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DIFFUSIVE MOVEMENT AND REACTIONS OF PHOSPHATE AND

ASSOCIATED CATIONS IN AN ACID SOIL AND IN

ALUMINUM-RICH SOIL-LIKE SYSTEMS

by

XIYING HAO

A Thesis
Submitted to the Faculty of Graduate Studies
In Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

Department of Soil Science
University of Manitoba
Winnipeg, Manitoba

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FACULTY OF GRADUATE STUDIES
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DIFFUSIVE MOVEMENT AND REACTIONS OF PHOSPHATE AND ASSOCIATED CATIONS

IN AN ACID SOIL AND IN ALUMINUM-RICH SOIL-LIKE SYSTEMS

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XIYING HAO

A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University

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Xiying Hao   1997 (c)

ABSTRACT

Hao, Xiying. Ph.D., The University of Manitoba, February, 1998. <u>Diffusive Movement and Reactions of Phosphate and Associated Cations in an Acid Soil and in Aluminum-Rich Soil-Like Systems</u>. Major Professor; C.M. Cho.

Phosphate availability and movement is very low in acid soil due to fixation reactions of aluminum with phosphate. This research proposed that P fixation reactions are controlled, among other factors, by hydrogen ion production/consumption. A series of experiments were designed to demonstrate the proposed research model through the study of one-dimensional diffusive movement and precipitation reactions of applied P fertilizer (and associated cations). The effects of exchangeable Al, gibbsite, lignosulphonate, and type of P fertilizer (KH_2PO_4, K_2HPO_4 and K_3PO_4) were investigated in a simulated soil consisting of acid-washed sand and various levels of Al-saturated cation exchange resin. The diffusive transport of P and associated cations were also studied in a limed and unlimed gibbsite-rich Oxisol.

When KH_2PO_4 was applied to the surface of columns with different levels of exchangeable Al, gibbsite, and lignosulphonate and incubated for various times, the soluble amount and movement of P decreased as levels of exchangeable Al increased. Gibbsite alone did not reduce movement of P, but the combination of gibbsite with exchangeable Al greatly reduced the movement of P. Lignosulphonate decreased the soluble amount and movement of P in columns with exchangeable Al, but the opposite

effect occurred in columns with both exchangeable Al and gibbsite, especially after four weeks. Studies using KH_2PO_4 in unlimed and limed gibbsite-rich Oxisol showed that P movement was very limited in both; liming had very little effect.

Among the three P fertilizers tested, P movement was greatest with KH_2PO_4, and least with K_3PO_4 in columns with exchangeable Al without gibbsite. But there was little difference among the three P fertilizers in columns with both exchangeable Al and gibbsite. However, P concentration was the highest for K_3PO_4 as time increased. Tripotassium phosphate and K_2HPO_4 were also very effective in increasing pH.

The pH values either increased or decreased depending on the initial pH and the presence or absence of H^+ ion producing/consuming materials in all experiments. Data obtained in these studies are consistent with the proposed research model showing that H^+ ion production/consumption is crucial to P fixation and movement.

ACKNOWLEDGEMENTS

FOREWORD

This dissertation was written in manuscript style as outlined in the Department of Soil Science Guide to Thesis Preparation for Graduate Students. All five of the following manuscripts are likely to be submitted for publication. The journal(s) to which they will be submitted have yet to be determined.

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LIST OF ABBREVIATIONS

CEC	Cation exchange capacity
d	Day
DKP	dipotassium phosphate (K_2HPO_4)
Extr	Extractable
h	Hour
K_{sp}	Solubility product
LS	Lignosulphonate
M	mole L^{-1}
MKP	Monopotassium phosphate (KH_2PO_4)
OX	Oxalate
TKP	Tripotassium phosphate (K_3PO_4)
wk	Week

1. INTRODUCTION

Phosphate (P) is an essential nutrient for plants and animals because of its role in vital life processes, such as photosynthesis in plants and energy transformations in all forms of life (Sanyal and Datta 1991). But many soils in their native state do not contain sufficient quantities of available phosphate to maximize crop yield (Barber 1995). As a result, farmers all over the world apply large amounts of P fertilizer in an effort to increase food production. However, only 10 to 20% of the P in fertilizers is utilized by crops in the year of application. The remaining P is not used by plants because P reacts rapidly with soil and is converted into relatively insoluble compounds (P fixation). As a result, much of the P does not move readily to plant roots where it can be utilized (limited P movement). Understanding P movement and fixation mechanisms in soil is crucial to the development of a sustainable and economically viable agriculture.

It is well understood that P fixation is a complex reaction between soil components and phosphate and depends on both the kind of soil and phosphate source (Kim et al. 1983). Hemwall (1957) pointed out that P fixation mechanisms are different in acid and alkaline soils, although it should be realized that the primary mechanisms involved in each occur to some extent in both. Phosphate fixation in alkaline and calcareous soils is usually attributed to the formation of P compounds of calcium. In acid soil, aluminum and iron plays an important role in P fixation.

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The type of P fertilizer used plays a important role not only in P fixation (Khasawneh et al. 1974) but also in soil degradation. The commonly used mono-basic P fertilizer may cause increased acidification in acid soils (Cho 1991).

Although the high P fixation capacity of acid soils has been attributed to the existence of exchangeable Al and Al oxides and hydroxides, the P fixation mechanism is still not fully understood. Phosphate fixation is generally believed to be caused by adsorption and precipitation reactions. The adsorption of P onto soil mineral surfaces has been regarded as the main mechanism of fixation, while precipitation reactions of P have been largely ignored. Barber (1995), however, pointed out that when P concentrations are higher than 5 mg L^{-1}, P fixation occurs mainly through precipitation reactions rather than adsorption. At the point of P fertilizer application, the concentration of phosphate can be as high as 10 M (or 310 g P L^{-1}) (Sample et al. 1980). Thus, precipitation of P is actually more important than adsorption in the movement and availability of fertilizer P added as granules or droplets to soil.

Understanding P movement is equally complex. First, one cannot study the movement of P without considering fixation reactions. In addition, the interactive and complex nature of these reactions, such as cation exchange, hydrolysis, dissociation and precipitation /dissolution after P fertilizer application, make it necessary to study the fate of all ions (cations and anions) involved in the reactions. However, interactions among ions have generally been ignored in past investigations of P movement.

Therefore, further studies are needed to better understand both P fixation and movement in acid soil. Through this effort, it may be possible to develop a better fertilizer or an improved application method for acid soils.

The objectives of this study are to:

- propose a phosphate fixation model for acid soils;

- test the model through examination of the effects of

    - hydrogen ion production or consumption

    - exchangeable Al, gibbsite and lignosulphonate and

    - type of P fertilizer

  on the movement and solution concentration of P and K; and

- suggest possible ways to improve phosphate fertilizer efficiency.

2. LITERATURE REVIEW

2.1 Aluminum Chemistry in Acid Soil

2.1.1 Introduction

An understanding of aluminum (Al) chemistry in soil is essential to the study of the mechanisms of P fixation and movement in acid soils. Aluminum has been considered to play a significant role in P fixation in acid soils (Hemwall 1957). Aluminum is also important because of its potential toxicity to plants, its interaction with phosphorus and other major plant nutrients (Stumm and Morgan 1981), its major role in soil colloid chemistry (Sposito 1981), and its effects on buffering of pH and alkalinity of natural waters (Cronan et al. 1990). Extensive reviews on soil Al chemistry have been published by several researchers (Huang 1988; McLean 1976; Ritchie 1994).

Aluminum forms amphoteric hydroxides that can dissolve in both acids and bases. In soil solution, Al exists as free ions, such as Al^{3+} and also as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, or $Al(OH)_4^-$ depending on pH, or as complexes, by reacting with F^-, SO_4^{2-}, phosphate and organic acid. The ionic species of Al can be adsorbed onto cation exchange sites, precipitate in inorganic salts, such as an Al-P precipitate, be incorporated into the structure of soil clay minerals, or exist as oxides or hydroxides. Aluminum could also exist as a hydroxy Al interlayer and as coatings on the edges and external planar surfaces.

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The concentration and activity of Al in soil solutions will not only depend on the mechanisms by which Al is distributed between solid and liquid. but also on its behavior in solution. The equilibrium solubility and speciation of Al in soil solution may be affected by pH, organic acids, metal ions, inorganic ligands. and the type of Al-containing solid (Arp and Ouimet 1986). Furthermore, soil is an open system in which the solution composition is continuously changing with time and space in response to losses and gains by percolation into and out of a volume of soil, plant uptake and release, atmospheric deposition and evaporation, application of amendments, and removal by vegetation. The quantity of Al in soil solution is also dynamic in time and space and the measurements we make only represent one point in the time and space of a pathway.

2.1.2 Aluminum in Soil Solution and Complex Formation

Total Amount: The total soluble Al in soil is usually between 10-350 μM. Levels greater than 1000 μM occur only in exceptional circumstances. such as in acid sulfate soils. Most of the Al is polymerized at concentrations greater than 1000 μM. The amount of Al^{3+} in soil solution is inversely correlated with pH (Adhikari and Si 1991; Menzies et al. 1994b; Patiram 1990).

Speciation: The chemistry of Al is complicated due to its hydrolysis; the proportion of each hydrolyzed species varies with solution pH. In aqueous solutions, Al^{3+} does not remain as free ions but is surrounded by six molecules of water forming $Al(H_2O)_6^{3+}$. As pH increases, protons are removed from the coordinated water molecules giving a series of hydrolysis products:

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H^+ \qquad [2.1]$$

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)_4(OH)_2^+ + 2\,H^+ \qquad [2.2]$$

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)_3(OH)_3^0 + 3\,H^+ \qquad [2.3]$$

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)_2(OH)_4^- + 4\,H^+ \qquad [2.4]$$

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)(OH)_5^{2-} + 5\,H^+ \qquad [2.5]$$
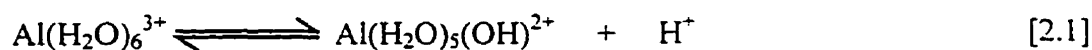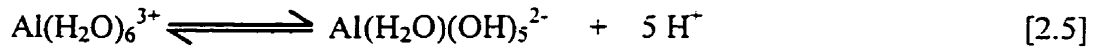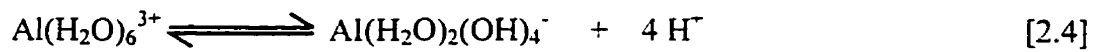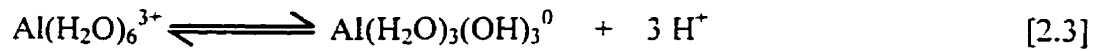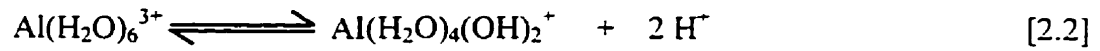
For simplicity, these hydrolysis species are generally written without the hydrated water. Figure 2.1 is a plot of activity (concentration) of Al hydrolysis species against pH using the equilibrium constants supplied by Lindsay (1979). Figure 2.2 shows the proportion of each Al hydrolysis species at different pH using the results from Figure 2.1. Together, Figures 2.1 and 2.2 show that the Al^{3+} species is dominant when the solution pH is below 4.5. $Al(OH)_2^+$ is dominant in the pH range of 4.5 to 5.7, $Al(OH)_3^0$ from 5.7 to 8.1, and $Al(OH)_4^-$ dominates for pH above 8.1.

Complexation: Aluminum can undergo several reactions with complexing agents. Figures 2.1 and 2.2 are only valid for solutions containing OH^- as the only complexing ligand. The presence of other anions that do not form complexes with Al, such as Cl^- or ClO_4^-, is permissible. But, most natural waters, or soil solutions, contain ligands other than OH^- that form complexes with Al. The extent of complexation will depend on the ionic strength and pH of the soil solution and the relative concentrations and complexing abilities of soluble ligands (Sposito 1981). Whether a ligand increases or decreases Al solubility depends on the particular Al-ligand complex and its tendency to remain in solution or to form a precipitate. Ligands that increase the overall solubility of Al include F^-, oxalate^{2-}, citrate^{3-}, fulvic acid, and silicate (monomeric) (McBride 1994). Ligands that decrease the overall solubility of Al include phosphate, sulfate, silicate (polymeric), and hydroxyl. Competition between Al and other cations is also important

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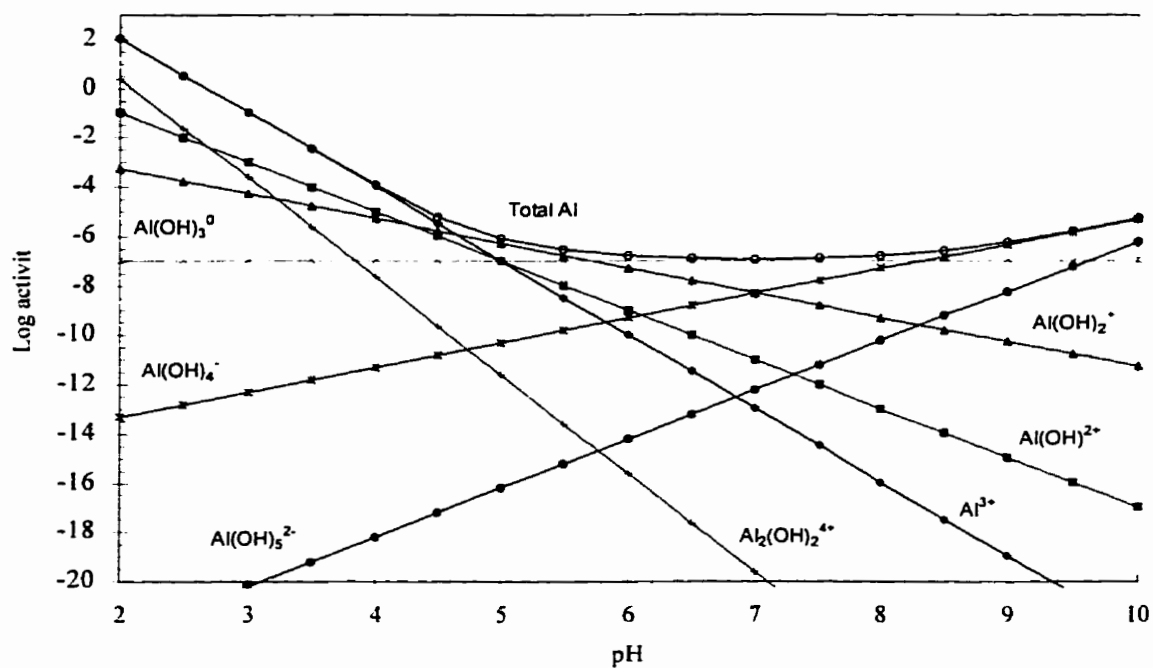
Figure 2.1 Concentration of the Al species in solution in equilibrium with gibbsite (using data from Lindsay 1979).
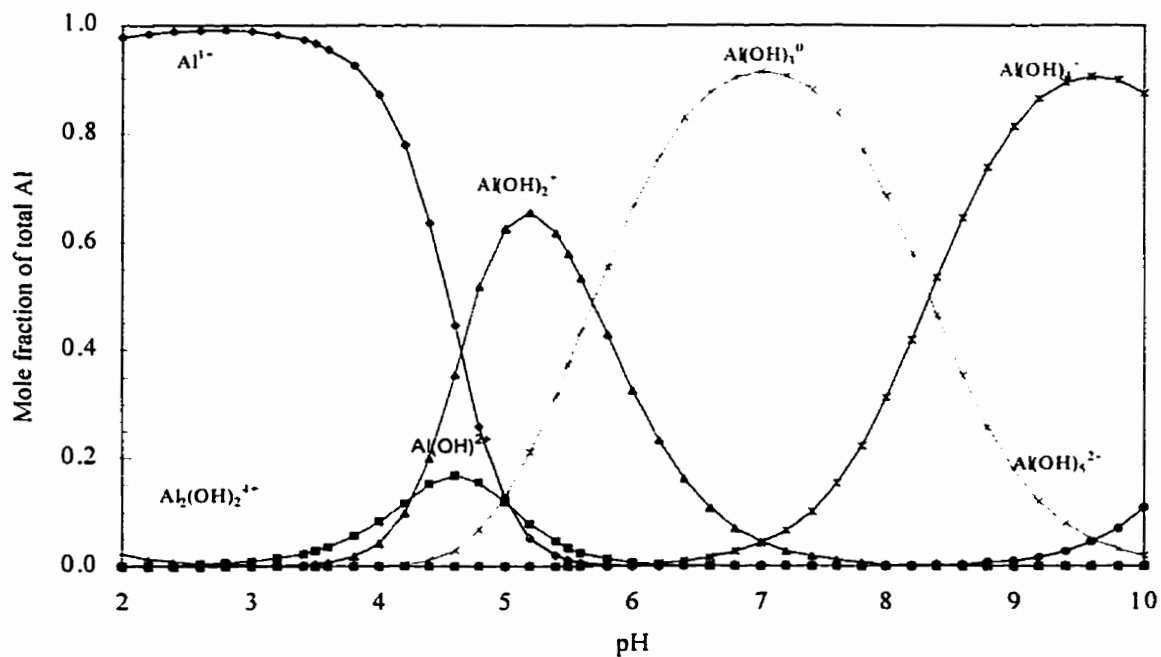
Figure 2.2 Effect of pH on the mole fractions of Al species in aqueous solution (using data from Lindsay 1979).

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in the formation of Al complexes in soil solution. The extent of competition depends on the equilibrium constant of the competing cation with the ligand relative to that of Al, and the concentration of other competing cations and Al in soil solution. There are competitions in ion exchange reactions among Al and other cations and all these affect Al complex formation in soil solution.

Fluoride has been reported to increase solubility of Al from gibbsite by a factor of about 24 at pH 4.5, and by a factor of 4 at pH 5.8 (Roberson and Hem 1969). Oxalate (a naturally occurring organic acid in soils) can increase the solubility of Al in soil through formation of stable complexes with Al (Fox and Comerford 1992). The effect of 10^{-3} M oxalate on Al solubility is shown in Figure 2.3. A comparison with Figure 2.1 reveals the dramatic effect of this complexing agent in boosting Al solubility, especially in the pH range of 5 to 7. Several Al-P complexes, such as $[Al(H_3PO_4)]^{3+}$ (Mortlock et al. 1993a; Mortlock et al. 1993b), $[AlOH(H_2PO_4)]^{2+}$, and $[Al(HPO_4)]^+$ (Stumm and Morgan 1981) are reported to exist.

Aluminum speciation in soil solution of an Spodosol is dominated by organic matter and fluoride complexes (David and Driscoll 1984). Aluminum-silica complexes can be an important part of the total dissolved Al concentration at pH values greater than 5 (Neal 1995).

Toxicity: Major toxic Al species are Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$, with Al^{3+} being most toxic to plant growth (McCray and Sumner 1990). Complexation of Al with various ligands is known to alter the toxicity effects of Al (Cameron et al. 1986; Hue et al. 1986). The presence of complexing inorganic and organic ligands such as fluoride,

8

3.0

4.0

5.0

- log activity

6.0

7.0

8.0

9.0

Al(OX)$_2$

total soluble Al

Al(OX)$_1$

Al(OH)$_2$$^+$

Al(OH)$_3$^{0}

Al(OX)$_3$^{3}

Al(OH)$_4$

Al^3$^+$

AlOH$_2$$^+$

solution pH

4   5   6   7   8   9   10
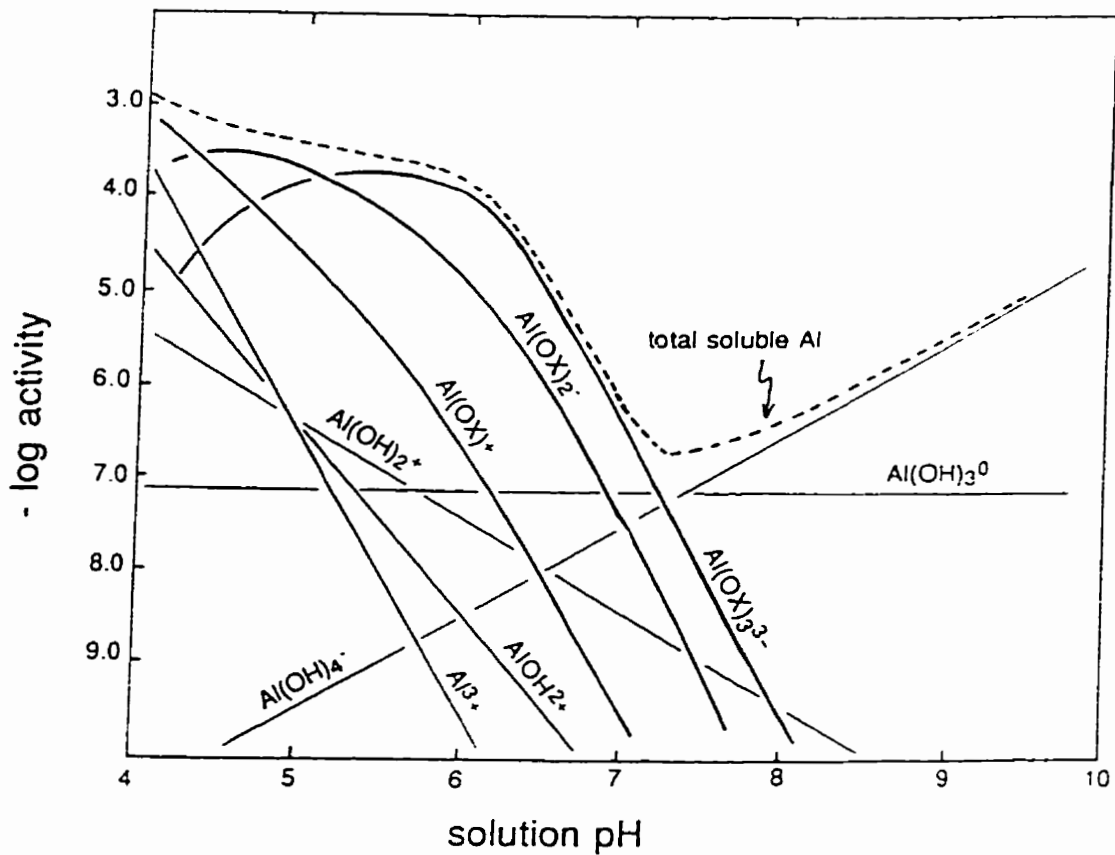
Figure 2.3 Concentration of the most significant species of soluble Al in an aqueous
solution of AlCl$_3$ and 10^{-3} M oxalic acid. assuming that gibbsite is present as
the solid phase at all pH values. The broken line depicts total soluble Al
(sum of all species concentrations). The oxalate anion (charge $= -2$) is
symbolized by OX (McBride 1994).

sulfate. phosphate, humic and fulvic acid. citrate and oxalate reduces the toxicity of Al

(Ritchie 1995).

2.1.3 Aluminum Minerals and Their Precipitation/Dissolution Reactions

Among the wide variety of Al minerals in soils. the oxide and hydroxides of Al

are by far the most significant. Extensive reviews on Al oxides and hydroxides have been

published (Hsu 1989; Zelazny and Jardine 1989). In cultivated soils. Al solution

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concentration is often controlled by the dissolution and precipitation of inorganic Al minerals (Helyar et al. 1993). Gibbsite is the most common and widely studied Al hydroxide in soil (Harsh and Doner 1985; Kittrick 1966; May et al. 1979; Ross and Turner 1971; Singh 1976) and is one of the major minerals in many Oxisols (Laterites and Lateritic soil and Latosols), which usually occur in humid tropical or subtropical uplands. Gibbsite is also a common but minor component in many Ultisols (Red-Yellow Podzolic soils), which are widespread in humid tropical, subtropical, and temperate regions. Other Al-bearing minerals in acid soil include Al sulfates, oxysulfates and aluminosilicates. Aluminum phosphates can form in soil that have been heavily fertilized with P fertilizer. Details about these Al-bearing minerals and their solubility can be found in Lindsay et al. (1989).

Under equilibrium conditions, the activity of Al in soil solution should be governed by the solubility of the Al-containing minerals. Gibbsite, being the most commonly found hydrous oxide in soils, has frequently been proposed as the solid phase form whose solubility controls Al activity in soil solution (Richard and Adams 1970). In support of this, Menzies (1994b), after studying 100 soils, found that the Al activity calculated in acid soils which received no lime application was comparable to the theoretical activity supported by the dissolution of gibbsite.

2.1.4 Adsorption and Exchange Reactions of Al

The total solution concentration of Al is affected not only by complexing reactions and the precipitation/dissolution of Al bearing minerals, but also by cation exchange reactions (adsorption/desorption) in soil. Aluminum can be adsorbed non-specifically at negatively charged sites in clay minerals and hydrous oxides of iron, Al

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and manganese. These are more commonly referred to as exchangeable Al. Aluminum is usually the dominant exchangeable cation in strongly acidic soils and this form constitutes a very substantial reserve of labile Al. The amount of exchangeable Al has been reported to be negatively correlated with the pH of soils (Adhikari and Si 1991; Menzies et al. 1994b; Patiram 1990).

2.1.5 Dynamic Nature of Al in Soil

The concentration and activity of Al (represented by $[Al^{3+}]$) in soil solution will not only depend on the mechanisms by which Al is distributed between solid and liquid phases, but also on its behavior in solution, and by the solubility of amorphous materials and crystalline minerals that are contained in these Al compounds (Lindsay 1979). Solution Al can also be affected by soluble organic and inorganic anions, and by insoluble forms of organic matter and negatively charged clay minerals and oxides that form strong to weak complexes with Al and Al-hydroxy ions (Hue et al. 1986; Thomas 1988). In theory, if equilibrium is attained among these dissolution-precipitation, adsorption-desorption, and complex formation-dissociation processes, a given system should have a characteristic Al^{3+} value in solution.

Disturbance of the system by changes in pH due to H^+ production, for example, should lead to a change in $[Al^{3+}]$ toward some new equilibrium value. However, equilibrium, or even approximate equilibrium or steady state, is not characteristic of soils. Soils are open systems receiving and discharging water and dissolved solutes, and receiving and losing carbon and nitrogen by biological processes. As a result, minerals and organic compounds in soil usually only achieve meta-stable equilibria or steady state.

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The conceptual model of the rate processes and soil Al forms involved in controlling Al^{3+} in the soil solution is illustrated in Figure 2.4 (Helyar et al. 1993). Figure 2.4 shows two Al pools. One is composed of inorganic solids containing Al. In the other, Al^{3+} and Al-hydroxy ions are complexed by inorganic and organic solid and solution compounds. The distinction between inorganic solid and adsorbed polymeric Al ions is necessarily arbitrary because there is no clear definition of the boundary between an adsorbed polymeric ion and a solid as the ion size increases. The soil solution Al^{3+} is depicted as being in equilibrium with the adsorbed and solution Al. This set of equilibria responds to the transport of Al to and from the exchangeable and solution pool by mass flow and dissolution from external sources.

According to this model, $[Al^{3+}]$ in the soil solution is controlled by the interaction among eight rate processes; the concept of organic matter (Bloom et al. 1979; Thomas 1988) or minerals (Lindsay 1979) uniquely controlling $[Al^{3+}]$ are simplifications of reality. Addition of organic matter to a soil (a change in rate r_6 in Figure 2.4) may affect Al^{3+} in several ways by changing the balance between the eight rate processes, but several other rates may still significantly affect the new steady state. The added organic matter could change the steady-state $[Al^{3+}]$ by (a) complexing solution Al faster than Al minerals dissolve and thus maintaining lower $[Al^{3+}]$ for a significant period (i.e. weeks to months) until mineral dissolution restores steady state; (b) adsorbing a major proportion of the Al from the most soluble Al mineral which might be an oxide or imperfectly crystalline oxides or alumino-silicate, thus allowing the next most soluble mineral to influence $[Al^{3+}]$; (c) causing an increase or decrease in soil pH, indirectly affecting $[Al^{3+}]$, or (d) inhibiting or catalyzing the rate of formation of Al minerals, affecting rate r_2. Mineral

Al(OH)$_3$ ion activity product $(Al^{3+})(OH^-)^3$

Soil Al minerals, oxides and amorphous compounds

Source/sink of materials used to increases the capacity of the soil solid phase to complex Al ion, e.g. $(CO_2 + H_2O)$ H^+, OH^-, soluble salts.

HIGH

Ion activity Product (soil)

LOW

* Unsaturated minerals (net dissolution)

Supersaturated minerals (net precipitation)

r_1

r_2

r_5 r_6

Soil and soil solution capacity to retain Al ion in complexed and solution forms

Soil Solution Al^{3+}

r_3

r_4

r_7 r_8

Source/sink for mass flow and diffusion of soluble Al to and from the soil layer

Source/sink of materials able to increase the capacity of the soil solution to contain Al e.g., H^+, OH^-, F^-, soluble salts, soluble organic matter

* The values of the Al(OH)$_3$ ion activity (soil) depends on the balance between the rate processes r_1 to r_8.

Figure 2.4 Conceptual model of the rate processes and soil Al forms involved in controlling Al^{3+} in the soil solution (Helyar et al. 1993).

solubility apparently controls Al chemistry in sub-soil, while organic substances control Al chemistry of surface soil (Cozzarelli et al. 1987). There is also evidence that acidification of soils depletes organically bound Al fairly quickly (Wesselink et al. 1996).

2.1.6 Liming Acid Soil

In acid soil, soluble Al can limit plant growth due to its toxic effects, resulting in reduced root extension and plant productivity (Wheeler et al. 1992). Liming or gypsum amendments are common and the purpose of such amendments is primarily to reduce the toxicity of Al and increase crop yield. Lime requirement can be defined as the quantity of lime required to reduce exchangeable and soluble Al^{3+} to a non-toxic level for the particular crop to be grown (McBride 1994). Soil pH rises nearly linearly with the quantity of lime added (McBride 1994). However, liming not only reduces Al toxicity and increases soil pH, but also induces changes in other soil chemical and physical characteristics.

Long term addition of gypsum ($CaSO_4.2H_2O$) decreased soil solution pH and increased electrical conductivity and concentration of Ca, Mg, Na, K and Al in the soil solution for 39 highly weathered Australian acid soils (Menzies et al. 1994a). On the other hand, liming significantly reduced the concentration of exchangeable (1 M KCl), extractable (0.01 M $CaCl_2$), and total soluble and monomeric Al (Slattery et al. 1995). The effective cation exchange capacity of a soil, measured as the sum of the exchangeable cations (Ca, Mg, Na, K, Al, and Mn), was also shown to increase with lime application and could be attributed to the increase in exchangeable Ca (Hochman et al. 1992). The increase in cation exchange capacity was probably due to the liming effect on the pH-

dependent variable charge on the minerals. Application of gypsum also reduced surface crusting and increased hydraulic conductivity (Sumner 1993).

2.2 Chemistry of Phosphate in Acid Soil

2.2.1 Introduction

A knowledge of the chemical behavior of phosphate (P) in soil is essential in order to understand its fixation and movement. The chemistry of P in soil is complex because each phosphate ion has the ability to form a multiplicity of compounds of various solubility. Total P in an average arable soil is approximately 0.1 percent by weight, of which only a very small part is usually in soil solution and available to plants. Plants absorb most of their phosphorous from the soil solution as the primary orthophosphate $(H_2PO_4^-)$, regardless of the original source of P. The P present in soil may be divided into four general categories:

1. P in soil solution;

2. P adsorbed on the surfaces of inorganic soil constituents and soil organic materials;

3. Minerals P; and,

4. Organic and microbial P.

The above classification is somewhat arbitrary. The phosphate in solution is affected by adsorption and desorption from oxide surfaces, dissolution and precipitation of P minerals, formation and dissociation of P complexes, and mineralization and immobilization of organic P. Soil is a dynamic system and is constantly changing. There have been extensive reviews on the chemistry of phosphorus transformation in soil

(Sanyal and Datta 1991), the fixation of P by soil (Hemwall 1957), and phosphate rocks for direct application to soils (Rajan et al. 1996). Only a brief summary will be presented here.

2.2.2 Soil Solution P

Orthophosphate is the common form of P in soil solution. The dissociation reaction of phosphate in solution is plotted in Figure 2.5 using equilibrium constants from Lindsay (1979). Figure 2.5 shows the relative abundance of the different ortho-phosphoric acid species as a function of pH. However, in soil solution there are several cations that form complexes with phosphate. In acid soil, the most common phosphate complexes are Al-P and Fe-P. Figure 2.6 shows that the proportion of phosphate species changes as Al species are introduced into the system. It has also been suggested that Al- and Fe-fulvic acid-phosphate complexes, Al peat phosphate complexes, and humic-Fe- (Al-) phosphate complexes exist in soil solution (Bloom 1981; Gerke 1992; Levesque and Schnitzer 1967).

The concentration of phosphate in soil solution is low when compared to the other two major plant nutrients, nitrogen and potassium. In cultivated soils, P concentration in soil solution is only about 0.03 mg kg^{-1}. The concentration of P in acid soil is largely influenced by the slow dissolution and re-precipitation of iron and Al containing minerals.

2.2.3 Adsorbed P

Phosphate adsorbs onto various surfaces of soil constituents. The adsorbed portion of P is also called labile P. Controversy exists over the amount of P that may be adsorbed on the surfaces of such soil constituents as Al and Fe oxides versus the amount
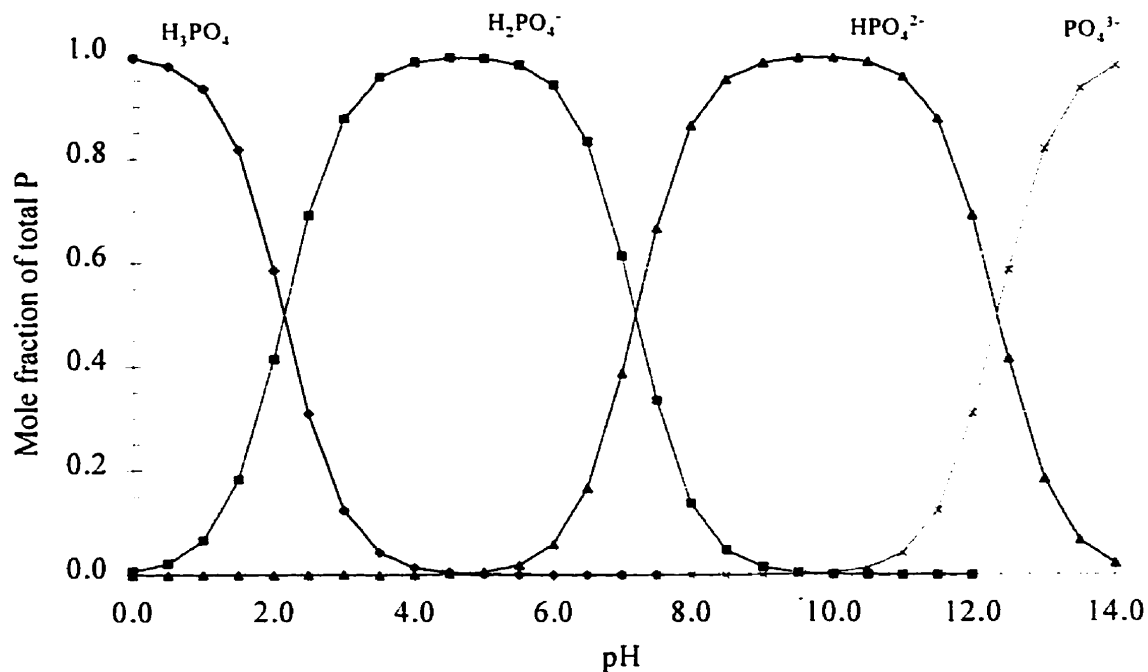
Figure 2.5 Effect of pH on the distribution of phosphate species (using data from
Lindsay 1979).
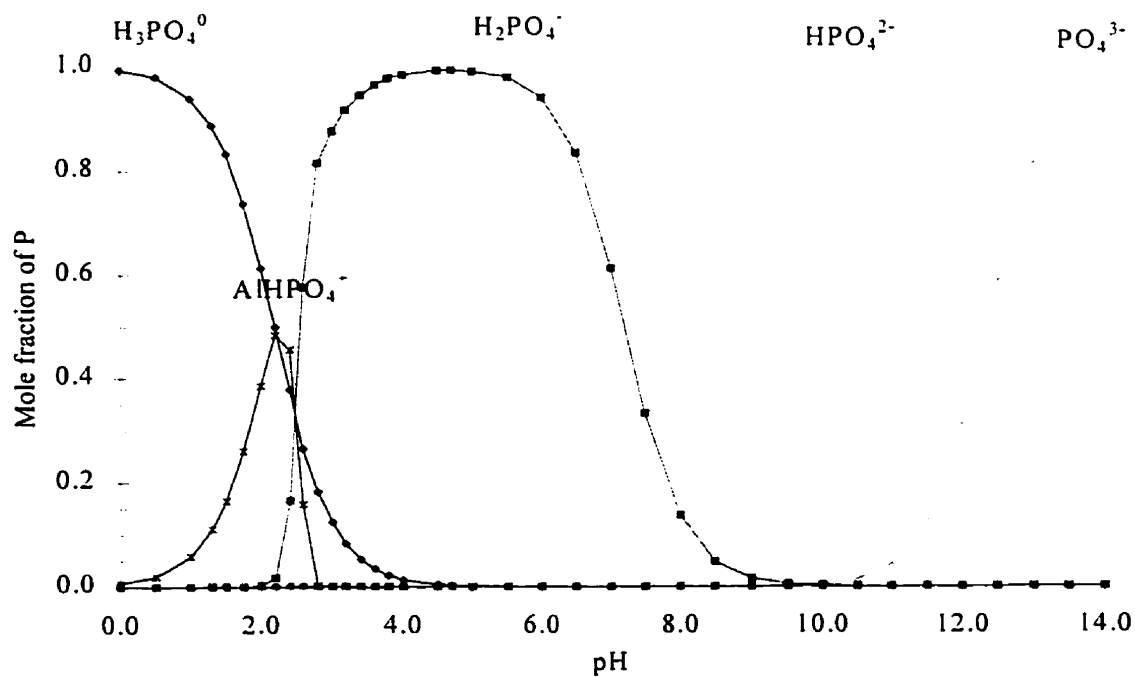
Figure 2.6 Effect of pH the distribution of phosphate species in the presence of
aluminum ions (Al^{3+} concentration is controlled by gibbsite, using data from
Lindsay 1979).

that is precipitated as discrete mineral forms. The amount of adsorbed P varies widely for different soils depending on the surface area and adsorption capacity of the soil. Numerous studies have been conducted to determine the amounts of P that soils can adsorb (discussed in Section 2.3.2.1).

2.2.4 Mineral P

There are numerous P minerals present in a soil before and after P fertilizer application. They are mainly minerals of P combined with Ca, Al and Fe. Calcium containing P minerals dominate in alkaline soils while Fe and Al containing P minerals dominate in acid soil. Lindsay et al. (1989) provides an excellent review on the various phosphate minerals in soil. Only the Al containing P mineral will be discussed here. It is believed that phosphate minerals such as, variscite, strengite or non-crystalline Fe and Al phosphates, may control the P levels in solution in acid soil.

Variscite ($AlPO_4 \cdot 2H_2O$) and taranakites (such as $H_6K_3Al_5(PO_4)_8 \cdot 18H_2O$ or $H_6(NH_4)_3Al_5(PO_4)_8 \cdot 18H_2O$) are the two most common Al-P minerals in acid soil. There are also reports on the existence of wavellite ($Al_3(PO_4)_2(OH)_3 \cdot 5H_2O$), cranadallite ($CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$) and sterrettite (($Al(OH)_2)_3HPO_4H_2PO_4$). Wavellite and cranadallite are considered to be naturally occurring secondary phosphate minerals resulting from weathering of apatite, while variscite, taranakite and sterrettite are the products of P fertilizer reactions in soil.

2.2.5 Soil Organic P

The amount of organic P in soil varies from 20 to 80% of the total P in the surface layer. The chemical nature of half of the organic P in soils is unknown. The compounds

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that have been identified are inositol phosphates, phospholipids, and nucleic acids. In addition to these three main groups, other groups of organic phosphates, phosphoprotein, and sugar phosphates are also proposed to exist in soil organic P (Dalal 1977). Organic P cannot be utilized by plants directly, but rather must be mineralized into an inorganic phosphate form before it can be used. Inorganic P can also be immobilized into organic P. The immobilization and mineralization of P in soil are largely due to the activity of soil micro-organisms. Depletion of organic P in soil is induced by cultivation due to increased aeration.

2.3 Phosphate Fixation in Acid Soil

2.3.1 Introduction

The fixation of phosphate generally implies the conversion of applied phosphate, which is water soluble, to a more insoluble form. The fixation process is composed of many complex reactions between soil components and phosphate, and these reactions depend on the kind of soil and the source of P. Furthermore, they have been shown to be non-equilibrium reactions and only partially reversible, the rate of reaction being concentration dependent. The overall reaction may continue for long time (van Riemsdijk and van der Zee 1995). It is generally believed that Ca plays an important role in P fixation in alkaline soil while Fe and Al play major roles in acid soil. There have been numerous studies to investigate P fixation and are summarized by Sanyal and Datta (1991) and Hemwall (1957).

2.3.2 Mechanisms of P Fixation

Phosphate fixation is generally believed to occur through two processes, adsorption and precipitation of P by soil constituents. Controversy exists over the amount of phosphate that may be adsorbed on the surfaces of such soil constituents as Al and iron oxides (Rajan et al. 1974) versus the amount that is precipitated as discrete mineral forms (Kim et al. 1983; van Riemsdijk et al. 1975). Phosphate is commonly believed to be adsorbed by oxide surfaces rather than precipitated in mineral forms when P level in soil solution is under-saturated with respect to P minerals.

When higher phosphate concentrations are maintained in the soil solution, such as near fertilizer particles, precipitation of phosphate as various iron and Al phosphates is believed to be the dominant process. However, in general, it is very difficult to determine the amount of P fixed into its different forms (van Riemsdijk and de Haan 1981). The term "sorption," which is the combined adsorption and surface precipitation of P, is used when the exact nature of the retention mechanism at a surface is unknown. Due to the low solubility of several P-containing minerals, precipitation may occur at very low P concentrations. Precipitation reactions probably play a much bigger role than adsorption processes in retention of applied fertilizer.

2.3.2.1 Adsorption

Adsorption is the process by which atoms, molecules, or ions are removed from the soil solution or soil atmosphere and retained on the surfaces of solids by chemical or physical binding (SSSA 1997). Adsorption does not include surface precipitation or polymerization processes (Sparks 1995).

Adsorption isotherms have been used to describe the relation between the activity or equilibrium concentration of the adsorbent and the quantity of an adsorbate on the surface at constant temperature. There are a number of models to describe the adsorption isotherms. However, for phosphate, the most commonly used equations to describe its adsorption isotherms are:

- Langmuir adsorption equation;

- Tempkin equation;

- Freundlich equation; and

- Mechanistic equation.

Detailed reviews of these models can be found in Sanyal and Datta (1991).

Extensive research has been conducted on the adsorption of phosphate by soil and various soil components. Phosphate might be adsorbed onto various surfaces. when the soil solution is not supersaturated with respect to any solid phosphate mineral. If this is the case, the process can be described as adsorption. However, many so-called adsorption studies are extended into the region of super-saturation, implying that in principle a precipitation mechanism may also contribute to the total P adsorption.

In acid soil, P adsorption is generally attributed to hydrous oxides of iron (Fe) and Al, and to layer lattice clays, particularly in tropical soils with low pH (Sanyal and Datta 1991). The adsorption of phosphate by iron and Al hydroxides has been studied very extensively (Barrow et al. 1981; Bloom 1981; Borggaard et al. 1990; Brennan et al. 1994; Chandler 1941; Goldberg and Sposito 1984; Helyar et al. 1976a; Helyar et al. 1976b; Kuo and Lotse 1974; Liu et al. 1984; Parfait 1977; Sims and Ellis 1983; Torrent

et al. 1990; Violante et al. 1991; Wada and Gunjigake 1979). The adsorption of P onto

mineral surfaces in soil is affected by several factors including pH, competing anions, and

soil mineralogy.

2.3.2.2 Precipitation

While the adsorption process may be regarded as that leading to net accumulation

at an interface, precipitation results in the formation of a solid phase from a strongly over-

saturated solution. Both processes cause loss of materials from the solution phase.

However, adsorption is essentially two-dimensional, whereas precipitation is inherently

three-dimensional. Distinguishing between the two processes in soil is difficult.

A number of early investigations of P chemistry in soil suggested the formation of

a variety of insoluble inorganic phosphates of Al and Fe in acid soils through

precipitation (Cole and Jackson 1950; Kittrick and Jackson 1956). Phosphate solution

concentrations (or activities) in soil have been correlated with different solubility

isotherms constructed from solubility product constants of various Al, Fe and Ca

phosphates (Lindsay et al. 1959a; Lindsay et al. 1959b). These solubility isotherms

indicate that in acid soil, variscite and strengite are the probable P minerals, whereas in

alkaline soils, several calcium P minerals govern the P concentration in soil solution.

When water soluble P is added to an acid soil, the concentration of P present in

soil solution will be higher than those associated with Al-P and Fe-P minerals. The soil

solution is thus supersaturated with respect to those minerals and they will precipitate.

Under field conditions, application of P fertilizer could increase the P solution

concentration to 1.5 to 6 M at the point of application, and the solution concentration of

the accompanying cations increases to as high as 1 to 12 M (Sample et al. 1980). The

solution pH may decrease to values near 1.0. These concentrated solutions, moving away from the application point, contact soil constituents and induce dissolution and/or exchange reactions of Al and Fe. This increases Al and/or Fe content ratios over other cations in solution of acid soils (Blanchar and Stearman 1984; Cho 1991; Sample et al. 1980). The added P then precipitates with the Al and/or Fe.

The initial reaction products of fertilizer P in acid soil are likely to be non-crystalline, meta-stable, and may slowly dissolve in soil solution under changing conditions with time. Eventually, crystalline products will be formed (Hetrick and Schwasb 1992). A further precipitation of the more stable reaction products is also possible. As the precipitation reaction progresses, the solution concentration reaches a point at which the more soluble precipitates dissolve to support the formation of less soluble products. Another possibility is that reaction products with different solubilities could be formed at the same time, but at a different rate. In other words, the reaction product, which is more soluble, could form at much greater rate than less soluble products such that the less soluble ones are not initially noticeable.

Phosphate concentration in soil solution will ultimately be controlled by the less soluble P minerals and the P concentration in soil solution will be lowered. Phosphate precipitation depends on factors such as pH, concentration of P, Al, Fe and Ca, competing ions, and reaction time. In the immediate vicinity of fertilizer granules, there are local conditions of low pH and high phosphate concentration that may cause dissolution of clays and precipitation of Al phosphate in acid soil. Even though P precipitation is a very important mechanism in P fixation, studies in this area are very limited. One reason is that soil is such a complicated system, making it very difficult to identify the reacting

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species and the final products. For example, three Al species (Al^{3+}, $Al(OH)^{2+}$ $Al(OH)_2^-$)

could possibly react with three phosphate species ($H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) in acid soil,

forming K-taranakite, if a P fertilizer such as KH_2PO_4 is added. No one knows for sure

which of the Al and phosphate ions are the reacting species. There are various ways to

write chemical equations for the formation of taranakite, but none has been quantitatively

proven to describe the phenomenon.

When a soluble calcium phosphate fertilizer is applied to an acid soil rich in Al,

the phosphate will be precipitated as $AlPO_4 \bullet 2H_2O$, referred to as variscite ($Ksp = 10^{-21}$)

by some researchers. The possible reactions could be written as:

$$Al^{3+} + H_2PO_4^- + 2\ H_2O \rightleftharpoons AlPO_4 \bullet 2H_2O(s) + 2H^+ \qquad [2.6a]$$

or as

$$Al(OH)_2^+ + H_2PO_4^- + 2H_2O \rightleftharpoons Al(OH)_2H_2PO_4 \bullet 2H_2O(s) \qquad [2.6b]$$
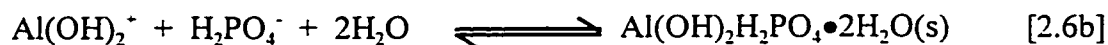
A non-crystalline analog of variscite was found to be the dominant P mineral in acid soil

where Ca phosphate fertilizer had been applied (Pierzynski et al. 1990a; Pierzynski et al.

1990b). While van Riemsdijk et al. (1975) suggested sterrettite as the Al-P reaction

product, Cole and Jackson (1950) found that variscite formation was favored at pH 3.8

but sterrettite formation was favored at pH 5.5.

Similarly, when fertilizers rich in potassium, such as KH_2PO_4, are applied,

taranakite (or its non-crystalline analog) will be formed (Lindsay et al. 1962). Kim et al.

(1983) suggested that taranakite should be written as $K_3[Al(OH)_2]_5(H_2PO_4)_8 \cdot 8H_2O$ instead

of $K_3H_6Al_5(PO_4)_8 \cdot 18H_2O$ because the $H_2PO_4^-$ ion is the predominant P species in acidic

solution. They also found that the mole ratio of H_2O in the precipitate varied from 18 to

48 due to the differences in degree of drying. Huang (1988) pointed out that formation of

taranakite was observed by reaction of Al hydroxide with concentrated K^- or NH_4^-

phosphate solutions, but these compounds hydrolyzed to non-crystalline Al phosphate

upon dilution and behaved as a slow releasing phosphate source rather than products of

fixation.

2.3.3 Factors Affecting P Fixation

Phosphate fixation is influenced by several factors. Numerous studies have been

conducted on the effects of pH (Eze and Loganathan 1990; Olila and Reddy 1995;

Staunton and Leprince 1996), ionic strength (Barrow and Shaw 1979; Evans Jr. and

Sorensen 1986), exchangeable cations (Curtin et al. 1993; Curtin et al. 1987; Russell et

al. 1988), non-crystalline Al and Fe minerals in soil (Yuan and Lavkulich 1994), organic

matter (Borggaard 1990) and reaction time (Barrow and Shaw 1975).

2.3.3.1 pH

Phosphate availability to plants in soil is optimal at or near pH 6.5. Soil pH

affects the abundance and solubility of Ca, Al and Fe in soil. In alkaline soil, Ca

phosphate formation decreases P solution concentration while formation of Al-phosphate

is responsible for the low concentration of P in solution in acid soil. Phosphate sorption

by soil has also been shown to be influenced by pH (Eze and Loganathan 1990; Olila and

Reddy 1995; White and Taylor 1977). In acid soil, the phosphate adsorption capacity

increases with acidity due to the protonation of surface Fe and Al functional groups in

clays and in oxides and hydroxides of Fe and Al (Edzwald et al. 1976). The amount of Al

that could potentially react with phosphate also increases with decreasing pH, thus

precipitation of Al-P would increase as pH decreases. Phosphate adsorption decreased

linearly with increases in pH for a Na-saturated soil, while minimum P adsorption

occurred at pH 5 to 5.5 for a Ca-saturated soil (Curtin et al. 1993). Montmorillonite fixes

increasing amounts of P as pH increases, whereas vermiculite fixes less P with increasing

pH (Hall and Baker 1971).

2.3.3.2 Organic Anions

Carboxylates, and the conjugate bases of organic acids, can play an important role

in improving the availability of soil phosphate (Staunton and Leprince 1996). Violante et

al. (1991) reported that adsorption of P onto freshly prepared Al oxides was greatly

reduced in the presence of oxalate. They attributed the reduction of P adsorption to the

strong competition of oxalate ions with phosphate for adsorbing sites on the Al oxide

surface. However, they did not consider the effect of complexation of Al by oxalate nor

the effect of pH on the solution concentration and distribution of Al species as illustrated

in Figure 2.3. There have been reports that some anions (F^-, tartrate, oxalate, EDTA and

citrate), with strong complexing ability with Al, decrease phosphate adsorption by

alumina and kaolinite over a wide range of pH (Chen et al. 1973). Staunton and Leprince

(1996) found that oxalate was more efficient in limiting the adsorption of freshly added

phosphate than desorbing native phosphate. Fox and Comerford (1992) found that Al

and P were continuously released following sequential addition of oxalate at low

concentration and concluded that, in forest soil, this could solubilize large amounts of P

and Al on an annual basis.

2.3.3.3 Clay Mineralogy

Highly weathered acid soils often have high P fixation abilities due to the

presence of large amounts of Al and Fe oxides and hydroxides. The Al and Fe oxides and

hydroxides have been recognized by many researchers as playing a significant role in P fixation (Borggaard et al. 1990; Hemwall 1957). Removal of the free Al and Fe oxide content of soil colloids reduces the magnitude of P fixation. The quantity of P adsorbed depends on the crystallinity of the Fe and Al oxides/hydroxide (Sims and Ellis 1983). As precipitated Fe and Al hydroxides age, they are converted to more crystalline compounds that have less surface area and fewer exposed hydroxyl groups which function in P adsorption. Because non-crystalline oxides and hydroxides are much more soluble than the crystalline forms, greater precipitation will take place when the solution concentration of Al and Fe are supported by non-crystalline Al and Fe oxides and hydroxides. There are also reports that phosphate is adsorbed on the $Al(OH)_3$ sites exposed on the edges and faces of the platey gibbsite crystals (Parfitt et al. 1977).

2.3.3.4 Exchangeable Cations

Exchangeable Al and Fe play a major role in P fixation in acid soil. One cmol of exchangeable Al per kg soil when hydrolyzed may fix up to 102 mg P kg^{-1} (Sanchez and Uehara 1980). High correlations between P fixation and level of exchangeable Al have been reported (Coleman et al. 1960; Syers et al. 1971). Russell et al. (1988) also found that P sorption increased with increasing exchangeable Al and decreased with increasing exchangeable Na for six Australian soils.

2.3.3.5 Soil Amendment

As discussed in Section 2.1.6, liming is commonly used to raise soil pH and reduce Al toxicity in acid soils. LeMare and Leon (1989) found the effects of liming on soil P adsorption was highly dependent on the type of soil used. The effect of liming on P fixation varies, with some studies showing increases, some decreases and others no

effect at all (Haynes and Ludecke 1981; Holford 1985; Holford and Crocker 1994; Martini and Mutters 1985; Ryan and Smillie 1975; Sanchez and Uehara 1980). Such widely differing results may be due to differences in soil clay mineralogy, initial P status. original pH and chemical properties of the soils studies. The effect of liming on P fixation seems to be influenced by two opposing factors. Increased pH due to liming decreases P adsorption by amphoteric adsorption surfaces and reduces exchangeable Al (a source for Al in solution). On the other hand, precipitation of Al at high pH can increase the P adsorbing surfaces in soil (Haynes 1984). As pointed out by Hall and Baker (1971), montmorillonite fixed increasing amounts of P as pH increased, while vermiculite fixed less P. Thus, addition of lime to soils containing clays that react with P, such as montmorillonite, will increase P fixation. For soil containing clays that react similarly to vermiculite, addition of lime prior to P addition will reduce the reactivity of Al through formation of stable interlayer Al polymers. These Al polymer interlayers effectively reduce the specific surface of reactive Al and P adsorption sites.

