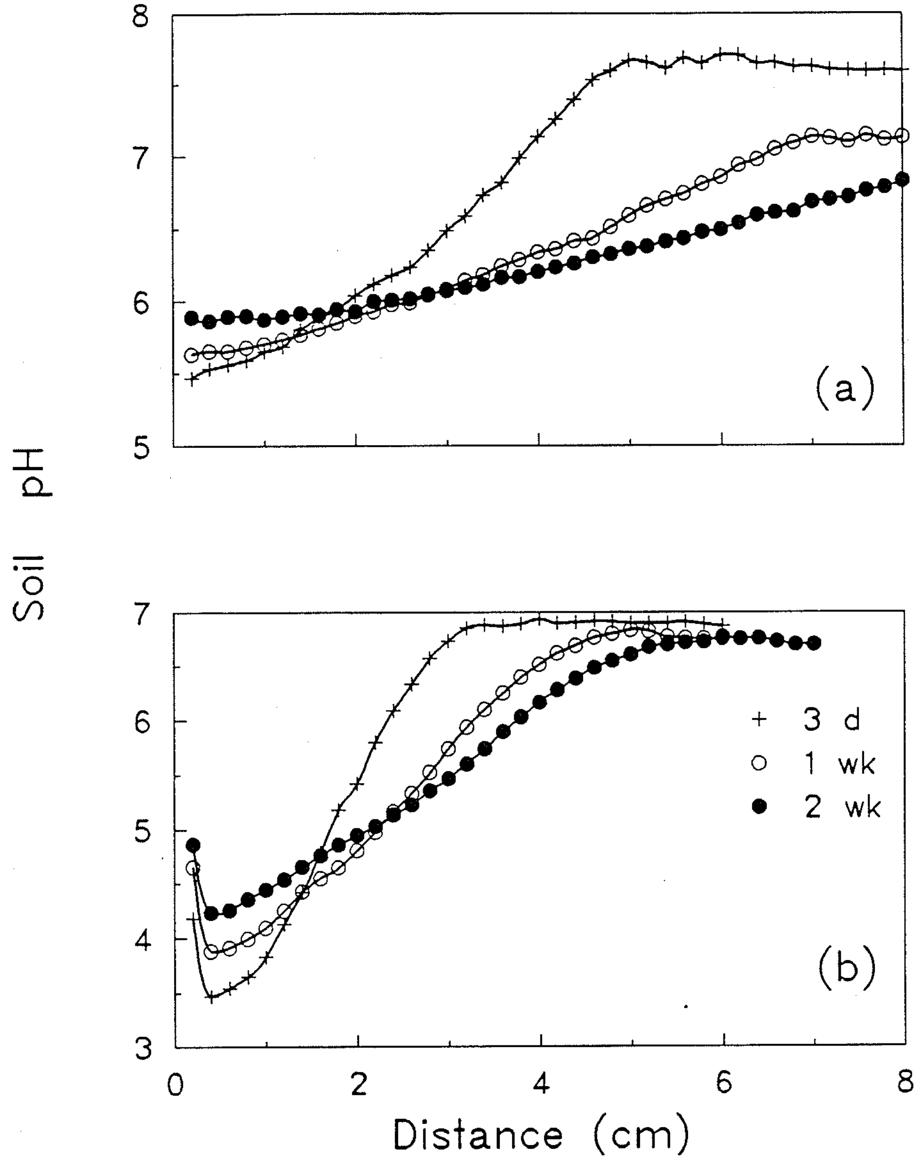

Figure 2.1 - pH of the resin-sand column with surface applied KH_2PO_4 at different times as affected by CEC; (a) CEC = 0, (b) CEC= 43 $cmol_c\ kg^{-1}$.

higher than 4 which was expected since the salt applied had totally dissolved by the third day.

In the control column, the highest H^+ ion concentration occurred at the top of the column and the pH profile of the column suggests that H^+ ion diffused down the column with a concomitant depression of pH below pH 7. With time, however, there was a rise in pH of the top 2 cm portion of the column as the hydrogen ion diffused down the soil column. Below this portion, there was a concomitant decline in pH as more and more H^+ ions moved from the top to the bottom of the column.

A similar pattern was observed in the column packed with 43 $cmol_c$ kg^{-1} resin-sand (Fig. 2.1b). The pH profile here differed from that of the control column in two ways. Firstly, the pH of this column was lower than the control column particularly at the top of the column. This can be attributed to the hydrogen ion production via the precipitation reaction. The lowering of pH following precipitation has previously been reported (Hsu and Rennie, 1962; Kim et al., 1983a). In their system, however, lower pH was attributed to the hydrolysis of Al^{3+} coming off the exchange site. We believe that the reaction of Ca^{2+} with the divalent phosphate ion caused a shift in the equilibrium shown below:

$$Ca^{2+} + HPO_4^{=} \rightleftharpoons CaHPO_{4(ppt)} \qquad [2.3]$$

$$H_2PO_4^{-} \rightleftharpoons HPO_4^{=} + H^+ \qquad [2.4]$$

Reaction [2.3] disturbed the equilibrium relation represented by reaction [2.4] causing a shift of [2.4] to the right with the production of a proton. Also, in the 43 $cmol_c$ kg^{-1} column, the pH of the top 2 mm section was higher than the section below . This is probably due to the dissolution of freshly precipitated $CaHPO_4$ during water extraction of the top 2 mm portion. The dissolution process reversed reaction [2.3] leading to a reversal of reaction [2.4] with the consumption of H^+ in the soil solution and a rise in soil pH. In the soil, application of the same amount of P would probably not lower the pH by the same magnitude due to the soil buffering action. The rise in pH at the top of the column with time shows that a lower pH in the fertilizer band is a short term phenomenon which will likely disappear with time.

Water and Acid Extractable P

In the water extractable fraction (Fig. 2.2a), maximum P concentration occurred at the top of the column and gradually declined down the column. This pattern of P distribution is similar to that obtained in soil columns by previous researchers (Hashimoto and Lehr, 1973; Khasawneh et al., 1974). A decrease in the level of water extractable P with time is a result of two processes: diffusion down the column; and precipitation reaction with solution calcium. The maximum distance travelled by P increased with time due to P movement from the top to the deeper portion of the column.

With the acid fraction the picture is somewhat different (Fig. 2.2b). Rather than the smooth curve obtained for the water extractable fraction, the precipitation of P seemed to occur exclusively at the first 2mm section of the column and the process was then apparently discontinuous. Although the low pH of the system will support a generally low level of precipitation, it is not clear why precipitation

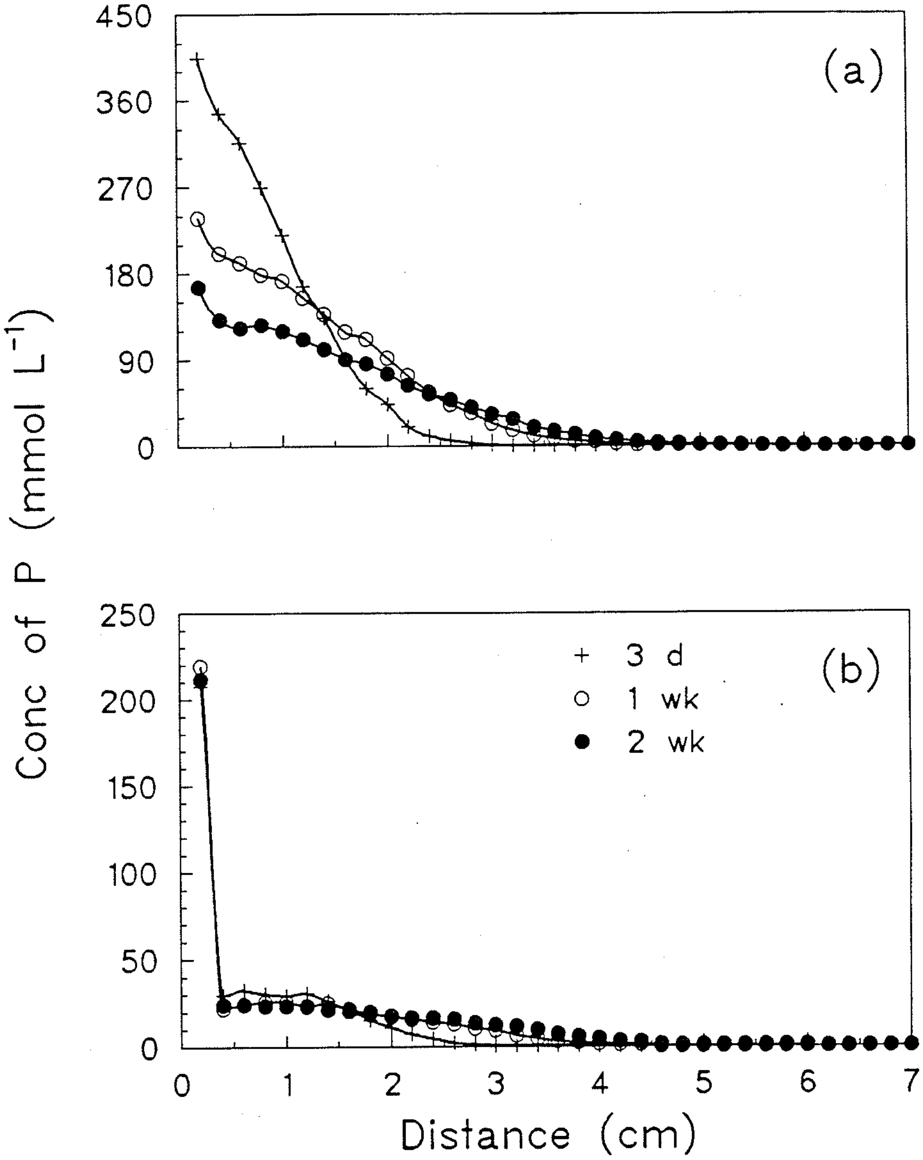

Figure 2.2 - Water- and acid-extractable phosphate distribution profiles in the column with a CEC of 43 $cmol_c$ kg^{-1}; (a) water-extractable P, (b) acid-extractable P.

was restricted to the top of the column. The levels of P and Ca^{2+} were high enough at the first 10 mm section of the column to promote precipitation (Figs. 2.2a and 2.6). A discontinuity in P profile during diffusion has been previously observed, (Bouldin and Black, 1958), and was attributed to the phenomenon of periodic precipitation. Whether the same phenomenon is operational here is uncertain.

A probable explanation is that the high level of P at the top of the column precipitated virtually all the solution Ca^{2+} creating a great sink for calcium. The concentration gradient of calcium is thus in opposite direction to those of P and K^+. As calcium diffused from the lower section to the top of the column in response to this gradient, it was precipitated by the high P pool. Counter diffusion of NH_4^+ and Ca^{2+} was observed by Sample et al., (1979). This was responsible for the increased acid-extractable calcium with time in the zone of banded DAP. There was a slight increase in the amount of acid-P with time (Fig. 2.2b) indicating an increased level of precipitation with time. This pattern is opposite to and compliments the profile obtained in the water extractable fraction.

The effect of CEC on both the water and the acid extractable P is shown in Fig. 2.3. Though the profile of precipitated P was not uniform throughout the column, the level was high enough to retard P movement with increasing CEC. In the absence of cation exchange resin (control) the phosphate ion has moved more than 8 cm down the column after 2 wk of incubation. The corresponding maximum depth of phosphate penetration was 6 and 4.5 cm for columns having a CEC of 21.5 and 43 $cmol_c\ kg^{-1}$, respectively. The maximum depth of phosphate penetration

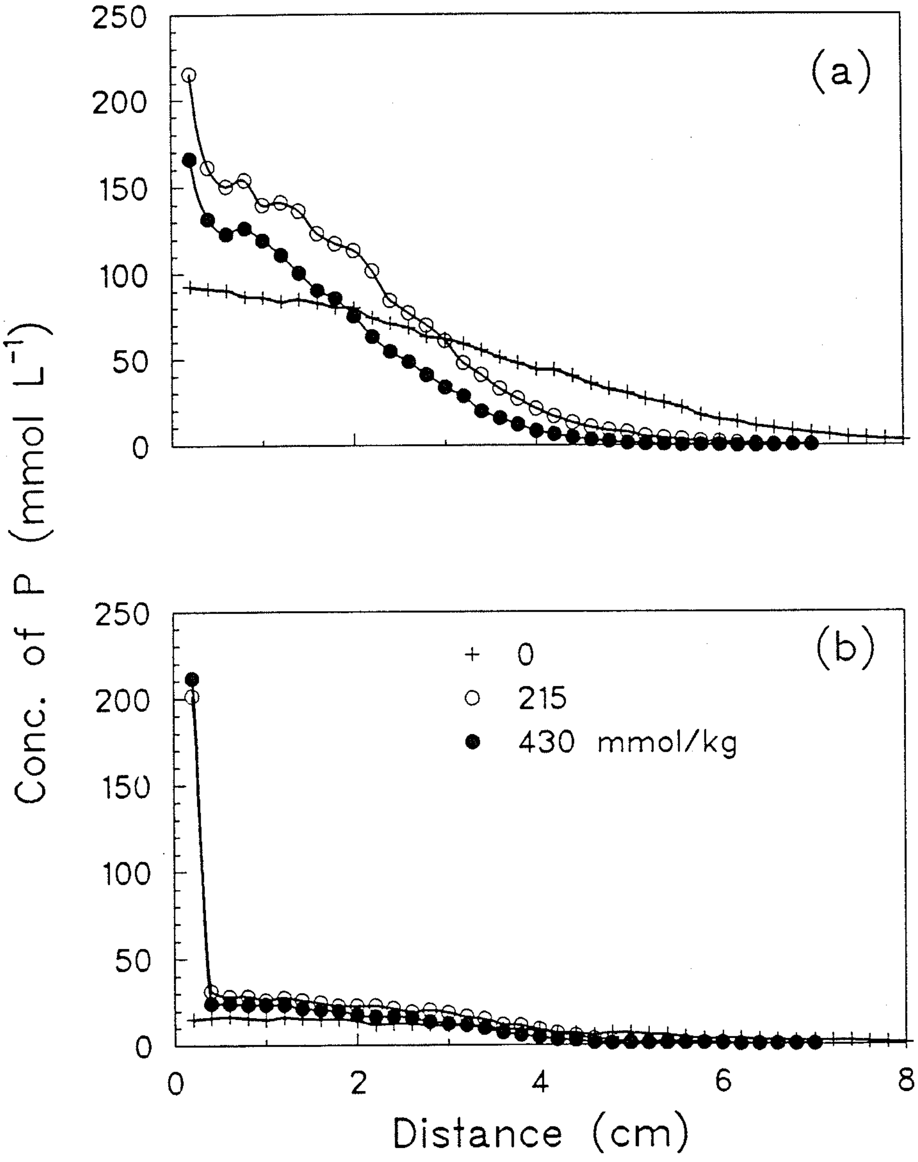

Figure 2.3 - Effect of CEC upon water- and acid-extractable P distribution profiles after 2 wk of incubation; (a) water-extractable P, (b) acid-extractable P.

was inversely related to the CEC of the column. This retardation was due to an increased level of P precipitation as a result of a higher solution Ca^{2+} concentration with an increased CEC (Fig. 2.6b).

Water and Acid Extractable K

The water-extractable K reflects the level in the soil solution while the acid-extractable K approximates what was on the exchange sites (Fig. 2.4). It was assumed that there was no K adsorption or precipitation in this system.

The water-extractable K profile resembled that obtained for P, with the maximum concentration at the top of the column. As with the phosphate ion, very rapid movement of K occurred in the first 3 days, but diffusion continued down the column at a reduced rate with time. The general features of the distribution patterns were established after 3 d of incubation. These distribution patterns retained their original form throughout the 2 wk of incubation.

The only difference between the profiles of water-extractable K and P was that the maximum distance travelled by K was less than that of P at any given time. K moved to a distance of 2, 3 and 4 cm after 3 d, 1 wk and 2 wk of incubation, respectively. The corresponding distance for P was 3, 4, 5 cm. This indicates that potassium was more retarded than phosphate in this system. The higher degree of retardation of potassium ions was due to the stoichiometry of the cation exchange versus P precipitation reactions as shown below:

$$\text{Ca-Resin} + 2K^{+} \rightleftharpoons K_2\text{-Resin} + Ca^{2+} \qquad [2.5]$$

$$Ca^{2+} + HPO_4^{=} \rightleftharpoons CaHPO_4 \qquad [2.6]$$

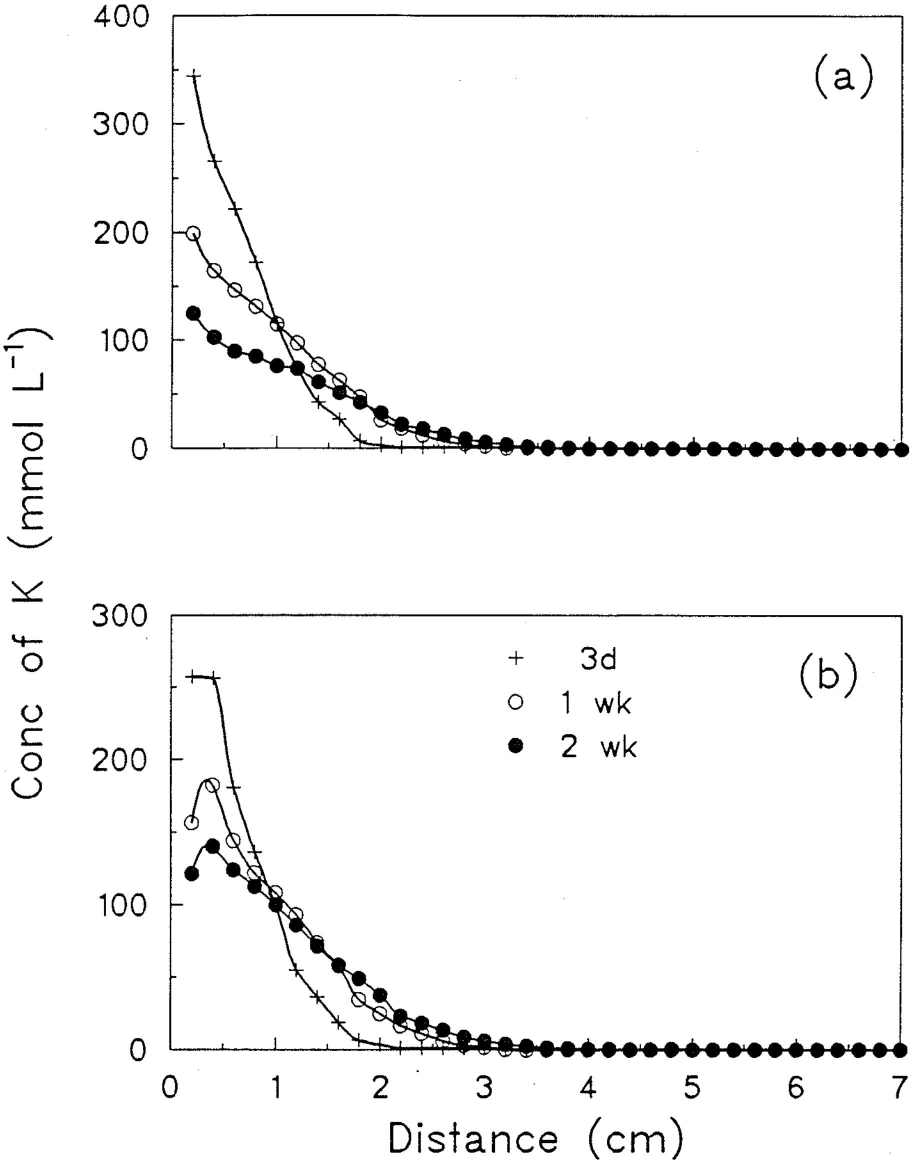

Figure 2.4 - Water- and acid-extractable potassium distribution profiles in the column with a CEC of 43 cmol$_c$ kg^{-1}; (a) water-extractable K$^+$, (b) acid-extractable K$^+$.

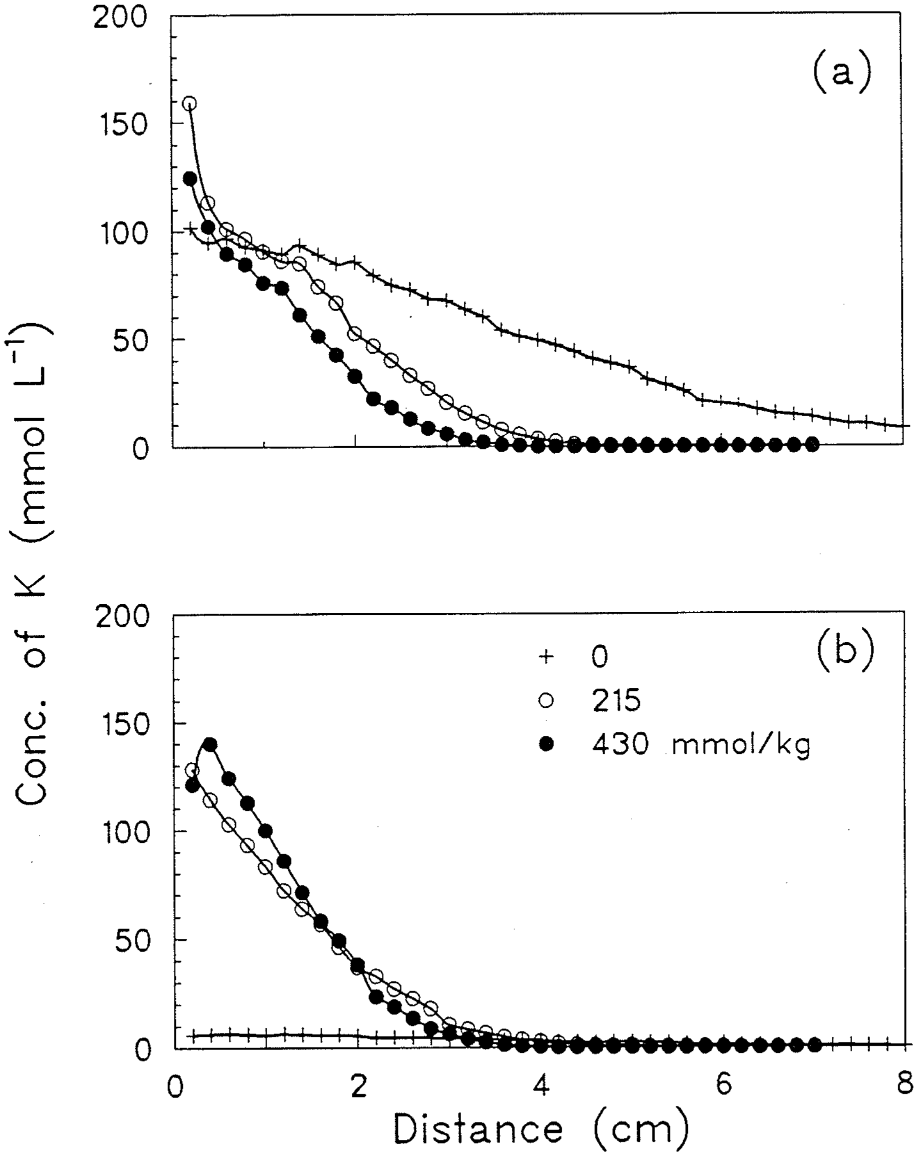

Figure 2.5 - Effect of CEC upon water- and acid-extractable K^+ distribution profiles after 2 wk of incubation; (a) water-extractable K, (b) acid-extractable K.

Unlike the acid-extractable P which increased with incubation time, the acid extractable K (Fig. 2.4b) declined with incubation time. A consideration of cation exchange reaction shows that this observation is consistent with the theory of cation exchange. The exchange reaction is very fast (Hater and Lehman, 1983; Kim et al., 1983a; b), and in this system may be considered to be instantaneous. Hence, there was a dynamic equilibrium between the amount of K in solution and K on the exchange sites. As the level of solution K declined due to diffusion, K came off the exchange site to maintain the equilibrium. This was not the case with acid extractable P because the P equilibrium was governed by the solubility product (K_{sp}). The amount of P in soil solution was far in excess of the K_{sp}, this ensured the accumulation of P precipitated with time. The effect of CEC on the movement of K was more pronounced than that of P (Fig. 2.5b). With higher CEC, more K^+ was exchanged for Ca^{2+} thus resulting in reduced K movement (Figs. 2.4 and 2.5).

