CHEMICAL CHARACTERIZATION OF PHOSPHATE DIFFUSION

IN A MULTI-IONIC ENVIRONMENT

BY

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ABSTRACT

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Low phosphate fertilizer efficiency in high pH soils is primarily due to the
retardation of P movement in the soil-P fertilizer reaction zone. This retarded movement
is caused by rapid reactivity and affinity of the applied P with soil components; more
importantly, the exchangeable Ca^{2+} and Mg^{2+} displaced into soil solution. These soil
components form a series of reaction products with P, with varying degree of solubility.
Measures that were taken to rectify this problem include the modification of the chemical
environment of soil-P fertilizer reaction zone through the co-application of non-
phosphatic salts with fertilizer P.

The objective of this study was to obtain fundamental information on the
influence of multi-ionic interactions on the solubility and diffusion of P in columns
containing a model soil system and two soil types. The study also aimed to identify the
salt combinations and factors that have the potential to enhance the solubility and
movement of P in calcareous soil condition. The model system consisted of a mixture of

inert quartz sand and Ca^{2+}-saturated cation-exchange resin (Amberlite IRP-69), buffered with $CaCO_3$. The study was divided into three distinct laboratory experiments to obtain comprehensive information on the effects of interactions of various ions, on the diffusive transport of P after two weeks of incubation. The first two sets of experiments were performed with the model system while the third experiment was conducted on two soils. The ions of interest included: NH_4^+, K^+, Mg^{2+}, NO_3^-, Cl^-, CO_3^{2-} and SO_4^{2-} in various combinations with orthophosphate fertilizer salts.

The objective of the first experiment was to investigate the chemical interactions and diffusive transport characteristics of P in the resin-sand columns, on addition of various sulphate salts with KH_2PO_4 and $NH_4H_2PO_4$. The addition of $(NH_4)_2SO_4$ to both P sources increased the solubility and diffusive movement of P in the reaction zone, compared to other treatments. The second experiment was conducted to examine the effect of cationic and anionic interactions on the solubility and diffusive transport of P in the resin-sand columns. Monopotassium phosphate (KH_2PO_4) was used as the P source in factorial combinations with three types of cations (K^+, NH_4^+, Mg^{2+}) and four types of anions (Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}). Phosphate solubility was greatest on addition of $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ to KH_2PO_4. However, depth of P movement was greater with the $(NH_4)_2SO_4$ treatment.

The objective of the third experiment was to examine the effects of the combination of various salts selected from the previous experiments, on the chemical diffusion and solubility of P in two soils with contrasting pH and cation exchange capacity (CEC). Co-application of non-phosphatic salts with P reduced the solubility of P in the low pH, high CEC soil while the addition of $(NH_4)_2SO_4$ salt produced the

greatest solubility and movement of P in the high pH, low CEC soil, compared to other salts.

The three experiments showed that the interaction of NH_4^+ and SO_4^{2-} was consistent at enhancing the water solubility and movement of P under a high soil pH condition. This effect was attributed to the combination of various mechanistic factors associated with $(NH_4)_2SO_4$ compound including significant pH reduction, cation exchange reaction of NH_4^+ with the exchangeable Ca^{2+}, and anionic competition of SO_4^{2-} with P for precipitation with Ca^{2+}. As such, dual banding of $(NH_4)_2SO_4$ salt with P fertilizer could have a positive influence on the availability of P in alkaline to calcareous soils.

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ACB	Ammonium carbonate ($(NH_4)_2CO_3$)
APP	Ammonium polyphosphates
APS	Ammonium phosphate-sulphate
ASU	Ammonium sulphate ($(NH_4)_2SO_4$)
AUP	Sulphuric acid, phosphoric acid and urea (14-14-0-4.4)
CEC	Cation exchange capacity
D_a	Apparent diffusion coefficient
DAP	Diammonium phosphate ($(NH_4)_2HPO_4$)
DCPD	Dicalcium phosphate dihydrate ($(CaHPO_4)_2.H_2O$)
D_e	Effective diffusion coefficient
d.f.	Degree of freedom
epm	Evolution per minute
KCB	Potassium carbonate (K_2CO_3)
KSU	Potassium sulphate (K_2SO_4)
L	Litre
M	mole L^{-1}
MAP	Monoammonium phosphate ($NH_4H_2PO_4$)
MCP	Monocalcium phosphate ($Ca(H_2PO_4)_2$)
MKP	Monopotassium phosphate (KH_2PO_4)
rpm	Revolution per minute
TSP	Triple super phosphate ($Ca(H_2PO_4)_2$)
UAN	Urea-ammonium nitrate
vs.	Versus

1. BACKGROUND INFORMATION

Concerted effort has been directed towards the study of the fate of phosphate fertilizer in the soil, and the identification of various mechanisms involved in the transport and transformation of fertilizer P. The fate of P following the application P fertilizer is important because of the significance of P in the nutritional requirements of crops, its limited level in the soil solution and low availability for crop uptake. Hao et al. (2000) stated that the retarded movement, rapid reactions and affinity of P for the various components of the soil matrix have been recognized as the most important limitations affecting the economic benefits of P fertilization.

Consistent over-fertilization of P in soils produces a great potential for significant losses of P to surface waters and shallow ground waters (Sharpley et al., 1994; Simard et al, 1995; Sims et al., 2000). High rates of P fertilizer application to agricultural soils to correct for P deficiency have been reported, particularly across Manitoba (Doyle and Cowell, 1993*a*). As such, more than 80% of the added P transforms into insoluble forms through various retention processes (Campbell et al., 1984) that reduce the movement and availability of the added P in soil solution. However, generally P is added at a rate similar to crop removal. Continuous loading of P fertilizer, accompanied by low crop uptake, causes a build up of residual soil P with an increased risk of P loss to the environment. Sims and Baker (2003) reported that the insoluble fraction of the applied P contributes to the labile P pool (in a short term) and the non-labile P forms (in the long

term). The former is the solid P phase that rapidly equilibrates with the soil solution or runoff and surface waters, while the latter pool slowly releases P into solution. The partitioning of insoluble P into the labile and non-labile forms therefore, has environmental implications (Sharpley et al., 1994; Simard et al, 1995; Sims et al., 2000).

According to Sharpley et al. (2000), one of the strategies for reducing the export of P from agricultural landscape is to limit the magnitude of P input, thereby lowering the amount of soluble P and residual P in surface runoff. For this strategy to work, efficiency of P uptake by crops must be increased (Kouboura et al., 1995). Although long term efficiency of P fertilizer is high, however, improving the efficiency of P uptake over a short term remains a challenging task for agronomists, soil chemists and fertility experts. Therefore, the overall agronomic and sustainable environmental goal is channelled towards optimizing the solubility of fertilizer P at the application site, and enhancing the movement of the soluble P in the reaction zone to the plant roots, to increase crop uptake of P.

Previous studies (Leikam et al., 1983; Westfall and Hanson, 1985; Beever and Racz, 1987; Ernani and Barber, 1991; Kouboura et al., 1995; Kumaragamage et al., 2004) have shown that it is possible to modify the chemical environment of soil-P fertilizer reaction zone in order to increase the solubility and movement of applied P in the soil solution, and consequently its uptake by crops. This is accomplished through mixing of non-phosphatic salts with fertilizer P as dual bands. Continuing from these past studies, it will be interesting to look at the interactions of various cations and anions associated with P fertilizer compound and the exchangeable cations, and how these multi-ionic interactions influence the soil pH, solubility, diffusive transport and transformation of P

and other accompanying ions in the dual bands. Therefore, the objectives of this study were to obtain fundamental information on the effect of multi-ionic interactions on the solubility and diffusive transport characteristics of P in various columns containing a model soil system and different soil types. The study also aimed to identify the salt combinations and the mechanistic factors that have the potential to improve the solubility and diffusive transport of P under calcareous soil conditions.

1.1 Overview of Cargill's Homogeneous NPS Fertilizer

Cargill Ltd. recently developed a multinutrient, homogeneous NPS granular fertilizer (13-33-0-15) to improve the efficiency of canola and wheat production in Canada and Australia. The ultimate objective of this formulation was to increase the uptake of phosphorus and sulphur, which are some of the most limiting nutrients in crop production, especially in western Canada (Nyborg et al., 1999; Doyle and Cowell, 1993*b*). The main components of the NPS fertilizer are monoammonium phosphate (MAP), ammonium sulphate (AS) and elemental sulphur (S°). The nutrient analysis of each granule consists of 13% nitrogen, 33% phosphate, 7.5% sulphate-sulphur and 7.5% elemental sulphur. One-fifth of the sulphate component of the granule is supplied as $CaSO_4$, which is 1.5% of the total product, while the remaining four-fifths come from the ammonium sulphate.

One of the unique features of Cargill's co-granulated NPS fertilizer is the inclusion of elemental sulphur. The elemental sulphur was manufactured by an

innovative technology that enables the sulphur component to form an "onion skin" coating on the granule. This innovation enhances the biological activity of the NPS fertilizer, as it allows the crop to capture the beneficial effect of sulphur oxidation on both S and P uptake. Similarly, the inclusion of elemental sulphur increases the nutrient concentration of the NPS fertilizer by 20% compared to conventional monoammonium phosphate and ammonium sulphate fertilizers (Kroeker, 2005).

Researchers at the University of Manitoba have conducted various studies on the agronomic effectiveness of Cargill's NPS fertilizer. He et al. (2002) evaluated the nutrient availability and potential seedling toxicity of this new fertilizer in incubation and growth chamber experiments. Both sets of experiments were conducted on two soils namely: Reinland very fine sand and Deadhorse clay. Treatment combinations on both experiments included a control, monoammonium phosphate (MAP) only, MAP plus elemental sulphur (Sº), MAP plus ammonium sulphate (AS) randomly distributed, MAP plus AS placed in intimate contact, and Cargill's NPS fertilizer.

The incubation experiment showed that there was no significant oxidation of elemental S from the NPS fertilizer during the incubation period. However, the chemical availability of P in the Deadhorse clay soil was greater with the NPS fertilizer compared to other treatments while the salt, ammonia and nitrite toxicity of the NPS fertilizer was intermediate between MAP only and MAP plus AS. Results from the growth chamber experiment indicated that none of the fertilizer treatments appeared to cause toxicity problems. The authors concluded that the availability of P from the new NPS fertilizer appeared to be excellent and similar to other types of MAP fertilizer, while the availability of S was intermediate between AS and Sº.

Further investigation on the agronomic evaluation of the NPS fertilizer was carried out with a field study (Kroeker, 2005). Results from the field experimentation showed that NPS fertilizer did not cause seedling injury on wheat and canola emergence at the rates applied in the study. The NPS fertilizer appeared to be an excellent source of P, with equivalent availability of P as that of conventional MAP fertilizers. However, there was no evidence that the inclusion of AS and elemental S in the NPS granule increased P availability in the field experiment. Although there was no measurable amount of oxidation of the elemental S component of the NPS, it was shown that the sulphate-S component, however, was available to crops (Kroeker, 2005).

While the previous studies examined the agronomic effectiveness and potential seedling toxicity of the NPS granule, the present study investigated the fundamental mechanism by which P movement and solubility is impacted by multi-ionic interactions in various dual bands containing N, P, K and S. This research also obtained information on ion transport in different columns packed with Ca^{2+}-saturated cation exchange resin-sand mixture and two soil types, using the methods of Akinremi and Cho (1991a; 1991b; 1993). It is expected that the information obtained from this study will contribute to a better understanding of the chemical environment of the Cargill's homogeneous NPS granule or any other dual band fertilizer containing N, P, K or S.

1.2 Fertilizer Use Efficiency of P and Environmental Sustainability

Phosphorus is one of the essential nutrients for crop production. However, it is not as available in soils with respect to its demand by crops, as compared to nitrogen and potassium. Havlin et al. (1999) documented that the total P in surface soils usually varies between approximately 0.1% in a P deficient soil and 0.5% in adequately supplied soil. Therefore, it is an agronomic necessity to supplement P level in the soil to meet crops demand at the appropriate time (Grant et al., 2001). Continuous use of phosphate fertilizer accompanied by low crop uptake, leads to a build up of residual soil P with an increased risk of P loss to the environment (Sharpley et al., 1994; Simard et al, 1995; Sims et al., 2000). The study of the fate of applied P in soil therefore, provides information that is pertinent to the efficiency of P fertilizer uptake by crops, effective recovery of applied P fertilizer from the insoluble phase, as well as risk of P loss to the adjacent water bodies.

According to Benbi (1987), increased efficiency of applied P fertilizer depends on increased solubility of P, and an increase in P movement to the plant roots from the fertilizer granules. This statement supports a previous finding by Silberbush and Barber (1984), that the concentration of P in soil solution was one of the most important variables that affected P diffusion to plant roots. There are two incentives for increasing the efficiency of crop utilization of P. First, P being an essential plant nutrient, proper P nutrition through an effective diffusion of the phosphate ions in the soil-P reaction zone will lead to increased P uptake and crop yield, and a reduced P fertilizer input cost. Secondly, increased movement and uptake of fertilizer P by the crop will reduce the soil

residual P, thereby reducing the potential for a significant loss of P from the soil through surface and subsurface pathways (Sharpley et al., 2000).

An important factor in the risk of P loss from soil to surface water is the level of soil residual P as measured by the soil P test (Sharpley, 1995; Sharpley et al., 1999; Flaten, 2003). Therefore, management practices employed in P fertilizer program should be directed at lowering the transformation of P into residual forms following the addition of P fertilizer.

1.3 Characterizing the Mode of P Transport in Soil: Chemical Diffusion

The most important mechanism of P movement in soil is diffusion (Barber et al., 1963; Barber, 1980; Tisdale et al., 1993). Such evidence was based on the consideration of the concentration of P in the soil solution, which is relatively low. Havlin et al. (1999) stated that the total P in surface soils usually varies between approximately 0.1% (in a P deficient soil) and 0.5% (in adequately supplied soil). There are other modes of P transport such as mass flow, particularly at the site of salt application where the dissolution of the added P occurs (Havlin et al., 1999).

According to Crank (1979), diffusion is a process by which a matter is transported from one part of a system to another as a result of random molecular motions. When a concentration gradient exists in a medium, net movement of solutes occurs by diffusion from regions of higher concentration to regions of lower concentration (Barber, 1995). Fick's first law of diffusion described the mathematical theory of diffusion in a

homogenous medium. This theory is based on the hypothesis that the rate of transfer of the diffusing substance through a unit area of a surface is proportional to the concentration gradient measured normal to the section, i.e.:

$$J = - D (dC) / (dx)$$ [1.1]

Where J is the rate of transfer per unit area of section i.e. diffusive flux, C is the concentration of the diffusing solute, x is the space coordinates measured normal to the section, and D is the diffusion coefficient of the solute in the medium. This equation only describes steady state diffusion process, in which the diffusive flux is stable as a result of a constant concentration gradient.

To describe the more common transient process, in which the solute is spreading out at one end and the concentration is changing at the other end, a separate equation is applied to the Fick's first law of diffusion. This equation is called the Continuity Equation:

$$dC / dt = - \blacktriangledown . J$$ [1.2]

The $\blacktriangledown$ term is a gradient operator in three dimensions, and t is time taken for the solute to diffuse from one region to the other. Combining equations [1.1] and [1.2], and considering only the x-dimension, we have:

$$dC / dt = - d / dx (J)$$ [1.3]

$$dC / dt = (- d / dx) (- D . (dC / dx))$$ [1.4]

Assuming that D is not a function of x:

$$dC / dt = D \, d^2C / dx^2$$ [1.5]

Equation [1.5] above is known as Fick's second law of diffusion in one dimension, e.g. diffusion along the x-coordinate. However, it describes only the transport

of solutes without chemical reaction. This equation alone is not sufficient to describe species that interacts with the medium. For instance, the transport of phosphate ion in soil is usually accompanied by the interaction of P with soil components (Bhadoria et al., 1991). Therefore, an additional term is included in order to completely describe the transport of P in soil. This term is referred to as the Chemical Reaction Term, denoted as ϕ. The complete equation describing the diffusion of phosphate ion in a soil medium is stated below as:

$$dC \,/\, dt = D\, d^2C \,/\, dx^2 \pm \phi \qquad\qquad [1.6]$$

The ϕ term could be negative or positive, depending on whether the chemical reaction is a sink or source of P.

Nye and Barber (1977) stated that the effective diffusion coefficient (D_e) used to describe ion movement in soil could be calculated as:

$$D_e = D_i\, \theta\, f\, (dC_1) \,/\, (dC_s) \qquad\qquad [1.7]$$

Here, D_e is the effective diffusion coefficient in soil measured in $cm^2\, s^{-1}$, D_i is the value of diffusion coefficient in water, θ is the volumetric water content, f is the tortuosity factor, C_1 and C_s are the concentration of the ion in solution and solid phase, respectively, and $(dC_1) \,/\, (dC_s)$ is the reciprocal of the soil buffer power for the ion in question.

Applying equation [1.7] to P transport in soil, it is apparent that a number of factors affect the diffusive movement of P in soil. These include: (1) tortuosity factor (the measure of crookedness or total length of the diffusion path of an ion travelling in soil continuum) (Hira and Singh, 1977), (2) chemical interactions of P with soil components (Lewis and Racz, 1969; Akinremi, 1990), (3) concentration and amount of P present at the source (Eghball et al., 1990; Bhadoria et al., 1991). These factors either

affect the effective diffusivity (D_e) or the concentration gradients of P in soil (Hao, 1998). As such, any fertilizer management practice that increases the equilibrium concentration of applied P in solution would consequently improve the diffusive movement and crop uptake of fertilizer P (de Camargo et al., 1979).