2.3.3.6 Management of Soil P

Phosphate deficiencies are usually remedied by application of phosphate fertilizers. Management of P is strongly inter-linked with soil characteristics such as soil pH, degree of weathering, amount and nature of clay minerals. and organic matter content. The extent of P fixation should also be considered, along with cropping patterns, when planning for P management practices (Sanyal and Datta 1991).

Band applications have long been recommended for P fertilizer both to minimize contact with the soil and to place the fertilizer close to young roots. Because of P precipitation in soil, P fertilizers are often placed in a band with the seed or about 5 cm to

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one or both sides of seeds and 5 cm below it. Initial high inputs of P have also been

suggested for acid soil due to its high P fixing capacity (Sanchez and Uehara 1980).

2.4 Transport of P in Soil

The movement of P in soil is very important to the supply of P for plant growth.

When fertilizer P is applied to the soil surface or placed in a band, its availability to the

plant roots depends on its rate of movement from the source into the surrounding soil

solution to the surface of the roots. The movement of applied P fertilizer in soil also

affects its efficiency by influencing the probability of root/P-fertilizer contact as well as

soil/P-fertilizer contact (Eghball et al. 1990). Applied P fertilizer in the soil typically

moves only a short distance (Akinremi and Cho 1991; Eghball et al. 1990; Hashimoto

and Lehr 1973). This movement is primarily by diffusion. Most of the P applied stays in

the top 5 cm even after excess poultry litter application (Lucero et al. 1995). The low

mobility of P in soil is due to the reactive nature of P with soil constituents which leaves

extremely low concentrations of P in soil solution.

2.4.1 Mechanisms of P Movement

There are generally three ways in which nutrient ions in soil may reach the root

surface: root interception, mass flow and diffusion. The importance of each mechanism

on the movement of ions depends on the ion itself and its concentration in soil solution.

Root interception and mass flow supply only about 10% or less of the P needed

for plant growth. The most important mechanism involving movement of P in soil is

diffusion (Tisdale et al. 1993). Diffusion is the process by which matter is transported

from one part of a system to another as a result of random molecular motions (Crank

1979). When a concentration gradient exists, net movement occurs by diffusion from locations of higher concentration to locations of low concentration (Barber 1995). The mathematical theory of diffusion in isotropic substances is therefore based on the hypothesis that the rate of transfer of the diffusing substance through a unit area of a section is proportional to the concentration gradient measured normal to the section, i.e.:

$$F = - D (dC) / (dx) \qquad [2.7]$$

where F is the rate of transfer per unit area of section (flux), C is the concentration of the diffusing substance, x is the space coordinate measured normal to the section, and D is the diffusion coefficient. Equation [2.7] is also called Fick's first law of diffusion. The fundamental differential equation of diffusion in an isotropic medium is derived from Equation [2.7]:

$$\partial C/\partial t = D (\partial^2 C) / (\partial x^2) \qquad [2.8]$$

where $\partial C/\partial t$ is the rate of change in concentration with time at a fixed distance. Equation [2.8] is called Fick's second law of diffusion.

The diffusion coefficient controls the rate of diffusion as demonstrated in Equations [2.7] and [2.8]. It has been reported that the diffusion coefficient of P is 0.89×10^{-5} cm^2 s^{-1} in water and 10^{-8} - 10^{-11} cm^2 s^{-1} in soil (Barber 1995). Nye and Barber (1977) suggested that the effective diffusion coefficient (D_e) used to describe ion movement in soil could be calculated as:

$$D_e = D_l \theta f(dC_l) / (dC_s) \qquad [2.9]$$

Here, D_e is the effective diffusion coefficient in soil, D_l is the value of D in water, θ is the volumetric soil water content, f is the tortuosity factor, and $(dC_l) / (dC_s)$ is the reciprocal

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of the soil buffer power for the ion in question. The relationship described in Equation [2.9] shows that as soil moisture content increases, D_e increases, which results in an increase in the diffusive flux, F. The effective diffusion coefficient (D_e) of P in soil is also directly related to the diffusion coefficient of P in water (D_l).

A number of factors can profoundly influence diffusive movement of P in soil. These factors include: (1) tortuosity factor (percentage volume of soil that is occupied by soil water and bulk density) (Hira and Singh 1977; Mahtab et al. 1971; Olsen et al. 1965), (2) chemical reaction of P with soil (Akinremi 1990; Lehr et al. 1957; Lewis and Racz 1969), (3) concentration and the amount of P present at the source (Bhadoria et al. 1991; Eghball et al. 1990; Kunishi and Taylor 1975; Lewis and Quirk 1967; Mahtab et al. 1971) and (4) temperature. All these factors either affect the effective diffusivity (D_e) or the P concentration gradients of P in soil.

2.4.2 Mathematical Models of P Movement in Soil

A chemical transport and transformation model for a particular chemical species embodies the following elements (Jury and Fluhler 1992):

1. A mass conservation law for the chemical species;

2. A division of mass into appropriate phases requiring separate description;

3. A flux law for each mobile phase, describing the rate of transport of chemical mass per unit area in that phase;

4. A series of inter-phase mass transfer laws describing movement between phases; and

5. A reaction term describing the rate of appearance or disappearance of mass per unit volume from the system.

The general equation describing the transport phenomenon of P in one-dimensional form can be written as (Cho 1991):

$$\partial(P)/\partial t = D\, \partial^2(P)/(\partial x^2) - v\, \partial(P)/(\partial x) + \phi \qquad [2.10]$$

where (P) is the concentration of phosphate in the soil solution and D is either the diffusion or dispersal coefficient, depending on whether v, the speed of the center of mass of the soil solution, is zero or not zero. The terms x and t stand for distance and time, respectively. The last term ϕ stands for either retention or release of solution phosphate, and is expressed as the rate of change in the solution phosphate concentration.

Numerous mathematical models have been developed over the years to describe the movement of P in soil. As Cho (1991) pointed out, the transport characteristics of phosphate are predominantly controlled by the term ϕ. As shown in Equation [2.10], the movement of fertilizer P is directly related to the diffusive movement (D $\partial^2(P)/(\partial x^2)$), the advective movement (- v $\partial(P)/(\partial x)$) and all sources and sinks (ϕ) of P. Since the P solution concentration is so low in soil, advective movement of P is very limited. To predict the transport of reactive solutes in soil, models that include all sources and sinks of P in soil are needed (Selim 1992). For phosphate, reactions that possibly affect sources and sinks of P are reversible and irreversible adsorption/desorption of P, precipitation of P minerals, and other mechanisms (e.g. biological transformations). Fixation and release reactions of P in soil are influenced by several soil properties, including bulk density, soil texture, pH, organic matter, and type and amount of dominant clay minerals as discussed in Section 2.3.3

2.4.3 Past Research on Mathematical Models of P Transport and Transformation

Several mathematical models have been developed in the past to predict the transport and transformation of P in soil. Distinguishing one model from another relies on how the sink and source term, ϕ, is treated. P reaction with soil matrix can be assumed to be instantaneous, (equilibrium model), time dependent (non-equilibrium model), or a combination of both (multi-reaction model).

2.4.3.1 Equilibrium Based Model

The equilibrium models are those for which P reaction with soil is assumed to be fast or instantaneous in nature and equilibrium is observed in a relatively short reaction time (de Camargo et al. 1979). The Langmuir and Freundlich models are perhaps the most commonly used equilibrium models for describing P retention or release in soil. In these models, adsorption is responsible for the retention of P in soil. The P transport model then becomes:

$$\partial(P)/\partial t = D\partial^2(P)/(\partial x^2) - v\partial(P)/(\partial x) + (\partial S_p)/(\partial t) \qquad [2.11]$$

where S_p is the amount of P adsorbed (-) or desorbed (+) from the soil matrix. $S_p = K_d C^b$ if the Freundlich adsorption isotherm is used and $S_p = V_{max}(P)/[1/K_l + (P)]$ if the Langmuir isotherm is used. K_d, b and K_l are constants and (P) is the concentration of P in solution.

2.4.3.2 Non-Equilibrium Based Model

Non-equilibrium models assume that P retention or release processes are time dependent. The most commonly used non-equilibrium models are based on first- or second-order reaction rates with the reactions being either reversible or irreversible

(Enfield and Ellis Jr. 1983; Enfield et al. 1981a; Enfield and Shew 1975; Gerritse 1989; van Riemsdijk et al. 1984). The P transport model with irreversible first order kinetics then becomes:

$$\partial(P)/\partial t = D\, \partial^2(P)\,/\,(\partial x^2) - v\, \partial(P)\,/\,(\partial x) - k(P) \qquad [2.12]$$

where $-k(P)$, irreversible first order kinetics, represents P retention due to precipitation.

2.4.3.3 Multi-Reaction Based Model

Mansell et al. (1977b) reported that neither reversible-instantaneous or kinetics adsorption-desorption processes adequately describe experimental data for phosphorus transport in the surface soil tested. Mansell at al. (1977a) developed a mathematical model of P transport by taking into consideration P in solution as well as immobilized (chemi-sorbed) and precipitated P. Models have been developed which consider both adsorption and precipitation of P in transport models (Enfield and Ellis Jr. 1983; Enfield et al. 1981b).

2.4.3.4 Muti-Reaction, Multi-ions Based Model

When fertilizer P is applied to the soil, P movement is affected by a series of reactions, including cation exchange, precipitation, dissolution, and adsorption. Since all these reactions are occurring simultaneously, the consequence of one reaction can have a great impact on the others. Thus, we cannot accurately model P movement without considering all the ions involved.

However, most models use one equation to describe the movement of P. This is inadequate. As Cho (1991) pointed out, most P-transport models do not include the effect of the exchangeable cations on phosphate transport in soil. In his model, four

transport equations are used to describe P movement in a Ca^{2+}-saturated, cation-exchange media. These four equations consider K^+, Ca^{2+}, H^+, and phosphate and the effect of cation exchange, $CaCO_3$ dissolution and Ca-P precipitation reactions on P movement. Cho's (1991) model is unique since it considers all ionic species involved in P reaction within the soil matrix. It is well known that any given ion does not move in isolation (electro-neutrality). A model based on thermodynamic concepts (in contrast to empirical ones) should follow the law of chemical equilibrium, the principle of mass balance and the principle of electro-neutrality (Schulthess and Sparks 1991). Cho's (1991) model is more realistic because it is the only one which considers electro-neutrality among all interacting ionic species in the transport model of phosphate rather than just P by itself.

3. PRELIMINARY EXPERIMENTS ON THE PRODUCTION OF H^+ IONS DURING THE PRECIPITATION OF ALUMINUM AND PHOSPHATE

Abstract

The production of H^+ or OH^- ions during aluminum and phosphate interaction is very important in the study of P fixation in acid soil. A series of experiments were designed to investigate the effect of solution pH on aluminum and phosphate precipitate formation and the production of H^+ or OH^- ions in aqueous solutions. Preliminary results showed that the production of H^+ or OH^- ions during aluminum and phosphate interaction was greatly dependent on the solution pH. When solution pH was low, H^+ ions were produced whereas if the solution pH was high, OH^- ions were produced. Precipitation of Al-P and the formation of taranakite were also pH dependent. Precipitation was slower and precipitates remained in a non-crystalline form longer at low pH than at high pH. The precipitates in a crystalline form did not dissolve in 1M HCl.

3.1 Introduction

Low P fertilizer use efficiency, due to phosphate fixation, is one of the most common agricultural problems. Most of the P fertilizer applied to soil very quickly becomes quite insoluble after application. However, the mechanisms of P fixation are still not fully understood. Phosphate adsorption onto clay surfaces has been stated as one of the main causes of decreasing P solubility and availability. However, most research

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indicates that adsorption only plays a role when soil P concentration is very low. In other

words, the concentration of P in soil solution has to be lower than that supported by the

solubility of P minerals.

Immediately after application, P concentration near a fertilizer granule is very

high. Sample et al. (1980) found that P concentration near a fertilizer band could be as

high as 4.5 M. Thus, precipitation of Al-P is the main mechanism that decreases fertilizer

P movement and availability in acid soils (McBride 1994). Cho (1991) pointed out that

H^+ ions are produced during phosphate precipitation and that H^+ ion production is a major

factor in the movement and availability of P in soil. Decreases in pH have been observed

in calcareous soil after P fertilizer application (Akinremi and Cho 1991; Sample et al.

1980). The decrease in pH in acidic soil after P fertilizer application has been attributed

to hydrolysis of $Al(OH)_3$ by some researchers (Hsu and Rennie 1962). However, the

significance of precipitation of Al-P on the production of H^+ ions may have been under-

estimated. Information on H^+ ion production and consumption is fundamental to the

understanding of mechanisms of P fixation in soil and, ultimately, fertilizer P use

efficiency.

The objectives of this experiment were to investigate:

1. the interactions between Al and P in aquatic solutions;

2. the production and fate of H^+ ions during the precipitation of Al-P; and

3. the formation of taranakite and its solubility in acidic medium.

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3.2 Materials and Methods

3.2.1 Experiment I: Change in Solution pH due to P and Al Interaction

Two phosphate solutions, 0.5 and 1 M, were prepared using KH_2PO_4. Aluminum

solutions of 0.06, 0.10, 0.14, 0.18, 0.22, 0.26, 0.30, 0.34, 0.38, 0.42, 0.46 and 0.50 M

were prepared using $AlCl_3$. Ten mL of either phosphate solution were added to 10 mL of

$AlCl_3$ solution of each concentration in a 50 mL centrifuge tube. After the mixing, the

pH values of the mixtures were measured using non-seepage combination electrodes

(Canlab). For comparison purposes, ten mL of distilled water, or 10 mL of 0.5 and 1 M

KCl solution, were mixed with 10 mL of Al solution of various concentrations. The pH

of these mixtures were measured in the same way. For comparison, the pH values of

these solutions after mixing were also calculated. The calculation was based on the

assumption that there are no interactions between the Al and P and the resulting pH is the

average of H^- ions concentration of the two solutions after mixing.

3.2.2 Experiment II: Titration of Phosphate with Aluminum Solutions at Varying pH Levels

Two phosphate solutions of 0.1 M were prepared using either KH_2PO_4 or K_2HPO_4.

The pH of the two solutions were adjusted using 1 M HCl or 1 M NaOH to pH values of

4.54 and 8.89 for KH_2PO_4 and K_2HPO_4, respectively. Three Al solutions of 0.01 M were

prepared using $AlCl_3$. The pH of the three Al solutions was adjusted in the same manner

as for phosphate to pH values of 3.00, 4.47 and 6.01.

Fifty mL of P solution was transferred into an Erlenmeyer flask and its pH

measured. The solution was then titrated with Al solution in 1 mL increments until 100

mL of solution had been added. After the addition of each mL of Al solution, the pH was

measured. The pH values during the titration were also calculated following the same procedures as in Experiment I.

3.2.3 Experiment III: Effect of Al Concentration on Al-P Precipitation and Crystallization

Solutions of Al and P similar to those used in experiment I were used to determined the time required for Al-P to precipitate and to crystallize. Solutions of $AlCl_3$ of 0.06, 0.1, 0.12, 0.14, 0.18, 0.22 and 0.26 M were added to the 0.5 M P solutions. Solutions of $AlCl_3$ of 0.3, 0.34, 0.38, 0.42, 0.46 and 0.5 M were added to the 1 M P solutions. Equal volumes, each of 20 mL of the Al and P solutions, were mixed in 50 mL centrifuge tubes. The final solution concentrations of Al were 0.03, 0.05, 0.06, 0.07, 0.09, 0.11 and 0.13 M at a P level of 0.25 M and 0.15, 0.17, 0.19, 0.21, 0.23, and 0.25 M at a P level of 0.5 M.

The length of time before Al-P precipitates appeared was determined by daily visual inspection of the solutions. The time of appearance of taranakite (the crystalline form of Al-P precipitate) was determined by X-ray diffraction analysis. Samples for X-ray diffraction analysis were prepared by washing the Al-P precipitate with ethanol, followed by air-drying on a glass slide. X-ray patterns were recorded in the 2-35° 2θ portion of the spectra.

The precipitates obtained above, aged for 2.5 years in the original solution, were used in the determination of the solubility of taranakite in acid. The precipitates (1 g in weight) were re-dispersed into 20 mL of distilled water or 1M HCl and shaken for

various periods of time and then centrifuged for 10 min. The solution was siphoned off and the remaining solid was dried at 40^0C and weighed.

3.3 Results and Discussion

3.3.1 Experiment I: Change in Solution pH due to P and Al Interaction

Adding 0.5 M KCl or distilled water to $AlCl_3$ solutions of various concentration increased pH only slightly (Figure 3.1). The slightly higher pH after the addition of H_2O or KCl to $AlCl_3$ solution was probably only due to dilution. In contrast to these relatively small changes, adding KH_2PO_4 caused a large decrease in pH. Thus, the interaction between KH_2PO_4 and $AlCl_3$ produced H^- ions, lowering pH. The magnitude of decrease in pH increased with increasing concentration of Al at both P levels. The decrease in pH was greater with 0.5 than with 1 M KH_2PO_4, suggesting that an excess of P was in the 1 M KH_2PO_4 solution.

3.3.2 Experiment II: Titration of Phosphate with Aluminum Solution at Varying pH Levels

The pH values obtained during the titration of P solutions (which had pH values of 4.54 and 8.89) with Al solutions of various pH values (3.00, 4.47, 6.01) are shown in Figure 3.2. Also shown are the calculated pH values based on the mixing of the two solutions with different pHs, but assuming no Al-P interaction. pH values were affected by the initial pH of the Al and P solutions and decreased with the volume of Al solution added during titration.

The pH of the solutions decreased with the volume of $AlCl_3$ added, when 0.1 M KH_2PO_4 (at pH 4.5) was titrated with Al solutions (pH of 3.00 and 4.47). On the other
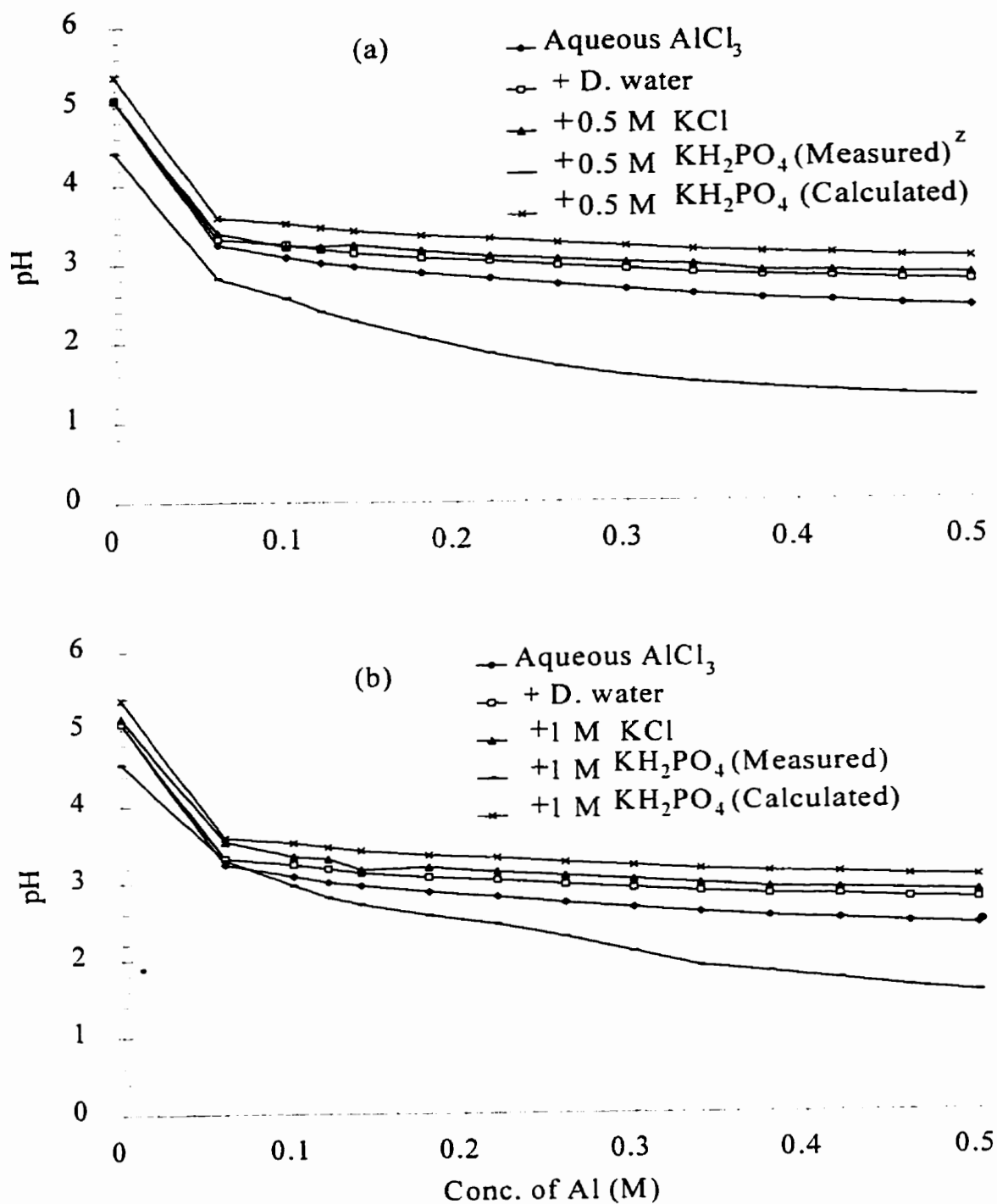
Figure 3.1 Effect of Al-P interaction on H^+ ions production (a) P concentration of 0.5 M and (b) P concentration of 1M. (initial pH values for distilled water, 0.5 M KCl, 1 M KCl, 0.5 M KH_2PO_4, and 1 M KH_2PO_4 are 5.9, 5.3, 5.3, 4.42, 4.55 respectively).

z Bassed on the mixing of the two solutions with different pH, but assuming no Al-P interaction.
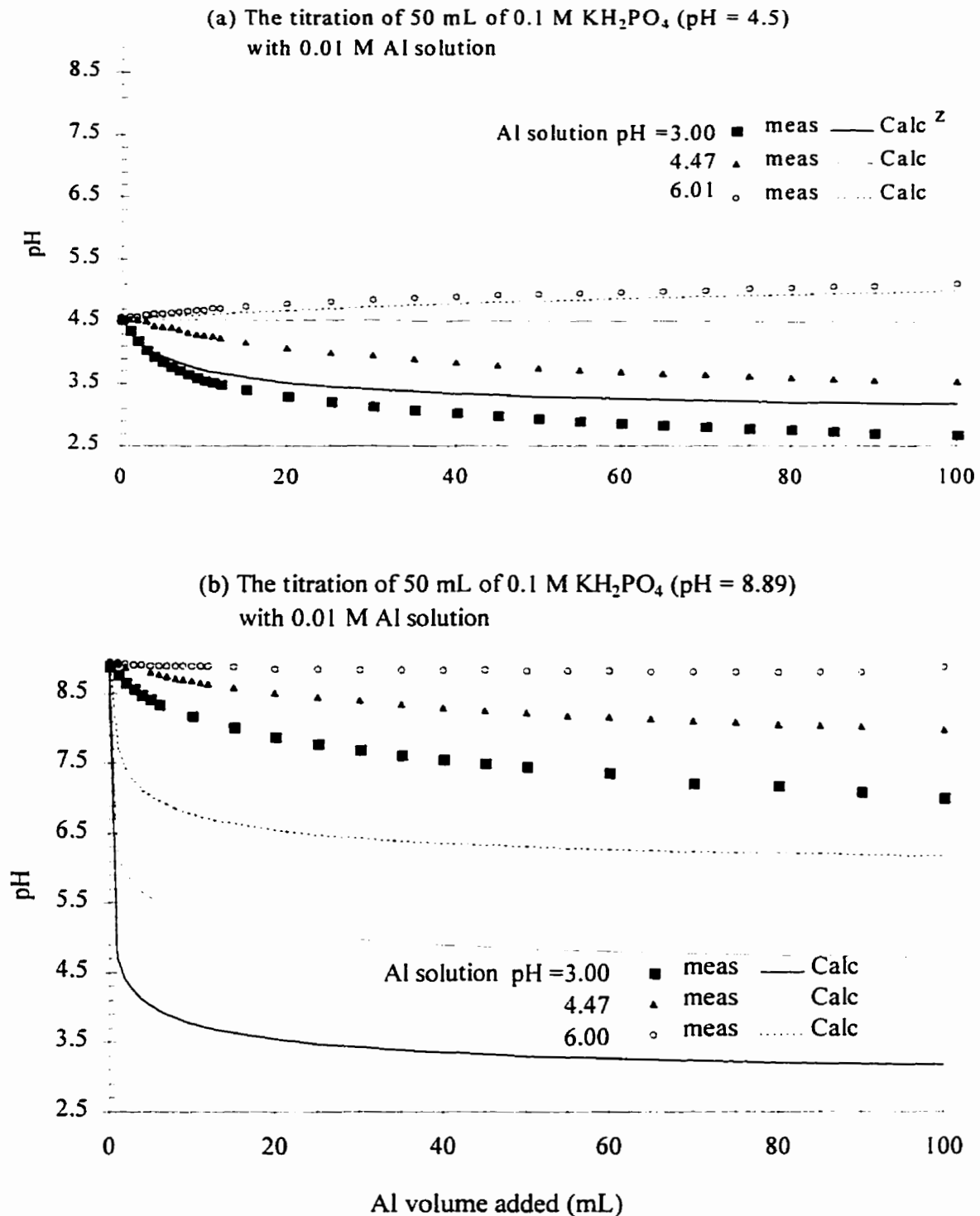
Figure 3.2 Titration curves of phosphate with Al as affected by initial pH.

z Bassed on the mixing of the two solutions with different pH, but assuming no Al-P interaction.

hand, the solution pH increased during titration when the Al solution had an initial pH of

6.01 (Figure 3.2a). The calculated pH values for the above titrations showed similar

trends, i.e., pH decreased with the addition of Al solution when the Al solution had an

initial pH of 3.00 and 4.47, and pH increased during the titration when the Al solution

had an initial pH of 6.01 (Figure 3.2a). However, both the observed decreases (with Al

solution at pH 3.00 and 4.47) and increases in pH (with Al solution at pH 6.01) were

much larger than the calculated pH values. Table 3.1 shows pH values of the solutions

before and after titration with $AlCl_3$. As expected, the calculated pH values (3.17) are

lower than the initial P solution of pH of 4.54 when it was combined with an Al solution

of pH 3.00. However, the observed pH value (2.68) was much lower than the pH values

of both solutions. Similarly, when the P solution with a pH value of 4.54 was titrated

with an Al solution of pH 4.47, the measured pH of 3.52 was much lower than the

calculated value (4.49). In contrast, when an Al solution of pH 6.01 was used, the

calculated pH of 4.99 was higher than the initial pH values of the P solution. However,

the measured value of 5.06 was only slightly higher than the calculated value. It is

evident that the observed pH values were lower than the calculated ones and this was a

result of the production of H⁻ ions.

The pH of the solution was observed to have decreased during titration when 0.1

M K_2HPO_4 at pH 8.89 was titrated with all three $AlCl_3$ solutions (Figure 3.2b). The

calculated pH values for the above titration showed similar trends, but were much lower

than measured values (Figure 3.2b). As stated previously, the calculated values of pH

were based on mixing the P and Al solutions of different pH without interaction between

Al and P. Thus, the observed pH values, which were higher than the calculated values,

Table 3.1 Final pH resulting from the titration of 0.1 M KH_2PO_4 and 0.1 M K_2HPO_4 with 0.01 M Al solution.

Initial pH			Final pH	
P source		$AlCl_3$	Measured (Al-P)	Calculated[w] (Al-P)
KH_2PO_4	4.54	3.00	2.68	3.17
	4.54	4.47	3.52	4.49
	4.54	6.01	5.06	4.99
K_2HPO_4	8.89	3.00	7.01	3.18
	8.89	4.47	7.99	4.72
	8.89	6.01[x]	8.88	6.19

x At pH 6.01, Al hydroxide would be expected and was observed in the solution.
w Based on the mixing of the two solutions with different pHs, but assuming no Al-P interaction

were due to the production of OH^- ions. The production of H^+ or OH^- ions were dependent on the initial pH of the system (Figure 3.2).

3.3.3 Experiment III: Effect of Al Concentration on Al-P Precipitation and Crystallization.

The time required for a precipitate to form and for the precipitate to convert to a crystalline form (taranakite) increased with increases in initial Al concentration and with decreasing pH for both phosphate concentrations (Table 3.2). There were very good correlations between the initial Al concentration and solution pH with the time needed for precipitation and crystallization (Tables 3.3 and 3.4). The increase in the time required for precipitation or crystallization with increasing initial Al concentration appears to contradict the law of mass action. Normally, the rate of Al-P formation should increase with increases in Al concentration at constant concentration of P. During the experiment, precipitates appeared immediately after addition of the first increment of Al solution. But, after adding more Al solution, the precipitate disappeared (low pH levels). It is

Table 3.2 Time required for precipitation and crystallization to occur as affected by solution pH.

initial Al Conc.	pH ppt	Time ppt	pH cry	Time cry
M		d		d
Initial P conc. at 0.25M KH₂PO				
0.03	2.68	0.1	2.60	9
0.05	2.46	0.1	2.38	9
0.06	2.33	1	2.27	9
0.07	2.21	4	2.13	9
0.09	1.95	9	1.95	16
0.11	1.75	9	1.75	16
Initial P conc. at 0.50M KH₂PO₄				
0.13	2.15	0.1	2.05	4
0.15	1.98	1	1.96	4
0.17	1.88	4	1.72	9
0.19	1.66	9	1.66	9
0.21	1.57	9	1.57	9
0.23	1.41	9	1.41	9
0.25	1.40	9	1.40	16

Table 3.3 Correlation analysis among Al concentration, pH and time required for precipitation and crystallization (KH_2PO_4 = 0.25 M).

	initial Al Conc.	pH_{ppt}	$Time_{ppt}$	pH_{cry}	$Time_{cry}$
initial Al Conc.	1.000				
pH_{ppt}	-0.999***^{v}	1.000			
$Time_{ppt}$	0.932***	-0.942***	1.000		
pH_{cry}	-0.996***	0.998***	-0.946**	1.000	
$Time_{cry}$	0.858*	-0.870*	0.941**	-0.862*	1.000

v Symbols *, ** and *** represents p = 0.05, 0.01, and 0.001, respectively.

Table 3.4 Correlation analysis among Al concentration, pH and time required for precipitation and crystallization (KH_2PO_4 = 0.5 M).

	initial Al Conc.	pH_{ppt}	$Time_{ppt}$	pH_{cry}	$Time_{cry}$
initial Al Conc.	1.000				
pH_{ppt}	-0.986***	1.000			
$Time_{ppt}$	0.903***	-0.944***	1.000		
pH_{cry}	-0.981***	0.982***	-0.927***	1.000	
$Time_{cry}$	0.879***	-0.814*	0.761*	-0.855**	1.000

suspected that the precipitate was stable at low Al concentration (corresponding to a higher pH). However, the precipitate became unstable and thus dissolved as Al concentration increased (corresponding to a lower pH). As the time of incubation progressed, a different form of Al-P solid, such as taranakite, probably formed and the quantity of precipitate formed increased with the concentration of Al solution as described by the law of mass action. Taranakite is very stable in acid as indicated by the amount left when it was shaken in 1 M HCl for a short time period (< 20 min, Figure 3.3).

The interaction of Al with phosphate is a complicated process and the results presented here show that the pH of the system can increase or decrease when P reacts with Al. The magnitude of increase or decrease in pH was dependent on the initial pH of the Al and P solutions. There are several hydrolyzed Al species (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3^0$) which could potentially interact with several phosphate ions ($H_3PO_4^0$, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}). Since the proportions of each Al and phosphate species are controlled by the pH of the system, the interaction of Al with P would, however, shift any such equilibrium and thus increase or decrease the concentration of the
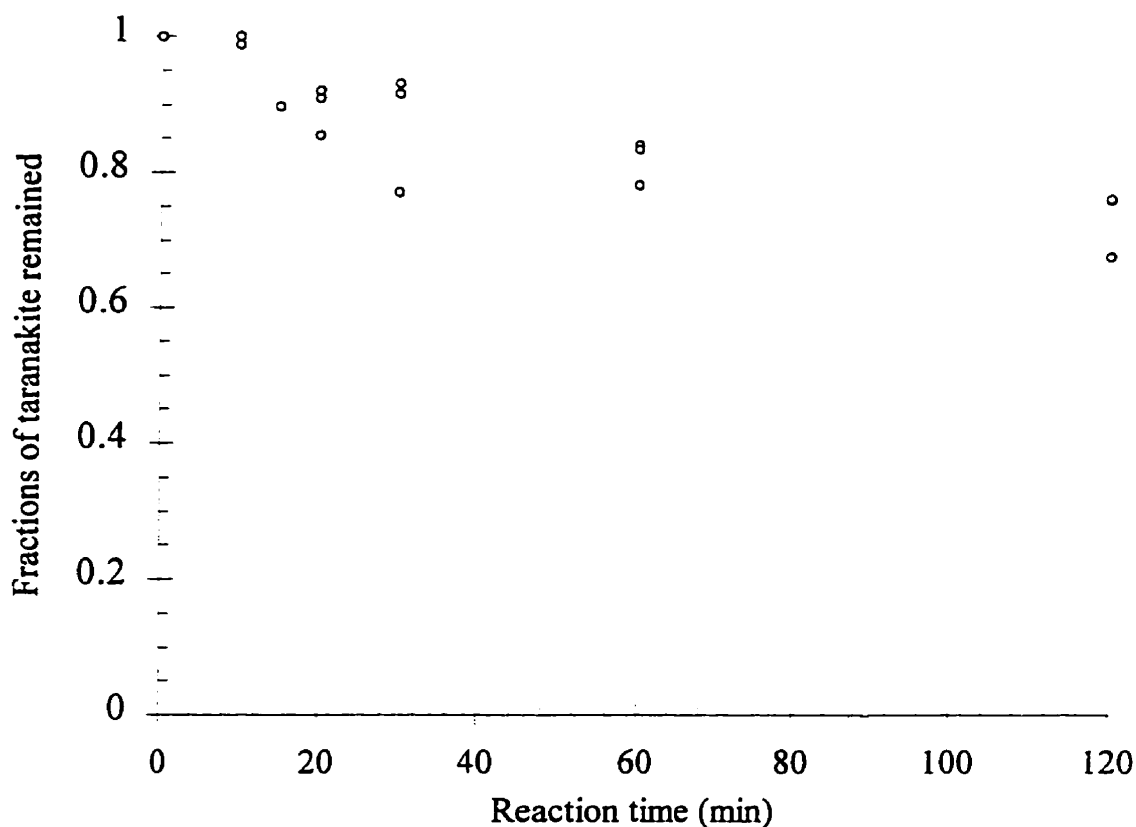
Figure 3.3 The solubility of taranakite in acid measured as the residual weight after reaction with 1 M HCl for various time of periods.

various species. Thus the pH could either increase or decrease as a result.

For experiment I, measured pH values are all lower than the calculated ones since the initial pH of the Al solution are all very low (2.7 to 3.2). At such low pH, majority of Al is in the Al^{3+} form. The equation for the formation of taranakite is commonly written as:

$$3K^+ + 5Al^{3+} + 8H_2PO_4^- + 18H_2O \rightleftharpoons H_6K_3Al_5(PO_4)_8 \bullet 18H_2O + 10H^- \quad [3.1]$$
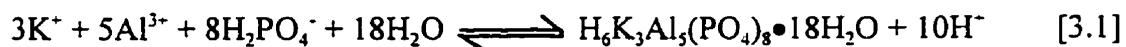
Equation [3.1] assumes that Al^{3+} and H_2PO_4 are the reacting species. But the equation could also be written as:

$$3K^+ + 5Al^{3+} + 6HPO_4^{2-} + 2PO_4^{3-} + 18H_2O \rightleftharpoons K_3Al_5(PO_4)_2(HPO_4)_6 \bullet 18H_2O \quad [3.2]$$

47
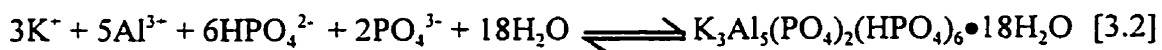
Thus, it is not known which are the reacting species. Equation [3.1] clearly shows the production of H^+ ions during the formation of taranakite. But there will also be production of H^+ ions in acid soil if equation [3.2] is true. Under low pH conditions, most phosphate is in the form of $H_2PO_4^-$ and $H_3PO_4^0$. The consumption of HPO_4^{2-} in equation [3.2] would cause the conversion of $H_2PO_4^-$ and $H_3PO_4^0$ to HPO_4^{2-} and thus produce H^+ ions.

Titrating phosphate solutions of varying pH with Al solutions showed that, under certain conditions, pH values were either higher or lower than the calculated pH values. The calculated values are obtained assuming no interaction between Al and P. Thus, there must have been interactions between Al and P because all measured pH values were different from those calculated. Instances in which the pH was lower than the calculated values resulted from H^+ ion production during Al-P interaction. However, instances in which the observed pH values were higher resulted from OH^- ion production. In other words, H^+ or OH^- ions were generated during Al-P interaction. Once again, the production of H^+ ions was observed when pH was initially low. The production of OH^- ions (or consumption of H^+ ions), on the other hand, was observed when pH was initially high. The H^+ or OH^- ions produced could be a result of one or more of the following processes:

1. formation of Al-P complexes;

2. hydrolysis of Al;

3. dissociation of phosphates;

4. formation of Al-P precipitate; and

5. adsorption of phosphate onto surfaces of Al hydroxides, especially when the

   Al solution had a pH value of 6.01.

All of the above processes could potentially affect H^+ or OH^- ion production during Al-P

interaction and the effects are strongly pH-dependent.

3.4 Summary and Conclusions

The interaction of Al and phosphate with the concomitant production of H^+ or OH^-

ions was investigated in pure solution in the laboratory. Differences between measured

and calculated pH values were observed in all experiments conducted. Thus, H^+ or OH^-

ions were produced during Al-P interaction. The differences in observed and calculated

pH were also dependent on the initial pH value of Al and P solutions. When the initial

pH values were low, hydrogen (H^+) ions were produced. When the initial pH values were

high, OH^- ions were produced (or H^+ ions were consumed). The production of H^+ or OH^-

ions also affected the time required for Al-P to precipitate and for the Al-P precipitate to

change from a X-ray amorphous form to a crystalline form. There was a significant and

strong negative relationship between the solution pH and time required for the precipitate

to form and the time required for the non-crystalline Al-P precipitate to form a taranakite.

4. MOVEMENT OF PHOSPHATE AND ASSOCIATED CATIONS IN ALUMINUM-RICH SOIL-LIKE SYSTEMS

Abstract

Phosphate fertilizers applied to soil are quickly converted into insoluble forms. Thus, phosphate availability to plants is rather limited. Although much work has been done, the phosphate fixation process is not yet fully understood. This research hypothesizes that phosphate fertilizer, when applied to Al-rich acidic soils, results in release of Al from cation exchange sites. The released Al reacts with phosphate, forming an insoluble salt while simultaneously releasing H^+. The released H^+ dissolves gibbsite and supplies more Al for phosphate fixation. This hypothesis was tested in a one-dimensional sand column containing an Al-saturated cation exchange resin with or without synthesized gibbsite. Columns with surface applied mono-potassium phosphate were incubated in a constant humidity chamber for various time periods. Both exchangeable Al and gibbsite retarded phosphate and potassium movement. The presence of exchangeable Al was essential to trigger P fixation. The combination of exchangeable Al and gibbsite had a far greater effect on phosphate movement and fixation than the sum of the individual effects. The cation exchange reaction and H^+/OH^- ion production or consumption played an important role in P movement and fixation reactions.

4.1 Introduction

Phosphate (P) fertilizer applied to soil typically moves only a short distance (Akinremi and Cho 1991; Eghball and Sander 1989; Eghball et al. 1990; Sharpley 1986) because of the tendency for P to react with certain soil constituents. Applying phosphate fertilizer to mineral soils usually results in an initial rapid conversion from water-soluble orthophosphate ($H_3PO_4^0$, $H_2PO_4^{1-}$, HPO_4^{2-} and PO_4^{3-}) to less soluble forms. Some of the applied phosphate remains in the soil solution, some becomes adsorbed to soil colloidal material, and some precipitates with cations such as Al, Fe and Ca. In highly weathered tropical acid soils, exchangeable Al and Al and Fe oxides and hydroxides are the main components responsible for P fixation.

When a granule of P fertilizer dissolves in the soil, the solution moving into the surrounding soil is highly concentrated with respect to P and associated cations (Sample et al. 1980). As this concentrated solution moves through the soil, cations, such as Al and Fe, associated with soil minerals in acid soils are dissolved or released through cation exchange reactions (Cho and Akinremi 1991; Lindsay et al. 1962). As the concentration of these cations increases, a point is reached at which precipitation of Al and Fe phosphates occurs. These reactions are the main mechanisms of P fixation near fertilizer granules and account for the low mobility of P in soil. Sanchez and Uehara (1980) reported that each 1 cmol of exchangeable Al per kg soil can fix up to 102 mg of P.

Gibbsite is one of the most common minerals in acid soils and is frequently proposed as the solid phase which controls Al activity in soil solution (Menzies et al. 1994a; Richard and Adams 1970). However, well crystallized gibbsite alone shows no P fixation ability (Burnham and Lopez-Hernandez 1982). Past P movement studies paid

little attention to the reactions of P with soil constituents, even though these reactions are detrimental to P movement. A single observation of P movement in soil is not sufficient; we also need to have scientific explanations for these observations. Thus, there is a need to examine the reactions and movement of associated cations in studying P movement.

Soil is a very complicated system and thus it is very difficult to differentiate among the effects of various sources of Al and/or Fe in P fixation. For example, is P precipitation due to Al and/or Fe from exchangeable sources or is it due to Al and/or Fe from mineral dissolution? If mineral dissolution occurs, which minerals would be dissolved? There is also the question of whether adsorption or precipitation of P is the main mechanism of P fixation. Soil is not an ideal medium in which to study or separate the effects of exchangeable cations and mineral dissolution on P fixation, since the source of the cation cannot be readily identified.

Cation exchange resins have been used to simulate soil conditions in studies of this nature (Akinremi and Cho 1991; Kim et al. 1983) for several reasons. First, cation exchange resins do not adsorb phosphate. Therefore, all P fixation is attributable to precipitation. Second, the type and the amount of cations on the exchange site can be controlled. Third, resins are uniform and homogeneous.

A series of experiments were designed using an Al-saturated cation exchange resin and laboratory synthesized gibbsite to:

1. examine the mechanism of P fixation in Al-rich acidic soils;

2. study the effect of cation exchange and H^+ ion production/consumption on Al-P fixation reactions; and

3. study P movement as affected by fixation reactions.

4.2 Research Model

Cations, applied as integral parts of phosphate fertilizer, exchange with cations on

the soil surfaces. It is hypothesized that when a phosphate fertilizer, such as KH_2PO_4, is

applied to a soil with exchange sites dominated by Al, the K^+ ion, because of its high

concentration, will release a considerable amount of exchangeable Al into the soil

solution. The Al released can react with the phosphate ion to form an insoluble salt,

presumably a taranakite, and at the same time release H^+ ions. The H^+ ions released can

then dissolve solid Al compounds (i.e., gibbsite $Al(OH)_3$). The dissolution of $Al(OH)_3$ by

H^+ supplies more Al for phosphate fixation. The reactions for the above model, outlined

in Figure 4.1 can be expressed as:

$$18\ KH_2PO_4 \rightleftharpoons 18\ K^+ + 18\ H_2PO_4^- \qquad [4.1]$$

$$15\ K^+ + Al_5\text{-Resin} \rightleftharpoons K_{15}\text{-Resin} + 5\ Al^{3+} \qquad [4.2]$$

$$5\ Al^{3+} + 3\ K^+ + 8\ H_2PO_4^- \rightleftharpoons K_3Al_5H_6(PO_4)_8\ (s) + 10\ H^+ \qquad [4.3]$$

$$10\ H^+ + 10\ Al(OH)_3(s) \rightleftharpoons 10\ Al(OH)_2^- + 10\ H_2O \qquad [4.4a]$$

or

$$10\ H^+ + 10\ Al(OH)_3(s) \rightleftharpoons 10\ AlOH^{2-} + 10\ H_2O + 10\ OH^- \quad [4.4b]$$
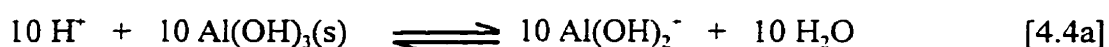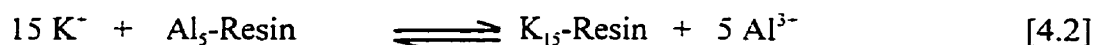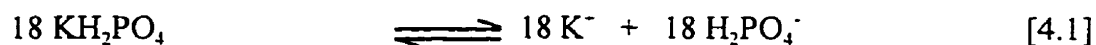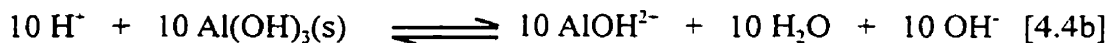
The degree of phosphate fixation depends on the level of exchangeable Al in soil, among

other things. This, in turn, determines the amount of soil Al initially liberated into

solution. Phosphate fixation also depends on the pH of the soil, which governs the

species distribution of both phosphate and Al ions. Phosphate fixation also depends on

the production and/or consumption of H^+ which determines the amount of Al that will be

(a) Exchangeable Al system
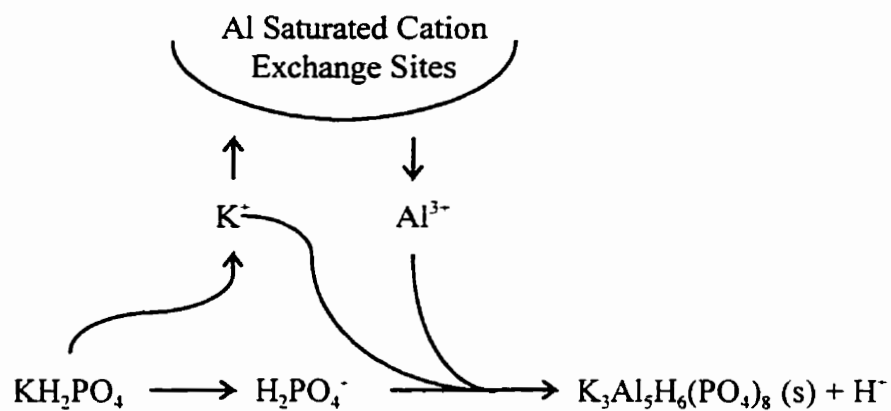
(b) Exchangeable Al and gibbsite system
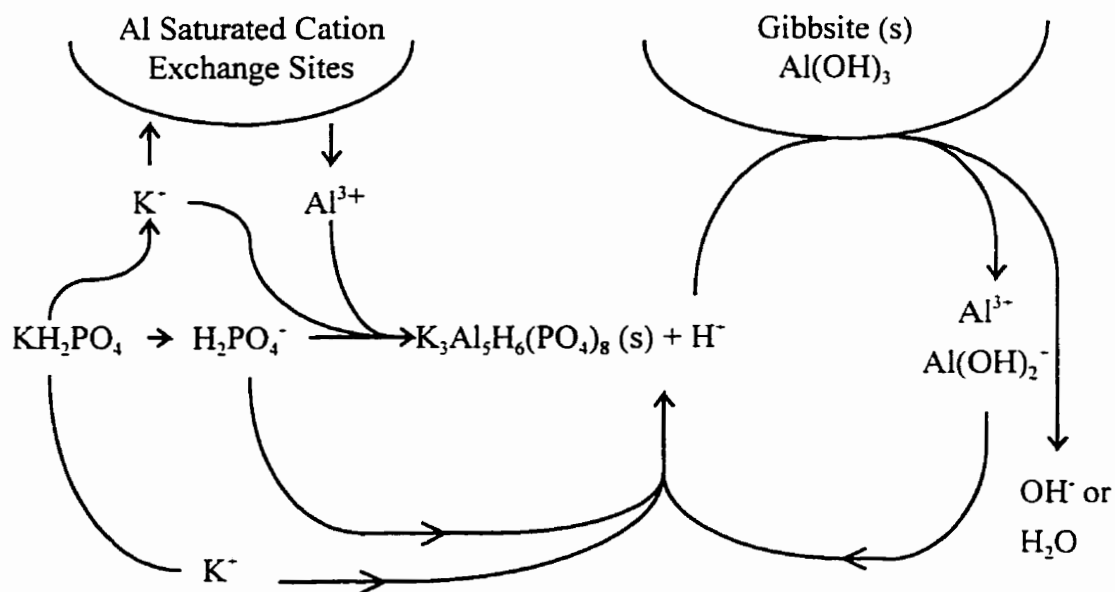
Figure 4.1 P fixation models in Aluminum rich systems

dissolved from solid forms. The rate of gibbsite dissolution in dilute acid has been reported to be comparable to the rate of decomposition for feldspars and increases with H^- ion concentration (Bloom and Erich 1987). Most researchers, studying phosphate-soil interaction, have concentrated on the interaction between solid Al or Fe compounds and the added water-soluble phosphate compound. However, laboratory studies have shown that the solid Fe or Al hydroxides, when aged, do not interact with water soluble phosphate as readily as generally observed for soils (Burnham and Lopez-Hernandez 1982).

This study attempts to clarify the roles of the H^- ion and the accompanying cation in the phosphate fertilizer on the movement and fixation of phosphate. The proposed hypothesis for phosphate fixation will be tested on a simulated soil system using sand and a cation exchange resin. The results will provide information on the types of reactions in a soil system during multi-ionic (K^-, P [$H_2PO_4^-$ and HPO_4^{2-}], Al [Al^{3-}, $AlOH^{2-}$, $Al(OH)_2^-$, $Al(OH)_3^0$], and H^-) diffusive transport. Particular attention will be paid to production or consumption of the H^+ ions during the processes of phosphate fixation and how this affects phosphate transport. A knowledge of the roles that exchangeable cations and H^- ions play in phosphate movement could help clarify the mechanisms and/or the dominant processes responsible for phosphate fixation in acidic soils.

4.3 Materials And Methods

To overcome the problems associated with the heterogeneous properties of soils, a system containing a cation exchange resin and gibbsite was chosen to simulate the

conditions similar to those prevailing in an acid soil. Two sets of experiments were designed to test the hypothesized model in Figure 4.1.

4.3.1 Experiment I: Effects of Exchangeable Al

The effects of exchangeable Al levels on P solution concentration and movement were studied. The systems consisted of a mixture of acid-washed sand and an Al-saturated cation exchange resin. The resin (Amberlite IR-120) had average diameters of 75 to 150 μm and a cation exchange capacity of 440 $cmol_c$ kg^{-1}. Saturation of the resin with Al followed the procedures outlined by Akinremi (1990). Briefly, a known amount of resin (40 g) was placed in a Buchner funnel and one liter of 0.5 M $AlCl_3$ solution was added in aliquots of 25 mL. The solution was removed by suction 5 min after its application. An additional 2 L of 0.025 M $AlCl_3$ solution in aliquots of 25 mL was then passed through the resin. The resin was washed with distilled water, until the silver nitrate test was negative for the chloride ion, and then air dried. The air-dry moisture content was determined. A sample of the air-dry resin was extracted with 1.0 M HCl. The chemical analysis of the extracts revealed the exchange sites were completely saturated with Al.

The acid-washed sand was thoroughly mixed with the Al-saturated resin in varying proportions to produce resin-sand mixtures with exchangeable Al levels of 0, 22, and 44 $cmol_c$ kg^{-1}. The mixture was moistened to field capacity water content with distilled water (Table 4.1) and thoroughly mixed. The mixture was placed into cylindrical columns constructed of paraffin, 4.5 cm in diameter and 10 cm long. Next, 0.2 g (1.47 mM) of KH_2PO_4 was applied uniformly to the surface of the resin-sand

mixture and the columns were incubated in a constant humidity chamber for various periods of time (Table 4.1). All treatments were conducted in duplicate.

After incubation, the columns were sectioned into 2 mm slices with a meat cutter. Samples were taken from each section for moisture content and chemical analysis. Approximately 1 g (dry weight) of the resin-sand mixture in each section was weighed into a 15 mL centrifuge tube. One mL of water was applied, and the pH of the mixture measured. Four mL of distilled water were then added. The samples were equilibrated by shaking for a period of 10 min and centrifuged. The clear solution was removed using a pipette. A second water-extraction was then conducted using 5 mL of distilled water as described above. The two water extractions were pooled. The concentration of P and K, measured in this fraction, were termed "the water-extractable fraction." The same resin-sand sample used for water-extraction was then subjected to three successive extractions using 5 mL 1M HCl. The three acid extracts were combined. The amount of P and K measured in this fraction were termed "the acid-extractable fraction." The water-

Table 4.1 Selected properties of the sand-resin columns and incubation periods.

Exchangeable Al levels	Bulk density	Field capacity Moisture content	pH	Incubation period
$cmol_c\ kg^{-1}$	$kg\ m^{-3}$	$kg\ kg^{-1}$		
0	1700	0.200	6.3	1 d, 3 d, 1 wk
22	1420	0.253	3.6	3 d, 1, 2, 4 wk
44	1250	0.302	3.6	3 d, 1, 2, 4 wk

extractable fraction approximates the amount of P and K in solution, whereas the acid-extractable fraction approximates the amounts of P and K in solid form.

The pH of the "soil" (1:1 in water) was determined using a sealed reference combination electrode made by Canlab. Phosphate in the extractants was determined by the modified ascorbic acid-ammonium molybdate method of Murphy and Riley (1962), while the extractable K^+ and Al^{3+} were determined using an atomic absorption spectrophotometer (Perkin-Elmer 1100B).

To further verify the changes in pH due to Al-P precipitation, a sub-experiment was designed. In this sub-experiment, 1.47 mM KCl instead of KH_2PO_4 was applied to the surface of a column with an exchangeable Al level of 22 $cmol_c$ kg^{-1} and incubated for 1 wk. All procedures were identical to those for the columns with KH_2PO_4.

4.3.2 Experiment II: Effects of Exchangeable Al and Gibbsite

The effect of gibbsite on P fixation and movement was studied using resin-sand-gibbsite mixtures. The columns consisted of the same materials and levels of exchangeable Al as used in Experiment I, except that 1.0% gibbsite was added to each column. Gibbsite was chosen because it is the most commonly found hydrous oxide in soils and is frequently proposed as the solid phase whose solubility controls Al activity in soil solution (Richard and Adams 1970).

The gibbsite was prepared by titrating 1 M $AlCl_3$ with 1 M Na(OH) to a pH of 6.0. The mixture was then washed daily by siphoning the clear water at the top of the container and replacing it with distilled water until the silver nitrate test for Cl^- was negative (about 2 wk). The pH of the solution was checked daily and, if the drop in pH was more than 1 unit, 1 M Na(OH) was added to adjust pH to 6.0. The gibbsite was aged

a total of 45 d at room temperature (22^0C). The final pH of the solution containing

gibbsite was 4.65. The gibbsite was dried and the air-dry moisture content was

determined. X-ray analysis showed that the gibbsite crystallized.