Water Soluble Ca

The low pH in this system allowed the accumulation of Ca^{2+} in the soil solution (Fig. 2.6) due to its inhibitory effect on P precipitation. At the pH range obtained in the soil column the predominant form of phosphate in solution was $H_2PO_4^-$. The concentration of the reactive species, $HPO_4^=$ was very low, as such, precipitation reaction with Ca^{2+} was low thereby allowing the accumulation of calcium in the soil solution. This build-up of exchangeable Ca^{2+} in the soil solution is described in the literature as the snow-plow effect (Starr and

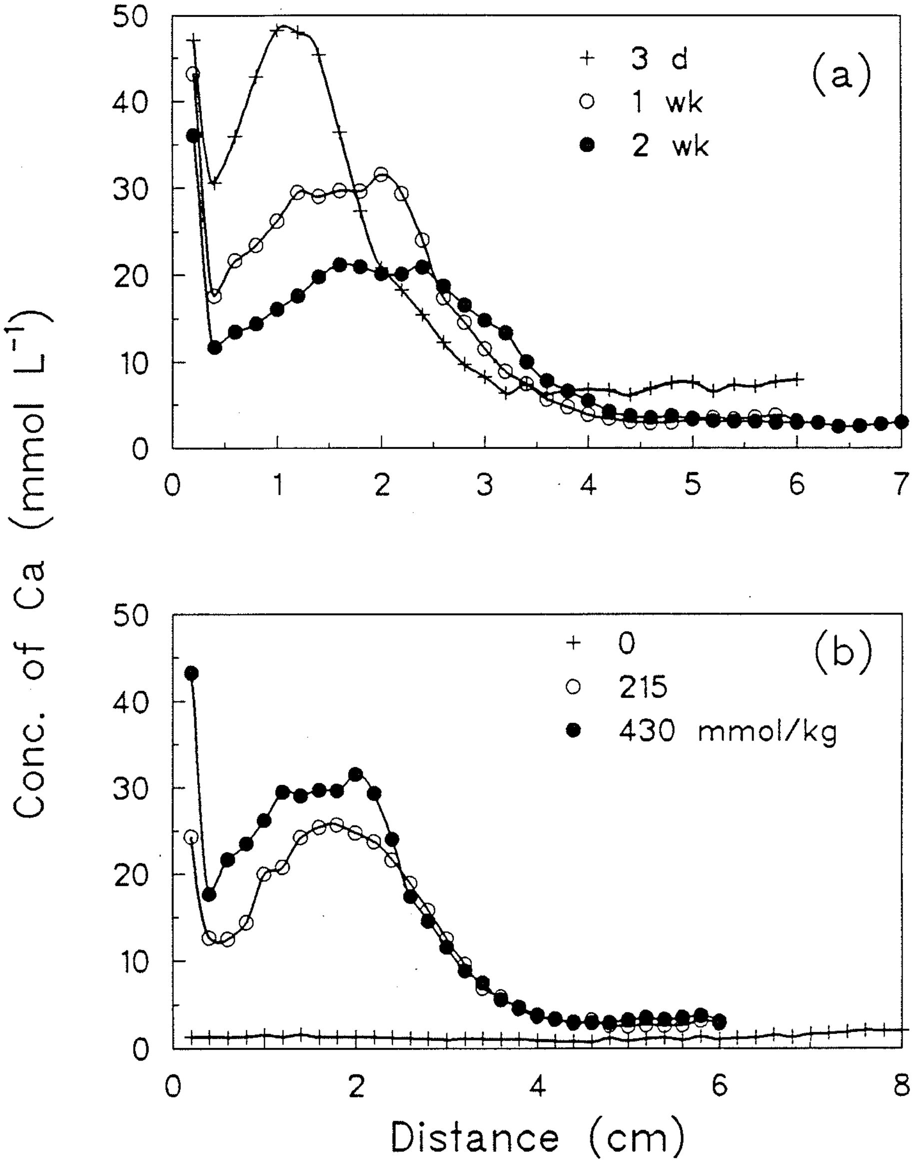

Figure 2.6 - Effect of time and CEC upon water-extractable Ca^{2+} distribution profiles; (a) effect of time (CEC = 43 $cmol_c$ kg^{-1}), (b) effect of CEC (time = 1 wk).

Parlange, 1979; Barry et al., 1983). The observed accumulation of calcium, which was hitherto not present in the soil solution, is an experimental validation of the theoretical development of the snow plow effect (Cho, 1985; Cho, 1990). Sample et al. (1979) reported that in soil columns treated with DAP there was a measurable displacement of Ca^{2+} from the first 2 mm section of the soil and their deposition at distances beyond 2 mm.

The highest level of Ca^{2+} occurred at the 3 d period. The calcium profile then changed with time as a result of diffusion in 2 directions, towards the top of the column, and down the soil column in response to the gradient. The concentration gradient of calcium towards the top of the column is evident from Figure 2.6a.

The presence of a high level of Ca^{2+} in the soil solution supports the assumption of calcium-phosphate precipitation. Also, the retardation of K and P as a result of exchange and precipitation reactions, respectively, is affirmed by the presence of Ca^{2+} in the solution. The effect of increasing the CEC on the level of water Ca^{2+} is shown in Fig. 2.6b. The higher the CEC the higher the solution Ca^{2+} which should be the case since more K^+ was found in exchangeable form as the result of acid-extractable K indicates (Fig. 2.5b).

Mass Balance of the Applied P and K

The mass balance of the added P and K extracted from the column was carried out to give an idea of how quantitative the extraction technique was. The exercise also provided a qualitative measure of the experimental error associated with the column sectioning, column extraction, P and K measurements. The results obtained are summarized in Tables 2.1 and 2.2 for P and K, respectively. The ionic mass balance was carried out by summing up the amount of P or K contained in each 2 mm section over the entire column. This was done separately for the water and the acid extractable fractions of the soil. The result of the summation represents approximately the area under the curves already presented. From Table 2.1 we see that extraction and analytical techniques were very good for P contained in the resin column. In general, the total amount extracted was higher than the amount added and this can be attributed to experimental error whose magnitude of course, appears very small. Water soluble P declined with time while acid extractable P increased with the incubation time, a trend clearly portrayed in the various plots presented earlier.

With respect to K, there was an under-estimation of the total K in the column by the experimental technique. The trend was apparent in all but one column. This may be due to incomplete extraction of K from the resin by the acid extractant. The fact that the values obtained in the column without resin was also below the added K seems to imply that the difference between added and total K was due to experimental error. It is reasonable to conclude from these two tables that the experimental error was very small and the extraction technique used in this experiment quantitatively recovered the added P and K.

Table 2.1 Mass balance of phosphorus in resin-sand column incubated with 0.2g potassium phosphate salt.

SAMPLING TIME	P ADDED (mg/column)	WATER P (mg/column)	ACID P (mg/column)	TOTAL P (mg/column)
[1]RESIN-0 (CEC = 0)				
3 DAYS	45.6[1]	42	4.5	46.5
1 WEEK	45.6	42	7.2	49.5
2 WEEKS	45.6	42.7	8.0	50.7
RESIN-20 (CEC = 21.5 cmol$_c$ kg^{-1})				
3 DAYS	45.6	39.8	7.6	47.4
1 WEEK	45.6	38.3	10.2	48.5
2 WEEKS	45.6	39.5	11	50.5
RESIN-40 (CEC = 43 cmol$_c$ kg^{-1})				
3 DAYS	45.6	42	9.3	51.3
1 WEEK	45.6	37.8	10.2	49.0
2 WEEKS	45.6	34.5	12.2	46.7
RESIN-60 (CEC = 64.5 cmol$_c$ kg^{-1})				
3 DAYS	45.6	39	8.3	47.3
1 WEEK	45.6	36.8	10.7	47.5
2 WEEKS	45.6	35.6	10.6	46.2

[1] Data represent average of 2 columns.

Table 2.2 Mass balance of potassium in resin-sand column incubated with 0.2g potassium phosphate salt.

SAMPLING TIME	K ADDED (mg/column)	WATER K (mg/column)	ACID K (mg/column)	TOTAL K (mg/column)
		RESIN-0 (CEC = 0)		
3 DAYS	57.3	49.4	4.4	53.8
1 WEEK	57.3	51.6	4.1	55.7
2 WEEKS	57.3	48.2	5.0	53.2
		RESIN-20 (CEC = 21.5 $cmol_c\ kg^{-1}$)		
3 DAYS	57.3	31.6	21.3	52.9
1 WEEK	57.3	28.4	24.4	52.8
2 WEEKS	57.3	27.2	22.2	49.4
		RESIN-40 (CEC = 43 $cmol_c\ kg^{-1}$)		
3 DAYS	57.3	32.5	27.1	59.6
1 WEEK	57.3	28	26.3	54.3
2 WEEKS	57.3	24	29.3	53.3
		RESIN-60 (CEC = 64.5 $cmol_c\ kg^{-1}$)		
3 DAYS	57.3	27.2	25.6	52.9
1 WEEK	57.3	22.6	29.7	52.3
2 WEEKS	57.3	21.7	28.5	50.2

SUMMARY AND CONCLUSION

In this study, KH_2PO_4 transport in a model system of calcium-saturated cation exchange resin was carried out. Both K and phosphate transport was retarded in the presence of exchangeable Ca^{2+} due probably to the ion-exchange for K and the formation of solid precipitate, $CaHPO_4$, for phosphate. Ca^{2+} which was not present in solution at the onset of the experiment, appeared in solution due to ion exchange reaction and reacted with phosphate. As the phosphate transport occurred, the pH of the media declined. The lowered pH retarded further precipitation of $CaHPO_4$. It is believed that the degree of retardation of P was low in this system due to the low pH.

Experiment II. - Phosphate Transport In Na-Saturated Exchange Resin.

INTRODUCTION

Two important and related questions arose from the results obtained in experiment I which required urgent answers. These are: (1) Was the difference in the P profile of the control column versus the columns containing Ca-saturated resin due to the exchangeable Ca or the presence of the resin?. (2) Did the acid-extractable P result from a precipitation reaction between Ca and P or an interaction between P and the resin?.

To provide answers to these questions, a column experiment was conducted in an identical fashion to those in experiment I. In this case, Na^+ rather than Ca^{2+} was the exchangeable cation. Na was used because it was expected to interact with added K, in the form of exchange reaction, but not form any precipitate with P. If this was the case, P transport should not be affected by the presence of resin while K should be retarded as usual.

The hypotheses formally stated are:

(a) P transport should not be influenced by CEC when Na is the exchange cation.

(b) With Na as the exchangeable cation, acid-extractable P level should be nil or similar to that obtained in the control column (without resin).

(c) K movement should be retarded due to ion exchange with Na.

MATERIALS AND METHOD

Experimental techniques adopted for this experiment has been stated earlier. The only difference was that Na^+-saturated cation exchange resin was utilized. Columns were incubated for a period of one week.

RESULTS AND DISCUSSION

The data obtained in this experiment are presented in Figures 2.7 and 2.8. The detailed discussion of the ionic profiles will not be undertaken since the pattern is similar to those presented earlier. Only the important features of the plots that addressed the questions raised will be pointed out.

A comparison of the water-extractable P at two different CEC is contained in Figure 2.7a. No significant difference was observed in P profile at the two CEC, indicating that the presence of the resin itself had no effect on P transport in the resin column. This is in agreement with the stated hypothesis, and was expected since Na^+ did not form a precipitate with the phosphate ion. Very small quantities of acid-extractable P, corresponding to about 10% of water-extractable P, was measured in the Na-saturated resin, which is negligible in comparison to the acid-extractable P when Ca^{2+} was the exchangeable cation. The amount of P in the acid fraction was just slightly higher than that obtained in the control column, where there was no exchange resin, in experiment I. It is possible that some of the phosphate ion could have been sorbed by the resin, in a manner similar to salt sorption by resin through osmosis. Also, there was no effect of CEC

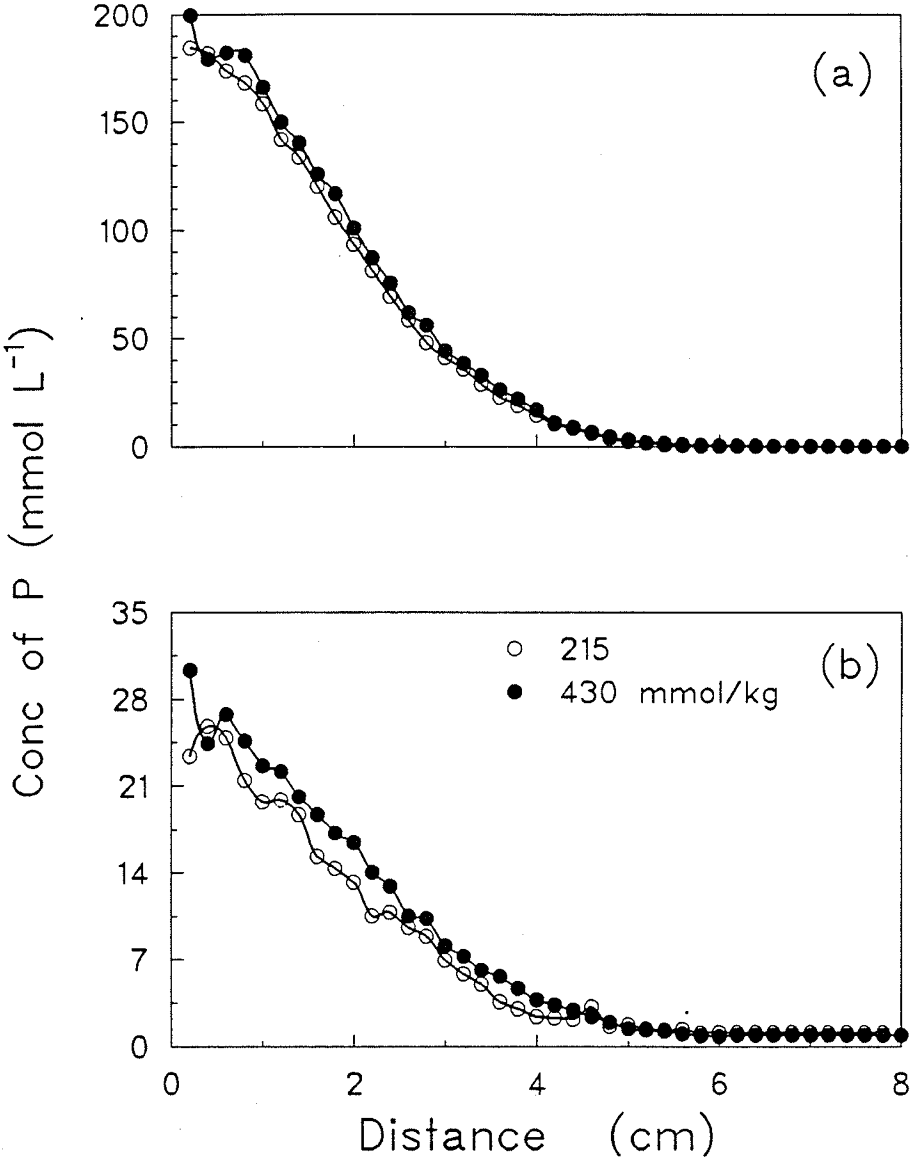

Figure 2.7 - Effect of CEC of Na-saturated resin column on the phosphate profile after 1 week of incubation; (a) water-extractable P, and (b) Acid-extractable P.

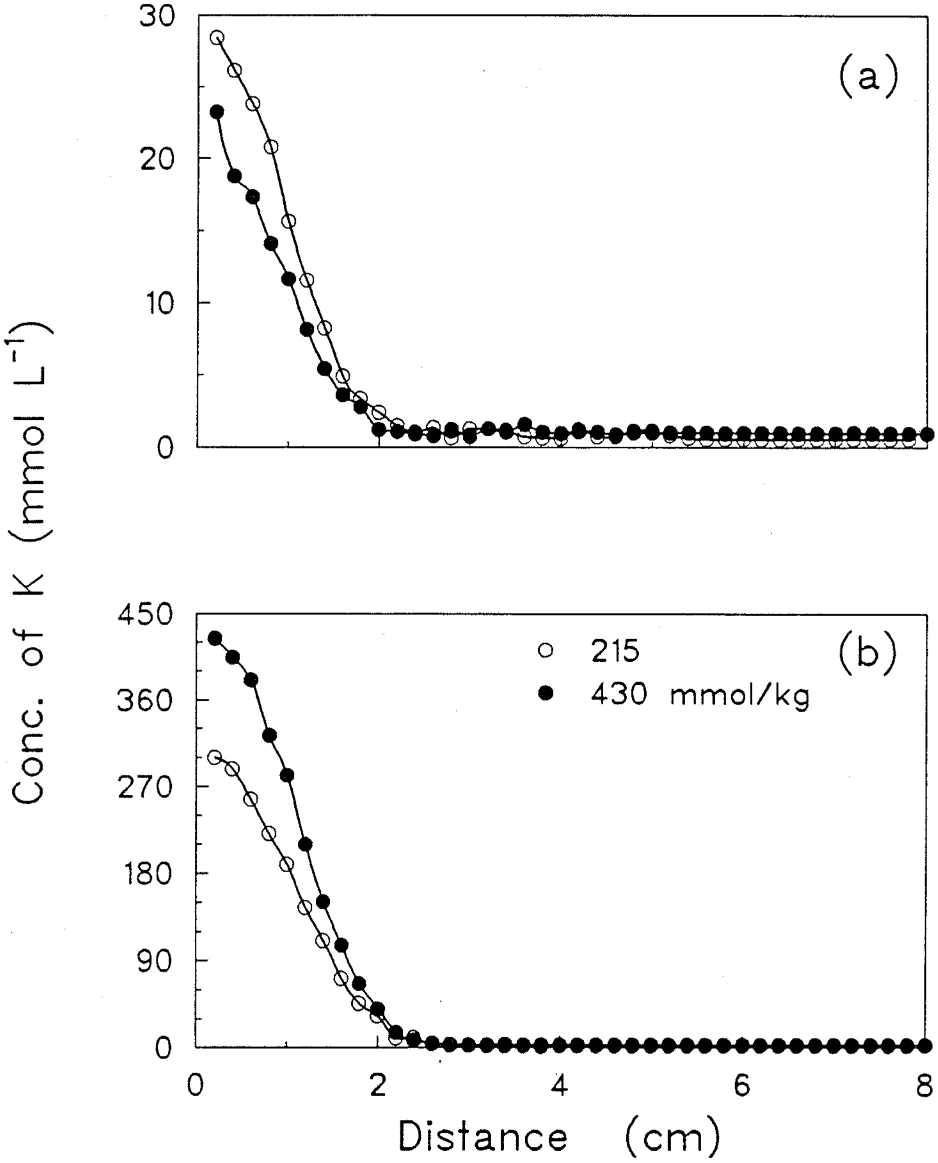

Figure 2.8 - Effect of CEC of Na-saturated resin column on the potassium profile after 1 week of incubation; (a) water-extractable K, and (b) Acid-extractable K.

on acid-P. This confirmed the argument that the high acid-P measured in the first 2 mm portion of Ca-saturated system was due to the Ca^{2+} ion and not the resin.

While P diffused to about 5 cm down the column, potassium only moved to a distance of 2 cm from the application site (Fig. 2.8). Thus, while phosphorus mobility can be said to be virtually unretarded in the presence of Na^{+}-saturated resin, this was not the case with K. A comparison between phosphate and potassium mobility in this system reveal the influence of ion exchange reactions on potassium mobility. The results shown in Figure 2.8 confirmed the hypothesis that K should be retarded as a result of ion exchange interaction with Na.

In the Na-saturated resin, the ratio of acid to water-K is much higher than was the case with Ca-saturated resin. For example, in the first 2 mm of the column containing Na-saturated resin, acid/water-K was about 15. The corresponding ratio of acid/water-K for the Ca-saturated column was 1. The preference of the exchanger for K over Na appears to be much higher than that for K over Ca.

SUMMARY AND CONCLUSION

When Na was the exchangeable cation, the movement of P was not influenced by CEC. Acid-extractable P in the Na-saturated column was very small and comparable in magnitude to the control column of experiment I. The mobility of the potassium ion was retarded compared to the phosphate ion as a result of its ion exchange interaction with the sodium ion. The result obtained in the study confirmed the hypotheses stated earlier.

Experiment III - The Diffusive Transport of Phosphate in a Calcium Carbonate-Cation Exchange Resin System.

INTRODUCTION

The wide occurrence of calcareous soils has generated interest in their study, especially with regard to their ability to sorb phosphate. Lewis and Racz (1969) reported that phosphate moved to a greater distance and at a more rapid rate in noncalcareous than in calcareous soils. This was attributed to a high pH and the precipitation of P by calcium.

In investigations of the mechanism and the magnitude of phosphate sorption in a calcareous soil, researchers in the past have used pure $CaCO_3$ (Cole et al., 1953; Kuo and Lotse, 1972; Griffin and Jurinak, 1973; Freeman and Rowell, 1981). It was assumed that knowledge gained from such a simple system could be applied to the soil. While it has been clearly demonstrated that $CaCO_3$ sorbs P, the magnitude of sorption reported is often small. Kuo and Lotse (1972) reported that the adsorption maximum of phosphate on $CaCO_3$ was 25 $\mu g\ g^{-1}$. Griffin and Jurinak (1973) working at a lower concentration range of P reported an adsorption maximum of 9 $\mu g\ g^{-1}$ for calcite. While these values may be large relative to soil solution P they are relatively insignificant in comparison to the level of P in a fertilizer band where the concentration is of the order of mole L^{-1} (Lindsay and Stephenson, 1959). It becomes obvious that the adsorption of P by $CaCO_3$ is not the dominant mechanism of P retention in a calcareous soil fertilized with P. Sorption studies indicate that the reaction of phosphate with $CaCO_3$ surfaces involves adsorption of a small amount of phosphate followed by precipitation of calcium phosphate at higher P levels (Cole et al., 1953; Griffin and Jurinak, 1973; Freeman and Rowell, 1981).

The study develops on the results of experiment I by examining the role of exchangeable cation and free $CaCO_3$ on the diffusive transport of phosphate in a calcium-saturated resin-mixture. $CaCO_3$ was chosen as the buffer to simulate a calcareous soil and also to permit the assessment of the relative contribution of calcium from $CaCO_3$ and calcium from the exchange sites to the precipitation and retardation of P movement. Information gained would be helpful in understanding the mechanism of P retention when calcareous soils are fertilized with P.

MATERIALS AND METHODS

An amberlite CG 120 resin with a CEC of 430 $cmol_c\ kg^{-1}$ was saturated with Ca^{2+} by repeated washing with 0.5 mol L^{-1} $CaCl_2$ solution. Details of the procedure have been presented earlier. Inert quartz sand was crushed with a shatter box to provide materials with a mesh size comparable with the resin. Sand particles that passed through a 150 mesh sieve were eliminated because of the possibility of this fraction exhibiting cation exchange characteristics.

Before mixing sand with the Ca-saturated resin, sand particles were coated with $CaCO_3$ by employing a technique similar to that described by Van Beek and Pal (1977) for a carborundum gypsum system. Briefly, the crushed sand was spread over a plastic tray and reagent grade $CaCO_3$ powder was added at a rate of 0.5%. These were thoroughly mixed, while water was sprayed over the mixture at intervals. The mixture was allowed to dry such that the $CaCO_3$ adhered to the sand particles. Random samples of this mixture were dissolved in 1 M HCl and analyzed for Ca^{2+} to test the uniformity of the mixture. Only uniformly mixed batches were used. The $CaCO_3$-coated sand was then mixed thoroughly with various amounts of Ca-saturated resin to produce a final mixture with CEC of 0, 21.5 and 43 $cmol_c\ kg^{-1}$. The 0 $cmol_c$ kg-1 mixture (that is, carbonated-sand with no resin) was the control treatment. Column preparation, incubation, sampling and analytic techniques are identical to those described for the last experiment.

RESULTS AND DISCUSSION

The Soil pH

The effectiveness of $CaCO_3$ as a buffer is evident when the pH at the top of the control column (Fig. 2.9a) is compared to the pH reported for an unbuffered system in experiment I. When KH_2PO_4 was added to the soil surface and incubated for various times, the pH near the site of the salt application in this study is one pH unit higher than those observed for the unbuffered system at all sampling periods. This is a significant reduction in hydrogen ion concentration, since the same amount of salt was applied in both experiments. The higher pH of this system should promote an increased level of precipitation through the prevalence of the divalent phosphate ion ($HPO_4^{=}$), the probable phosphate species involved in precipitation reaction with Ca^{2+} (Cho, 1990).

The hydrogen ion concentration was highest close to the application site and declined with increasing distance from the application

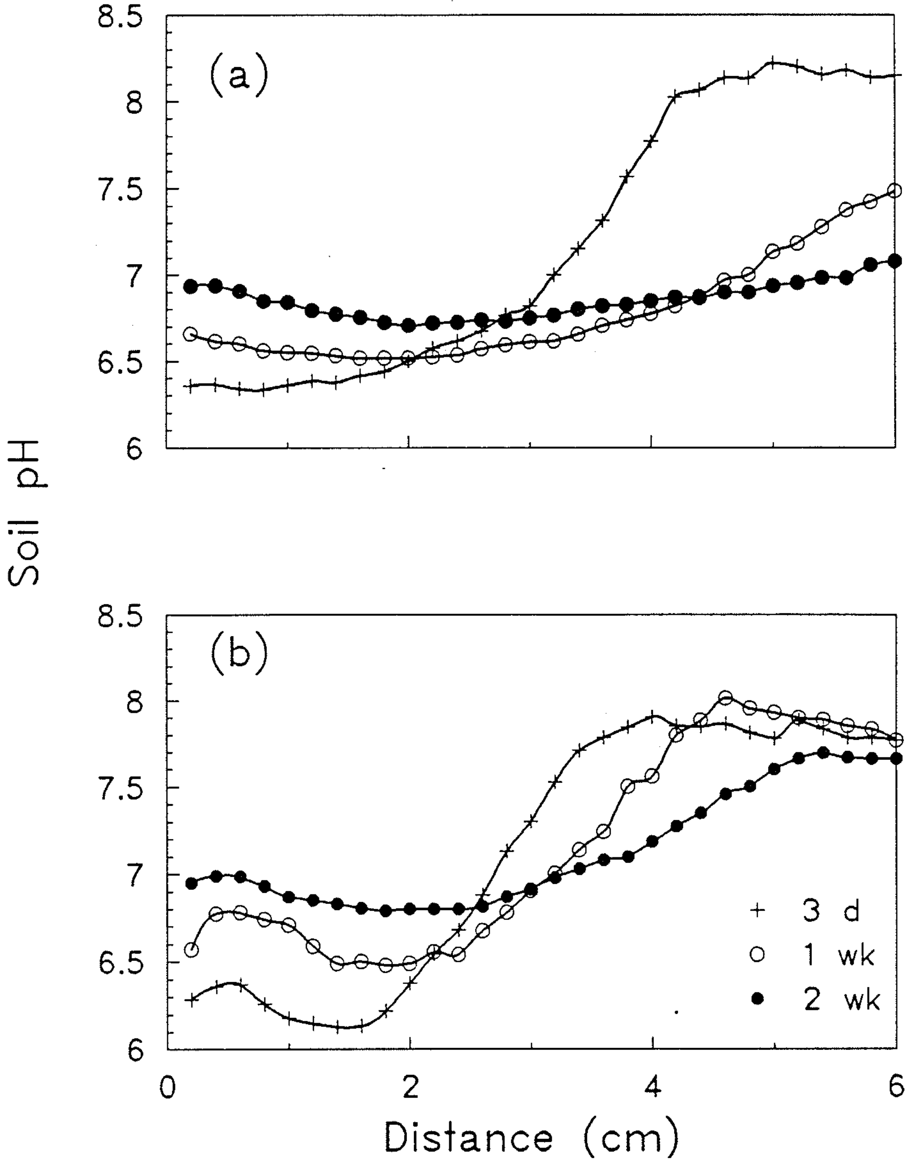

Figure 2.9 - pH of the carbonated resin column with surface applied KH_2PO_4 at different times; (a) CEC= 0, (b) CEC = 21.5 $cmol_c\ kg^{-1}$.

site. The shape and general features of the pH profile was similar to that obtained in experiment I. The mobility of the H^+ ion was exhibited by the rising pH at the top of the column with incubation time and a corresponding decline in pH down the column.