The movement of P in soil has a significant influence on the supply of P for crop uptake and utilization. Eghball et al. (1990) reported that on addition of fertilizer P to the soil surface or placement of fertilizer P in a band, the availability of P to the plant roots depends on the movement of P from the point of salt application into the surrounding soil solution. Eghball et al. (1990) also showed that the movement of applied P in the soil affects the efficiency of P fertilizer through the influence of P movement on the probability of root- and soil-P fertilizer contact. Diffusive movement of P fertilizer also influences the residual P build-ups and the longevity of fertilizer P in soil. Fan and MacKenzie (1993) evaluated the interaction of urea and triple superphosphate (TSP) on urea hydrolysis and P transformations, under a laboratory incubation experiment. They concluded that the diffusion and transformations of phosphate ion from the fertilizer band have a significant effect on availability of fertilizer P to crops.

1.4 Effect of Dual Band Application on P Solubility and Movement

Past studies (Leikam et al., 1983; Westfall and Hanson, 1985; Beever and Racz, 1987; Ernani and Barber, 1991; Akinremi and Cho, 1993; Kouboura et al., 1995; Kumaragamage et al., 2004) have shown that the application of non-phosphatic salts with P compounds modifies the concentration of ionic species in the soil solution, and at the same time, pH changes may occur (Isensee and Walsh, 1971; Teng and Timmer, 1995). These pH changes have a number of consequences. First, they alter the solubilities of fertilizer P and its reaction products (Sample et al., 1980). Secondly, pH changes influence the interactions of P with soil constituents and other ions. This has been shown to either increase or decrease the availability of fertilizer P, depending on the original pH status of the soil (Ernani and Barber, 1991; Akinremi and Cho, 1993).

Westfall and Hanson (1985) studied the effect of band application of N and P, and acid based fertilizer on soil pH and availability of P, Fe and Zn in the soil-fertilizer reaction zones of a slightly acid soil and a calcareous soil, respectively. The treatment combinations consist of ammonium polyphosphate (APP) alone, ammonium hydroxide (NH_4OH) plus APP, and AUP (sulphuric acid, phosphoric acid and urea; 14-14-0-4.4). In the reaction zone of the calcareous soil, they observed that none of the fertilizers applied produced significant changes in pH. This was attributed to the buffering effect of the free lime present in the soil. However, the dual N-P band (NH_4OH plus APP) and the AUP treatment produced higher $NaHCO_3$-extractable P concentration measured 10 days after application, as compared to the effect of APP alone treatment. Beyond 10 days, the level of extractable P in the AUP injection zone dropped rapidly below the level observed in the dual N-P band and APP alone treatment, respectively. Although their results did

not substantiate the acidifying effect of acid based fertilizer on calcareous soils, it otherwise showed that the dual N and P enhanced the solubility of P in the calcareous soil.

Beever and Racz (1987) conducted similar experiments on the effects of various N fertilizers combined with monoammonium phosphate (MAP) on pH and P solubility. The results showed that solution pH in the calcareous Almasippi soil did not vary greatly with treatments. However, the solubility of P in the entire fertilizer reaction zone increased with application of urea, ammonium hydroxide or acidified urea. On the other hand, a decrease in P solubility occurred when an acidic N fertilizer such as ammonium sulphate or ammonium nitrate was added. The results further showed that urea (alkaline N fertilizer) generally increased P solubility to a greater extent than the acidified urea in all instances.

Kouboura et al. (1995) reported that the application of ammoniacal forms of N along with P enhanced the availability of P compared to the application of P alone, when both N and P were applied together in the same injection zone in acid soil and in alkaline soil. The P source was ammonium polyphosphate (APP), while the N source was urea ammonium nitrate (UAN). The sampling times were 1, 4, 12, 24, and 36 weeks. The results indicated that the pH of both soils decreased in the first 12 weeks due to the nitrification of the component NH_4^+ in the treatments. However, the soil pH increased during the remaining incubation period; which was attributed to the neutralizing effect of $CaCO_3$ in the soil. The dual application of APP+UAN resulted in higher concentration of total available and extractable P than for APP alone. These differences were attributed to the effect of each treatment on pH changes. The authors stated that the greater reduction

in pH observed for both soils on addition APP+UAN compared to APP alone possibly allowed the formation of more soluble P reaction products. They suggested that the increased solubility of the solid phase P would improve the fertilizer use efficiency of P.

Kouboura et al. (1995) concluded that methods of fertilizer application that can increase P fertilizer use efficiency are of considerable interest for both economic and environmental reasons. This assertion was based on the earlier findings reported by Leikam et al. (1983) who showed that significant advantages on crop yield of wheat (*Triticum astivum L.*) resulted from pre-plant dual application, using urea ammonium nitrate (UAN) with APP, compared with P application alone. In contrast, Fixen and Wolkowski (1981) found little advantage for the dual application of N-P starter when they compared dual application of N and P using anhydrous NH_3 and APP with a conventional band placement of N and P for corn (*Zea mays L.*).

Factors contributing to the positive influence of N-P interactions on P availability in alkaline soils had been documented by various researchers. Some of these factors are attributed to certain chemical effects due to reduction in soil pH. Effects of pH lowering due to the interaction of N and P in alkaline to calcareous soils include increased $H_2PO_4^-$/HPO_4^{2-} ratios in the soil solution (Miller et al., 1970) and increased solubility of P fertilizer reaction products in the soil (Hanson and Westfall, 1985; 1986). Other factors are due to physiological effects. These include enhanced root growth in the fertilized reaction zone (Grunes et al., 1958); NH_4^+-enhancement of P uptake by roots (Miller and Ohlrogge, 1958); and rhizocylinder acidification caused by root uptake of NH_4-N (Kirkby and Mengel, 1967). These physiological phenomena of NH_4-N and P interactions are

generally referred to as "ammonium ion effect" (Sheppard and Racz, 1980; Leikam et al., 1983; Sangakkara and Cho, 1987).

1.5 Factors Affecting the Interactions of Phosphate in the Soil

The sequence of events following the addition of P fertilizer to soil was described by Sample et al. (1980). Past works have shown that the fate of the applied P depends on its interactions with the associated cations and anions in the P fertilizer compound (Akinremi and Cho, 1993; Kumaragamage et al., 2004), and the soil exchangeable cations and minerals (Akinremi and Cho, 1991a; 1991b; Hao et al., 2000). Details on the chemical factors affecting the interactions of applied P in the soil-P reaction zone are described below.

1.5.1 Effect of Soil pH on Phosphate Interactions

In their review, Sample et al. (1980) reported that the pH of the soil-P fertilizer inter-phase, known as the reaction zone, greatly influence the chemodynamics of P reactions. Such reactions include: the dissolution kinetics of P fertilizer, the degree of dissolution - either complete or partial dissolution, rate or extent of P movement from the point of application, as well as the chemistry of the reaction products formed. As such, the magnitude of phosphate retention process is strongly influenced by the acidity of the soil solution. This claim was also supported by Lindsay (1979), who stated that the

reaction of exchangeable cations with the added P in soil solution is a function of the prevailing soil pH. This form of P interaction is defined as precipitation, which can be described as the formation of discrete, solid materials. Phosphate in the soil solution interacts with the reactive cations displaced from the exchange sites to form less soluble P compounds. The stability of the end product of precipitation reaction is highly pH dependent.

Soil pH has a significant influence on the distribution of phosphate species in soil solution (Schachtman et al., 1998; Havlin et al., 1999). Hinsinger (2001) defined the speciation of P as the distribution of phosphate ion into various ionic species in solution. This distribution is primarily determined by solution pH. The relevant domains to most soils are characterized by the $H_2PO_4^-$ and HPO_4^{2-} species, respectively. Below pH 6.0 units, most orthophosphates will be present as the monovalent ($H_2PO_4^-$) species. However, the divalent (HPO_4^{2-}) species will be present in smaller proportion. At neutral pH scale there are approximately equal concentrations of both species in solution, while above 7.2 units the divalent (HPO_4^{2-}) species is the predominant form of phosphate species. Therefore, the addition of P fertilizers with acidifying effects would enhance the dominance of the $H_2PO_4^-$ species in soil solution.

According to Hinsinger's (2001) review, trivalent Fe^{3+} and Al^{3+} occur in large concentrations in the solutions of acid soils because of the increased solubility of Fe and Al oxides. Conversely, in neutral and alkaline soils, Ca^{2+} and Mg^{2+} are the dominant cations in soil solution. Based on the discussions stated above, it is obvious that soil pH management is an important tool for assessing the fate of applied phosphates in the soil.

Therefore, the distribution and availability of applied P are much dependent on the prevailing soil pH and the dominant exchangeable cation.

1.5.2 The Roles of Cation-Exchange Reactions on Phosphate Interactions

The magnitude of P concentration in soil solution is strongly related to the characteristic interactions of the associated cation in P compound with the soil exchangeable cations (Fixen and Grove, 1990; Akinremi and Cho, 1991a). The accompanying cations undergo cation exchange reactions with soil exchangeable Mg/Ca in alkaline and calcareous soils or with the exchangeable Fe/Al in acid soils (Khasawneh et al., 1974; Sample et al., 1980; Akinremi and Cho, 1991a and 1991b; Ro and Cho, 2000; Hao et al., 2000). Some peculiar properties of the accompanying cation, such as the valency, ionic radius, and hydrated radius respectively, determine the degree of displacement of the soil exchangeable cations into soil solution. The displaced cations consequently determine the overall solubility of P in the reaction zone (Sample et al., 1980; Akinremi and Cho, 1991a and 1991b).

The significance of cation exchange reactions on the precipitation of P had been reported by some researchers. Sample et al. (1979) investigated the effect of the accompanying NH_4^+ in various ammonium phosphate fertilizers. The results showed that as the granule dissolved in a moist soil; the solution moving into the surrounding soil was highly concentrated with P and the associated NH_4^+. As this movement continued by diffusion, some of the Ca^{2+} ions on the exchangeable sites of the soil continuum within the first 6.0 mm were displaced into solution through exchange reactions with NH_4^+ to

form precipitates with P. As the solution diffused outward, the displacement of Ca^{2+} accumulates at the front of solution, ahead of the bulk of the soluble P. This cation exchange and displacement phenomenon was termed as the "snow-plow" effect. Greater diffusion of P occurred as much of the soil exchangeable Ca^{2+}/Mg^{2+} or Al^{3+}/Fe^{3+} are "plowed" off the exchange sites. However, the movement of P was eventually impeded due to back-flow of the displaced cations. They observed that the precipitation of P was more pronounced because the displaced cations came from the solution and not from the exchange sites. In conclusion, the researchers suggested that the accompanying NH_4^+ is only advantageous if there is no back diffusion of the displaced exchangeable cations.

Akinremi (1990) investigated the effect of cation exchange reactions on the movement of phosphate ion in the reaction zone of Ca- and Na-saturated exchange resins treated with KH_2PO_4 salt, respectively. In the Ca-saturated resin system, the results showed that the movement of P was significantly retarded because the HPO_4^{2-} ion was precipitated by the reactive Ca^{2+} displaced into solution by the accompanying K^+. In contrast, the Na-saturated resin system had no significant effect on P retardation because the displaced Na^+ did not form precipitate with the phosphate ion (HPO_4^{2-}).

Akinremi and Cho (1993) also conducted a series of experiments to investigate multi-ionic diffusive transport in various columns packed with Ca-saturated resin-sand mixture. Monopotassium phosphate (KH_2PO_4) alone, and in combination with KCl were applied to the surface of the soil columns. The results showed that the mobility and solubility of the added P was significantly reduced in the presence of KCl. This was attributed to increased precipitation of P with Ca^{2+} displaced from the exchange sites by

K^+. Further retardation occurred when the rate of KCl was increased. They concluded that the availability of P to plants could be adversely affected in mixed P-K bands.

Hao (1998) investigated the diffusive movement and reactions of phosphate and associated cations in a simulated Al-rich acid soil. The results indicated that P transport was retarded in the presence of exchangeable Al due to the ion-exchange reactions between the exchangeable Al and the associated K^+ in KH_2PO_4 salt. This observation was also supported by the experimental evidence shown by Ro and Cho (2000) in a model system of acid soil. Their results indicated that exchangeable Al^{3+} released through ion-exchange reactions are involved in the precipitation of phosphate in the model system. The results also revealed that P transport was retarded in the presence of Al_2O_3, and further retardation occurred in the presence of exchangeable Al^{3+} and solid Al_2O_3. They concluded that the H^+ ion produced from Al-P precipitation reactions dissolved the solid Al_2O_3, giving rise to more Al^{3+} in solution.

In general, the results obtained from these studies indicate that the extent of P movement is generally governed by the dominant exchangeable cation and its characteristic ion-exchange reaction with the cation that accompanies phosphorus. It is important to note that the cation associated with P compounds must maintain electro-neutrality. Thus, the concentration of the accompanying cation in the solution is also altered. Akinremi (1990) and Hao (1998) showed that associated K^+ in KH_2PO_4 has direct and indirect effect on P retention through its ion exchange reactions with the exchangeable Ca^{2+} and Al^{3+}, respectively. However, the role of other cations such as Mg^{2+} and NH_4^+ has not been studied extensively. Therefore, it will be interesting to

investigate the influence of various cations associated with different non-phosphatic salts on the fate of P in a calcareous soil system.

1.5.3 The Roles of Anionic Competition on Phosphate Interactions

The accompanying anions in the phosphate fertilizer compounds directly affect the dynamics of P in soil solution by competing with P for (1) adsorption sites (Satnam et al., 1996) and (2) precipitation reactions with Ca/Mg in high pH soils (Kumaragamage et al., 2004) or Al/Fe in acid soils (Hao et al., 2000). This phenomenon is referred to as anionic competition.

In a recent study, Kumaragamage et al. (2004) mixed monocalcium phosphate (MCP) fertilizer with ammonium sulphate, magnesium sulphate and urea respectively, to investigate the diffusion of P in a calcareous soil (Gleyed Rego Black Chernozem). In agreement with model predictions (Cho, 1985; 1991), the solubility of MCP was increased by more than two-fold when mixed with ammonium sulphate or magnesium sulphate, and by 1.2- fold when mixed with urea. The differences between the performance of sulphate salts and urea on P solubility were attributed to the competition between SO_4^{2-} and P for precipitation with Ca^{2+}. The results indicated that sulphate ion competed strongly with P, reducing the magnitude of Ca-P precipitation reactions.

Singh and Jones (1976) equilibrated soils for 6 days with different aqueous solutions of phosphate in the presence of molybdate, sulphate, chloride and nitrate salts, respectively. The results showed that phosphate adsorption decreased significantly in the presence of molybdate and sulphate in the equilibrium solution. Conversely, effect of

nitrate and chloride were not significant, indicating that P adsorption was not affected by the presence of nitrate and chloride addition in the equilibrium solutions.

Satnam et al. (1996) observed similar results. They examined the competitive effect of molybdate, sulphate, nitrate and chloride on phosphate adsorption in different soils. They reported that phosphate adsorption decreased significantly in the presence of molybdate and sulphate in the equilibrium solution. The Langmuir adsorption isotherm parameters employed to characterize their data showed that, with the presence of molybdate and sulphate in the equilibrated solution, phosphate was held in less quantity with weaker bond strength. Hence, more P was in solution and available for plant uptake. However, they indicated that the Langmuir adsorption isotherm is not sufficient to explain the overall mechanisms occurring in this system. As such, retention processes other than adsorption may be responsible for this observation. Nevertheless, the results showed that the effectiveness of these anions to reduce P adsorption was in the order of $MoO_4^{2-} > SO_4^{2-} > NO_3^- = Cl^-$. The differences in the competitiveness of these anions were attributed to the differences in their reaction mechanisms. Significant effects of MoO_4^{2-} and SO_4^{2-} were due to their similar ligand exchange reactions with the divalent phosphate (Parfitt, 1978; Rajan, 1978).

Lefroy et al. (1995) conducted a leaching experiment to demonstrate the movement and distribution of P in a dual-band of KH_2PO_4 and Na_2SO_4. The salts combination was applied to weathered acid soils: low-sorbing gleyed podzolic (Aquic haplustalf) and a medium-sorbing red earth (Haplohumult) packed into different columns. In the low-sorbing soil column, the addition of sulphate enhanced the downward movement of the applied P, and resulted in significantly high amounts of P in the

leachate. They suggested that the coexistence of two or more anions in soil solution can have significant effect on the effective mobility of each ion because they compete for adsorption sites. Murali and Eylmore (1983) also observed that the accompanying sulphate significantly increased the mobility and leaching losses of the less mobile P. Since P is usually strongly sorbed to soil surfaces, they concluded that co-application of sulphate with P compound decreased the retention of P in the soil, and therefore enhanced the downward movement of P in the soil column.

1.5.4 Interactions due to Ionic Concentration and Ionic Strength

Akinremi and Cho (1993) investigated the retardation of P movement in various soil columns. They found that the K^+ associated with KH_2PO_4 displaced sufficient Ca^{2+} from the exchanger to form Ca-P precipitates, which consequently immobilized P in the column. Significant retardation of P movement occurred when KCl was added with the KH_2PO_4 salt, while further retardation occurred when the rate of KCl was doubled from 0.11 g to 0.22 g. Therefore, increase in ionic concentration due to additional K^+ ion in the system displaced much Ca^{2+} into solution, which caused substantial retardation of P movement.

Ernani and Barber (1991) predicted the effect of banding KCl with P on P supply to the plant roots. Their experiment focused on the quantification of the effect of banding KCl with monocalcium phosphate $(Ca(H_2PO_4)_2)$ to predict P uptake. They hypothesized that interactions of P in soil may be affected by the ionic strength of the soil solution. Thus, P supply to plant roots would be influenced by other nutrients banded with P in the

same granule. The results showed that the addition of KCl displaced Ca^{2+} from the exchange sites of the less weathered soils and the more highly weathered soils and thereby increased the concentration of Ca^{2+} in the soil solution. For the more highly weathered soils, the addition of KCl increased soil solution P when pH was below 5.0 and decreased it when pH was above 5.0. Hence, the increased solubility of P in the more highly weathered soils with pH less than 5.0 implied that P existed as $H_2PO_4^-$. As such, the partitioning of P into the monovalent species at pH less than 5.0 possibly reduced the magnitude of Ca-P precipitation reaction.