A sub-experiment using KCl instead of KH_2PO_4 was also carried out with the

columns consisting of 22 $cmol_c$ kg^{-1} exchangeable Al and 1% gibbsite. Instead of

KH_2PO_4, 1.47 mM of KCl was surface-applied and incubated for 1 wk. Experimental

techniques and procedures used were as outlined for Experiment I.

4.4 Results And Discussion

4.4.1 Experiment I: Effects of Exchangeable Al

4.4.1.1 Water- and Acid-extractable P

The distribution profiles of water-extractable P in the column were affected by

both the levels of exchangeable Al and time of incubation (Figure 4.2). The

concentration of water-extractable P was highest at the surface (15 μM g^{-1}) and decreased

with depth to zero at about 6.5 cm for the columns with no exchangeable Al

(exchangeable Al level = 0 $cmol_c$ kg^{-1}) after 1 d of incubation. The concentration of

water-extractable P at the surface of the column decreased with time of incubation

whereas the concentration of water-soluble P at the bottom of the column increased.

After 1 wk of incubation the concentration of water soluble P was nearly uniform within

the columns with no exchangeable Al; the concentrations of P at the surface and bottom

of the column were about 7-8 μM g^{-1} and 5 μM g^{-1}, respectively. The distribution

patterns obtained after 3 d of incubation were between those observed at 1 d and 1 wk.

The concentrations of water-extractable P for the columns with exchangeable Al levels of

Figure 4.2 Distribution of water-extractable P in various resin-sand mixtures as affected by time of incubation and levels of exchangeable Al.

22 and 44 cmol$_c$ kg^{-1} were also highest near the surface and decreased with depth. However, the downward movement of P was greatly reduced when compared to those observed with no exchangeable Al (Figure 4.2a). The reduction was greater for the columns with 44 cmol$_c$ kg^{-1} of exchangeable Al (Figure 4.2c), than for columns with 22 cml$_c$ kg^{-1} of exchangeable Al (Figure 4.2b). Even after 4 wk of incubation, phosphate moved only 5 cm and 3.9 cm in column with exchangeable Al levels of 22 and 44 cmol$_c$ kg^{-1}, respectively. The differences in the depths of P movement were small among the four different incubation times for columns with 22 and 44 cmol$_c$ kg^{-1}. The concentration of water-extractable P near the surface for the columns with exchangeable Al levels of 22 (Figure 4.2b) and 44 cmol$_c$ kg^{-1} (Figure 4.2c) decreased with time of incubation. This was also observed for the columns with no exchangeable Al (Figure 4.2a). The decrease in water-extractable P near the surface of columns without exchangeable Al was due to diffusion to lower depths. However, for the columns with exchangeable Al (Figure 4.2b and 4.2c), the reduction in water soluble P near the surface was probably due to a combination of downward diffusion and precipitation of P as Al-P.

The distribution profiles of acid-extractable P, which are the water-insoluble fractions, were also affected by levels of exchangeable Al and time of incubation (Figure 4.3). There was virtually no acid-extractable P for the columns with no exchangeable Al (Figure 4.3a). The distribution of acid-extractable P in columns with 22 cmol$_c$ kg^{-1} were quite different (Figure 4.3b) than in columns with 44 cmol$_c$ kg^{-1} exchangeable Al (Figure 4.3c). Most of the P was concentrated in the top 3 cm of the column with 44 cmol$_c$ kg^{-1} exchangeable Al, whereas a large amount of P penetrated to depths of 3 to 6 cm in the columns with 22 cmol$_c$ kg^{-1} of exchangeable Al. Acid-extractable P was also lower in the
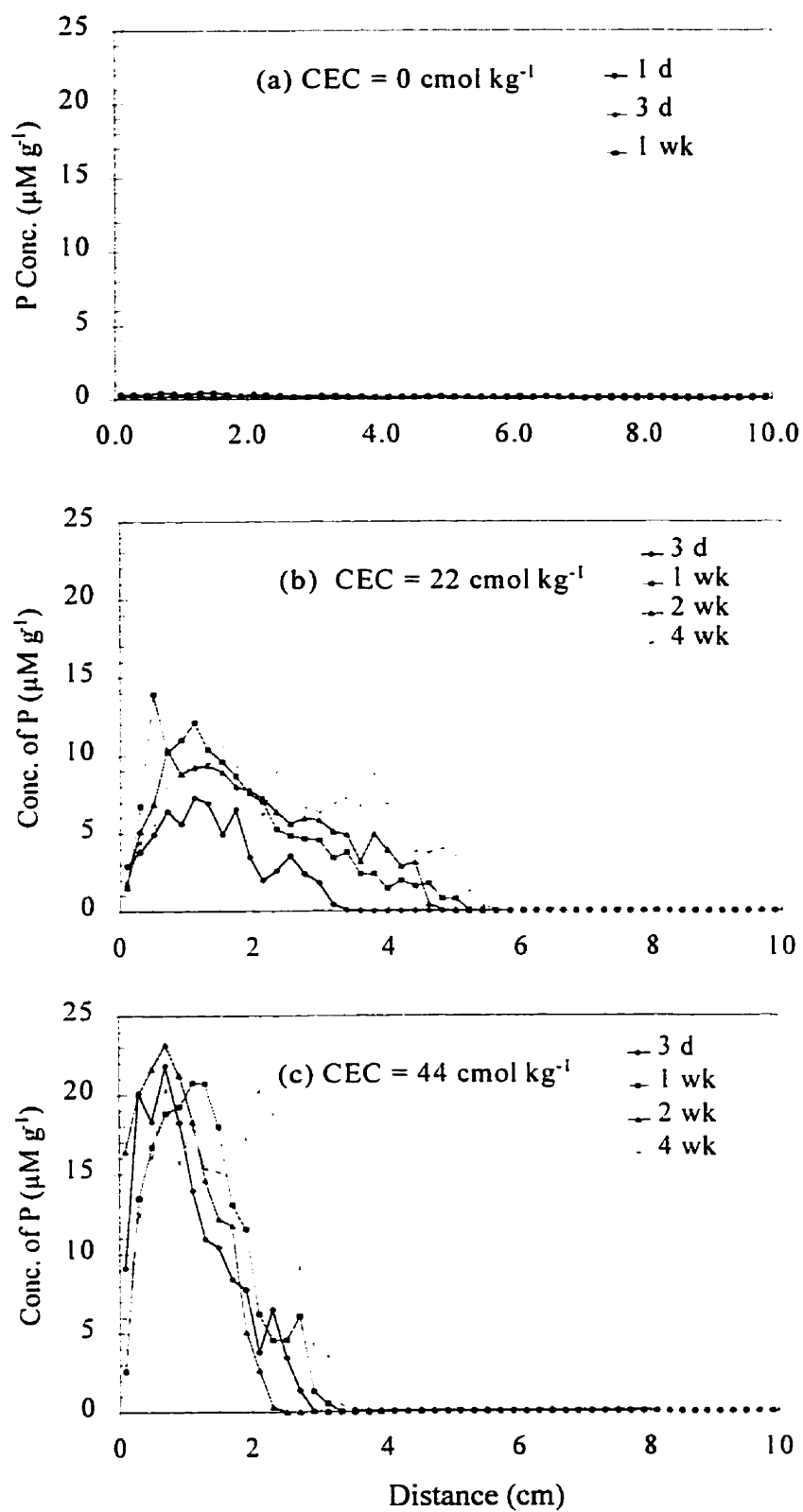
Figure 4.3 Distribution of acid-extractable P in various resin-sand mixture as affected by time of incubation and levels of exchangeable Al.

0 to 1 cm depth than in layers immediately below 1 cm for both exchangeable Al levels. The differences in distribution patterns were probably the result of differences in magnitude of Al-P precipitation as well as the rate of downward diffusion due to differences in exchangeable Al levels. More of the P would be precipitated at the surface of the column, due to the greater supply of Al from the cation exchange, for the columns with 44 $cmol_c$ kg^{-1} exchangeable Al as described in Equation [4.2]. Thus, there would be more acid-extractable P (precipitated) and less water-extractable P. Another implication of the higher precipitation with 44 than with 22 $cmol_c$ kg^{-1} exchangeable Al was that downward movement of P was reduced. Chemical interaction of an element reduces its mobility, because the total quantity of the element in soluble form is constantly decreasing due to interactions. Since only the soluble form is subject to diffusive transport, the magnitude of element transport would naturally decrease due to interaction.

4.4.1.2 Water- and Acid-extractable K

The distribution of water-extractable K (Figure 4.4) resembled those obtained for water-extractable P (Figure 4.2) and was affected by levels of exchangeable Al and time of incubation. For columns with no exchangeable Al and incubated for 1 d, the concentration of water-extractable K was highest at the surface (12 μM g^{-1}), and decreased gradually with depth to zero at 7.0 cm. The concentration of water-extractable K in the columns tended to become almost uniform over the entire depth of column after 1 wk of incubation. For columns with exchangeable Al levels of 22 and 44 $cmol_c$ kg^{-1}, the maximum concentrations of water-extractable K were also near the surface and decreased with depth. The downward movement of K was greatly reduced by the exchange resin and the distance the K traveled was inversely related to the levels of
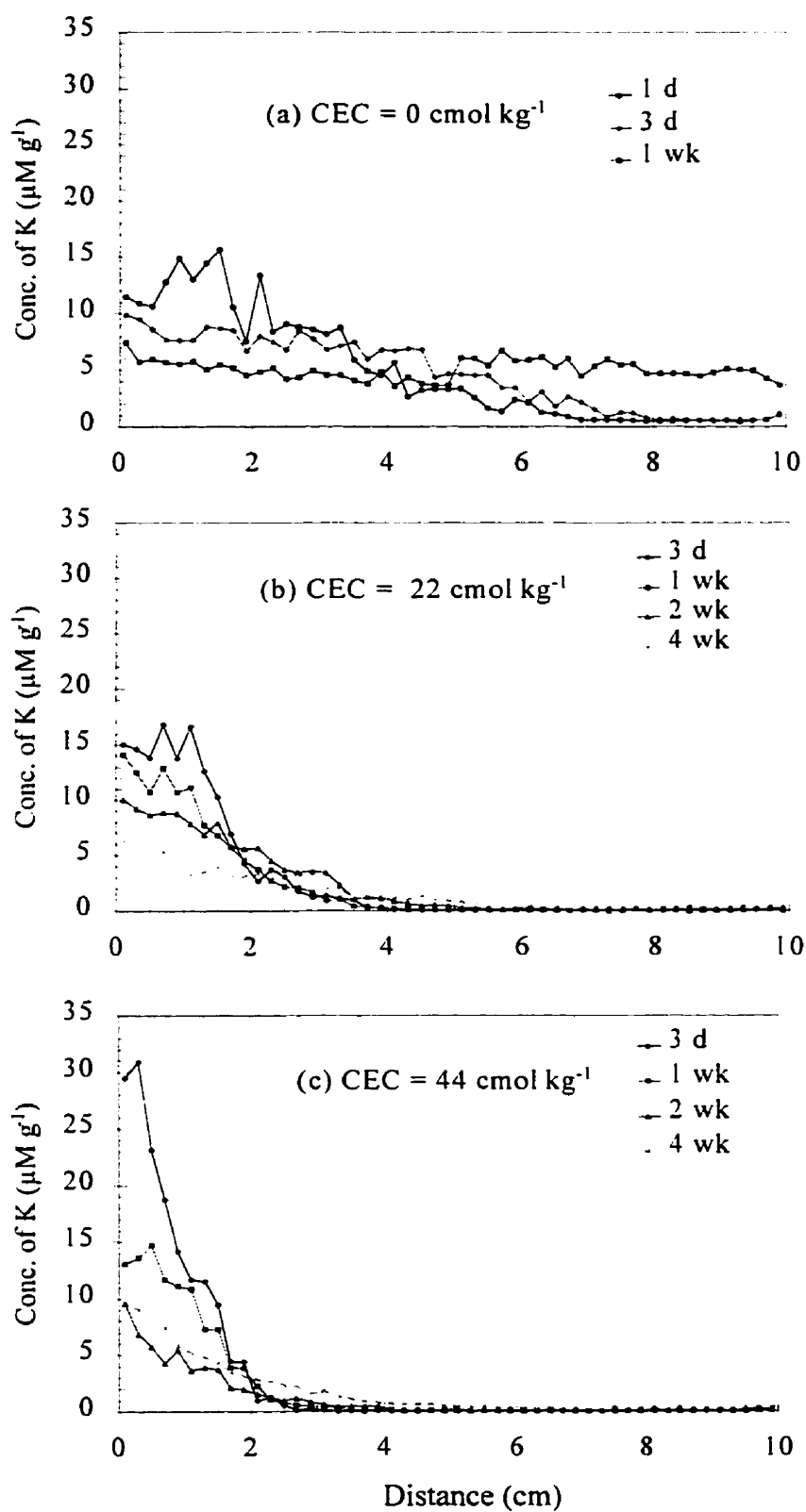
Figure 4.4 Distribution of water-extractable K in various resin-sand mixtures as affected by time of incubation and levels of exchangeable Al.

exchangeable Al. The K^+ ions moved all way down to the bottom of the columns after 1 wk in the column without exchangeable Al. But the movement of K^+ ions were only 4.0 and 2.7 cm after 1 wk for columns with exchangeable Al levels of 22 and 44 $cmol_c$ kg^{-1}, respectively. Differences in the depth of K^+ movement were small among incubation periods in columns with exchangeable Al.

Acid-extractable K^+ was virtually zero for the columns without exchangeable Al (Figure 4.5a). The extremely low levels of acid-extractable K in columns with no exchangeable Al reflects the nature of the columns. Because they could not adsorb K^+, all the K^+ ions remained in solution. The distribution of acid-extractable K was very similar to that of water-extractable K for the columns with exchangeable Al (Figure 4.5b and 4.5c). Maximum concentrations of acid-extractable K occurred at the surface of the column and decreased with depth. K moved slightly more in the columns with 22 $cmol_c$ kg^{-1} than with 44 $cmol_c$ kg^{-1} exchangeable Al.

4.4.1.3 Recovery of P and K

The amount of water- and acid-extractable P and K in the entire columns after 1 and 4 wk of incubation are summarized in Tables 4.2 and 4.3, respectively. The percentage of P recovered was quite high for all treatments, ranging from 87% to 100% (Table 4.2). The columns with no exchangeable Al had the highest recovery of P (100%) while the columns with 22 $cmol_c$ kg^{-1} exchangeable Al had the lowest recovery. Water-extractable P decreased and acid-extractable P increased with time. The recovery of K (Table 4.3) was very similar to that of P. The columns with no exchangeable Al had the highest K recovery (94%) while the columns with an exchangeable Al level of 22 $cmol_c$ kg^{-1} had lowest recovery after 1 wk of incubation. Similar to P, water-extractable K

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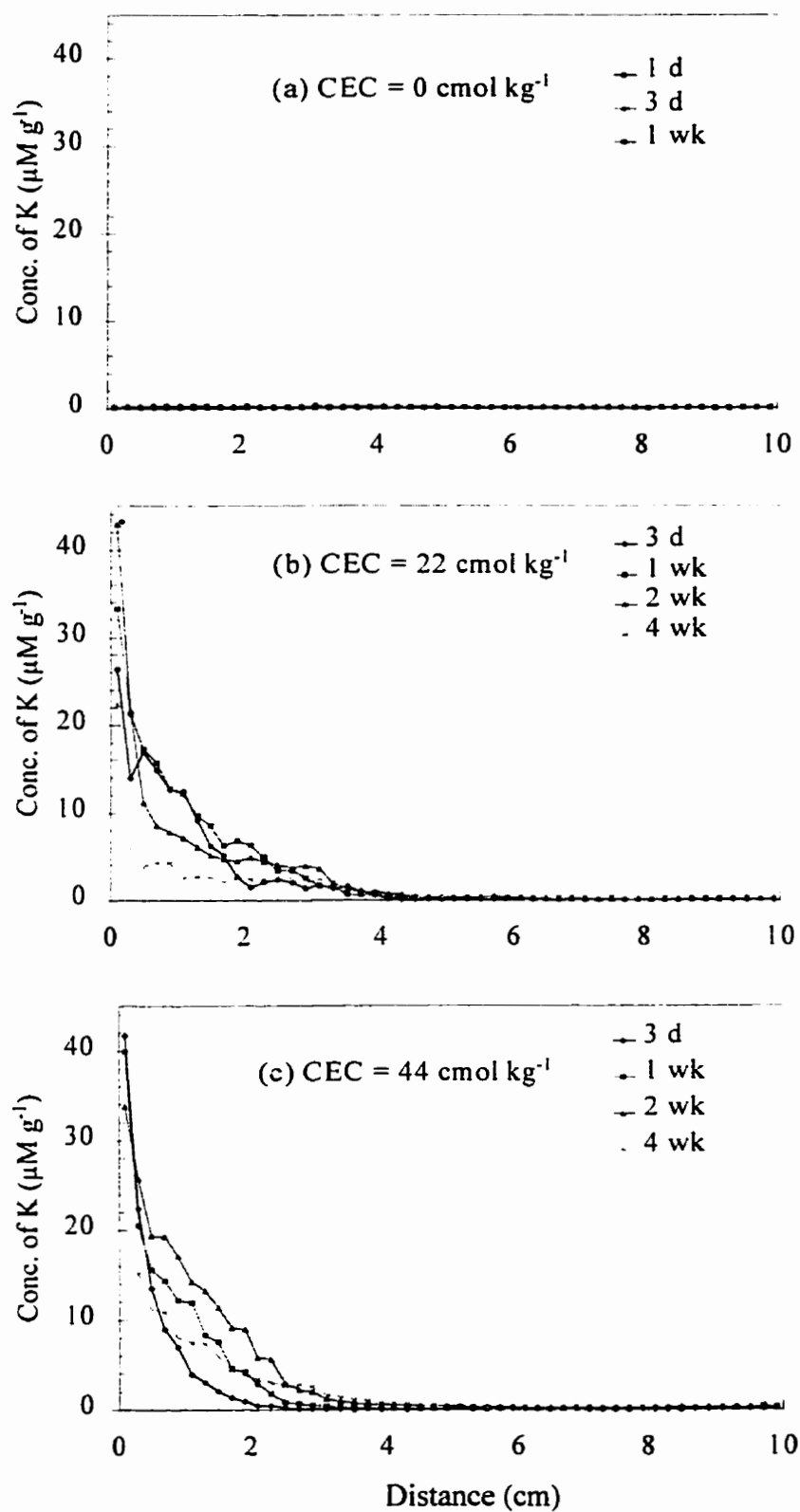
Figure 4.5 Distribution of acid-extractable K in various resin-sand mixture as affected by time of incubation and levels of exchangeable Al.

Table 4.2 Recovery of water- and acid-extractable P as affected by level of exchangeable Al and time of incubation.

CEC levels	P added	Water-extr. P	Acid-extr. P	Total P recovered	Percentage recovered
cmol kg^{-1}		mM column^{-1}			
		1 wk			
0	1.47	1.45	0.03	1.48	100.9
22	1.47	0.73	0.55	1.27	86.7
44	1.47	0.67	0.71	1.37	93.4
		4 wk			
0					
22	1.47	0.62	0.67	1.29	87.5
44	1.47	0.47	0.87	1.33	90.8

Table 4.3 Recovery of water- and acid-extractable K as affected by level of exchangeable Al and time of incubation.

CEC levels	K added	Water-extr. K	Acid-extr. K	Total K recovered	Percentage recovered
cmol kg^{-1}		mM column^{-1}			
		1 wk			
0	1.47	1.36	0.02	1.38	94.0
22	1.47	0.50	0.79	1.29	87.5
44	1.47	0.43	1.03	1.45	98.7
		4 wk			
0					
22	1.47	0.33	0.40	0.73	49.4
44	1.47	0.34	0.84	1.19	80.6

decreased and acid-extractable K increased with time of incubation.

For columns with no exchangeable Al, the observed 100% recovery of P was due to the nature of the columns. Since there are no P fixation or K exchange reactions, all P and K were recoverable. The low recovery of P and K in columns with exchangeable Al was most likely due to precipitation reactions creating acid-insoluble taranakite.

4.4.1.4 Soil pH

The pH of the resin-sand column decreased on application of P fertilizer for all three levels of exchangeable Al (Figure 4.6). The magnitude of change in pH after KH_2PO_4 application, however, was affected by both the levels of exchangeable Al and time of incubation. In the columns without exchangeable Al (pure sand), the pH assumed that of the applied KH_2PO_4. As a result, the pH decreased 1 d after P fertilizer application, from 6.3 to 4.5 (Figure 4.6a). Over time, the pH increased in the top 5 cm portion of the column and decreased at the bottom such that after 1 wk of incubation, the pH was uniform (4.6) throughout the column.

pH also decreased near the surface in columns with exchangeable Al, from about 3.5 to 3.0 (Figure 4.6b and 4.6c). The depth of pH changes resulting from KH_2PO_4 fertilizer application was shallower with increasing levels of exchangeable Al (Figure 4.6). The zone from which H^- was produced was restricted to where Al-P interaction. Over time, the pH increased near the surface and decreased in the lower part of column as more and more H^- ions, generated from Al-P precipitation reactions, diffused downward. It should be noted that more H^- ions are needed to lower pH from 3.5 to 2.5 than from 6.5 to 5.5. Specifically, 2.84×10^{-3} M H^- ions are required to lower the pH from 3.5 to 2.5 while only 2.84×10^{-6} M H^- ions are needed to lower pH from 6.5 to 5.5. Thus, there
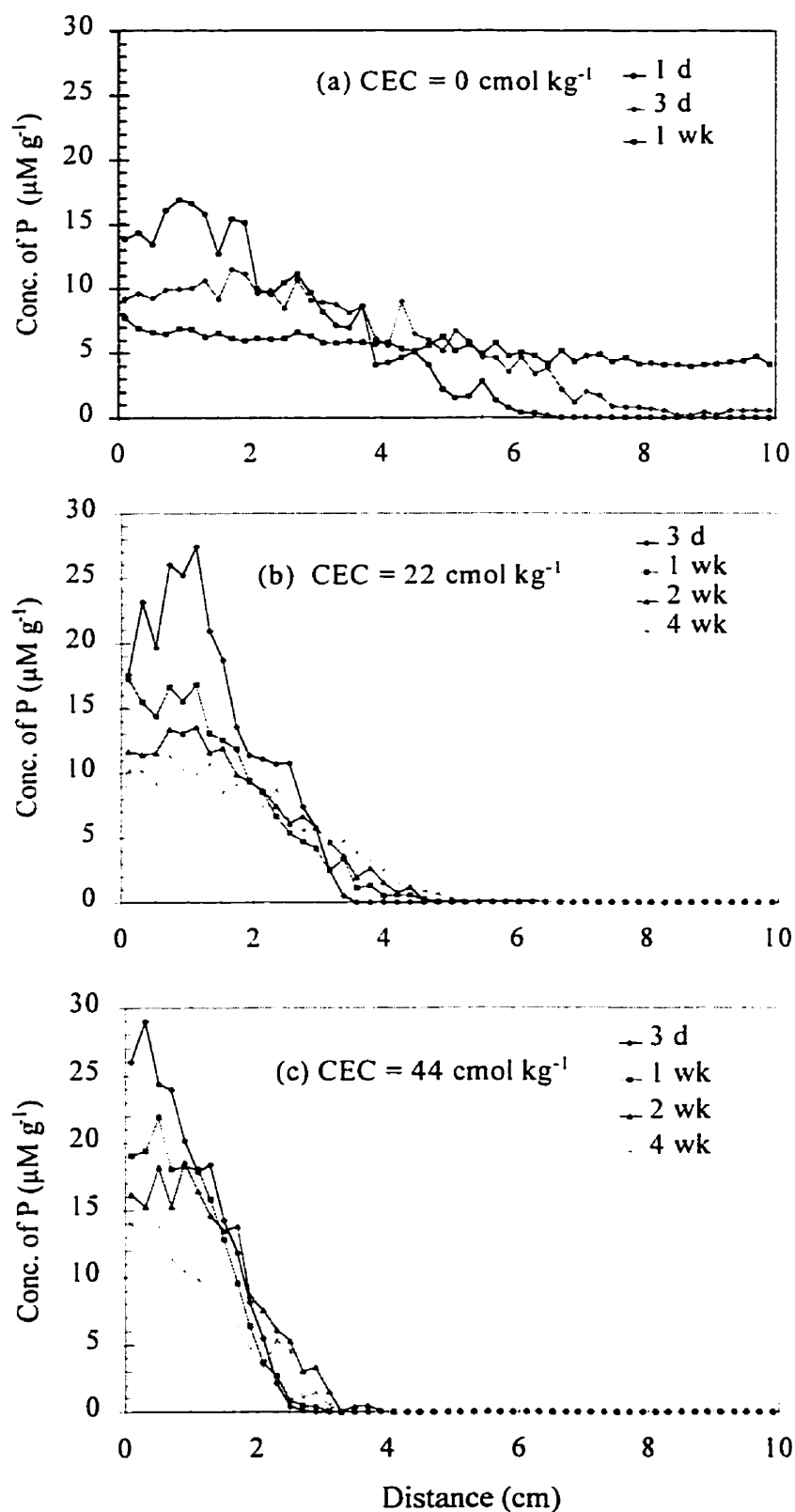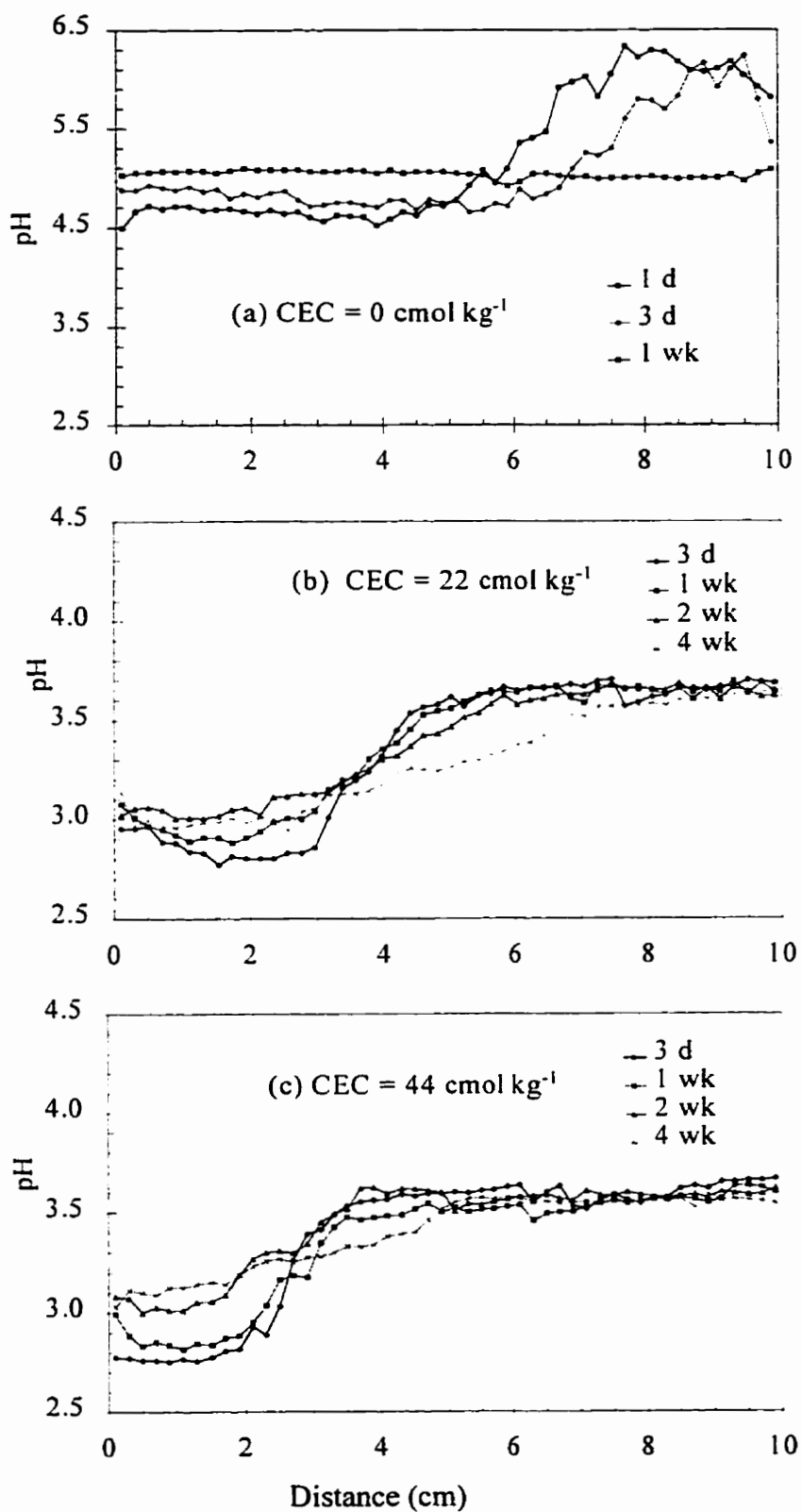
Figure 4.6 Distribution of pH in various resin-sand mixtures as affected by time of incubation and levels of exchangeable Al.

were more H$^+$ ions produced in columns with than without exchangeable Al.

Some researchers have suggested that the reduction in pH results from the hydrolysis of Al^{3+} (Hsu and Rennie 1962). To examine this, the pH profiles obtained with the surface application of KH$_2$PO$_4$ (1.47 mM column^{-1}) were compared with those of KCl (with equal molar K application rate) at an exchangeable Al level of 22 cmol$_c$ kg^{-1} after 1 wk of incubation. The pH at the top of the column with KCl did not decrease much, if at all, when compared to that with KH$_2$PO$_4$ (Figure 4.7). The lowest point in pH 4.7).

Figure 4.8 shows the distribution of Al and K in the columns with 22 cmol$_c$ kg^{-1} of exchangeable Al after application of equal molar amounts of KCl and KH$_2$PO$_4$ and 1 wk incubation. The information presented in Figure 4.8 helps explain the observed pH profiles. The highest concentration of water-extractable K was near the surface of the column and then decreased with depth for both KCl and KH$_2$PO$_4$. However, the decrease
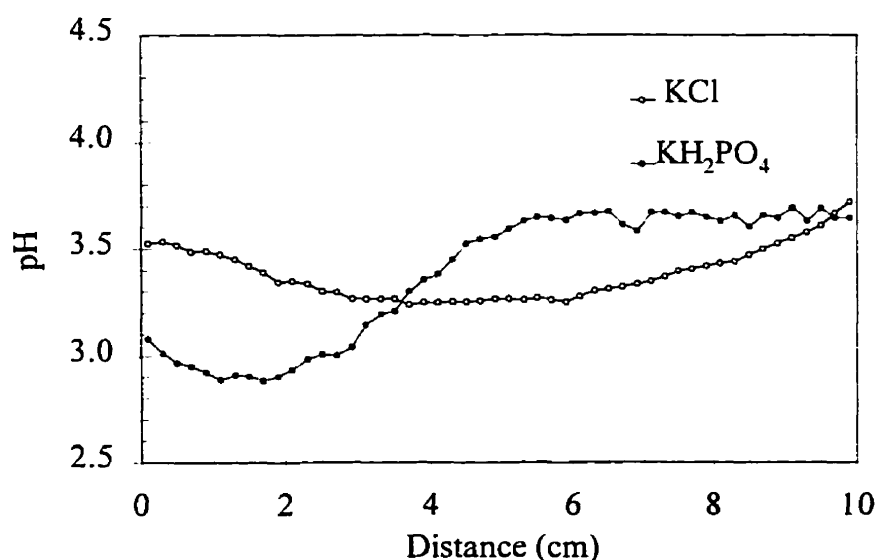
Figure 4.7 Distribution of pH as affected by type of salt applied in columns with 22 cmol$_c$ kg^{-1} exchangeable Al after 1 wk of incubation.

was in the middle for the column with KCl, but near the surface with KH_2PO_4 (Figure

was more gradual with KCl than with KH_2PO_4. The distance K^- ions moved was also

greater for KCl (6.0 cm) than for KH_2PO_4 (4.0 cm). The distribution of acid-extractable

K should have very similar patterns for KCl and KH_2PO_4 if there were only cation

exchange and Al hydrolysis reactions, but KH_2PO_4 application resulted in a much higher

solution K^+ concentration near the surface than KCl. The Al distribution patterns were

very similar for KCl and KH_2PO_4 applications, except at Al concentration is slightly

lower for KCl and higher for KH_2PO_4 application near the surface than those at the lower

part of the column.

The addition of KCl induces a cation exchange reaction of K^- ions for Al^{3-} ions

and subsequent hydrolysis of Al^{3+}, as well as the diffusive movement of Al and H^- ions.

Initially, a high concentration of K from KCl releases exchangeable Al^{3-} and H^- ions near

the surface. The Al^{3+} and H^- ions released can then diffuse downward. As the K^- moves

downward, solution K^- concentration at the surface decreases with time. Since some of

the Al^{3-} and H^- ions in solution will readsorb on exchange sites in order to maintain

equilibrium, the pH at the surface will increase slightly compared to the layers

immediately below. The pH in the column was lowest at the depth to which K ions had

moved (around 6 cm, Figure 4.8a). The gradual increase in pH below 6 cm was probably

the result of diffusive movement of Al^{3-} and H^- ions due to the concentration gradient.

The pH at the surface of the column was lower with KH_2PO_4 than with KCl (Figure 4.7).

The lower surface pH cannot be explained by Al^{3-} hydrolysis alone. Aluminum and

phosphate interaction definitely reduced pH substantially. The Al-P interaction initiates

reactions which shift or dictate equilibrium in the solution and alter pH. First, Al-P

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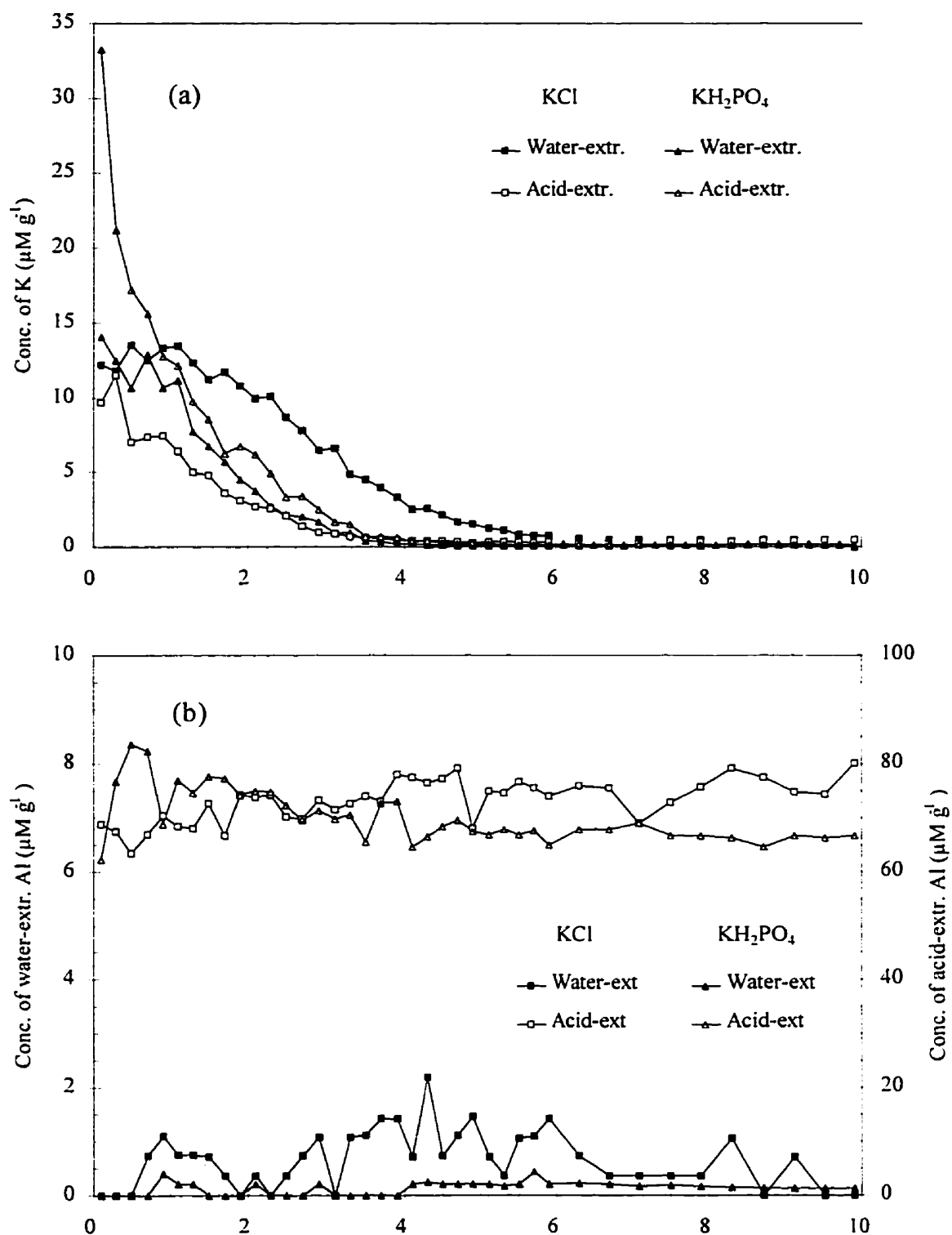
Figure 4.8 Distribution of water- and acid-extractable K (a) and Al (b) as affected by type of salt applied in columns with 22 $cmol_c$ kg^{-1} exchangeable Al after 1 wk of incubation.

interaction will increase the rate of the K-Al exchange reaction since the exchangeable Al

released is precipitated by P. Figures 4.8a indeed show a higher acid-extractable K near

the surface of the columns with KH_2PO_4 than with KCl. It is reasonable to assume that

most of the acid-extractable K was exchangeable K. If Al hydrolysis played a role in the

reduction of pH, then the precipitation of Al-P would magnify this role. Second, most of

the exchangeable Al ions released are used up during Al-P precipitation as indicated by

the low water-extractable Al (Figure 4.8b). As illustrated in Equation [4.3], the formation

of 1 mole of taranakite will produce 10 H^+ ions. Third, the dissociation of phosphate

could also generate H^+ ions. At an initial pH of 3.6, 98% of phosphate is in the form of

$H_2PO_4^-$, with about 2% as H_3PO_4. As more and more $H_2PO_4^-$ precipitated, $H_3PO_4^0$

dissociated to $H_2PO_4^-$ with the release of H^+ ions.

Equation [4.3] assumed that Al^{3+} and $H_2PO_4^-$ were the reaction species for

taranakite formation, but other species of Al and phosphate could also possibly form

taranakite. There is insufficient evidence to support one or the other. For example,

equation [4.3] could be written as:

$$5\,Al(OH)_2^- + 3\,K^+ + 8\,H_2PO_4^- \rightleftharpoons K_3(Al(OH)_2)_5(H_2PO_4)_8 \qquad [4.5]$$

$$5\,Al^{3+} + 3\,K^+ + 8\,HPO_4^{2-} \rightleftharpoons K_3H_6Al_5(PO_4)_8 + 2\,H^- \qquad [4.6]$$

or

$$5\,Al^{3+} + 3\,K^+ + 6\,HPO_4^{2-} + 2\,PO_4^{3-} \rightleftharpoons K_3H_6Al_5(PO_4)_8 \qquad [4.7]$$

Since the structure of the taranakite is unknown, but the unit cell presumably consists of

Al and PO_4 tetrahedra, there is no direct evidence to support which of the above reactions

is correct.

Water-extractable phosphate represents phosphorus which is immediately available for plant uptake in the soil system. All of the KH_2PO_4 applied remained in the solution (high water-extractable and near zero acid-extractable P and K) when there was no exchangeable Al in the system (Figures 4.2a, 4.3a, 4.4a, and 4.5a and Tables 4.2 and 4.3). As exchangeable Al increased, the concentration and the total amount of acid-extractable P and K increased near the surface. The results reflect increased Al-P precipitation at the surface due to greater exchange of K^+ ions for Al. It is very reasonable to assume that the supply of Al was the main factor controlling Al-P precipitation, because P concentration near the surface (point of application) was very high. To precipitate the same amount of Al, the phosphate had to travel a greater distance in columns with an exchangeable Al level of 22 $cmol_c$ kg^{-1} than in columns with an exchangeable Al level of 44 $cmol_c$ kg^{-1}. This was confirmed by the lower concentration of acid-extractable P ($\approx 10\mu M$ g^{-1}) near the surface and the greater depth of penetration of P (5 cm) for columns with 22 $cmol_c$ kg^{-1} exchangeable Al than in the columns with 44 $cmol_c$ kg^{-1}. Greater precipitation of Al-P at the higher levels of exchangeable Al would also generate more H^+ ions near the surface, resulting in a lower pH (Figure 4.6c and 4.6b).

The low acid-extractable P in the top three layers (Figure 4.3b and 4.3c) compared to layers immediately below could be due to the conversion of some of the Al-P precipitate from non-crystalline form to taranakite (Bohn and Peech 1969). This conversion would be very likely because K^+ concentration was high in the system. Acid-

extractable P would decrease as more and more of the non-crystalline form of Al-P precipitate was converted to taranakite near the surface.

The lower total recovery of P for columns with 22 than 44 $cmol_c$ kg^{-1} was probably due to the differences in the rate of conversion of non-crystalline Al-P precipitate to taranakite. Laboratory studies in pure solutions revealed that the rate of taranakite formation was positively correlated to pH, i.e., the higher the pH, the faster the rate of taranakite formation (Section 3.3.3). The columns with exchangeable Al levels of 22 $cmol_c$ kg^{-1} had a relatively higher pH (Figure 4.6) than the 44 $cmol_c$ kg^{-1} columns. The higher pH in the 22 $cmol_c$ kg^{-1} columns would have favored a higher rate of taranakite formation and a lower recovery of P. Another possibility is that when the exchangeable Al level was at 44 $cmol_c$ kg^{-1}, a compound other than taranakite may have been formed. More K^+ ions would be adsorbed to exchange sites at the higher CEC, resulting a much lower solution concentration of K^+. Thus, from the K^+ concentration perspective, there would be less taranakite formed at the 44 than at the 22 $cmol_c$ kg^{-1} level of exchangeable Al. It is also possible that the Al-P precipitate was not taranakite at 44 $cmol_c$ kg^{-1} level of exchangeable Al.

4.4.2 Experiment II: Effects of Exchangeable Al and Gibbsite

Experiments were conducted to determine the relative effects of Al from two sources, exchange sites and the dissolution of gibbsite, on concentrations and movement of P and K ions and the pH of the system.

4.4.2.1 Water- and Acid-extractable P

Distribution of water-extractable P was affected by both level of exchangeable Al and time of incubation (Figure 4.9). Water-extractable P in columns with gibbsite was
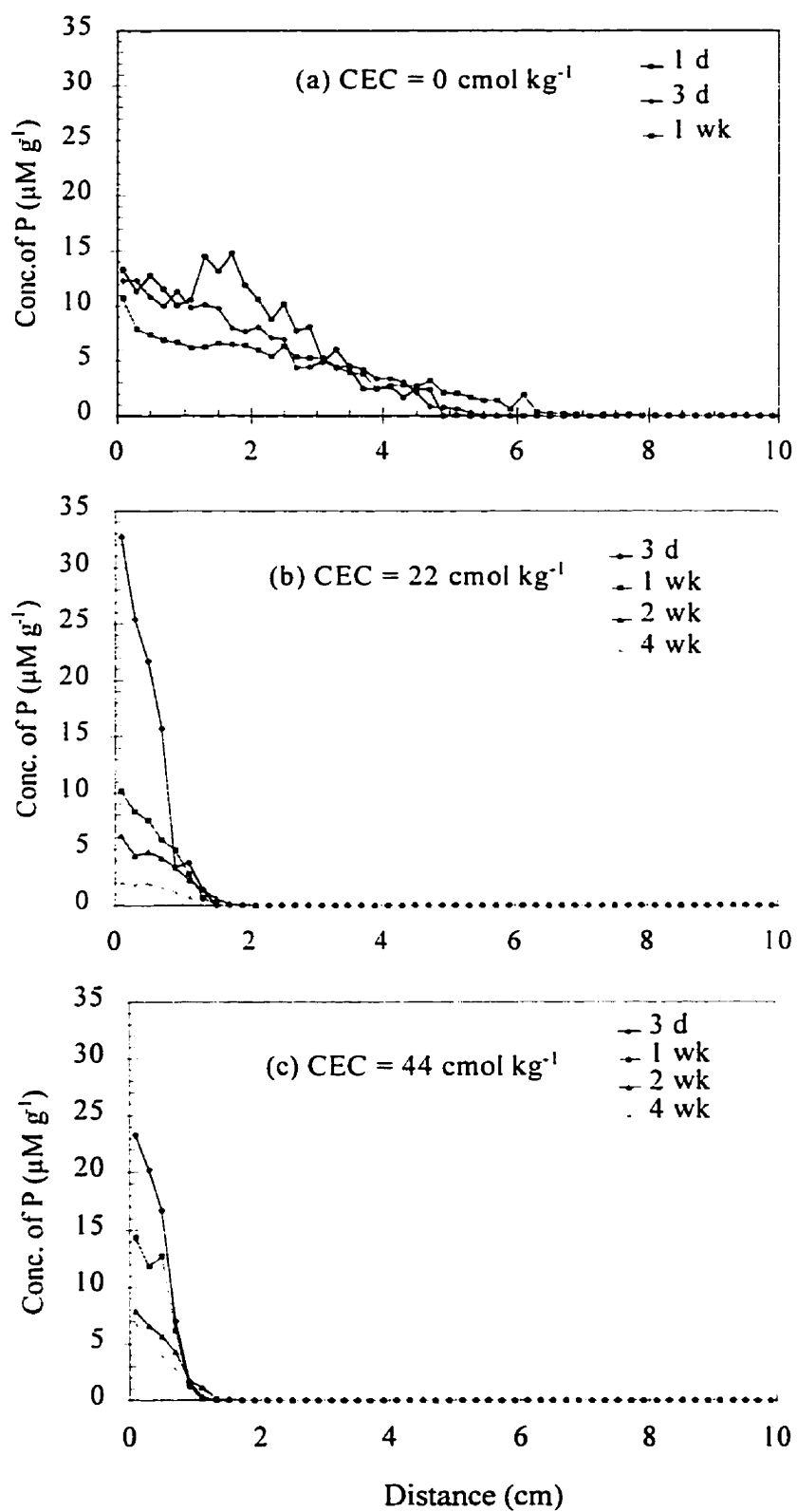
Figure 4.9 Distribution of water-extractable P in various resin-sand and gibbsite mixtures as affected by time of incubation and levels of exchangeable Al.

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considerably less than in columns with only exchangeable Al. Phosphate penetrated to much greater depths in columns without gibbsite than for corresponding columns with gibbsite. Concentration of water soluble P at the surface decreased at a greater rate in columns with gibbsite than in columns without gibbsite as time of incubation increased from 3 d to 4 wk.

When there was 1% gibbsite and no exchangeable Al in the columns, the concentration of water-extractable P was highest at the surface (15 μM g^{-1}) and decreased gradually downward, reaching zero around 5.5 cm depth after 1 d of incubation. After 1 wk of incubation, the concentration of water-extractable P was still highest at the surface, but its magnitude had dropped to 10 μM g^{-1}. There was not much downward movement of P after 3 d as indicated by the very similar depths of P movement at 1 d and 1 wk (Figure 4.9a).

For the columns with exchangeable Al levels of 22 and 44 cM$_c$ kg^{-1}, the maximum concentrations of water-extractable P were also near the surface and decreased with depth (Figure 4.9b and 4.9c). However, the downward movement of P was greatly reduced and the reduction was more evident for the columns with 44 cmol$_c$ kg^{-1} of exchangeable Al. Even after 4 wk of incubation, P moved only 1.7 cm and 1.3 cm for exchangeable Al levels of 22 and 44 cmol$_c$ kg^{-1}, respectively. In contrast, P moved 5.0 and 3.9 cm for exchangeable Al levels of 22 and 44 cmol$_c$ kg^{-1}, respectively, in columns without gibbsite (Figure 4.2). There were virtually no differences in the depth of P movement among the four different time of incubations for columns with 22 and 44 cmol$_c$ kg^{-1}. The concentration of water-extractable P near the surface for columns with exchangeable Al levels of 22 (Figure 4.9b) and 44 cmol$_c$ kg^{-1} (Figure 4.9c) decreased with time of

incubation, similar to what was observed with zero exchangeable Al (Figure 4.9a). However, the magnitude of decrease was much greater. The movement of P was much greater (6 cm after 1 wk of incubation period) for columns with no exchangeable Al than for columns with exchangeable Al.

The distribution profiles of acid-extractable P are shown in Figure 4.10. It is evident that the concentration of acid-extractable P was affected by levels of exchangeable Al. Unlike the columns with only exchangeable Al, the distribution of acid-extractable P was not affected by the time of incubation when gibbsite was present. The concentration of acid-extractable P near the surface was inversely related to the CEC, with a maximum of about 70 μM g^{-1} for the column with 44 $cmol_c$ kg^{-1} exchangeable Al. The maximum concentrations of acid-extractable P were observed near the surface and decreased with depth for the columns with exchangeable Al levels of 22 and 44 $cmol_c$ kg^{-1} (Figure 4.10b and 4.10c). There were only small differences in the distribution profiles of acid-extractable P among the different incubation periods.

4.4.2.2 Water- and Acid-extractable K

Results of water- and acid-extractable K (Figures 4.11, and 4.12) followed very similar patterns to those of P. The concentration of water-extractable K (Figure 4.11) was highest at the surface and constantly decreased with time and depth. The concentration of acid-extractable K was also highest at the surface and decreased with depth. However, there was little difference as time of incubation increased. Results of K profiles were consistent with those for P and need not be discussed in detail here.
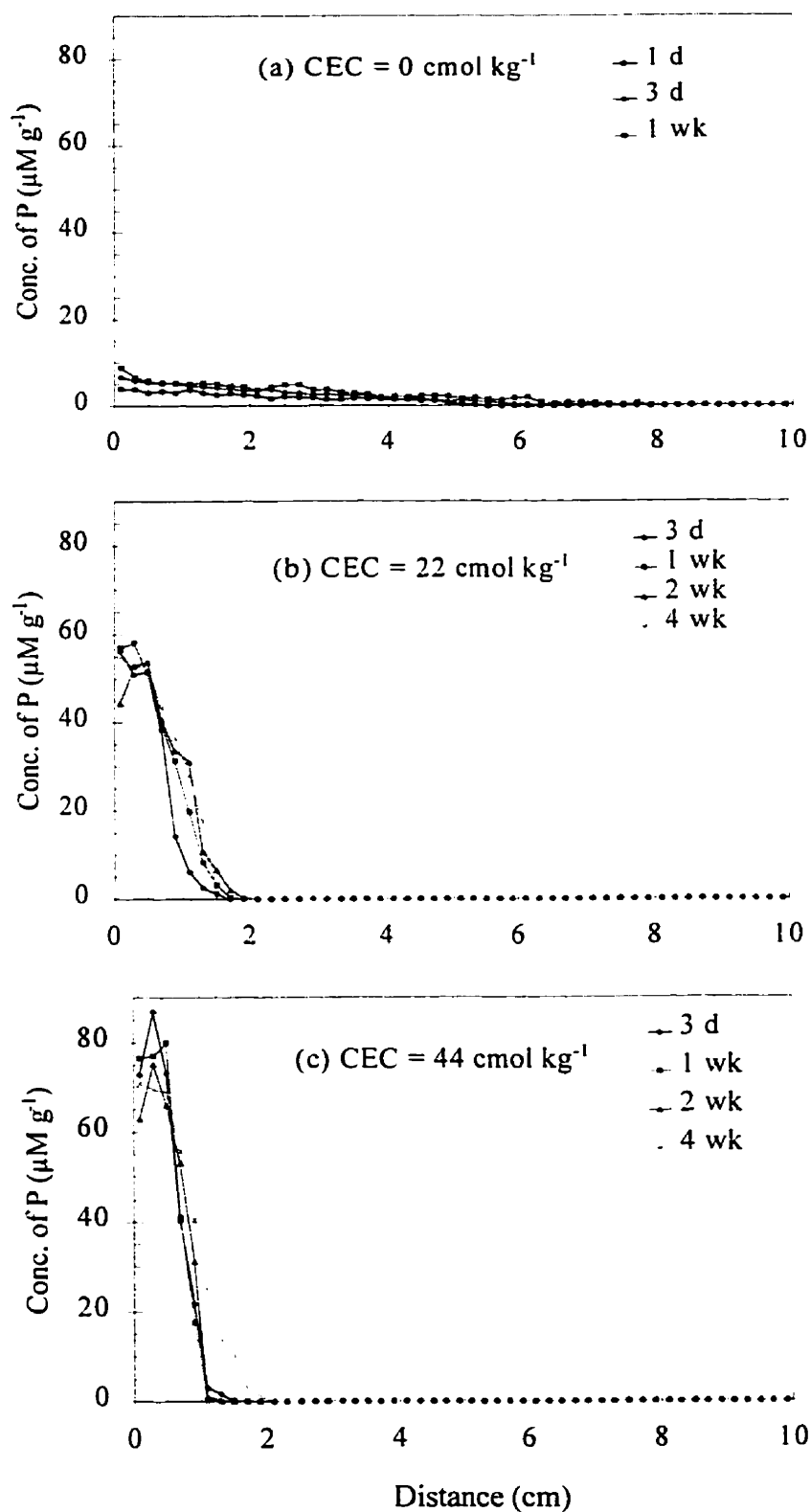
Figure 4.10 Distribution of acid-extractable P in various resin-sand and gibbsite mixtures as affected by time of incubation and levels of exchangeable Al.