The pH of the background soil (portion of the column not affected by H^+ movement) as shown in the 3 d profile of the control column was about 8.3. This is very close to the pH 8.4 reported for a solution that is in equilibrium with $CaCO_3$ and atmospheric CO_2 (Griffin and Jurinak, 1973b), indicating that the soil solution is in equilibrium with $CaCO_3$. The reduction of pH below 8.3 along the soil column was due to the hydrogen ion from the applied salt. In columns containing Ca^{2+}-saturated cation exchange resin (21.5 $cmol_c\ kg^{-1}$) a slightly different pattern of pH distribution was obtained (Fig. 2.9b). The magnitude of average depth of H^+ penetration, measured as the distance from surface to the mid-point of sharp increase in pH, was considerably lower in the column containing exchange resin compared to the control. For example, the average depth of H^+ penetration for $CaCO_3$-sand mixture was about 3.5 cm after 3 d of incubation. The value was about 2.8 cm with cation exchange resin.

As a result of the buffering action of $CaCO_3$, there was only a slight effect of CEC on the pH profile of the column. This was not the case in the unbuffered system where there was a significant reduction in pH with an increase in the CEC attributed to precipitation reactions. The rise in pH at the top of the column with time resulted from hydrogen ion movement away from the application site and the simultaneous consumption of hydrogen by the buffer.

Water-Extractable P

The values of water-extractable phosphorus are shown in Fig. 2.10. Phosphate moved to a greater depth in the absence of cation exchange resin and the magnitude of transport of surface applied phosphorus was slightly less than that observed without $CaCO_3$ in experiment I (Fig. 2.3a). Thus, addition of 0.5% $CaCO_3$ decreased the mobility of surface applied phosphorus slightly.

The CEC affected the movement of P two ways when the water-extractable P in the control column (Fig. 2.10a) is compared to those in the columns with exchange resin (Fig. 2.10b). Firstly, phosphorus movement in the control column at any point in time was greater than those in columns containing both $CaCO_3$ and Ca-saturated resin. This was due to an increased amount of precipitated P in columns with resin, over the soil column containing $CaCO_3$ alone. This resulted in an increased retardation of P movement with exchange resin. Secondly, in the control column, the reduction in the level of P with time at the upper portion of the column (2 cm from the top) was accompanied by an increase in the concentration of P at the lower segment of the column, indicating the continuous diffusion of phosphate from the top to the bottom of the column. This behaviour is similar to that observed for unbuffered resin system. However, in the carbonated column containing exchange resin, this was not the case. The level of P at the top of the column declined with time without a corresponding increase down the soil column, indicating that the reduction was not due to diffusion, rather, it was a conversion from the water-extractable P to acid-extractable P with time.

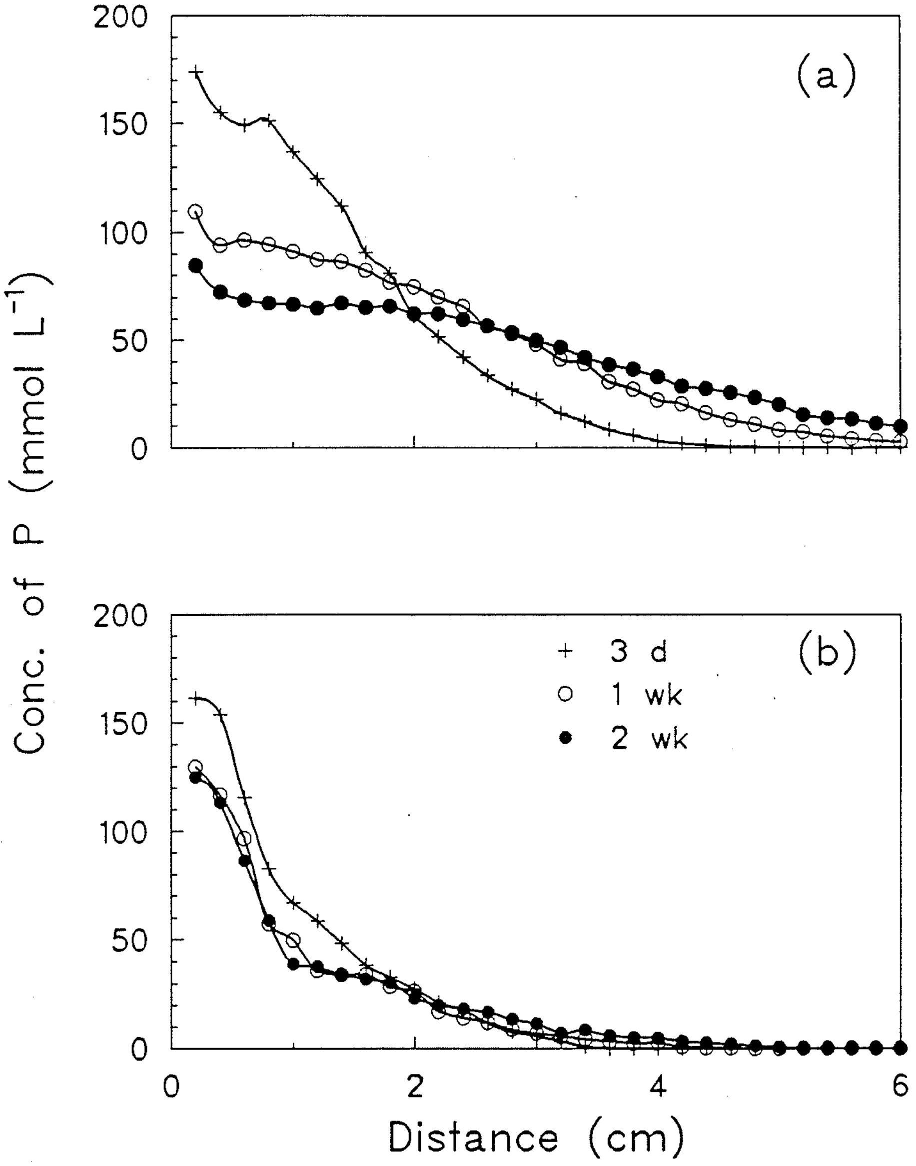

Figure 2.10 - Water-extractable phosphate profiles in the carbonated resin column with time; (a) CEC= 0, (b) CEC = 21.5 $cmol_c$ kg^{-1}.

In general, there was only a small change in the overall P profile from 3 d to 2 wk in the columns containing exchange resin, suggesting a fast rate process in the system. This should be the case if there were an abundance of Ca^{2+} ion and divalent phosphate ion (due to a favourable pH regime - pH > 6). These conditions were met in this case, and by the 3 d period the transformation was almost complete with little or no change with time. Hashimoto and Lehr (1973) observed that the general features of P distribution patterns were established by the first week and maintained throughout the 4 wk incubation. They suggested that long incubation periods, particularly under conditions simulating band placement are not necessary to compare the agronomic effectiveness of different phosphates.

The difference in the P profiles of the control column versus those containing exchange resin further confirmed the conclusion made from experiment I regarding the role of cation exchange on the transport of the phosphate ion.

Acid-Extractable P

The relative contribution of $CaCO_3$ and exchangeable Ca to precipitation of P can be deduced from the values of acid extractable P shown in Figure 2.11. In the columns containing only $CaCO_3$ (Fig. 2.11a), P precipitation was limited to the application site similar to the pattern obtained with the unbuffered exchange resin (Experiment I).

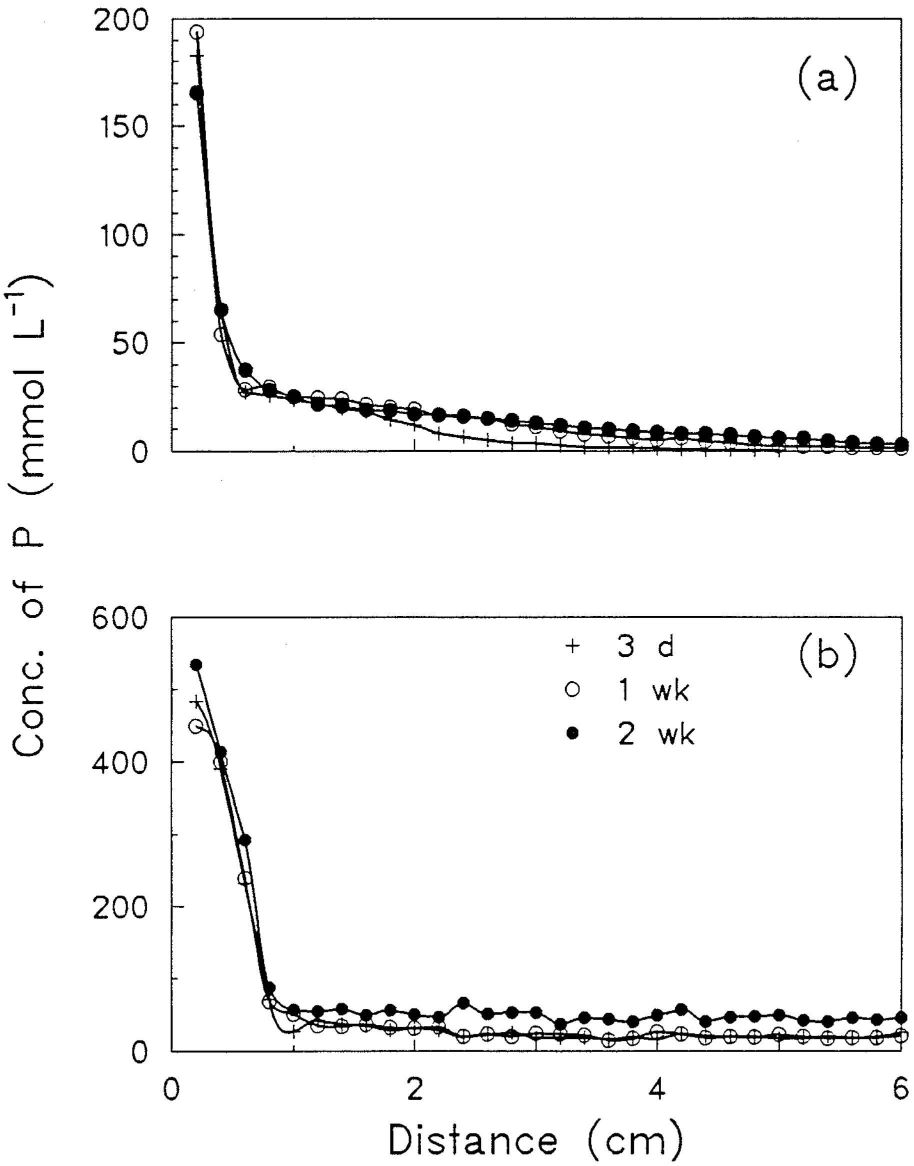

Figure 2.11 - Acid-extractable phosphate profiles in the carbonated resin column with time; (a) CEC = 0, (b) CEC = 21.5 cmol$_c$ kg^{-1}.

The magnitude of surface precipitated P ranged from 160 to 190 mmol L^{-1}. In the columns containing both $CaCO_3$ and Ca-saturated resin (Fig.2.11b), the zone of precipitation extended to 1 cm from the top of the column and the amount of P precipitated at the top of the column alone ranged from 450 to 600 mmol L^{-1}. The combination of these two effects was a much higher level of precipitated P in columns with resin and $CaCO_3$ than in columns with $CaCO_3$ alone. This difference would explain the retardation of P in the presence of exchange resin discussed earlier. Since the pH of both systems was similar, due to the buffering action of $CaCO_3$, and the same amount of P was added, it can be concluded that exchangeable Ca^{2+} was responsible for the elevated levels of precipitation and retardation of phosphate diffusion and to emphasize its importance over that of $CaCO_3$.

The higher level of precipitation in the buffered system supports the explanation given in experiment I that the low pH of the unbuffered system was responsible for the low level of precipitated P. Thus, the pH of the system is quite important in determining the fate of P because of its influence on the ratio of $H_2PO4^-/HPO_4^=$ in solution as was discussed by Cho (1990).

In carbonated soils with similar pH and CEC levels, the amount of P precipitation may not be as high because of the accessibility of exchangeable Ca^{2+} in the soil compared to the resin. The Ca^{2+} on the exchange sites of the resin are probably more accessible, hence, can be more easily replaced by K^+ than those in the soil system. Also, the selectivity coefficient of K^+-Ca^{2+} exchange may not be similar in the two systems. The effect of selectivity coefficient on solution K^+ and

Ca^{2+} has been clearly demonstrated with mathematical models describing cation transport with exchange reaction (Cho, 1985; Cho, 1990).

Water-Extractable K

Figure 2.12a shows the distribution of water soluble K^+ at three different times in the control column (with 0.5% $CaCO_3$ only). The results indicate that the mobility of K^+ was high and similar to that of P (Fig. 2.10a) suggesting that P and K moved together. Such behaviour is referred to as salt diffusion and was observed when diammonium phosphate (DAP) was applied to soil column (Sample et al., 1979). The difference between the K profiles in Fig. 2.12a as compared to Fig. 2.12b was due to ion exchange interaction with Ca^{2+}, resulting in the retardation of K in column containing Ca-saturated exchange resin.

Acid-Extractable K

The acid-extractable K represents what was left on the exchange sites after water extraction. The exchangeable K level in the column declined in tandem with the reduction of the solution K with time. There was a small amount of acid extractable K in the control column containing no exchange resin (Fig. 2.13a). Since it was assumed that there was no precipitation of K in this system, the acid-K in the control column would either represent K adsorption by the fine sand or incomplete extraction of solution-K by water. In any case, the amount was quite small compared to the column with exchange resin and can be assumed to be negligible. Acid-extractable K in the column with cation exchange resin (Fig. 2.13b) was quite high. The concentration at the

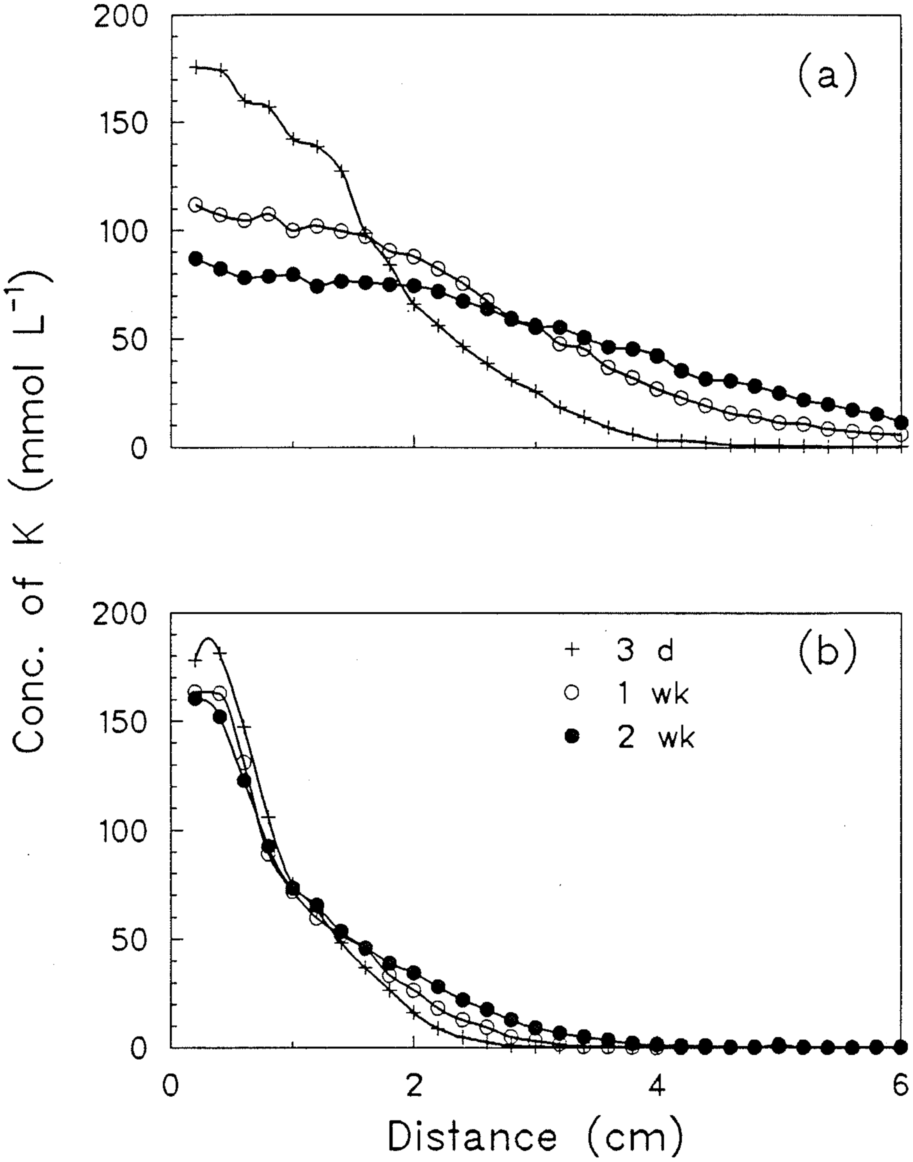

Figure 2.12 - Water-extractable potassium profiles in the carbonated resin column with time; (a) CEC = 0, (b) CEC = 21.5 $\text{cmol}_c\ \text{kg}^{-1}$.

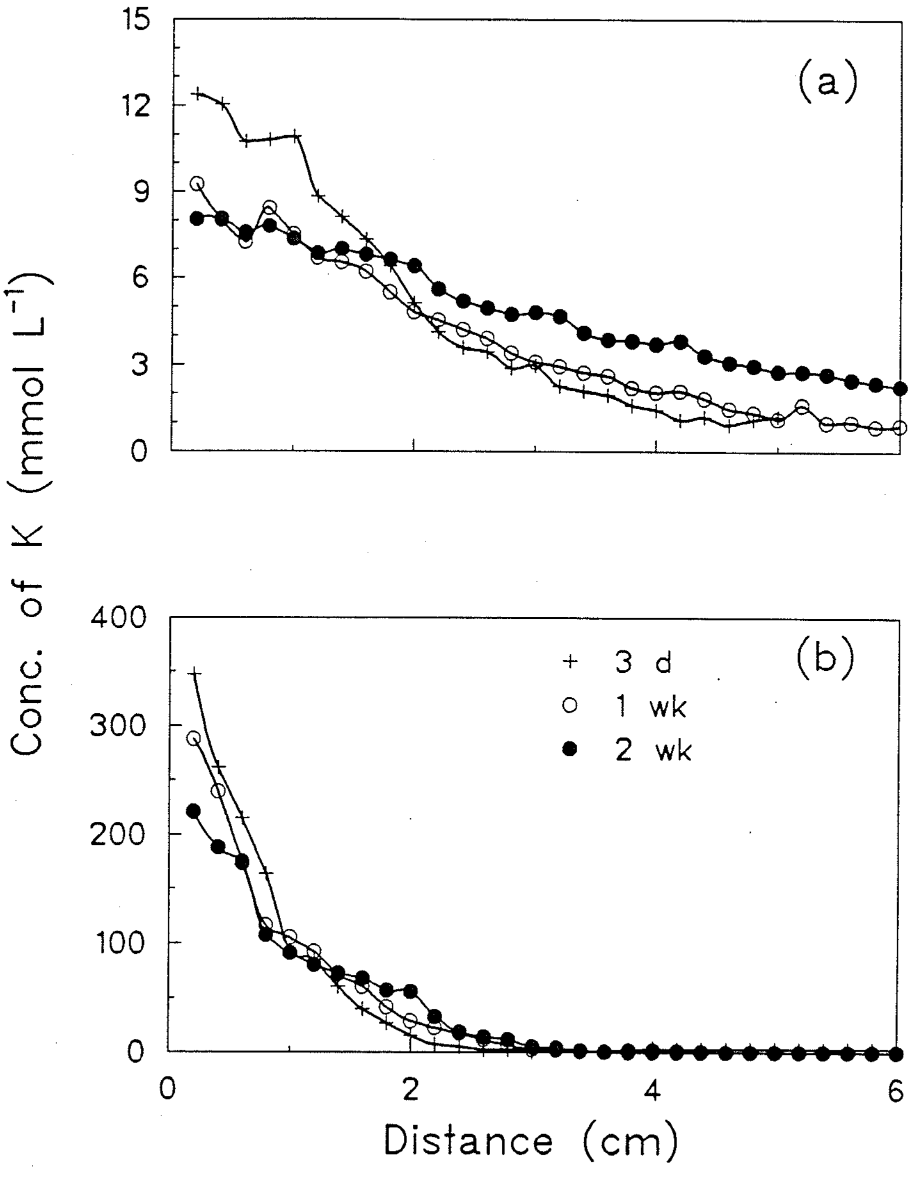

Figure 2.13 - Acid-extractable potassium profiles in the carbonated resin column with time; (a) CEC = 0, (b) CEC = 21.5 cmol$_c$ kg^{-1}.

surface was initially high but decreased with time. The profile suggested that the acid-soluble K^+ travelled downward with time in a similar manner as water-soluble K^+. If all the Ca^{2+} liberated from the exchange sites was precipitated as $CaHPO_4$ in situ, then the acid-extractable P should be one-half of acid-extractable K, since two potassium ions replaced one calcium ion, at any point in the column. A comparison of Figure 2.13b (acid-extractable K), with Figure 2.11b (precipitated $CaHPO_4$) shows that this was not the case, especially at the top of the column, implying that the Ca^{2+} precipitated at the surface came from the lower portion of the column or from sources other than exchange sites.

Water-Extractable Ca^{2+}

The build-up of Ca^{2+} in the soil solution as a result of ion exchange with K^+ was reported in the last experiment. This build-up, referred to as snow-plow, was not observed in this experiment (Fig. 2.14). This is probably because the high pH of the buffered system promoted a high rate of precipitation leading to the consumption of solution Ca^{2+}. This high rate of precipitation did not permit the accumulation of Ca^{2+} in the soil solution. This was also the case in soil system, to be discussed later, where the snow-plow effect was not observed because of Ca^{2+} consumption.

In the control column, calcium concentration was highest at the top of the column and decreased with distance from the application site. The effect of H^+ on the dissolution of $CaCO_3$ is probably responsible for the profile of Ca^{2+} obtained. The combination of $CaCO_3$

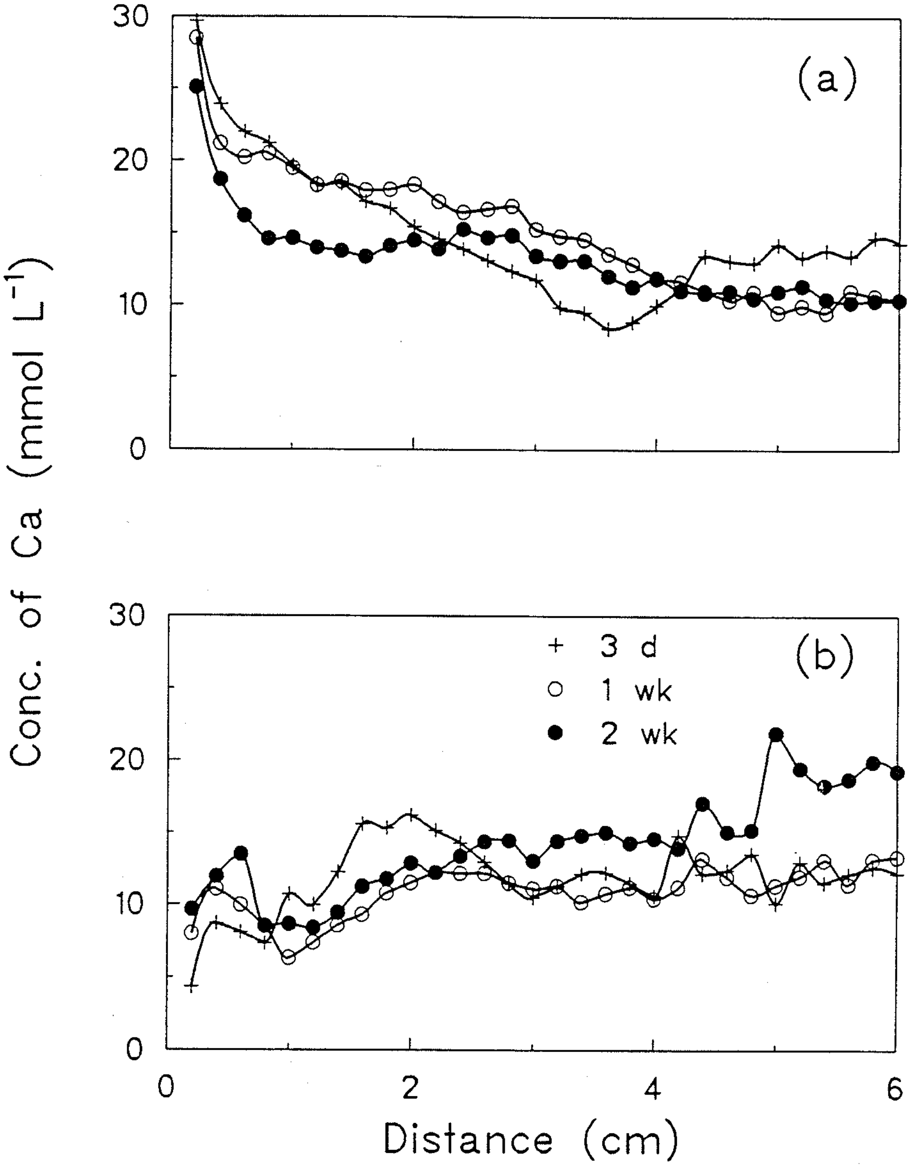

Figure 2.14 - Water-extractable calcium profiles in the carbonated resin column with time; (a) CEC = 0, (b) CEC = 21.5 $cmol_c$ kg^{-1}.

and Ca^{2+}-saturated exchange resin did not produce a smooth distribution of Ca^{2+} indicating that the system is more complex.