In addition to the effect of soil pH, Ernani and Barber (1991) showed that the increased solubility of P in the more highly weathered soil with low pH was due to the increase in ionic strength on addition of KCl. It is possible that the presence of KCl in the soil solution prevented the association of Ca^{2+} and HPO_4^{2-} to form precipitates. Therefore, increase in ionic strength on addition of KCl resulted in thermodynamic interference on Ca-P reactions, which consequently decreased the activity coefficient of Ca^{2+} and HPO_4^{2-}, thereby increasing the concentration of HPO_4^{2-} in the soil solution. Conversely, the reduced solubility of P in the more highly weathered soils when pH was above 5.0 suggested that significant part of the added P existed as HPO_4^{2-} in the soil solution, which enhanced Ca-P precipitation.

Ernani and Barber (1991) employed the Barber-Cushman mechanistic nutrient uptake model to predict P uptake (Barber and Cushman, 1981). The model revealed that the addition of KCl increased the predicted uptake of P in the more highly weathered soils with low pH, and decreased P uptake in the less weathered soils with high pH. They concluded that increase in the electrolyte strength following the addition of KCl to the

highly weathered soils influenced the concentration of P in the soil solution and the predicted P uptake, while the direction of effect was determined by the soil pH.

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2. SOLUBILITY AND TRANSPORT OF PHOSPHATE IN VARIOUS NPKS COMBINATIONS

2.1 Abstract

We hypothesized that a key strategy for increasing the availability of phosphate in calcareous soil is to prevent its tie up by soil calcium either by excluding Ca^{2+} from the reaction zone or by lowering the reaction zone pH to preclude Ca-P precipitation or by introducing a competitive anion with P for Ca precipitation. This strategy can be accomplished by modifying the chemical environment of the soil-P fertilizer reaction zone through various nutrients banding with P. This study investigated the solubility and diffusive transport characteristics of P in the dual application of various sulphate salts with monopotassium phosphate and monoammonium phosphate salts, using a model system of calcareous soil columns. The model soil system consists of a mixture of quartz sand and Ca^{2+}-saturated cation-exchange resin (Amberlite IRP-69) to provide a CEC of 22 $cmol_c$ Ca^{2+} Kg^{-1}, buffered with $CaCO_3$. The pH of the final mixture was approximately 8.8. Treatment combinations were replicated by a factorial approach. One factor was P sources at two levels: $NH_4H_2PO_4$ and KH_2PO_4, denoted as MAP and MKP, respectively. The other factor consisted of three sulphate levels: Control, $(NH_4)_2SO_4$ and K_2SO_4, denoted as ALONE, ASU and KSU, respectively. An equivalent concentration of P (45.6 mg P per column) was applied to the surface of each column for

each of the P sources. For the sulphate treatments, approximately 141 mg SO_4-S per column was added to each phosphate salt. After two weeks of incubation, each column was sectioned at 3 mm interval to a depth of 7.5 cm and extracted with water, followed by 1 M HCl. The pH profiles showed that all treatments in the MAP system depressed the background pH by 1.4 units within the first 1.2 cm depth. However, H^+ ion moved deeper into the columns on addition of either of the SO_4 salts. While the pattern of H^+ ion movement was similar on addition of the SO_4 salts to MKP system, the pH of the column containing $(NH_4)_2SO_4$ or K_2SO_4 was lower than that of MKP ALONE at every point in the column. The addition of $(NH_4)_2SO_4$ or K_2SO_4 to $NH_4H_2PO_4$ increased the solubility of P ($P < 0.05$) by 43% and 21%, compared to $NH_4H_2PO_4$ alone, respectively. The maximum depth traversed by P in the MAP system was 4.2 cm. The addition of $(NH_4)_2SO_4$ or K_2SO_4 to KH_2PO_4 also increased the solubility of P in the reaction zone by 48% and 41% of the amount of P in KH_2PO_4 alone. However, the maximum depth of P movement (4.0 cm) in the MKP system was slightly less than in the MAP system. The study also revealed the effect of ionic competition between NH_4^+ and K^+ when both cations were added together in the same band. It was shown that each cation enhanced the solubility and transport of the other in the soil column. These results suggested that the combination of the roles of the accompanying ions in the SO_4 salts and pH reduction could have a positive influence on the availability of P in calcareous soil.

2.2 Introduction

A large portion of the applied P transforms into insoluble forms through various retention processes (Campbell et al., 1984; Sharpley et al., 1994; Simard et al., 1995; Sims et al., 2000). These retention processes consequently reduce the movement of the added P in the soil-P fertilizer reaction zone and the availability of P in soil solution for crop uptake. In calcareous soil, the solubility and movement of P are retarded by the combined interactions of exchangeable Ca displaced into solution and the reactive Ca^{2+} from $CaCO_3$, with the divalent phosphate ion (HPO_4^{2-}) (Akinremi and Cho, 1991b; 1993; Kumaragamage et al., 2004). Therefore, it is important to identify the chemical mechanisms that have the potential to optimize fertilizer use efficiency of phosphate fertilizer in calcareous soils. Increasing the fertilizer efficiency of P is possible through an enhanced movement of P in the soil-P fertilizer reaction zones (Benbi, 1987).

Researchers have used soil columns to study one-dimensional diffusive transport of P and the role of accompanying ions on the fate of P (Khasawneh et al., 1974; Akinremi and Cho, 1991a; 1991b; 1993; Hao et al., 2000). In the present study, we hypothesized that a key strategy for increasing the availability of phosphate in calcareous soil is to prevent its tie up by soil calcium either by excluding Ca^{2+} from the reaction zone or by lowering the reaction zone pH to prevent Ca-P precipitation. It is also possible to introduce an anion that can compete with P for precipitation reaction with Ca^{2+}. These strategies can be accomplished by modifying the chemical environment of the soil-P fertilizer reaction zone through co-application of various salts with P fertilizer.

Kumaragamage et al. (2004), in a study that used soil columns, reported that the addition of $(NH_4)_2SO_4$ or $MgSO_4$ to monocalcium phosphate (MCP) fertilizer increased

the mobility of P. This was attributed to anionic competition of sulphate with phosphate for Ca^{2+} precipitation. In contrast, other researchers observed reduced solubility of P and a retardation of P movement. Akinremi and Cho (1993) observed a significant retardation of P movement when KCl was co-applied with KH_2PO_4 salt in a model system of calcareous soil. Ernani and Barber (1991) also observed a decrease in P solubility on addition of KCl to monocalcium phosphate in the less weathered or highly weathered soils with neutral to high pH.

The differences in the effect of salt addition on the solubility and mobility of P in these studies may be attributed to the effects of various factors. Such factors include: the chemical composition of the salt added, the characteristic interactions of the accompanying ions with P and soil components (Akinremi and Cho, 1993; Kumaragamage et al., 2004) and their effect on soil pH changes (Teng and Timmer, 1995). How the combination of these factors affects the solubility and diffusive movement of P is unknown. As such, comprehensive information has not been provided on the combined role of various cations and anions associated with P compound, and their effect on the solubility and transport of P. It is also necessary to examine how multi-ionic interactions influence the chemical environment of soil-P reaction zone and the fate of P and the accompanying ions.

The present study attempts to obtain this information by using a model soil system of cation exchange resin-sand mixture packed into various columns. This model soil system precludes the interferences due to wide variation in the chemical composition of soil. The information gathered from the chemical characterization of NPKS band using the model soil system will also help to identify the nutrient formulation and the

chemical factors that have the potential to improve P fertility management on high pH soils of Manitoba. This is also in part of the objectives of Cargill's new NPS fertilizer formulation. Therefore, the objectives of this study were to investigate the solubility and diffusive transport characteristics of P and the accompanying ions (1) in monoammonium phosphate and monopotassium phosphate salt, and (2) in the dual application of ammonium sulphate and potassium sulphate salt with each of the phosphate salts, respectively.

2.3 Materials and Methods

2.3.1 Preparation of the Model System

The experiment was conducted using a model system of Ca-saturated cation exchange resin-sand mixture. The resin (Amberlite IRP-69; sulfonic acid functionality; CEC 430 $cmol_c$ Kg^{-1}; 30-150 μm in diameter) was saturated with Ca^{2+} to simulate a base saturated soil using the procedure of Akinremi and Cho (1991a). Briefly, 40g of the resin was placed in a Büchner funnel, and leached by suction with approximately 1000 mL of 0.5 mol L^{-1} $CaCl_2$ solution in aliquots of 50 mL. This was followed by further leaching with 1000 mL of 0.025 mol L^{-1} $CaCl_2$, also in aliquots of 50 mL.

Following the leaching procedure, the resin was washed with distilled water until silver nitrate test was negative for chloride ion.

$$Ag(NO_3)_2 + CaCl_2 \longrightarrow Ca(NO_3)_2 + AgCl_2 \qquad\qquad [2.1]$$

The resin was air dried and extracted with either 1.0 M neutral NH_4OAc or 1.0 M HCl to verify complete saturation of the exchange sites by Ca^{2+}. The CEC of the resin was reduced to a level comparable to that of soil by mixing it with industrial grade inert quartz sand (Unimin Silica Sand, Unimin Corporation, Le Seur, MN). The sand was crushed with a pulverizing soil grinder, and dry-sieved to produce materials with particle size in the range of 50-150 μm, similar to that of the resin. Particles finer than 50 μm were eliminated as these may possess cation exchange capability.

The sand was washed with 5% concentrated HCl, and then rinsed with distilled water until the pH was near neutral (approximately 6.8) and air dried. Prior to mixing with the resin, the crushed sand was spread out on a plastic tray and coated with 0.5% of reagent-grade $CaCO_3$ powder using the technique similar to that described by Akinremi and Cho (1991b). The addition of the $CaCO_3$ was necessary to simulate a calcareous soil system and to provide buffer for the system. The carbonated-sand was mixed thoroughly with a known amount of Ca-saturated resin, at a resin to sand ratio of 1:20 to produce a final mixture with a CEC of 22 $cmol_c$ Ca^{2+} Kg^{-1}. The pH of the final mixture was 8.8.

2.3.2 Description of the Soil Column

The column was made up of a rectangular block of wax-petroleum jelly mixture, prepared using the method of Khasawneh and Soileau (1969). The column was 10 cm high with a cylindrical cavity of 4.5 cm diameter, which was closed at the bottom with an acrylic plate. A known quantity of the resin-sand mixture was packed into the cavity of

the wax column at a bulk density of 1.4 Mg m^{-3}, and wetted at the surface to a water content of 25% by weight. This was allowed to equilibrate for 48 hours prior to treatment application.

2.3.3 Treatment Combinations

The experiment was carried out using a factorial design with one factor being two sources of P: $NH_4H_2PO_4$ and KH_2PO_4, (denoted as MAP and MKP system, respectively), in combination with the other factor as three sources of sulphate: Control, $(NH_4)_2SO_4$ and KH_2SO_4 (denoted as ALONE, ASU and KSU, respectively). The factorial combinations yielded six treatments (Table 2.1) with two replications for a total of 12 columns. An equivalent concentration of P (45.6 mg P per column) was applied to the surface of each column for each of the P sources (Akinremi and Cho, 1991a), and approximately 141 mg SO_4-S per column was added to each phosphate salt for the treatments containing the dual bands, respectively. The amount of SO_4^{2-} added to the soil column was equivalent to that of P as 1.47 mmol per column.

All sources of P and SO_4^{2-} were added as reagent grade salts, with both P and SO_4^{2-} salts mixed together prior to addition to the soil (resin-sand mixture) surface. The mixture was then applied as uniformly as possible to the soil surface using a spatula, to simulate a one-dimensional diffusive movement. The columns were arranged in an upright position and placed on a raised stand inside a rubber tub with free water at the bottom. The rubber tub was properly sealed (to prevent moisture loss to the surrounding through evaporation), and then set in an incubator (Fisher Low Temperature Incubator,

Model 307) for a period of two weeks at constant temperature (20 ºC) and controlled humidity.

Table 2.1 Treatment combinations and mass of salts per column

System	Mass of salt per column
MAP System	$NH_4H_2PO_4$ (0.17 g)
	$NH_4H_2PO_4$ (0.17 g) + $(NH_4)_2SO_4$ (0.19 g)
	$NH_4H_2PO_4$ (0.17 g) + K_2SO_4 (0.26 g)
MKP System	KH_2PO_4 (0.20 g)
	KH_2PO_4 (0.20 g) + $(NH_4)_2SO_4$ (0.19 g)
	KH_2PO_4 (0.20 g) + K_2SO_4 (0.26 g)

2.3.4 Chemical Analysis and Measurements

After two weeks of incubation, the resin-sand column was sectioned at 3 mm interval to a depth of 7.5 cm using a meat cutter (Model UL8, International Edge Tool Co., Roseland, NJ). Exactly 2 g of the sample (moist weight) from each section was weighed into a centrifuge tube for chemical analyses, while the remaining portion was collected into a pre-weighed moisture can to determine the gravimetric water content. The total weight of the sample and the moisture can was measured immediately, after which the can and soil were set into an oven at 105 ºC for 48 hours. After 48 hours, the weight of the oven-dry sample was measured to account for the amount of moisture loss.

These measurements were used to calculate the gravimetric water content for each sample.

Approximately 2 mL of deionized water was added to the sample in the centrifuge tube, and placed on a Vortex machine for 30 seconds. The pH of the mixture was then measured with an Accument Model AR50 digital pH meter (Fisher Scientific Ltd., Winnipeg, MB, Canada) fitted with a combination electrode. The electrode was rinsed with 5 mL of water into the tube and extra 3 mL of water was added to bring the total amount of water to 10 mL at a soil to solution ratio of 1:5.

The mixture was shaken for 15 minutes at 150 epm and centrifuged at 3500 rpm for 5 minutes. The clear solution was filtered and defined as the "water extractable fraction". The soil residue from the water-extraction was further extracted with 1 M HCl in two successions of 20 mL each. Following the two acid extractions, the soil on the filter paper was further rinsed with two aliquots of 10 mL of the acid. The acid extracts were combined and defined as the "acid extractable fraction". The water extractable fraction approximates what is in the soil solution, i.e. the mobile phase, while the acid extractable fraction approximates what is in the solid, i.e. the immobile phase.

Concentration of phosphate in the extracts was determined by the ascorbic acid-ammonium molybdate method of Murphy and Riley (1962), while the concentration of SO_4-S was measured by turbidimetry method (Jones, 2001). The NH_4-N content in the sample was determined by an Autoanalyzer with the automated phenate method (Greenbert et al., 1992), while K^+ and Ca^{2+} were determined by the Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES) machine. The concentration of each

ion in each segment was plotted against distance to provide the distribution of these ions in the soil column.

3.3.3 Statistical Analysis

Effect of treatment means on the concentration of each ion in the water-extractable and acid-extractable fractions was compared using the Least Significant Difference (LSD) test at 0.05 level of significance. Also, the main effect of each factor (P sources and SO_4^{2-} salts, respectively) and the interactions between factors were analyzed by two-factor analysis of variance (ANOVA), using the General Linear Models (GLM) procedure of SAS software for Windows, version 9.1 (SAS Institute, Inc., Cary, NC).

2.4 Results and Discussion

Sample extraction of the cation exchange resin revealed the degree of saturation of the resin by Ca^{2+} after leaching with 0.5 mol L^{-1} $CaCl_2$ solution. As stated earlier, the cation exchange capacity (CEC) of the resin was originally 430 $cmol_c$ Kg^{-1}. Extraction with the 1.0 M NH_4OAc indicated that the exchange site of the resin was saturated by approximately 426 ± 21 $cmol_c$ Ca^{2+} Kg^{-1}, while the extraction with 1.0 M HCl indicated a saturation of 314 ± 24 $cmol_c$ Ca^{2+} Kg^{-1}. These results showed that NH_4OAc was more effective at extracting the exchangeable Ca^{2+} from the resin than HCl. Similar

differences in the extraction abilities of NH_4OAc and HCl have been reported by Akinremi and Cho (1991a). The value of the NH_4OAc extraction also showed that the exchange sites on the resin was completely saturated with Ca^{2+}.

The gravimetric water content was generally uniform throughout the soil columns (Figure 2.1). The average value obtained from each column was within $\pm$ 2.00 g g^{-1} of the amount of water added (25.0 g g^{-1}) to the resin-sand surface. The uniformity of water content distribution in the system confirmed that the ions moved in the columns mainly by diffusion and not by mass flow. It is possible that osmotic attraction of liquid and vapour phases occurred at the site of salt application (the first 3 mm segment of the column) during salts dissolution (Sample et al., 1980; Havlin et al., 1999).

2.4.1 The pH Profiles

The background pH of the mixture was approximately 8.8, which is similar to the pH of 8.3 observed by Akinremi and Cho (1991b) and the pH of 8.4 reported by Griffin and Jurinak (1973) for a solution that is in equilibrium with $CaCO_3$ and atmospheric CO_2. The high pH of this system is expected to promote the precipitation of phosphate through the prevalence of the divalent orthophosphate (HPO_4^{2-}) at this pH range. The HPO_4^{2-} is the phosphate species involved in precipitation reaction with Ca^{2+} (Cho, 1991; Akinremi and Cho, 1993; Schachtman et al., 1998; Havlin et al., 1999).

All treatments in both MAP and MKP systems depressed the pH of the carbonated resin-sand mixture below the initial pH (Figure 2.2). This was due to the production of H^+ ion from the dissolution of the salts and possibly from precipitation

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Figure 2.1 Gravimetric water content following 2 weeks of incubation in resin-sand columns treated with dual application of P and sulphate salts.

Figure 2.2 Distribution of H^{+} ion following 2 weeks of incubation in resin-sand columns
treated with dual application of P and sulphate salts.

reaction between Ca and P (Akinremi and Cho, 1991a; Cho, 1991). The hydrogen ion concentration was greatest close to the application site and declined with increasing distance from the surface, as indicated by the increase in pH profiles with depth. Sample et al. (1980) described the pH of a solution in equilibrium with $NH_4H_2PO_4$ and KH_2PO_4 as 3.5 and 4.0 respectively. However, the pH observed on the addition of these salts to the soil columns was higher than the pH of the equilibrium solution of the salts, showing the buffering effect of $CaCO_3$ on column pH.