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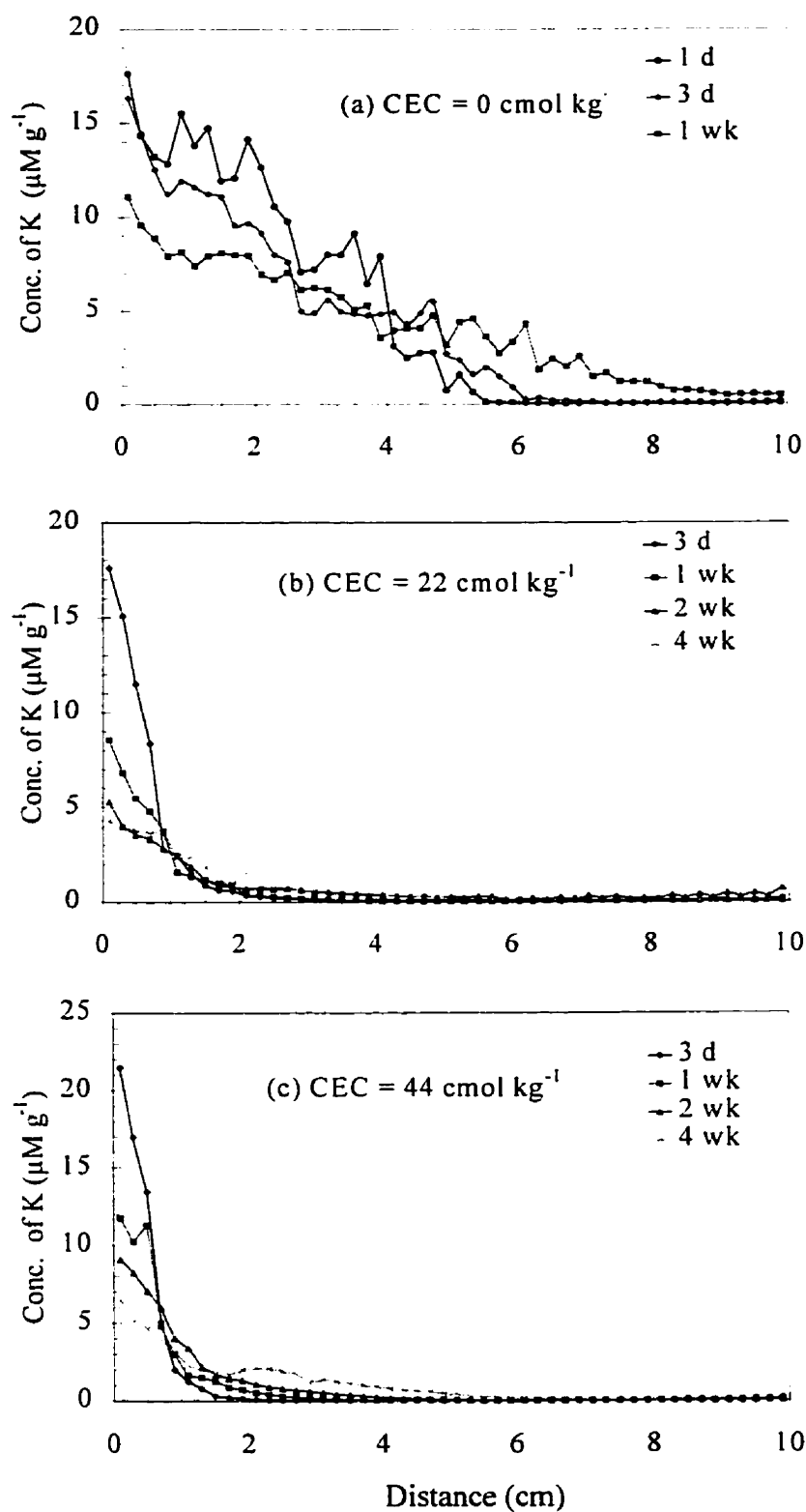
Figure 4.11 Distribution of water-extractable K in various resin-sand and gibbsite mixtures as affected by time of incubation and levels of exchangeable Al.
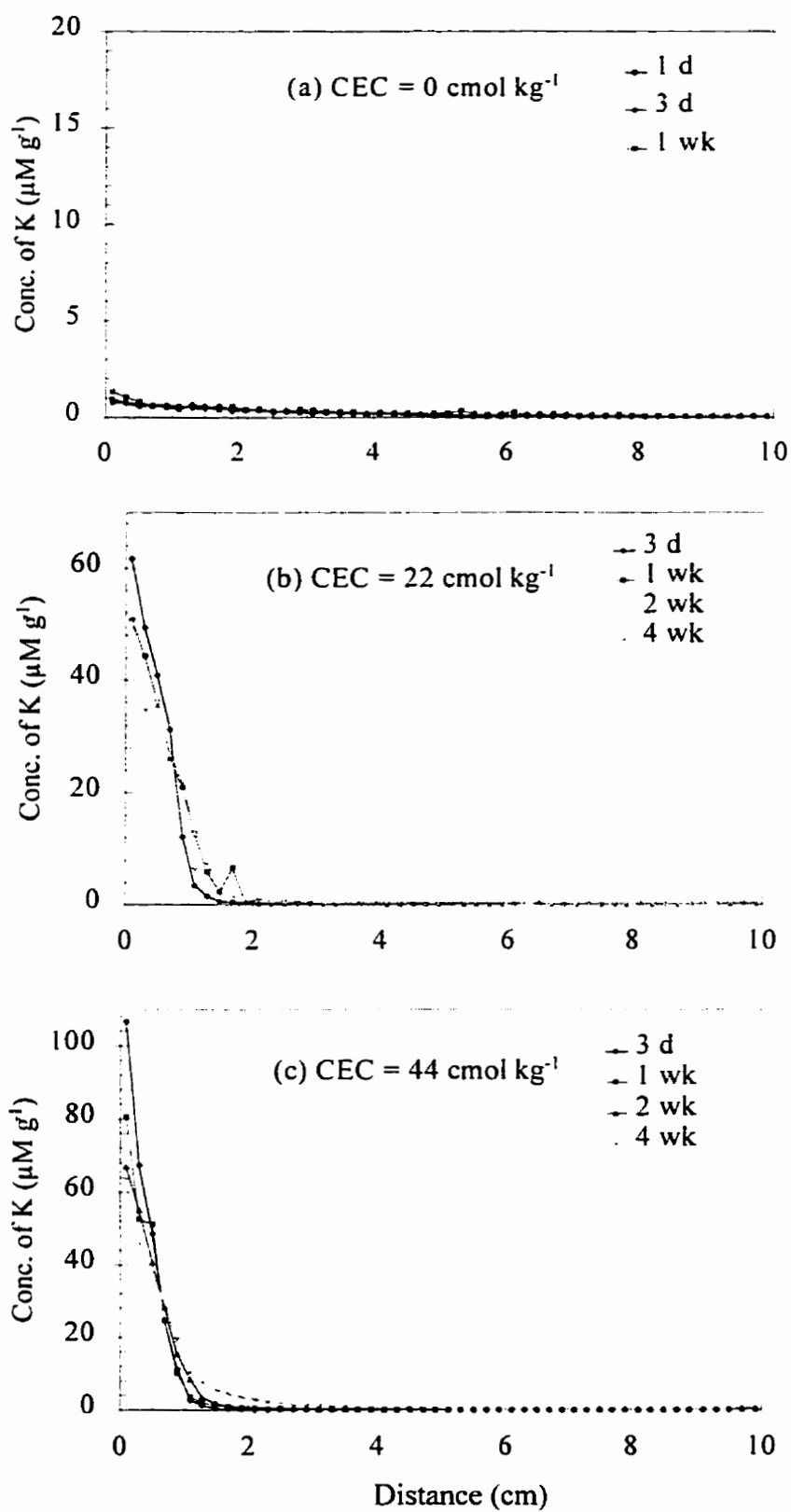
Figure 4.12 Distribution of acid-extractable K in various resin-sand and gibbsite mixtures as affected by time of incubation and levels of exchangeable Al.

4.4.2.3 Recovery of P and K

The amount of P and K for the entire column at 1 wk and 4 wk of incubation

periods are summarized in Tables 4.4 and Table 4.5, respectively. The percentage of P

recovered was quite high (> 90%) in all cases. Generally, water-extractable P decreased

while acid-extractable P increased over time. The recovery of K (Table 4.5) was very

similar to that of P, but the water-extractable K did not decrease much over time and the

total recoveries were slightly lower than P.

4.4.2.4 Soil pH

The pH values near the surface increased as a result of the surface application of

KH_2PO_4 fertilizer for all columns with gibbsite (Figure 4.13). This was opposite to

columns without gibbsite, where pH decreased for all columns after P addition

(Figure4.6). The magnitude of change in pH, however, was affected by both the levels of

exchangeable Al and incubation period as observed for the column without gibbsite

The pH values of the medium increased when KH_2PO_4 was added to the sand-

gibbsite mixture without any exchangeable Al. The pH values near the surface continued

to increase and the depth to which pH changed increased with time of incubation. But in

the columns with exchangeable Al, the pH increased near the surface as result of the

application of KH_2PO_4 (Figure 4.13b and 4.13c). The pH values continued to increase at

the surface with the time of incubation. In contrast to the columns with no exchangeable

Al, the depth to which pH change occurred was very shallow (less than 3 cm) and not

affected by incubation period when the exchangeable Al levels were 22 and 44 $cmol_c$ kg^{-1}.

The increase in pH near the surface was greatest when the exchangeable Al level was

zero and least when the exchangeable Al level was 44 $cmol_c$ kg^{-1}. This was

Table 4.4 Recovery of water- and acid-extractable P as affected by levels of exchangeable Al and time of incubation when there was 1% gibbsite.

CEC levels	P added	Water-extr. P	Acid-extr. P	Total P recovered	Percentage recovered
cmol kg^{-1}			mM column^{-1}		
			1 wk		
0	1.47	0.78	0.63	1.41	95.8
22	1.47	0.18	1.22	1.40	95.2
44	1.47	0.19	1.16	1.35	91.6
			4 wk		
0					
22	1.47	0.04	1.30	1.34	91.3
44	1.47	0.08	1.43	1.51	102.4

Table 4.5 Recovery of water- and acid-extractable K as affected by levels of exchangeable Al and time of incubation when there was 1% gibbsite.

CEC levels	K added	Water-extr. K	Acid-extr. K	Total K recovered	Percentage recovered
cmol kg^{-1}			mM column^{-1}		
			1 wk		
0	1.47	1.13	0.07	1.22	82.2
22	1.47	0.17	0.96	1.13	76.8
44	1.47	0.20	0.91	1.12	75.9
			4 wk		
0					
22	1.47	0.17	0.88	1.05	71.6
44	1.47	0.21	0.96	1.17	79.9
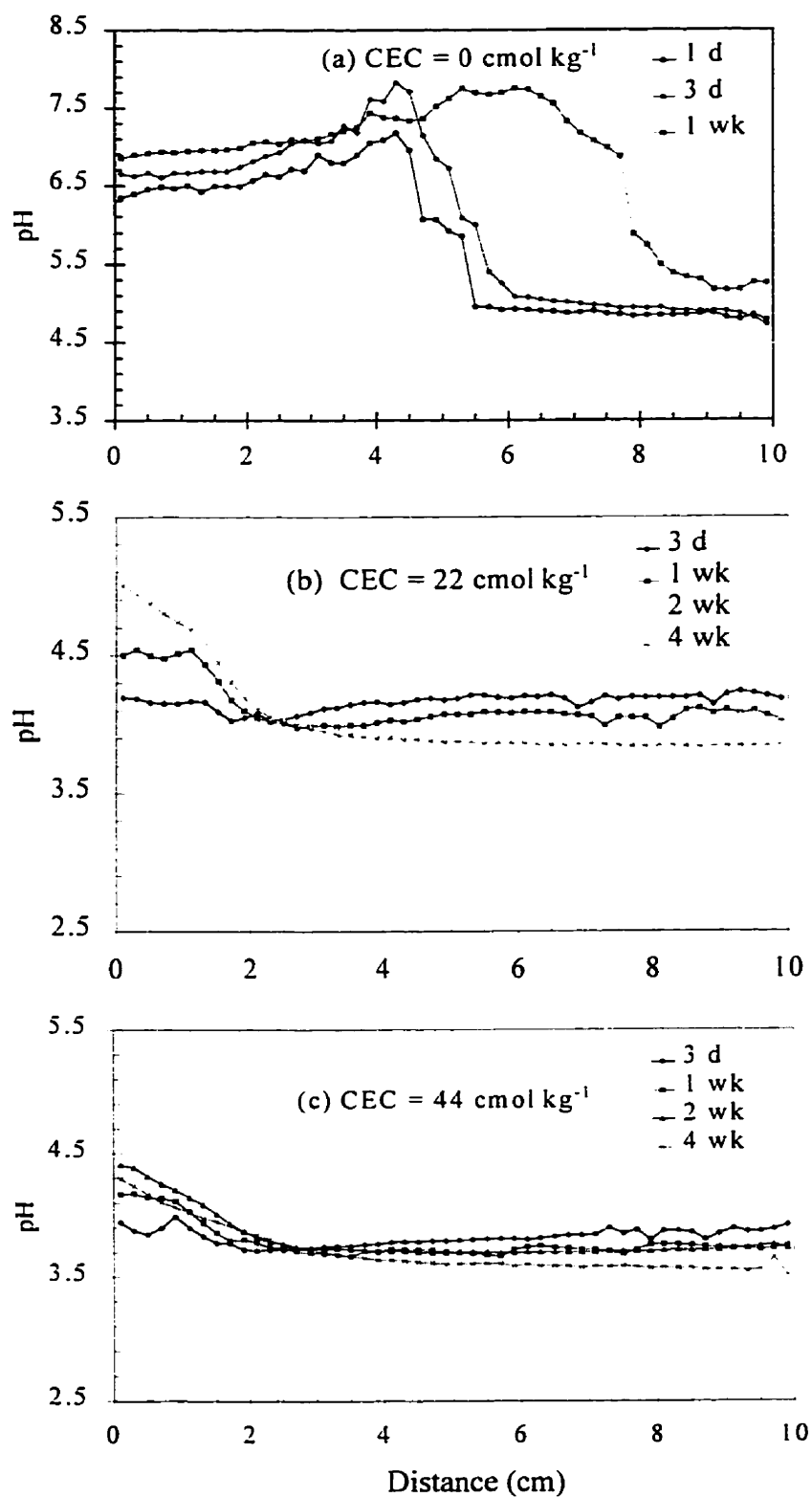
Figure 4.13 Distribution of pH in various resin-sand and gibbsite mixtures as affected by time of incubation and levels of exchangeable Al.

because more H^+ ions were consumed to raise a unit of pH at lower that at higher pH. Consequently, the increase in pH will be less at initially low pH conditions.

The pH profiles for equal molar concentration of KH_2PO_4 and KCl added to columns with 22 $cmol_c$ kg^{-1} exchangeable Al level and 1% gibbsite were also obtained (Figure 4.14). The pH value decreased when KCl was added. The pH was fairly uniformly low (3.7) down to a depth of 5 cm, then increased slightly toward the background pH (4.1) at the bottom of the column. In contrast, pH values near the surface with KH_2PO_4 increased above background levels. The pH value increased to 4.5 in the top 1.1 cm layer, then decreased with depth and approached the background value of 4.1 at a depth of 2 cm.
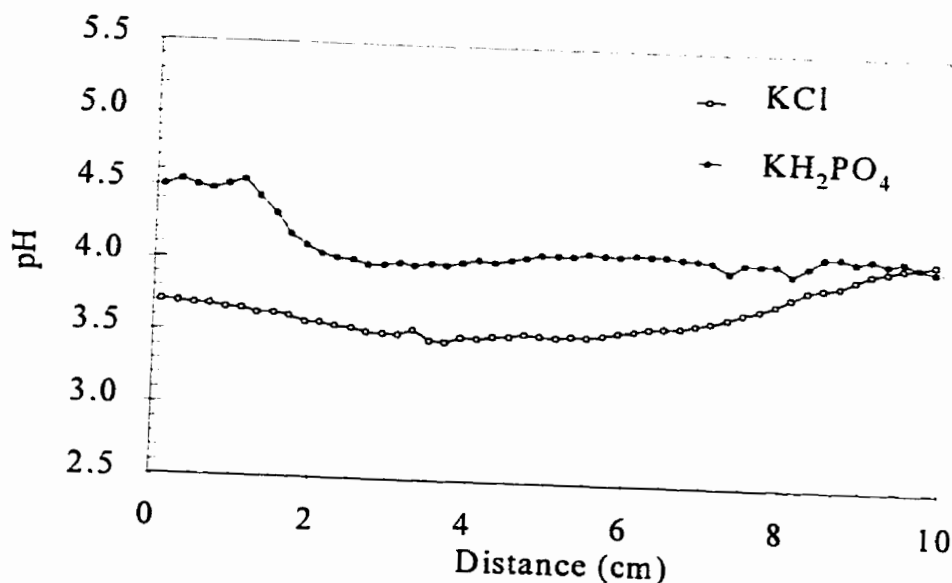
Figure 4.14 Distribution of pH as affected by type of salt applied in column with 22 $cmol_c$ kg^{-1} exchangeable Al and 1% gibbsite after 1 wk of incubation.

To help to explain the observed pH profiles, the concentration of water- and acid-extractable K and Al for equal molar applications of KCl and KH_2PO_4 are presented in Figure 4.15. The concentration of both water- and acid-extractable K was highest near the surface for both KCl and KH_2PO_4 (Figure 4.15a). However, the decrease in concentration with depth was more gradual for KCl than for KH_2PO_4. The concentrations decreased with depth and reached zero at 2 cm for KH_2PO_4 and 5.7 cm for KCl. The concentration of acid-extractable K near the surface was higher for KH_2PO_4 than for KCl, whereas the reverse was true for water-extractable K.

The concentration of water-extractable Al was about 25 to 40 μM g^{-1} while acid-extractable Al concentration was about 80 μM g^{-1} throughout the column with KCl (Figure 4.15b). However, the water-extractable Al concentration was almost zero in the top 1.7 cm and then increased dramatically to background levels of 25 μM g^{-1} at a depth of 2 cm with KH_2PO_4. The acid-extractable Al concentration was slightly higher near the surface and near that of the background level (80 μM g^{-1}) at lower depths.

The decrease in pH near the surface of columns with KCl was the result of cation exchange of K$^-$ for Al ions and subsequent hydrolysis of Al. The pH curves were very similar to KCl in the columns with 22 cmol$_c$ kg^{-1} exchangeable Al, whether or not gibbsite was present. The observed similarities were due to the same interactions occurring with and without gibbsite. However, increases in pH were observed with KH_2PO_4 when gibbsite was present in the column. The high surface pH could be due to either the dissolution of gibbsite or hydrolysis of Al.

It should be kept in mind that the production of H$^-$ or OH$^-$ ions greatly depends on the initial pH of the solution. Soil pH increased near the surface where Al-P interaction
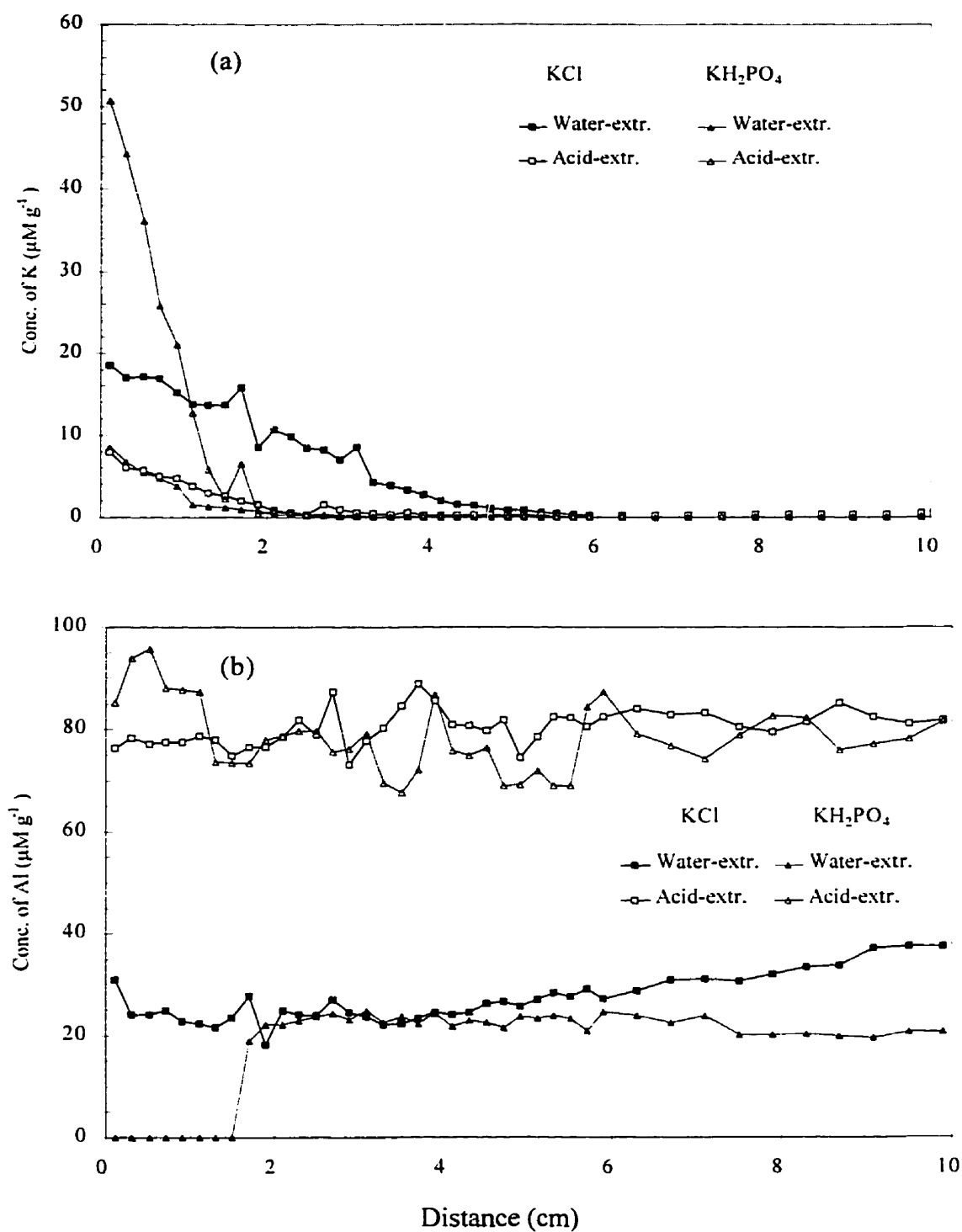
Figure 4.15 Distribution of K (a) and Al (b) as affected by type of salt applied in column
with 22 cmol$_c$ kg^{-1} exchangeable Al and 1% gibbsite after 1 wk of
incubation.

was most profound for all three levels of exchangeable Al when gibbsite was present. The increase in pH could be a result of the dissolution of gibbsite during Al-P precipitation. Ligand exchange could also increase soil pH, but will not play a significant role since the P concentration in this experiment was very high and precipitation would greatly exceed ligand exchange reactions (Sample et al. 1980). As hypothesized, and observed in the columns with sand-resin mixture, the H^- ions were most likely released during the precipitation of Al-P. The H^- ions produced could cause dissolution of gibbsite. The dissolution of gibbsite would then supply more Al for P precipitation with the concomitant release of OH^-. The pH will increase as the OH^- is produced.

The hydrolysis of Al will also play a role in elevating pH. Since the background pH was 4.1 for the columns with 1% gibbsite, as compared to 3.6 for columns without gibbsite, there would be an increasing proportion of $Al(OH)_2^-$ species and a decreasing proportion of Al^{3+} species as pH increased. If Al^{3+} is the reacting Al species with P to form an Al-P precipitate, more and more $Al(OH)_2^-$ would be converted to Al^{3+} in order to maintain equilibrium (Al hydrolysis) during precipitation of Al-P. The conversion of $Al(OH)_2^-$ to Al^{3+} could also release hydroxyl ions (OH^-). Since the columns with 1% gibbsite had a relatively high concentration of Al in solution (25 μM g^{-1}, Figure 4.15b), the production of OH^- from Al hydrolysis was very possible. Once again, the precipitation of P by Al is the reaction which initiated Al hydrolysis and the ultimate production of OH^- ions.

Results from Experiment II were obtained using columns with 1% gibbsite in combination with 0, 22, and 44 $cmol_c$ kg^{-1} levels of exchangeable Al. For the columns with no exchangeable Al, the resulting P profile was caused solely by the addition of

gibbsite. Since the gibbsite used contained quite a large amount of water-soluble Al (25 μM g^{-1}, Figure 4.15b), considerable P precipitated (0.63 mM column^{-1} or 42.9% applied P, from Table 4.4) after 1 wk. However, with both exchangeable Al and gibbsite, almost all the P applied was precipitated (1.2 mM column^{-1}, > 80% P applied) after 1 wk. When there was no exchangeable Al, P had moved to 6 cm after only 1 wk of incubation. But P movement was less than 2 cm when there were 22 and 44 cmol$_c$ kg^{-1} exchangeable Al in the column. The differences could be due to several factors, such as the supply of Al and the effect of pH on Al hydrolysis and speciation as well as phosphate dissociation.

For columns with only gibbsite and no exchangeable Al, the initial Al-P will generate less H$^-$ since its background pH is much higher (5.0, Figure 4.13a) than the columns with both exchangeable Al and gibbsite (4.1, Figures 4.13b and 4.13c). As discussed in Chapter 2, the speciation of Al and dissociation of phosphate are pH dependent; lower pH means more Al is in the Al^{3+} form instead of Al(OH)$_2^-$. Thus, there would be more H$^-$ ions produced at the lower pH during Al-P precipitation. More H$^-$ production would mean more gibbsite dissolution, which supplies more Al for precipitation of Al-P. Thus, a higher acid-extractable P would result in columns with exchangeable Al levels of 22 and 44 cmol$_c$ kg^{-1} than those without exchangeable Al.

A lower pH also means a greater proportion of phosphate was in the form of H$_3$PO$_4^0$. The precipitation reactions would consume H$_2$PO$_4^-$ as described in Equations [4.1] to [4.4]. Such consumption would convert H$_3$PO$_4^0$ into H$_2$PO$_4^-$, generating H$^-$ ions. This could lead to more gibbsite dissolution and Al-P precipitation at lower initial pH levels. The addition of gibbsite evidently reduced P concentration and movement in the soil system tested. A comparison of the P distribution profiles for columns with

exchangeable Al and gibbsite (Figures 4.9 and 4.10) with results of the P distribution in the columns with only exchangeable Al (Figures 4.2 and 4.3), reveals these differences. First, the concentration of water-extractable P was generally lower and acid-extractable P was higher in the presence of gibbsite. Second, differences in the acid-extractable P distributions in the presence of gibbsite narrowed over time. Third, P did not move downwards as much for columns with both exchangeable Al and gibbsite as those with only exchangeable Al.

The results obtained for columns with both exchangeable Al and gibbsite could be partly explained by the supply of Al for Al-P precipitation reactions. The gibbsite used in this experiment contained an appreciable amount of soluble Al, as illustrated in Figure 4.15. The Al solution concentration in the columns with 1% gibbsite was about 25 $\mu M\ g^{-1}$ (Figure 4.15) as compared to < 1 $\mu M\ g^{-1}$ (Figure 4.8) in the columns without gibbsite. Thus, there would be more precipitation of Al-P in the system with gibbsite, resulting in lower levels of water-extractable and higher levels of acid-extractable P. As demonstrated in Figure 4.6, H^+ ions were produced during the Al-P interaction in the absence of gibbsite. H^+ ions could dissolve gibbsite and supply more Al for P fixation in the presence of gibbsite.

Due to the soluble Al associated with the gibbsite, considerable P precipitation would occur without the relying entirely on the exchange reactions to release Al. In other words, the precipitation reaction of Al-P was more dependent on the rate of downward diffusion of P from the surface than on the rate of Al supply from the exchange. Under these conditions, the effects of time of incubation became very small as indicated by the

small differences in acid-extractable P (Figure 4.10) and depth of P movement among different time of incubations (Figure 4.9) in columns with gibbsite.

4.5 Summary and Conclusions

In this study, KH_2PO_4 transport in Al-saturated resin-sand columns at different exchangeable Al levels, with or without gibbsite, was investigated. Both K and P transport was retarded in the presence of exchangeable Al and gibbsite due to the ion-exchange and precipitation reactions. When there was no gibbsite in the columns, the movement and solution concentration of P and K decreased as the exchangeable Al levels increased. When there was no exchangeable Al but only gibbsite in the column, the movement and solution concentration of P was reduced only slightly. However, when there are both exchangeable Al and gibbsite in the columns, the movement and solution concentration of P and K was greatly reduced. The combination of exchangeable Al and gibbsite had far greater effect than the sum of the individual effects.

Results obtained in the two experiments confirmed the proposed P fixation model that shows H^- ions being produced during P fixation and then dissolving gibbsite providing more Al for P fixation. The pH of the system decreased when only exchangeable Al was present, but in the columns with 1% gibbsite the pH increased due to Al-P precipitation, gibbsite dissolution, Al hydrolysis and phosphate association/dissociation.

5. EFFECTS OF LIGNOSULPHONATE ON THE MOVEMENT OF PHOSPHATE AND ASSOCIATED CATIONS IN ALUMINUM-RICH SOIL-LIKE SYSTEMS

Abstract

The availability and movement of inorganic phosphate fertilizer is usually low due to precipitation and adsorption reactions in soil. For some soils, adding organic matter has been shown to reduce such reactions. Lignosulphonate (LS), which is produced from acid sulfite pulping processes, has similar characteristics to soil organic materials. An experiment was designed to study the effects of LS on P movement in a simulated acid soil containing Al-saturated cation exchange resin and acid-washed fine sand. The resulting simulated soil had a cation exchange capacity of 22 $cmol_c$ kg^{-1} and had no or 1% gibbsite. Movement of surface applied mono-potassium phosphate was studied in soil columns, either with 2% LS or without LS. Lignosulphonate reduced phosphate fixation and sustained a higher water-extractable phosphate concentration near the surface of the columns, but had no significant effect on downward phosphate movement in the columns with gibbsite. Lignosulphonate reduced the solution concentration of P near the surface and reduced phosphate movement in the columns without gibbsite. The results suggested that the application of LS may be beneficial to P nutrition in gibbsite-rich soils.

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5.1 Introduction

The phyto-availability of P fertilizer is very low due to its fixation reactions and limited movement, especially in acid soils. The limited movement and rapid reactions of phosphate fertilizer in the soil have been the most important limitations affecting the economic benefits of phosphate fertilization. An understanding of P fixation mechanisms and movement in soil are crucial to efficient utilization of P fertilizer resulting a sustainable and economical development of agriculture. In acid soil, P fixation is mainly due to the precipitation of phosphate by soluble Al and Fe.

A high concentration of Al^{3+} in soil solution is not only toxic to plant growth, but is also responsible for reduced P availability. The soil solution Al^{3+} can be affected by the solubility of Al containing minerals (Menzies et al. 1994b; Richard and Adams 1970), by exchangeable Al (Adhikari and Si 1991; Patiram 1990), and by the concentrations of ligands that form soluble complexes with Al (McBride 1994).

Increased P availability has been achieved by adding organic materials (Iyamuremye and Dick 1996). Organic materials tend to compete with P ions for adsorption sites on colloids and complex cations such as Fe and Al, thereby reducing P fixation (Hue 1991; Hue et al. 1986). Lignosulphonate (LS) is a water soluble lignin-based waste product from pulp and paper processing. Traditionally, LS is treated as a waste and disposed of either by burning or by discharge into aquatic systems. Since LS is a source of organic materials, applying LS to agricultural land can be beneficial by improving soil structure (Buylov et al. 1980), increasing fertilizer N availability (Meier et al. 1993), and reducing ammonia volatilization from urea fertilizer (Al-Kanani et al.

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1994). Lignosulphonate also decreases P fixation in calcareous soils. The decrease was attributed to competition of LS for P adsorption sites (Xie et al. 1991; Xie et al. 1993). LS also increased phosphate uptake by corn when applied together with P fertilizer (Xie et al. 1995).

Lignosulphonate has negatively charged sulphonate, hydroxyl, carboxylate, and phenolate groups throughout the molecule (Stapanian and Shea 1986). Xie et al. (1991) suggested that although LS has the potential to complex cations and/or occupy P adsorption sites, the acidic characteristics of LS may result in greater dissolution of Al and Fe. This would cause rapid precipitation and formation of insoluble Al- and Fe-P in soil.

Soil is a very complicated system and it is very difficult to differentiate the effects of different sources of Al and Fe on P fixation. For example, the effects of exchangeable Al and Fe versus those of Al and Fe from the dissolution of Al and Fe minerals are very difficult to separate. There is also the question of whether adsorption or precipitation of P is the main mechanism in P fixation. Soil is not the ideal medium to study the effect of exchangeable cations versus mineral dissolution on P fixation. Instead, cation exchange resins have been used to simulate soil conditions (Akinremi and Cho 1991; Kim et al. 1983) because resins are uniform, homogeneous and do not adsorb phosphate. Thus, all P fixed is by precipitation. The type and amount of cation on the exchange site can also be controlled with resins.

In this study, a model for P fixation in acid soils rich in gibbsite and exchangeable Al is proposed (Figure 5.1). The model proposes that when a phosphate fertilizer, such as KH_2PO_4, is applied to a soil with its exchange sites dominated by Al, the K^- ion will

(a) Exchangeable Al system
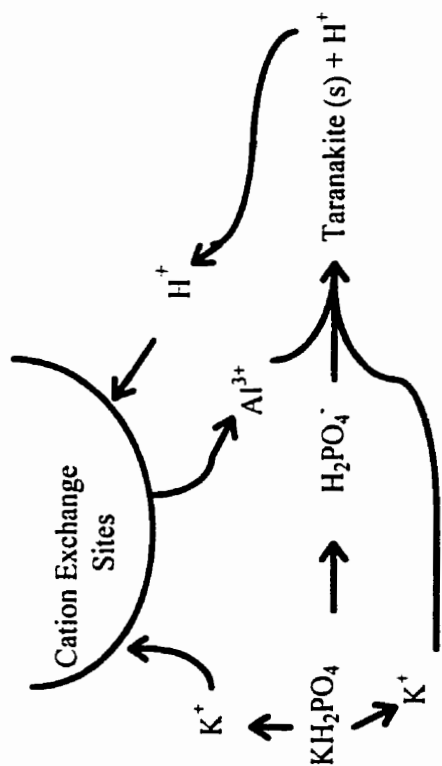
(b) Exchangeable Al plus gibbsite system

(c) Exchangeable Al plus LS system
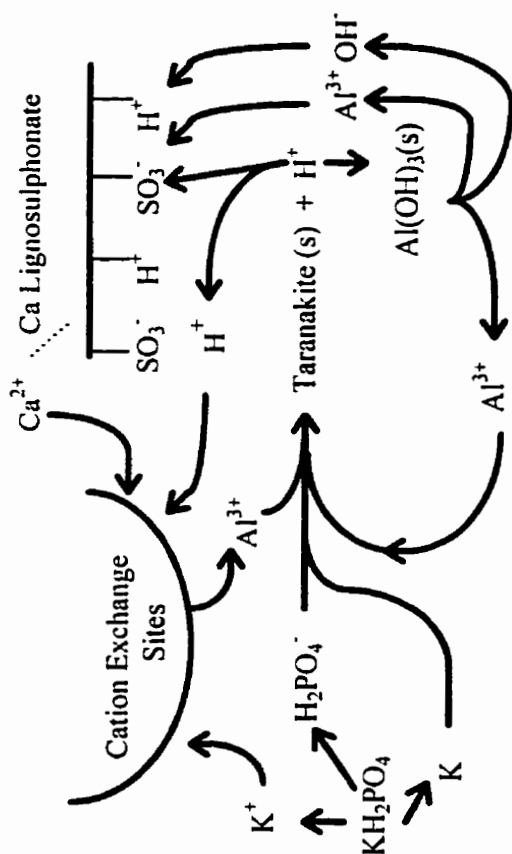
(d) Exchangeable aluminum plus LS and gibbsite system

Figure 5.1 Phosphate fixation model for an aluminum-rich system

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exchange with considerable amounts of Al, thus causing Al release to the soil solution.

The Al in solution combines with the phosphate ions to form an insoluble salt releasing

H^- ions. The H^- released can dissolve solid Al compounds, e.g., gibbsite. The

dissolution of gibbsite by H^- supplies more Al ions for phosphate fixation, thus further

retarding phosphorus movement. LS could be a complexing agent for Al and a source or

sink for H^- and OH^- ions, thereby affecting phosphate fixation and P solubility. Thus,

studies were conducted to determine the effect of LS on the movement and fixation of

phosphate in an Al-rich acid soil.

5.2 Material and Methods

One-dimensional P diffusion was studied using a simulated soil-like system. The

simulated "soil" was made from acid-washed sand ($< 150\mu m$) and an Al saturated resin.

A strongly acidic cation-exchange resin (Amerlite IR-120 Plus, Sigma Chemical Co., St

Louis, MO) with a wet mesh of 100-200 (diameter = 75 to 150 μm) and a CEC of 440

$cmol_c$ kg^{-1} was mixed with the acid-washed sand. To simulate conditions similar to an

acid soil, the resin was saturated with Al^{3+} using the method of Akinremi (1990). The

resulting soil-like system has a cation exchange capacity of 22 $cmol_c$ kg^{-1}.

The experiment used calcium LS in slurry form, containing 50% solid, with a pH

of 5.5. Gibbsite was prepared in the laboratory by titration of 1 M $AlCl_3$ with 1 M NaOH

to a pH of 6. The precipitate was aged for 45 days at room temperature (22^0C). The

mixture was washed daily until all chloride was gone. X-ray analysis showed that

gibbsite was well crystallized after 45 days of aging.

The experiment used a 2x2 factorial design giving four types of soil systems:

- "soil" plus 2% LS and 1% gibbsite (LS2G1)

- "soil" plus 2% LS with no gibbsite (LS2G0)

- "soil" with no LS and 1% gibbsite (LS0G1)

- "soil" alone, with no added LS or gibbsite (LS0G0)

All dry materials were first thoroughly mixed for each treatment. Distilled water and LS (as required) were added to achieve a moisture content of field capacity (0.25 kg kg^{-1}). Finally, the "soil" was packed to a density of about 1.42 g cm^{-3} into wax columns, 4.5 cm in diameter and 10 cm long. Phosphate fertilizer (0.2 g of KH_2PO_4) was applied to the surface after 17 h. Four columns for each treatment were made and incubated in a constant humidity chamber. Two columns of each treatment were analyzed after 1 wk of incubation and the other two after 4 wk.

The columns were cut into 2 mm slices with a meat cutter (Model UL8, International Edge Tool Co., Roseland, NJ) and samples taken from each slice for moisture content and chemical analysis. Approximately 1 g of the resin-sand mixture from each section was placed into a centrifuge tube. One mL of water was added to each tube and the mixture was thoroughly mixed with a vertex mixer. The pH (1:1 in water) was measured after 10 min. An additional 4 mL of water was then added, the mixtures shaken for ten min, and then centrifuged for 10 min at room temperature. The solution was removed with a pipette, 5 mL distilled water was added, and the sample was extracted as outlined above. The extracts obtained were combined and termed "the water-extractable fraction." The same sample was then successively extracted with three 5mL portions of 1 M HCl. The acid extractions were combined and termed "the acid-

extractable fraction." The water-extractable fraction approximates P in soil solution

(mobile phase), while the acid-extractable fraction approximates that which is non-water

soluble (less mobile and immobile phases).

The pH of the "soil" (1:1 in water) was determined using a non-seepage

combination electrode (Canlab). The extractable P was determined by the ascorbic acid-

ammonium molybdate method of Murphy and Riley (1962). Potassium and Al

concentration in the extracts were determined using an atomic absorption

spectrophotometer (Model 1100b, Perkin-Elmer, Norwalk, CT).

5.3 Results and Discussions

5.3.1 Water- and Acid-extractable P

The maximum water-extractable P concentration occurred at the top of the

columns and gradually declined with depth for all treatments and times of incubation

(Figure 5.2). The distribution pattern of P was similar to those obtained by other

researchers (Akinremi and Cho 1991; Eghball et al. 1990; Hashimoto and Lehr 1973).

The highest concentration of water-extractable P at the surface (20 μM g^{-1}) occurred in

the samples with LS and without gibbsite (LS2G0). The concentration of water-

extractable P at the surface after 1 wk of incubation was in the order of LS2G0 > LS0G0

> LS2G1 > LS0G1 (Figure 5.2a). The depth of P movement was in the order of LS0G0

>> LS2G0 > LS2G1 > LS0G1 for the same time of incubation period (Figure 5.2a).

The distribution profiles for water-extractable P after 4 wk of incubation were

similar to those obtained after 1 wk of incubation, but the concentrations at the surface

decreased. The maximum concentrations of water-extractable P were again at the

Figure 5.2 Effect of LS on the distribution of water-soluble P in Al-saturated cation exchange resin and sand columns with and without gibbsite.

surface. However, there was virtually no difference in the concentration of water-extractable P at the surface with and without LS in sample (LS0G0 and LS2G0). Phosphate in the columns without LS moved to greater depths than those with LS when gibbsite was not present (Figure 5.2b).

There was considerable difference in the effects of LS on P movement for the columns with 1% gibbsite and those without. In the columns without gibbsite, the addition of LS (LS2G0) generally decreased the water-extractable P and the depth of P movement. In the columns with gibbsite, adding LS (LS2G1) increased water-extractable P near the surface of the column. However, the difference narrowed over time. Addition of gibbsite generally decreased the concentration of water-extractable P at the surface as well as the depth of P movement, regardless of the level of LS.

The concentration of acid-extractable P was highest for LS0G1 and lowest for LS0G0 column after 1 wk of incubation (Figure 5.3). As incubation progressed, there was very little change in distribution profiles of acid-extractable P for all treatments at 4 wk. The magnitude of acid-extractable P at the surface increased in the reverse order as that of water-extractable P, i.e., LS0G1 > LS2G1 > LS2G0 > LS0G0 (Figure 5.3). This was expected, because the acid-extractable P fraction represents precipitation of Al-P and thus a decrease in water-extractable P. Columns with gibbsite generally had higher acid-extractable and lower water-extractable P than those without gibbsite.

5.3.2 Water- and Acid-extractable K

The water-extractable K reflects the level of K^- in the soil solution. The patterns of water-extractable K resembled those obtained for P, with maximum concentrations

Figure 5.3 Effect of LS on the distribution of acid-soluble P in Al-saturated cation exchange resin and sand columns with and without gibbsite.

near the surface and a gradual decrease with depth (Figure 5.4). The concentration of water-extractable K near the surface was much higher for columns with 2% LS (LS2G0 and LS2G1) than for columns without LS for both incubation periods. The concentrations of water-extractable K at the surface of the column decreased over time, as was observed for P.

The high water-extractable K when LS was added to the system was probably due to competitive cation exchange reaction of Ca^{2+} from the LS competing with K^- for exchange sites. Due to the competition of Ca^{2+} with K^+ for exchange sites, more K^+ ions were left in the soil solution with LS (Figure 5.4, LS2G0, LS2G1) than without LS (Figure 5.4, LS0G0, LS0G1). Water-extractable K^+ concentration decreased with time of incubation as a result of adsorption onto the exchange sites, downward movement or precipitation as taranakite. Acid-extractable K^- concentration at the surface was generally lower with LS than without. This again was due to competitive cation exchange reactions (Figure 5.5).

5.3.3 Mass Balance of Applied P and K

The total amount of water-extractable P decreased with time whereas acid-extractable P increased (Table 5.1). The decrease in water-extractable P reflects the continuous precipitation of the added P as Al-P. The addition of LS generally increased the total water-extractable P in the columns with gibbsite whereas LS decreased water-extractable P in the columns without gibbsite. Recoveries of less than 100% are probably due to the formation of acid insoluble taranakite (Chapter 3). In contrast, the addition of LS always increased water-extractable K^- due to the competition between Ca^{2+} and K^- for exchange sites, leaving more K in solution (Table 5.2).
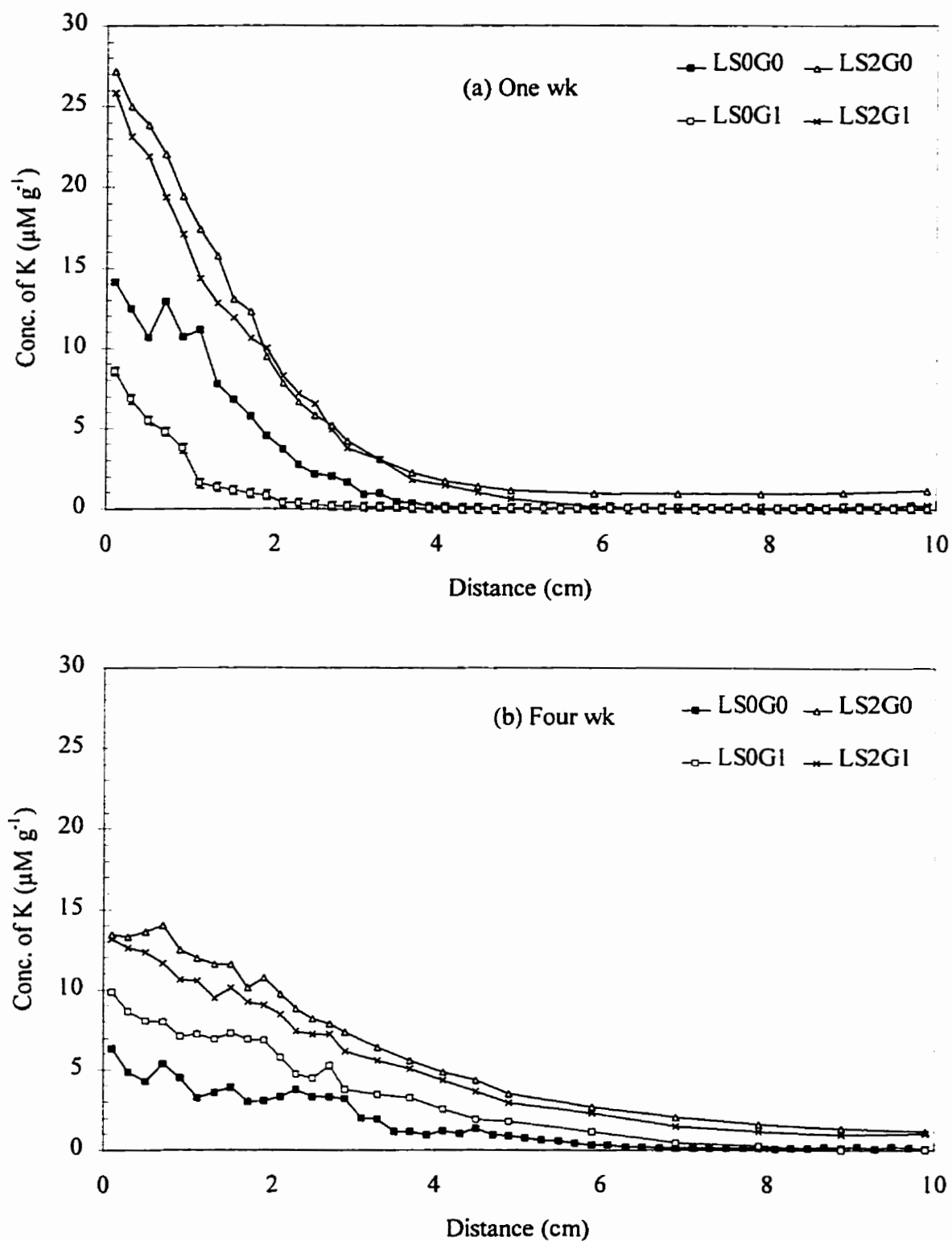
Figure 5.4 Effect of LS on the distribution of water-soluble K in Al-saturated cation exchange resin and sand columns with and without gibbsite.
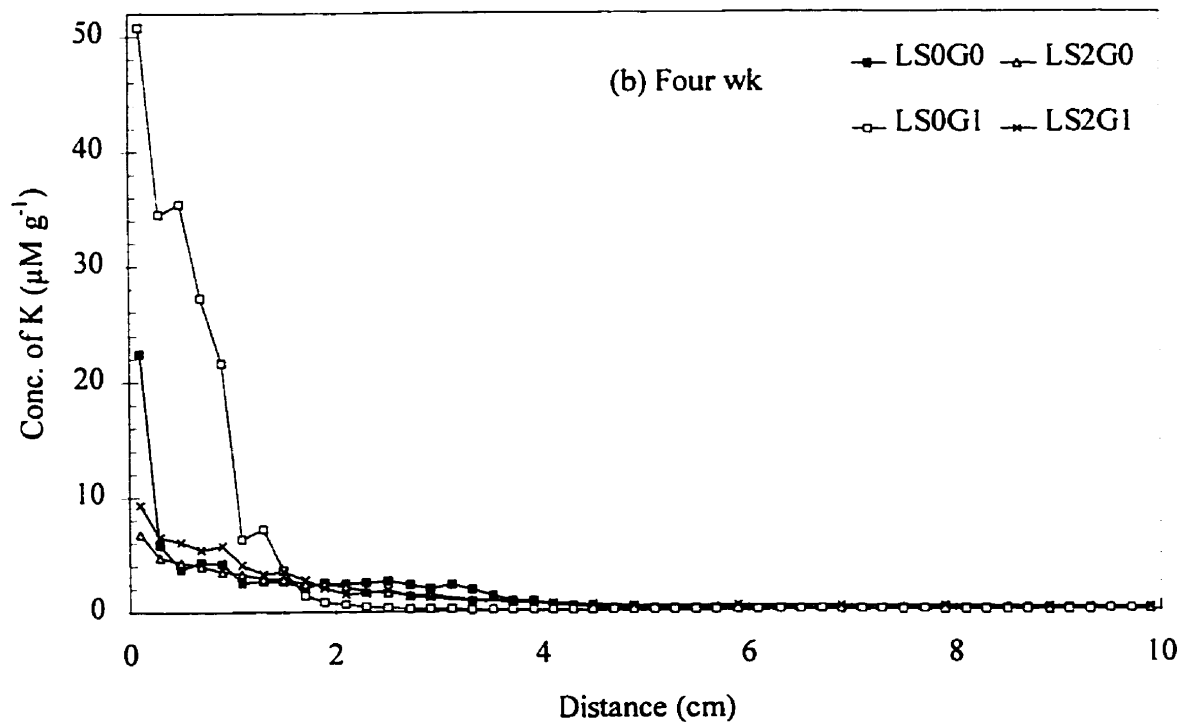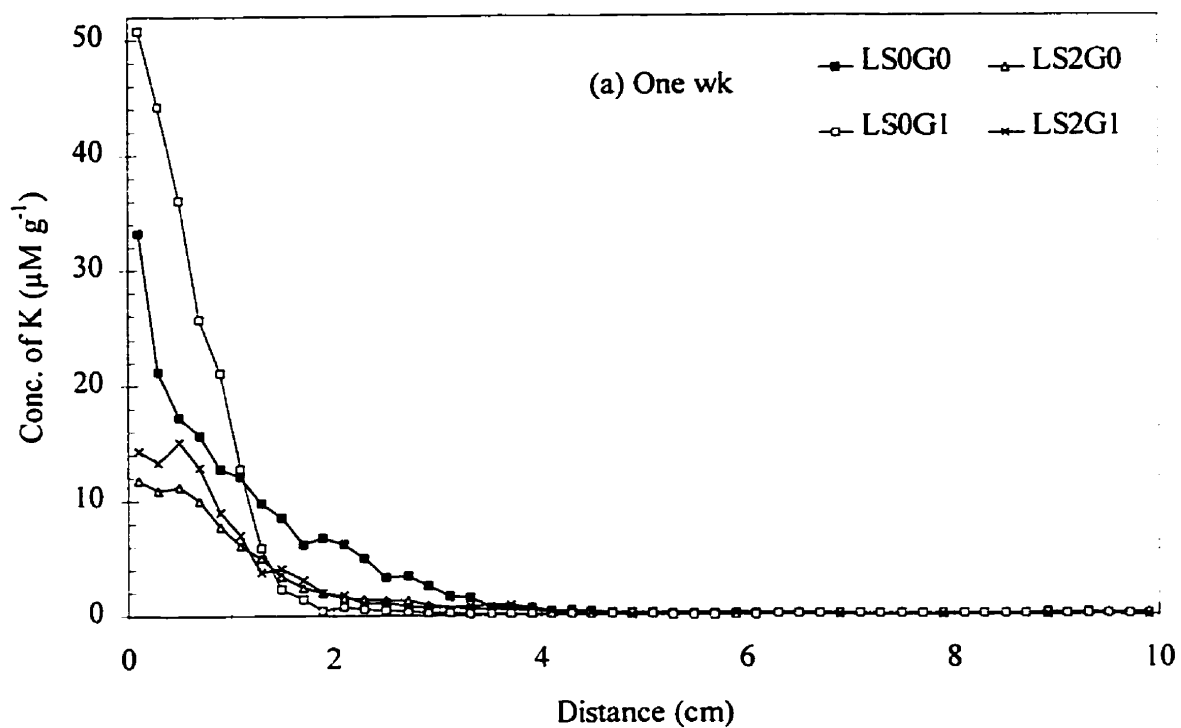
Figure 5.5 Effect of LS on the distribution of acid-soluble K in Al-saturated cation exchange resin and sand columns with and without gibbsite.

Table 5.1 Recovery of water- and acid-extractable P as affected by LS in Al-saturated cation exchange resin and sand columns with and without gibbsite.

| Treatments | | P added | Water-extr P | Acid-extr P | Total P recovered | Percentage Recovered |
LS	Gibbsite					
			mM column^{-1}			
			1 wk			
0	0	1.470	0.826	0.625	1.450	98.7
2%	0	1.470	0.571	0.786	1.357	92.3
0	1%	1.470	0.182	1.217	1.400	95.2
2%	1%	1.470	0.283	1.096	1.379	93.8
			4 wk			
0	0	1.470	0.702	0.764	1.465	99.7
2%	0	1.470	0.375	1.133	1.508	102.6
0	1%	1.470	0.043	1.300	1.343	91.3
2%	1%	1.470	0.057	1.222	1.278	87.0

Table 5.2 Recovery of water- and acid-extractable K as affected by LS in Al-saturated cation exchange resin and sand columns with and without gibbsite.

| Treatments | | K added | Water-extr K | Acid-extr K | Total K recovered | Percentage Recovered |
LS	Gibbsite					
			mM column^{-1}			
			1 wk			
0	0	1.47	0.52	0.79	1.31	89.3
2%	0	1.47	1.18	0.39	1.57	106.7
0	1%	1.47	0.18	0.93	1.11	75.2
2%	1%	1.47	0.99	0.43	1.42	96.4
			4 wk			
0	0	1.47	0.35	0.35	0.70	47.5
2%	0	1.47	0.87	0.17	1.03	70.2
0	1%	1.47	0.17	0.88	1.05	71.6
2%	1%	1.47	0.82	0.17	0.99	67.5

5.3.4 Water- and Acid-extractable Al

The concentration of water-extractable Al near the surface was highest for columns with LS (Figure 5.6). The concentration of water-extractable Al near the surface was near zero for columns without LS (LS0G0 and LS0G1). In contrast to the results for P and K, the concentration of water-extractable Al was low at the surface and increased with depth, except for columns with neither LS nor gibbsite (LS0G0). Concentrations of Al in the LS0G0 columns were very low and constant throughout the column. The concentration of water-extractable Al increased with depth more gradually for columns with LS. For the columns with gibbsite, but without LS, the concentration of Al remained near zero to a depth of 1.3 cm, then increased very rapidly to background levels (around 20 to 25 μM g^{-1}). Increasing the time of incubation had little effect on these patterns. The background level of Al is defined as the Al concentration at the bottom part of columns, where there were no Al-P interactions and thus which also represents Al concentration before the P application.