SUMMARY AND CONCLUSION

When $CaCO_3$ was used as a buffer, the pH of the Ca-saturated resin was maintained at a level which support the precipitation of P. This resulted in a high level of precipitation in columns containing $CaCO_3$ alone or $CaCO_3$ in combination with exchange resin. The exchangeable Ca^{2+} contributed more to P precipitation than calcium from $CaCO_3$. The higher level of P precipitation resulted in the retardation of P movement as shown by the extent of P movement in this study. This demonstrates the role of ion exchange on the transport of anionic species in a system where the cation on the exchange can form a precipitate with the anion. Whether or not such precipitation reaction would occur, and its magnitude in the soil, would be dictated by the cation composition on the exchange complex, the pH reaction of the applied salt and the accessibility of the soil cation to the cation accompanying the phosphate ion.

CHAPTER III

Experiment IV - Phosphorus Transport In Calcareous and NonCalcareous Soils

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INTRODUCTION

The column experiments performed with Ca^{2+}-saturated ion exchange resin, revealed interesting results about phosphate transport in a system where Ca^{2+} was the dominant exchangeable cation. The flushing out (snow-plow) of exchangeable calcium by the applied KH_2PO_4 was observed. Though P was not adsorbed, its mobility was nevertheless retarded as a result of the influence of ion exchange reaction on anion transport. The effect of salt pH on the level of precipitation through its direct effect on the ratio of monovalent to divalent phosphate ion was demonstrated.

An exchange resin was utilized to provide information on phosphate movement and interaction in a model system. Cation exchange resins are known to have ion exchange behavior similar to those of soil clay (Hsu and Rennie 1962a). The investigation was extended to natural soils so as to determine the extent to which some of the reactions (ion exchange, precipitation, H^+ transport) already observed occur in the soil.

In this experiment, the diffusive transport of phosphate in two calcareous soils (Libau and Graysville II series) and a noncalcareous soil (Pipestone) was studied with the aid of ^{32}P labelled KH_2PO_4. It has been observed (Cho et al. 1970) that ^{31}P and ^{32}P would travel differently under convective (advective) condition, since the isotopic exchange of ^{32}P with native soil P retards the movement of ^{32}P while such retardation does not exist with ^{31}P. Isotopic exchange retardation is most noticeable if solution P concentration is low and native soil P content is high, and is almost invisible if solution P concentration is very high. The use of ^{32}P to trace applied P movement is justified only if the fertilizer P concentration is very high so that the retardation of ^{32}P as compared to ^{31}P is negligibly small. Such a condition was reasonably met in this experiment. The labelled form of KH_2PO_4 was utilized because it is possible to distinguish between the applied P and the native soil P. This will increase the precision of P measurement in the soil column while eliminating the necessity for a control experiment.

A study of this nature will help in a better understanding of the mechanisms of P interactions in the fertilizer band. It is also expected to furnish information on how a particular P salt might behave depending upon the CEC of the soil, the composition of cations on the exchange complex and the pH reaction of the salt.

MATERIALS AND METHOD

This experiment was performed in an identical fashion to those reported earlier and as such the details will not be repeated here. The only difference was that the salt utilized was labelled with carrier free ^{32}P.

The following procedure was utilized to label the salt with ^{32}P. 50 g of KH_2PO_4 was weighed into a 250 mL glass beaker. 50 mL of water was added and mixed into a paste. 1 mL of H_3PO_4 containing 3.7×10^7 Bq of carrier-free ^{32}P was then added to the beaker and thoroughly mixed. The mixture was allowed to evaporate under a radiant heat source. The salt, after drying, was ground with a pestle and mortar to obtain a very fine powder.

Three of the six soils used for the sorption studies in chapter I were utilized in this experiment. These were made up of two calcareous soils (Libau and Graysville II series) and a noncalcareous soil (Pipestone). Details of soil preparation methods and soil properties were described earlier in chapter I. Each soil was packed into a wax column, having a cylindrical cavity, at a bulk density of 1.2 Mg m^{-3} and wetted to field capacity. The field capacity of these soils and other pertinent properties are listed in Table 1.1. The soils were allowed to equilibrate for 48 h on a perforated desiccator plate with free water at the bottom. After equilibration 0.2 g of labelled KH_2PO_4 was applied as uniformly as possible to the surface of each column. This was then incubated in the desiccator for the desired period of time. Duplicate columns were prepared for sampling for each of the 3 soils at each sampling period. Soil column sectioning, sampling and extraction were identical to that described for the two previous experiments. The amount of ^{32}P in the extracted solution was measured using a scintillation counter (Beckman model 7500), in a liquid scintillation cocktail (Beckman).

A known concentration of P (100 $\mu g\ g^{-1}$) was prepared in a 250 mL volumetric flask from the same stock of labelled KH_2PO_4 salt applied to the soil columns. One mL of this solution was added to 4 mL of scintillation cocktail, thoroughly mixed in a plastic scintillation vial, and counted as the standard. One mL of distilled water was similarly added to 4 mL of scintillation cocktail and counted as a blank. The soil extracts (water and acid), after the appropriate dilution were treated in a similar manner and were counted at the same time with the standard and the blank. The specific activity of the standard allowed the determination of P in the sample after correcting for the background count.

The K and Ca in the extract were measured with an atomic absorption spectrophotometer after allowing sufficient time for the ^{32}P in the sample to decay to reasonable levels. The combination of this with the dilution of the extract, ensured that the activity of the solution to be measured was not significantly different from that of the background.

RESULTS AND DISCUSSION

The information gathered from the two earlier studies using cation exchange resins will be useful in explaining ionic distribution of phosphate, calcium and potassium observed in the soil. However, direct comparison of the ionic profiles in the soil to that obtained from the resin columns would not be carried out.

Certain similarities undoubtedly exist in the chemical nature of the resin and the soil systems, the two systems are, however, not identical. The fundamental differences existing between them have to be borne in mind to make meaningful interpretation. For example, the resin system had its exchange complex made homo-ionic with Ca^{2+}. This ensured that the interaction between the applied K and the exchangeable Ca^{2+} was binary exchange. The exchange complex of the soil on the other hand though dominated by Ca^{2+}, contained other cations such as K^+, Mg^{2+} and Na^+ (Table 1.1). Therefore, the ion exchange reaction is bound to be more complicated in the soil than in the resin. For the purpose of this experiment attention was focused mainly on K-Ca exchange. While this might have been the dominant exchange reaction in the soil it was not exclusively so.

Soil pH

The pH of the soil is a measure of the hydrogen ion activity in the soil solution. The pH profile of the 3 soils is shown in Figure 3.1. The KH_2PO_4 salt applied to the surface of the column is an acidic fertilizer and the hydrogen ion from the dissolution and ionization of the salt depressed the soil pH below that of the original soil pH. Hence, the lowest pH was obtained close to the site of application. There was hydrogen ion movement down the column with a reduction of soil pH below that of the background in the portion of the column influence by the applied salt.

The pH profiles obtained in these soils appeared to be influenced by two soil parameters. The first was the original pH of the soil and the second was the $CaCO_3$ content which acted as a buffer in these soils. The pH of the Libau, Graysville II and Pipestone as shown in Table 1.1 are 7.6, 8 and 7.5 while the carbonate content are 8, 2 and < 1 % $CaCO_3$, respectively. It is evident from Fig. 3.1. that the calcareous soils were well buffered against pH change compared to the noncalcareous soil. The change in pH at the soil surface following the salt application bore a direct relationship to the $CaCO_3$ content of these 3 soils.

The Libau series with 8 % $CaCO_3$ content had the least pH change following the application of KH_2PO_4. After 3 d of incubation the

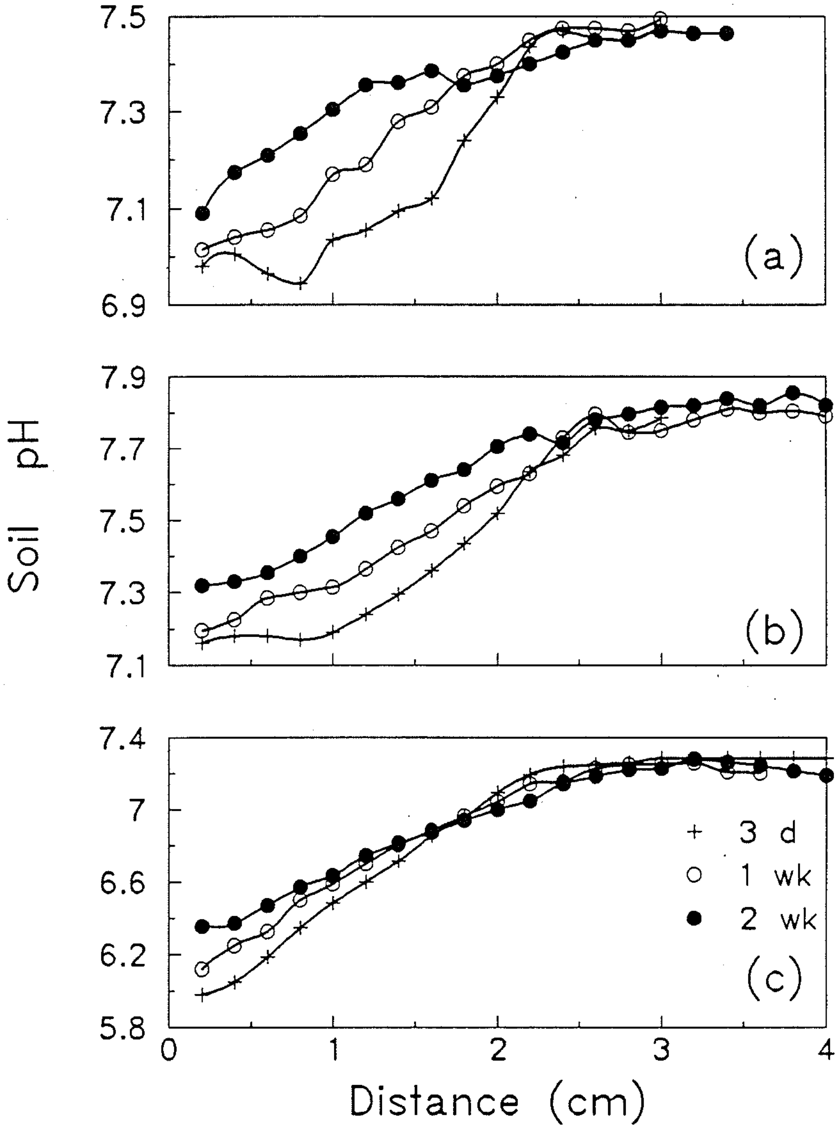

Figure 3.1 - The pH of calcareous and noncalcareous soils following the surface application of KH_2PO_4; (a) Libau, (b) Graysville, and (c) Pipestone.

surface pH decreased from 7.6 to 7, a change of 0.6 unit of pH. With the Graysville II series the pH declined from 8.0 to 7.2 after the same period of incubation while for the noncalcareous Pipestone, the change in pH was from 7.5 to 6 after 3 d. It should be pointed out that the Libau series and Graysville II series have similar chemical properties (CEC exchangeable Ca, Mg, etc.) except for the $CaCO_3$ content. A comparison of the ionic profiles of these two soils should reveal the influence of calcium carbonate content.

While pH at the surface of the two calcareous soils were quite similar after incubation, the change in pH was not. The buffering action of $CaCO_3$ on pH change following the application of KH_2PO_4 is well demonstrated by the pH profile obtained in this study and support the results obtained in experiment III.

The following reactions were postulated by Plummer et al. (1978), and restated by Warfvinge and Sverdup (1989) for the dissolution of $CaCO_3$ in soil:

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \quad [3.1]$$

$$CaCO_3 + H_2O \rightleftharpoons Ca^{2+} + HCO_3^- + OH^- \quad [3.2]$$

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \quad [3.3]$$

Limestone in soils reacts with dissolved species in the soil solution producing two moles of acid neutralizing capacity (ANC) and one mole of calcium ions for each mole of calcium carbonate that dissolved.

The transport of H^+ ion in the soil did not follow the pattern observed for the resin system and this may be due to the high buffering capacity of these soils. Whereas the pH profile in the exchange resin was sigmoidal, the profiles from the soils were curvilinear. In the resin system the rise in pH in the first 2 cm portion of the column with time was followed by a concomitant depression of pH down the column; an indication of H^+ ion diffusive movement with time. In these soils, there was no appreciable H^+ ion diffusion beyond the 3 d period. While a rise in pH was observed with time, this rise appeared to emanate from H^+ ion consumption rather than movement since this rise was not followed by a decline in pH at any portion of the column with time. It was only in the Pipestone column (soil with the lowest pH buffer capacity) that the pH profile had a semblance to that obtained in the resin system.

The soil pH obtained after the application of KH_2PO_4 to these 3 soils while probably not detrimental to plant growth is nevertheless quite important. The importance is derived from its indirect effect on the magnitude of $CaHPO_4$ precipitation through its direct effect on the ratio of $H_2PO4^-/HPO_4^=$ in the soil solution. The dissolution of KH_2PO_4 and speciation of the phosphate ion is given by:

$$KH_2PO_4 \rightleftharpoons K^+ + H_2PO_4^- \qquad [3.4]$$

$$H_2PO_4^- \rightleftharpoons HPO_4^= + H^+ \qquad [3.5]$$

While the equilibrium relation in equation [3.4] is governed by the solubility of KH_2PO_4 that of [3.5] is governed by the second dissociation constant of H_3PO_4, such that:

$$([H^+] \times [HPO_4^=])/[H_2PO_4^-] = K_2 = 10^{-7.2} \qquad [3.6]$$

$$(HPO_4^=)/(H_2PO_4^-) = K_2/[H^+] \qquad [3.7]$$

When the solution pH is 7.2 then the ratio $HPO_4^=/H_2PO_4^-$ is unity. A unit change in pH represents 10 times change in the concentration of the mono and divalent phosphate ions depending on the direction of the pH change. Since $HPO_4^=$ is the probable species reacting with Ca to form DCPD its relative abundance in solution is governed by the pH of the soil. There is 10 times more $HPO_4^=$ ion in the soil solution at pH 7.2 than at pH 6.2 under constant total phosphate concentration. Given the same Ca concentration, there should be more precipitation and retardation of P movement with increased soil pH. The pH change resulting from fertilizer P application may not affect plant growth directly, the magnitude may be such that it enhanced the precipitation reaction of P with soil Ca^{2+} thereby reducing P mobility and availability to plants.

The above discussion shows the need to take a multi-ionic approach in studying the behaviour and transport of ions in the soil. To be able to understand the reactions of phosphate ion in a system as complex as the soil it may not suffice to pay attention, solely, to the phosphate ion.

Water-Extractable P

The profile of P obtained when the soil columns were sectioned and extracted with water is shown in Fig. 3.2 for the 3 soils. It should be pointed out that these P profiles are not as smooth as those obtained in the resin system owing to the complex nature of the soil system and its interaction with the added phosphate. Nevertheless, some of the features that were observed with the resin and calcium carbonate-resin experiments were exhibited by the profiles of P shown in Figure 3.2.

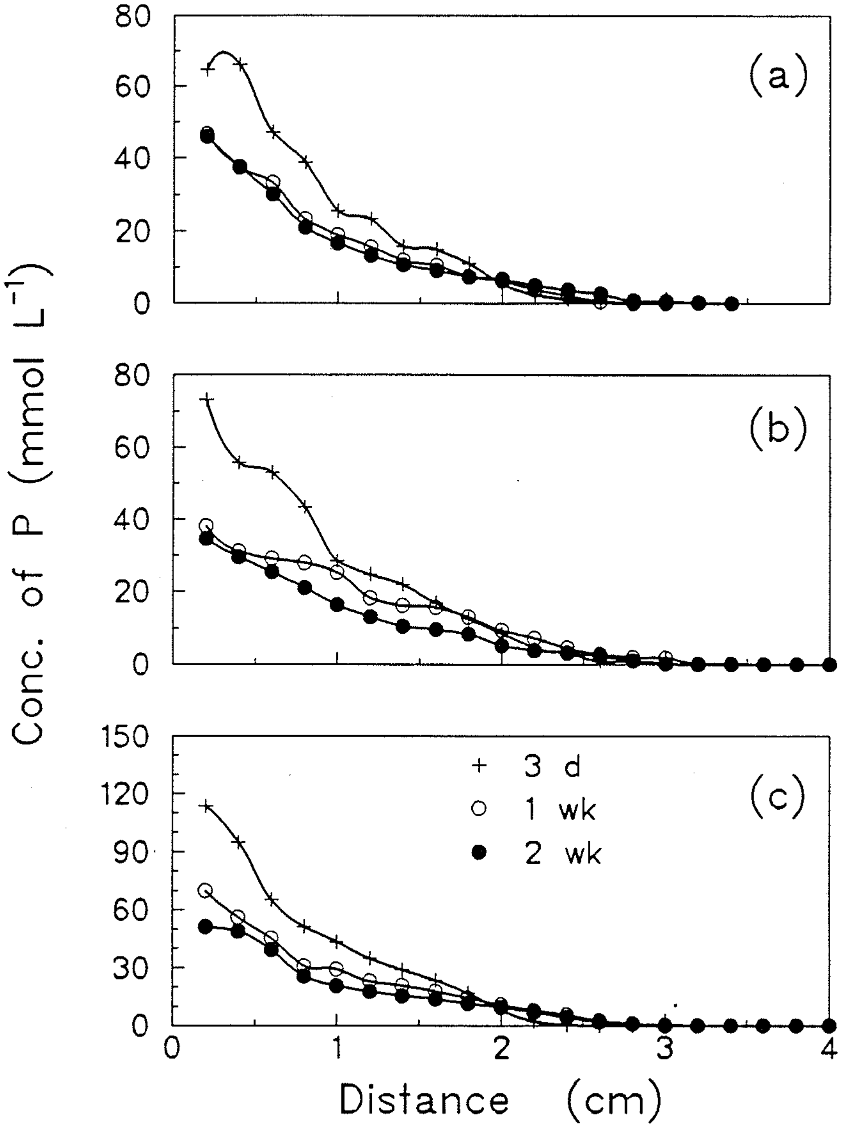

Figure 3.2 - The water-extractable P in calcareous and noncalcareous soils following the surface application of KH_2PO_4; (a) Libau, (b) Graysville II and (c) Pipestone.

The similarity in the characteristics of the two calcareous soils [Libau and Graysville II, Fig 3.2 (a) and (b)] is portrayed by the P profile obtained with time in the columns packed with the two soils. The maximum distance moved by P was roughly the same in all the 3 soils irrespective of CEC or the carbonate content of the soils. The water extractable P was higher in the noncalcareous soil than in the calcareous soils. This was probably due to the higher amount of precipitated P in the calcareous soil compared to the noncalcareous soil as will be seen later.

As was the case with hydrogen ion concentration, the water-extractable P declined with time after 3 d. In the resin system the decline in the water-P was a result of the twin processes of diffusion and precipitation with time. In the soil, there was very little diffusion of phosphate after 3 d and the decline in water-P level was due, mainly, to precipitation. An identical feature was observed with calcium carbonate-cation exchange resin columns (Experiment III).

The results of this experiment showed the high capacity of the soil to fix (precipitate) P as long as there is an ample supply of Ca^{2+}. Though the experiment was terminated after 2 wk there is no doubt that the precipitation reaction would have continued over longer periods of time (Hashimoto et al., 1973). It will therefore be difficult to speak about saturating the soil with P where the soil system has a large reserve of Ca^{2+} on its exchange sites. This may explain the apparent rejuvenation of the soils' ability to sorb P which has come as a surprise to many researchers (Kao and Blanchar, 1973; Enfield and Ellis, 1983). In soils where Ca^{2+} predominates on the exchange sites, equilibrium with respect to P concentration can be achieved when the supply of Ca^{2+} becomes limiting. Such a situation may arise from the exchange reaction equilibrium whereby the potassium ion in the soil solution has attained a dynamic equilibrium with Ca^{2+} on the exchange sites. As long as the supply of calcium is not limiting, however, precipitation reaction will continue to remove P from soil solution albeit at a declining rate.

The CEC of the noncalcareous soil (Pipestone series) is about twice the CEC of the two calcareous soils (Table 1.1), however, no noticeable influence of CEC upon P diffusive transport was observed. This was not the case with the exchange resin in Experiment I where P retardation increased with an increase in CEC. Some of the probable reasons for this observation include the fact that the exchangeable Ca^{2+} of these soils are of the same order of magnitude, though a large difference exist in the exchange capacities of the three soils. For the mobility and immobilization of P in soils, therefore, the absolute magnitude of the CEC may not be as important as the proportion of calcium on the exchange sites. Also, the calcareous soils had a source of calcium other than the exchange sites which could have masked any influence of the Ca^{2+} from the exchange sites.

Acid-Extractable P

The acid extractable P, which was the portion of P extracted with 0.1 N HCl after the water extraction is a measure of the precipitated P in the soil column following the addition of KH_2PO_4 (Fig. 3.3). It should be pointed out that the partition of the total P into water

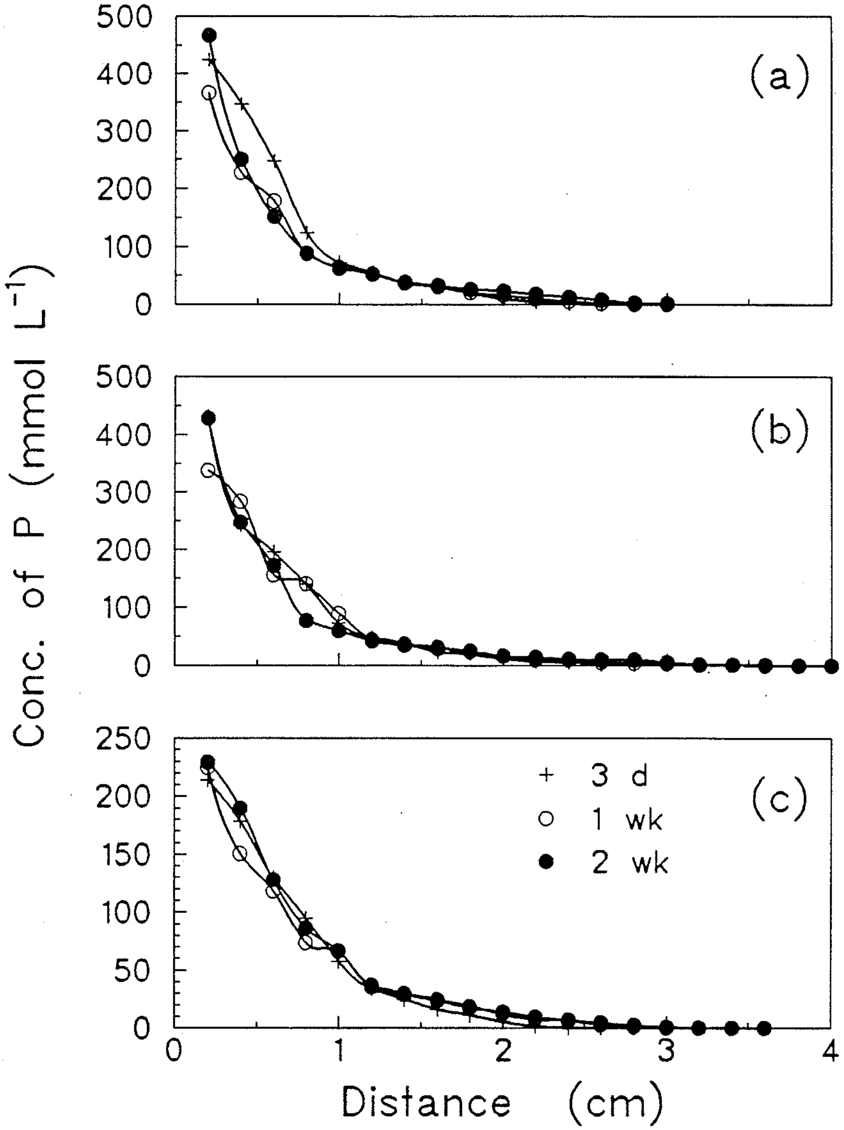

Figure 3.3 - The acid-extractable P in calcareous and noncalcareous soils following the surface application of KH_2PO_4; (a) Libau, (b) Graysville II and (c) Pipestone.

extractable and acid extractable P is an experimental convenience rather than a precise measurement of soil solution P and precipitated P. The data obtained were at best an approximation of this ideal values because of experimental limitations involved in measuring solution P and precipitated P. A detailed discussion of these limitations will be carried out in the next chapter.