There was no significant difference in pH among the treatments at the site of salt application, i.e. the first 3 mm depth of the column, in the MAP system, as the pH of all columns was reduced from 8.8 to 7.4 after two weeks of incubation (Figure 2.2a). The pH of the columns remained similar in all treatments from the soil surface to a depth 1.2 cm. At greater depths, however, the pH of the MAP+ASU treatment became slightly higher than that of MAP ALONE or MAP+KSU within the first 1.2 - 3.9 cm segments of the column. Beyond 4.0 cm depth, differences in the pattern of H^+ ion movement disappeared until a depth of 5.4 cm.

While the addition of SO_4^{2-} salts with MAP reduced the pH of the column to a depth of 7.5 cm, the pH of MAP ALONE treatment was similar to the background pH at the region beyond 5.4 cm depth (Figure 2.2a). It is evident that more H^+ ion was produced following the addition of SO_4^{2-} salts than with MAP ALONE. This H^+ ion also diffused down the column reducing the pH of the column. According to Cho (1991), a potential sink for the H^+ ion produced from these salts is the dissolution of $CaCO_3$, which acted as pH buffer in the system.

The pH profile in MKP system was similar to that of MAP system except that the addition of ASU or KSU to MKP reduced the pH of the column beyond that of MKP ALONE throughout the entire column (Figure 2.2b), including shallow depths. While the pH of the column with MKP ALONE was reduced to a depth of 5.1 cm, those with ASU and KSU were lowered throughout the entire column. Overall, the pH profiles showed that H^+ ion movement was similar in both MKP+ASU and MKP+KSU treatments. Similar to the MAP system, more H^+ ion was produced with the addition of ASU or KSU to MKP which consequently reduced the pH of the MKP system at every point in the column compared to MKP ALONE. However, in both systems, the pH was still high enough to support precipitation reaction between Ca and P (Akinremi and Cho, 1991b).

2.4.2 Water Extractable Phosphorus

Statistical analysis indicated that the effect of both P sources (MAP and MKP) on the solubility and precipitation of P was not significantly different from each other at $P < 0.05$ (Table 2.2). However, effect of SO_4^{2-} salts on the water solubility of P was significant, but there was no significant effect on the precipitation of P. Similarly, there was no significant interaction ($P < 0.05$) between the main effect of the P sources and the SO_4^{2-} salts.

Maximum concentration of water-extractable P occurred at the site of application (the first 3 mm segment) in all columns. Thereafter, the concentrations of P in both systems generally declined with depth conforming to a typical diffusion profile (Figure 2.3).

Table 2.2 General Linear Model analysis on water-extractable and acid-extractable P in resin-sand columns after 2 weeks of incubation

Source of variation	d.f.	[‡]Water P	[ℓ]Acid P
		Mean square value	
P source	1	4.41 *ns*	1.82 *ns*
Salts	2	17.09 *	2.11 *ns*
P X Salts	2	0.97 *ns*	0.82 *ns*
Error	6	3.03	5.96

[‡] Water-extractable P. The data represent average of two columns.
[ℓ] Acid-extractable P. The data represent average of two columns.
* indicates significance at $P < 0.05$; *ns* indicates not significant ($P < 0.05$).

At the site of salt application, highest concentration of soluble P occurred in the MAP+ASU treatment, followed by MAP+KSU and MAP ALONE treatment (Figure 2.3a). The water-extractable P in the MAP+KSU and MAP ALONE also showed a steeper decline in P concentration compared to the MAP+ASU. Although the depth of P penetration was similar in all the treatments to about 4.2 cm, the addition of both SO_4 salts to MAP increased the overall concentration of soluble P in the reaction zone. Estimates of the diffusion curves in the first 3.6 cm depth of the column indicated that MAP+ASU treatment increased the solubility of P by 53% over that for the P measured in MAP ALONE, while MAP+KSU treatment increased solution P by 28% within this zone. Based on these diffusion profiles the estimated order of P solubility in the MAP system was MAP+ASU > MAP+KSU > MAP ALONE.

(a) MAP System

Concentration of P (mmol L^{-1})

(b) MKP System

Concentration of P (mmol L^{-1})

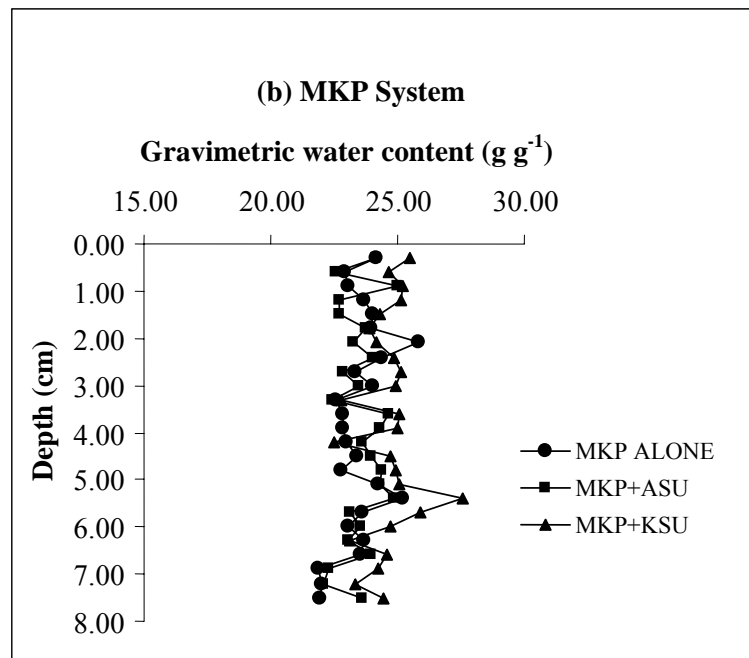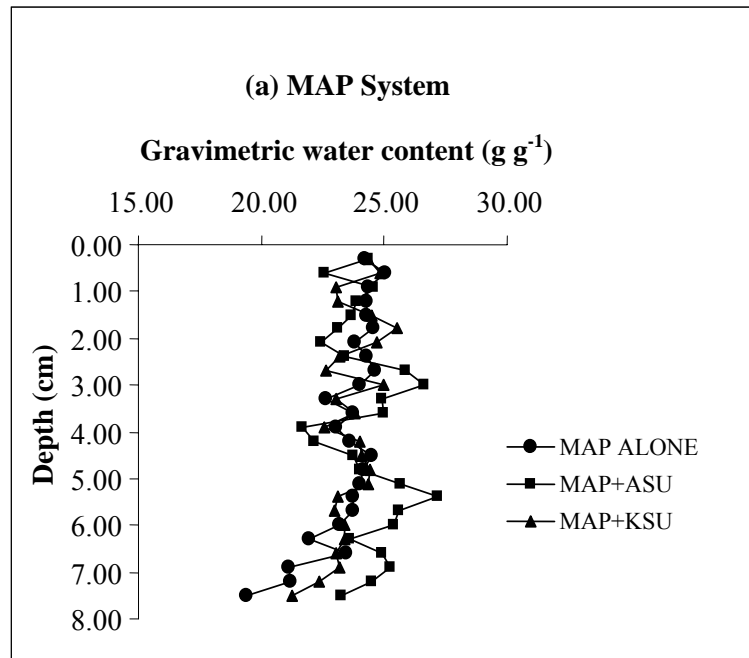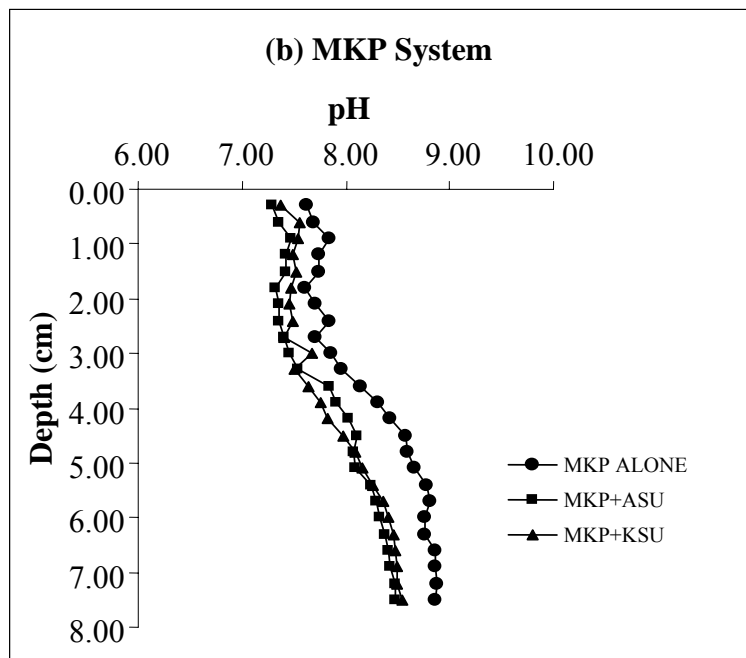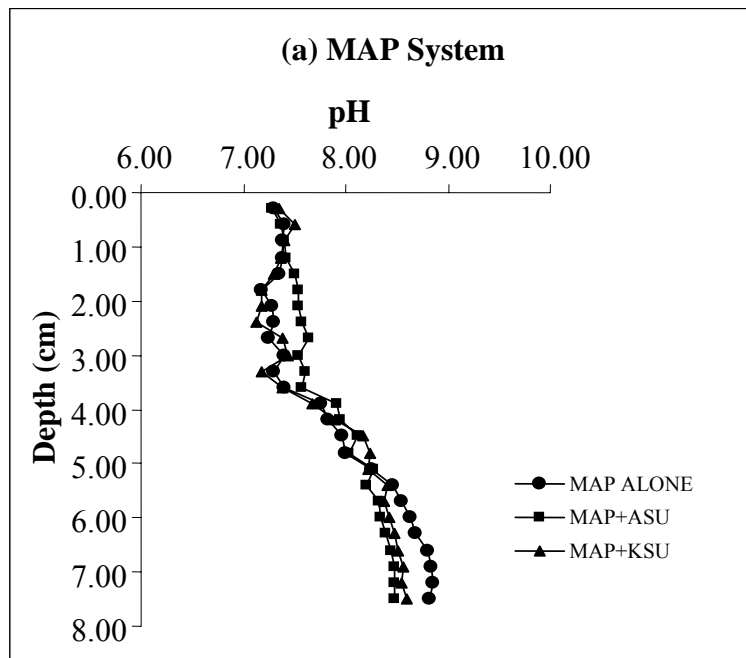Figure 2.3 Distribution of water-extractable P following 2 weeks of incubation in resin-sand columns treated with dual application of P and sulphate salts.

In the MKP system, the concentration of water-extractable P at the site of application followed the order: MKP ALONE > MKP+ASU > MKP+KSU, respectively (Figure 2.3b). The concentration of P in solution gradually declined as P diffused into the column, travelling as deep as 4.0 cm. Although the maximum depth of P penetration (4.0 cm) was similar in all treatments, the pattern of P solubility differed among treatments. Similar to the MAP system, the addition of SO_4 salts to MKP enhanced the solubility of P in the first 3.0 cm depth of the column. Within this segment of the soil column, MKP+ASU increased the solubility of P by 56% while MKP+KSU increased the solution concentration of P by 40% of the P measured in the MKP ALONE treatment. It appeared that the addition of ASU and KSU had similar effects on the transport and distribution of P in the MKP treated columns (Figure 2.3b), unlike the superiority of ASU to KSU that was observed in the MAP system (Figure 2.3a).

Also, the maximum depth of P penetration was slightly less (4.0 cm) in the MKP system compared to the MAP system (4.2 cm). The pH reduction was not strongly correlated with P solubility in some treatments. It is evident that the lowering of pH is not the only way of optimizing P solubility in high pH soils. As such, factors other than pH lowering may be involved. Overall, the data suggest that the co-application of $(NH_4)_2SO_4$ salt with P fertilizer would increase the solubility and diffusion of P in calcareous soil, possibly through an ion competition effect. It is possible that the presence of SO_4^{2-} in the soil solution competed with P for precipitation with Ca^{2+}.

Similar observations on the influence of $(NH_4)_2SO_4$ on the availability of P in calcareous soil had been reported by various researchers (Hammond, 1997; Kumaragamage, 2004). The movement and solubility of P from MKP was enhanced in

the presence of ASU and KSU, more so in the MAP system. Akinremi and Cho (1993) showed that when KCl salt was added with MKP, the accompanying K^+ replaced Ca^{2+} from the exchange site, thereby retarding the movement of P through subsequent precipitation reaction between Ca and P. This may reflect a cation effect on exchange reactions and subsequent P movement and solubility. It appeared that K^+ (from KSU) may be more efficient than NH_4^+ (from ASU) in displacing Ca^{2+} from the exchange complex, which reduced the movement of P through Ca-P precipitation reaction. It is also possible that part of the added NH_4^+ co-existed as NH_3 in the soil solution due to the prevailing high pH conditions in the resin-sand column, thereby reducing the effectiveness of NH_4^+ on the exchange sites. These results would explain the greater retardation of P movement with KSU compared to ASU treatment as clearly shown in the MAP system.

Kumaragamage (1990) also observed differences in the influence of K_2SO_4, $MgSO_4$ and $(NH_4)_2SO_4$ on availability of P, when these sulphate salts were co-applied with monocalcium phosphate to various soils. This author concluded that K_2SO_4 was not as effective in enhancing the diffusion and solubility of phosphate in solution, compared to the other two sulphate salts.

2.4.3 Acid Extractable Phosphorus

The P measured in the acid fraction represents the amount of P that was precipitated by Ca^{2+} from the exchange sites and Ca^{2+} from the dissolution of $CaCO_3$. This form of P exists probably as dicalcium phosphate dihydrate (DCPD) (Akinremi and Cho, 1991a; 1991b). The acid-extractable P profiles for both systems (Figure 2.4) showed that significant precipitation occurred at the surface and throughout the reaction zone. The acid-extractable profiles showed that the zone of Ca-P precipitation extended to the same depth (approximately 4.0 cm) traversed by water-extractable P in both systems.

The concentration of acid-extractable P at the site of application (the first 3 mm depth of the column) in the MAP system ranged from 62 mmol L^{-1} in MAP+ASU, 95 mmol L^{-1} (MAP+KSU) and 114 mmol L^{-1} (MAP ALONE). A similar order was found in the MKP system, except that the concentrations were higher: 96 mmol L^{-1} (MKP+ASU), 135 mmol L^{-1} (MKP+KSU) and 152 mmol L^{-1} (MKP ALONE), respectively. These values indicated that the precipitation of P by Ca^{2+} followed the same trend in both systems. The values also showed that P was more strongly precipitated at the site of application in MKP system compared to MAP system, a reflection of cation effects from K^+ versus NH_4^+.

Although the magnitude of Ca-P precipitation at the surface of the columns (the first 3 mm depth) followed the same trend in both systems, certain differences, however, were noticeable among treatments. At the first 3 mm depth, the concentration acid-extractable P in MAP+ASU treatment was by 46% less than the amount of acid-extractable P measured in MAP ALOE, and 35% less than that of MAP+KSU,
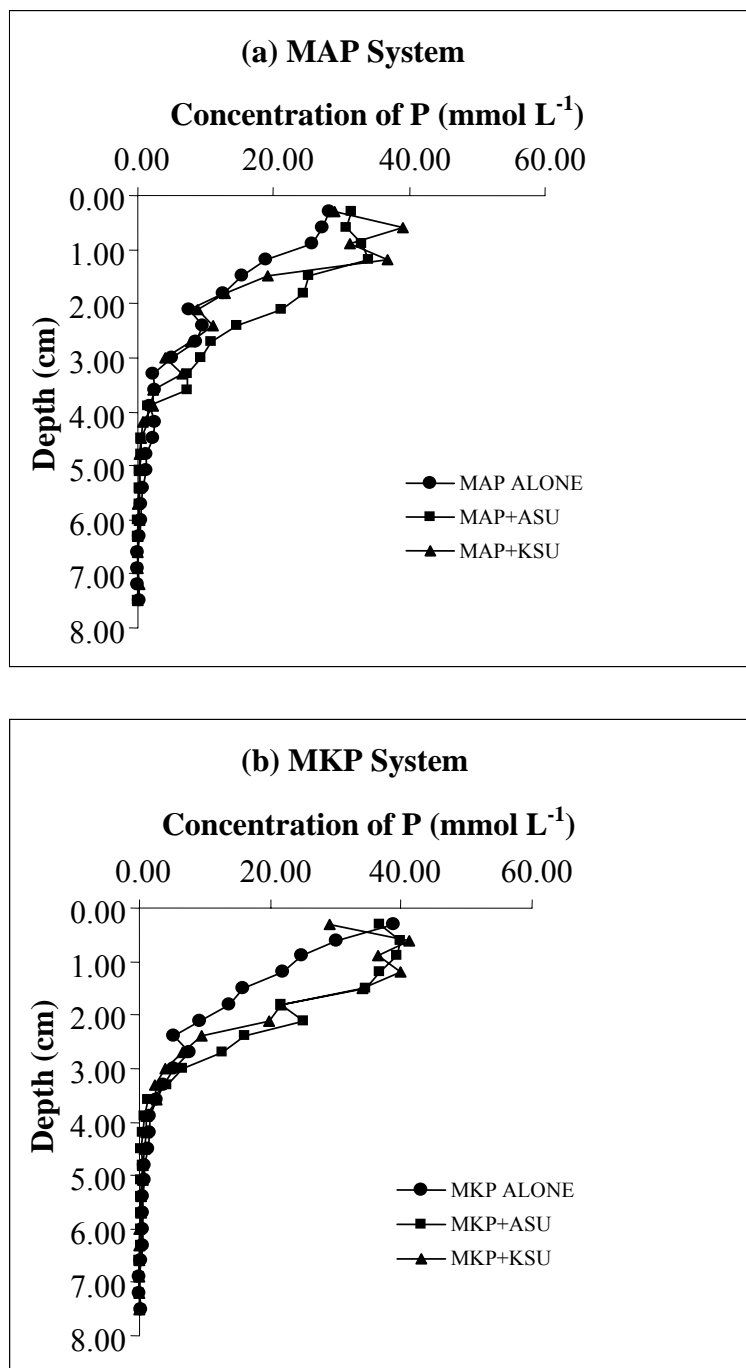
Figure 2.4 Distribution of acid-extractable P following 2 weeks of incubation in
resin-sand columns treated with dual application of P and sulphate salts.

respectively. However, the concentration of acid-extractable P increased sharply in MAP+ASU with second increment in depth, resulting in the greatest precipitation of P in MAP+ASU treatment in the top 1.5 cm portion of the column (Figure 2.4a). The concentration of acid-extractable P in MAP+ASU, however, declined steeply with further increments in depth and was very low beyond 1.5 cm depth while MAP+KSU and MAP ALONE maintained a gradual decline in the concentration of acid-extractable P down the column.