Water-soluble Al decreased where P penetrated for all treatments (Figure 5.6), most likely resulting from precipitation of Al-P. Adding LS increased the Al^{3+} concentration near the surface. The concentration of water-extractable Al near the surface was still quite high (> 2.5 μM g^{-1}) for the columns with LS (LS2G0 and LS2G1) when compared to columns without LS (LS0G0, LS0G1), whose values were < 1 μM g^{-1}. The increase in concentration of water-extractable Al^{3+} near the surface when added P interacted with Al was probably due to the complexation of Al^{3+} by the LS.

The background level of water soluble Al^{3+} increased considerably for columns without gibbsite when LS was added (compare LS0G0 to LS2G0). The Ca^{2+} from the
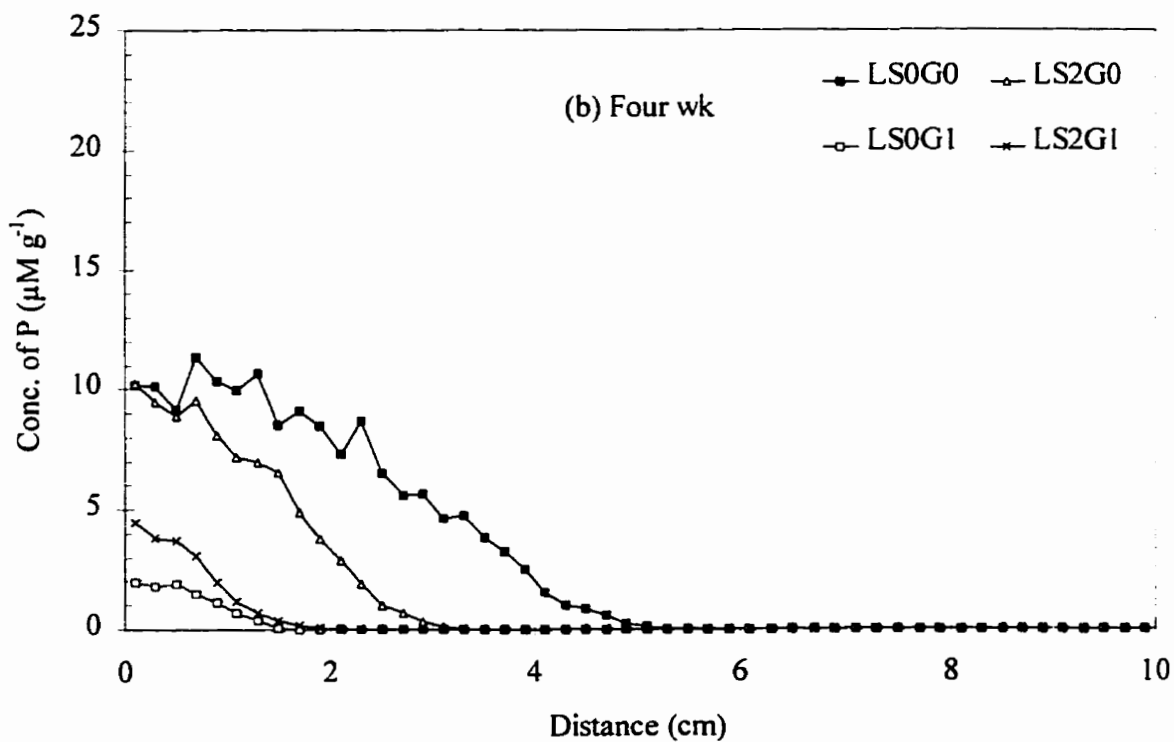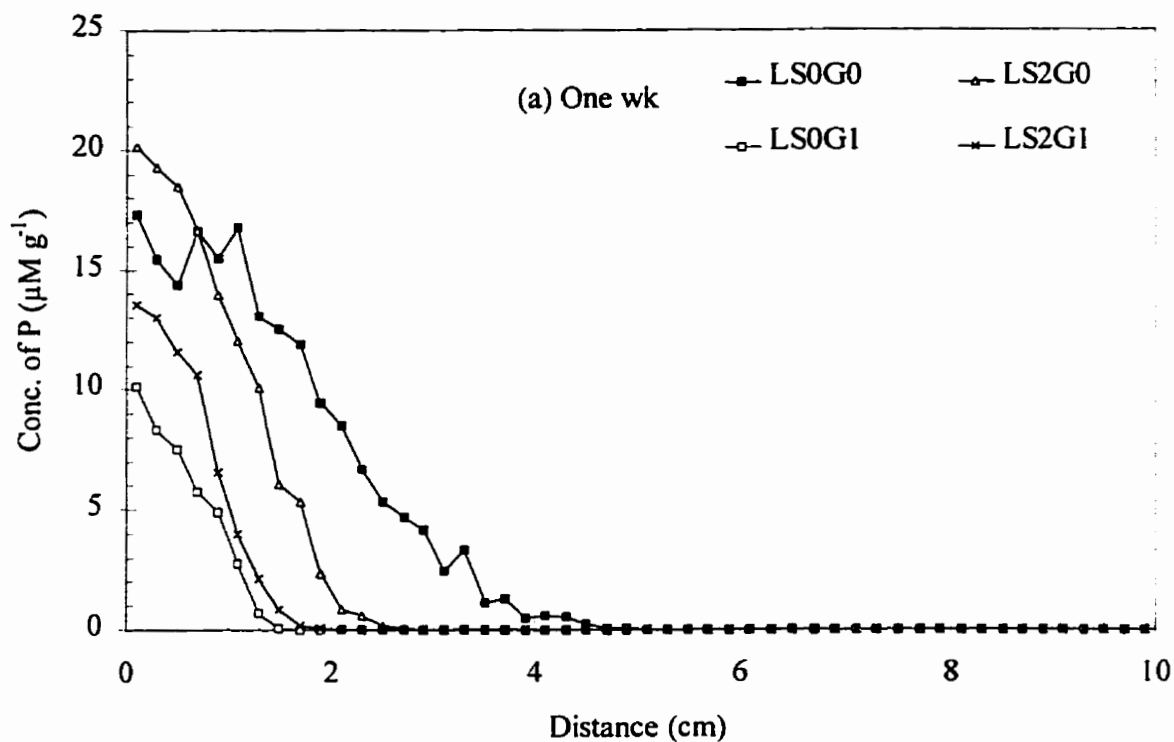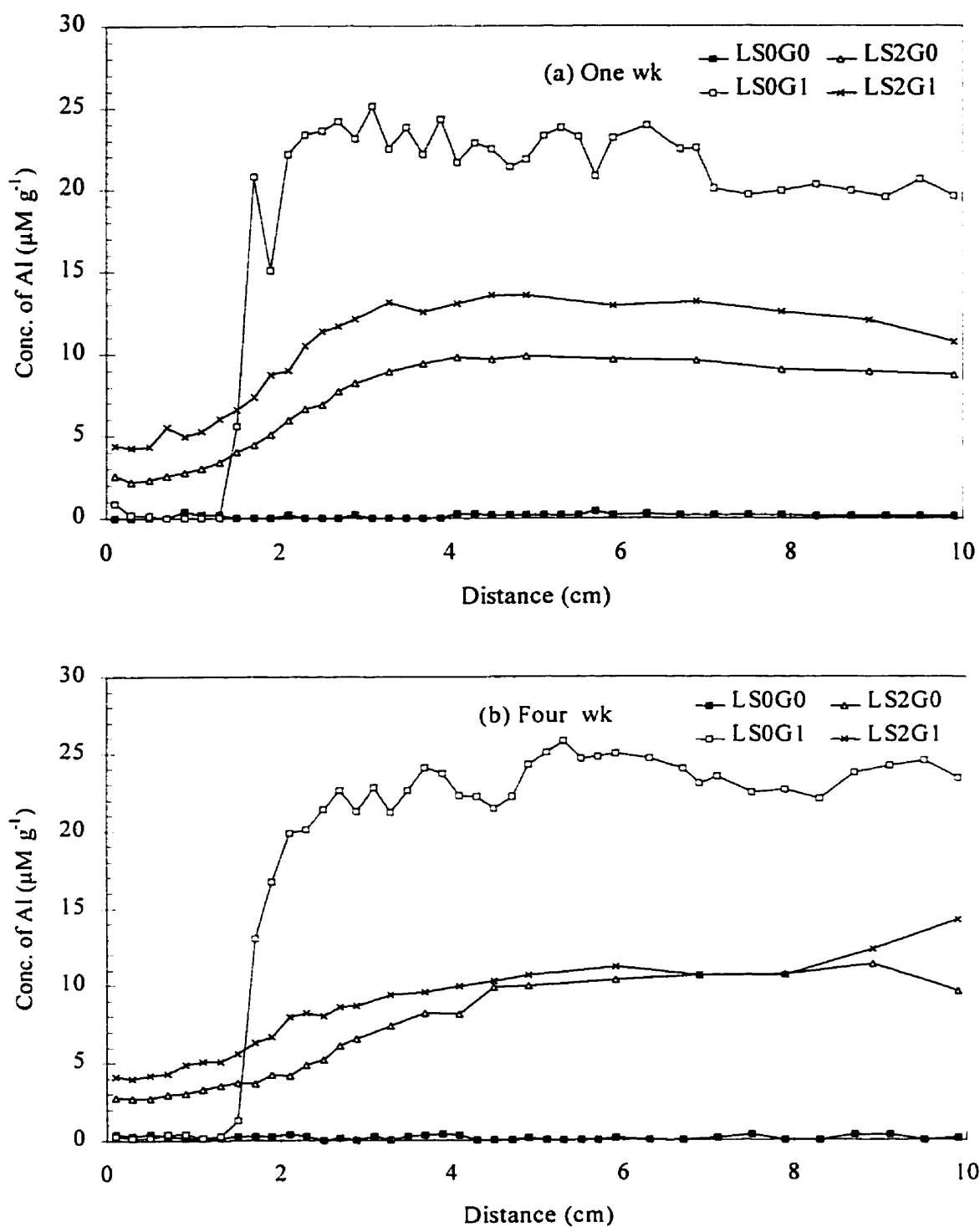
Figure 5.6 Effect of LS on the distribution of water-soluble Al in Al-saturated cation exchange resin and sand columns with and without gibbsite.

Ca-LS exchanged for Al on exchange sites, resulting in a higher level of water-extractable Al. However, in the columns with gibbsite, the addition of LS lowered the Al in solution (compare LS0G1 to LS2G1).

The background levels of water-extractable Al were generally higher for columns with gibbsite (LS0G1 and LS2G1) than without (LS0G0 and LS2G0). The differences can be attributed to the high water soluble Al in the gibbsite used for the experiment. The greater solubility of laboratory-prepared samples than commercially available gibbsite have been attributed to a greater concentration of structure defects in the crystals (Bloom and Weaver 1982).

The background level of acid-extractable Al at the bottom of the column reflects the amount of Al on the exchange sites (Figure 5.7). However, at the top of the columns, where Al-P precipitation occurred, the level of acid-extractable Al includes both the amount of Al on exchange sites as well as the amount of Al-P precipitates that are soluble in 1 M HCl. Considerable amounts of Al were precipitated by P as indicated by the high value of acid-extractable Al near the surface, especially for columns with gibbsite (Figure 5.7).

5.3.5 Soil pH

The pH profiles for both the 1 and 4 wk of incubation periods are shown in Figure 5.8. In the absence of gibbsite (LS0G0 and LS2G0), the pH decreased at the surface when KH_2PO_4 was added to columns for both incubation periods. The decrease in pH was greater in columns with LS than without. In the absence of LS, the pH decreased with depth and reached a minimum at a depth of 1.9 cm (pH = 2.9) and then increased with depth until it reached the background level at a depth of 5.5 cm at 1 wk of
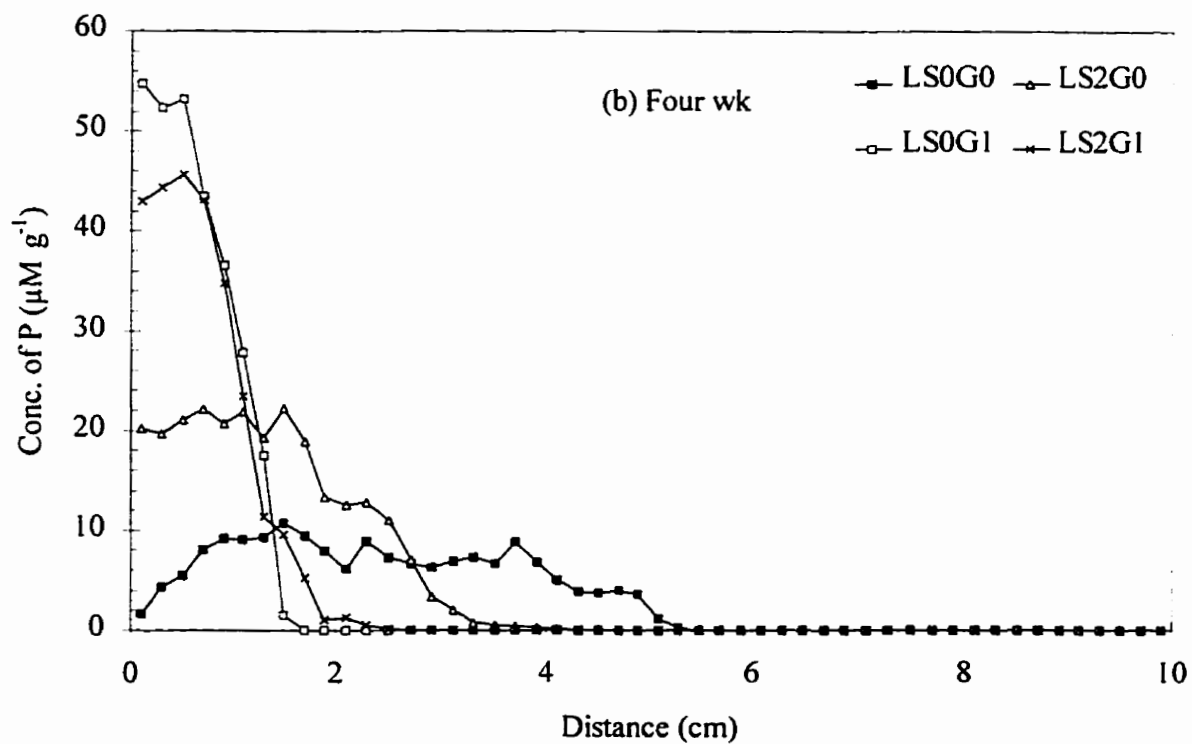
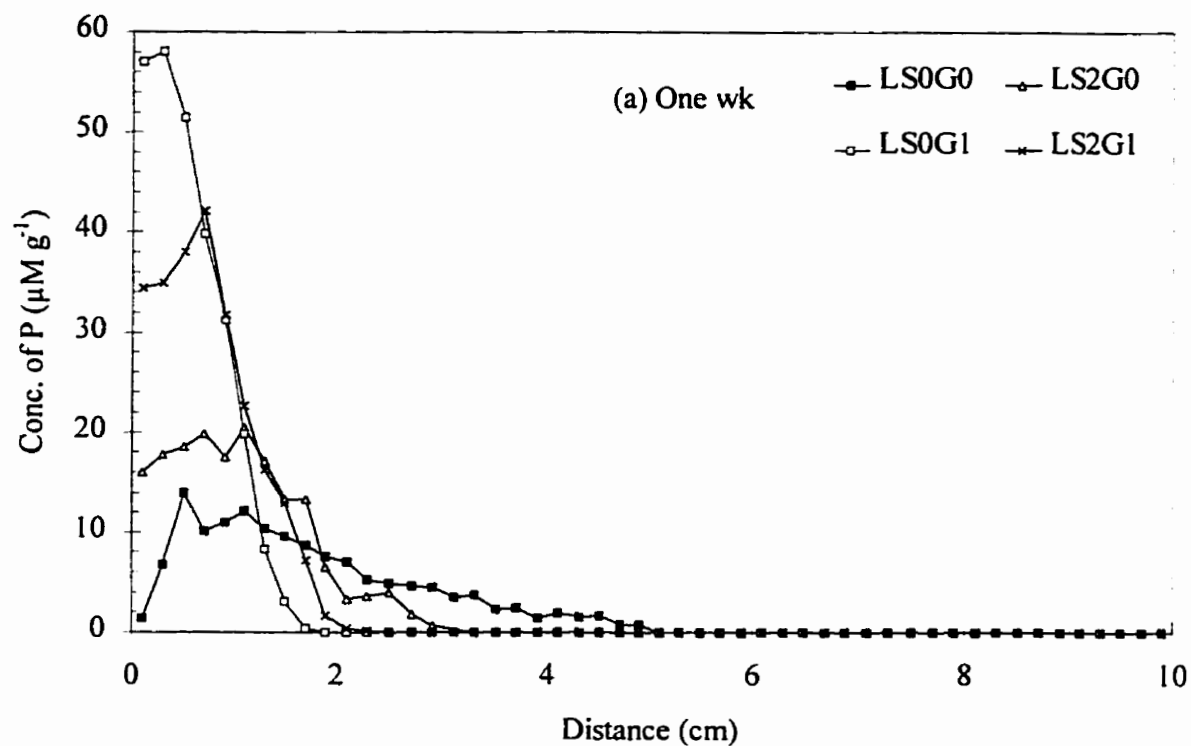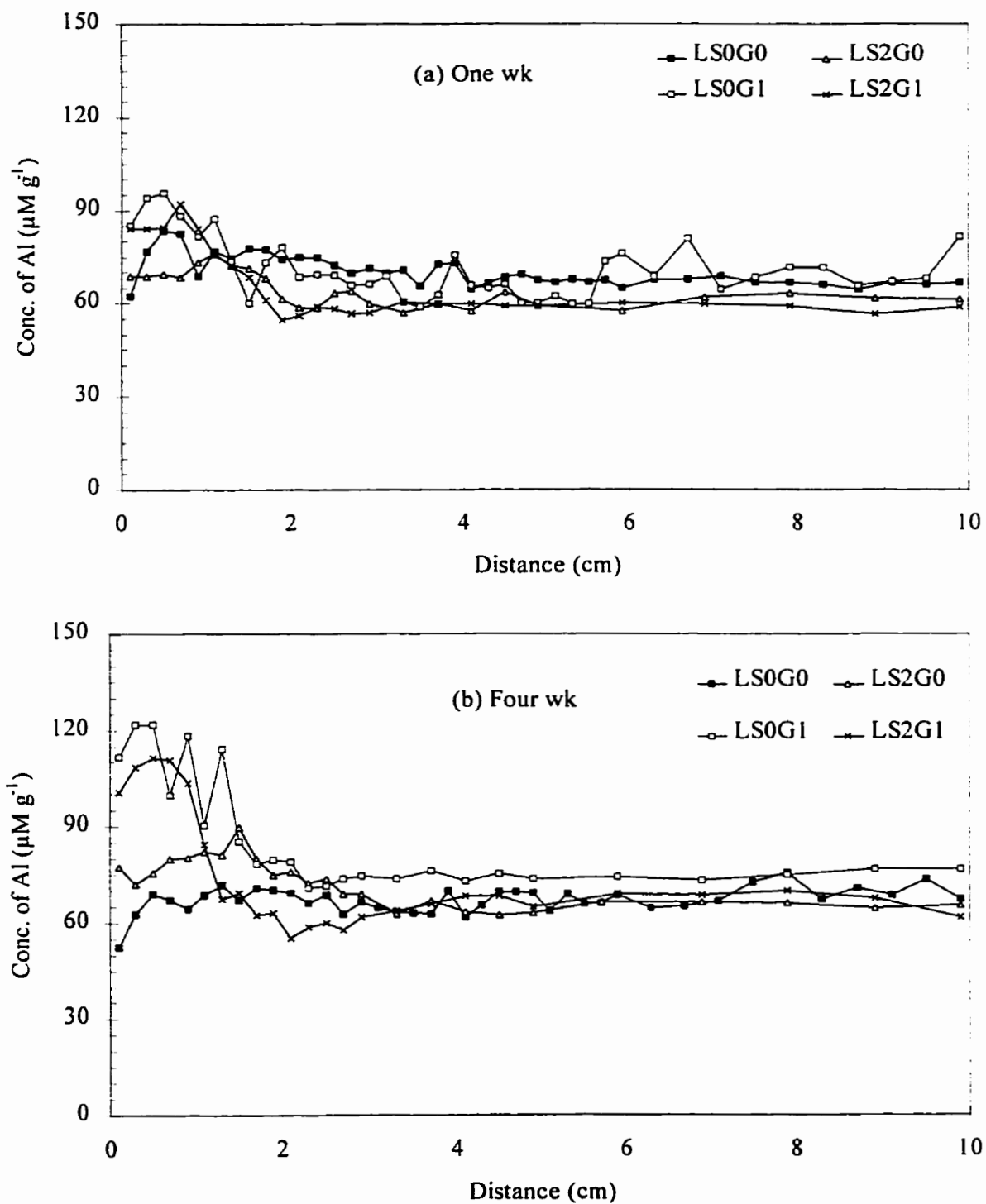Figure 5.7 Effect of LS on the distribution of acid-soluble Al in Al-saturated cation exchange resin and sand columns with and without gibbsite.

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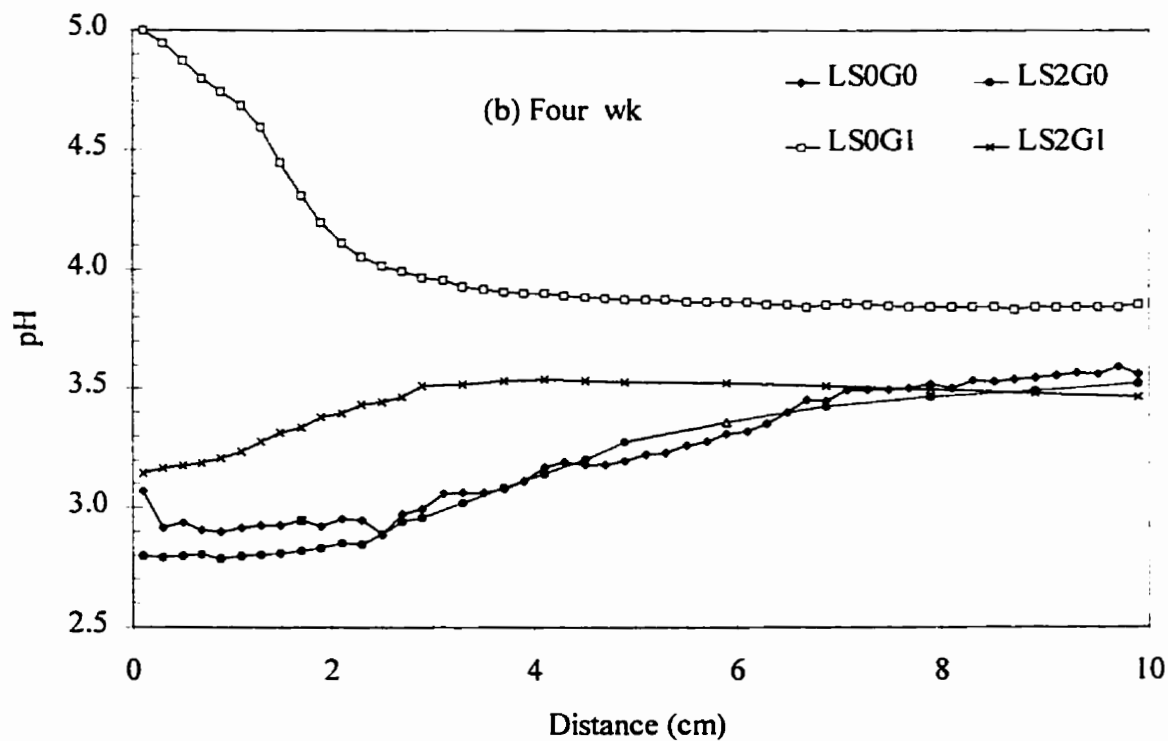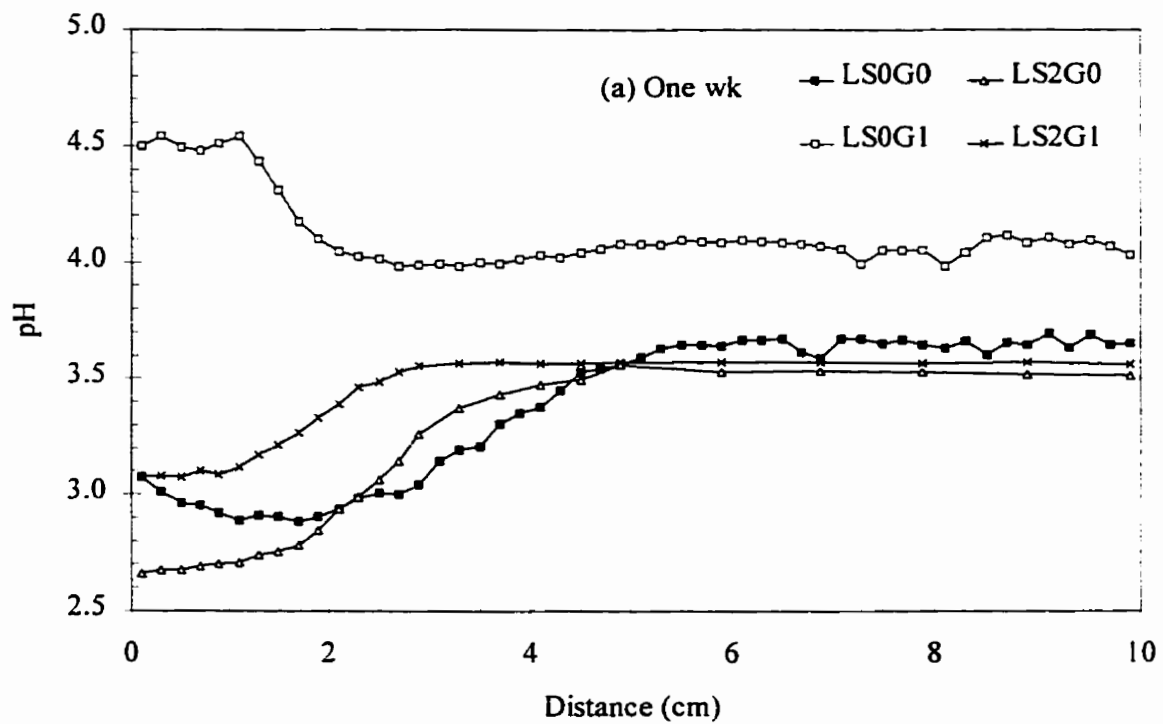
Figure 5.8 Effect of LS on the profile of pH in Al-saturated cation exchange resin and sand columns with and without gibbsite.

incubation. In the presence of LS, the pH values were much lower at the surface and it increased gradually with depth and reached the background level at a depth of 5.0 cm. However, pH at the surface increased in the column without LS (LS0G1) whereas pH decreased in the column with LS (LS2G1) in the presence of gibbsite.

The pH profiles observed are a function of processes such as cation exchange reactions, Al hydrolysis, phosphate dissociation, Al and phosphate complex formation, and Al-P precipitation reactions. As shown below, in the Al^{3+}-saturated resin system, the reaction of Al^{3+} with phosphate ions caused a shift in the equilibrium to the right with the production of hydrogen ions:

$$5 Al^{3+} + 3 K^+ + 8 H_2PO_4^- \rightleftharpoons K_3 Al_5H_6(PO_4)_8 (s) + 10H^- \qquad [5.1]$$

The above reaction occurred without gibbsite and LS, since only exchangeable Al existed in the column. Thus, the pH of columns decreased as a result of the production of H^- ions. The slightly lower pH for columns without gibbsite, but with LS, for both incubation periods was due to competitive cation exchange reactions. The Ca^{2-} from LS would reduce the amount of H^- on the exchange complex due to competition, with the result that more H^- ions remained in solution. This was reflected in the lower pH near the surface for the LS treated columns (LS2G0, Figure 5.8). When gibbsite was present in the soil system (LS0G1), the H^- ions released by the initial precipitation of Al-P dissolved gibbsite releasing OH^- and Al^{3+} or $Al(OH)^{2+}$ ions into solution and thus increasing the pH.

The decrease in pH with both LS and gibbsite, but increase with gibbsite only, could be due to a number of factors. First, the treatment with both LS and gibbsite had a much higher Al solution concentration than that with neither LS nor gibbsite (Figure 5.6).

Thus, more OH⁻ ions would be required to increase pH by one unit for solutions with high

Al concentration than for solutions with low Al concentration. Second, functional groups

of LS act as a pH buffer and could complex most of the H⁻ produced during Al-P

precipitation reactions. If more H⁻ ions were complexed, there would be less free H⁻ ions

and thus less gibbsite dissolution and OH⁻ production. This is consistent with the lower

precipitation of Al-P for columns with gibbsite where LS was also added. Third, the LS

could complex OH⁻ ions and thus less OH⁻ will be free in soil solution. Finally, the

background pH of columns with LS added was also much lower than those without LS,

when gibbsite was in the columns. Less OH⁻ will be produced during fixation and

gibbsite dissolution at low than at high pH. The low background pH with LS was

probably caused by Ca^{2+} exchange reactions, releasing Al^{3+} and H⁻ from exchange sites

into the soil solution, thereby lowering pH. The production of H⁻ or OH⁻ ions during the

Al-P precipitation reaction are greatly dependent on the initial pH of the system. These

observations confirmed the hypothesized model outlined in Figure 5.1.

The results clearly show that LS buffered the pH of the system through its

functional groups (Figure 5.8). LS can act as a buffer by accepting either H⁻ or OH⁻, so

that the pH of the system does not change drastically during H⁻ or OH⁻ production.

Gibbsite decreased the concentration of P in solution and the movement of P

(Figure 5.2). The lower water-extractable P in the columns with gibbsite was attributed

to the gibbsite being an unlimited source of Al, greatly accelerating P fixation. The total

amount of water-extractable P was also generally lower, and acid-extractable P higher,

with gibbsite than without (Table 5.1). High acid- and low water-extractable P suggests

that there was more precipitation of Al-P with gibbsite than without. The greater

precipitation with gibbsite was probably due to dissolution of the gibbsite which favored Al for precipitation with P. There were considerably higher amounts of water-extractable Al in the columns with gibbsite than in columns without gibbsite.

The effect of LS on phosphate concentration and movement were greatly dependent on the presence or absence of gibbsite. LS increased Al-P precipitation without gibbsite, but decreased precipitation with gibbsite. The decrease in water-extractable P with LS and no gibbsite is probably due to the accelerated release of exchangeable Al as well as the lower pH caused by the addition of LS. The Ca^{2+} added in the LS probably released Al from the exchange sites at a much greater rate than K. Since the release of Al was increased with LS, the precipitation of Al-P increased. Thus, water-extractable P was reduced and the downward diffusion of P was retarded. Similar results were observed by Akinremi and Cho (1993) with a calcareous soil. In their experiment, KCl was added with KH_2PO_4 in a Ca^{2+} saturated resin-sand system. The addition of KCl increased P fixation as a result of the accelerated release of Ca^{2+} from the exchange sites and increased precipitation of Ca-P.

In the columns with gibbsite, adding LS increased water-extractable P near the surface of the columns relative to columns without LS. However, the difference narrowed over time. The increased water-extractable P could be attributed to several factors. First, LS acts as a buffer for the H^+ initially released from the precipitation of Al-P, and much of the H^+ released was complexed by LS. This reduces the supply of Al from the dissolution of gibbsite, thereby reducing P fixation. Xie et al. (1993) observed a decreased dissolution of Ca as well as decreased P retention when NH_4LS was added to a calcium-rich soil (soil pH of 5.7). While adding LS would promote Al^{3+} release from the

exchange sites, which could increase P fixation, the effects of accelerated Al release from the exchange sites were not significant compared to the reduction in gibbsite dissolution. The net result is a reduction in P fixation. Second, LS can complex Al in the solution and effectively reduce the amount of Al available for the precipitation of Al-P. Third, LS may act as a bridge taking Al^{3+} ions out of solution forming Al-LS-gibbsite. Indeed, the water-extractable Al was greatly reduced.

A decrease in the level of water-extractable P over time was also observed. This was a result of downward diffusion in the column and precipitation of Al-P. The depth of P movement increased with time. Depth of P movement was reduced by adding LS to columns without gibbsite while no noticeable effect was observed in the columns with gibbsite.

The practical implication of these results is that application of LS to acid soils rich in gibbsite will enhance the bio-availability of P, since it increased water-extractable P in the simulated soil. However, for soils high in exchangeable Al and low in gibbsite, adding LS may not increase bio-availability of P to plants.

The findings are consistent with the proposed model's description of the P fixation process in Al-rich systems when LS is added. As demonstrated in the columns with only exchangeable Al, adding LS increased the release of exchangeable Al and thus increased P fixation. In contrast, in the columns with both gibbsite and exchangeable Al, the complexation of H^+ and Al ions by LS reduced the Al availability for precipitation of Al-P. This should be beneficial for P nutrition of crops. Complexation of Al by LS could also speed up the gibbsite dissolution process causing more Al leaching and reducing Al toxicity in long term. Further study is needed to examine the mechanisms by

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which LS increases P bio-availability in gibbsite-rich soils and the conditions under which the application of LS to agricultural land could be beneficial. The research should also be expanded to include natural soils and soils rich in Fe oxides.

5.4 Summary and Conclusions

In this study, the effects of LS on KH_2PO_4 transport in a Al-saturated cation exchange resin mixed with fine sand, in the presence or absence of gibbsite, were investigated. In the columns with no gibbsite, adding LS increased P fixation through accelerated release of Al by cation exchange reactions. In the columns with gibbsite, adding LS decreased P fixation by complexing H^+ ions and thus reducing gibbsite dissolution and P fixation. The experimental results support the proposed research model. The resin-sand column with gibbsite closely reflected an acid soil, and this research showed that adding LS will increase fertilizer P availability in a gibbsite-rich acid soil. Given these results, land disposal of LS may be an economically viable and a less environmentally damaging alternative to the traditional disposal methods such as burning or discharge into the aquatic environment.

6. PHOSPHATE MOVEMENT AND AVAILABILITY

IN A GIBBSITE-RICH OXISOL

Abstract

The movement of phosphate (P) is limited by its low solubility due to precipitation and other fixation processes. The fixation of P is a complex reaction with Al (Al) and iron (Fe) playing a major role in acid soil. This study was conducted to test the proposed phosphate fixation mechanisms and to examine the one-dimensional diffusive movement and solubility of applied phosphate fertilizer in a gibbsite-rich soil column. The soil sample used in this study, a loamy sand, was obtained from the west coast of Australia, 150 km south of Perth. Soil columns, with surface applied KH_2PO_4, were incubated in a constant humidity chamber for various time periods. The movement of phosphate was less than 1.9 cm even after 4 wk of incubation. The solution concentration of phosphate near the surface continued to decrease during the incubation period. Solution pH, Al and Fe concentration were elevated near the surface as a result of phosphate fertilizer application. This increase was attributed to the dissolution of Al and Fe oxides and hydroxides by the H^+ ions produced during the phosphate fixation reaction as proposed in the research model.

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6.1 Introduction

Acid soils, developed under humid conditions, have Al^{3+} occupying a large proportion of the exchange sites. Two fundamental factors limit the fertility of acid soils, impoverished nutrients status (e.g., deficiency of P, Mo, S, K, Ca, Cu, or Zn) and the presence of phyto-toxic substances (e.g., soluble Al and Mn) (Haynes 1984). In particular, phosphate presents special difficulties because it is subject to strong fixation by the soil component. The movement of applied P fertilizer in soil also affects its efficiency by influencing the probability of root/P-fertilizer contact as well as soil/P-fertilizer contact (Eghball et al. 1990). The movement of phosphate fertilizers is very limited in many soils because of their tendency to react with soil constituents. The movement of P in soil is mainly through diffusion (Barber et al. 1963).

Experiments with an Al-saturated cation exchange resin have shown that phosphate movement and solution concentration were affected by both the levels of exchangeable Al and the presence of gibbsite (Chapter 4). In those experiments, the release of exchangeable Al after the application of KH_2PO_4 was observed and phosphate mobility was retarded as a result of cation exchange reactions and subsequent Al-P precipitation. In this experiment, the reaction and the diffusive transport of phosphate in a gibbsite-rich acid Oxisol was studied.

6.2 Materials and Methods

A gibbsite-rich surface soil, obtained from approximately 150 km south of Perth Australia, was used. Vegetation cover is predominately Eucalyptus marginata (*Jarrah*) and Eucalyptus calophylla (*Marri*). The pertinent soil properties are listed in Table 6.1.

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The experiment was performed as outlined in Chapter 4. Soil at field capacity moisture content was packed into cylindrical columns made of wax with inner diameters of 4.5 cm and height of 10 cm. Seventeen hours later, 0.2 g (equivalent to 1.47 mM) of KH_2PO_4 was applied to the soil surface in each column. Soil columns were incubated for 3 d, 1 wk, 2 wk and 4 wk. After incubation, the columns were sectioned into 2 mm slices with a meat cutter. Samples were taken from each section for moisture content and chemical

Table 6.1 Some physical and chemical properties of the soil used.

Property	
Texture	Loamy sand
	78.2% sand
	16.8% silt
	5.0% clay
$pH_{(1:2)}$	5.5 in water
	5.01 in 0.01 M $CaCl_2$
CEC ($cmol_c$ kg^{-1})	2.35-3.24
	Al 60%
	Fe 30%
Saturated paste (mM L^{-1})	Al 0.44
	Fe 0.017
	Ca 0.047
Field capacity (kg kg^{-1})	0.13
Dominant mineral (in clay fraction)	gibbsite
Bulk density (kg m^{-3})	1860
Vegetation cover	Eucalyptus
Organic matter	< 0.5%

analysis. Three soil samples of approximately 1 g each from each section were weighed into 15 mL centrifuge tubes. One mL of distilled water was applied to each tube, and the pH of each mixture was measured. An additional 4 mL of distilled water was then added and the samples were equilibrated with shaking for a period of 10 min and centrifuged. The clear solution was removed using a pipette. A second water-extraction was conducted using 5 mL of distilled water as described above. The two water extractions were combined. The concentration of P, K, Al, Fe, and Ca measured in this fraction were called "the water-extractable fraction." One of the three initial samples was used for acid-extraction, a second was used for ammonium oxalate-extraction and the third was used for barium chloride-extraction. The samples were extracted successively three times with 5 mL 1 M HCl, 0.25 M ammonium oxalate (NH_4OX, light color with pH value of 6.65) or 0.25 M BaCl.

Extractable K, Fe Al and Ca were measured using an atomic absorption spectrophotometer (Perkin-Elmer 1100b). Phosphate concentration was determined using a spectrophotometer (Spectronic 301 by Milton Ray) according to the modified method of Murphy and Riley (1962). Results reported are the average of two columns.

6.3 Results and Discussion

6.3.1 Extractable P

The maximum concentration of water-extractable P was found near the surface and decreased with depth for all incubation periods (Figure 6.1). The concentration of water-extractable P (Figure 6.1a) near the surface decreased with time of incubation, from around 22 μM g^{-1} after 3 d to 8 μM g^{-1} after 4 wk of incubation. Phosphate movement
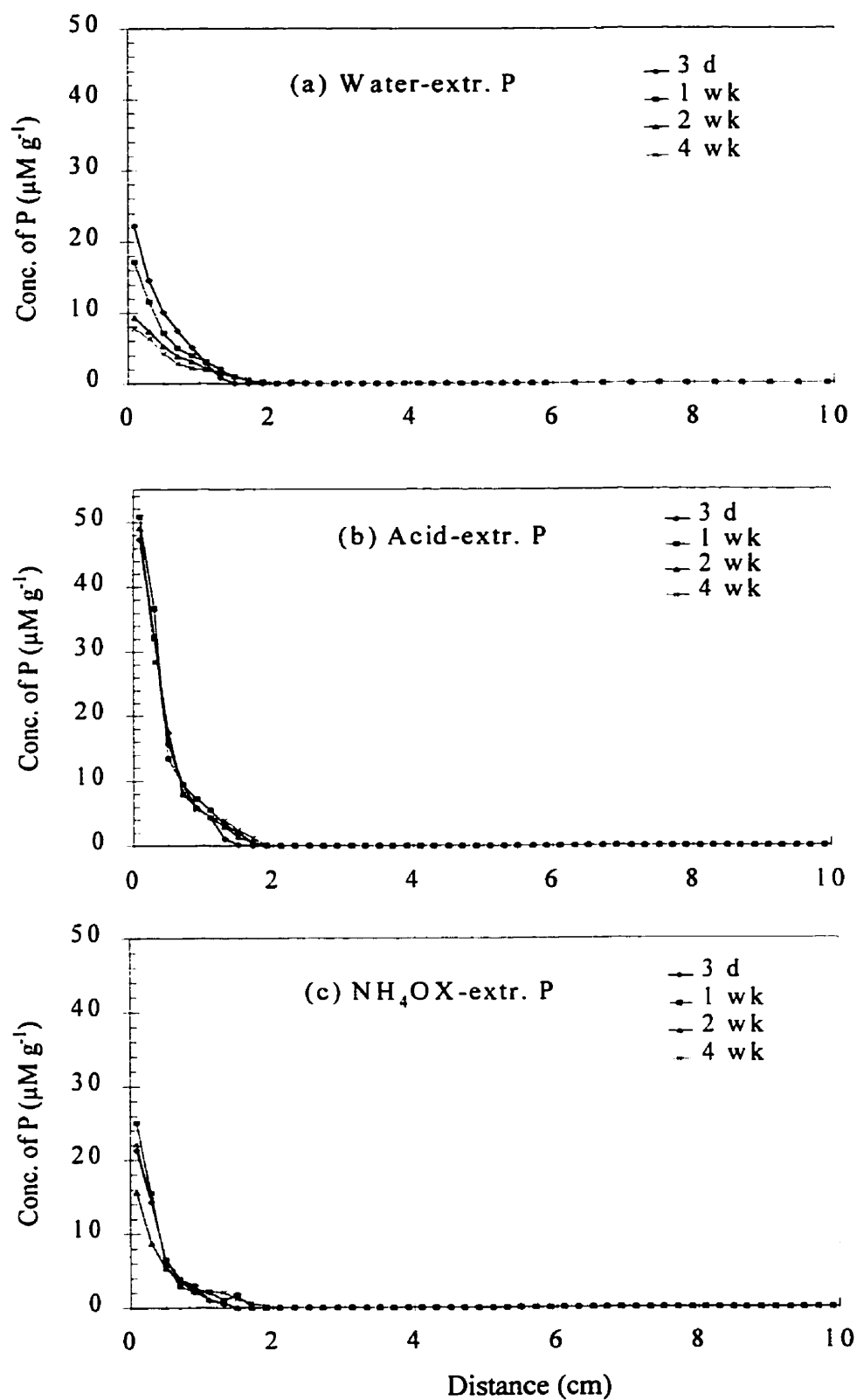
Figure 6.1 Distribution of water-, acid- and NH₄OX-extractable P in soil columns treated with KH₂PO₄ and incubated for various times.

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was very limited and there was little difference in the depth of P movement with time of incubation. The depth to which P had moved was less than 1.9 cm even after 4 wk of incubation.

The maximum P concentrations for the acid- and NH_4OX-extractable fractions also occurred at the surface (Figures 6.1b and 6.1c). There was also little or no variation in the distribution of acid- and NH_4OX-extractable P with time of incubation. However, there was almost twice as much acid-extractable phosphate as NH_4OX-extractable P near the surface.

In this experiment, acid-extractable P was assumed to represent the fraction of P that had been precipitated, but not yet converted to acid-insoluble crystalline taranakite. Precipitation of P, rather than sorption processes, would dominate due to the very high initial concentration of P. The amount of P extracted by NH_4OX represents the amount of P adsorbed on non-crystalline Al and Fe material in the soil as suggested by Yuan and Lavkulich (1994) and Freese et al. (1992). As illustrated by McBride (1994), oxalate is a very good complexing agent of Al and can increase Al concentration in solution by as much as 100 times around pH 6 (Figure 2.3). The soil solution concentration of P was in the range of 20 μM g^{-1}, which is the equivalent of 200 mM, since the average moisture content of soil was 0.10 kg kg^{-1}. Effectively, some of the precipitated Al-P will be dissolved in the presence of oxalate due to its strong complexing ability.

The small differences in acid-extractable P among different incubation periods suggests that the precipitation reaction was initially very rapid. This is probably due to the high levels of P near the site of application and the high solution Al concentration released from exchange sites. At the time of application, the soil solution concentration

of P was 2450 mM if all P applied is thoroughly mixed within the top 2 mm layer of soil. Although precipitation continued after the third day of incubation, as indicated by the decline in water-soluble P concentration, it was at a much reduced rate. The higher amount of acid- than NH_4OX-extractable P was due to the stronger extracting ability of 1M HCl than 0.25 M NH_4OX.

There was very little downward diffusion of P after 3 d of incubation. The decline in P solution concentration was mainly due to precipitation reactions since the solution concentration of P was very high (> 5 mg kg^{-1}).

The level of both water-extractable and acid-extractable P and the depth of P movement for the Oxisol used here were very similar to values reported in Chapter 4 for a simulated soil (resin-sand system with 22 cmol kg^{-1} CEC and 1% gibbsite). This experiment showed that the Oxisol used has a very high capacity to fix P, even though the CEC of the soil is very low.

Figure 6.2 shows the ratio of acid- to water-extractable P in the columns at different incubation times. Ratios for all four incubation periods were highest at the surface and decreased with depth. The ratios near the surface also increased from 2 at 3 d to 6.5 after 4 wk of incubation.

A high ratio of acid to water-extractable P near the surface indicates that the Al-P precipitation reaction is very localized since the water-extractable P was also highest near the surface. The increases in acid- over water-extractable P reflect the continued precipitation of Al-P.
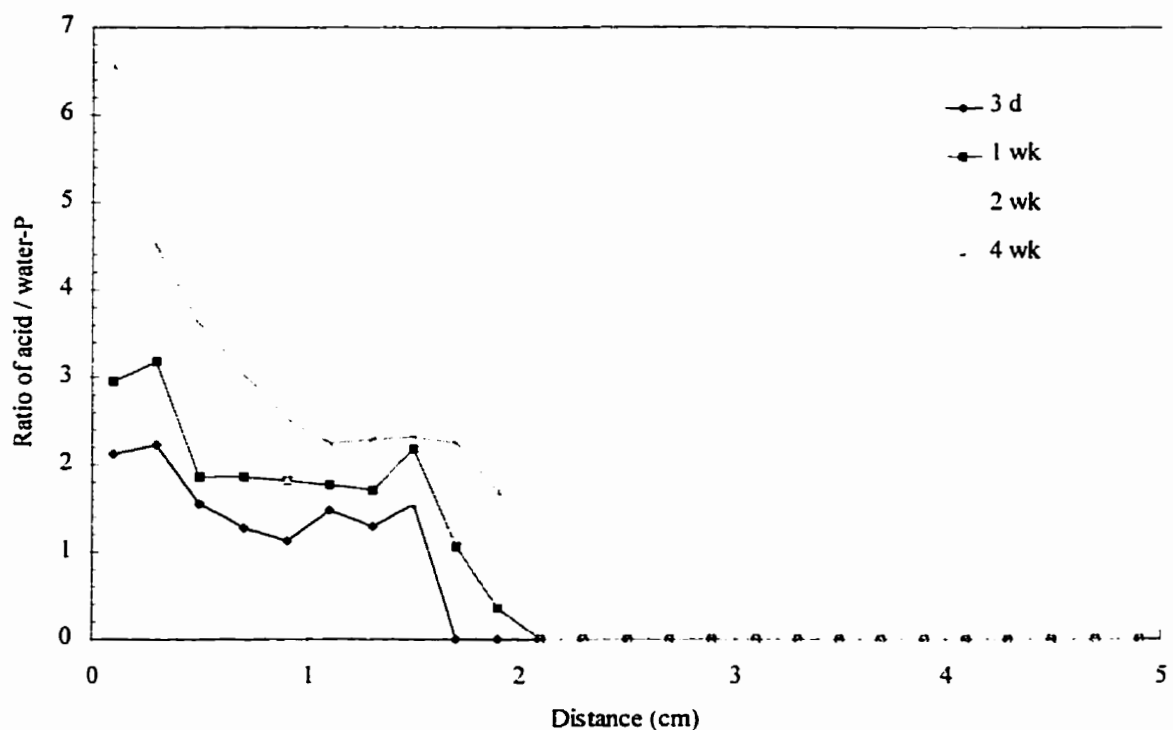
Figure 6.2 The ratio of acid- to water-extractable P in soil columns treated with KH_2PO_4 and incubated for various times.

6.3.2 Extractable K

Water-, acid- and barium chloride-extractable K profiles are shown in Figure 6.3. The distribution of K was very similar to that of P. The maximum concentrations of water-, acid- and barium chloride-extractable K were near the surface and decreased with depth. The concentration of water-extractable K near the surface decreased continuously with time of incubation. The decrease in water-extractable K concentration was probably due to precipitation of Al-P and formation of a K-taranakite. The concentration of water-extractable K was higher than that of P near the surface and did not decrease as rapidly as

Figure 6.3 Distribution of water-, acid- and BaCl$_2$-extractable K in soil columns treated with KH$_2$PO$_4$ and incubated for various times.

P concentration with time of incubation. The concentration of water-extractable K in the soil at any point in the column was higher than the concentration of water-extractable P. This indicated that the K front was ahead of the P front in the soil solution.

There was a strong relationship between water-extractable P and K concentrations (Figure 6.4). The regression equation suggests that there were 1.38 and 1.43 of K^+ ions in the soil solution for each P ion at 1 and 4 wk of incubation, respectively.

Barium chloride-extractable K represents the exchangeable fraction of K and it increased over time at the surface for up to 2 wk, then decreased slightly at 4 wk. Similar to acid-extractable P, the acid-extractable K profiles did not vary much over the incubation periods.
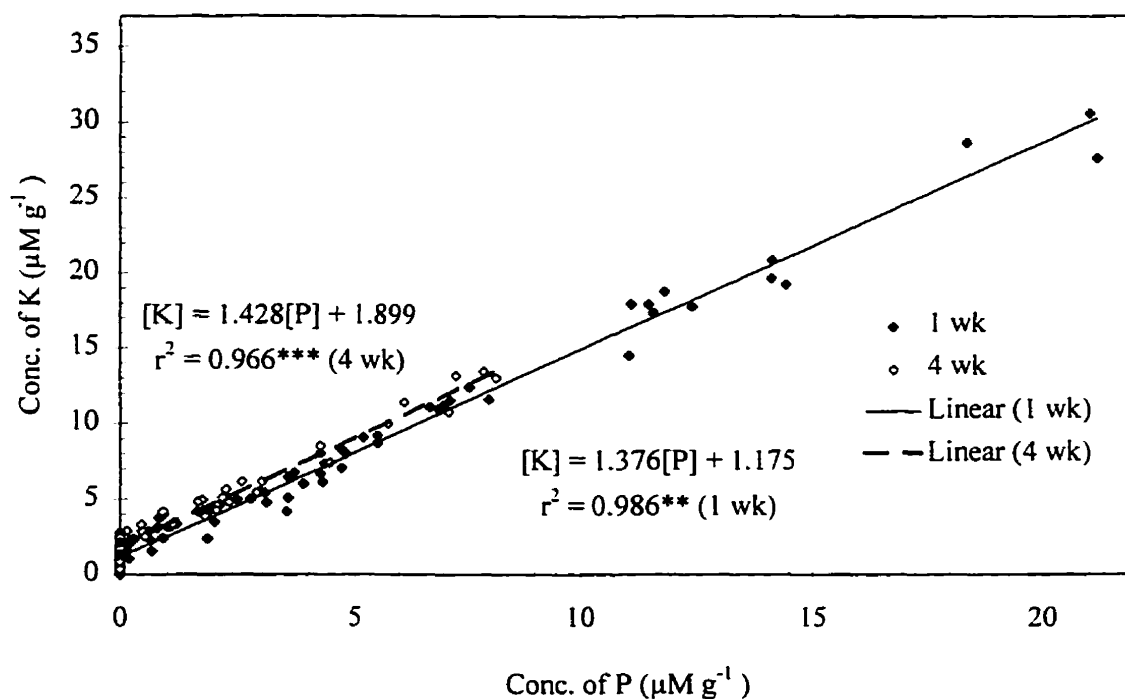
Figure 6.4 Relationships between water-extractable P and K at 1 and 4 wk after KH_2PO_4 application.

6.3.3 Mass Balance of Applied P and K

The total amounts of water- and acid-extractable P and K in the entire column, are

summarized in Tables 6.2 and 6.3, respectively. Water-extractable and total P recovered

decreased with time of incubation (Tables 6.2). The acid-extractable P was highest after

1 wk of incubation. The total P recovered was much lower than that obtained for the

resin-sand mixture columns (Chapter 4).

The difference in the amount of P recovered from the soil versus the resin-sand

mixture could be due to crystalline taranakite formation, which was favored in the soil

Table 6.2 Recovery of water- and acid-extractable P as affected by time of incubation in the Oxisol.

Time of incubation	Water-P	Acid-P	Total P recovered	Percentage of P recovered
		mM column^{-1}		
0 d	1.470			
3 d	0.375	0.690	1.064	72.4
1 wk	0.306	0.761	1.067	72.6
2 wk	0.202	0.728	0.930	63.3
4 wk	0.170	0.725	0.885	60.2

Table 6.3 Recovery of water- and acid-extractable K as affected by time of incubation in the Oxisol.

Time of incubation	Water-K	Acid-K	Total K recovered	Percentage of K recovered
		mM column^{-1}		
0 d	1.470			
3 d	0.581	0.448	1.028	70.0
1 wk	0.546	0.525	1.071	72.9
2 wk	0.488	0.518	0.998	67.9
4 wk	0.444	0.591	1.034	70.4

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due to a higher pH. As discussed in Chapter 3, crystalline taranakite is insoluble in 1 M HCl. Thus there will be less P recovered for the soil than for the resin-sand columns.

The total recovery of K (Table 6.3) was very similar to those obtained for P. The water-extractable K decreased and acid-extractable K increased over time. Total K recovered was slightly higher than that for P. The formation of each taranakite molecule requires eight phosphate ions and three K^- ions. Thus, there will be more K^- than P left in the soil solution.

The amount of P recovered decreased over time whereas that of K did not. If taranakite is the final product of the precipitation of Al-P, the recovery for both P and K should decrease with time. This suggests that Al-P precipitates other than taranakite might have been formed. Further studies are needed to identify the phosphate reaction product(s).

6.3.4 Extractable Al, Fe and Ca Profiles

The concentration of water-extractable Al was around 10 μM g^{-1} at the surface, increased to a maximum of about 35 μM g^{-1} at around 2 cm depth and then decreased with depth (Figure 6.5a). Water-extractable Al concentration was highest where P had penetrated. The maximum values of water-extractable Al were almost 10 times that of background levels (i.e., the level observed at the bottom part of the soil column where phosphate fertilizer application has no impact). The concentration of both acid- and NH_4OX-extractable Al was highest at the surface, decreased with depth, and reached background levels about 2 cm from the surface.