In this experiment it was assumed that the acid-extractable P represented P precipitated as DCPD, rather than adsorbed P. The rationale for this assumption has been discussed earlier but probably is worth reiterating here for the soil system. The most important factor favouring P precipitation rather than sorption processes is the concentration range of P. The P concentration was in the range of mmol L^{-1} where it is generally agreed upon that precipitation process predominates (Sample et al., 1980). Also, the adsorption process is assumed to be a reversible process with a reduced P concentration leading to desorption. The precipitation reaction, on the other hand, is not governed by P concentration alone but also by the solubility product of the solid phase. As long as the ionic activity products of Ca and P in the soil solution exceeded the solubility product for DCPD, precipitation would continue regardless of whether or not the solution P concentration was declining. A sharp decline in the water-soluble P with time produced no corresponding decrease in solid phase P, rather, the trend was for acid P to increase slightly with time (Fig. 3.3).

In agreement with the lower levels of water P in calcareous soils than the noncalcareous soil, the acid-P in calcareous soils was higher than the noncalcareous soils. This was expected for the conservation of P mass since equal amounts of P was added to all soils. The higher magnitude of acid-P in the calcareous soils than in the noncalcareous soil was probably due to the higher amount of precipitated phosphate.

The precipitated P profile changed only slightly with time after 3 d of incubation. This suggests that the precipitation reaction was initially very rapid. This could have resulted from the high levels of P near the band and a high solution Ca displaced from exchange sites by a high K concentration at the early stages of incubation. Also, the hydrogen ion from the dissolution of the applied salt lead to the dissolution of $CaCO_3$ and the supply of calcium to drive phosphate precipitation reaction. Although precipitation continued after the third day of incubation, as indicated by the declining P profile, it was at a much reduced rate.

With DCPD as the precipitated phase, the supply of applied P to plants will be governed by the chemistry of DCPD in the soil. DCPD is a relatively soluble P source (Bell and Black, 1970 a and b; Strong and Racz, 1970). The conversion of the added P to DCPD has been shown to be very rapid in the soil. It is reasonable to assume that the short term need of plants will be met from this form rather than directly from the applied P salt in a Ca-saturated system. This will very likely be the case where some time span exists between fertilizer application and planting. Dicalcium phosphate dihydrate is metastable and undergoes reactions with the soil solution until apatite is formed (Lehr and Brown, 1958; Strong and Racz, 1970). The rate of this reaction is, however, very slow that within a growing season DCPD will likely be the dominant P phase present.

The magnitude of precipitated P obtained in the calcareous soils (Fig. 3.3) is very similar to the values shown in Figure 2.11b for the calcium carbonate-cation exchange resin system.

Ratio of Acid/Water-P

The ratio of acid-extractable to water-extractable P in the column at different incubation times is shown in Figure 3.4. The calcareous soils have a similar ratio of acid to water P in all portions of the soil column. This is expected, due to the similarities in their water and acid P discussed earlier. The ratio for Pipestone is much lower than that of the calcareous soils as a result of lower level of precipitated P and higher levels of water-P in this soil.

A common feature of this plot is that higher ratios were obtained close to the application site in all the soils. For the calcareous soils, the region with a high ratio extended from the top of the column to about 1 cm down the column. The ratio then gradually declined and remained virtually constant with depth. It is known that the highest water-P in any part of the column existed close to the top of the column. A high ratio of acid to water P in this region indicates that the precipitation reaction is very localized in the calcareous soils with most of it occurring within 1 cm from the application site. The increase in this ratio with time was due to an increase in the amount of P precipitated (though at decreasing rate) and a decline in water-extractable P with time. Both of these factors accentuated the ratio with time. It should be noted, also, that the effective time for the

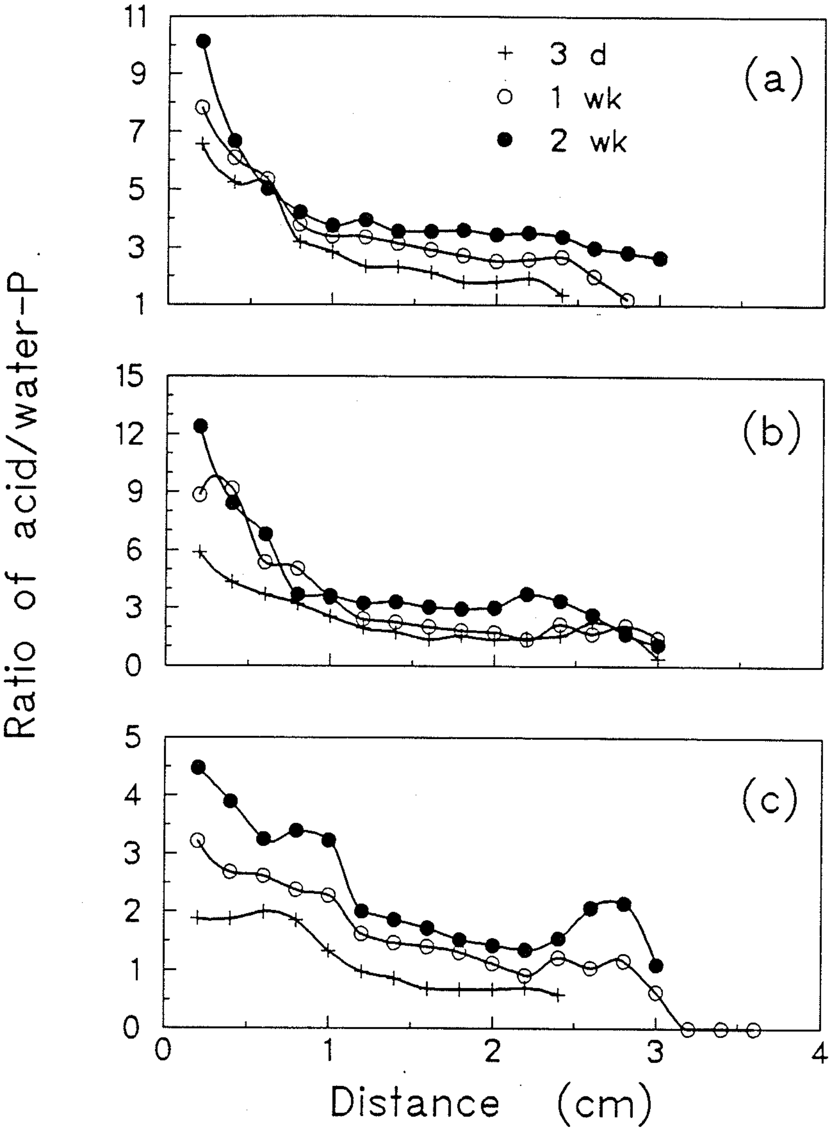

Figure 3.4 - The ratio of acid-extractable to water-extractable P in the soils following the surface application of KH_2PO_4; (a) Libau, (b) Graysville II and (c) Pipestone.

interaction of P and the soil at various distance was highest at the surface and declined with distance since P has to diffuse from the soil surface.

In the Pipestone soil, the picture is slightly different from what was observed in the calcareous soils as the precipitated P did not appear as localized. The plot for the pipestone soil had a gradual decline with distance away from the application site. Also, there appeared to be a deposition of $CaHPO_4$ at a distance 1 cm away from the application site. This trend appeared for all the incubation periods.

Water-Extractable K

The water-extractable K in the soil at any point in the column was higher than the water-extractable P in all the soils (Fig. 3.5). This indicated that the K front was ahead of P in the soil solution. The reverse was obtained in the resin column where K mobility was more retarded, as a result on ion exchange with Ca. In the soil, the relatively high "native" K on the exchange sites and in solution could have masked the retardation of the added K. Unlike exchange resin, ion exchange in the soil was not confined to K-Ca exchange. There is the possibility of K to K exchange which will manifest itself like a system without interaction, hence, no retardation of K.

The similarity that has been observed in the ionic distribution in both calcareous soils was also evident in K profile. The concentration of K in the Graysville II series was slightly higher than that in the Libau series (Table 1.1). With respect to the extent of K movement, there was no noticeable difference in all the soils.

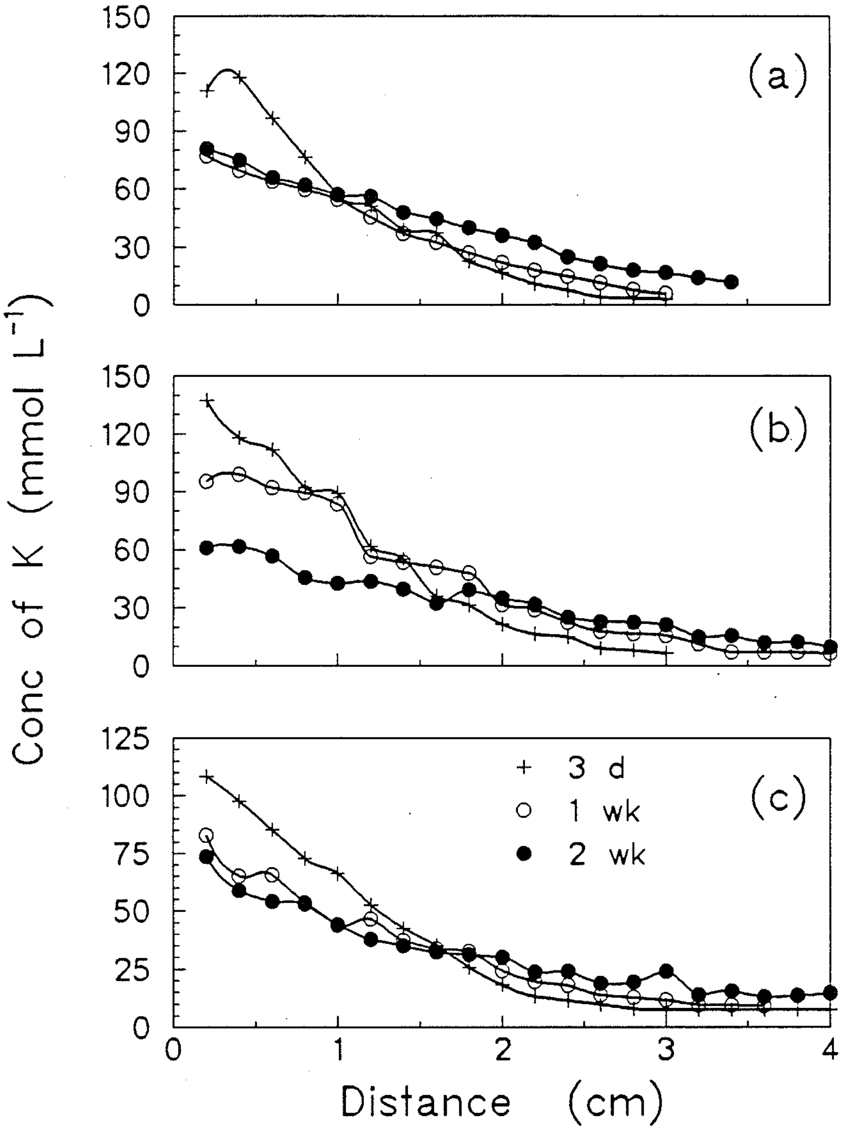

Figure 3.5 - The water-extractable K in calcareous and noncalcareous soils following the surface application of KH_2PO_4; (a) Libau, (b) Graysville and (c) Pipestone.

The profile of potassium obtained with time in these soils differed from that of P as a result of the different reactions the two ions participated in. Ion exchange is a rather fast process whereas precipitation reaction is a slow and continuous process. The loss of K from the solution with time, as indicated by the decline in the water extractable K, was due mainly to diffusion as opposed to an ion exchange reaction. This was deduced from the fact that a decline in water extractable potassium at the top of the column (1 - 1.5 cm) was followed by a rise below this depth. This was not the case with P. The features of K obtained in the soil system parallel those observed in the previous resin experiments.

Acid-Extractable K

The acid-extractable K was not measured because of the large pool of soil exchange K which will make the interpretation of the result quite difficult.

Water-Extractable Ca

The concentration of calcium extracted with water after the application of KH_2PO_4 to the soil surface is shown for all the 3 soils in Figure 3.6. The magnitude of solution calcium obtained in the soil columns was similar to that reported for the carbonated system in experiment III. Ca distribution in the columns packed with the Libau soil series, a calcareous soil, was similar to that obtained in the Pipestone soil a noncalcareous soil. The water-extractable calcium showed a wider variation along the column than any other ion measured.

This may be strictly due to experimental error, variability in the $CaCO_3$ content of sample etc. In the Libau soil series, the maximum concentration was obtained at the top of the column, and the amount then levelled off along the column. The high concentration of calcium near the site of application could be due to exchangeable Ca from ion exchange reaction, dissolution of $CaCO_3$ in calcareous soil or dissolution of freshly precipitated phosphate during the water extraction process. The level of calcium along the column appeared to rise with time. Because of the variability however, no conclusion could be drawn.

The snow plow effect of K-Ca exchange which was well demonstrated in the unbuffered resin experiment was not observed in the soil columns. Since large amount of precipitated P was found in the soil, it is reasonable to assume that this P was in association with Ca. The large consumption of Ca^{2+} as a result of a precipitation reaction with P prevented the build-up of solution Ca^{2+}. A similar result was obtained with the carbonate resin system.

Transport models that take ion exchange reaction into consideration predict Ca accumulation in the soil solution during the diffusion process (Cho, 1985). These models, however, did not account for Ca^{2+} ion disappearance from solution through precipitation reaction with P, as their main focus was cation exchange. The snow plow profile of Ca obtained in experiment I was a confirmation of such models. Such result was, however, fortuitously obtained as a result of the low P precipitation and a low pH in the unbuffered system. The Ca^{2+} profile obtained in experiments III and IV would be more realistic since in

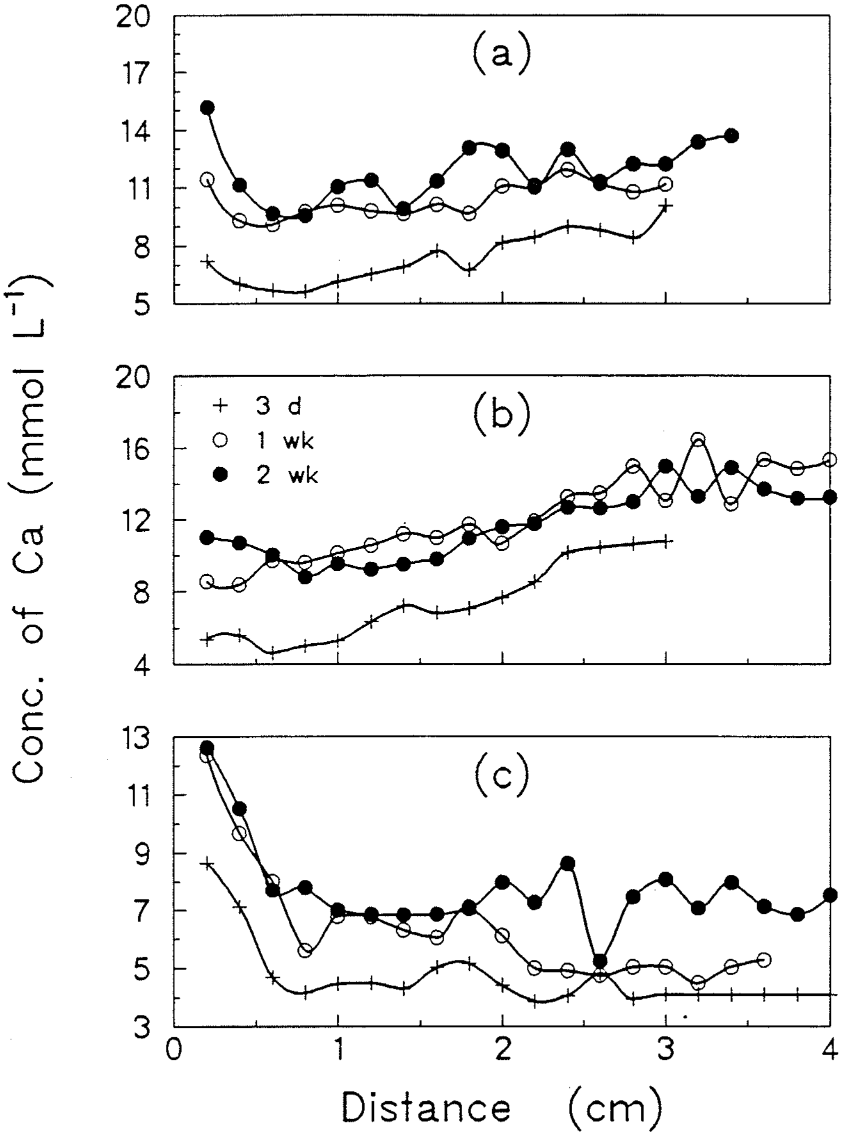

Figure 3.6 - The water-extractable Ca in calcareous and noncalcareous soils following the surface application of KH_2PO_4; (a) Libau, (b) Graysville II and (c) Pipestone.

the soil, the pH is reasonably well buffered and the consumption of calcium would occur.

The level of Ca^{2+} remaining in the soil solution when compared to the magnitude of Ca^{2+} associated with precipitated P leads one to conclude that virtually all the Ca^{2+} liberated from the exchange complex was precipitated by the available P. Also, when the amounts of solution Ca^{2+} is compared to the solution P along the soil column, it becomes obvious that the calcium concentration limits the rate of P precipitation after 3 d of incubation. The ability of the accompanying cation, K in this case, to replace Ca^{2+} will then play an important role in the rate of transformation of the added P to DCPD.

With the above results, the application of a salt such as KH_2PO_4 to a well buffered soil containing a large pool of exchangeable Ca^{2+} leads to a transformation of the added salt. The cation associated with the phosphate ion replaces some of the Ca^{2+} on the exchange sites and within a short period of time the applied P salt is quantitatively converted to less soluble form such as DCPD.

SUMMARY AND CONCLUSION

Many of the results obtained in pure resin system were observed for natural soil column indicating that such pure system could provide vital information on the complex soil system. The buffering capacity of the soil, as indicated by pH change resulting from P salt application, was closely related to the $CaCO_3$ content of the soil. The calcareous soil had a higher pH than the noncalcareous soil even where both soil had similar background pHs.

Higher level of precipitated P was obtained in calcareous soils than in noncalcareous soil suggesting the role of both exchangeable and nonexchangeable Ca^{2+} sources. Very rapid rate of P precipitation was obtained in all the soils as a result of high pH and a high supply of Ca^{2+} by the soils. The results show that the exchange reaction has an influence on the conversion of applied P to less soluble form via the supply of exchangeable Ca^{2+}.

By comparing the results obtained in the resin system to that of the soil system, it can be concluded that the same set of reactions gave rise to the distribution of ions obtained in both systems. Very likely, DCPD was the reaction product and the amounts formed were similar, especially in the calcium carbonate-resin system and the calcareous soils.

CHAPTER IV

Mathematical Model For Phosphate Transport In A Calcium-Saturated System

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INTRODUCTION

Many models have been formulated that attempt to analyze the transport of P in the soil. The dominant reaction of P taken into consideration by the existing models is adsorption which is accounted for by the use of equilibrium relationships, kinetic equations, or a combination thereof. The customary phosphate transport equation in an interaction medium is expressed by a single equation, in which the ionic phosphate is assumed to interact with a stationary solid surface.

The model to be presented shortly is one that takes a different approach to the description of phosphate diffusive transport, a multi-ionic approach. As much as possible the model takes into consideration all the ionic species that are present in the soil solution and account for their interaction. By so doing, any given ion does not move in isolation, rather, its transport and interaction affect other ions present in the solution. This results in the coupling of the transport equations for all the interacting species present in the soil solution. The solution to the resulting equations can only be obtained through numerical analysis and computer programming.

The model also takes into account the transport of hydrogen ion, production and consumption of the H^+ ion. This is a unique feature of the model to be presented. Quite often, hydrogen transport and mass balance is neglected because of its relatively low concentration in comparison to other ions in the system. For example, the pH of a Ca-saturated resin system with KH_2PO_4 added to the surface ranged from pH 4 to 7 which represent a concentration of 0.1 to 1 x 10^{-4} mmol L^{-1} of H^+ ion. This is numerically insignificant in comparison to other ionic species, and is the basis for the neglect. The hydrogen ion, however, plays an important role on P transport above and beyond that indicated by its intensity. This is due to the involvement of H^+ in many solution equilibria as already discussed in the resin experiment. The pH thus affects the rate of P precipitation by its influence on the ionic form of P present in the soil solution. Furthermore, the precipitation reaction also results in hydrogen ion production due to the consumption of the divalent phosphate ion and the resultant deprotonation of the monovalent phosphate ion [Equations 2.3 and 2.4). All these interactions were explicitly taken care of by the model.

After the mathematical model has been presented and its main equations described, a test of the model will be carried out. This test will take the form of a comparison of the experimental results, already presented, with the output generated from the model.

MODEL FORMULATION

In this model, n equations representing n interacting ionic species in solution are required to completely describe the transport of phosphate in a multi-ionic environment. The model to be presented takes care of the cation accompanying phosphorus e.g. K in KH_2PO_4, which will be refereed to as cation A. The cation resident on the exchange sites e.g. Ca^{2+}, will be referred to as cation B. For a base saturated soil, the exchange sites is for the most part dominated by the Ca^{2+}. In acid soils where Al^{3+} and/or Fe^{3+} predominate, this model is also applicable. An equation is necessary for phosphate ions which though comprising of monovalent ($H_2PO_4^-$) and divalent ($HPO_4^=$) ions will be regarded as a single species in the model. Speciation of phosphate ions is possible if the pH of the system is known. Another anionic species taken into consideration is carbonate ($HCO_3^- + CO_3^=$) which may be present in calcareous soil and may be formed as a result of CO_2 dissolution and calcium build-up in the soil solution. The fifth and last equation represents the transport of hydrogen ion.

The general form of the proposed transport equations are:

$$\begin{aligned}
\partial A/\partial t &= D\ \partial^2 A/\partial x^2 - \partial S_A/\partial t \\
\partial B/\partial t &= D\ \partial^2 B/\partial x^2 - \partial S_B/\partial t - \partial S_{BC}/\partial t - \partial S_{Bq}/\partial t \\
\partial C/\partial t &= D\ \partial^2 C/\partial x^2 - \partial S_C/\partial t - \partial S_{BC}/\partial t \\
\partial q/\partial t &= D\ \partial^2 q/\partial x^2 + \partial S_q/\partial t - \partial S_{Bq}/\partial t \\
\partial H/\partial t &= D\ \partial^2 H/\partial x^2 + \Phi H_1 + \Phi H_2 + \Phi H_3 .
\end{aligned} \tag*{[4.1]}$$

Where A stands for the applied cation, K, concentration. In this model, potassium is involved in diffusion from the point of application and ion exchange interaction with exchangeable calcium. Of course, it is possible to have more interaction terms for K, for example, in soils with high potassium fixing capacity. This can be taken care of if an equation representing the interaction can be formulated. No such K interaction was considered in this model. S_A stands for the concentration of potassium in the exchangeable form.

B stands for calcium concentration which is involved in diffusion, ion exchange with solution K, precipitation reaction with solution phosphorus and reaction with $CO_3^=$ to form $CaCO_3$. Hence, in the soil solution there is a competition between phosphate and carbonate ions for Ca^{2+}. The formulated model can also be applied to situations where more than one salt was applied e.g. sulphate banded with phosphate.

There will also be competition between the sulphate and phosphate ions for calcium. S_B stands for calcium on the exchange sites, S_{BC} and S_{Bq} represent precipitated $CaHPO_4$ and $CaCO_3$ concentrations respectively.

C stands for the phosphate ion concentration which can diffuse in the soil solution from the point of application. The phosphate ion can be precipitated as $CaHPO_4$ or can be adsorbed by the soil surface. Hence, this model also considers the classical phosphorus adsorption. An important extension of the classical transport model is the inclusion of a precipitation term for phosphorus. This will explicitly account for the influence of cation exchange reactions on P transport. Such treatment has never been attempted in the literature. In this model, the $CaCO_3$ surface was assumed to be responsible for P adsorption. This will be the predominant sorption surface in a calcareous soil. In other soils, such as those containing significant amount of Fe and Al oxides, sorption equations can be used without the specification of the sorption surface. Such treatment has already been carried out and discussed in Chapter 1. S_C represents the adsorbed phosphate (C) concentration.

q stands for carbonate concentration (e.g. in calcareous soil) and it may also represent sulphate when it is banded along with phosphate fertilizer. Carbonate is involved in diffusion, precipitation as $CaCO_3$ and formation from dissolved CO_2. This model does not consider the dissolution of $CaCO_3$ which may be important especially with an acidic fertilizer such as KH_2PO_4. This represents a limitation of the model, which can be corrected by incorporating carbonate equilibria into the model. This modification will however not be attempted in this discussion. Experimental results have shown that moderate amounts of P can be precipitated in the presence of $CaCO_3$ alone (experiment 2). The Ca^{2+} obviously came from $CaCO_3$ dissolution when free calcite was present. S_{Bq} represents the consumption of CO_3 through $CaCO_3$ precipitation while S_q represents the formation of CO_3 from CO_2 dissolution.