The acid-extractable P profiles of the MKP system (Figure 2.4b) were similar to those of MAP system, particularly with the addition of ASU. At the site of application, the concentration of acid-extractable P in MKP+ASU was less than that of MKP ALONE and MKP+KSU by 37% and 30%, respectively. The acid-extractable P in MKP+ASU, however, increased with second increment in depth, compared to MKP ALONE or MKP+KSU. Unlike in the MAP system, the concentration of the solid phase P in MKP+ASU and MKP+KSU declined steeply within a shorter distance (in the first 1.0 cm segment) from the peak. Generally, the region of Ca-P precipitation in the MKP system was restricted to the top 4.0 cm depth of the column.

2.4.4 Water and Acid Extractable Sulphate

In the resin-sand columns, the only sources of sulphate were KSU and ASU, therefore extraction data are presented for these treatments only. In general, maximum concentration of water-extractable SO_4^{2-} occurred at the surface of the sulphate treated columns and declined gradually with depth (Figure 2.5). In the MAP system, the water solubility of SO_4^{2-} in the first 3.0 cm depth was higher with ASU than with KSU (Figure 2.5a). Beyond 3.0 cm depth, the pattern of SO_4^{2-} movement was similar in both treatments as SO_4^{2-} moved throughout the entire depth of the column sectioned.

Unlike P, whose movement was restricted to about 4.2 cm depth, SO_4^{2-} moved deeper into the soil column with measurable concentration of SO_4^{2-} at the 7.5 cm depth. As such, SO_4^{2-} was more mobile and less retarded in MAP system compared to phosphate ion. This is similar to the results of Lefroy et al. (1995), who reported a greater mobility of SO_4^{2-} in soil, compared to P. Although we have hypothesized that SO_4^{2-} competed with P for Ca^{2+}, the extent of Ca-SO_4^{2-} precipitation was smaller than that of P as shown by the greater mobility of SO_4^{2-} in the system.

The features of SO_4^{2-} distribution and movement in the MKP system (Figure 2.5b) were similar to the MAP system. However, unlike the MAP system, there were no marked differences in the distribution of SO_4^{2-} between ASU and KSU at any point in the entire column of the MKP system. The profile also showed that SO_4^{2-} travelled through the entire 7.5 cm depth of the column.

The SO_4^{2-} recovered from the acid extract probably represents solid $CaSO_4$ resulting from the precipitation reaction between SO_4^{2-} and the reactive Ca^{2+} in the resin-sand system. The profiles showed that the magnitude of solid $CaSO_4$ precipitate in both

(a) MAP System

Concentration of SO$_4^{2-}$ (mmol L^{-1})

(b) MKP System

Concentration of SO$_4^{2-}$ (mmol L^{-1})
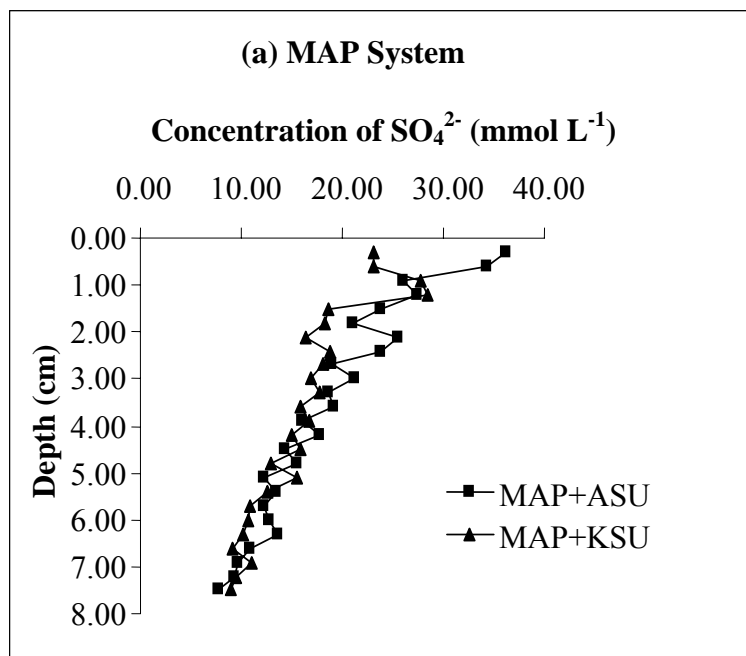
Figure 2.5 Distribution of water-extractable SO$_4^{2-}$ following 2 weeks of incubation in resin-sand columns treated with dual application of P and sulphate salts.

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systems declined gradually from the site of application down into the column (Figure 2.6). Both profiles on Figure 2.6 suggest that the reactive Ca^{2+} was precipitated by SO_4^{2} throughout the entire depth traversed by SO_4^{2-} in the column, as considerable amount of acid-extractable SO_4^{2-} was still detectable at the lower region of the column. This is in contrast to P whose region of precipitation was limited to 4.0 cm from the soil surface. However, the concentration of acid-extractable P was higher than that of acid-extractable SO_4^{2-} especially in the top 4.0 cm depth of the column for both systems, confirming that P out-competed SO_4^{2-} for Ca^{2+}.

Although there were no significant differences in the pattern of Ca-SO_4 precipitation between ASU and KSU in both systems, a higher concentration of precipitated SO_4^{2-} occurred at the surface of the columns in the MAP system. The concentration of acid-extractable SO_4^{2-} in the first 2.0 cm segment of the column containing MAP+KSU treatment was greater than that of the MAP+ASU by 22%. Similarly, in the first 3.0 cm segment of MAP system, the concentration of water-extractable SO_4^{2-} in the MAP+ASU treatment was 23% greater than that in the MAP+KSU (Figure 2.5a).

The greater concentration of acid-extractable SO_4^{2-} in the first 2.0 cm depth of MAP+KSU column compared to that of MAP+ASU, further confirmed that the K^+ associated with KSU was more effective than the corresponding NH_4^+ in ASU in replacing Ca^{2+}. Hence, the preference of the exchange system for K^+ caused a substantial displacement of the exchangeable Ca^{2+} to react with SO_4^{2-} within the first 2.0 cm depth of the column in MAP+KSU treatment. Conversely, the distribution of acid-extractable
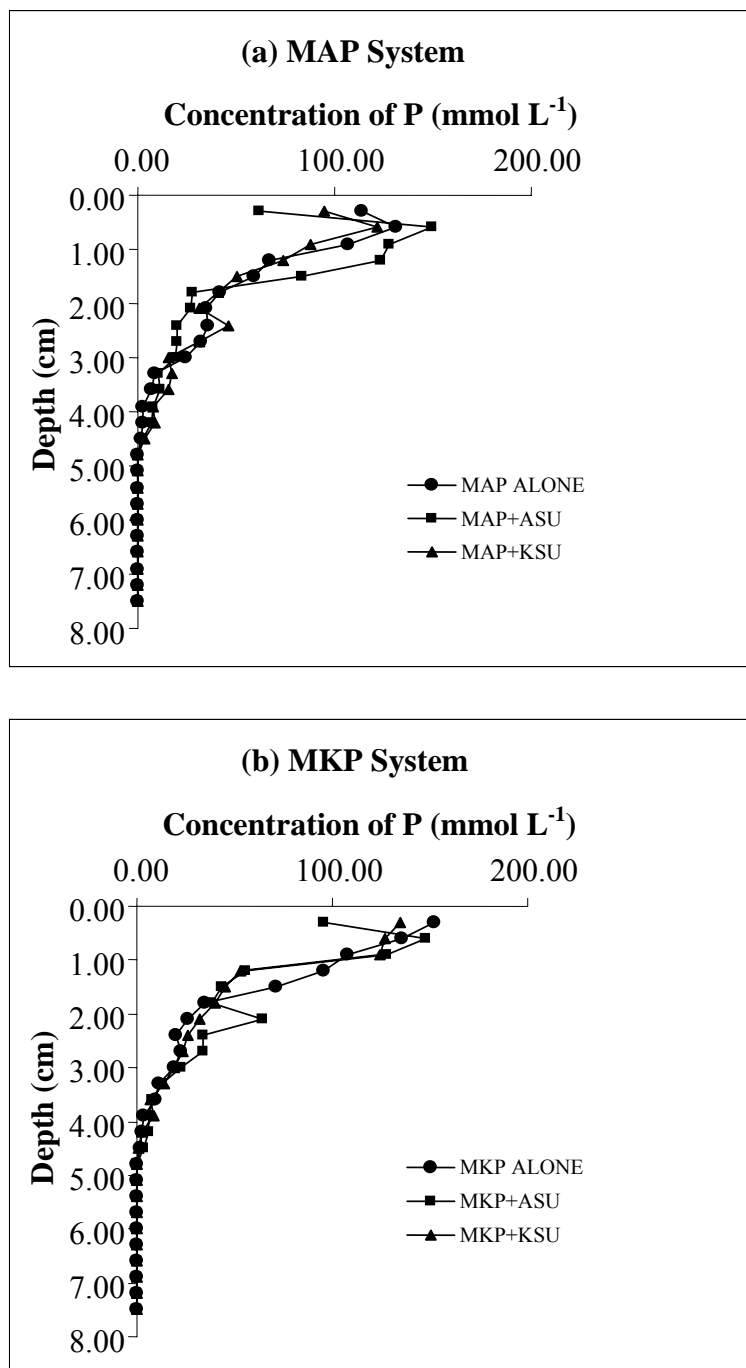
Figure 2.6 Distribution of acid-extractable SO_4^{2-} following 2 weeks of incubation in resin-sand columns treated with dual application of P and sulphate salts.

SO_4^{2-} was similar on addition of ASU or KSU to MKP throughout the entire section of the column in the MKP system (Figure 2.6b).

2.4.5 Water and Acid Extractable Ammonium-Nitrogen

The distribution profiles of both extracts (water and acid) were characterized by maximum concentration of NH_4^+ at the site of application and a gradual decline with depth (Figure 2.7). The amount of NH_4^+ ion in the various segments of the column was proportional to the rate of application of nitrogen in each treatment. The MAP ALONE and MAP+KSU treatments both contained the same amount of NH_4-N. Although the concentration of water-extractable NH_4^+ (approximately 52 mmol L^{-1}) at the surface of MAP ALONE was similar to that of MAP+KSU treatment, however, there were differences in the pattern of NH_4^+ ion movement between these two treatments at the region beyond 1.0 cm depth of the column.

More NH_4^+ was recovered from the water-extractable fraction of MAP+KSU treatment compared to that of MAP ALONE, in spite of adding similar amounts of NH_4-N to both treatments. Similarly, ammonium ion moved deeper into the column of MAP+KSU treatment to a maximum depth of 6.0 cm, while the movement of NH_4^+ ion in the MAP ALONE was limited to the 4.0 cm depth (Figure 2.7a). The greater solubility and depth of penetration of NH_4^+ ion in MAP+KSU treatment compared to MAP ALONE was due to cation competition. In MAP+KSU treatment, the component two moles of K^+ ion in K_2SO_4 competed with one mole of NH_4^+ for exchange sites, thereby increasing the concentration of NH_4^+ in solution. This study thus demonstrates that the
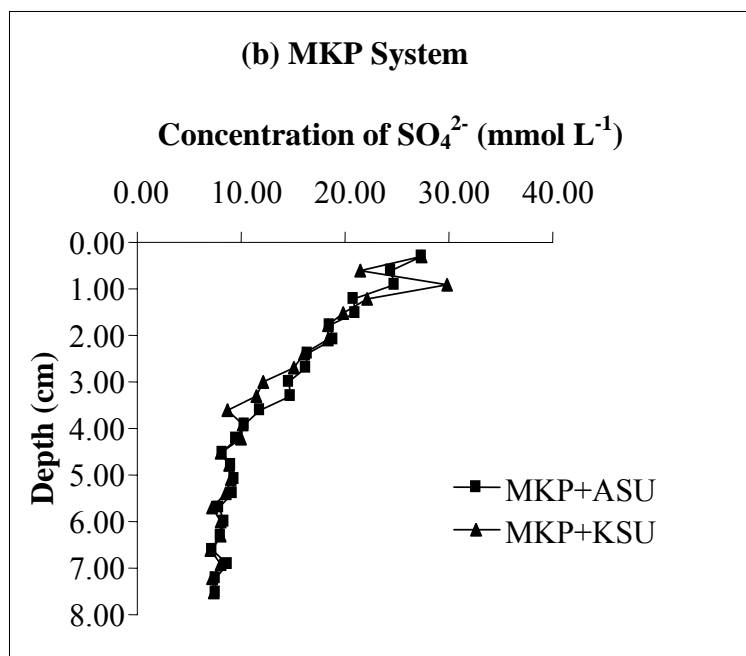
Figure 2.7 Distribution of extractable NH₄-N following 2 weeks of incubation in resin-sand columns treated with dual application of P and SO₄ salts.

solubility and diffusive transport of cation in soil solution can be significantly impacted by the addition of another cation.

The concentration of NH_4^+ at the site of application was 126 mmol L^{-1} and 168 mmol L^{-1} in MKP+ASU and MAP+ASU treatment, respectively (Figure 2.7a). Based on stoichiometry, there are two moles of N in one mole of MKP plus one mole of ASU, while one mole of MAP+ASU treatment contained three moles of N. Thus, the greater solubility and subsequent diffusion of NH_4^+ ion in MAP+ASU over MKP+ASU treatment was due to the effect of higher ionic concentration of NH_4-N in MAP+ASU treatment. However, detectable amount of NH_4^+ was measured at 7.5 cm in both treatments.

The maximum depth of NH_4^+ penetration in MAP ALONE (Figure 2.7a) was similar to the depth of penetration for P in MAP ALONE treatment (Figure 2.3a), as both ions were restricted to approximately 4.0 cm depth of the column. However, the depth of penetration of NH_4^+ ion increased greatly ahead of P in MAP+KSU as a result of the effect of cation competition between K^+ and NH_4^+, and greater depth of NH_4^+ penetration occurred in MKP+ASU and MAP+ASU compared to MAP ALONE or MAP+KSU as a result of higher ionic concentration of NH_4-N. Increased diffusion of NH_4^+ ahead of P was also reported by Sample et al. (1979).

The acid-extractable NH_4^+ profile (Figure 2.7b) represents the portion of NH_4^+ that replaced Ca^{2+} on the exchange complex. The profile in Figure 2.7b was complementary to the water-extractable fractions (Figure 2.7a), particularly for MAP ALONE and MAP+KSU treatments in the first 2.0 cm depth of the column. The MAP ALONE treatment had a higher concentration of acid-extractable NH_4^+ than MAP+KSU

treatment; even though both treatments contained the same amount of NH_4-N. The higher concentration of acid-extractable NH_4^+ in MAP ALONE suggested that there was a higher level of exchange reaction between NH_4^+ and Ca^{2+} in the MAP ALONE treatment, especially near the application site, while the addition of KSU to MAP reduced the activity of NH_4^+ on the exchange sites. As such, Figure 2.7b confirmed the effect of ionic competition between NH_4^+ and K^+ as seen in the differences in water-extractable fraction between MAP ALONE and MAP+KSU treatment (Figure 2.7a).

The trend of exchangeable NH_4^+ in MKP+ASU and MAP+ASU was similar to that of the water-extractable NH_4^+. This may be attributed primarily to the difference in the application rates. Generally, the concentration of exchangeable NH_4^+ at the surface followed the order: 114 mmol L^{-1} (MAP ALONE), 90 mmol L^{-1} (MAP+ASU), 73 mmol L^{-1} (MKP+ASU), and 41 mmol L^{-1} (MAP+KSU), respectively. However, the concentration of exchangeable NH_4^+ in MAP ALONE treatment dropped considerably within 2.0 cm from the surface and close to zero at the 4.0 cm depth (Figure 2.7b). On the other hand, the zone of cation exchange reactions of NH_4^+ in MAP+ASU and MKP+ASU treatment extended to approximately 7.0 cm depth of the column.

2.4.6 Water and Acid Extractable Potassium

The water-extractable K^+ profile (Figure 2.8a) reflects the level of potassium ion in soil solution. This profile resembles that obtained for NH_4^+ (Figure 2.7a). The features of K^+ distribution in solution were also characterized with maximum concentration at the top of the column, with a smooth, gradual decrease in concentration of K^+ with depth. At the site of salt application, the highest concentration of water-extractable K^+ (184 mmol L^{-1}) occurred in the MKP+KSU treatment, followed by MAP+KSU (105 mmol L^{-1}).

The concentration of water-extractable K^+ was similar at the surface in MKP+ASU and MKP ALONE treatment as 69 mmol L^{-1} and 71 mmol L^{-1} of K^+ was measured respectively. Although similar amount of K^+ was added to both MKP ALONE and MKP+ASU treatment, the movement of K^+ was significantly retarded in the MKP ALONE compared to MKP+ASU treatment (Figure 2.8a); similar to what was observed for NH_4^+ in the MAP system.