The presence of a peak in water-extractable Al suggests that the interaction of applied P with soil caused an increase in Al in solution. This can be explained by the

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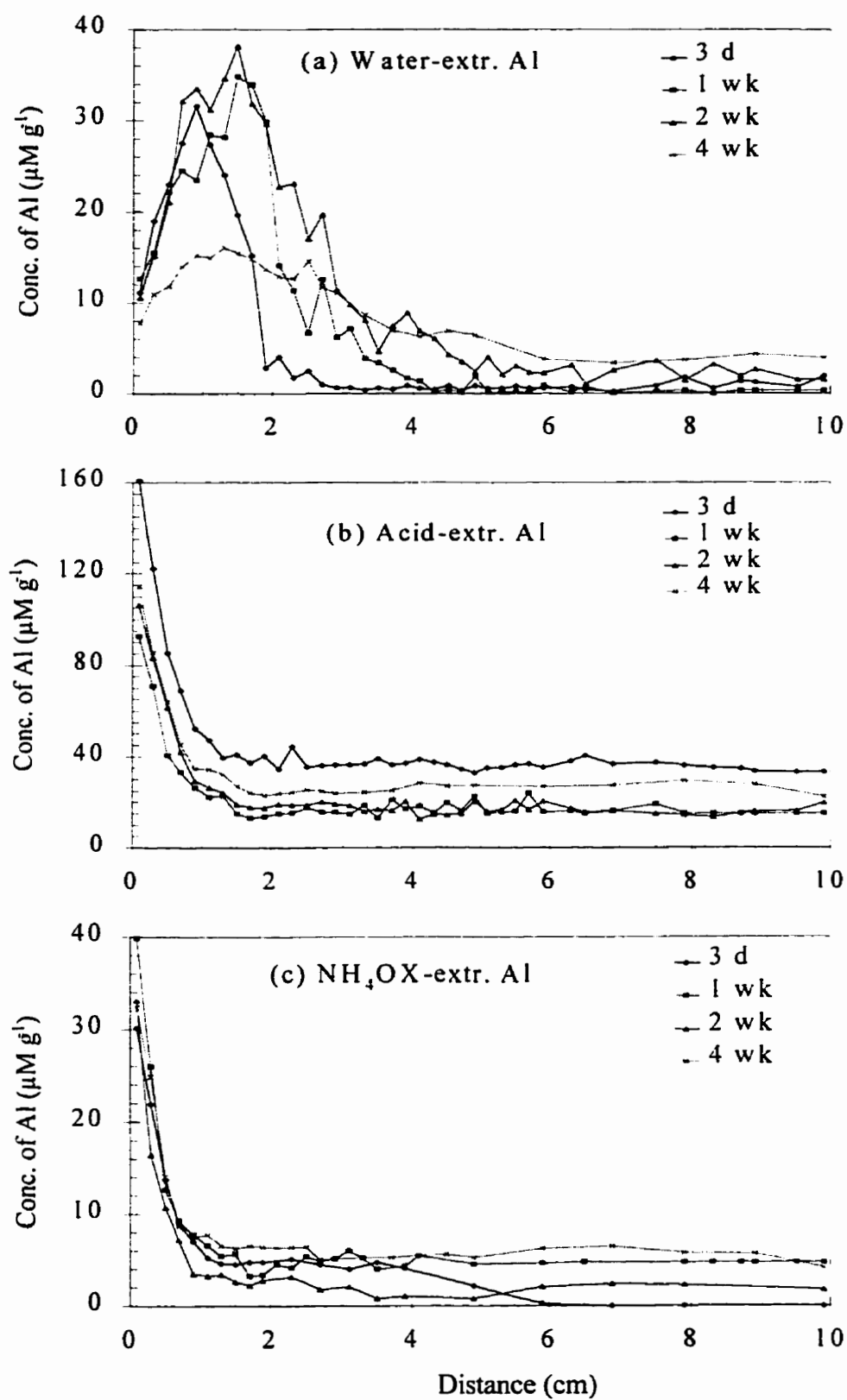
Figure 6.5 Distribution of water-, acid- and NH$_4$OX-extractable Al in soil columns
treated with KH$_2$PO$_4$ and incubated for various times.

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release of exchangeable Al and dissolution of Al-bearing minerals. Given the extremely low CEC (3 cmol kg^{-1}) and exchangeable Al (less than 2 cmol kg^{-1}) of the soil used, the maximum Al that could be released into soil solution is only about 20 μM g^{-1} if all exchangeable Al were replaced by K$^-$ ions. Thus, the exchange reaction alone cannot explain the increased Al concentration in soil solution. The increase in concentration of Al in solution also cannot be explained by the ligand exchange theory of P fixation. Ligand exchange results in replacement of OH$^-$ in surfaces by H$_2$PO$_4^-$ ions without any effect on Al concentration. Thus, since the soil was rich in gibbsite, it was very likely that gibbsite dissolution caused the increases in Al concentration where P had penetrated. The precipitation of P by Al released protons (thus lowering pH in the absence of gibbsite) is demonstrated in Chapter 4. These protons cause dissolution of gibbsite, thus increasing the Al concentration in soil solution.

Increases in acid- and NH$_4$OX-extractable Al (Figure 6.5) near the surface further confirms that Al-P precipitation was responsible for P fixation in the soil studied. NH$_4$OX extracts the amorphous forms of Al, while acid extracts all Al-P precipitates which are soluble in acid. The high acid-extractable Al at the surface also suggests that Al might have moved to the site of Al-P precipitation.

The distribution pattern of water-extractable Fe was similar to that of Al (Figure 6.6). However, the maximum concentrations were much lower. For Al, the maximum concentration was around 35 μM g^{-1} whereas for iron, the maximum concentration was about 7 μM g^{-1}. Acid- and NH$_4$OX-extractable Fe changed very little from the background levels, indicating that Fe did not play a major role in P fixation. This is also
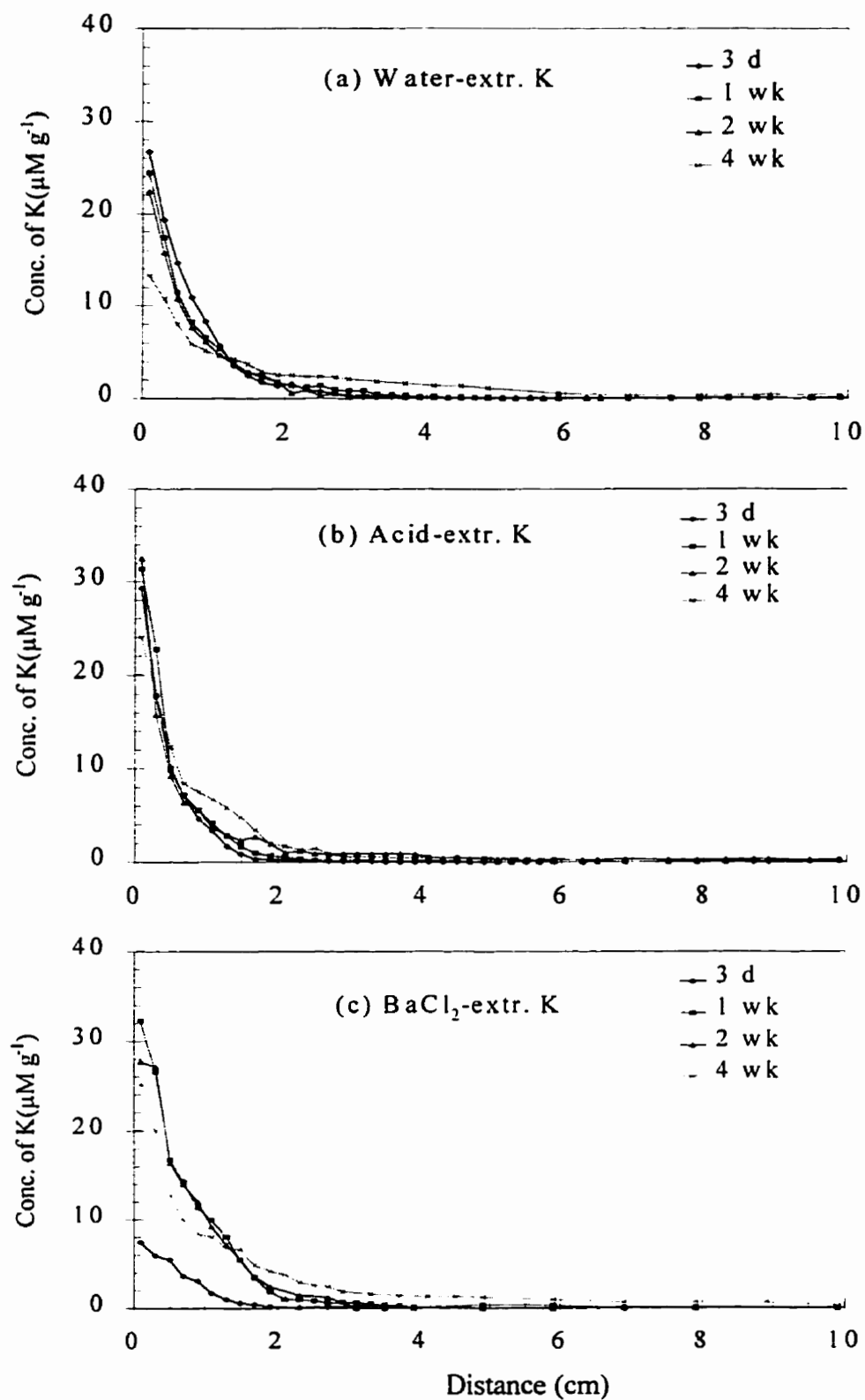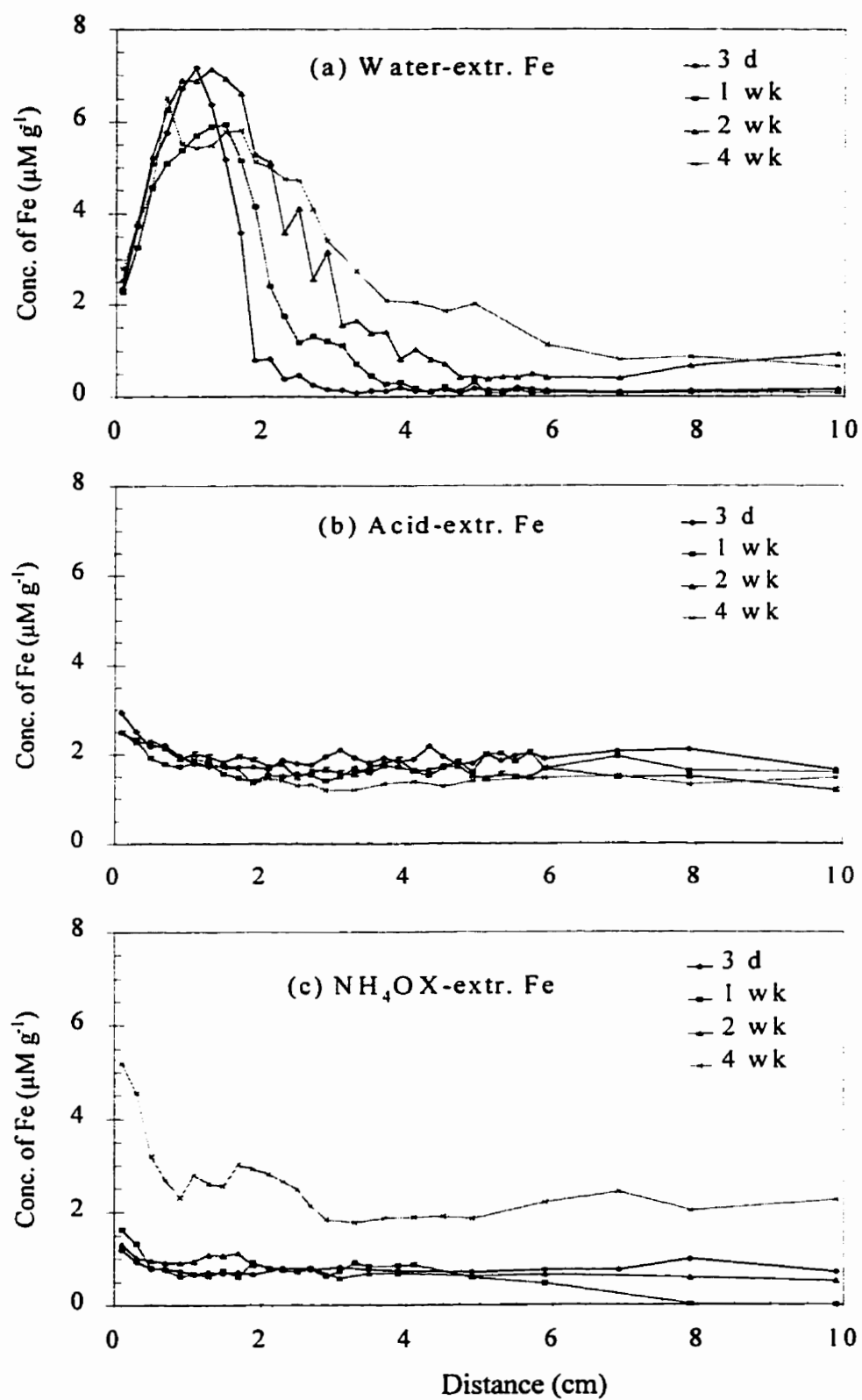
Figure 6.6 Distribution of water-, acid- and NH₄OX-extractable Fe in soil columns treated with KH₂PO₄ and incubated for various times.

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in agreement with the mineral analysis of the soil, which showed that gibbsite was the dominate mineral in the clay fraction.

There was a strong relationship between the concentrations of Al and Fe in soil solution (Figure 6.7). The regression equation showed that $[Fe] = 0.2117[Al] + 0.0708$, and $r^2 = 0.935^{***}$ (significant at 0.001p level).

Water-extractable Ca was less and acid-extractable Ca^{2+} was greater than background levels in the region to which P had penetrated (Figure 6.8). However, the concentration of both water- and acid-extractable Ca^{2+} was very low ($< 0.1 \mu M$ g^{-1}), indicating that Ca did not play a significant role in P fixation. Sloan et al. (1995) also

$$(Fe) = 0.212(Al) + 0.0708$$
$$r^2 = 0.935**$$

Conc. of Fe ($\mu M g^{-1}$)

Conc. of Al (μM g^{-1})
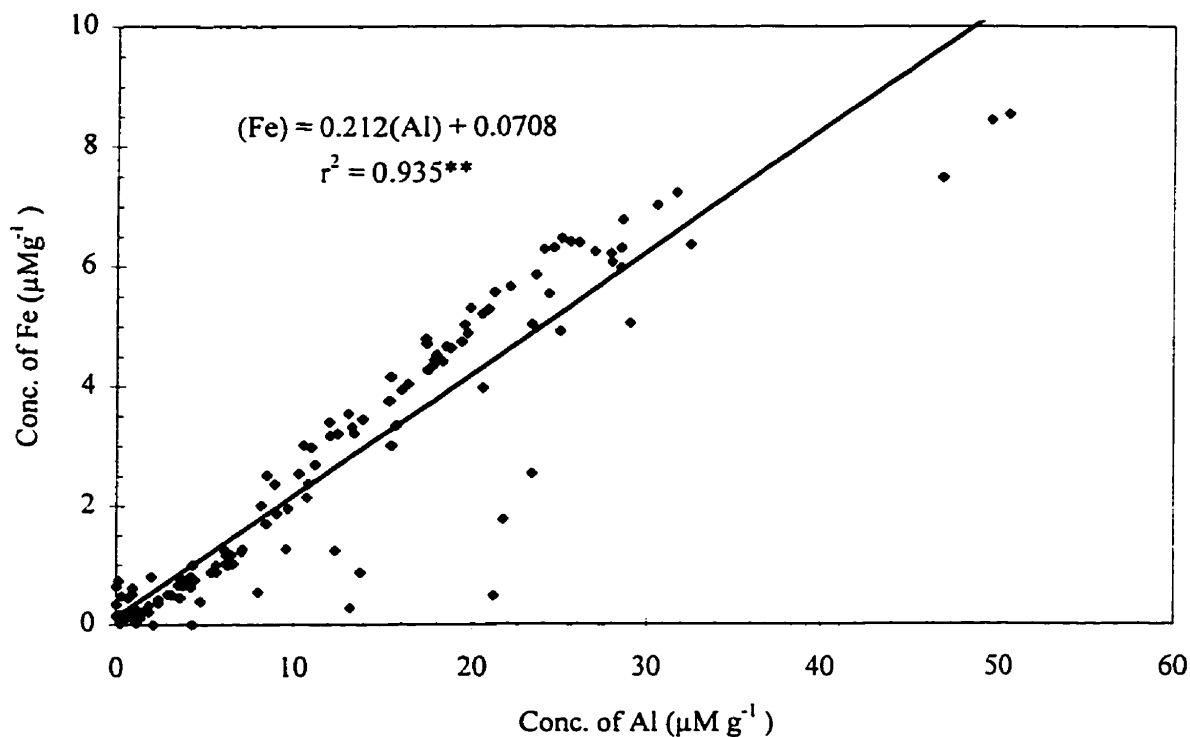
Figure 6.7 Relationship between water-extractable Al and Fe 1 wk after KH_2PO_4 application.

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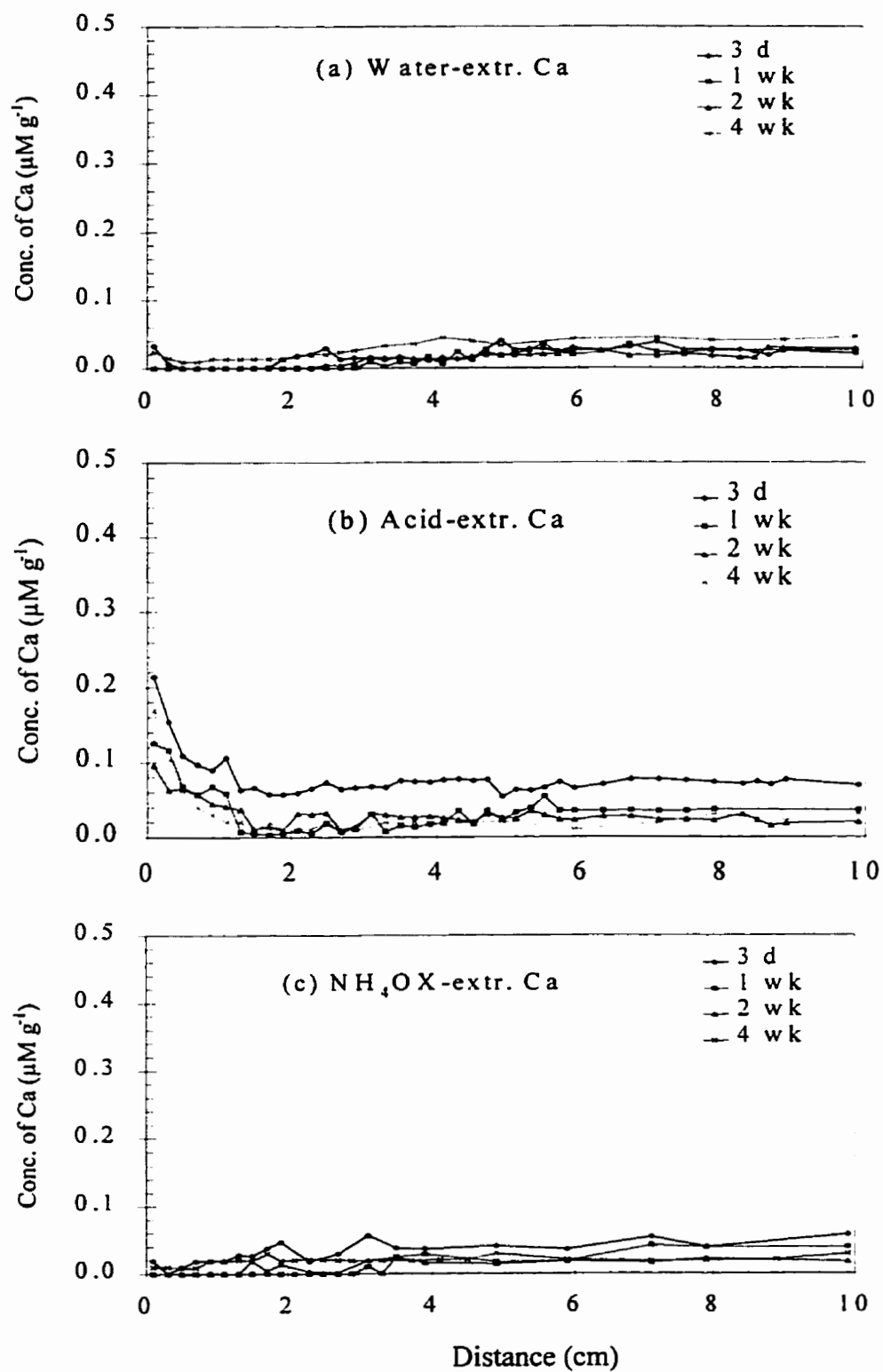
Figure 6.8 Distribution of water-, acid- and NH$_4$OX-extractable Ca in soil columns treated with KH$_2$PO$_4$ and incubated for various times.

found that soil solution was under-saturated with respect to Ca and Mg phosphates for the soil used.

6.3.5 Soil pH

The application of KH_2PO_4 to the surface of the soil column increased pH near the surface (Figure 6.9) The depth to which the pH was altered increased with time of incubation. The increase in pH could be due to Al hydrolysis, production of hydroxyl during P fixation, and/or the dissolution of gibbsite.

The formation of taranakite is normally written as:

$$5Al^{3+} + 3K^+ + 8H_2PO_4^- + 18H_2O \rightleftharpoons K_3Al_5H_6(PO_4)_8.18H_2O \,(S) + 10H^+ \qquad [6.1]$$

or as

$$5Al(OH)_2^+ + 3K^+ + 8H_2PO_4^- + 18H_2O \rightleftharpoons K_3Al_5H_6(PO_4)_8.18H_2O \,(S) + 10H_2O \quad [6.2]$$
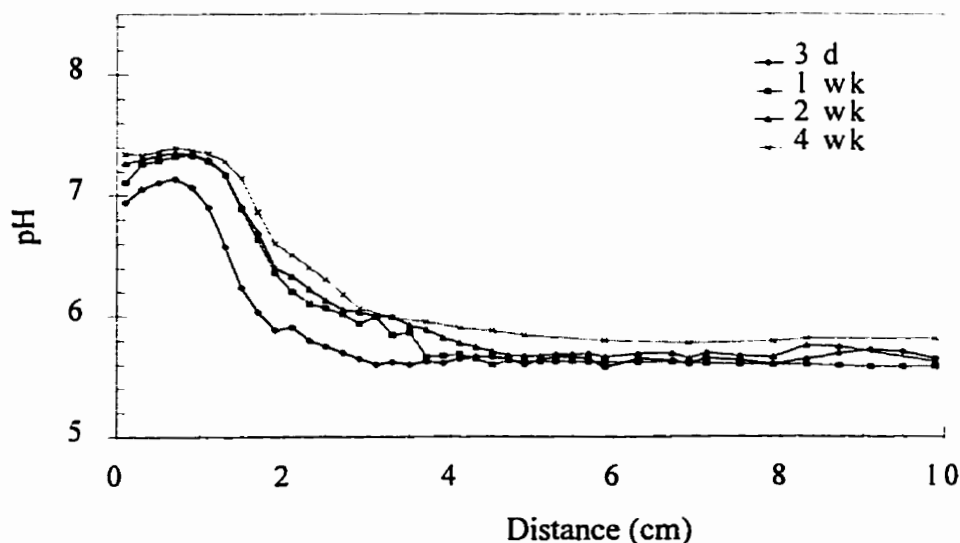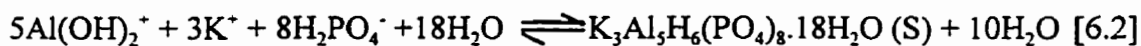
Figure 6.9 Distribution of pH in soil columns treated with KH_2PO_4 and incubated for various times.

If it is assumed that Al^{3+} ions were used during the precipitation of Al-P, then the production of one molecule of taranakite requires five ions of Al^{3+} and eight ions of $H_2PO_4^-$ with the resultant production of ten H^+ ions. $Al(OH)_2^+$ was the dominant ionic Al form when initial soil pH was 5. As Al^{3+} ions were consumed with continued precipitation of Al-P, more $Al(OH)_2^+$ and $Al(OH)^{2+}$ ions were converted into Al^{3+} releasing OH^- ions. Thus, if exchangeable Al was solely responsible for the precipitation of Al-P, then the pH of the soil solution should have decreased because more H^+ than OH^- ions were produced. On the other hand, if five molecules of $Al(OH)_3$ (gibbsite) are converted to five $Al(OH)_2^+$ ions, the process requires five H^+ ions. Five $Al(OH)_2^+$ ions would produce ten OH^- ions in order to form Al^{3+}. Consequently, the net result is the production of five OH^- ions in order to sustain the formation of taranakite from $Al(OH)_3$ and $H_2PO_4^-$.

It could be argued that OH^- is released due to ligand exchange. However, hydroxyl ion release from ligand exchange was not a major factor, as demonstrated by the distribution profile of Al. Ligand exchange will not cause an increase in water soluble Al, and thus the peak of Al observed in the soil solution is contrary to the results expected if ligand exchange had occurred. Also, ligand exchange would not play a major role in increasing soil pH near the P fertilizer band where P concentration is very high since the amount of OH available for ligand exchange would be relatively low.

Distribution patterns of water-extractable P, K, Al, Fe Ca and soil pH after 1 wk of incubation are summarized in Figure 6.10. Several phenomenon were observed. First,
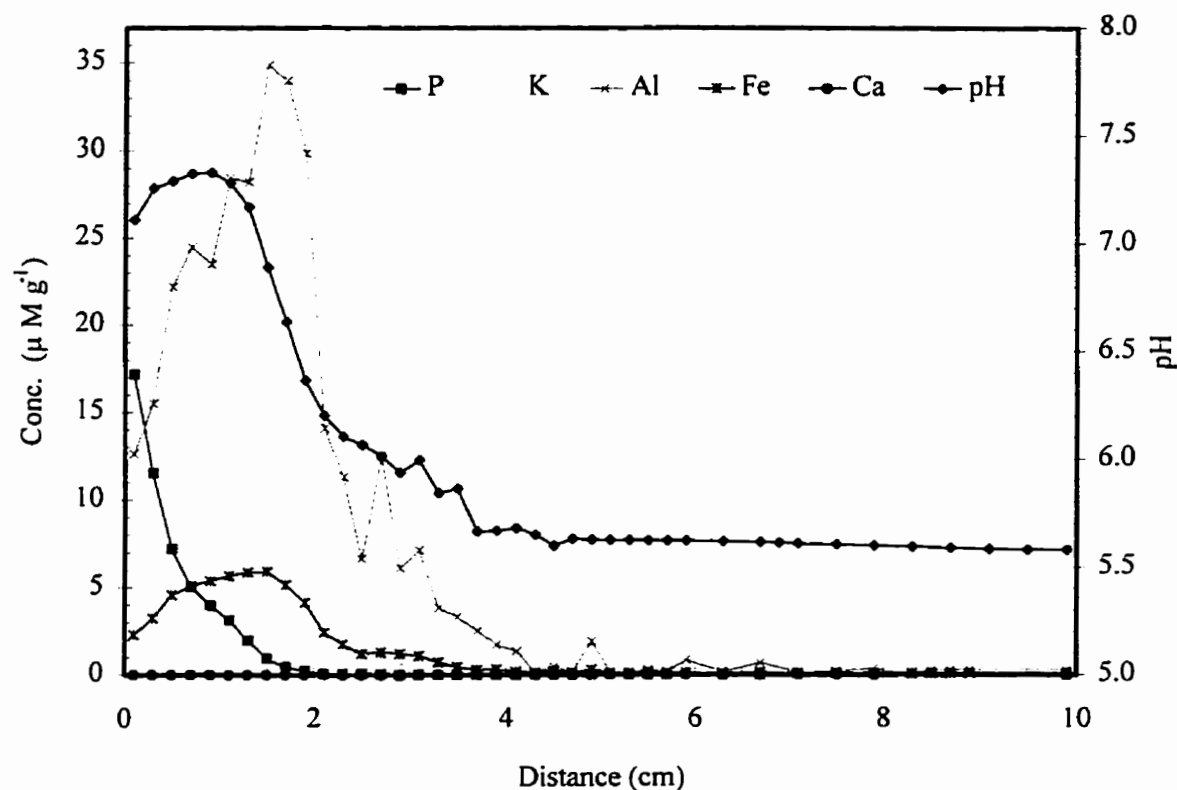
Figure 6.10 Distribution of water-extractable P, K, Al, Fe and Ca and pH in soil columns
treated with KH_2PO_4 and incubated for 1 wk.

the maximum solution concentrations of phosphate and potassium occurred near the

surface. Second, the movement of phosphate and potassium in the Oxisol was minimal

(less than 1.9 cm). Third, the pH and solution concentration of Fe and Al had maximum

values at about 1 to 2 cm depth, with the peak for pH lagging behind those for Fe and Al.

Fourth, the concentration of Ca in solution was relatively low. The distribution patterns

were very similar for other incubation periods, except that the concentration of P and K

near the surface decreased over time (Figures 6.1 and 6.3).

The limited movement (< 1.9 cm) of phosphate in soil (Figure 6.1) indicates that the Oxisol used had a very high P fixation ability. As discussed in Chapter 2, phosphate fixation, at high concentrations of P resulting from fertilizer application, was controlled by Al-P precipitation rather than adsorption in acid soil. The proposed fixation mechanism was demonstrated in a simulated soil with a Al-saturated cation exchange resin-sand and gibbsite (Chapter 4) and further here with the gibbsite-rich Oxisol. When KH_2PO_4 fertilizer was applied to soil, the fertilizer dissolved in the soil solution to produce K^+ ions. The K^+ ions then underwent cation exchange reactions and released Al ions from exchange sites into the soil solution. As observed in Chapter 4, H^+ ions were produced during Al-P precipitation reactions in the system when there was only exchangeable Al without gibbsite. The H^+ ions could then dissolve gibbsite, releasing more Al ions for phosphate fixation reactions. The dissolution of gibbsite in the Oxisol was confirmed by the increased Al solution concentration (Figure 6.5a). The increases in solution Fe observed are also attributed to the dissolution of Fe oxides.

The increase in pH after P application would benefit plant growth and reduce the toxicity of Al, since Al^{3+} is the most toxic form of Al. The pH of over 7 observed near the P fertilizer application band could also affect the P and cation species of Al and Fe present in soil solution (Figure 6.10). One surprising aspect of this study is the amount of water-soluble Al and Fe in soil at such a high pH. Normally, the cation forms of Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^-$ and Fe^{3+}, $Fe(OH)^{2+}$, and $Fe(OH)_2^-$ would not exist when the soil pH is above 6. It is suspected that the elevated water-extractable Al at the high pH probably existed as $Al(OH)_3^0$, $Al(OH)_4^-$, or $Al(OH)_5^{2-}$ and Fe as $Fe(OH)_3^0$, $Fe(OH)_4^-$ or $Fe(OH)_5^{2-}$ (Lindsay 1979).

The increase in concentration of cations such as Al and Fe in soil after fertilizer application is also known as the Snow Plow effect (Cho 1985). As Cho (1985) pointed out, as the displacing cations (K^- ions in this study) advanced, Al^{3+} and Fe^{3+} ions were replaced from the soil exchange sites and their concentration in the soil solution increased with the maximum concentration just ahead of the advancing ions (K^-). It was observed that the location of Al and Fe peaks were ahead of the K^- and H^- ions (Snow Plow effect). Al and Fe do not participate in ion-exchange because the soil was always in equilibrium with those ions. On other hand, K^+ and H^- ions are involved with the cation exchange reactions and are thereby retarded. Thus, the mobility of K^- and H^- ions is reduced.

6.4 Summary and Conclusions

A gibbsite-rich acid Oxisol was used to study the one-dimensional diffusive transport of P and associated cations in the laboratory. The downward movement of both P and K was very limited, less than 1.9 cm after 4 wk of incubation. The solution concentration of P and K near the surface continued to decrease during the incubation period. Solution pH, Al and Fe concentration were elevated near the surface as a result of phosphate fertilizer application. This increase was attributed to the dissolution of Al and Fe oxides and hydroxides which, according to the research model, was caused by proton production during phosphate precipitation reactions. The precipitation reactions are the dominant processes for P fixation in the gibbsite-rich acid soil studied here.

7. PHOSPHATE MOVEMENT AND AVAILABILITY IN A LIMED OXISOL

Abstract

Aluminum (Al) plays an important role in the movement and fixation of phosphate in acid soils. This study was conducted to determine what effect liming an acid soil has on phosphate movement. The soil sample used in this study, a loamy sand, was obtained from the west coast of Australia 150 km south of Perth. The soil was limed at a rate of 5 g kg^{-1} to obtain a soil pH of 7.1 (measured in water with soil to water ratio of 1 to 2). Soil columns were treated with KH_2PO_4 (surface application) and incubated in a constant humidity chamber for various periods of time. The movement of phosphate was very limited (less than 1.5 cm as compared to 1.9 cm for the unlimed soil). The concentration of phosphate in soil solution near the surface decreased with time of incubation. Solution pH, Al and Fe concentration increased near the surface as a result of phosphate fertilizer application. The dissolution of Al and Fe oxides and hydroxides were proposed as the cause for the increases in solution pH, Al and Fe concentrations.

7.1 Introduction

One of the problems associated with acid soils is Al toxicity. The management of Al toxicity involves treating of the soil to reduce the Al^{3+} activity in the soil solution to non-toxic levels. Liming is one of the most common management practices used to raise soil pH and reduce Al toxicity in acid soils. Liming-induced changes in soil chemical and physical properties also improve conditions for plant growth (Menzies et al. 1994a). Positive benefits of increased crop yield due to liming have been demonstrated (Dolling et al. 1991; Holford and Crocker 1994). The cation exchange capacity (CEC) of a soil

has been shown to increase with lime application (Hochman et al. 1992), while the extractable (by sodium acetate) Al. Fe and H decreased (Ryan and Smillie 1975).

Another important and commonly advocated reason for liming is to increase phosphate availability (Sanchez and Uehara 1980). Liming of soils has been shown to both increase extractable P (Holford 1985; Holford and Crocker 1994; Martini and Mutters 1985; Ryan and Smillie 1975; Sanchez and Uehara 1980) as well as decrease it (Mendoza et al. 1995). LeMare and Leon (1989) found the effects of liming on soil P adsorption was highly dependent on the type of soil used. They used five soils and found that liming increased P adsorption for two soils, decreased P adsorption for two soils, and had no effect on P adsorption for the fifth. The effects of liming on phosphate availability was also found to be pH dependent (Naidu et al. 1990). Very few studies have dealt with the effect of liming on movement of applied P. The objectives of this experiment were therefore to investigate the effect of liming on P movement as well as to determine the effect of P application on soil pH and cations in soil solution in a limed soil.

7.2 Materials and Methods

A gibbsite-rich surface Oxisol, obtained from approximately 150 km south of Perth Australia, was used. Vegetation cover is predominately Eucalyptus Marginata (*Jarrah*) and Eucalyptus Calophylla (*Marri*). The pertinent soil properties and experimental methodology are as outlined in Table 6.1. Soil was limed at a rate of 5 g kg^{-1} with $CaCO_3$ and thoroughly mixed before the soil was packed into the wax columns.

The resulting soil pH after lime amendment was 7.1 (in water with soil to water ratio of 1 to 2).

7.3 Results and Discussion

7.3.1 Extractable P

The concentration of water-extractable P was highest near the surface and decreased with depth for all incubation periods (Figure 7.1a). The concentration of water-extractable P near the surface decreased with time of incubation, from around 22 $\mu M \, g^{-1}$ after 3 d of incubation to 6 $\mu M \, g^{-1}$ after 4 wk of incubation. There was very little difference in depth of P movement with time of incubation. The depth to which P had moved was less than 1.5 cm even after 4 wk of incubation.

The maximum concentrations of acid- and NH_4OX-extractable P fractions also occurred at the surface. There was little or no variation in distribution of acid-extractable P with time of incubation. This is probably due to the high levels of P near the site of application and very rapid initial precipitations. The concentration of NH_4OX-extractable P near the surface, however, decreased with time. NH_4OX-extractable P near the surface was about 20 $\mu M \, g^{-1}$ after the 1 wk of incubation and decreased to 10 $\mu M \, g^{-1}$ after 2 to 4 wk of incubation (Figure 7.1c). The acid-extractable P was much higher than NH_4OX- or water-extractable P near the surface. The level of both water- and acid-extractable P and the depth of P movement for the limed Oxisol was very similar to the unlimed Oxisol reported in Chapter 6.

Ratios of acid- to water-extractable P for all four incubation periods decreased slightly with increasing soil depth (Figure 7.2). The ratio increased with time, from a ratio of 2.0 after 3 d incubation to a ratio of 4.0 after 4 wk of incubation.

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Figure 7.1 Distribution of water-, acid and NH_4OX-extractable P in limed soil treated
with KH_2PO_4 and incubated for various times.

7.3.2 Extractable K

The maximum concentrations of K extracted by water, acid and $BaCl_2$ were near the surface and decreased with depth (Figure 7.3). Whereas the concentration of water-extractable K near the surface decreased with time, the acid- and barium extractable K did not change very much. There was a strong correlation between solution concentration of P and K (Figure 7.4). The relationship between water-extractable P and K after 1 wk and 4 wk of incubation periods is shown in Figure 7.4.
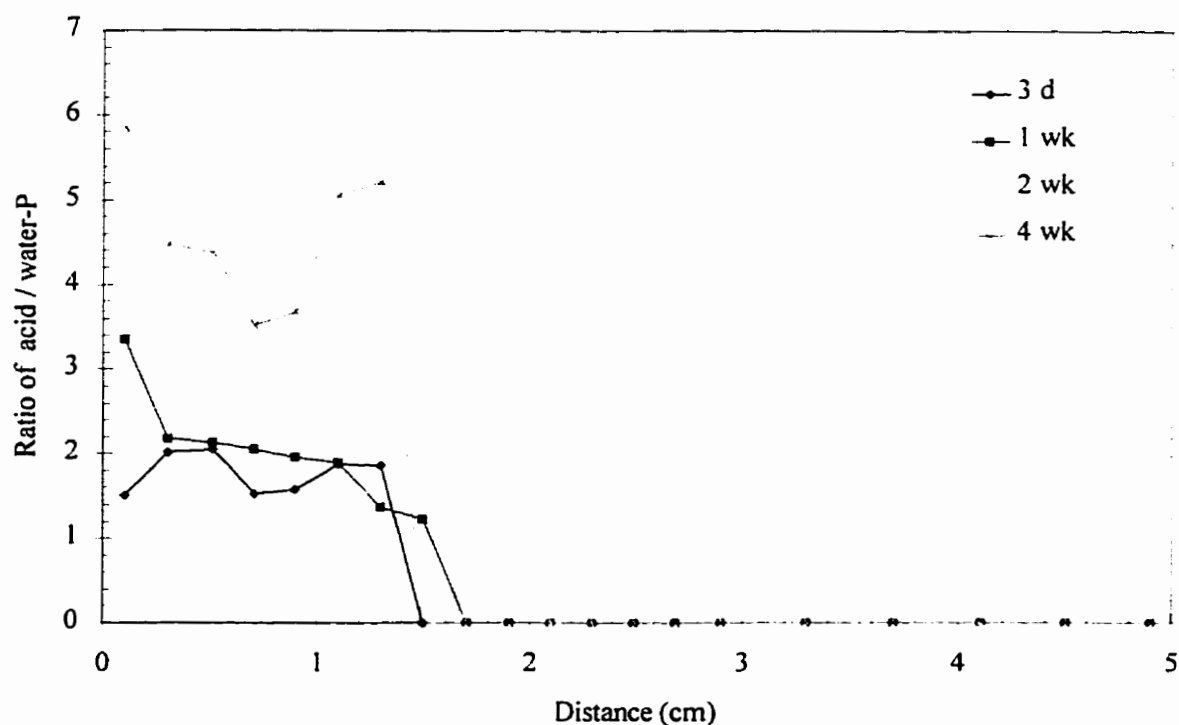
Figure 7.2 Ratio of acid- to water-extractable P in limed soil treated with KH_2PO_4 and incubated for various times.
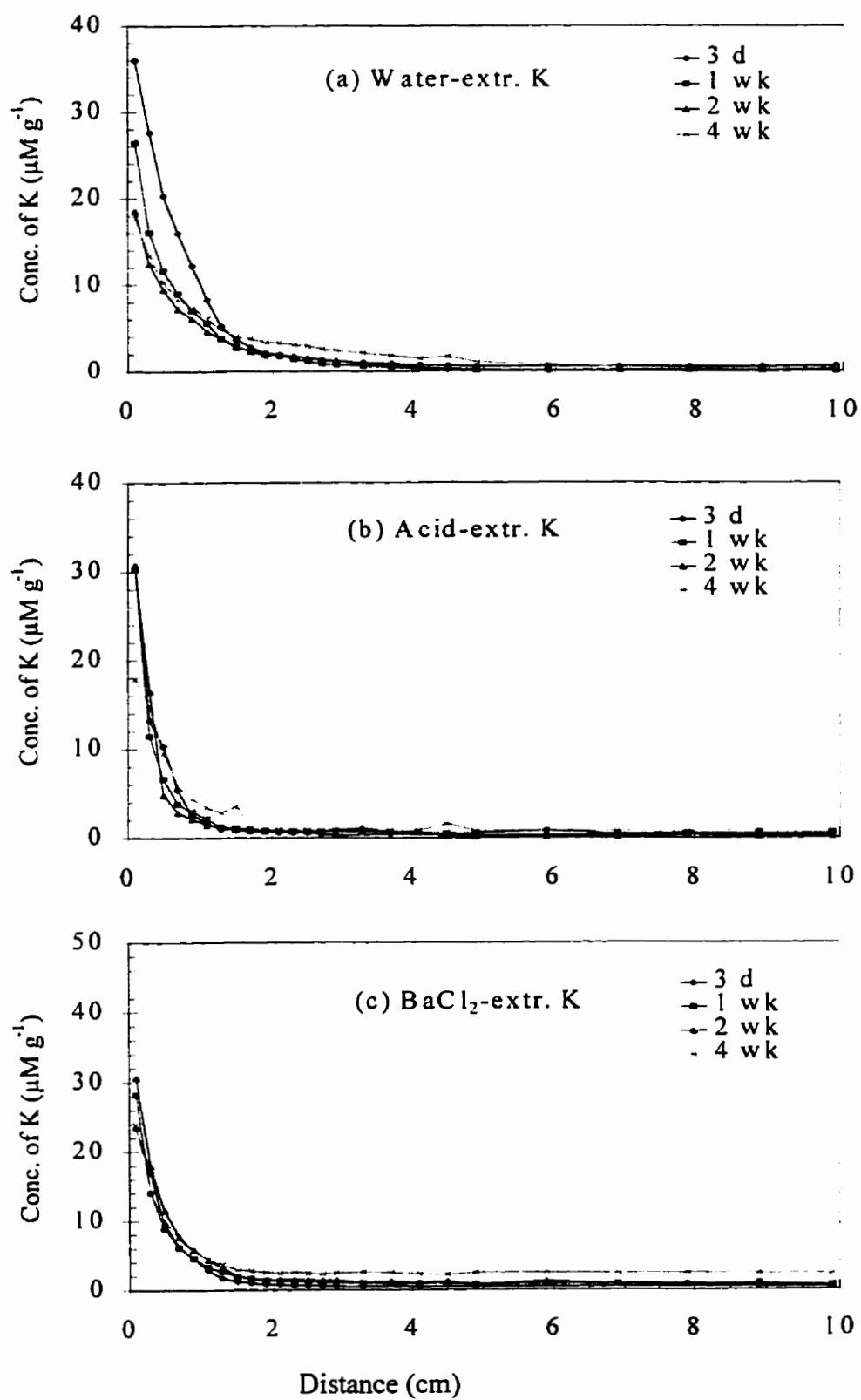
Figure 7.3 Distribution of water-, acid and BaCl$_2$-extractable K in limed soil treated with KH$_2$PO$_4$ and incubated for various times.

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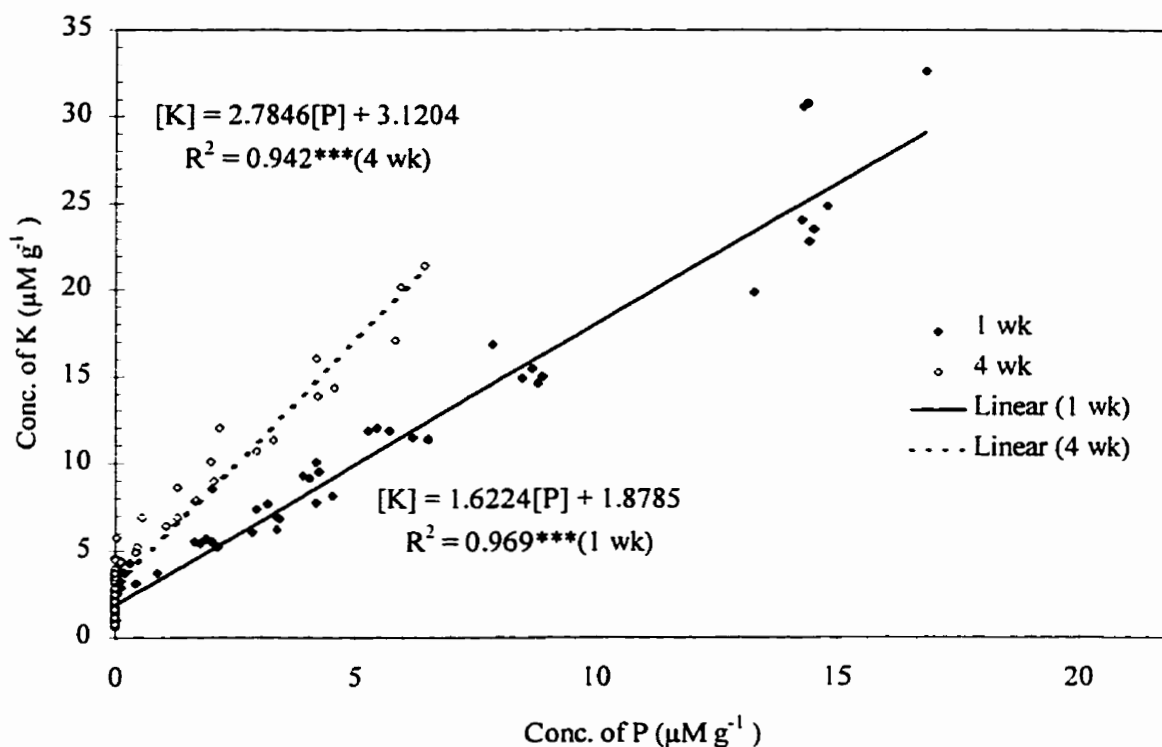
Figure 7.4 Relationship between water-extractable P and K in limed soil at 1 and 4 wk after KH_2PO_4 application.

7.3.3 Mass Balance of Applied P and K

The total amount of water- and acid-extractable P and K in the columns for all four incubation periods are shown in Tables 7.1 and 7.2, respectively. Water-extractable P decreased over time. The acid-extractable P remained relatively constant for the first 3 wk (6.0 to 6.3 mM column^{-1}), and then decreased to much lower values (4.8 mM column^{-1}). The total P recovered also decreased over time. The decreases in water-extractable P, as discussed earlier, were the result of continuous precipitation of Al-P, whereas decreases in total P recovered were a result of continuous conversion of acid-soluble Al-P to taranakite or other acid-insoluble forms of Al-P precipitate over time.

Table 7.1 Mass balance of P for soil columns with 0.5% lime application.

Time of incubation	Water-P	Acid-P	Total P recovered	Percentage of P recovered
		mM column^{-1}		
0 d	1.470			
3 d	0.359	0.625	0.984	66.9
1 wk	0.235	0.602	0.837	57.0
2 wk	0.195	0.624	0.818	55.7
4 wk	0.109	0.478	0.584	39.8

Table 7.2 Mass balance of K for soil columns with 0.5% lime application.

Time of incubation	Water-K	Acid-K	Total K recovered	Percentage of K recovered
		mM column^{-1}		
0 d	1.470			
3 d	0.799	0.383	1.182	80.4
1 wk	0.543	0.337	0.880	59.8
2 wk	0.463	0.396	0.860	58.5
4 wk	0.579	0.351	0.931	63.3

Patterns for K recovery over time (Table 7.2) were similar to those observed for P (Table 7.1). However, the values for total recovery as well as water-extractable K were much higher than those obtained for P.

7.3.4 Extractable Al, Fe and Ca

The concentration of water-extractable Al increased with depth to a maximum of 15 to 18 μM g^{-1} at a depth of 1 cm, and then decreased with depth down to background level of 6 μM g^{-1} at about 2.1 cm (Figure 7.5). Water-extractable Al concentrations were highest where P had penetrated. The maximum values of water-extractable Al were
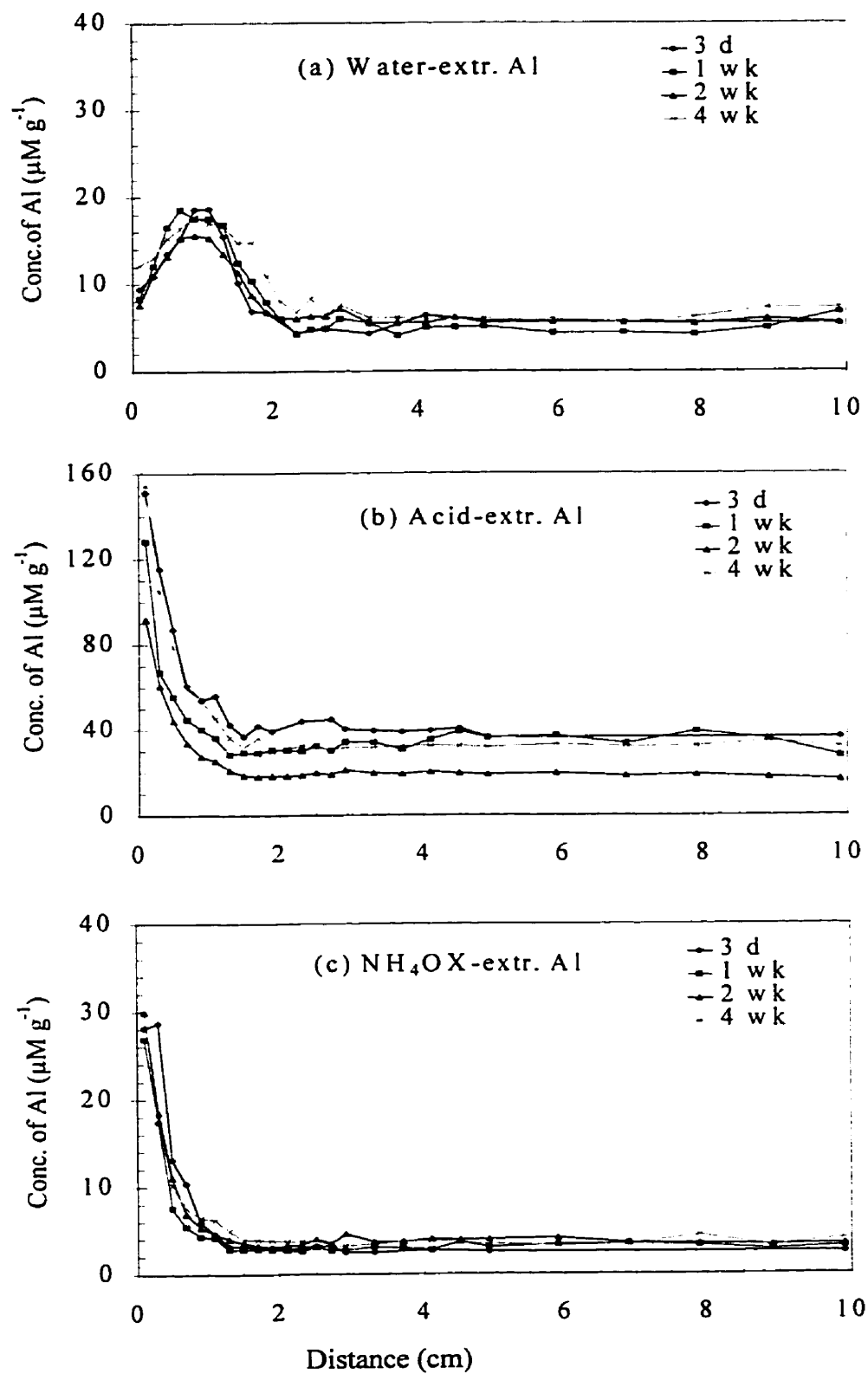
Figure 7.5 Distribution of water-, acid and NH$_4$OX-extractable Al in limed soil treated with KH$_2$PO$_4$ and incubated for various times.

almost 4 times those of background levels. Concentration of both acid- and NH_4OX extractable Al were highest at the surface and decreased with depth, down to the background level (near zero) at 1.5 cm. There was very little difference among the Al distribution profiles measured at the four incubation periods for all three extraction methods.

Similar patterns were observed for Fe (Figure 7.6) as for Al (Figure 7.5). The maximum concentration of water-extractable Fe was found where P had penetrated. There was a strong relationship between concentration of Al and Fe in soil solution (Figure 7.7). The regression equation showed that $[Fe] = 0.229[Al] + 0.650$ and $r^2 = 0.708***$ (significant at 0.001p level). A decrease in water-extractable Ca and an increase in acid-extractable Ca where P had penetrated were observed (Figure 7.8). The increase in acid-extractable Ca was so small (< 2 μM g^{-1}) when compared to Al (about 100 μM g^{-1}) that Ca cannot play a significant role in P fixation.