H stands for hydrogen ion concentration which is involved in diffusion from the fertilizer band where hydrogen producing fertilizer is applied. It is also produced and consumed by several reactions in the soil. ΦH_1, ΦH_2, ΦH_3 represent the production of proton from the precipitation of $CaHPO_4$, $CaCO_3$ and CO_2 dissolution, respectively. In equation [4.1] D stands for the diffusion coefficient of porous materials in $cm^2\ s^{-1}$, x stands for distance in cm and t for time in s.

The units of A, B and C are in mmol L^{-1} while those of S_A, S_B, S_C, S_{Bq}, S_q are also expressed in the solution concentration unit of mmol L^{-1} by multiplying the solid phase concentration (mmol g^{-1}) with the ratio of bulk density to volumetric moisture content (Cho, 1985).

Assumptions of the Model

Before discussing the various equations describing the interaction terms in equation [4.1], it is necessary to point out some of the underlying assumptions of this model. Some of these assumptions help in reducing the mathematical complexity of the resultant model.

Ion exchange process because of its rapid nature (Kim et al., 1983; Ogwada and Sparks, 1986) was assumed to be governed by local equilibrium with the equilibrium condition adequately described by a selectivity coefficient. Both the selectivity coefficient and the cation exchange capacity (CEC) were assumed constant during the transport process. The contribution of H^+ ion to ion exchange reaction was assumed to be negligible as a result of its low concentration relative to K^+ or Ca^{2+}. Precipitation of phosphate as $CaHPO_4$, and the carbonate as $CaCO_3$ were assumed to be described by a second order reaction equation with the residual concentration controlled by the solubility product of the solid phase. Local equilibrium assumption was also made for the adsorption of P onto carbonate surface since this is a surface reaction with fast rate. A Langmuir type adsorption isotherm was chosen to describe the sorption process.

Ion Exchange

In a system where the exchange complex is saturated with calcium, the ion exchange reaction with the surface applied KH_2PO_4 can be represented as:

$$2K^+ + CaR_2 \rightleftharpoons 2KR + Ca^{2+} \qquad [4.2]$$

This equilibrium can be represented by the conditional equilibrium constant or the selectivity coefficient.

$$k = BS^2{}_A/(A^2S_B) \qquad [4.3]$$

where k is the selectivity coefficient, $B = Ca^{2+}$, $A = K^+$, $S_B = Ca\text{-}R_2$, $S_A = K\text{-}R$

$$S_A = \surd((y^2 + 2Ry))-y \qquad [4.4]$$

In equation [4.4] $y = kA^2/4B$ and R which represents the cation exchange capacity (CEC) is expressed in $mmol_c\ L^{-1}$, so that $S_A + 2S_B = R$

The interaction term $\partial S_A/\partial t$ in equation [4.1] can be obtained by differentiating equation [4.4] with respect to time. S_A from equation [4.4] can be substituted into equation [4.3) to obtain S_B, from which $\partial S_B/\partial t$ can be derived. A similar relationship was used by Cho (1985).

P Adsorption Term

The classical Langmuir adsorption isotherm was chosen to describe the adsorption of P onto calcium carbonate particles. The equation is given by:

$$S_C = K_r R_r C/(1 + K_r C) \qquad [4.5]$$

where K_r is the "affinity factor" and R_r is the adsorption maximum. Differentiating equation [4.5] with respect to time yields

$$\partial S_C/\partial t = K_r R_r/(1 + K_r C)^2 \ \partial C/\partial t \qquad [4.6]$$

which was then incorporated into equation [4.1].

Because $CaCO_3$ was assumed to be responsible for sorption, the Ca^{2+} on the calcite surface will probably determine the maximum P sorption capacity. Ca was assumed to be responsible for phosphate sorption as the studies of Amer et al. (1985) and Griffin and Jurinak (1974) indicated. In this model, the value for R_r will be chosen to be 1 % $CaCO_3$ content and expressed in solution concentration unit.

Of course, to use this model for any soil with P sorption capacity, one need not specify the surface responsible for sorption. All that is needed is the P sorption parameters for that particular soil as derived in a P sorption study. These parameters can be used as input into the model to take care of P sorption by the soil.

Precipitation Reaction For P and CO_3 (SO_4)

The precipitation reaction represented by $\partial S_{BC}/\partial t$ and $\partial S_{Bq}/\partial t$ in equation [4.1] corresponds to the rate of formation of $CaHPO_4$ and $CaCO_3$ respectively. A second order reaction was chosen to describe the rate of precipitation which depends on the concentration of Ca, P and CO_3 in the solution. In the model, the concentrations of $HPO_4^=$ and $CO_3^=$ are the driving force for precipitation of $CaHPO_4$ and $CaCO_3$ respectively and not the total quantity of phosphate or carbonate. However, quantities that are measurable are C, the sum of $H_2PO_4^-$ and $HPO_4^=$, and q is the sum of HCO_3^- and $CO_3^=$ within the pH range to be encountered in soil. There is thus a need to express the amount of divalent phosphate and carbonate ions in term of the measurable quantity C and q respectively. This was achieved by noting that the fraction of C existing as $HPO_4^=$ is a function of pH and expressing this explicitly as shown below

$$H_2PO_4^- \rightleftharpoons HPO_4^= + H^+$$

$$K_c = (HPO_4^=)(H)/(H_2PO_4^-)$$

$$H_2PO_4^= = K_c\ (H_2PO_4^-)/(H)$$

$$\text{Since } C = H_2PO_4^- + HPO_4^=$$

$$f_c = HPO_4^=/C = K_c/(K_c + [H]) \qquad [4.7]$$

where f_c is the fraction of C in the form of $HPO_4^=$ and K_c is the second dissociation constant of phosphoric acid.

Similarly:

$$f_q = CO_3^=/q = K_q/(K_q + [H]) \qquad [4.8]$$

Here, f_q is the fraction of q in the form of $CO_3^=$ and K_q is the second dissociation constant of carbonic acid.

The precipitation reaction is thus a function of pH as explicitly expressed in the rate equations. The lower the pH (high $[H^+]$), the lower is the rate of precipitation as a result of the low level of divalent ionic species during the precipitation reaction.

The rate expression is given by:

$$\partial S_{BC}/\partial t = r_c(HPO_4^{=})\ (B - B_{eq}) = r_c f_c C(B - B_{eq}) \qquad [4.9]$$

$$\partial S_{Bq}/\partial t = r_q\ (CO_3^{=})(B - B_{eq}) = r_q f_q q(B - B_{eq}) \qquad [4.10]$$

r_c and r_q in the above equations stand for the second order rate constants for the precipitation of $CaHPO_4$ and $CaCO_3$, respectively. B_{eq} is the equilibrium concentration of calcium which for this model is taken to be the background Ca content of the soil before the salt application or the water extractable Ca of the soil.

There is the dissolution of CO_2 from the atmosphere as a result of $CO_3^{=}$ consumption by the precipitation reaction which may reduce its concentration below that supported by atmospheric CO_2. The $CO_3^{=}$ formation is represented by:

$$dS_q/dt = r_a\ (q_{eq} - q) \qquad [4.11]$$

where r_a is the rate constant and q_{eq} is the carbonate concentration in equilibrium with CO_2 of the atmosphere.

H^+ Production Terms

The uniqueness of this model is the explicit form by which it expresses the role of H^+ ion concentration on P and $CO_3^{=}$ precipitation. The other side of the coin, however, is that precipitation reaction leads to the production of hydrogen which the model also uniquely takes account of. The production of H^+ from the precipitation reactions is a consequence of the consumption of the divalent phosphate and carbonate ions and the resultant effect on the equilibrium relation represented by the dissociation reactions shown below:

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^=$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^=$$

The rate of precipitation of P and $CO_3^=$ are expressed by equation [4.9] and [4.10] respectively. It should be noted that the rates of H^+ production represented as ΦH_1 and ΦH_2 in equation [4.13] are not equal to rate expressions of equations [4.9] and [4.10]. This is because the rate of precipitation is driven partly by the concentration of divalent phosphate and carbonate ions in the soil solution on one hand, while H^+ production rate is driven by the concentration of monovalent ion on the other hand as indicated by the above dissociation reaction. To take account of this fact, the rate of H^+ production is given by:

$$\Phi H_1 = (1 - f_c)\ dS_{BC}/dt \tag*{[4.12]}$$

$$\Phi H_2 = (1 - f_q)\ dS_{Bq}/dt \tag*{[4.13]}$$

where ΦH_1 and ΦH_2 stand for the rate of H^+ production due to $CaHPO_4$ and $CaCO_3$ precipitation, respectively. $(1 - f_c)$ and $(1 - f_q)$ are the fractions of C and q in the monovalent HPO_4^- and HCO_3^- respectively.

As a result of the buffering action of the soil, the H^+ ion produced does not stay in solution as H^+, rather, it combines with OH^- or other proton acceptors in the soil. An empirical relation shown below was adopted to account for the "buffering" phenomena.

$$\text{buff} = \exp(-2.0(\text{pH} - 6.0)) \tag*{[4.14]}$$

when equation [4.14] is multiplied by the rate of H^+ production represented by equations [4.12] and [4.13], an empirical net rate of H^+ production due to precipitation reactions in the soil is obtained.

$$\Phi H_1 = \text{buff}\ (1 - f_c)\ dS_{BC}/dt \qquad [4.15]$$

$$\Phi H_2 = \text{buff}\ (1 - f_c)\ dS_{Bq}/dt \qquad [4.16]$$

The model does account for the loss of the produced H^+ ion due to the soil buffering action by a reduction in the rate of hydrogen production. Equations [4.15] and [4.16] also reveal the pH dependent characteristic of H^+ production. When the soil pH is very low or very high, H^+ production is quite small or negligible. ΦH_3 which is the rate of H production resulting from CO_2 dissolution is related to the $CO_3^=$ formation dS_q/dt by the proportionality constant. For each ion of HCO_3^- produced from CO_2, one ion of H^+ is produced while $CO_3^=$ produced results in 2 ions of H produced. The combined effect is given by:

$$2f_q + (1 - f_q) = (1 + f_q)$$

such that:

$$\Phi H_3 = dS_q/dt\ (1 + f_q) \qquad [4.17]$$

where $(1 + f_q)$ is the proportionality constant between ΦH_3 and dS_q/dt

Relationships expressed by equations [4.2 - 4.17] were substituted into equation [4.1] to produce a set of transport equations that represent the model. The boundary and initial conditions simulating the situation where KH_2PO_4 was uniformly applied to a soil surface was chosen to be:

(1) $t <= t_{ch}$ and $x = 0$.

$A = A_o$, $B = B_o$, $C = C_o$, $q = q_o$ and $H = H_o$

(2) $t = 0$ and $0 < x < = L$

$A = A_i$, $B = B_i$, $C = C_i$ $q = q_i$ and $H = Hi$ [4.18]

(3) $t > t_{ch}$ and $x = 0$

no - flux for every ionic specie.

(4) $t >= 0$ and $x = L$

no - flux for every specie.

t in equation [4.18] stands for time, x stands for distance from the soil surface perpendicular to the surface, L = length of the soil column, suffix i stands for the initial ionic concentration before the application of the salt, suffix o represents concentration at the top resulting from the salt application, t_{ch} stands for the change-over time from constant boundary to no flux boundary conditions. Simply put, t_{ch} represents the time it takes the salt to totally dissolve or disappear from the soil surface. The choice of A_i and B_i was such that the exchange complex was saturated with B (Ca^{2+}).

An analytical solution cannot be obtained to the set of equations describing this model. Numerical method was used to approximate the equations, subject to boundary conditions [4.18] and adopting the Crank-Nicholson technique. Thomas algorithm was combined with iteration to solve for the five dependent variables at fixed time and position. Along with this, the distribution of $CaHPO_4$, $CaCO_3$, adsorbed P and exchangeable K were obtained.

Major Assumptions of Column Experiment

The basic assumptions made that allow comparison of experimental results to that from the model are stated below:

(1) Diffusion process was assumed to be solely responsible for ion transport, that is, no convection or mass flow. This assumption is necessary since the model takes into consideration only diffusion equations. In practice, conformity to this assumption was achieved by

incubating the soil column at field capacity after allowing enough time for moisture equilibration so that there was no net moisture movement in the soil column. Also, it was ensured that columns were not mechanically disturbed after the salt application. Moisture content measurement carried out after the desired incubation period showed very little variation along the column.

(2) Concentration of the soil solution in contact with the added salt was assumed equal to that predicted by the solubility product of the salt. That is, as long as the salt existed, a constant concentration equal to the K_{sp} is maintained in solution at the soil surface. This assumption is possible because of the soluble nature of the applied salt which ensures that the rate of dissolution is orders of magnitude higher than the rate of diffusion (Bouldin and Black, 1954).

(3) K applied along with the phosphate ion is assumed to take part in only ion exchange interaction with Ca^{2+}, that is, no precipitation, co-precipitation of K and P, or adsorption of K by the column constituents. For the resin column, this assumption holds, but may not hold for some soils. In such cases, a term describing the other forms of potassium interaction can be incorporated into the model.

Limitations of Experimental Measurements

Since the test of the formulated model involved a comparison of the model output and experimentally determined ionic profiles, a condition necessary for a valid comparison is that both techniques measure the same quantity. Not only must the unit of measurement be identical, but also the partitioning and measurement of the ionic profile in the solution and solid phases by the experimental techniques have to be such that it is comparable to the model output.

With respect to the model there is no problem, since the output is structured to give the actual solution composition in mmol L^{-1} and the solid phase profile can have an output in the same unit. The main problem, however, is to determine the ionic concentration in the soil solution that is in equilibrium with the various solid phases in the soil column experiment. Herein lies the limitation of experimental measurements. That is, how to accurately determine the solution concentration and solid phase concentration in the soil column at a fixed time and position without the introduction of artifacts that are not due to the transport phenomenon itself but rather are imposed by the sectioning and analytical method adopted?. In other words, it is extremely difficult, if not impossible, to determine the solution concentration, for example, of a soil incubated at field capacity.

This problem was clearly stated by Sposito (1986) in his definition of soil solution that: "from the point of view of chemical thermodynamics, the soil solution is a unique phase only if it can be isolated from soil and studied experimentally. The problem of isolating the true soil solution has not yet been solved, but several preferred methods of removing aqueous phases from bulk soils for laboratory study have been established as operational compromises between chemical accuracy and analytical convenience".

The usual technique of extracting sliced soil column with water and then acid, as adopted in this study, while expedient, no doubt, changes the chemistry such that the interpretation of "water-extractable" and "acid-extractable" as representing solution and solid phase distribution respectively has to be tempered with great caution.

For example, the resin column was incubated with the moisture content at field capacity. This corresponds to a moisture content of 14 - 15 % on oven dry basis. Water extraction involved the addition of 10 mL of water to 1 g of soil. This changes the solid to water ratio from 1 : 0.15 during diffusion to approximately 1:10 during water extraction, corresponding to a 66 times dilution. The concentration of the ionic species in solution during extraction is thus 66 times lower than what they were originally in the soil column. With freshly precipitated $CaHPO_4$ and $CaCO_3$ present, such dilution will no doubt lead to dissolution. The resultant effect of which is an over estimation of solution P concentration and an underestimation of the amount of P in the solid phase. The extent of departure from the original state in the column depends on the magnitude of dilution and the final P concentration after dilution. The higher the dilution factor the greater is the magnitude of error.

If the P concentration in the final solution is still very high, say above the K_{sp} of $CaHPO_4$, then it can be assumed that little or no dissolution will result. But even under this condition, the validity of such an assumption is questionable.

Dissolution of precipitated form is not the only problem associated with water extraction and dilution, the partitioning of cation into solution and exchangeable form is also affected by dilution. The principle of electroselectivity (Helfferich, 1962) stipulates that for monovalent-divalent (e.g. K^+-Ca^{2+}) ion exchange process, there is a natural tendency for the exchanger to prefer the divalent ion to the monovalent ion. For example, the lower the total ionic concentration the higher is the preference for Ca^{2+} over K^+ in the soil solution (Helfferich, 1962). Diluting a solution containing both K^+ and Ca^{2+} will as a consequence of electroselectivity cause a shift of ionic composition on the exchange sites such that more Ca^{2+} will reside on the complex while K^+ comes to the solution. This will occur even when the selectivity coefficient is assumed to be constant. From the view point of chemical analysis, the solution K and exchangeable Ca^{2+} will be overestimated while underestimating solution Ca and exchangeable K.

The above discussion, though not exhaustive, points out some of the problems encountered in the use of measured value to represent the actual value of a system. Some of these problems can be reduced by minimizing dilution or avoiding it totally, if at all possible. To overcome these limitations, the test of the model will not involve a comparison of water or acid compositions, rather, the two will be summed to give total ionic composition as a function of time and distance from the column surface. Since the mass balance already discussed (chapter 3) indicated that the analytical technique was good, summing up will overcome the problem of underestimation and overestimation resulting from partitioning into water and acid fractions.

Parameters Chosen For Calculation

The parameters to be used will depend on the soil column to be modelled. Data generated from experiment 1 were tested. For the columns containing no exchange resin (control column), only ionic diffusion took place with no interaction among ions in the system. This represents the simplest case.

Of all the parameters needed, two are unknown, - the diffusion coefficient (D) and the change over time from constant to no-flux boundary condition (t_{ch}). P diffusion coefficient in free water is 8.7 x 10^{-6} cm^2 s^{-1} (Wild, 1981). The value for the soil column should, however, be much lower than this because of the effects of moisture content, tortuosity, and bulk density on the diffusion coefficient. The model was calibrated by obtaining values of D and t_{ch} such that the 3 d experimental curve of P was fitted to that predicted from the model. These parameters were then used to test the data obtained after 1 wk and 2 wk of incubation in the control column.

The result of this calibration produced a diffusion coefficient of 0.0135 cm^2 hr^{-1} and change over time of 8.5 hours. The obtained D is about one-half of the D in free water and was considered reasonable.

Parameters for P diffusion in the sand columns are:

$D = 0.0315$ cm^2 hr^{-1} $t_{ch} = 8.5$ h R (CEC) = 0 $mmol_c$ L^{-1}

A_o (K^+) = 1700 mmol L^{-1} B_o (Ca^{2+}) = 0.001 mmol L^{-1}

C_o (P) = 1700 mmol L^{-1} pH_o = 4 for KH_2PO_4 (From Lindsay et al., 1962).

A_i = 0.001, B_i = 0.001 C_i = 0.001 mmol L^{-1} pH_i = 7.

All rate constants and selectivity coefficient were made zero since there was no ionic interaction in this system.

Results From The Model For The Control Column

The results obtained from the model (t = 72, 168 and 336 h) are shown in Figures 4.1 to 4.3 for phosphate, potassium and hydrogen ions, respectively. The 3 d plot is trivial since the experimental data were fitted to the model in order to obtain the needed parameters. Figures 4.2 and 4.3 showed a good fit between the experimental data and the output from the model for phosphorus and potassium. Both the maximum concentration and the maximum depth of ion penetration were well predicted by the model.

The fit between the predicted pH and the experimentally measured pH profiles was not as good as those obtained for P and K above. The discrepancy between the predicted and the measured pH is a reflection of the difficulty of accounting for proton in the soil solution. The acidity close to the surface of the soil column was generally over-predicted by the model with a resultant under-prediction down the column. This pattern suggest that the model did not totally account for all the pathways of proton loss in the system. When all the ions in solution are taken together, the model can be said to predict very adequately the ionic profiles in the soil column.

This good agreement was expected for two obvious reasons. Firstly, the control system represents a very simple system with no chemical interaction. Since ion diffusion was the only process controlling ionic distribution, complication due to chemical reactions was avoided. Secondly, the experimental technique and chemical analysis yielded good results with a small experimental error which

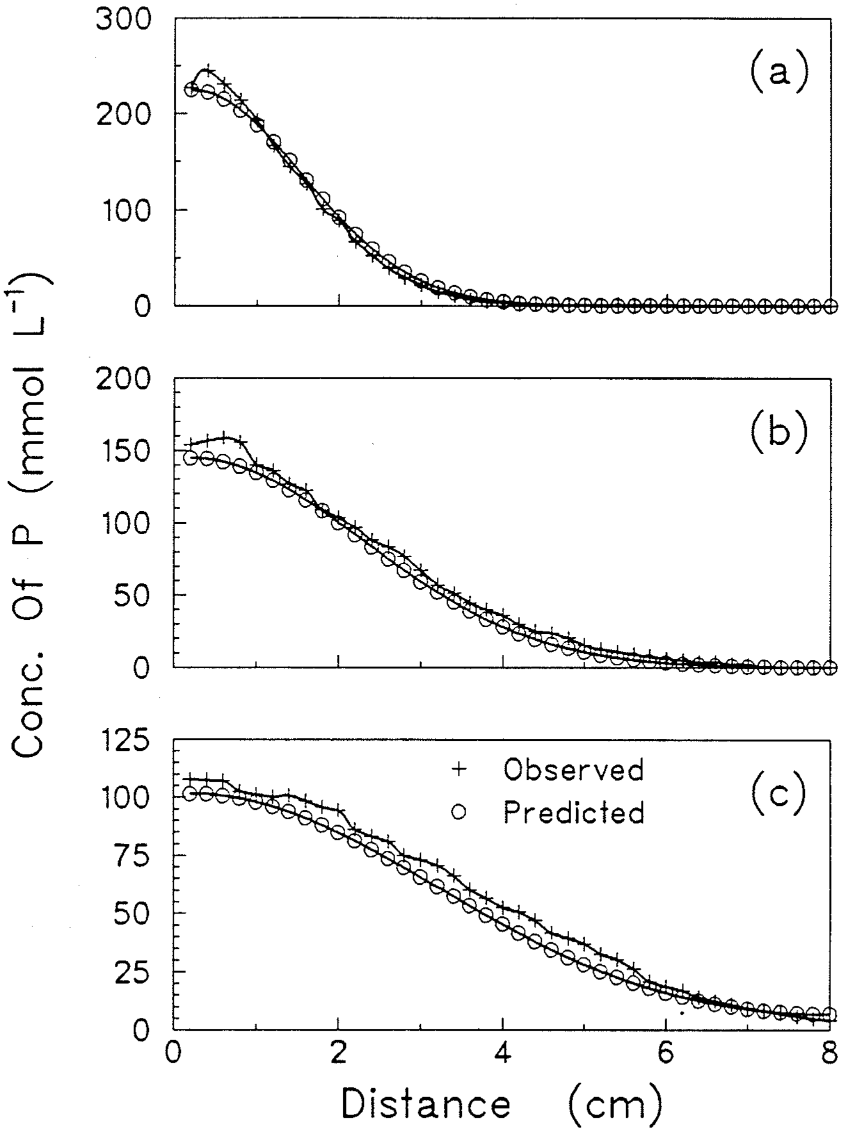

Figure 4.1 - Comparison between experimentally measured and predicted P profiles in sand column; (a) 3 days, (b) 1 week, and (c) 2 weeks.

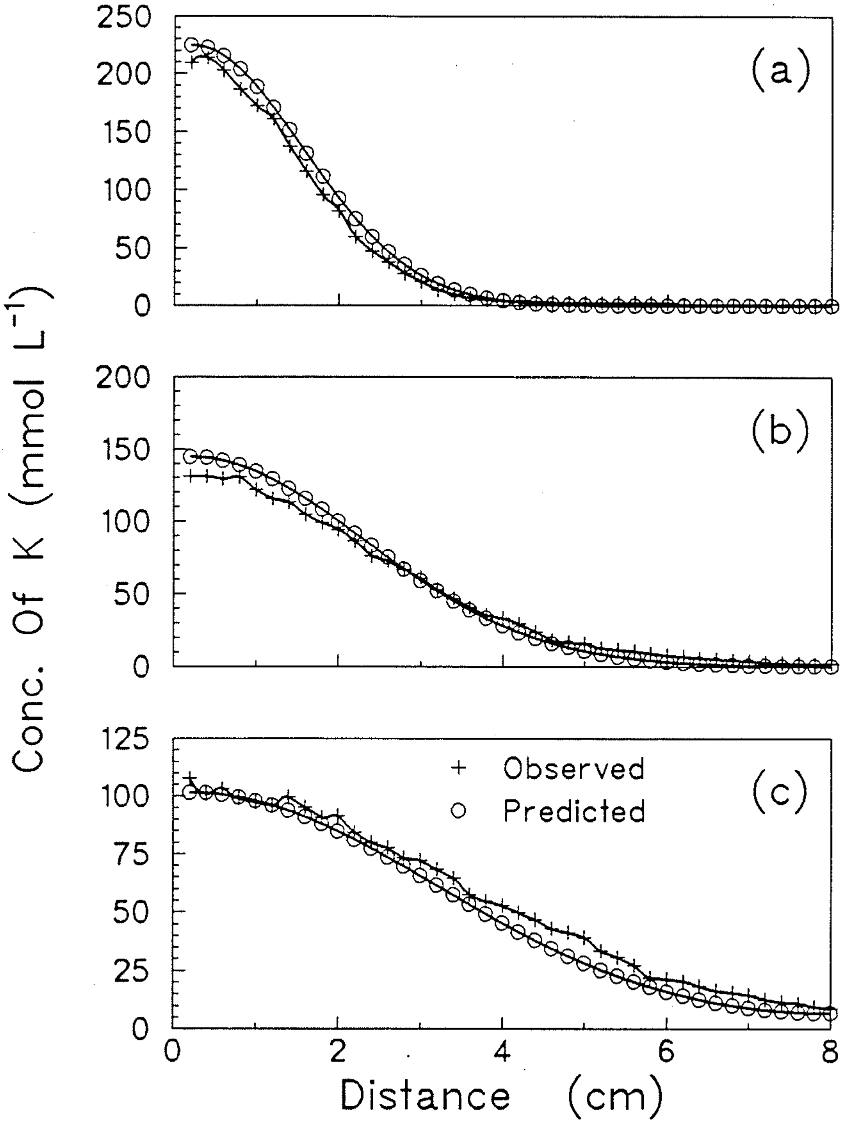

Figure 4.2 - Comparison between experimentally measured and predicted K profiles in sand column; (a) 3 days, (b) 1 week, and (c) 2 weeks.