While the maximum depth of K^+ penetration was 4.0 cm in the MKP ALONE treatment, K^+ moved to a depth of 5.0 cm in the MKP+ASU treatment. As such, solution concentration of K was higher at any point in the column for MKP+ASU compared to MKP ALONE treatment. The reason for the greater concentration of water-extractable K^+ in MKP+ASU treatment was cationic competition between K^+ and NH_4^+ for exchange sites; the two moles of NH_4^+ ion in ASU competed with the one mole of K^+ in MKP for the exchange sites. Hence, the presence of NH_4^+ ion reduced the amount of K^+ on the exchange sites, which consequently increased the amount of K^+ in the soil solution phase
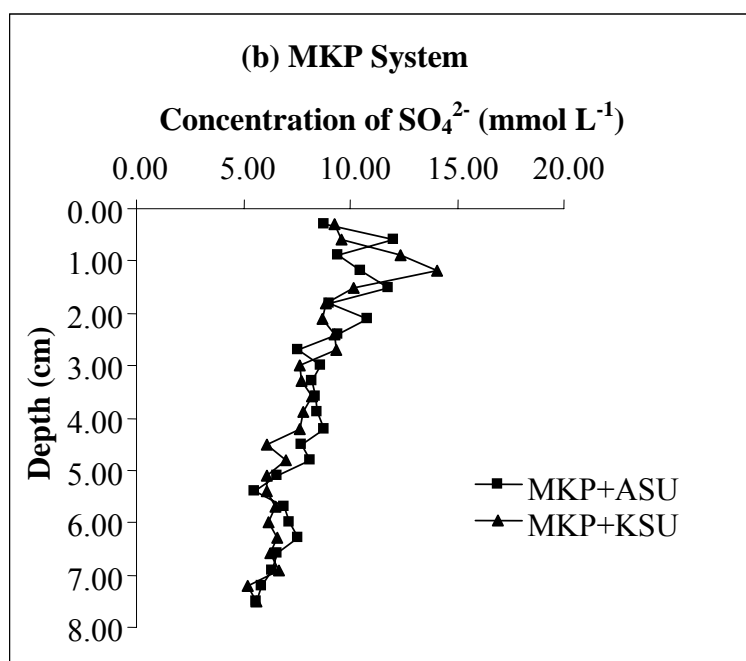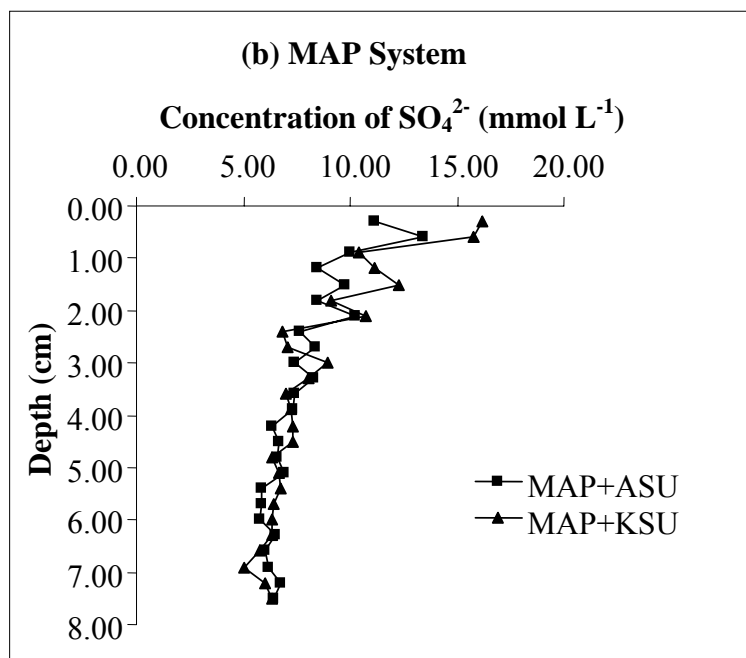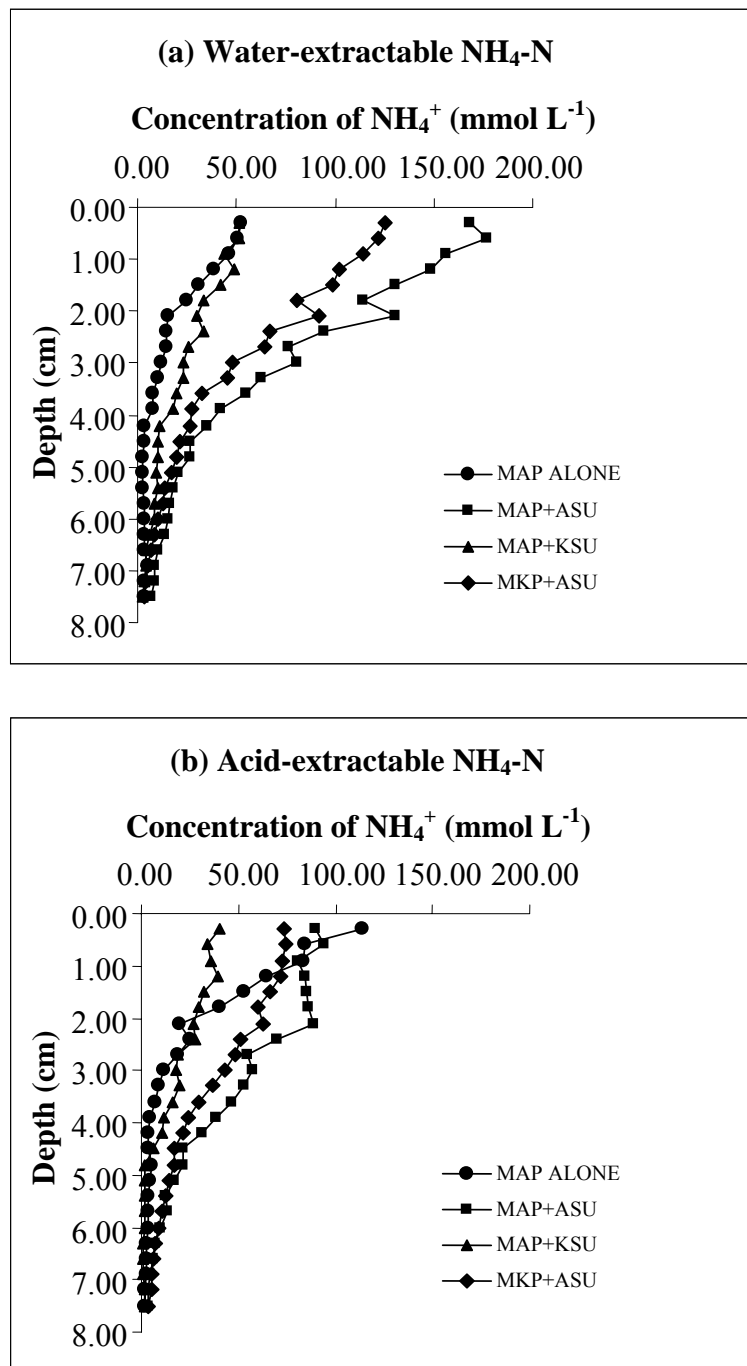
Figure 2.8 Distribution of extractable K^{+} following 2 weeks of incubation in resin-sand columns treated with dual application of P and SO$_4$ salts.

and the diffusive movement of K^+ ion in MAP+ASU treatment, in comparison to MKP ALONE.

The concentration of water-extractable K^+ and depth of K^+ penetration increased as the amount of added K^+ increased in MAP+KSU and MKP+KSU treatments, compared to MKP ALONE (Figure 2.8a). These results suggest that the combination of the effects due to ionic competition between NH_4^+ and K^+ for the exchange sites, and higher concentration of K^+ added in the MAP+KSU treatment resulted in a greater water solubility and mobility of K^+ in the solution phase, compared to MKP ALONE. On the other hand, the greatest water-extractable K^+ and maximum depth of K^+ movement measured in MKP+KSU were due to higher concentration of K^+ added in the MKP+KSU treatment, compared to other treatments. While the depth of K^+ movement was greater than that of P in MKP+ASU, MKP+KSU and MAP+KSU, the maximum depth traversed by K^+ in MKP ALONE treatment was similar to that recorded for P in the MKP system (Figure 2.3b), as the diffusion of both ions was limited to 4.0 cm depth of the column.

The acid-extractable K approximates the K^+ ion on the exchange sites after two weeks of incubation (Figure 2.8b). The underlying assumption is that there was no K^+ adsorption or precipitation in this system (Akinremi and Cho, 1991*a*). Figure 2.8b also showed that cation exchange reaction between K^+ and Ca^{2+} extended over the same region traversed by K^+ in each treatment.

The pattern of acid-extractable K^+ in the MKP ALONE and MKP+ASU columns was complementary to their corresponding water-extractable fractions in Figure 2.8a. As such, the exchangeable K^+ within the top 1.0 cm depth was higher in MKP ALONE compared to MKP+ASU and MAP+KSU treatment, respectively. These results indicated

that K^+ in MKP ALONE treatment was actively involved in cation exchange reaction with Ca^{2+} at the region close to the application site. Similar to what was observed with NH_4^+, the higher concentration of exchangeable K^+ in the MKP ALONE column compared to that in the MKP+ASU column, in spite of adding similar amount of K^+ to both columns, confirmed the role of ionic competition between NH_4^+ and K^+ for the exchange sites in enhancing the diffusive transport of K^+. The concentration of exchangeable K^+ in MKP+KSU treatment was consistent with the water-extractable profile based on the higher application rate of K^+ in this treatment.

The significant finding of this study is that it is possible to modify the solubility and diffusive transport of a cation by the mode of application of fertilizer elements. If cation movement and solubility is to be promoted, then banding another cation with it in a dual band will achieve this objective. However, this will not occur unless the two cations are added in the same band. This may then explain the observation that intimate contact between salts is needed to observe improved solubility of ions in soil (Hammond, 1997), as compared to random application of fertilizer elements. On the other hand, if retardation and restricted movement of a cation is the objective of the fertilizer management, then adding the cation alone or ensuring its separation from other cations will also achieve this objective. This study provides us with techniques to optimize the agronomic effectiveness of dual band fertilizers such as the Cargill's homogeneous NPS formulation.

2.4.7 Water Soluble Calcium

In the MAP system (Figure 2.9a), the addition of sulphate salts to $NH_4H_2PO_4$ increased the concentration of calcium in the soil solution compared to the application of MAP ALONE treatment. This suggests that the additional cations supplied by these sulphate salts displaced Ca^{2+} from the exchange complex. The pattern of water soluble Ca^{2+} was slightly different for the two sulphate salts in the MAP system (Figure 2.9a), as the concentration of Ca^{2+} was higher at the region close to the application site in MAP+ASU compared to MAP+KSU treatment. Thereafter, the concentration of water-extractable Ca^{2+} increased in MAP+KSU column and was consistently higher than the amount of solution Ca^{2+} in the corresponding MAP+ASU treatment throughout the remaining portion of the soil column. The summation of the concentration of water-extractable Ca^{2+} over the entire 7.5 cm depth of the columns in MAP system indicated that similar amount of Ca^{2+} was displaced into solution in both SO_4^{2-} treatments, i.e. 395 and 394 mmol Ca^{2+} L^{-1} in MAP+ASU and MAP+KSU, respectively.

It is possible that the differences in the concentration of Ca^{2+} between MAP+ASU and MAP+KSU at different portions of the column were due to pH effects on the dissolution of $CaCO_3$. However, Figure 2.2a showed that the magnitude of pH reduction was similar between the two sulphate salts within the first 1.2 cm segment and also from 4.2 cm depth down into the column, respectively. As such, the different concentration of Ca^{2+} between the two SO_4^{2-} treatments may be attributed to the presence of the displaced Ca^{2+} from the exchange complex of the chemical resin by the accompanying cation in each SO_4^{2-} salt.
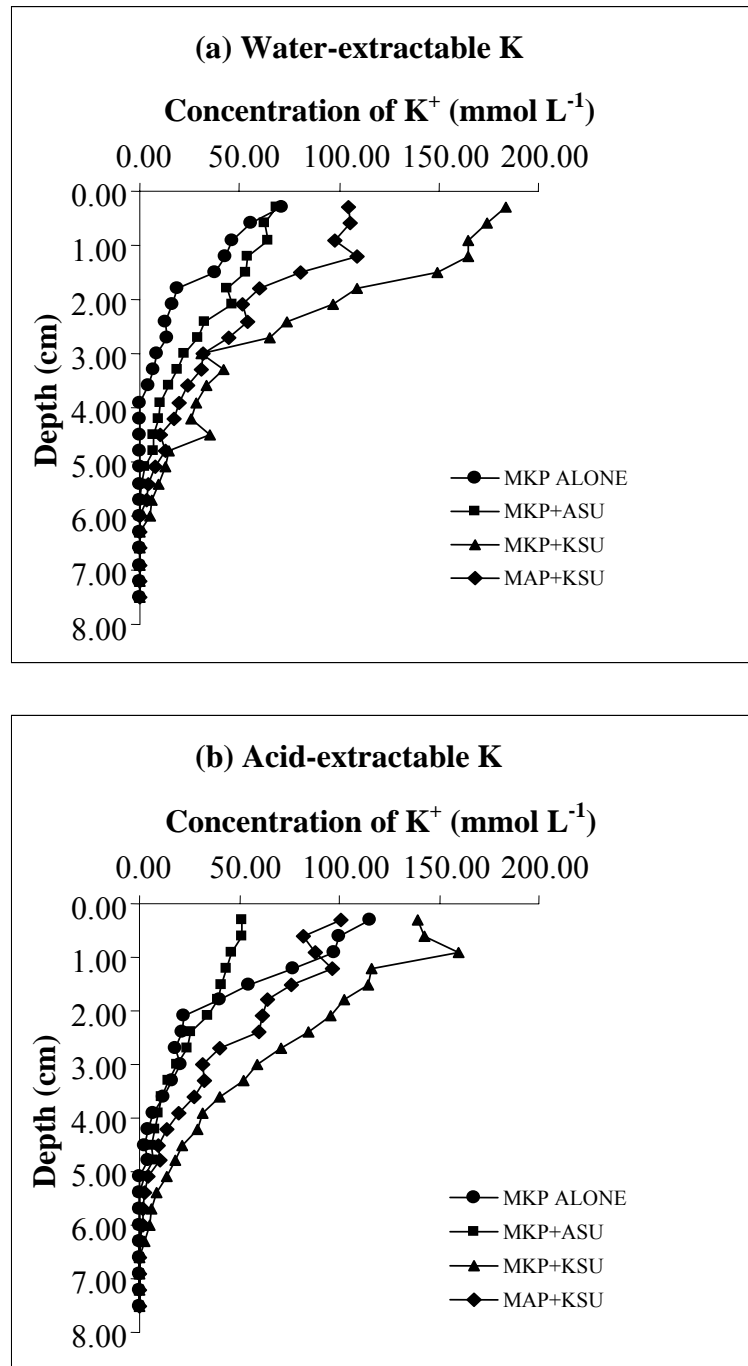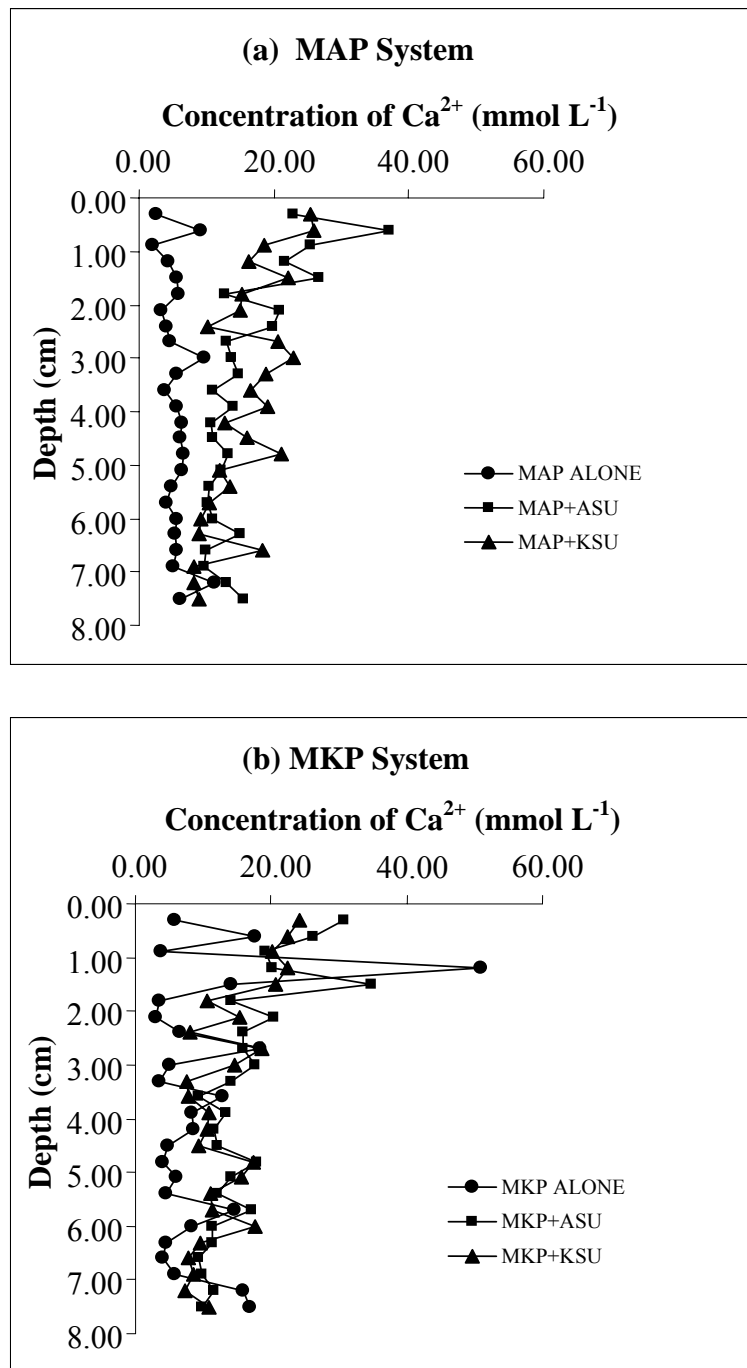
Figure 2.9 Distribution of water-extractable Ca^{2+} following 2 weeks of incubation in resin-sand columns treated with dual application of P and SO$_4$ salts.