7.3.5 Soil pH

The background level of pH was increased from 5.5 in the original soil to 7.1 in limed soil (Figure 7.9). There was a further increase in pH near the surface after the application of P fertilizer. The maximum increase in pH occurred at 1.1 cm depth and was very sharp after 3 d. As incubation progressed, pH near the surface decreased and the peak broadened. As previously discussed in Chapter 6, phosphate fixation after fertilizer application was controlled by Al-P precipitation, rather than adsorption, in acid soil. The dissolution of gibbsite in the Oxisol was confirmed by the increase in concentration of Al in soil solution in the position in the column where Al-P interaction occurred (Figure 7.5a).
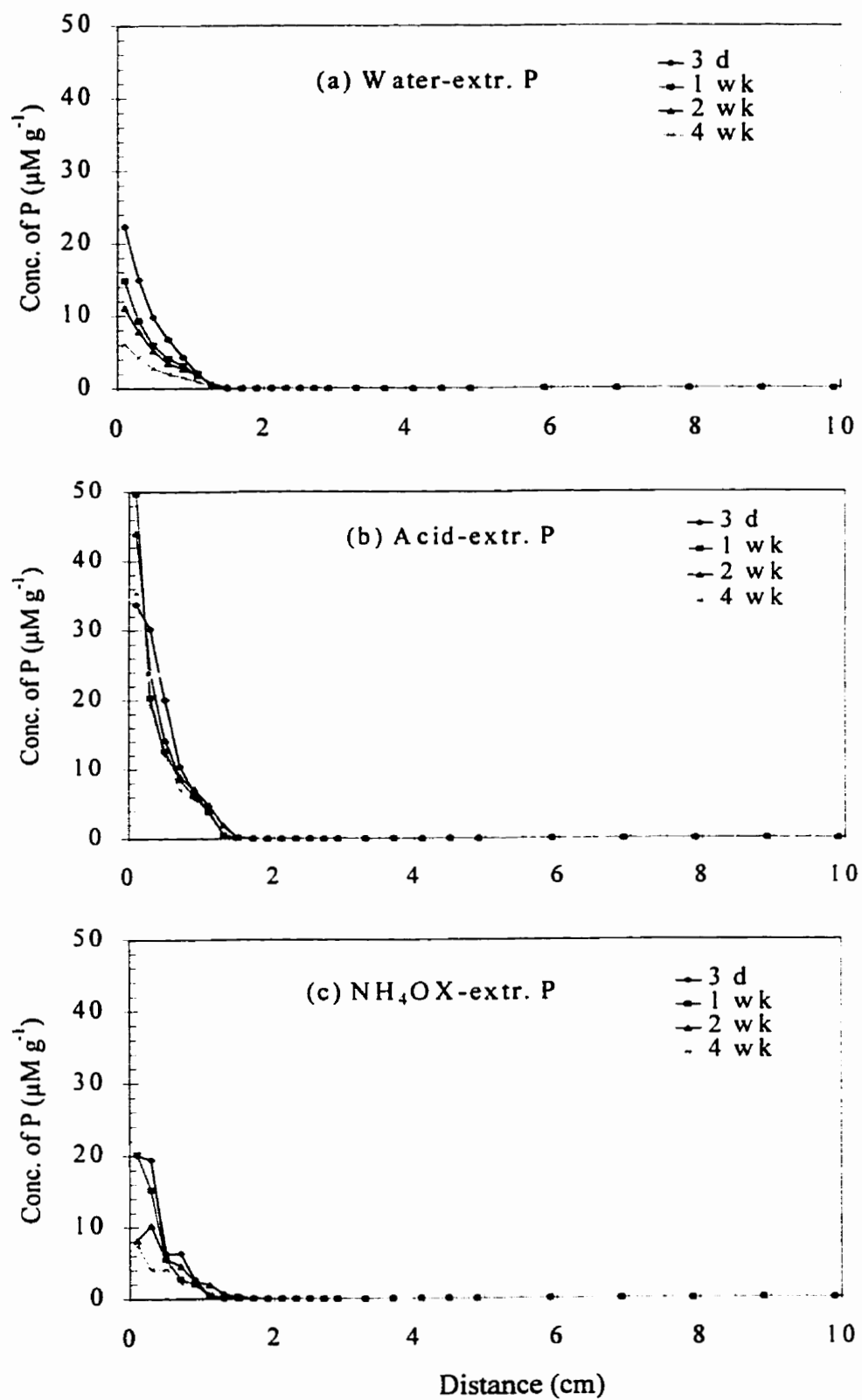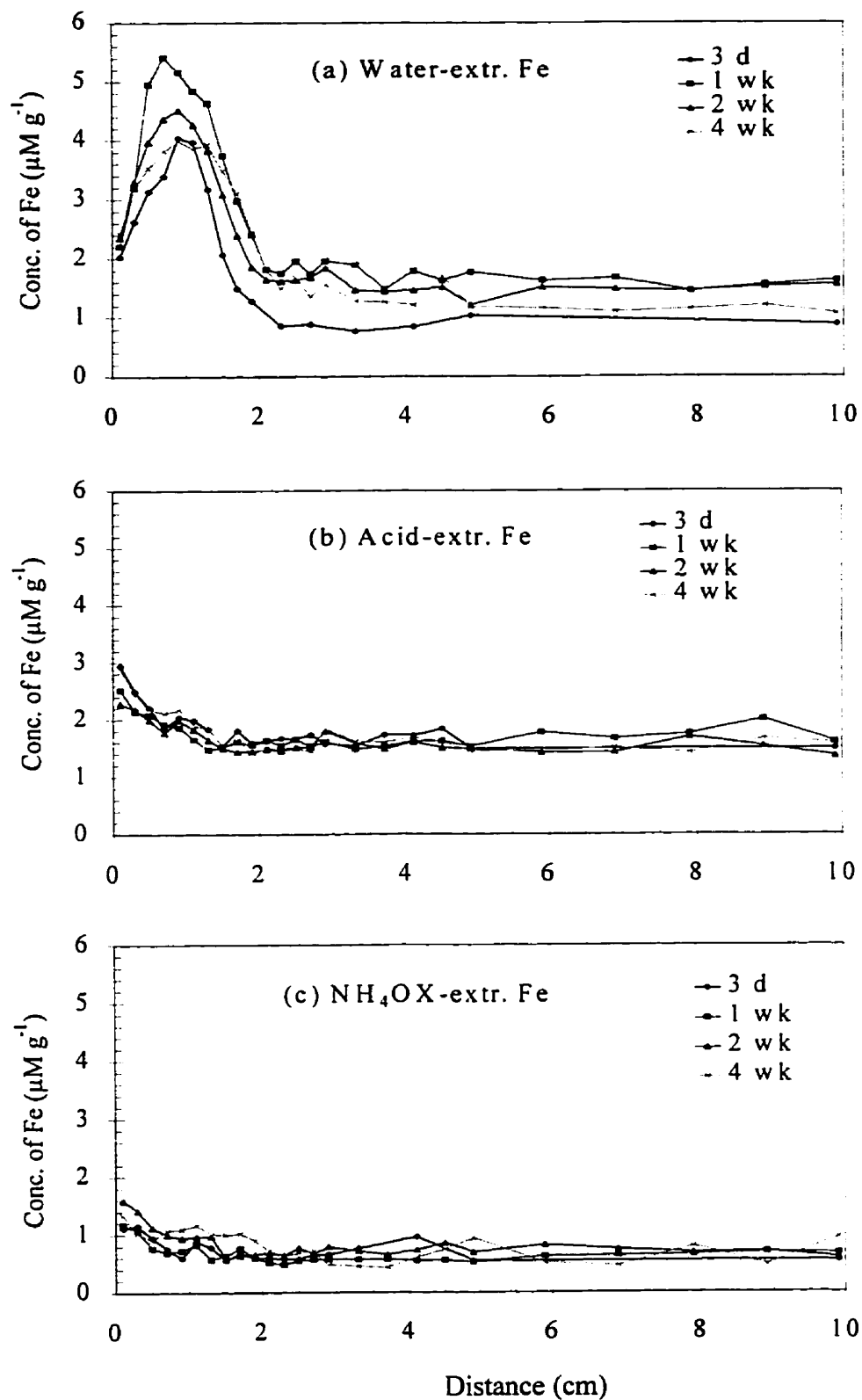
Figure 7.6 Distribution of water-, acid and NH_4OX extractable Fe in limed soil treated with KH_2PO_4 and incubated for various times.

$$(Fe) = 0.2293(Al) + 0.6497$$
$$R^2 = 0.7082***$$
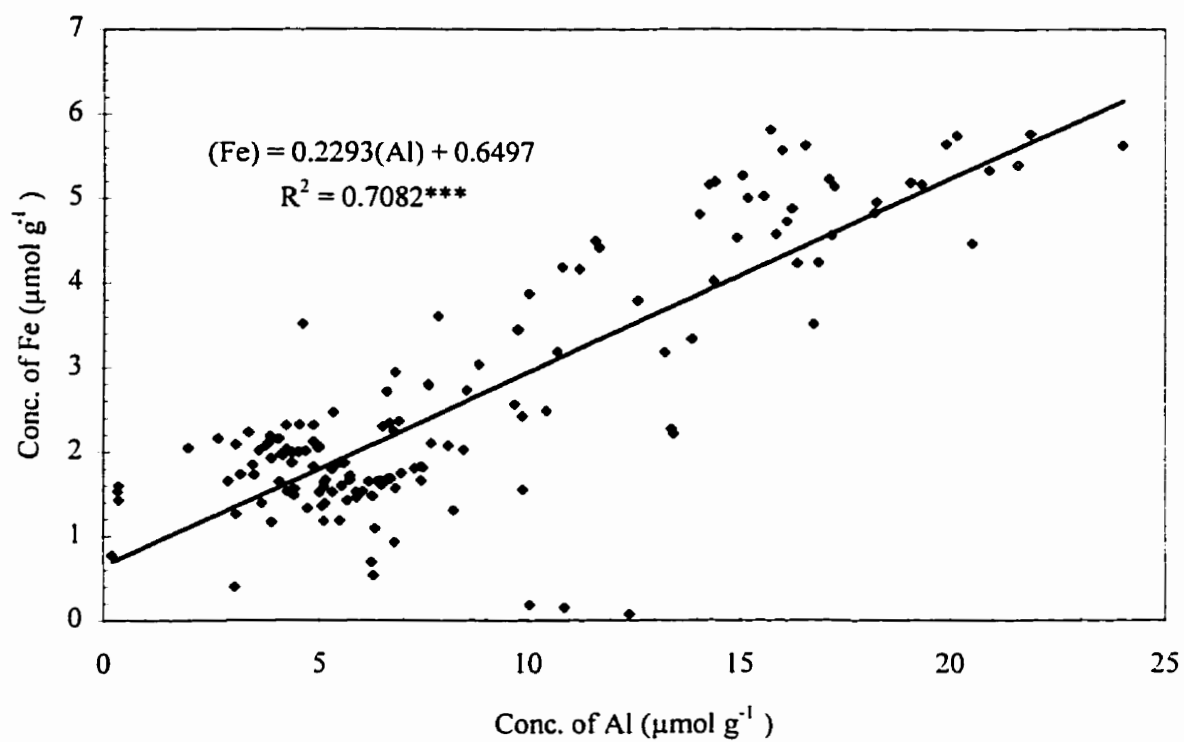
Figure 7.7 Relationship between water-extractable Al and Fe in limed soil 1 wk after KH_2PO_4 application.

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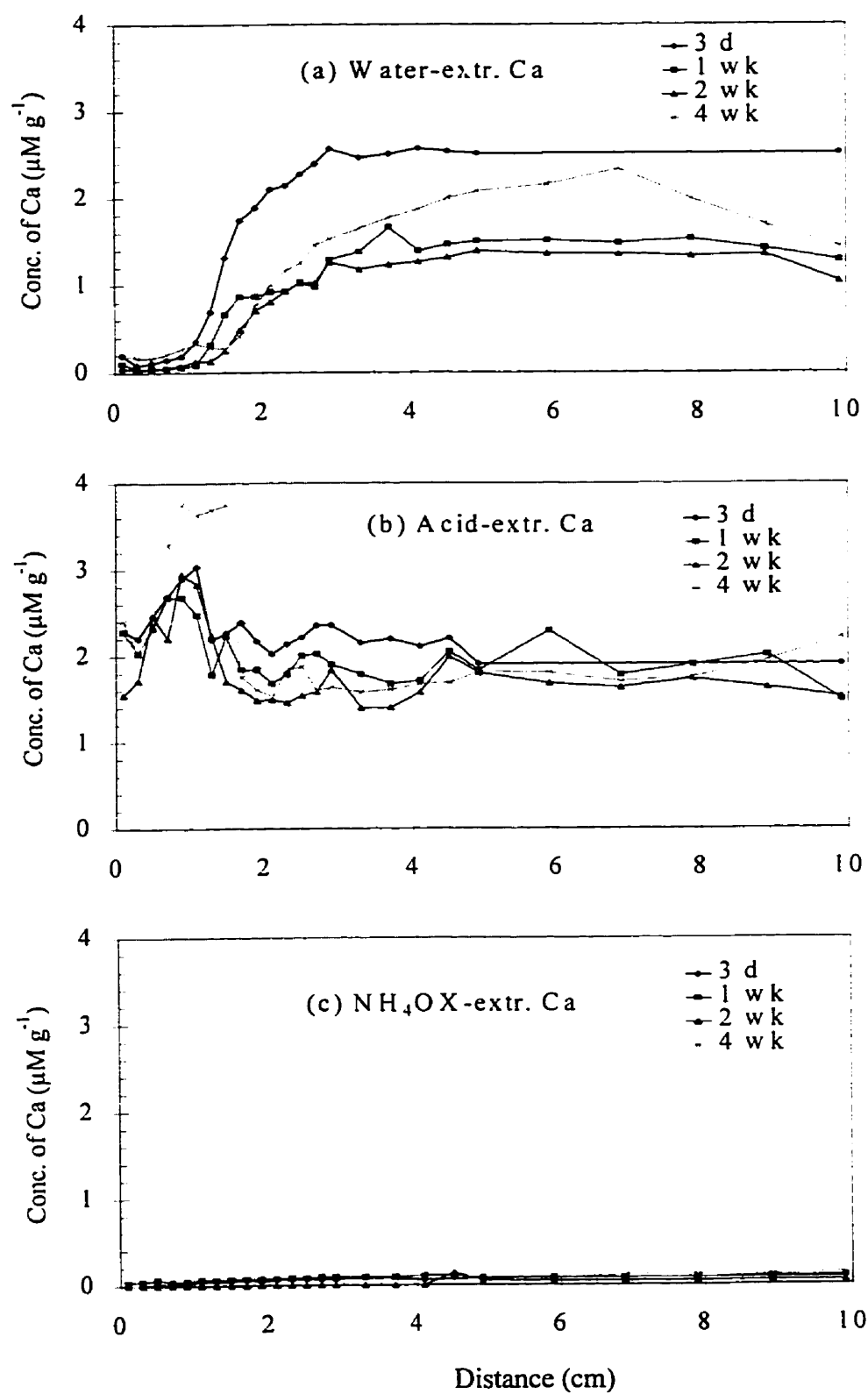
Figure 7.8 Distribution of water-, acid and oxalate extractable Ca in limed soil treated with KH_2PO_4 at various times of incubation.
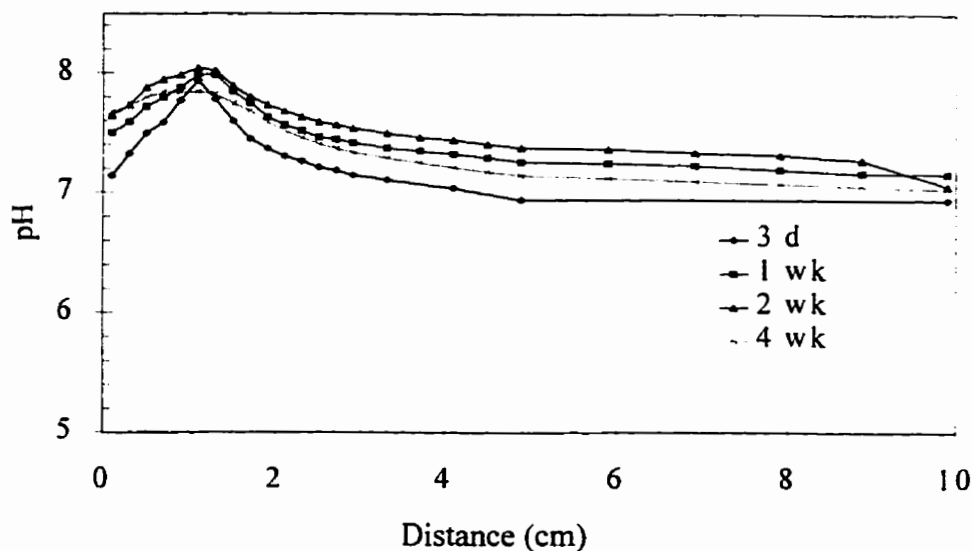
Figure 7.9 Distribution of pH in limed soil treated with KH_2PO_4 and incubated for various times.

When KH_2PO_4 fertilizer was surface applied to limed soil, the solution concentration near the surface and the total amount of water-extractable P decreased with the time of incubation (Figure 7.1a and Table 7.1). The movement of phosphate in soil was very limited. After 4 wk of incubation, it moved less than 1.5 cm. This is a good indication that the limed Oxisol had a very high P fixation ability.

Liming has no significant effect on the concentration of water- and acid-extractable P. Water- and acid-extractable P distributions for limed and unlimed soils were virtually identical (Figures 6.1a and 7.1a). The exception is after 4 wk, where water-extractable P was slightly higher for unlimed soil (8 μM g^{-1}) than for limed soil (6 μM g^{-1}). The movement of phosphate was reduced by liming. Phosphate had moved

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to 1.9 cm in unlimed soil, but only to about 1.5 cm in limed soil. The NH$_4$OX-extractable P decreased slightly after liming.

The ratios of acid- to water-extractable P for all four incubation periods were highest at the surface and decreased with depth for limed soil (Figure 7.2), similar to those observed in unlimed soil (Chapter 6). However, the decrease was much more gradual for the limed than unlimed soil.

The distribution patterns of K were very similar in limed and unlimed soils. However, the concentration of water-extractable K was generally higher, and exchangeable K lower, for limed soil than for unlimed soil. This is probably due to cation competition since Ca ions were introduced when lime was added.

The regression equation in Figure 7.4 shows that for every P ion there are 1.62 and 2.78 K$^+$ ions in the soil solution at 1 and 4 wk, respectively. These figures are much higher than the values of 1.38 and 1.43 obtained for unlimed soil, because the competitive cation exchange reactions leave more K$^+$ ions in solution for the limed soil. For limed soil, there was also an increasing likelihood of Ca-P precipitation rather than taranakite formation. This, too, could lead to a higher K to P ratio in soil solution.

The decrease in total P recovery for limed soil compared to the original soil was probably due to the higher pH of the limed soil. The higher pH supports a faster rate of conversion of a non-crystalline Al-P precipitate to acid-insoluble taranakite (Chapter 3). The decrease in total K recovery for limed soil (except after 3 d of incubation) compared to the original soil was also probably due to taranakite formation.

Even though the P concentration at the surface did not change much for limed soil compared to the original soil for the first 2 wk after P fertilizer application, the maximum

concentration of water-extractable Al was not as high as in the original soil. The concentration of maximum water-extractable Al was only about 18 μM g^{-1}, compared to the original soil where the maximum value was about 35 μM g^{-1}. The maximum solution concentration of Al did not decrease and move downward in limed soil as observed in the original soil. It is possible the differences in Al concentration between the original and limed Oxisol was due to differences in the soil pH.

The background level of water-extractable Al increased from around 2 - 4 μM g^{-1} in the original to 6 - 8 μM g^{-1} in the limed Oxisol. This was in contrast to the common belief that liming decreases total solution concentrations of Al (Haynes 1984; Ritchie 1989). The increased background level of water soluble Al could be due to Ca^{2+} exchange for Al^{3+} and the formation of a precipitate that is much more soluble than gibbsite. There were no differences in acid- and NH_4OX-extractable Al profiles for limed and unlimed soil.

The increases in solution Fe observed could be attributed to the dissolution of Fe oxides and hydroxides. The maximum value of water-extractable Fe was slightly lower in limed (5 μM g^{-1}) than unlimed (7 μM g^{-1}) soil. The acid- and NH_4OX-extractable Fe was virtually identical for both limed and unlimed soils. The background level of water-extractable Ca increased from less than 0.1 μM g^{-1} to about 2 μM g^{-1} due to the addition of $CaCO_3$ (Figure 7.8).

The increase in background pH resulted from hydroxyl (OH^-) production after lime ($CaCO_3$) application. The OH^- production can be expressed as :

$$CaCO_3 + H_2O \longrightarrow Ca^{2+} + 2\ OH^- + CO_2(g)\uparrow$$
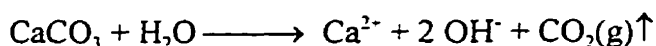
The increase in pH after P fertilizer application resulted from Al-P interactions. Those reactions, as discussed in Chapters 4 and 6, could include Al-P precipitation, Al hydrolysis, and gibbsite dissolution. The smaller increase in pH after P fertilizer application in limed than original soil was due to the greater amount of OH^{-1} ions needed to raise pH by one unit at higher pH conditions.

The above discussion shows that pH is a very important factor in Al-P precipitation reactions. The change in pH after application of P fertilizer can affect the solution P concentration and the concentration of cations species, such as Al and Fe present in soil solution. Figure 7.10 clearly shows that there are peaks of water-
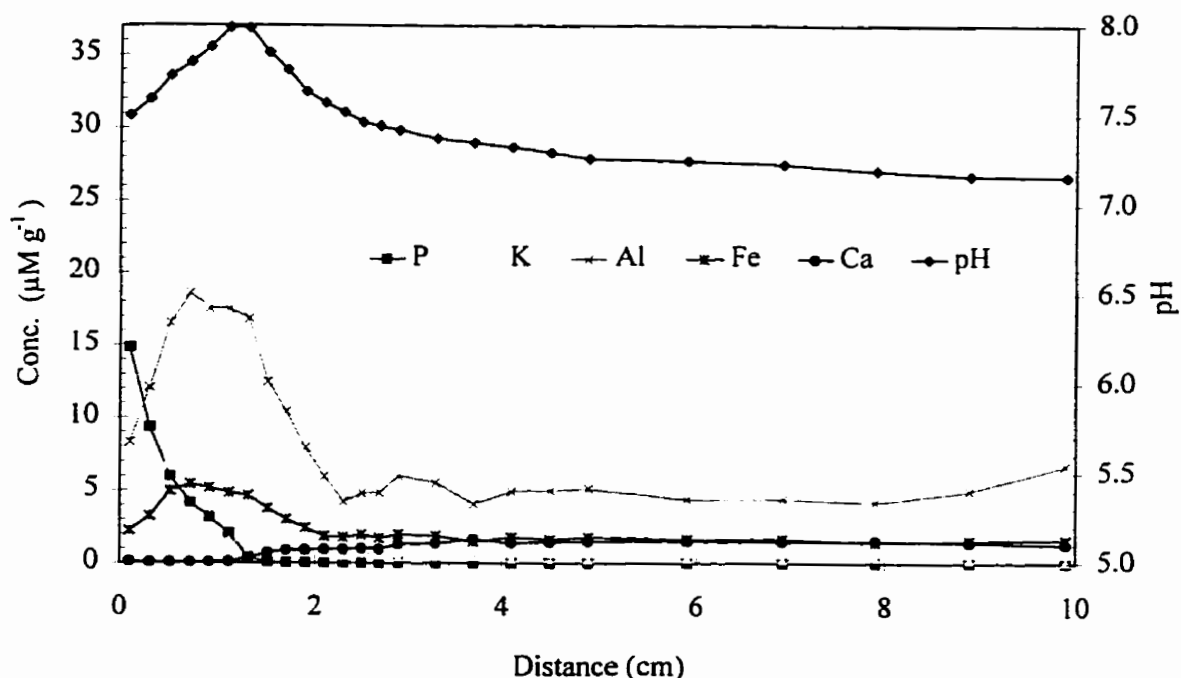
Figure 7.10 Distribution of water-extractable P, K, Al, Fe and Ca and pH in limed soil columns treated with KH_2PO_4 and incubated for 1 wk.

extractable Al and Fe in the regions of Al-P reactions and the peaks were concurrent with changes in pH. It was observed that the location of Al and Fe peaks were ahead of the K^- and H^- ions (Snow Plow effect). As discussed in Chapter 6, Al and Fe do not participate in ion exchange because the soil was always in equilibrium with those ions. On other hand, K^- and H^- ions are in involved with the cation exchange reactions. Thus, the mobility of H^- is slowed down.

The pH increase after P fertilizer application will benefit plant growth and reduce the toxic effects of Al, since Al^{3+} is the most toxic form of Al and its concentration decreases with increasing pH. The decrease in pH over time near the surface indicates that pH changes were not a long term event.

7.4 Summary and Conclusions

A limed gibbsite-rich acid Oxisol was used to study the one-dimensional diffusive transport of P and associated cations in the laboratory. The distribution profiles and the concentration of water- and acid-extractable P and cations, such as Al, K, Fe and Ca, at different times of incubation were investigated in soil columns. The results showed that the downward diffusive movement of both P and K is very limited, less than 1.5 cm for the limed soil after 4 wk of incubation. The concentration of soluble P and K at the surface decreased with time and depth as observed for the original unlimed soil. The solution concentration of Al and Fe and pH had a maximum value where P had penetrated. The maximum concentration of Fe and Al were lower in limed than in the original unlimed soil. The solution concentration of Ca was lowered, and acid-

extractable Ca was elevated, near the surface, but the concentration of Ca was very low, even in limed soil, and it probably did not play a significant role in P fixation.

Al-P precipitation reaction was proposed as the main mechanism for P fixation in a limed acid soil. As this precipitation continued, more and more phosphate ions were taken out of soil solution, resulting in a decrease in P concentration near surface. The Al and Fe solution concentrations were increased during the Al-P (Fe-P) precipitation process as result of the dissolution of oxides and hydroxides.

8. MOVEMENT, AVAILABILITY AND EFFECTS ON SOIL ACIDITY OF THREE PHOSPHATE FERTILIZERS

Abstract

Phosphate (P) movement in soil is limited by rapid fixation processes and its low solubility. This study was conducted to investigate how phosphate movement in an Al-rich acidic soil is affected by phosphate species, and the effects of fertilizer application on soil pH. One-dimensional phosphate transport was studied with mono-, di- and tri-potassium phosphates (MKP, DKP, and TKP) in a simulated soil column. The simulated soil consisted of an Al-saturated cation exchange resin and acid-washed sand, with and without 1% gibbsite. The CEC of the simulated soil was 22 $cmol_c kg^{-1}$. Quantities of P equivalent to 1.47 mM were surface applied to each column and incubated for 1 and 4 wk in a constant humidity chamber.

Depth of phosphate movement was greatest with MKP and least with TKP in the absence of gibbsite. When gibbsite was added to the soil system, there was little difference in the depth of P movement for the various types of phosphate fertilizer. The amount of water soluble phosphate remaining in the soil system also decreased from MKP to DKP to TKP for the system without gibbsite. But the order was reversed when gibbsite was added and the columns were incubated for 4 wk. Thus, the transport of

phosphate was affected by the phosphate species, the time of incubation and the presence or absence of gibbsite.

Application of TKP resulted in the highest soil pH, while application of MKP resulted in the lowest soil pH. This indicates that TKP is a better fertilizer to use in preventing soil acidification.

8.1 Introduction

Acidity is a major limitation to soil productivity in much of the world. Two of the most common problems associated with high acidity in soil are Al toxicity and phosphorus (P) deficiency. Since many highly weathered tropical acid soils in their native state do not contain sufficient available P to maximize crop yield, application of phosphate fertilizer has been used in an effort to increase crop yields. However, P fixation (transformation of soluble forms of P into less soluble forms) is a frequent problem in acid soils (Sanchez and Uehara 1980). Highly weathered acidic tropical soils are very rich in Al. Each cmol of exchangeable Al per kg of soil could fix up to 102 mg of P and soils rich in Al oxides and hydroxides have very high P fixation capacities (Sanchez and Uehara 1980). One of the common management strategies for acidic soils is to apply an initially very large amount of P fertilizer. Rates of 500 to 1000 kg P ha^{-1} yr^{-1} have been used on acid soils (Sanchez and Uehara 1980), compared to the normal 60 kg P ha^{-1} yr^{-1} usually applied to non-acidic soils. However, heavy application of P fertilizer can result in soil acidification.

Soil acidification due to P fertilizer application has been well documented (Helyar and Porter 1989). The commonly used mono-basic P fertilizer ($NH_4H_2PO_4$, KH_2PO_4 and

$Ca(H_2PO_4)_2$) is one source of acidification of soil (Cho 1991; Kennedy 1992; McBride 1994), although it has not received as much attention as N fertilizer. In acid soil, the mono-basic P fertilizer reaction with soil can be represented as:

$$H_2PO_4^- + Al^{3+} \rightleftharpoons AlPO_4(s) + 2H^- \qquad [8.1]$$
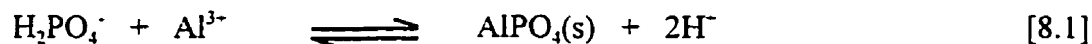
The hydrogen ions produced during the Al-P fixation reaction would lower soil pH. Past research has shown that toxicity of Al increases with decreasing pH (Cameron et al. 1986). Thus, excess application of mono-basic P fertilizer could potentially increase the toxic effect of Al.

The objective of this study was to examine the movement and solution concentration of phosphate and associated cations after the application of KH_2PO_4 (MKP), K_2HPO_4 (DKP) and K_3HPO_4 (TKP) in acidic soil and their effect on soil acidity.

8.2 Materials and Methods

A resin-sand mixture was used to simulate an acid soil. An Al-saturated cation exchange resin was mixed with acid-washed sand to give a cation exchange capacity of 22 cmol$_c$ kg^{-1}. Gibbsite, at 1% w/w, was added to one-half of the treatments. The preparation of gibbsite is outlined in Chapter 4.

Dry mixtures of sand, cation exchange resin and gibbsite were thoroughly mixed and then distilled water was added to bring the moisture content to field capacity (0.25 kg kg^{-1}). The moistened mixture was packed into cylindrical columns made of wax to a bulk density of 1.42 g cm^{-3}. The soil column was 4.5 cm in diameter and 10 cm long. The soil columns were placed into a constant humidity chamber for 17 hours prior to phosphate fertilizer application.

Three different types of phosphate fertilizers, KH_2PO_4 (MKP), K_2HPO_4 (DKP) or K_3PO_4 (TKP), were added to the surface of the column at rates of 0.2, 0.256 and 0.312 grams per column (equivalent to 1.47 mM P per column), respectively. The columns were incubated for 1 and 4 wk and each soil column was sliced into 2 mm thick sections with a meat cutter. The water content of each slice was determined.

To measure the pH, approximately 1 g (oven-dry weight) of each sample was placed into a centrifuge tube, one ml of water was added, and the mixture thoroughly mixed with a vertex (Genie 2 by Fisher Scientific). The pH was then measured using a non-leakage combination electrode (Canlab). An additional 4 ml of water was added, the mixtures shaken for ten minutes, and then centrifuged at 8000 RPM for ten minutes. The solutions were removed with a pipette and 5 mL of distilled water was added and the samples extracted as noted above. The two extracts were combined and termed "the water-extractable fraction." After water extraction, the solid sample remaining in the tube was successively extracted with three portions of 5 mL of 1 M HCl. The three acid extractions were combined and termed "the acid-extractable fraction." The water-extractable fraction approximates P in the soil solution and dissolved P from solid phases, while the acid-extractable fraction approximates that in the solid phase and not readily soluble in water. $BaCl_2$-extractable Al, representing the exchangeable Al, was also measured. Phosphate was determined by the modified ascorbic acid-ammonium molybdate method of Murphy and Riley (1962) while the extractable K^- and Al^{3-} were determined using an atomic absorption spectrophotometer (Perkin-Elmer 1100B).

8.3 Results and Discussion

8.3.1 Phosphate Distribution

8.3.1.1 Water-extractable P

The distribution patterns of water-extractable P in columns without gibbsite were related to the type of phosphate compound added (Figure 8.1). The concentration of P in solution and the depth of movement of P was the highest with MKP and decreased with basicity of the phosphate applied for both incubation periods. The water-extractable P concentration was highest ($17\mu M$ g^{-1}) at the surface, decreased gradually to zero around 4.7 cm depth for columns with MKP incubated for 1 wk. For DKP, the P concentration was 10.5 μM g^{-1} at the surface. The concentration of water-extractable P increased slightly to a depth of 0.5 cm, then decreased in a pattern similar to that for MKP to zero at a depth of 3.1 cm. For TKP, the P concentration was 3.5 μM g^{-1} at the surface, increased to 7 μM g^{-1} at a depth of 0.7 cm, then decreased to zero at a depth of 2.3 cm.

As noted above, the distribution of water-extractable P was similar for both times of incubation. However, the concentration of water-extractable P generally declined from 1 to 4 wk. The maximum concentrations near the surface decreased from 17.0, 10.5, and 3.5 μM g^{-1} at 1 wk to 10.0, 9.5, and 2.5 μM g^{-1} at four wk for MKP, DKP and TKP, respectively. The maximum depth of penetration of water-extractable P also moved further downward from 4.7, 3.1 and 2.3 cm at 1 wk to 5.1, 3.5 and 2.7 cm at 4 wk for MKP, DKP and TKP, respectively. The movement of phosphate was quite slow after 1 wk as indicated by the small differences in the depth of phosphate movement between 1 and 4 wk of incubation. Generally, water-extractable P was highest near the surface for MKP among the three phosphate compounds, regardless of incubation period.

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Figure 8.1 Distribution of water-extractable P in columns treated with KH_2PO_4, K_2HPO_4, and K_3PO_4 without gibbsite at (a) one and (b) four wk of incubation.

The concentration of water-extractable P in columns with gibbsite was usually lower than in columns with only exchangeable Al (Figure 8.1 and 8.2). The distribution of water-extractable P was affected by the type of phosphate compound added. For MKP, the distribution of P for columns with gibbsite (Figure 8.2a) were similar to those observed without gibbsite (Figure 8.1a) for the 1 wk of incubation. The maximum water-extractable P was highest at the surface (10 μM g^{-1}) and decreased gradually with depth to zero at a depth of 1.5 cm for MKP. When DKP was applied, water-extractable P was highest at the surface (7.0 μM g^{-1}) and decreased with depth to zero at 1.5 cm similar to patterns observed with MKP. For TKP, columns with gibbsite showed very similar patterns to those without gibbsite. Specifically, the P concentration was 3.0 μM g^{-1} at the surface, increased to 5.0 μM g^{-1} at a depth of 0.6 cm, and then decreased with depth to zero at 1.5 cm. In contrast to results obtained for the columns with only exchangeable Al (Figure 8.1a), the depth of P movement was not affected by the type of phosphate compounds applied in the columns containing both exchangeable Al and gibbsite.

Water-extractable P was the highest (Figure 8.2a) after 1 wk, but the lowest after 4 wk (Figure 8.2b), of incubation for MKP among the three fertilizers used . The decrease in water-extractable P concentration with DKP and TKP from 1 wk (7.0, and 2.7 μM g^{-1}) to 4 wk (3.7 and 2.0 μM g^{-1}) of incubation was much less than that observed with MKP (which decreased from 10 to 2.0 μM g^{-1} from 1 to 4 wk).

The presence of gibbsite had a great impact on P reactions. With gibbsite, the concentration of water-extractable P was generally lower; the differences in the water-extractable P distribution patterns among the three phosphates became less distinctive over time; water-extractable P movement was more retarded; and the depth of P
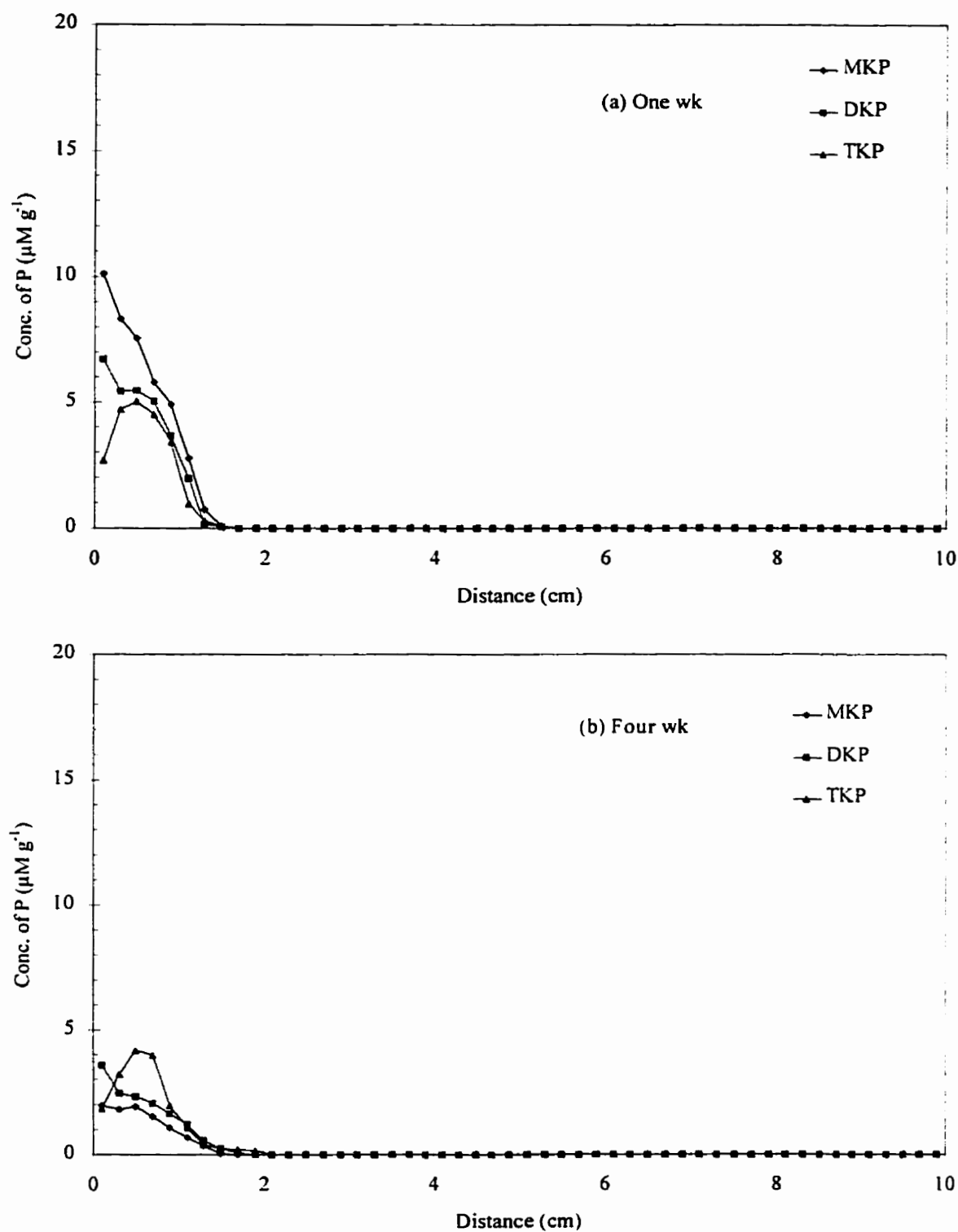
Figure 8.2 Distribution of water-extractable P in columns treated with KH_2PO_4, K_2HPO_4, and K_3PO_4 with gibbsite at (a) one and (b) four wk of incubation.

movement was not affected by the type of phosphate compound.

8.3.1.2 Acid-extractable P

Acid-extractable P at the surface of the columns with only exchangeable Al was highest with TKP and lowest with MKP after 1 wk of incubation (Figure 8.3a). Below 1.5 cm, acid-extractable P was lowest with TKP and highest with MKP. Similar patterns were observed after 4 wk of incubation (Figure 8.3b). In the surface region (0 to 2 cm depth), acid-extractable P content was the highest for TKP and lowest for MKP, while the reverse was true below 2 cm. The reduction in acid-extractable P near the surface (from 35 μM g^{-1} to 15 μM g^{-1}) was much greater for DKP than for MKP and TKP as time of incubation increased from 1 wk to 4 wk.

The distribution patterns of acid-extractable P (Figure 8.4) in the columns with exchangeable Al and gibbsite were quite different from those columns with only exchangeable Al (Figure 8.3). The acid-extractable P decreased in the order MKP, DKP. and TKP for the top 1 cm of the columns for both incubation periods. Below 1 cm depth, there were virtually no differences in acid-extractable P among the three phosphate compounds.

8.3.1.3 Phosphate Recovery

The portion of added phosphate, which was extracted (recovered), is summarized in Tables 8.1 and 8.2. The amount of P in each 2 mm section over the entire column was summed. This was done separately for the water and acid-extractable fractions.

The total P recovered was quite high (98.7 to 99%) for MKP and DKP after 1 wk of incubation for columns with only exchangeable Al (Table 8. 1). The recovery, however, was only 77% for TKP. The percentage of P recovered remained very high for

Figure 8.3 Distribution of acid-extractable P in columns treated with KH_2PO_4, K_2HPO_4, and K_3PO_4 without gibbsite at (a) one and (b) four wk of incubation.
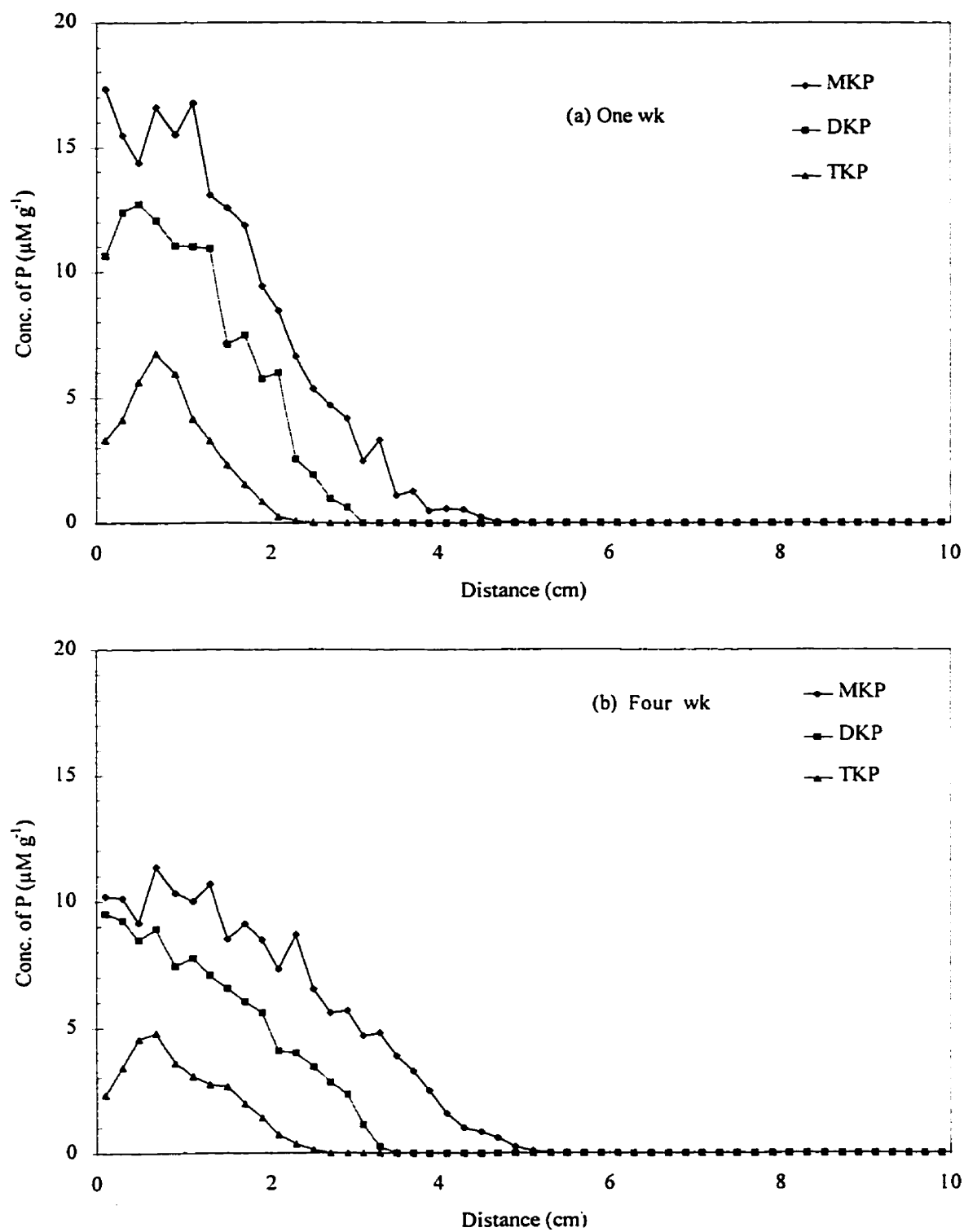
Figure 8.4 Distribution of acid-extractable P in columns treated with KH_2PO_4, K_2HPO_4, and K_3PO_4 with gibbsite at (a) one and (b) four wk of incubation.

Table 8.1 Mass balance of phosphate for columns with only exchangeable Al.

Treatment	P added	Water-ext P	Acid-ext P	Total P recovered	Percentage of P recovered
			$(mM \ column^{-1})$		
			1 wk		
KH_2PO_4	1.47	0.826	0.625	1.450	98.7
K_2HPO_4	1.47	0.512	0.943	1.455	99.0
K_3PO_4	1.47	0.173	0.960	1.133	77.1
			4 wk		
KH_2PO_4	1.47	0.702	0.763	1.464	99.6
K_2HPO_4	1.47	0.428	0.722	1.150	78.2
K_3PO_4	1.47	0.143	0.984	1.127	76.7

Table 8.2 Mass balance of phosphate for columns with both exchangeable Al and gibbsite.

Treatment	P added	Water-ext P	Acid-ext P	Total P recovered	Percentage of P recovered
			$(mM \ column^{-1})$		
			1 wk		
KH_2PO_4	1.47	0.182	1.217	1.400	95.2
K_2HPO_4	1.47	0.129	1.034	1.163	79.1
K_3PO_4	1.47	0.098	0.867	0.965	65.6
			4 wk		
KH_2PO_4	1.47	0.043	1.300	1.343	91.3
K_2HPO_4	1.47	0.064	1.159	1.223	83.2
K_3PO_4	1.47	0.078	1.000	1.078	73.3

MKP, but dropped to 78.2% for DKP after 4 wk. Percent recovered remained constant with time of incubation for TKP. In general, total P recovered decreased with increased basicity of the phosphate compounds.

For columns with both exchangeable Al and gibbsite, the recovery of phosphate was still highest for MKP and lowest for TKP. There was very little difference in the amounts of P recovered between the two incubation periods. The percentages recovered were generally lower for the columns with gibbsite than for the columns with only exchangeable Al.

The total water-extractable P fraction decreased from MKP to TKP, when there was no gibbsite in the column (Table 8.1). When gibbsite was added, the above pattern was true only for the 1 wk of incubation. Water-extractable P was highest for TKP after a 4 wk of incubation. The acid-extractable P fraction increased from MKP to TKP fertilizer when there was no gibbsite, whereas the opposite trend was observed with gibbsite. As demonstrated in Chapter 3, the rate of taranakite formation increases with pH. Since water and 1 M HCl may only extract a portion of Al-P precipitates, a decrease in P recovery from MKP to TKP fertilizer may be due to the increased formation of taranakite at higher pH. The percentage of P recovered would also be lower for columns with both exchangeable Al and gibbsite because columns with gibbsite had a slightly higher pH (4.1) than columns with only exchangeable Al (3.5). The decrease in P recovery over time was probably due to the conversion of non-crystalline Al-P to acid-insoluble taranakite.

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8.3.2 Aluminum Status

8.3.2.1 Water-extractable Al

The background concentration of water-extractable Al was very low for both incubation periods for the columns with only exchangeable Al (Figure 8.5). Application of TKP generally increased the Al concentration at the surface with concentration peaks of 5.4 and 3.6 μM g^{-1} at a depth of 0.5 cm for 1 wk and 4 wk of incubation, respectively. There was a slight increase in Al concentration near the surface after the application of DKP. Application of MKP had no observable effect on water-extractable Al.

Water-extractable Al decreased near the surface for columns with both exchangeable Al and gibbsite when phosphate fertilizer was applied (Figure 8.6). The background Al concentration was quite high ($20\mu M$ g^{-1}) due to the gibbsite used in this experiment. A peak of Al (around 4 μM g^{-1}) was also observed at a depth of 0.5 cm for the columns with TKP.

8.3.2.2 BaCl₂- and Acid-extractable Al

$BaCl_2$-extractable Al represents the exchangeable Al fraction. $BaCl_2$-extractable Al was lowest at the surface, increased with depth to the point of P penetration, and then remained constant throughout the remainder of the column (Figure 8.7). Application of TKP resulted in the lowest exchangeable Al concentration at the surface of the column among the three phosphate fertilizers used.

The reduction in $BaCl_2$-extractable Al near the surface was due to cation exchange of the K^- ion for Al on exchange sites after phosphate fertilizer application. The greatest reduction in exchangeable Al was associated with the application of TKP, which contained the highest ratio of K to P. This further suggests that Al-P precipitation would
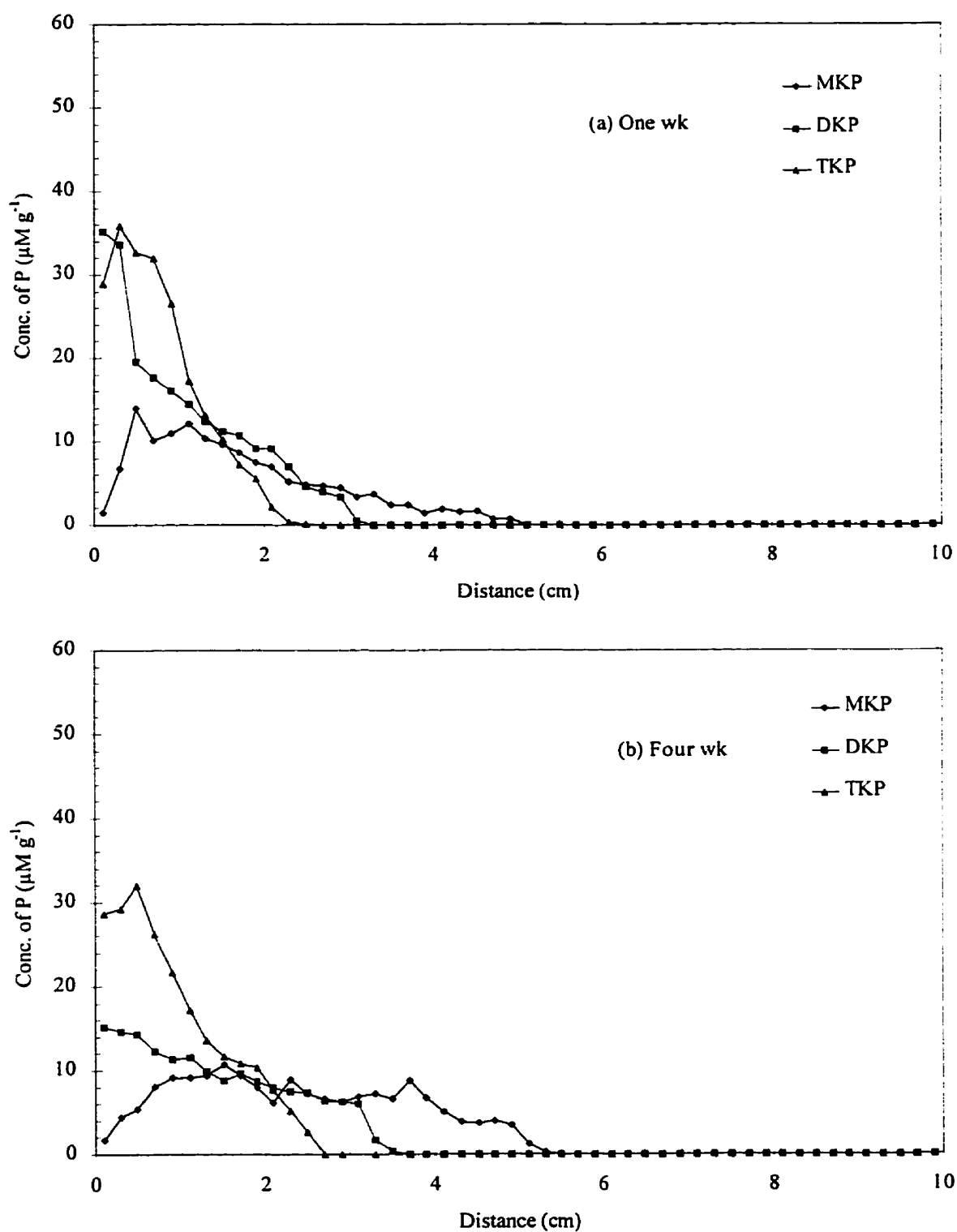
Figure 8.5 Distribution of water-extractable Al in columns treated with KH_2PO_4, K_2HPO_4, and K_3PO_4 without gibbsite at (a) one and (b) four wk of incubation.