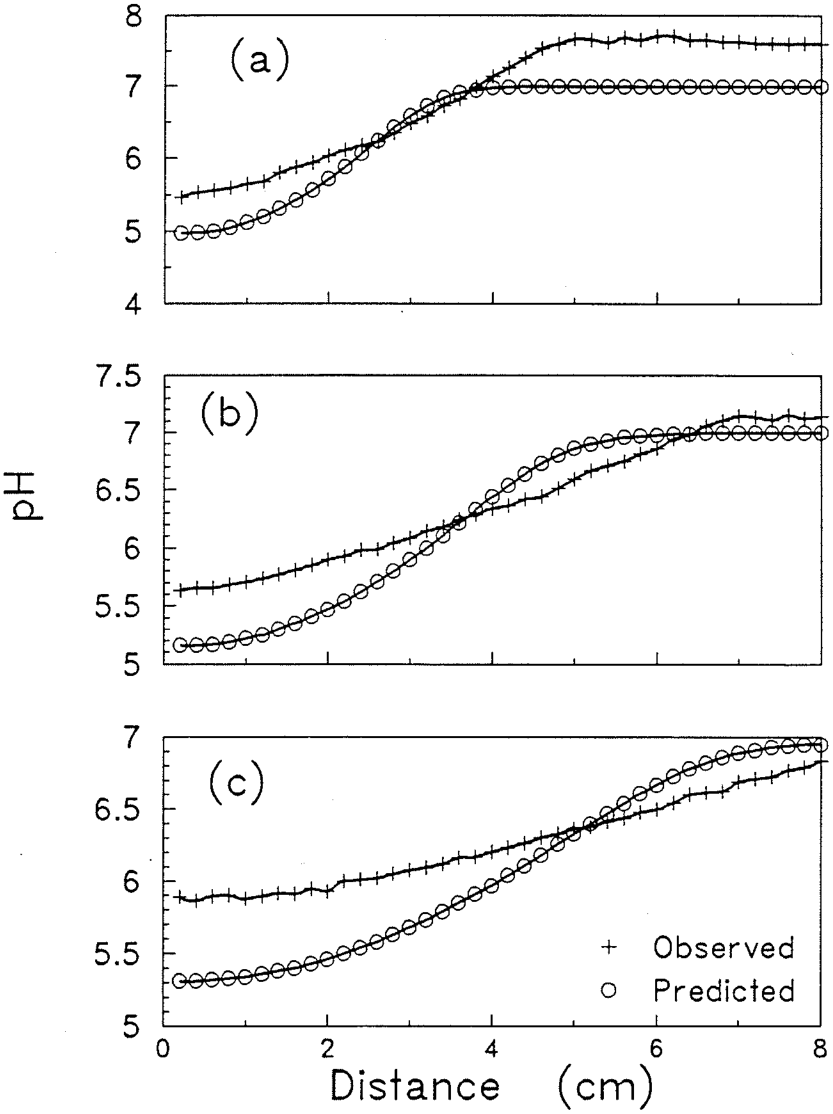

Figure 4.3 - Comparison between experimentally measured and predicted pH profiles in sand column; (a) 3 days, (b) 1 week, and (c) 2 weeks.

made comparison easier. The absence of any solid phase also removedthe problem associated with water or acid extraction already discussed.

Modelling of P Transport in Cation Exchange Resin System

The values of D and t_{ch} obtained from the control column were utilized for the columns containing Ca^{2+}-saturated exchange resin. This was possible since experimental treatments were identical in both cases. However, the values for the selectivity coefficient (K) of K-Ca exchange and the second order rate constant (K_s) for the precipitation of $CaHPO_4$ were not measured experimentally, but obtained using a technique similar to that utilized for obtaining D and t_{ch}. With the experimental data obtained after 3 d, in the column with a CEC of 21.5 $cmol_c\ kg^{-1}$, the values of K and K_s were obtained that gave the best fit between model output and experimental data.

The testing of the model was carried out by calculating output for the 1 wk and 2 wk incubation periods. Also, all the parameters obtained were used to test the data obtained in the columns with a CEC of 43 $cmol_c\ kg^{-1}$ for the 3 d, 1 wk, and 2 wk data. The curve fitting procedure described above yielded a selectivity coefficient value for K-Ca exchange and a second order rate constant for P precipitation of 1 and 0.01, respectively.

Parameters For Simulating Resin Column Data

$D = 0.0135\ cm^2\ h^{-1}$ $t_{ch} = 8.5\ h$

R (CEC) = 21.5 $cmol_c\ kg^{-1}$ = 1340 $mmol_c\ L^{-1}$ (15 % moisture content)

K = 1 Ks = 0.01

A_o (K^+) = 1700 mmol L^{-1} B_o (Ca^{2+}) = 0.001 mmol L^{-1}

C_o (P) = 1700 mmol L^{-1} pH_o = 4 for KH_2PO_4 (From Lindsay et al. 1962).

A_i = 0.001, B_i = 0.001 C_i = 0.001 mmol L^{-1} pH_i = 7.

For the column with a CEC of 43 $cmol_c$ kg^{-1},

R = 2680 $mmol_c$ L^{-1} (15 % moisture content) and other parameters remained the same as those stated above for the previous calculations.

Results From The Model

As mentioned earlier, except for Ca, the total ionic concentration of the species were compared. Water-extractable P and K were summed with the acid-extractable P and K, respectively, to obtain the total P and the total K in each section of the soil column. In a similar manner, precipitated P and solution P from the model output were summed up so were the predicted solution K and exchangeable K. The summation process was possible because these quantities were expressed in same unit of mmol L^{-1}.

The experimental results, presented in a different fashion in chapter 2, were plotted alongside the output from the model in Figures 4.4 to 4.7. Only the model output for the soil column with a CEC of 43 $cmol_c$ kg^{-1} represents, in a strict sense, the test of the model. For in this case, the column parameters and the experimental data were independent. As such, only these results will be discussed in detail. The results obtained for column with a CEC of 21.5 $cmol_c$ kg^{-1} is presented in Appendix C and the general features are similar to the results to be discussed.

A plot of the total phosphate concentration in the column is shown in Figure 4.4 for 3 d, 1 wk, and 2 wk of incubation. The phosphate profile predicted from the model compared well with the experimental result over distance and time. A divergence in the P concentration between the model output and the experimental results was apparent especially at distances close to the top of the column. The model under-predicted the P levels in the first 1 cm section of the column which translated to an increase in the depth of penetration of P from the model than was obtained from the experiment.

Various reasons might be responsible for this observation, chief among which was the lack of uniformity of P precipitation along the soil column in the column experiment. From the resin experiment, it was observed that P precipitation appeared limited to the top 2 mm section of the column. This discontinuity was apparently not due to the partitioning into water/acid extractable as indicated by the sharp rise in the total P level, when the two fractions (water and acid) were summed up. If the discontinuity was an artifact of the extraction technique, then the summation of the water and acid P should get rid of this anomaly. The fact that it persisted indicated that it is a reflection of the column condition. The model on the other hand assumed a uniform precipitation of P along the entire column, as such there is bound to be a discrepancy of the nature reflected in Figure 4.4. Also, the rate of precipitation of P obtained for the model might be lower than the actual experimental rate, this would also manifest itself in this manner. With increased time however, the experimental and predicted P profile converged except for the first experimental data point representing the zone of localised P precipitation.

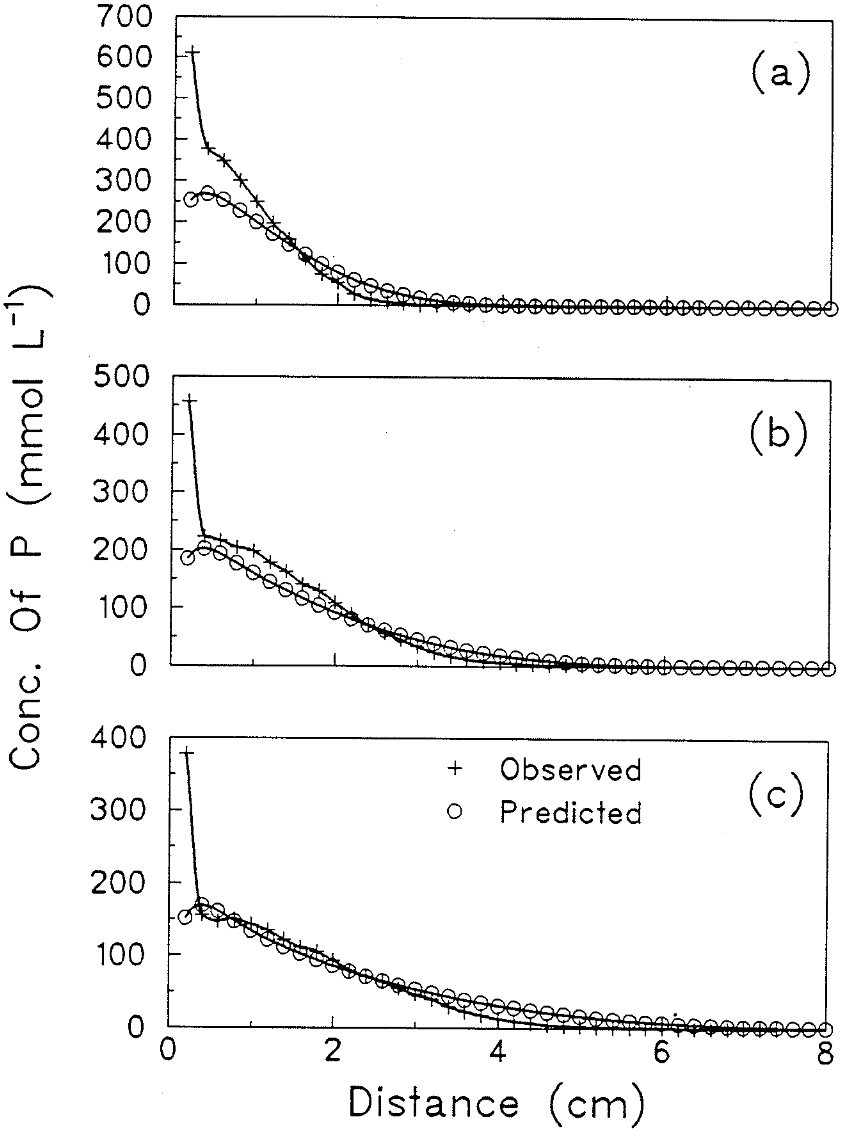

Figure 4.4 - Comparison between experimentally measured and predicted P profiles in resin-sand column; (a) 3 days, (b) 1 week, and (c) 2 weeks.

Figure 4.5 shows the solution Ca^{2+} obtained from the experiment and the model. The "snow plow" effect of exchangeable Ca^{2+} previously discussed was very well predicted by the formulated model. Very good agreement was obtained for the 3 d calcium profile, any discrepancy can be attributed to experimental error. For the 1 wk and 2 wk solution Ca, the agreement between the model and experimental was not as good. The model in general under-predicted the calcium level in solution, but the general feature of Ca^{2+} profile was displayed by the model. The discrepancy existing in the Ca profile is indirectly related to the P profile already discussed. The P profile was used to standardize the model and obtain the necessary parameters such as the rate constant. Standardization resulted in a high rate of P precipitation which consumed solution Ca^{2+} in the model and this with time is reflected by a lower Ca level predicted by the model. There is also the possibility of $CaHPO_4$ dissolution during extraction leading to an overestimation of solution Ca^{2+}. These problems will likely increase in magnitude with time as reflected by the plots.

A good relationship between the predicted K profile and the experimentally measured K profile were observed after 3 d. This is an indication that the value of the selectivity coefficient used in the model is reasonable. After 3 d, however, substantial divergence occurred in the two K profiles, with the model over-predicting the levels of K in the soil column. The discrepancy here, is suspected to be due to experimental error especially with the acid-extractable K. It appeared as if the extraction of K by the acid was incomplete. Since the area under the curves have to be same for K with time, it is

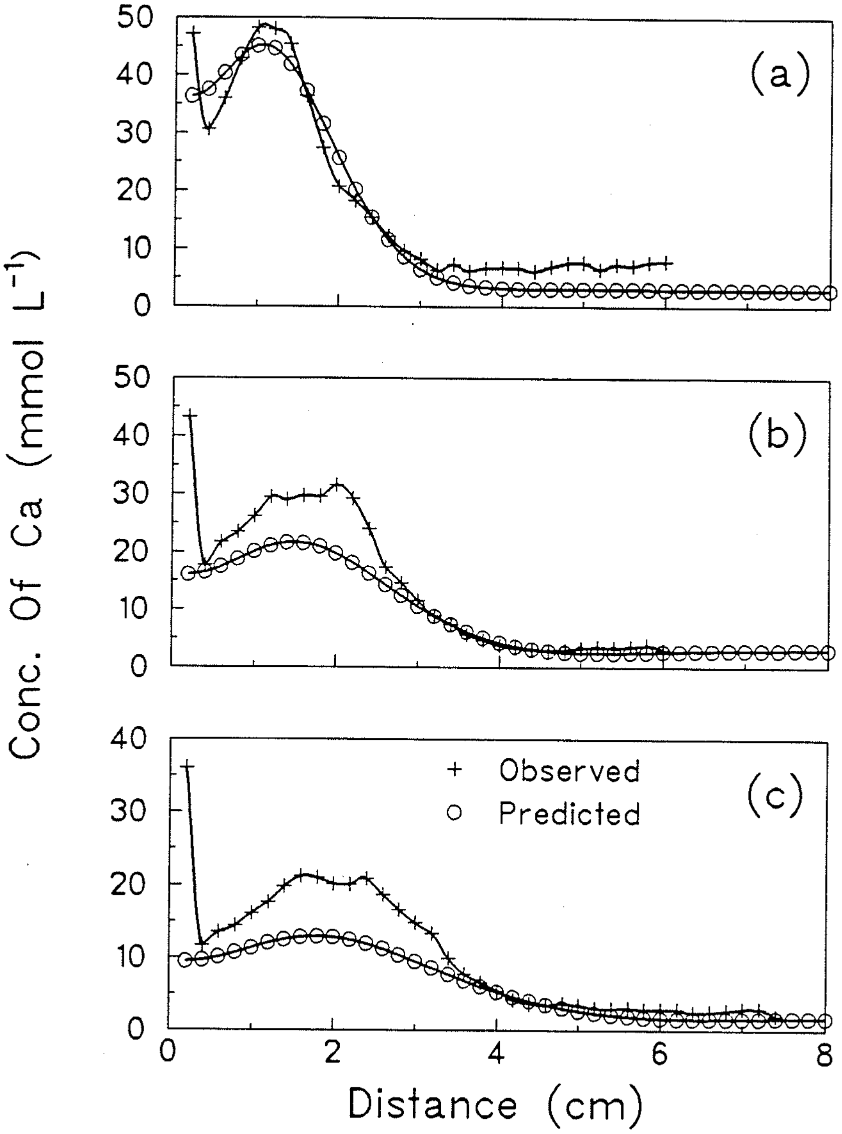

Figure 4.5 - Comparison between experimentally measured and predicted Ca profiles in resin-sand column; (a) 3 days, (b) 1 week, and (c) 2 weeks.

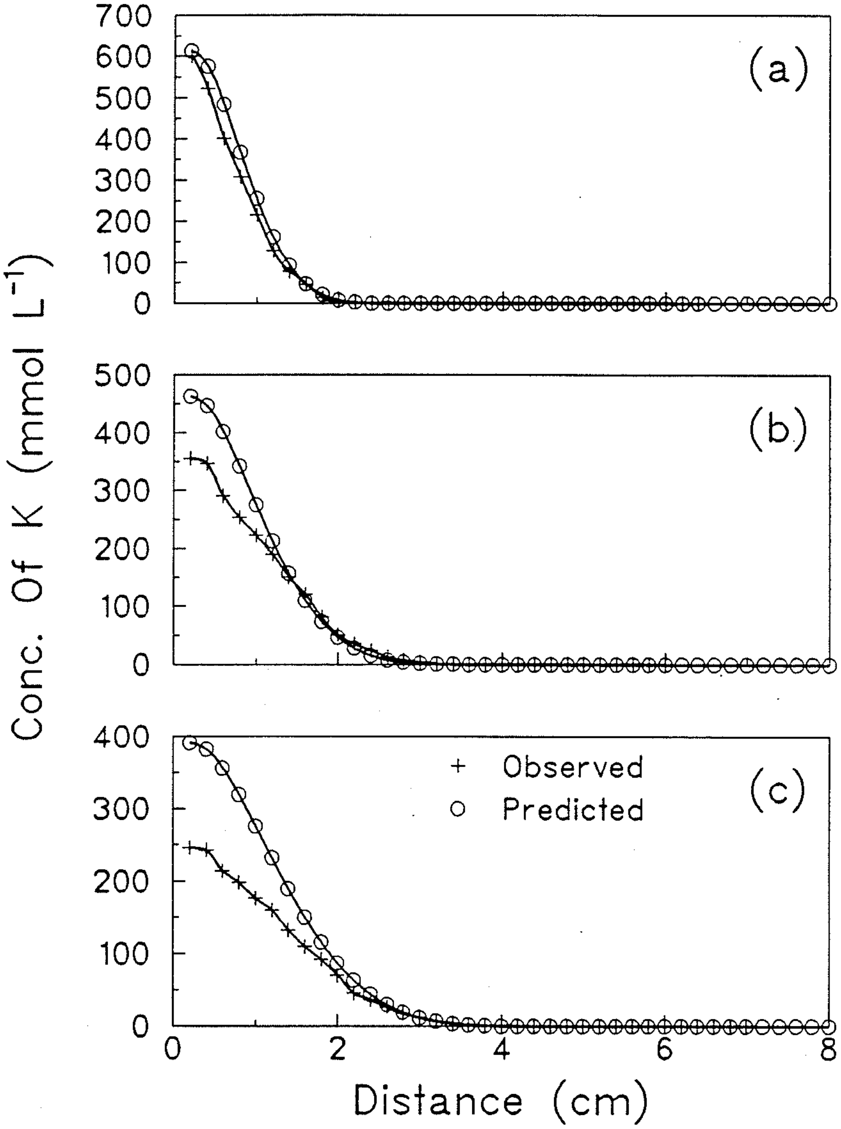

Figure 4.6 - Comparison between experimentally measured and predicted K profiles in resin-sand column; (a) 3 days, (b) 1 week, and (c) 2 weeks.

impossible to obtain an equal level of K from both the experimental data and the model after 3 d, only for the amount of K from the model to be higher with time. Either mass has been created (by the model) or loss in the experimental system. If we assumed that the model did not create mass, then the experimental technique was in error. Successive leaching of resin by the acid would have ensured completed extraction of K as opposed to a batch-type of extraction.

The pH profile is shown in Figure 4.7 for both the experimental results and the model output. The agreement between the model and the experimental results appears better than that obtained for the control column. The model, in this case, under-predicted the hydrogen ion concentration in the first 2 cm section of the profile while over-predicting H^+ concentration below this depth. The extent of H^+ ion penetration however seems to be well predicted by the model.

Because the model did not take into consideration the dissolution of $CaCO_3$ contained in the soil, and it has already been shown that substantial precipitation of $CaHPO_4$ can occur in carbonated system, the model was not be used to simulate the data obtained from carbonated resin system and the soils.

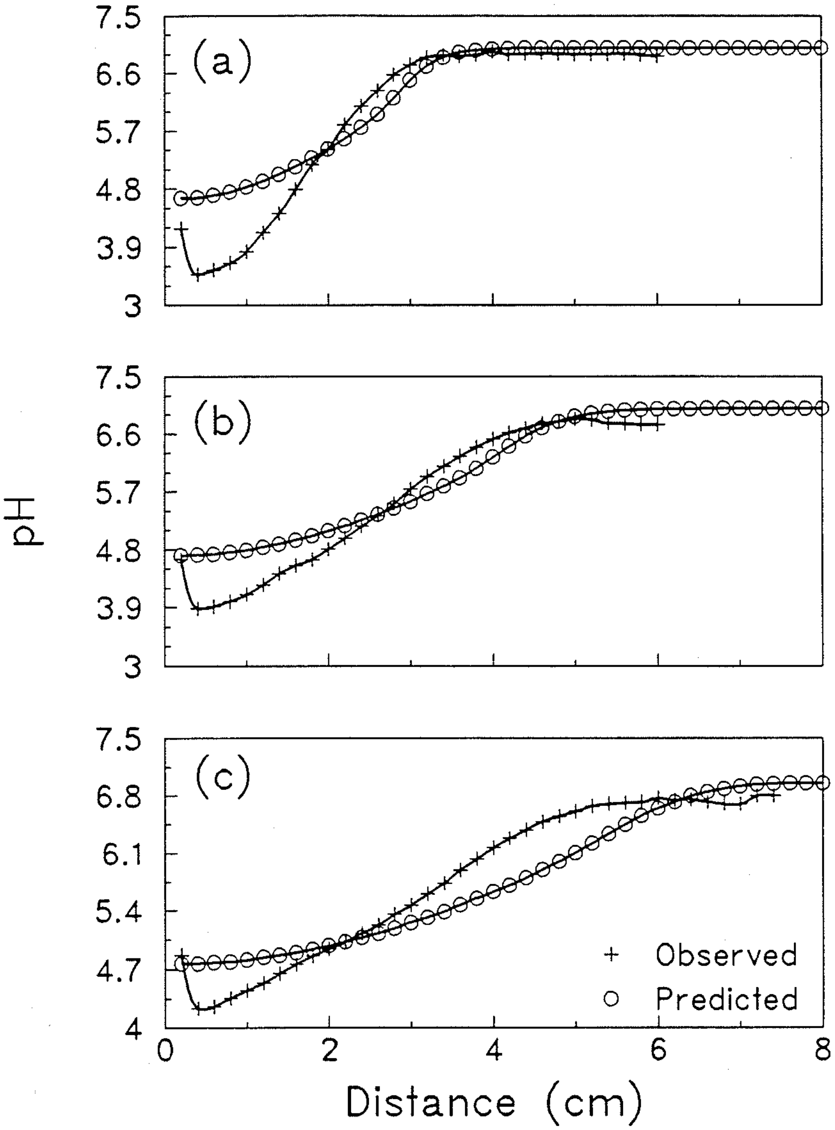

Figure 4.7 - Comparison between experimentally measured and predicted pH profiles in resin-sand column; (a) 3 days, (b) 1 week, and (c) 2 weeks.

SUMMARY AND CONCLUSION

The test of the model carried out so far suggested that the model is rigorous enough for modelling multi-ionic system. In general, the ionic profiles predicted by the model compared well with the profiles generated from column experiments. The model has to be modified in order to be applicable to calcareous soils. By obtaining soil parameters like the rate constant and the selectivity coefficient independently, better simulation of experimental results is expected.

The simulation of experimental results by the formulated model implied that the reactions included in the model were probably the important ones controlling P distribution following the application of a P salt.

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Appendix A

The Transport equation without the advective term is given by

$$\partial C/\partial t = D\partial^2 C/\partial x^2 - \rho/\theta\ \partial S/\partial t \qquad [A.1]$$

where C is the solution P, S is the adsorbed P, T is the time, x is the distance in the direction of diffusion, ρ is the bulk density and θ is the volumetric moisture content. D is the diffusion coefficient.

Using the Freundlich isotherm to describe P sorption with the local equilibrium assumption we have

$$S = aC^n \qquad [A.2]$$

$$\partial S/\partial t = \partial S/\partial C.\partial C/\partial t \qquad [A.3]$$

$$\partial S/\partial C = anC^{n-1} = K_1 \qquad [A.4]$$

Therefore,

$$\partial S/\partial t = \partial C/\partial t.anC^{n-1} = \partial C/\partial t.K_1 \qquad [A.5]$$

For the Langmuir isotherm

$$\partial S/\partial C = K_2 = Kb/\ (1 + KC)^2 \qquad [A.6]$$

For Cubic Polynomial

$$\partial S/\partial C = K_3 = b + 2gC + 3DC^2 \qquad [A.7]$$

For Gunary

$$\partial C/\partial t = K_4 = \frac{(A + D\ \sqrt{C}/2)}{(BC + A + D\sqrt{C})^2} \qquad [A.8]$$

Taking the Freundlich isotherm as an example, equation [A.5] is substituted into equation [A.1] to produce:

$$\partial C/\partial t = D\partial^2 C/\partial x^2 - \rho/\theta\ \partial C/\partial t\ .\ K_1 \qquad [A.9]$$

where $K_1 = anC^{n-1}$

rearranging equation [A.9] will produce:

$$\partial C/\partial t\ (1 + K_1\ \rho/\theta) = D\partial^2 C/\partial x^2 \qquad [A.10]$$

Equation [A.10] can be written in the difference form using the Crank Nicholson approximation as:

$$(C_i^{j+1} - C_i^j)\ [1 + K_1\ \rho/\theta] =$$

$$D\Delta t/2(\Delta x)^2\{C_{i-1}^{j+1} - 2C_i^{j+1} + C_{i+1}^{j+1} + C_{i-1}^j - 2C_i^j + C_{i+1}^j\} \qquad [A.11]$$

where the superscript j represents time and the subscript i represents the distance.

let $2(\Delta x)^2/(D\Delta T) = q$

and multiply both sides of equation [A.11] by q we have

$$(C_i^{j+1} - C_i^j)\ [1 + k\ p/\theta]q = \{\ldots\ldots.\} \qquad [A.12]$$

Collecting all terms with the superscript j + 1 to one side and terms with the superscript j to the other gives:

$$C_{i-1}^{j+1} - [2+q+qk\rho/\theta]\ C_i^{j+1} + C_{i+1}^{j+1} = -C_{i-1}^j + (2-q-kq\rho/\theta]\ C_i^j - C_{i+1}^j \qquad [A.13]$$

By letting i run from 1 to n (where n is the number of subdivisions of the distance) equation A.13 gives a system of tridiagonal algebraic equations which can be solved using the Thomas algorithm. Similarly, k_2, k_3 and k_4 can each be substituted into equation [A.1] to obtain the calculated profiles of P when these isotherms has been incoporated into the transport equation.