Figure 2.9b also showed that the concentration of Ca^{2+} in soil solution was lower in MKP ALONE column compared to the amount of Ca^{2+} measured in the columns where ASU and KSU were added. Similar to the MAP system, the amount of solution Ca^{2+} was slightly higher in the top 2.4 cm on addition of ASU to the MKP system as compared to the addition of KSU. However, there was no marked difference in the concentration of solution Ca^{2+} between MKP+ASU and MKP+KSU treatments in the remaining segment of the soil column. The mean concentration of water-extractable Ca^{2+} over the entire 7.5 cm depth of the column of the MKP+ASU treatment was 60% and 18% greater than for the MKP ALONE and MKP+KSU treatments, respectively.

Overall, the water-extractable Ca^{2+} profiles in both systems did not produce a smooth diffusion curve for Ca^{2+} as observed for other ions shown earlier. Similar features of solution Ca^{2+} due to cation effect were reported by Akinremi and Cho (1993) when KCl was added to KH_2PO_4. However, unlike the retardation of P movement observed on addition of KCl to KH_2PO_4 by Akinremi and Cho (1993), interactions of SO_4^{2-} in these columns enhanced the solubility and diffusion of P.

It is worth noting that the water-extractable Ca^{2+} alone can not provide conclusive information about the displacing power of a cation, since Ca^{2+} in solution could be from the dissolution of $CaCO_3$ or from the dissolution of freshly precipitated DCPD or gypsum. Conversely, exchangeable Ca^{2+} would have provided us with comprehensive information on the fate of Ca^{2+} as influenced by cation exchange reactions. Nevertheless, the mean concentration of water-extractable Ca^{2+} was greater in MKP ALONE column (252 mmol Ca^{2+} L^{-1}) compared to MAP ALONE treatment (139 mmol Ca^{2+} L^{-1}), indicating that K^+ was generally more effective than NH_4^+ in displacing Ca^{2+}.

It was expected that the highly alkaline condition of this buffered system would prevent the accumulation of Ca^{2+} in the solution phase of the resin-sand system. This expectation was based on the hypothesis that, the combination of the displaced Ca^{2+} and free Ca^{2+} from the dissolved $CaCO_3$ would result in a high level of Ca-P precipitation in the resin-sand column. This was reflected in the marked precipitation of Ca^{2+} with the added P in the form of HPO_4^{2-} (Figure 2.4) under the existing high pH condition of the soil columns, as well as the precipitation of Ca^{2+} with SO_4^{2-} associated with ASU and KSU respectively. Therefore, the famous "snow-plow" phenomenon described in past studies (Starr and Parlange, 1979; Barry et al., 1983; Cho, 1985; Akinremi and Cho, 1991a) was not observed for Ca^{2+} distribution in the MAP and MKP systems in our experiment.

These results further confirmed the effect of ionic concentration on the displacement of the exchangeable Ca^{2+} into soil solution by the additional cations in the SO_4^{2-} salts. Similarly, greater reduction in pH on addition of SO_4^{2-} salts to both P sources (Figure 2.2) possibly introduced Ca^{2+} into the column solution through the dissolution of $CaCO_3$, thereby increasing the concentration of water-extractable Ca^{2+}.

2.4.8 Mass Balance of the Applied Ions

The mass balance was calculated for the applied ions to quantify the recovery of the applied salts through the extraction procedure, as well as errors associated with the column sectioning, column extractions and measurements of the ions. The technique employed in the calculation was similar to that used by Akinremi and Cho (1991*a*). The values shown on Tables 2.3-2.6 represent the summation of the ionic masses for the individual ion analyzed in each 3 mm section, over the entire 7.5 cm depth of the column. This was done separately for the water and acid extractable fractions.

Similar amounts of water-extractable P were recovered from the columns treated with MAP ALONE and MKP ALONE (Table 2.3). The addition of ASU to either MAP or MKP increased the water solubility of P by 43% and 48% respectively, while the solubility of P increased by 21% and 41% on addition of KSU to MAP or MKP, respectively. Statistical analysis of the treatment means also indicated that there was a significant treatment effect on the water-extractable P. Although the effect of sulphate species on the water-extractable P was statistically similar in MAP+ASU, MAP+KSU and MKP+KSU treatment, the addition of ASU to MKP was the only treatment in which the water-extractable P was significantly greater than for MAP ALONE or MKP ALONE ($P < 0.05$).

The portion of the added P recovered from the acid-extractable P fraction was greater than that of the water extracts by a ratio of 3:1 on the average, indicating that P was significantly precipitated perhaps as solid DCPD in the buffered resin-sand system (Table 2.3). The concentration of acid-extractable P in the soil columns ranged from 32.1

Table 2.3 Mass balance of P in resin-sand columns after 2 weeks of incubation

Treatment	[‡]Water P (mg)	[ℓ]Acid P (mg)	Total P (mg)	Input P (mg)	% Recovery
$NH_4H_2PO_4$	8.7 *b*	33.7 *a*	42. 5	45.6	93
$NH_4H_2PO_4 + (NH_4)_2SO_4$	12.5 *ab*	34.2 *a*	46.7	45.6	103
$(NH_4)H_2PO_4 + K_2SO_4$	10.5 *ab*	32.1 *a*	42.6	45.6	94
KH_2PO_4	9.1 *b*	34.7 *a*	43.8	45.6	96
$KH_2PO_4 + (NH_4)_2SO_4$	13.5 *a*	33.9 *a*	47.4	45.6	104
$KH_2PO_4 + K_2SO_4$	12.8 *ab*	33.7 *a*	46.5	45.6	102

[‡]Water-extractable P. The data represent average of two columns.
[ℓ]Acid-extractable P. The data represent average of two columns.
Means with the same letter are not statistically different according to Least Significant
Difference (LSD) test ($P < 0.05$).

Table 2.4 Mass balance of SO_4^{2-} in resin-sand columns after 2 weeks of incubation

Treatment	[‡]Water SO_4^{2-} (mg)	[ℓ]Acid SO_4^{2-} (mg)	Total SO_4^{2-} (mg)	Input SO_4^{2-} (mg)	% Recovery
$NH_4H_2PO_4 + (NH_4)_2SO_4$	70.9 *a*	29.1 *b*	99.9	141.1	71
$NH_4H_2PO_4 + K_2SO_4$	60.8 *b*	32.5 *a*	93.3	140.8	66
$KH_2PO_4 + (NH_4)_2SO_4$	51.2 *c*	31.6 *ab*	82.8	141.1	59
$KH_2PO_4 + K_2SO_4$	51.7 *c*	30.0 *ab*	81.7	141.1	58

[‡] Water-extractable SO_4^{2-}. The data represent average of two columns.
[ℓ] Acid-extractable SO_4^{2-}. The data represent average of two columns.
Means with the same letter are not statistically different according to Least Significant
Difference (LSD) test ($P < 0.05$).

mg P per column (in MAP+KSU treatment) to 34.7 mg P per column (in MKP ALONE treatment). However, statistical analysis of the treatment means at $P < 0.05$ did not indicate any significant difference in acid-extractable P among treatments. This was probably due to the small number of replicates (two) and experimental errors, coupled with variability in the magnitude of precipitation along the soil column. In general, the percentage recovery of the total extractable P in each column was close to the amount of P added. The over- or under-recovery of P in some columns may be attributed to experimental error whose magnitude appears small.

The sum of water-extractable SO_4^{2-} in the soil columns (Table 2.4) indicated that the greatest water solubility of SO_4^{2-} occurred on addition of ASU to MAP, while the concentration of water-extractable SO_4^{2-} was least and similar in the MKP system. In the MAP system, the trend of SO_4^{2-} recovered from the acid fraction was complementary to the water-extractable SO_4^{2-}, as the amount of precipitated SO_4^{2-} in MAP+KSU was greater than that observed in MAP+ASU treatment ($P < 0.05$). However, there was no significant difference in the acid-extractable SO_4^{2-} between MAP+ASU and MKP+ASU or MKP+KSU and also between MAP+KSU and MKP+ASU or MKP+KSU ($P < 0.05$).

Although a similar amount (1.47 mmol per column) of P and SO_4^{2-} was added to the soil columns, the amount of P precipitated in the columns was approximately 74% of the added P while the amount of precipitated SO_4^{2-} ranged between 21-23% of the added SO_4^{2-}. These results confirmed that P out-competed SO_4^{2-} for Ca^{2+}. However, unlike P, the values of the extractable SO_4^{2-} were under-recovered from the soil columns. These deficits in the percentage recovery of SO_4^{2-} were probably not due solely to experimental errors. A number of reasons could explain the under-recovery of SO_4^{2-} in the columns.

Firstly, it may be due to incomplete sectioning of the total depth of the column. The profiles of SO_4^{2-} distribution showed that SO_4^{2-} ions moved beyond the region of the column sectioned (7.5 cm), and this consequently limits the recovery of the true value of SO_4^{2-} added. Secondly, it is possible that the acid extraction procedure employed in this experiment was not effective at recovering the precipitated $CaSO_4$. In spite of the incomplete recovery of SO_4^{2-}, the presence of acid-extractable SO_4^{2-} supports the hypothesis that the precipitation of SO_4^{2-} with Ca^{2+} would enhance P solubility.

Although similar amounts of NH_4-N were added to MAP ALONE and MAP+KSU treatments, the addition of KSU to the MAP system increased the water-extractable concentration of NH_4^+ by 45% over that of MAP ALONE treatment (Table 2.5). Similarly, MAP+ASU and MKP+ASU treatment increased the water solubility of NH_4^+ by 3.4-fold and 2.1-fold respectively, compared to the MAP ALONE treatment. The combination of the effect of cation competition between NH_4^+ and K^+ for exchange sites, and ionic concentration due to higher stoichiometry moles of NH_4-N was responsible for the greater concentration of water-extractable NH_4^+ observed in MAP+KSU, MAP+ASU and MKP+ASU, respectively.

The trend of water-extractable K^+ in Table 2.6 was similar to that of NH_4^+ (Table 2.5) as MKP+ASU increased the water-extractable K^+ by 60% above that of MKP ALONE treatment. The addition of MKP+KSU and MAP+KSU treatments also increased the water-extractable K^+ by 4.4-fold and 1.6-fold respectively, compared to MKP ALONE treatment. As such, the same explanation as for the mass balance of NH_4^+ in Table 2.5 may hold for the greater concentration of water-extractable K^+ in MKP+ASU, MKP+KSU and MAP+KSU.

Table 2.5 Mass balance of NH_4^+ in resin-sand columns after 2 weeks of incubation

Treatment	[‡]Water NH_4^+ (mg)	[ℓ]Acid NH_4^+ (mg)	Total NH_4^+ (mg)	Input NH_4^+ (mg)	% Recovery
$NH_4H_2PO_4$	8.2	12.9	21.2	20.6	103
$NH_4H_2PO_4 + (NH_4)_2SO_4$	36.6	24.1	60.7	61.7	98
$NH_4H_2PO_4 + K_2SO_4$	11.9	8.5	20.4	20.5	100
$KH_2PO_4 + (NH_4)_2SO_4$	25.6	18.4	44.1	41.2	107

[‡]Water-extractable NH_4^+. The data represent average of two columns.
[ℓ]Acid-extractable NH_4^+. The data represent average of two columns.

Table 2.6 Mass balance of K^+ in resin-sand columns after 2 weeks of incubation

Treatment	[‡]Water K^+ (mg)	[ℓ]Acid K^+ (mg)	Total K^+ (mg)	Input K^+ (mg)	% Recovery
KH_2PO_4	20.6	37.5	58.1	57.5	101
$KH_2PO_4 + (NH_4)_2SO_4$	33.5	26.4	59.9	57.4	104
$KH_2PO_4 + K_2SO_4$	111.2	83.9	195.2	172.3	113
$NH_4H_2PO_4 + K_2SO_4$	54.1	51.4	105.5	114.6	92

[‡]Water-extractable K^+. The data represent average of two columns.
[ℓ]Acid-extractable K^+. The data represent average of two columns.

2.5 Summary and Conclusions

This study examined the roles of the accompanying cations and anions in the dual application of different sulphate salts with MAP and MKP salt. The results showed that the accompanying ions in each treatment influenced the H^+ ion distribution and overall solubility and diffusion of P in the buffered resin-sand system.

The addition of all treatments produced a zone of significant pH reduction in the top 6.0 cm depth of the column in both MAP and MKP systems. Although the magnitude of pH reduction was slightly greater in MAP+KSU compared to MAP+ASU treatment, the overall movement of H^+ ion was similar between MKP+ASU and MKP+KSU. In general, there was an increase in the depth of H^+ ion movement on addition of sulphate salts to both systems, compared to adding either of the phosphate salt alone.

The addition of SO_4^{2-} salts to both MAP and MKP systems increased the solubility of P ($P < 0.05$) and its movement, compared to the phosphate salts alone. This suggests that the co-application of SO_4^{2-} with P fertilizer would increase the solubility of P in calcareous soil, by competing with P for Ca^{2+} precipitation. Although the addition of K_2SO_4 had the greatest effect on pH reduction in the MAP system, there was a greater water solubility and diffusive movement of P on addition of $(NH_4)_2SO_4$ to P in both systems. The differences in the effect of $(NH_4)_2SO_4$ and K_2SO_4 on P solubility and movement may be attributed to the role of the associated cation in each SO_4^{2-} salt. Nevertheless, the results showed that SO_4^{2-} in both $(NH_4)_2SO_4$ and K_2SO_4 diffused farther into the columns than P and the accompanying cations, K^+ and NH_4^+ respectively.

Effect of ionic competition between K^+ and NH_4^+ was also observed on the distribution of each of these cations in the water-extractable and acid-extractable fraction.

It was shown that K^+ associated with K_2SO_4 enhanced the concentration of water-extractable NH_4^+ in MAP+KSU treatment compared to MAP ALONE by competing with NH_4^+ for the cation exchange sites. Similar effects of NH_4^+ associated with $(NH_4)_2SO_4$ on the greater concentration of water-extractable K^+ in MKP+ASU, compared to MKP ALONE were also observed. As such, it is possible to increase the solubility and diffusive transport of a cation by introducing another cation through a dual band fertilizer application, as both cations undergo cationic competition phenomenon to modify the solubility and movement of each other.

Overall, the results showed that the coupled interactions of the accompanying NH_4^+ and SO_4^{2-} significantly increased the water-extractable P and the diffusive movement of P in the buffered resin-sand column. These results suggested that, anions such as sulphate species associated with P in the same fertilizer band can increase the solution concentration and diffusive movement of P in alkaline to calcareous soils. This mechanism was due to ionic competition between the two anions (HPO_4^{2-} and SO_4^{2-}, respectively) for precipitation with soil Ca^{2+}.

It was also shown that K^+ from K_2SO_4 was more efficient than NH_4^+ from $(NH_4)_2SO_4$ in terms of cation exchange reactions. This possibly resulted in greater retardation of P movement with KSU compared to ASU particularly in the MAP system. As such, the banding of $(NH_4)_2SO_4$ salt with fertilizer P might enhance the solubility and movement of P in calcareous soils.

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3. CHARACTERIZING CATION AND ANION INTERACTIONS ON PHOSPHATE TRANSPORT

3.1 Abstract

Mixing various salts with fertilizer P modifies the chemical environment of the soil-P fertilizer reaction zone, due to induced changes in the pH status and the reactions of P with soil components and other ions. These interactions consequently affect the concentration and movement of phosphate species in soil solution. The objective of this study was to examine the effect of cationic and anionic interactions on the solubility and diffusive movement of P in a model system of calcareous soil columns. The model system consists of a mixture of inert quartz sand and Ca^{2+}-saturated cation-exchange resin (Amberlite IRP-69), buffered with $CaCO_3$. The CEC of the final mixture was 22 $cmol_c$ Ca^{2+} Kg^{-1}, while the pH was approximately 9.4. Treatments were replicated by a factorial approach. Three types of cations (K^+, NH_4^+, and Mg^{2+}) were combined with four types of anions (NO_3^-, Cl^-, SO_4^{2-}, and CO_3^{2-}). Each combination of cations and anions were added with 0.4 g of KH_2PO_4 (91.2 mg P per column) to the surface of a column that was packed with the resin-sand mixture. Following two weeks of incubation, soil columns were sectioned at 3 mm intervals to a depth of 7.5 cm and extracted with water, followed by 1 M HCl. The soil pH in each section was determined and soil extract was measured for inorganic P. While the column pH at the surface was

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depressed from 9.4 to 7.1 by KH_2PO_4 alone, the soil pH remained unchanged at 9.1 on addition of K_2CO_3 to KH_2PO_4. However, the addition of $MgCl_2$ to KH_2PO_4 resulted in the greatest concentration and depth of H^+ ion penetration compared to other treatments. Treatment combinations in the Mg^{2+} system produced the greatest movement of H^+ ion, compared to either K^+ or NH_4^+ system. ANOVA results showed that interactions exist between the effects of the cation systems and the corresponding anions ($P < 0.05$) on the solubility and precipitation of P. The addition of $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ to KH_2PO_4 produced the greatest concentration of water-extractable P ($P < 0.05$), followed by the addition of K_2SO_4, while the least water solubility of P occurred with the addition of K_2CO_3. Except for $KH_2PO_4+MgSO_4$ treatment, other treatments in the Mg^{2+} system reduced the overall solubility of P compared to KH_2PO_4 alone. The co-application of SO_4^{2-} salts with KH_2PO_4 enhanced the diffusive movement of P compared to the depth of P penetration with other salts, as P travelled to 5.1, 6.0 and 7.5 cm depth on addition of K_2SO_4, $(NH_4)_2SO_4$ and $MgSO_4$ to KH_2PO_4, respectively. Although the solubility of P was low in the Mg^{2+} system, maximum depth of P transport occurred in this system. These results suggest that interactions of the accompanying NH_4^+ and SO_4^{2-} in the soil-P fertilizer reaction zone, and the consequent pH reduction due to salt effects, would enhance the solubility and diffusive movement of phosphate ions in a calcareous soil system.