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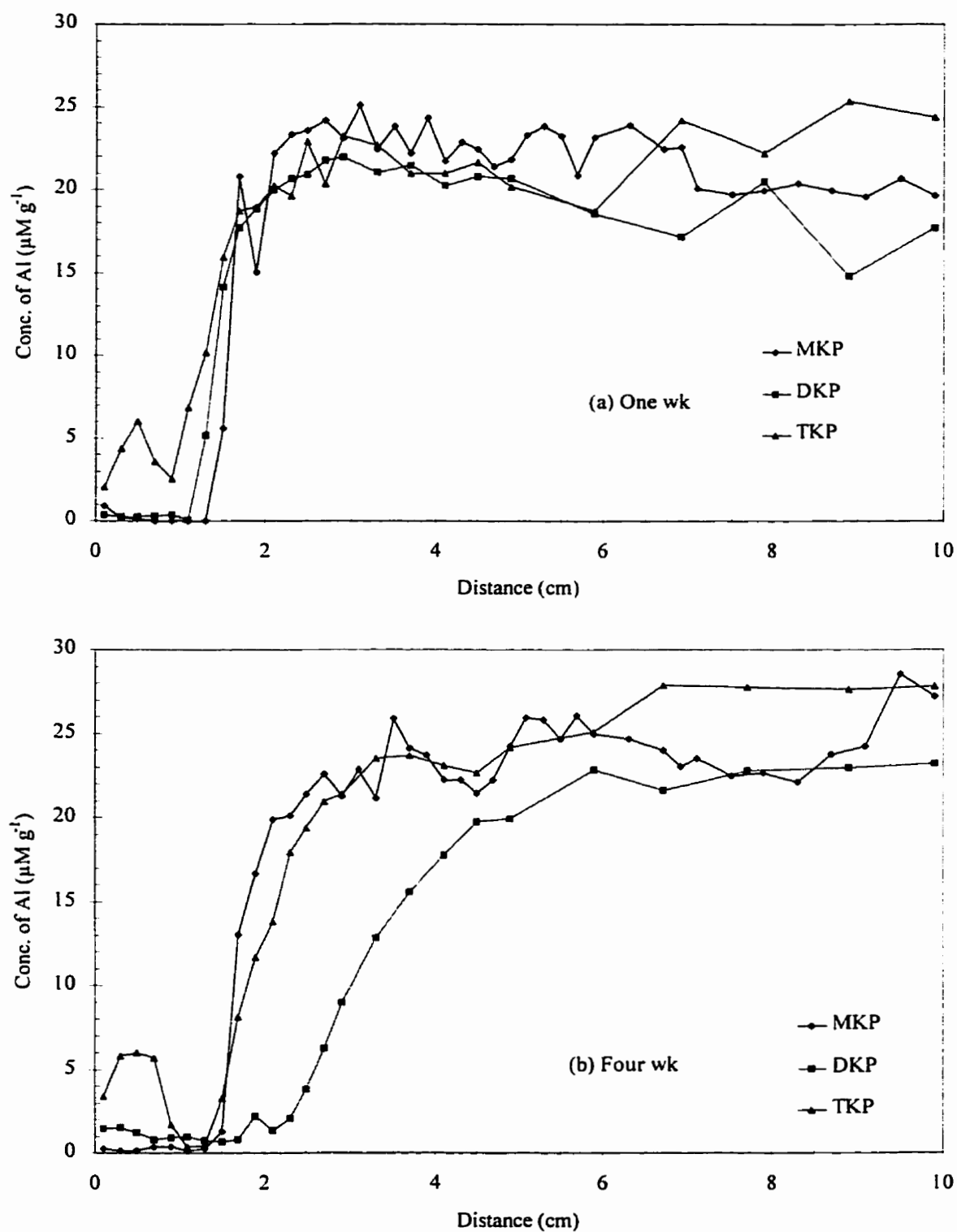
Figure 8.6 Distribution of water-extractable Al in columns treated with KH_2PO_4, K_2HPO_4, and K_3PO_4 with gibbsite at (a) one and (b) four wk of incubation.
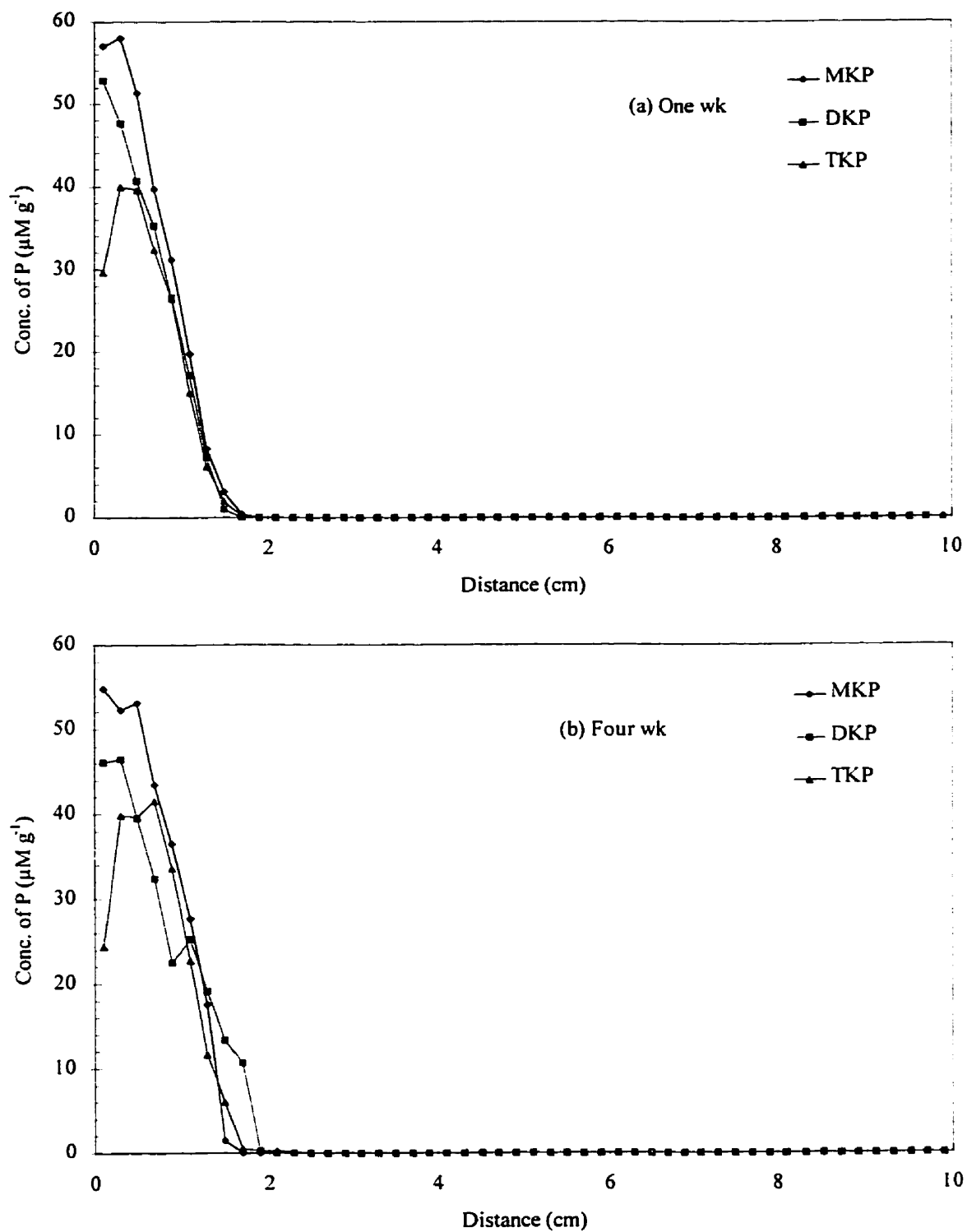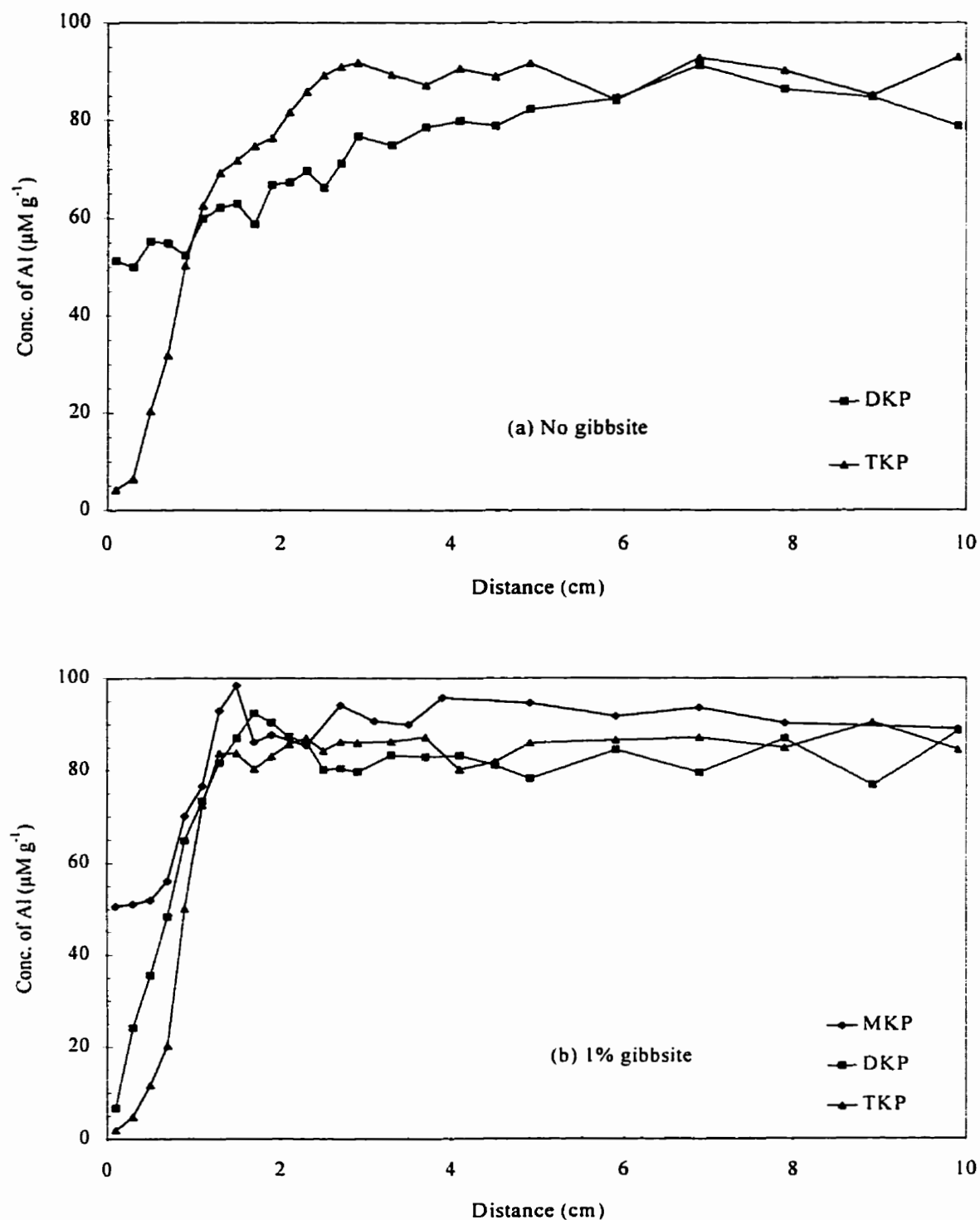
Figure 8.7 Distribution of BaCl$_2$-extractable Al in columns treated with KH$_2$PO$_4$, K$_2$HPO$_4$, and K$_3$PO$_4$ (a) without gibbsite (b) with gibbsite at four wk of incubation.

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be greater for TKP since the supply of Al from exchange sites would be the greatest. The low water-extractable P in the columns with TKP application confirmed this hypothesis.

Only a slight increase in acid-extractable Al occurred in surface layers for columns with only exchangeable Al (Figure 8.8). In contrast, adding P to the columns with both exchangeable Al and gibbsite resulted in a more noticeable increase in acid-extractable Al at the surface of the columns (Figure 8.9). The high acid-extractable Al near the surface was most likely result of the dissolution of non-crystalline Al-P as the exchangeable Al was very low in the same region. The very high acid-extractable Al near the surface suggests that some of the Al may have moved upwards, especially for the columns with both exchangeable Al and gibbsite.

8.3.3 Soil Acidity

Soil pH was affected by type of phosphate fertilizer and the presence or absence of gibbsite (Figures 8.10 and 8.11). Soil pH values, at the surface, were lowest for MKP, and increased with basicity of phosphate fertilizers for both incubation periods for columns with only exchangeable Al. Addition of MKP decreased soil pH to the depth of about 5 cm at 1 wk of incubation (Figure 8.10). On the other hand, addition of TKP increased soil pH in the same region.. The differences in surface pH among the three phosphate fertilizers narrowed with time of incubation, but the effects were similar to that obtained for 1 wk of incubation. The surface pH dropped from 6.0 to 5.3 for TKP, 4.5 to 4.0 for DKP and remained the same for MKP from 1 wk to 4 wk of incubation. The depth to which pH had changed as a result of phosphate application was also affected by the type of phosphate compound. MKP affected soil pH to the greatest depth, especially after 4 wk of incubation. The depths to which pH had changed due to phosphate
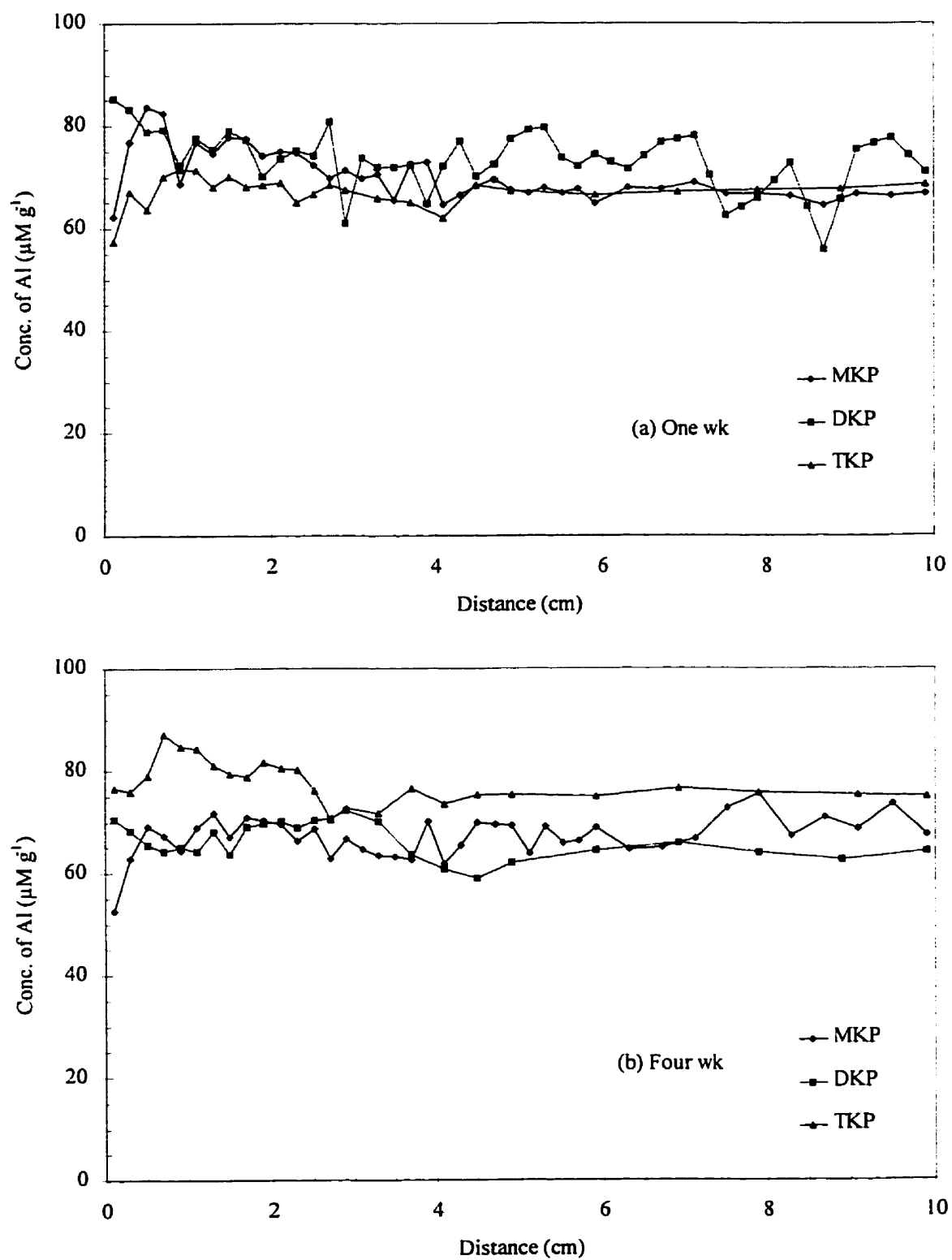
Figure 8.8 Distribution of acid-extractable Al in columns treated with KH_2PO_4, K_2HPO_4, and K_3PO_4 without gibbsite at (a) one and (b) four wk of incubation.
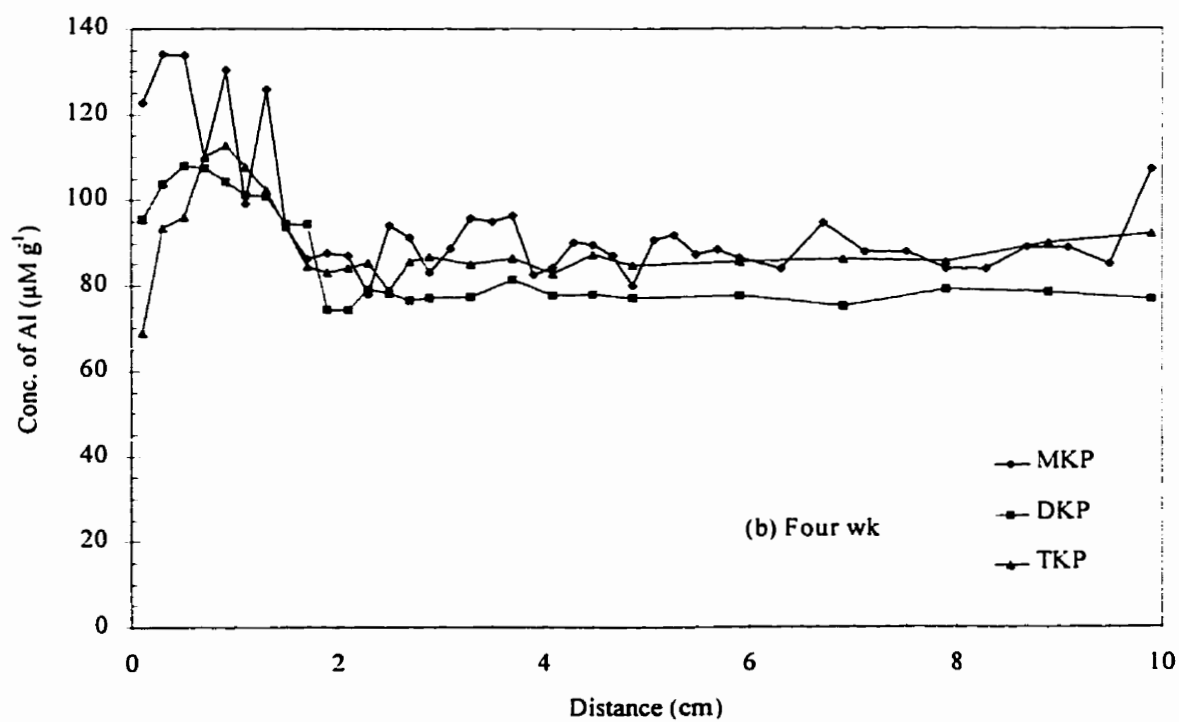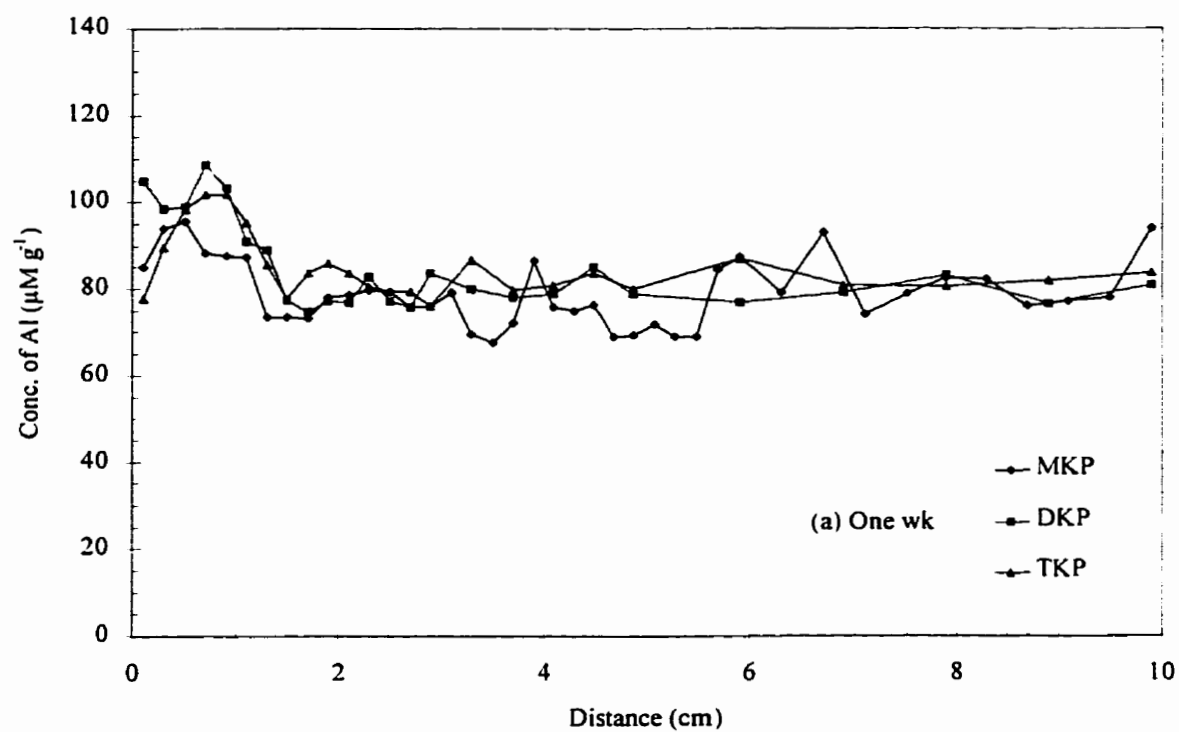
Figure 8.9 Distribution of acid-extractable Al treated with KH_2PO_4, K_2HPO_4, and K_3PO_4 with gibbsite at (a) one and (b) four wk of incubation.
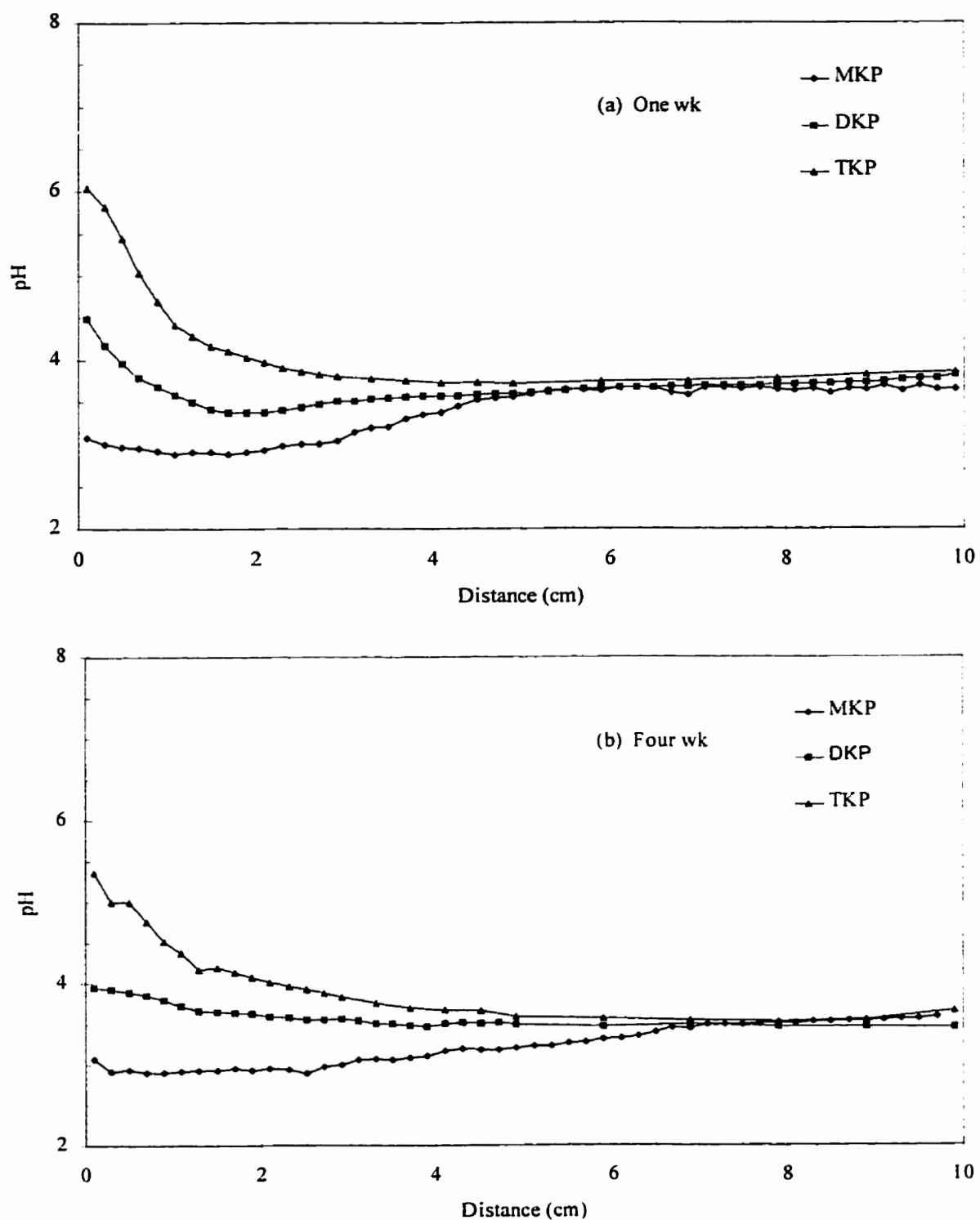
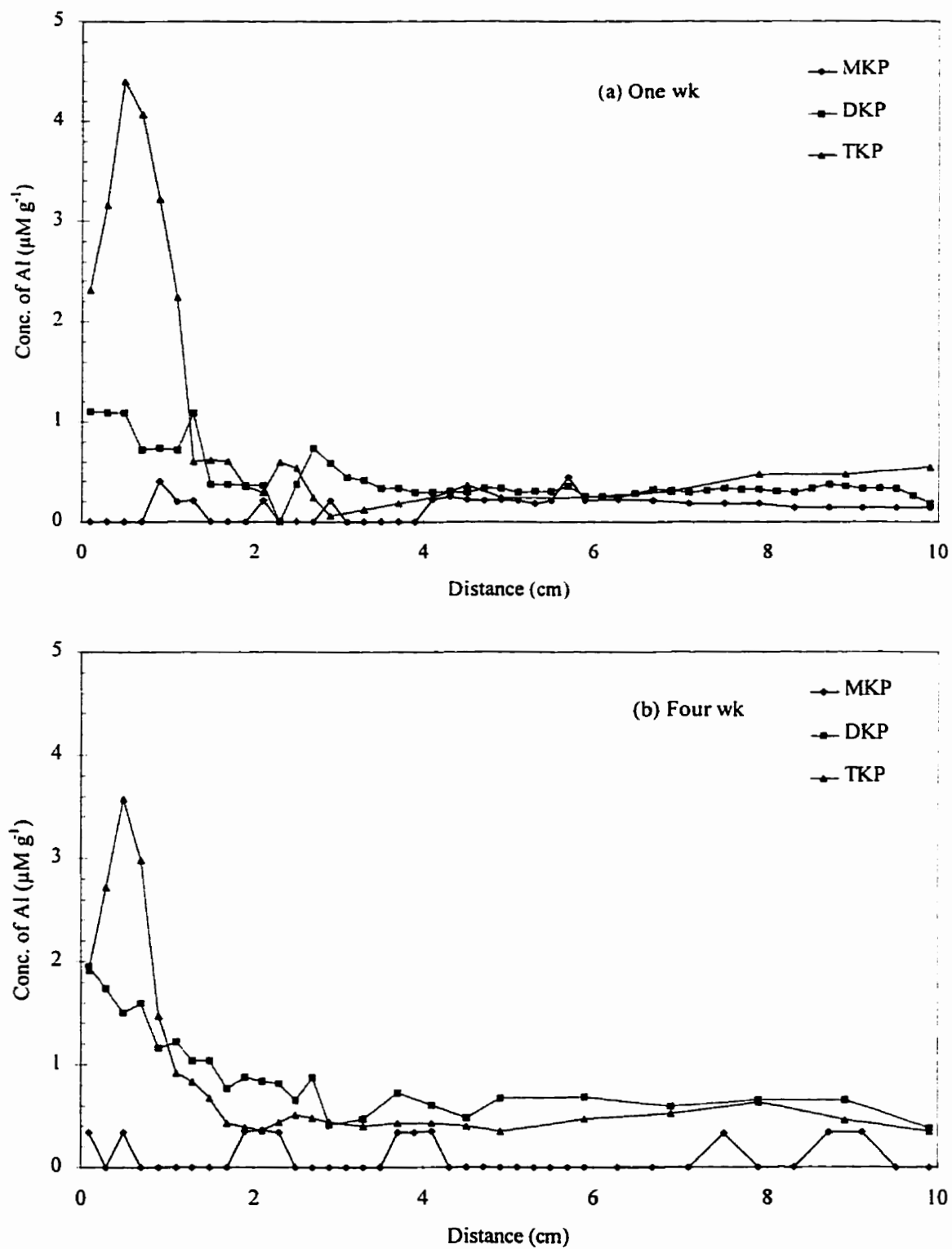Figure 8.10 Distribution of pH in columns treated with KH_2PO_4, K_2HPO_4, and K_3PO_4 without gibbsite at (a) one and (b) four wk of incubation..

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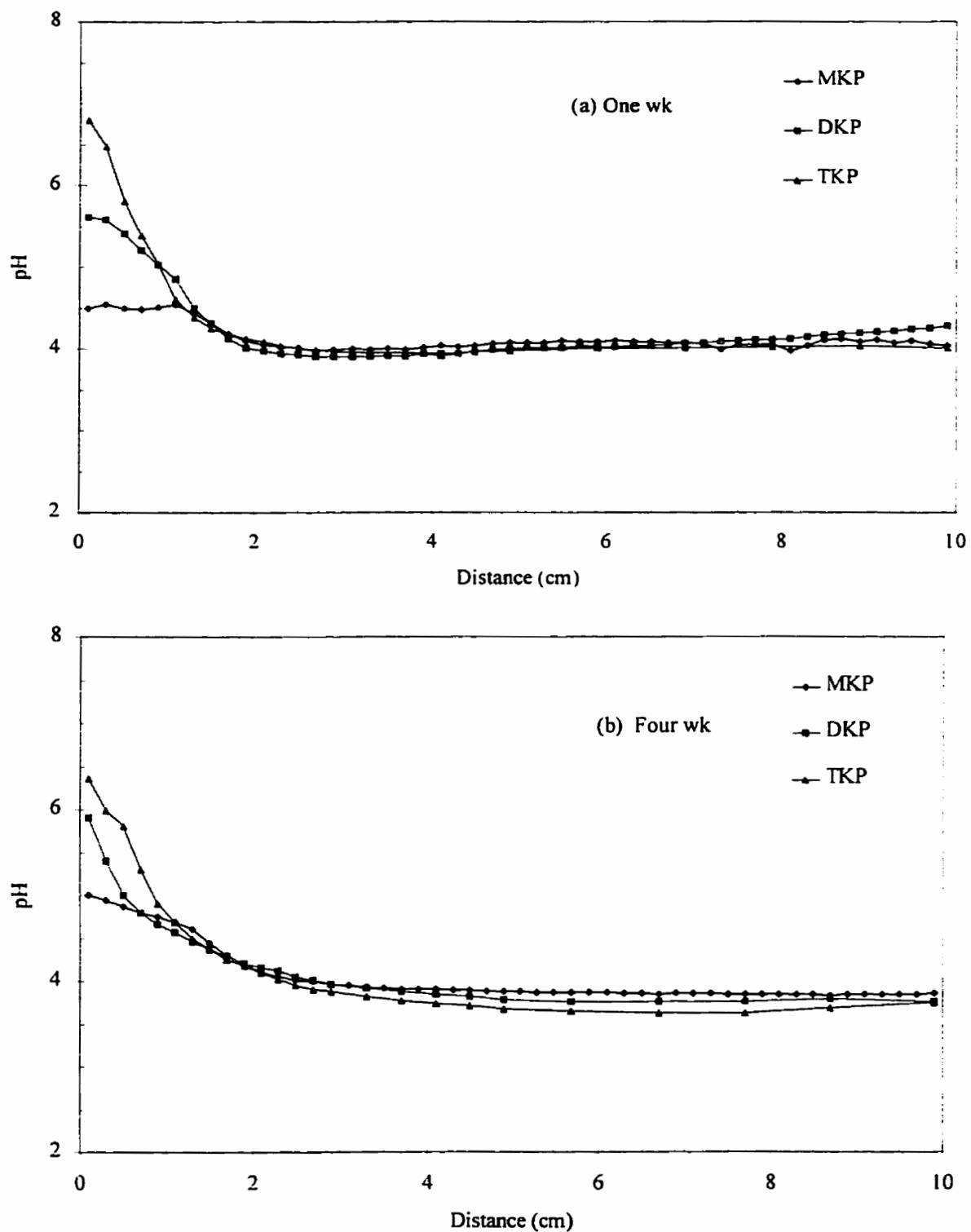
Figure 8.11 Distribution of pH in columns treated with KH_2PO_4, K_2HPO_4, and K_3PO_4 with gibbsite at (a) one and (b) four wk of incubation.

application were consistent with the results for depths of P movement. The greatest depth of P movement and the depth of pH change were observed with MKP application, whereas TKP produced the least movement and least depth to which pH was affected.

Soil pH values at the surface were also the lowest for MKP, and increased with the basicity of phosphate fertilizers for columns with both exchangeable Al and gibbsite for both incubation periods (Figure 8.11). In contrast to findings with exchangeable Al only, the pH near the surface was elevated for all three type of phosphate compounds for all columns with gibbsite (Figure 8.11). TKP was the most effective in raising the surface pH. As the time of incubation progressed, the difference in surface pH among three phosphate fertilizer applications narrowed. The surface pH dropped from 6.7 to 6.3 for TKP, but increased from 5.6 to 5.9 for DKP and from 4.5 to 5.0 for MKP. The differences in surface pH values were smaller among the three phosphate fertilizer in the columns with gibbsite than those with only exchangeable Al. The depth to which pH had changed was very shallow and was not affected by the type of phosphate compounds applied, when compared to the columns with only exchangeable Al. For columns with only exchangeable Al, the depth of pH change was much greater and was dependent on type of phosphate compounds applied.

The depths to which pH had changed (Figure 8.11) due to phosphate application were consistent with the results for depths of P movement (Figure 8.3). The depth of both P movement and pH changes were shallow and not affected by the types of phosphate fertilizer used for the columns with both exchangeable Al and gibbsite.

The pH was generally higher in columns with both exchangeable Al and gibbsite (Figure 8.11) for all three phosphate fertilizer applications than in the columns with only

exchangeable Al (Figure 8.10). The background pH, where phosphate did not affect pH (below 4 cm depth), was higher for the columns with both exchangeable Al and gibbsite (pH was 4.0) than for the columns with only exchangeable Al (pH 3.5). The depths of pH change due to addition of phosphate were generally greater than the depth of phosphate movement (see Figures 8.1 and 8.2) indicating that H^+ or OH^- ions had moved ahead of phosphate ions. This was more pronounced after 4 wk of incubation than after 1 wk.

For columns with only exchangeable Al, the lowering of pH with MKP probably resulted from H^+ ions production from the precipitation of Al-P as described in Equation [8.1]. The phosphate (PO_4^{3-}) in TKP would be converted to $H_2PO_4^-$. When applied to the columns with a pH of 3.5, an increase in pH would occur as a result of consumption of H^- ions by PO_4^{3-}. Thus, the pH was highest near the soil surface with TKP application among the three phosphates added (Figure 8.10).

There are several possible reasons for increased pH near the surface after the addition of phosphate fertilizer for the columns with both exchangeable Al and gibbsite. First, when Al^{3+} are consumed due to precipitation with phosphate, additional $Al(OH)_3$ would be dissolved releasing hydroxyl ions into soil solution. This would cause elevated pH in columns with gibbsite. Second, the initial pH of the columns will play a role in H^- or OH^- ion production or consumption. With gibbsite, the initial pH was 4.0 as opposed to 3.5 for columns without gibbsite. Since Al hydrolysis is a function of pH, there will be more $AlOH^{2+}$ and $Al(OH)_2^-$ at a higher pH. Thus, Al-P precipitation will produce fewer H^+ ions at a pH of 4.0 than at 3.5, where 96.5% of Al species is Al^{3+}.

The faster downward movement of H^- ions than phosphate could be due to several factors. First, H^- ions do not participate in any precipitation reactions directly, so their

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movement will not be retarded. Second, in order to keep electro-neutrality, there should

be an $Al(OH)_2^-$ ion moving upwards for every H^- ion that moves downwards if the anion

(phosphate) is stationary. Indeed, this was confirmed by the fact that higher

concentrations of acid-extractable Al were found (Figures 8.8 and 8.9) where pH was

affected than where pH was the same as the initial state.

The results obtained show that the presence of gibbsite reduced P solution

concentration and retarded P movement in the resin-sand columns. Therefore, results for

the columns with and without gibbsite will be discussed separately.

8.3.3.1 Columns with Only Exchangeable Al (No Gibbsite)

Water-extractable phosphate is considered to represent phosphate which is

immediately available for plant uptake from the soil system. Total water-extractable P

(Table 8.1), as well as the solution concentration near the surface and depth of movement

of P (Figure 8.1), was highest for MKP for both incubation periods in the columns with

only exchangeable Al. In contrast, total water-extractable P and solution P concentration

near the surface and movement of P was least for TKP. The observed results could be

due to the rate of release of exchangeable Al into the solution as well as the effect of pH

on phosphate speciation.

For every molecule of PO_4^{3-} added as K_3PO_4, three K^- ions are added that would

release one Al^{3-} ion into soil solution from the exchange sites. The Al^{3-} released could

precipitate one phosphate ion as follows:

$$8\ K_3PO_4 \rightleftharpoons 24\ K^- + 8\ PO_4^{3-} \qquad [8.2]$$

$$15\ K^- + Al_5\text{-Resin} \rightleftharpoons 5\ Al^{3-} + K_{15}\text{-Resin} \qquad [8.3]$$

$$8 \ PO_4^{3-} + 16 \ H_2O \quad \rightleftharpoons \quad 8 \ H_2PO_4^- + \ 16 \ OH^- \qquad \qquad [8.4]$$

$$3 \ K^- + 8 \ H_2PO_4^- \ + \ 5 \ Al^{3+} \quad \rightleftharpoons \quad K_3 \ H_6 \ Al_5 \ (PO_4)_8 \ (s) \quad + \ 10 \ H^- \qquad [8.5]$$
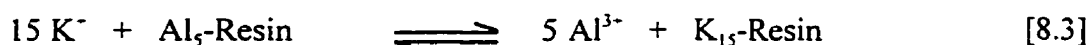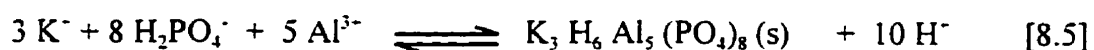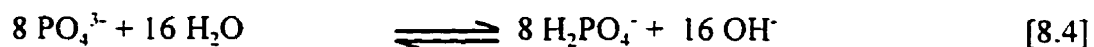
Thus, the net result of one molecule of taranakite formation is the consumption of eighteen K^-, eight PO_4^{3-}, five Al^{3+} ions and the production of six OH^- and six K^- ions. The above equations were written with the assumption that Al^{3+} and $H_2PO_4^-$ were the reacting species during the formation of taranakite. For MKP fertilizer, there is only one K^- ion for every phosphate ion, and since it takes fifteen K^- ions to release five Al^{3+} ions from exchange site into soil solution, ten phosphate ions will be left if all Al released from exchange sites is used in the formation of taranakite. There are also ten H^- ions produced during the formation of taranakite, which probably did occur because the K^- solution concentration was relatively high when the phosphate fertilizer was initially applied. The low water-extractable Al near the surface (Figure 8.5) suggests that all of the Al released from the exchange sites was consumed through Al-P precipitation. Thus, there would be higher water-extractable P left in the solution for MKP than for TKP fertilizer if all Al^{3+} released near the surface was used for Al-P precipitation.

The observed P profiles could be also due to the effect of the P species present. Since the $H_3PO_4^0$ species does not react with Al, the higher the proportion of $H_3PO_4^0$, the slower the Al-P precipitation if the total P concentration is not altered. The pH values near the surface were 3, 4.5 and 6 for MKP, DKP and TKP, respectively. The corresponding fraction of P as $H_3PO_4^0$ are 12.4%, 0.4% and 0.01%. Even though initially the same amount of P (1.47 mM column^{-1}) was applied, a greater portion of P would be in the non-reactive form of $H_3PO_4^0$ for the columns with MKP since its surface pH is much

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lower. Since the concentration of $H_2PO_4^-$, and HPO_4^{2-} will be relatively lower, a slower rate of precipitation of Al-P and higher water-extractable P profiles would be observed.

Increased precipitation of Al-P would leave less P for downward diffusion. Since diffusion is a concentration-gradient driven process, the higher the concentration gradient, the faster the rate of diffusion. Aluminum-P precipitates in the columns were greater and the water-soluble P concentration near the surface was lower with TKP than with MKP (Figure 8.1). The lower surface concentration of P would result in a slower downward diffusion of P. Thus, the depth of P movement was the lowest for columns with TKP fertilizer.

The depth of P movement could also be affected by the fraction of $H_3PO_4^0$ species in the solution, since $H_3PO_4^0$ species do not react with Al. As discussed above, a higher proportion of $H_3PO_4^0$ species, as in the case for MKP, would result in an increased downward movement of $H_3PO_4^0$.

Results obtained for acid-extractable P were consistent with the proposed research model. Increased acid-extractable P reflects greater precipitation of P, resulting in a lower water-extractable P. TKP resulted in more Al-P precipitation and less diffusion of P. Thus, its recovery as acid-extractable P was greatest (Table 1) and concentrated at the top of the column (Figures 8.1 and 8.3). In contrast, the lowest level of Al-P precipitation and diffusion would have occurred with MKP and thus its recovery as acid-extractable P was the least (Table 8.1, Figures 8.1 and 8.3). The concentration of water-extractable P at the surface decreased from 1 wk to 4 wk. This was due to both continued precipitation of P and the downward diffusion process.

8.3.3.2 Columns with Both Exchangeable Al and 1% Gibbsite

Phosphate retention in columns with gibbsite was different than in those without. First, the concentration of water-extractable P was usually lower and the acid-extractable P was higher with gibbsite than without. Second, the differences in the water- and the acid-extractable P distribution among three phosphate fertilizers were narrowed. Third, P did not move as readily in columns with gibbsite. Fourth, the depth of P penetration was not affected by the type of phosphate compound used in the presence of gibbsite, while it was greatly reduced with increasing basicity of phosphate compound in columns without gibbsite.

The results obtained for columns with both exchangeable Al and gibbsite can be partly explained by the supply of Al for precipitation reactions of Al-P. The gibbsite used in this experiment contained an appreciable amount of soluble Al. as illustrated in Figures 8.5 and 8.6. The Al solution concentration in the columns with gibbsite was about 20 μM g^{-1} (Figure 8.6), as compared to < 1 μM g^{-1} (Figure 8.5) in those without. Thus, there would be more Al-P precipitation in the system with gibbsite than without, and a lower water-extractable and higher acid-extractable P content. Due to the supply of Al from gibbsite, the P precipitated would be enhanced without entirely relying on the exchange reaction to furnish Al. In other words, the precipitation of Al-P was more dependent on the rate of downward diffusion of P rather than the rate of Al supply from the exchange sites. Under these conditions, the differences in the effect of phosphate fertilizer (or amount of K added per mole of P) became very small as indicated by the small differences in amounts of water- and acid-extractable P and the depth of P movement among the three phosphate fertilizers (Figures 8.2, and 8.4). For the columns

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with both exchangeable Al and gibbsite, there was no downward movement after 1 wk of incubation. This may be due to the extremely high Al concentration in solution with gibbsite in the system.

The concentration near the surface (Figure 8.2) and the total amount (Table 8.2) of water-extractable P were highest for MKP after 1 wk, but lowest after four wk of incubation. The reversal in trend can be explained by the factors which may be limiting the rate of Al-P formation, i.e., the rate of Al and P supply. After 1 wk, P supply was plentiful and Al-P precipitation was mainly controlled by the release of exchangeable Al from the exchange site after the Al in solution was initially used up. Since TKP had three times more K^+ ions than MKP fertilizer per mole of P, three times as much Al is released from the exchange site for TKP. This would result in rapid precipitation of Al-P. In addition to the exchange reactions, Al^{3+} in solution may have moved upwards in columns with gibbsite providing Al for precipitation. Aluminum in columns without gibbsite would be more limited.

It is speculated that after 4 wk of incubation, the water-soluble P was greatly reduced. Since the supply of Al from exchange sites or solution Al^{3+} would no longer be a limiting factor, and since there were more H^+ ions produced during the initial precipitation of Al-P with MKP fertilizer, there would have been more gibbsite dissolution resulting in more precipitation of Al-P. Thus, water-extractable P was lowest for columns with MKP fertilizer after 4 wk of incubation.

The conversion of the Al-P precipitate from non-crystalline to crystalline form seemed faster at higher pH than at lower pH. At higher pH (TKP fertilizer application),

there will be a faster rate conversion of Al-P precipitates to taranakite, which is insoluble in 1 M HCl. This would also result in a lower acid and total P recovery.

8.4 Implications

Acidic precipitation and farm management practices that disrupt the carbon, nitrogen, and sulfur cycles have apparently resulted in contemporary acidification rates that are much higher than rates estimated to occur in their absence. Agricultural production on acidic soils may be severely limited by unavailability of nutrients or toxicity problems. The implication of this study is that MKP fertilizer is the most soluble and has high initial availability in the soil. But it will not be as available as more basic phosphate after a short period of time. In contrast, the bio-availability shortly after application of TKP and DKP may not be as high as for MKP, but their availability would not decrease as rapidly with time as for MKP. This information is especially relevant to areas which have both acid soils and limited amounts of fertilizer. Another advantage to using DKP and TKP fertilizer is that there will be a very low possibility of soil acidification, and thus reduced toxicity of Al. It is well known that Al^{3+} is the most toxic species and is most prevalent at low soil pH. TKP fertilizer not only supplies P to plants over long periods of time, but also acts as a very effective neutralizing agent increasing soil pH and thereby reducing Al toxicity. DKP and TKP are therefore much better fertilizers than MKP for acid soils.

8.5 Summary and Conclusions

The diffusive movement and availability of phosphate was directly related to the type of phosphate compounds as well as the amount of Al readily available for Al-P precipitation. In the columns with only exchangeable Al and no gibbsite, phosphate movement and availability decreased in the order from MKP to DKP and TKP fertilizers. In the columns with both exchangeable Al and gibbsite, there was not much difference among the three phosphate compounds tested. TKP and DKP fertilizers would not only supply P over longer periods of time for plant growth, but also would be a very effective neutralizing agent and increase soil pH while reducing Al toxicity. DKP and TKP are much better fertilizers than MKP for acid soils.

9. SUMMARY AND CONCLUSIONS

The studies reported herein were designed to investigate the effects of exchangeable Al, gibbsite, lignosulphonate and the type of P fertilizer on the movement and reaction of phosphate and associated cations in an acid soil and in a simulated Al-rich acid soil. The simulated soil, consisting of acid-washed sand and Al-saturated cation exchange resin (with or without gibbsite), was used to distinguish the effects of exchangeable Al from the those from Al hydroxides.

For simulated soil columns, pH, the movement of P and K, and the amount of water-extractable P and K were affected by the levels of exchangeable Al and the presence or absence of gibbsite. Adding KH_2PO_4 to an Al-saturated cation exchange resin-sand mixture (simulated soil) decreased the pH of the system. The decrease in pH at the surface of the columns increased with the level of exchangeable Al. This reduction in pH was due to (1) exchange reactions and the hydrolysis of Al^{3+}, (2) the production of H^+, and (3) the retardation of H^+ ion movement during precipitation reactions. Both the movement of P and K and the amount of water soluble P and K decreased with the level of exchangeable Al.

The addition of 1% gibbsite to resin-sand mixtures, to permit assessment of its contribution to P fixation, increased P precipitation. In addition, the movement of P and K were greatly reduced. However, the pH increased after KH_2PO_4 application, due to the

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initial higher pH and dissolution of gibbsite in the columns with both exchangeable Al and gibbsite.

The introduction of lignosulphonate (LS) into the simulated soil columns both increased and decreased pH, movement of P and K, and the amount of water-extractable P depending on the incubation periods and the presence or absence of gibbsite. The addition of LS to the columns with exchangeable Al and no gibbsite increased P fixation through accelerated release of Al by cation exchange reactions. Thus, the amount of soluble P and movement of P were decreased. However, the opposite effect occurred in the columns containing both exchangeable Al and gibbsite, especially after four weeks of incubation. The addition of LS decreased P fixation as LS complexed H^- ions and thus reduced gibbsite dissolution and P fixation.

Three P fertilizers, KH_2PO_4, K_2HPO_4, and K_3PO_4, were also tested in the simulated soil columns. In the columns with exchangeable Al and no gibbsite, P movement and solubility was greatest with KH_2PO_4, and least with K_3PO_4. In the columns with both exchangeable Al and gibbsite, there was little or no difference among the three P fertilizers tested. However, the solution concentration of P was highest for K_3PO_4 as the incubation period increased. K_3PO_4 and K_2HPO_4 were also very effective neutralizing agents and increased soil pH while reducing Al toxicity.

Experiments conducted with a gibbsite-rich acid Oxisol revealed that movement of P was very limited and the solution concentration of P near the surface continually decreased during the incubation period. The solution concentrations of Al and Fe and the pH increased after the application of P fertilizer and had maximum values where P had penetrated. The increases in Al, Fe and pH resulted from the dissolution of Al and Fe

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oxides and hydroxides. The results obtained from the Oxisol used were very consistent with those from the simulated column containing both exchangeable Al and gibbsite. Liming had very little effect on P movement and availability in the Oxisol, but reduce water-extractable Al.

The results confirmed the proposed research models. There are cation exchange reactions, H^- or OH^+ production, and Al oxides or hydroxides dissolution occurring concurrently with the Al-P precipitation fixation reactions. The study of P fixation and movement must take into account all of above reactions.

From the findings of this study, it appears that there is considerable potential for improving fertilizer P availability in soil. The production or consumption of H^- ions is crucial to P fixation, and further investigation is needed. The causes and possible reactions involved in increasing solution concentration of P in the presence of LS in the simulated soil need to be further elucidated. The results obtained in the simulated soil should also be tested in a wide variety of acid soils with different clay mineralogies and CEC.

10. CONTRIBUTION TO KNOWLEDGE

The movement and reaction of phosphate fertilizer in the soil have been regarded as most important for the economic application of phosphate fertilizers. Understanding mechanisms of fixation and movement of P in soil are crucial to a sustainable and economic development of agriculture. The interactive, complex nature of reactions, such as cation exchange, hydrolysis, dissociation and precipitation/dissolution reactions in soil after P fertilizer application, and impact of these reactions on P movement make it necessary to study all ions (cations and anions) and the reactions involved in the study of P transport in acid soil.

Results obtained in this study confirmed the proposed fixation mechanisms of phosphate in acid soil. There are cation exchange reactions, H^- or OH^- production, Al hydrolysis phosphate dissociation/association and Al oxides or hydroxides dissolution occurring concurrently with the Al-P precipitation fixation reactions. The study of P fixation and movement must take into account all of above reactions. Through a series of experiments, we suggest that protons generated during fixation reaction of phosphate could dissolve Al oxides and hydroxides and supply more Al for P fixation. This has significant implications for the study of P fixation and offers the potential to improve P availability to plants. As demonstrated in this study, H^- ion production or consumption is the key to P fixation. If we could reduce H^- ion production, such as by using more basic P fertilizer (K_3PO_4), or increase H^- consumption by using organic matter to complex the

H⁺, there would be less Al and Fe oxides and hydroxides dissolution. This means less Al and Fe ions are available for P fixation.

The results of these studies are obviously of great agronomic importance. These results suggest that K_3PO_4 is a better fertilizer to use in acid soil than KH_2PO_4, since K_3PO_4 maintains a higher solution concentration over longer periods of time and also raises soil pH to a more desirable level for plant growth than the commonly used MKP (KH_2PO_4). Application of LS, a by-product of paper pulp industry, is beneficial in gibbsite-rich soil as indicated by the higher P solution concentration as time of incubation progressed. The limited impact of liming on P movement and solution concentration suggests that it is not essential to lime soil prior to P fertilizer application.

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IMAGE EVALUATION
TEST TARGET (QA-3)

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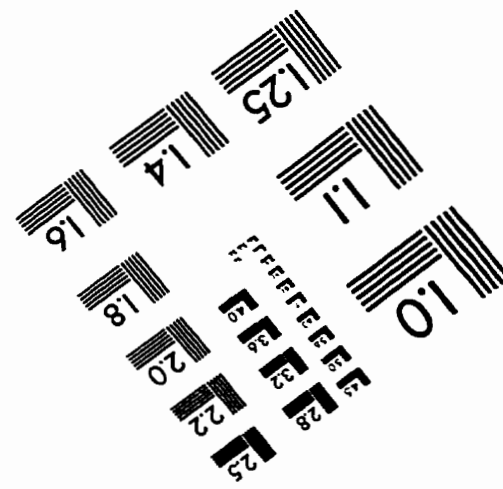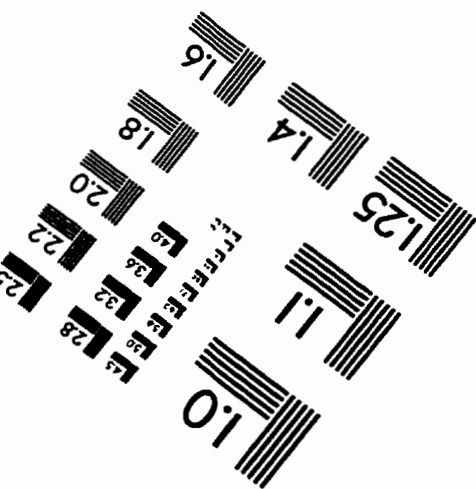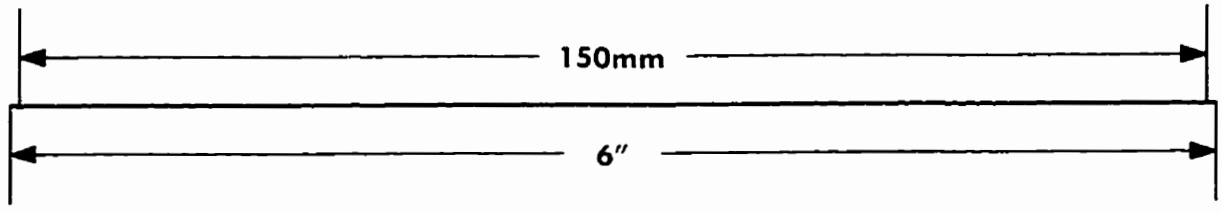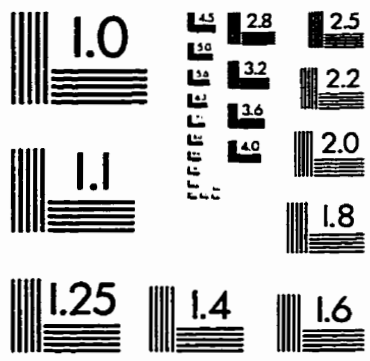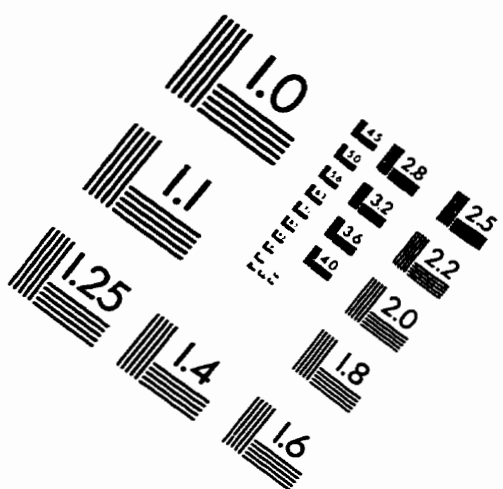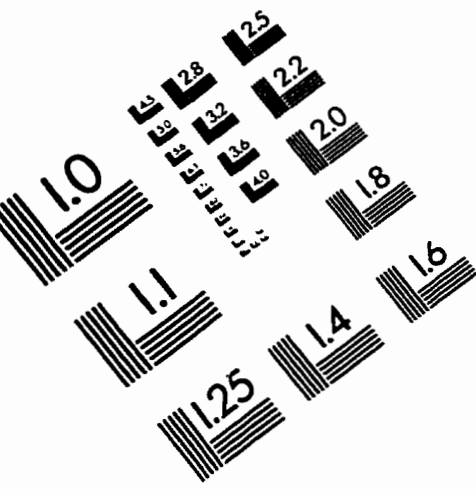
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