Appendix B

Phosphorus adsorption data with time in calcareous and noncalcareous soils

Libau Series

Time	†10		20		30		40	
(hr)	‡ADS	CONC	ADS	CONC	ADS	CONC	ADS	CONC
0.0	0.0	10.0	0.0	20.0	0.0	30.0	0.0	40.0
0.5	42.2	5.8	65.7	13.4	97.3	20.3	110.0	29.0
1.0	46.1	5.4	75.8	12.4	107.7	19.2	126.3	27.4
2.0	50.1	5.0	88.7	11.1	114.5	18.6	135.8	26.4
4.0	52.5	4.8	95.0	10.5	121.5	17.9	144.0	25.6
6.0	53.5	4.7	99.6	10.0	127.0	17.3	149.0	25.1
12.0	61.7	3.8	102.0	9.8	137.4	16.3	162.1	23.8
18.0	62.9	3.7	110.2	9.0	154.7	14.5	173.0	22.7
24.0	63.8	3.6	111.7	8.8	147.0	15.3	179.2	22.1
48.0	69.4	3.1	119.3	8.1	159.0	14.1	193.4	20.7

Time	50.0		100.0		250.0		500.0	
(hr)	ADS	CONC	ADS	CONC	ADS	CONC	ADS	CONC
0.0	0.0	50.0	0.0	100.0	0.0	250.0	0.0	500.0
0.5	108.9	39.1	144.4	85.6	289.0	221.1	327.4	467.3
1.0	145.4	35.5	167.5	83.3	324.5	217.6	373.8	462.6
2.0	154.8	34.5	180.1	82.0	334.5	216.6	424.3	457.6
4.0	163.2	33.7	242.4	75.8	345.6	215.4	491.5	450.9
6.0	169.1	33.1	261.2	73.9	362.0	213.8	518.8	448.1
12.0	189.6	31.0	294.6	70.5	378.6	212.1	515.6	448.4
18.0	206.1	29.4	309.3	69.1	440.4	206.0	480.1	452.0
24.0	211.9	28.8	301.1	69.9	430.1	207.0	616.0	438.4
48.0	225.5	27.5	327.4	67.3	469.2	203.1	757.4	424.3

†Applied Phosphate concentration in μg P ml^{-1}

‡ADS stands for adsorbed P in μg P g^{-1} soil, while CONC stands for equilibrium P concentration in μg P ml^{-1}.

McCreary series

Time	10		20		30		40	
(hr)	ADS	CONC	ADS	CONC	ADS	CONC	ADS	CONC
0.0	0.0	10.0	0.0	20.0	0.0	30.0	0.0	40.0
0.5	24.0	7.6	47.3	15.3	71.2	22.9	86.3	31.4
1.0	31.8	6.8	56.9	14.3	78.8	22.1	103.4	29.7
2.0	34.6	6.5	64.4	13.6	85.0	21.5	119.8	28.0
4.0	38.3	6.2	71.4	12.9	93.3	20.7	129.7	27.0
6.0	40.6	5.9	80.3	12.0	109.3	19.1	136.7	26.3
12.0	44.6	5.5	84.1	11.6	114.5	18.6	144.6	25.5
18.0	46.4	5.4	93.1	10.7	133.0	16.7	160.3	24.0
24.0	46.5	5.4	94.3	10.6	127.5	17.3	167.3	23.3
48.0	51.5	4.9	101.2	9.9	149.2	15.1	180.4	22.0

Time	50.0		100.0		250.0		500.0	
(hr)	ADS	CONC	ADS	CONC	ADS	CONC	ADS	CONC
0.0	0.0	50.0	0.0	100.0	0.0	250.0	0.0	500.0
0.5	92.5	40.7	157.2	84.3	272.4	222.8	358.5	464.2
1.0	111.7	38.8	179.8	82.0	291.7	220.8	418.2	458.2
2.0	132.7	36.7	185.0	81.5	297.9	220.2	483.1	451.7
4.0	146.2	35.4	245.7	75.4	345.6	215.4	336.4	466.4
6.0	150.6	34.9	263.6	73.6	382.9	211.7	467.0	453.3
12.0	174.7	32.5	297.0	70.3	426.0	207.4	648.8	435.1
18.0	191.6	30.8	315.7	68.4	460.0	204.0	664.1	433.6
24.0	196.2	30.4	311.7	68.8	471.3	202.9	729.6	427.0
48.0	217.7	28.2	319.3	68.1	524.8	197.5	868.6	413.1

Portage Clay Loam

Time	10		20		30		40	
(hr)	ADS	CONC	ADS	CONC	ADS	CONC	ADS	CONC
0.0	0.0	10.0	0.0	20.0	0.0	30.0	0.0	40.0
0.5	23.9	7.6	42.2	15.8	62.5	23.8	77.3	32.3
1.0	30.0	7.0	51.0	14.9	70.3	23.0	91.1	30.9
2.0	31.3	6.9	61.5	13.9	81.7	21.8	101.0	29.9
4.0	35.6	6.4	66.2	13.4	89.0	21.1	109.6	29.0
6.0	36.9	6.3	70.7	12.9	93.4	20.7	113.7	28.6
12.0	40.0	6.0	73.3	12.7	99.2	20.1	115.3	28.5
18.0	42.9	5.7	80.0	12.0	107.1	19.3	121.9	27.8
24.0	43.2	5.7	82.4	11.8	102.4	19.8	134.2	26.6
48.0	46.5	5.4	86.3	11.4	124.5	17.6	140.6	25.9

Time	50		100		250		500	
(hr)	ADS	CONC	ADS	CONC	ADS	CONC	ADS	CONC
0.0	0.0	50.0	0.0	100.0	0.0	250.0	0.0	500.0
0.5	75.3	42.5	128.4	87.2	207.0	229.3	244.4	475.6
1.0	97.4	40.3	131.0	86.9	189.3	231.1	234.0	476.6
2.0	111.2	38.9	143.3	85.7	222.1	227.8	388.2	461.2
4.0	119.0	38.1	186.1	81.4	263.3	223.7	372.2	462.8
6.0	124.0	37.6	215.5	78.5	280.0	222.0	344.2	465.6
12.0	134.3	36.6	223.6	77.6	288.0	221.2	418.3	458.2
18.0	155.3	34.5	245.7	75.4	364.5	213.6	464.0	453.6
24.0	162.8	33.7	246.9	75.3	358.0	214.2	504.7	449.5
48.0	167.7	33.2	240.7	75.9	390.9	210.9	635.5	436.5

Pipestone

Time	10		20		30		40	
(hr)	ADS	CONC	ADS	CONC	ADS	CONC	ADS	CONC
0.0	0.0	10.0	0.0	20.0	0.0	30.0	0.0	40.0
0.5	4.0	9.6	20.3	18.0	34.4	26.6	46.7	35.3
1.0	5.1	9.5	23.2	17.7	32.5	26.8	49.0	35.1
2.0	5.1	9.5	29.0	17.1	41.1	25.9	60.6	33.9
4.0	6.7	9.3	32.0	16.8	46.7	25.3	63.8	33.6
6.0	9.5	9.1	33.0	16.7	48.8	25.1	69.6	33.0
12.0	13.6	8.6	35.3	16.5	45.0	25.5	72.9	32.7
18.0	13.9	8.6	37.0	16.3	55.7	24.4	74.1	32.6
24.0	12.7	8.7	41.3	15.9	50.8	24.9	78.6	32.1
48.0	17.5	8.3	44.2	15.6	74.4	22.6	87.2	31.3

Time	50		100		250		500	
(hr)	ADS	CONC	ADS	CONC	ADS	CONC	ADS	CONC
0.0	0.0	50.0	0.0	100.0	0.0	250.0	0.0	500.0
0.5	41.3	45.9	83.2	91.7	111.9	238.8	182.1	481.8
1.0	43.4	45.7	58.1	94.2	126.8	237.3	234.0	476.6
2.0	59.6	44.0	62.2	93.8	120.5	238.0	254.7	474.5
4.0	71.1	42.9	108.7	89.1	156.2	234.4	218.6	478.1
6.0	65.9	43.4	139.7	86.0	158.7	234.1	257.7	474.2
12.0	80.6	41.9	149.4	85.1	222.1	227.8	274.9	472.5
18.0	85.6	41.4	156.0	84.4	184.7	231.5	341.1	465.9
24.0	94.7	40.5	142.4	85.8	263.3	223.7	398.3	460.2
48.0	104.1	39.6	157.2	84.3	292.1	220.8	492.4	450.8

Noncalcareous Graysville I series

Time	10		20		30		40	
(hr)	ADS	CONC	ADS	CONC	ADS	CONC	ADS	CONC
0.0	0.0	10.0	0.0	20.0	0.0	30.0	0.0	40.0
0.5	0.3	10.0	8.2	19.2	11.0	28.9	15.2	38.5
1.0	0.9	9.9	7.9	19.2	12.2	28.8	19.9	38.0
2.0	0.1	10.0	13.3	18.7	14.7	28.5	21.3	37.9
4.0	2.1	9.8	16.3	18.4	25.2	27.5	23.0	37.7
6.0	2.6	9.7	15.0	18.5	23.6	27.6	27.0	37.3
12.0	3.2	9.7	18.5	18.2	22.3	27.8	33.4	36.7
18.0	4.7	9.5	19.6	18.0	28.0	27.2	37.4	36.3
24.0	2.9	9.7	21.0	17.9	26.8	27.3	34.8	36.5
48.0	6.7	9.3	22.8	17.7	38.7	26.1	44.8	35.5

Time	50		100		250		500	
(hr)	ADS	CONC	ADS	CONC	ADS	CONC	ADS	CONC
0.0	0.0	50.0	0.0	100.0	0.0	250.0	0.0	500.0
0.5	9.8	49.0	17.5	98.3	9.6	249.0	88.7	491.1
1.0	14.3	48.6	9.9	99.0	0.0	250.0	109.5	489.1
2.0	19.1	48.1	9.9	99.0	22.6	247.7	119.8	488.0
4.0	29.0	47.1	40.2	96.0	30.6	246.9	98.9	490.1
6.0	36.4	46.4	59.8	94.0	20.1	248.0	78.9	492.1
12.0	43.9	45.6	69.5	93.1	28.6	247.1	65.0	493.5
18.0	48.4	45.2	74.4	92.6	37.7	246.2	125.0	487.5
24.0	48.0	45.2	84.9	91.5	129.5	237.1	169.4	483.1
48.0	54.2	44.6	91.7	90.8	197.4	230.3	259.2	474.1

Appendix C

Model output for the column with a CEC of 21.5 $cmol_c\ kg^{-1}$.

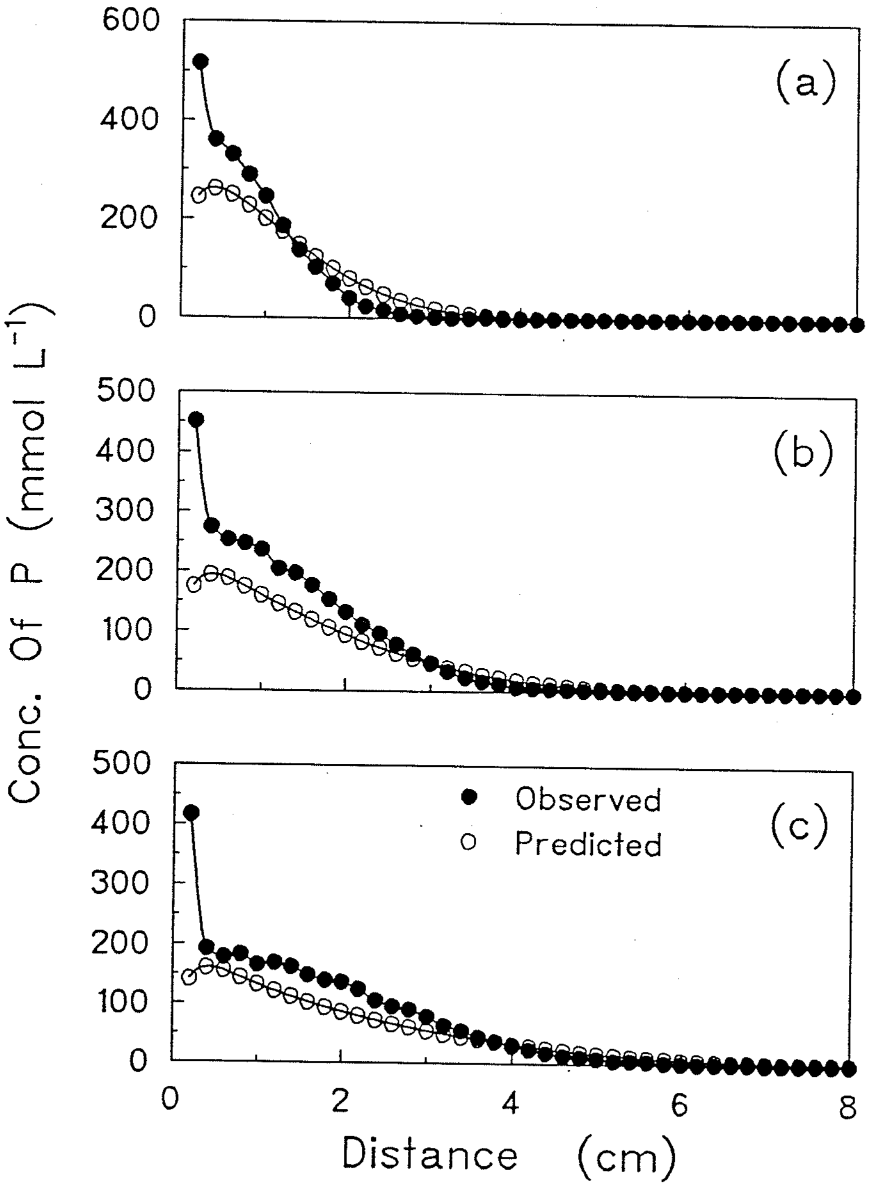

Figure C.1 - Comparison between experimentally measured and predicted P profiles in resin-sand column; (a) 3 days, (b) 1 week, and (c) 2 weeks.

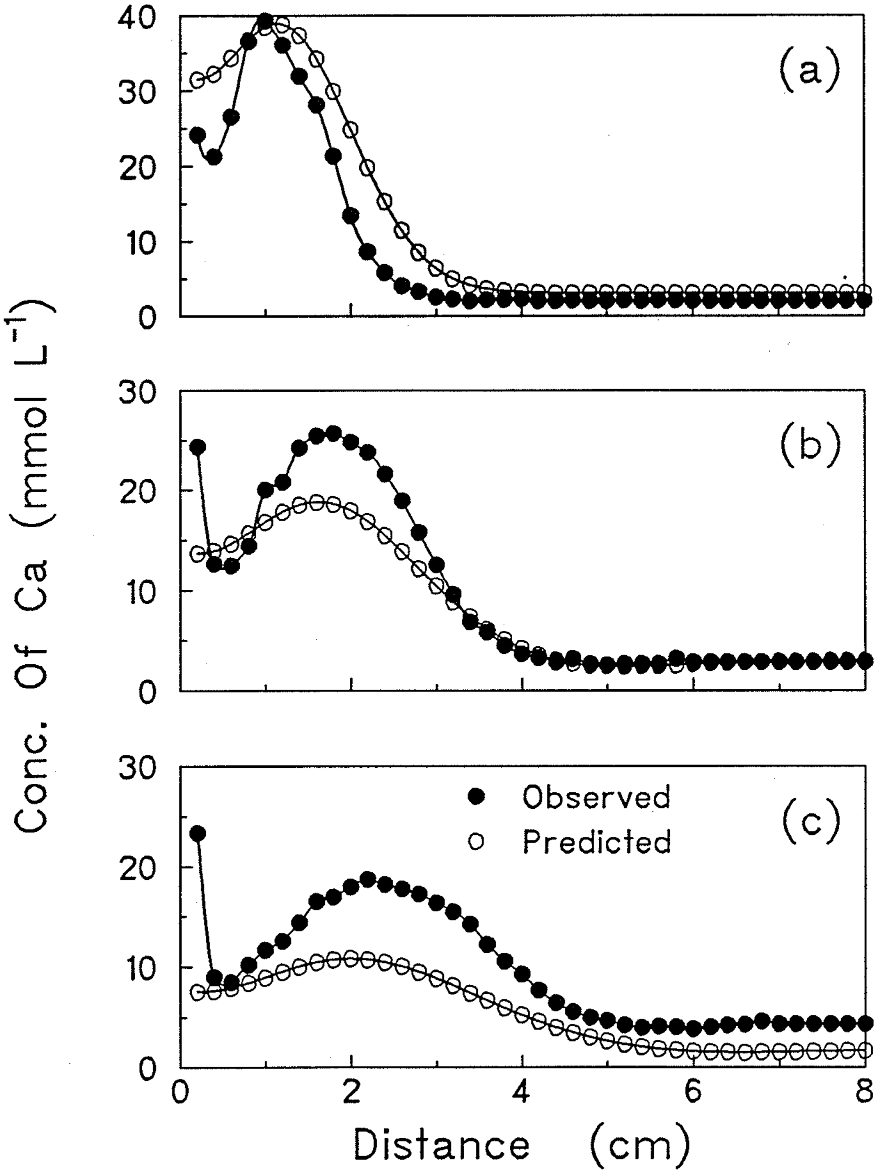

Figure C.2 - Comparison between experimentally measured and predicted Ca profiles in resin-sand column; (a) 3 days, (b) 1 week, and (c) 2 weeks.

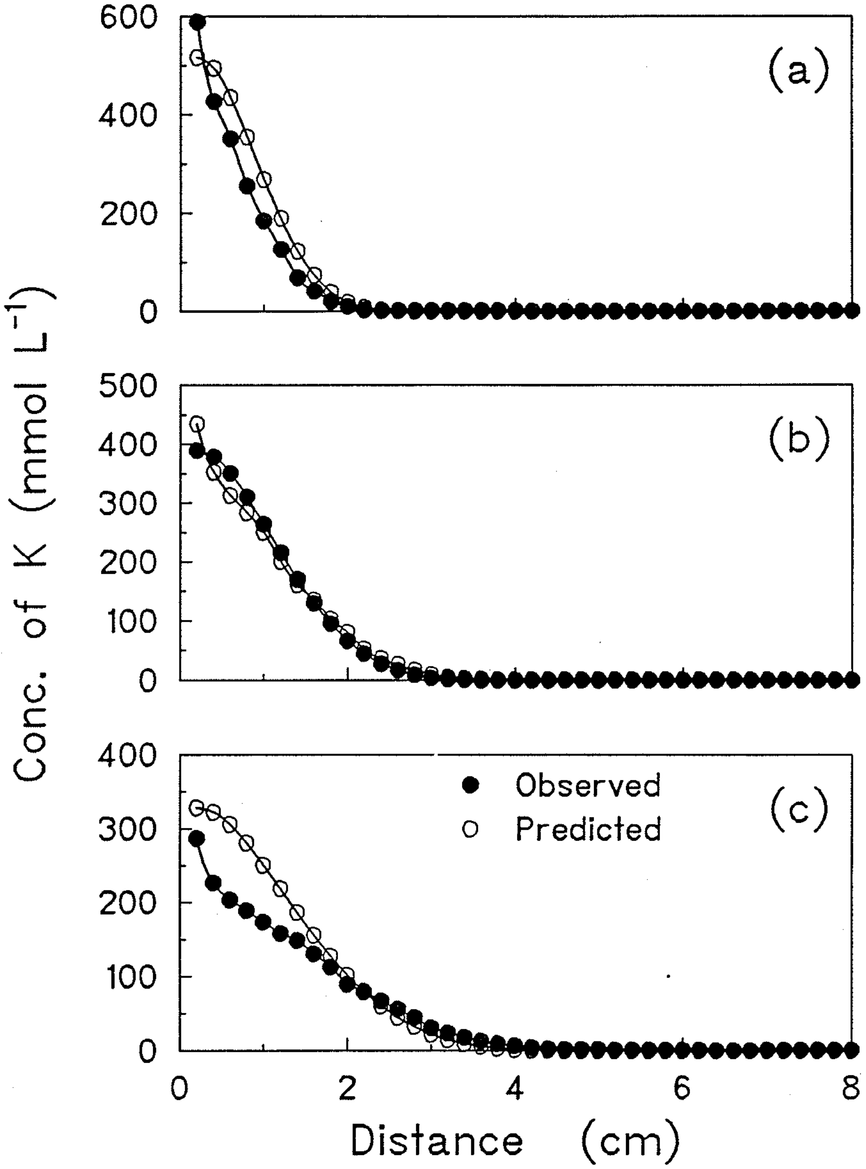

Figure C.3 - Comparison between experimentally measured and predicted K profiles in resin-sand column; (a) 3 days, (b) 1 week, and (c) 2 weeks.

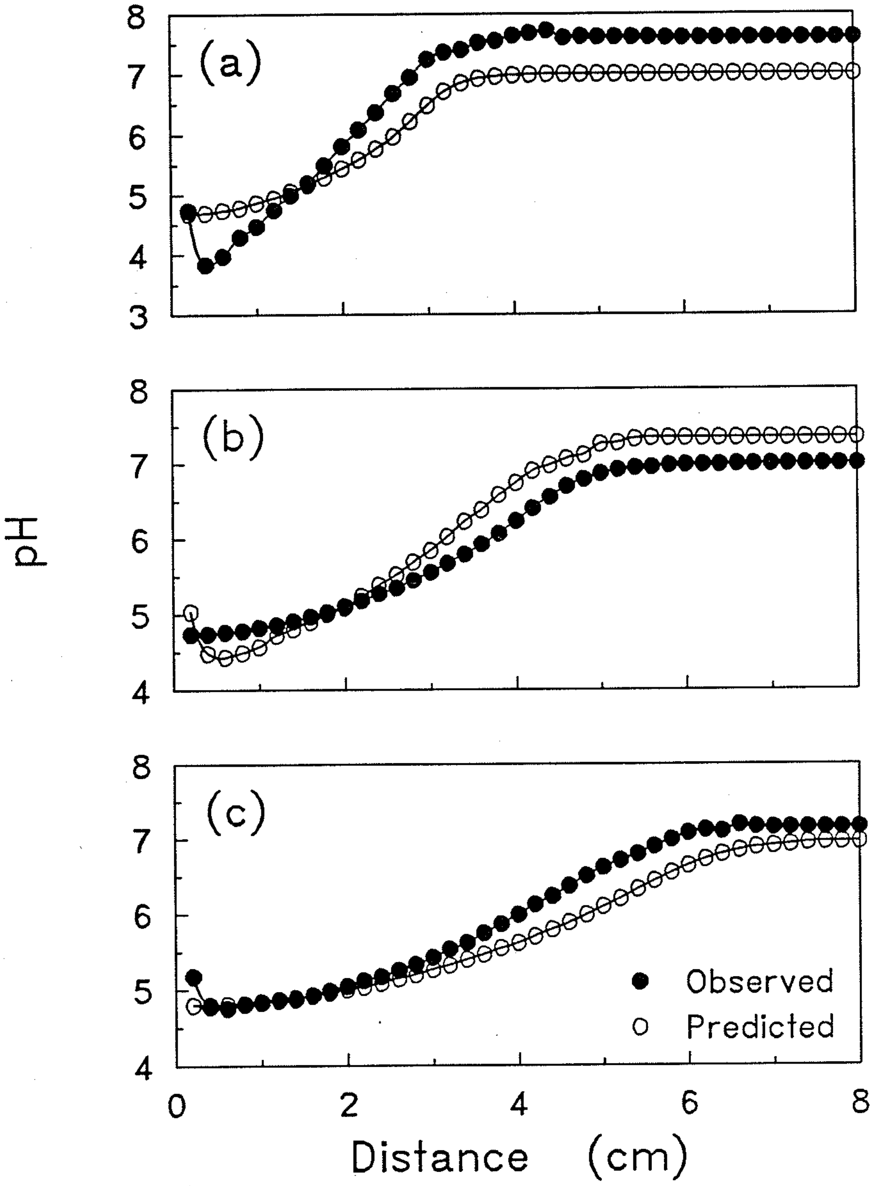

Figure C.4 - Comparison between experimentally measured and predicted pH profiles in resin-sand column; (a) 3 days, (b) 1 week, and (c) 2 weeks.