3.2 Introduction

Certain chemical processes in the soil-P fertilizer reaction zone have been shown to affect the fate of added P (Akinremi and Cho, 1991*a*; 1991*b*; 1993; Hao et al., 2000; Ro and Cho, 2000; Kumaragamage et al., 2004). These processes are: diffusive flux, cation exchange reactions, anion competition and chemical precipitation of P. These processes are the fundamental chemical factors that determine the overall availability of P in the reaction zone for crop uptake. Among the processes stated above, diffusion has the most limiting effect on crop utilization of P fertilizer (Eghball et al., 1990; Fan and MacKenzie, 1993).

According to Khasawneh et al. (1974), the common orthophosphate fertilizers exhibit limited mobility in soils because of their tendency to react with soil minerals or with cations derived from soil minerals. Hence, one of the strategies employed to control these processes is the modification of the chemical environment of the soil-P fertilizer reaction zone through a co-application of non-phosphatic salt with P fertilizer (Leikam et al., 1983; Westfall and Hanson, 1985; Beever and Racz, 1987; Ernani and Barber, 1991; Kouboura et al., 1995; Kumaragamage et al., 2004).

Having recognized the fundamental processes that control the fate of P in the soil-P reaction zone, the ultimate agronomic and environmental goal is to optimize the solubility of fertilizer P at the application site and enhance its movement towards plant roots. Consequently, this goal may improve the efficiency of P uptake. Early studies showed that the uptake of fertilizer P can be influenced by banding other nutrients with P. An increase in P uptake was observed following the addition of NH_4-N, rather than calcium to phosphate fertilizer band (Leikam et al., 1983; Hanson and Westfall, 1985;

Beever and Racz, 1987).   On the other hand, other researchers observed reduced

solubility and retardation of P movement. Akinremi and Cho (1991*a*; 1991*b*; 1993)

reported that the cation associated with P has a significant effect on the solubility and

mobility of P in soil-P reaction zone.   Their results confirmed that the displacement of

Ca^{2+} from the exchange sites by K^+ associated with P resulted in reduced movement of P,

due to the precipitation of P by the displaced Ca^{2+}.

Hammond (1997) reported that of all the salts evaluated, ammonium sulphate was

the most effective at increasing P utilization when banded with monoammonium

phosphate fertilizer. A similar observation was reported by Kumaragamage et al. (2004).

Their incubation experiment using soil columns revealed that the addition of $(NH_4)_2SO_4$

or $MgSO_4$ to monocalcium phosphate (MCP) fertilizer increased the solubility and

movement of P, compared to the effect of co-application of urea with MCP or MCP

alone.   More importantly, their results clearly demonstrated the role of associated SO_4^{2-}

anion on P solubility.

While other researchers had reported the roles of cationic interactions, such as

that between K^+ and Ca^{2+} (Akinremi and Cho, 1993) and the effect of anions such as

SO_4^{2-} (Kumaragamage et al., 2004) on the fate of P in calcareous soils, little information

is available on the influence of various cationic and anionic compositions on P movement

and solubility.   In the previous chapter of this study, we investigated the roles of multi-

ionic interactions of K^+, NH_4^+ and SO_4^{2-} on the solubility and diffusive transport of P in a

model system of calcareous soil condition.

It is necessary to generate information on the effect of multi-ionic interactions on

P solubility and transport by using a synthetic soil system, as this will prevent the

interferences due to complexity of chemical properties in natural soils. This study is part of the overall goal of evaluating the agronomic efficiency of Cargill's new NPS fertilizer formulation and providing fundamental information on the chemical environment that mimics that of the NPS fertilizer. Therefore, the objectives of this study were to examine the roles of various cationic and anionic compositions in a P fertilizer band on H^+ ion distribution, and their interactions on the solubility, diffusive transport and chemical precipitation of P in a cation exchange resin-sand system buffered with $CaCO_3$.

3.3 Materials and Methods

Preparation of the resin-sand mixture and wax columns used in this experiment was similar to the previous study. As such, details on these aspects will not be repeated in this study. However, the treatment combinations in this study were modified to conform to the objectives stated.

3.3.1 Treatment Combinations and Mass of Salt per Column

Treatment combinations were replicated by a factorial approach. One factor being cations of three types (K^+, NH_4^+, and Mg^{2+}) in combinations with anions of four types (NO_3^-, Cl^-, SO_4^{2-}, and CO_3^{2-}). The anion/cation combinations were added with approximately 0.4 g of KH_2PO_4 salt, which was equivalent to 91.2 mg P per column, to the resin-sand columns. The treatment combinations were grouped according to the cation systems and denoted as: potassium, ammonium and magnesium system. Reagent

grade salts were used for all treatments. Salts were thoroughly mixed together prior to application (particularly for the treatments containing the dual bands) and applied uniformly to the soil (resin-sand mixture) surface using a spatula, to simulate a one-dimensional diffusive movement. The treatment combinations and mass of each salt per column are shown in Table 3.1.

Table 3.1 Treatment combinations and mass of salts per column

Cation System	Treatment	Salt
Control	1	KH_2PO_4 (0.4 g)
Potassium	2	KH_2PO_4 (0.4 g) + KCl (0.22 g)
	3	KH_2PO_4 (0.4 g) + KNO_3 (0.29 g)
	4	KH_2PO_4 (0.4 g) + K_2SO_4 (0.26 g)
	5	KH_2PO_4 (0.4 g) + K_2CO_3 (0.20 g)
Ammonium	6	KH_2PO_4 (0.4 g) + NH_4Cl (0.16 g)
	7	KH_2PO_4 (0.4 g) + NH_4NO_3 (0.24 g)
	8	KH_2PO_4 (0.4 g) + $(NH_4)_2SO_4$ (0.19 g)
	9	KH_2PO_4 (0.4 g) + $(NH_4)_2CO_3$ (0.14 g)
Magnesium	10	KH_2PO_4 (0.4 g) + $MgCl_2·6H_2O$ (0.30 g)
	11	KH_2PO_4 (0.4 g) + $Mg(NO_3)_2·6H_2O$ (0.38 g)
	12	KH_2PO_4 (0.4 g) + $MgSO_4·7H_2O$ (0.36 g)
	13	KH_2PO_4 (0.4 g) + $MgCO_3$ (0.124g)

3.3.2 Chemical Analysis and Measurements

After two weeks of incubation, column segmentation and sample extractions followed the same procedure outlined in the previous study. The H^+ ion concentration in the mixture was measured with an Accument Model AR50 digital pH meter (Fisher Scientific Ltd., Winnipeg, MB, Canada) fitted with a combination electrode, while the concentration of phosphate in the extracts was determined by the ascorbic acid-ammonium molybdate method of Murphy and Riley (1962). The amount of P measured in the water-extracts (1:5 soil to solution ratio) represents the concentration of P in solution and that of acid-extracts (1 *M* HCl) approximates the precipitated P. The concentration of ions measured in each segment was plotted against distance to provide the distribution of these ions in the soil column.

3.3.3 Statistical Analysis

Effect of treatments means on P solubility and precipitation was compared using the Least Significant Difference (LSD) test at 0.05 level of significance. Also, the main effect of each factor (cation and anion, respectively) and the interactions between factors were analyzed by two-factor analysis of variance (ANOVA), using the General Linear Models (GLM) procedure of SAS software for Windows, version 9.1 (SAS Institute, Inc., Cary, NC).

3.4 Results and Discussion

The gravimetric water content was uniform throughout the entire depth of the resin-sand column in each treatment and the distribution features were similar between systems (Figure 3.1 a-c). The average value obtained from each column (approximately 23.5 g of water g^{-1} soil) was slightly lower than the actual amount of water added (25.0 g of water g^{-1} soil). The uniformity of water content distribution in the columns ensured that the ions moved mainly by diffusion and not by mass flow.

3.4.1 Effect of Salt Addition on Hydrogen Ion Distribution

The background pH of the resin-sand mixture was approximately 9.4; slightly higher than the background pH (8.8) measured in the previous experiment. Although same amount (0.5%) of $CaCO_3$ was added to the quartz sand in both experiments, the reason for the slight difference in pH may be attributed to error inherent in the pH electrode. Similarly, the high pH of the resin-sand mixture for this experiment is expected to favour high level of precipitation reaction between the divalent orthophosphate (HPO_4^{2-}) species and the displaced Ca^{2+} in solution (Cho, 1991; Akinremi and Cho, 1991*b*; Schachtman et al., 1998; Havlin et al., 1999).

The addition of KH_2PO_4 ALONE treatment reduced the column pH at the surface to approximately 7.1 after two weeks of incubation (Figure 3.2 a-c). The pH remained below 7.5 in the top 4.2 cm segment of the KH_2PO_4 ALONE column. However, between 4.2 cm and 6.0 cm, a sharp increase in pH by 1.3 units indicated the extent to which H^+
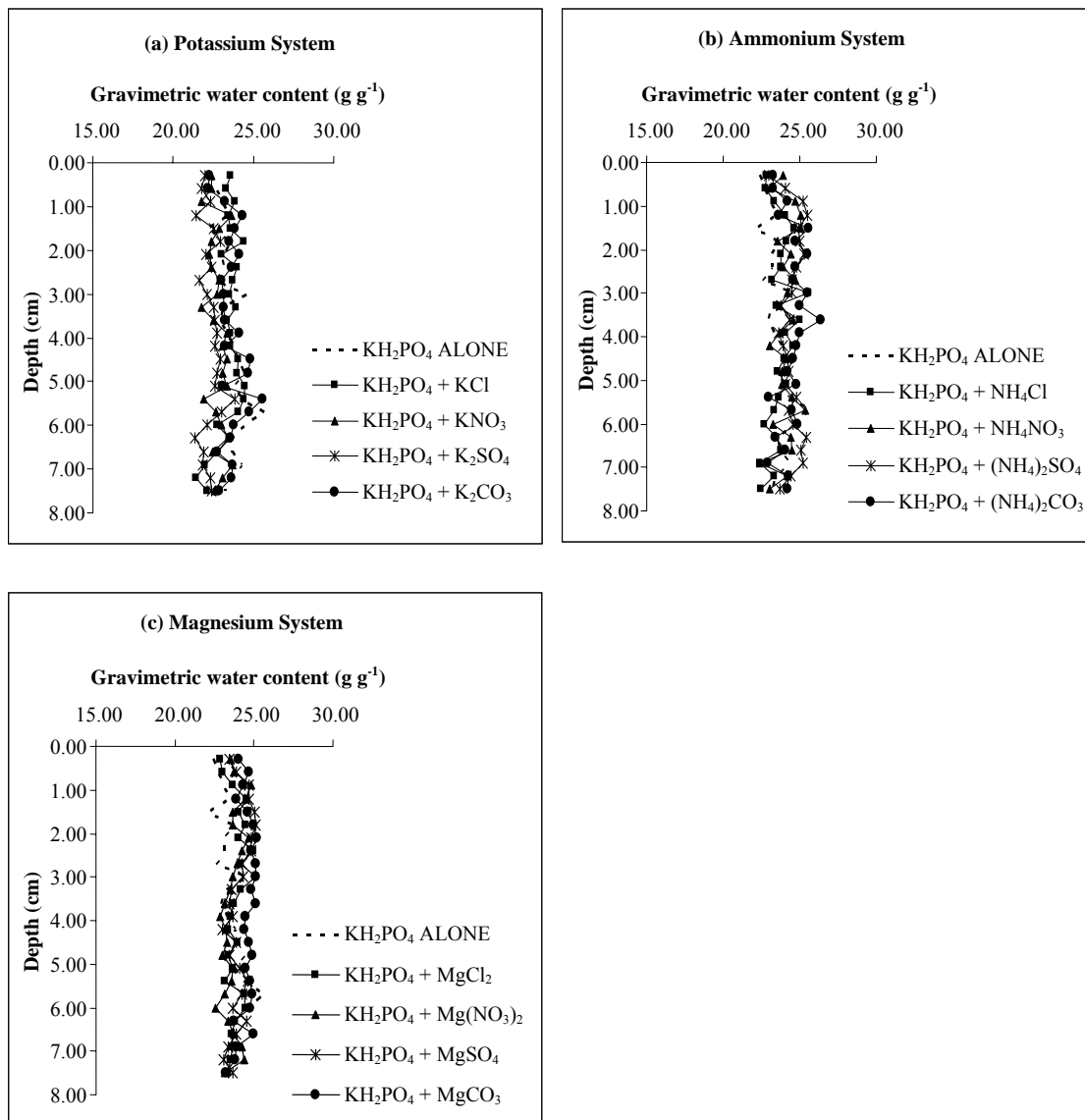
Figure 3.1 Gravimetric water content in resin-sand columns after 2 weeks of
incubation with dual band P.
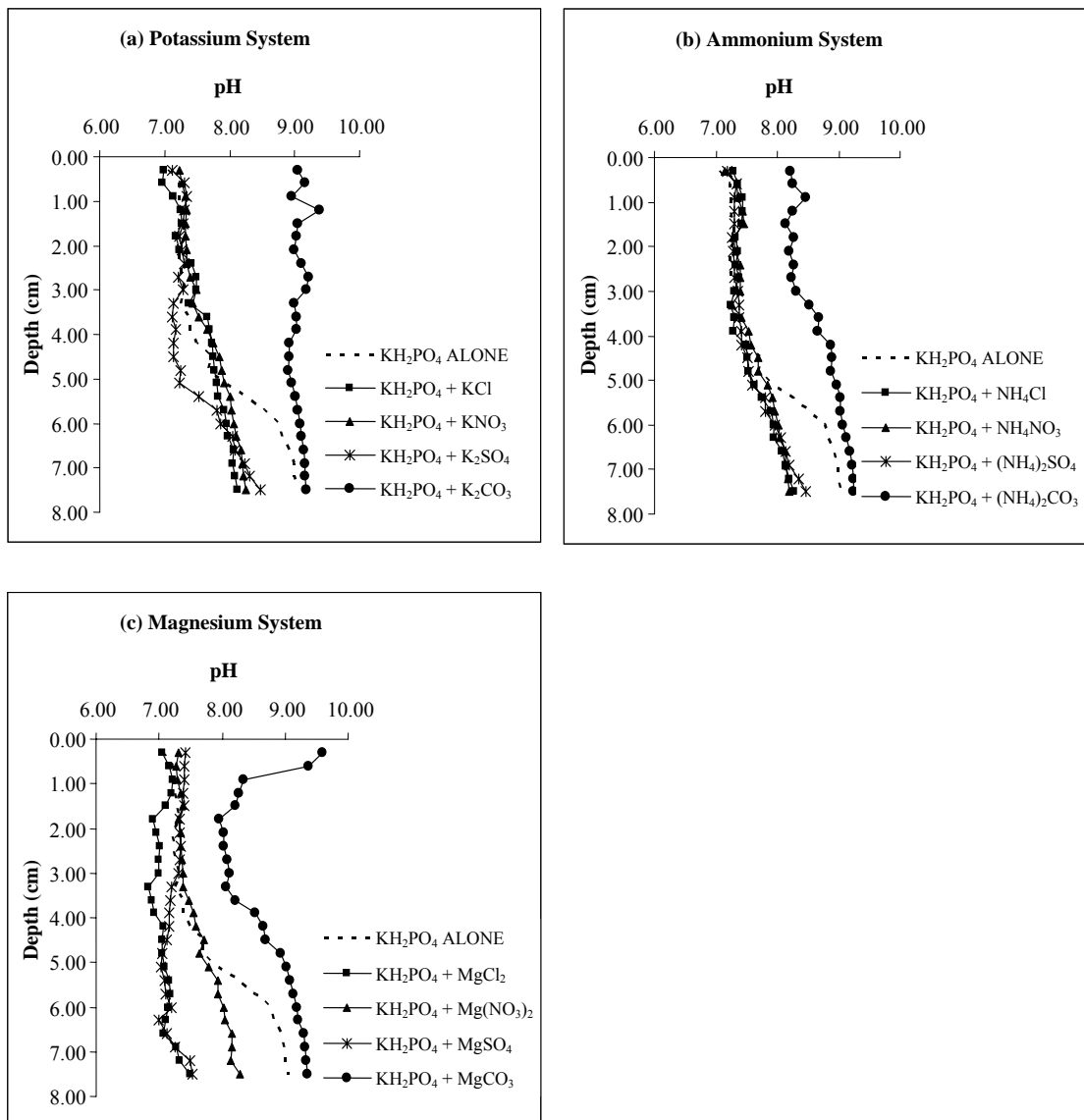
Figure 3.2 Distribution of H^+ ion in the resin-sand system after 2 weeks of incubation with dual band P.

ion produced at the top of the column by the dissolution of KH_2PO_4 had moved downwards to modify the background pH. Below 6.0 cm, the column pH was approximately 8.8, similar to the background pH. This result is consistent with the effect of KH_2PO_4 alone on column pH observed in the previous experiment, and also in agreement with the acidifying effect of KH_2PO_4 salt reported by Lindsay et al. (1962).

Except for the K_2CO_3 salt, the combination of other non-phosphatic salts with P in the potassium system produced H^+ ion concentration and movement that were similar to that of the KH_2PO_4 alone in the top 3.3 cm depth (Figure 3.2a). Beyond 3.3 cm zone, the pattern of H^+ ion distribution diverged in the column containing the K_2SO_4 salt resulting in a lower pH between 3.3 and 6.0 cm, compared to other treatments. In the column where KCl or KNO_3 was added, the pH remained uniform in the top 5.1 cm depth of the column and was still similar to that of the column containing KH_2PO_4 alone. However, beyond 5.7 cm down to the remaining portion of the column, the pattern of H^+ ion movement in KCl and KNO_3 columns were similar to that obtained for K_2SO_4.

The pH profile produced on addition of K_2CO_3 to KH_2PO_4 was substantially different from the other treatments. The addition of K_2CO_3 increased the column pH at the surface by 2.0 units compared to adding KH_2PO_4 alone, and the pH was similar to the background pH at every point in the column. Unlike in the other non-phosphatic salts, the H^+ ion produced from the dissolution KH_2PO_4 appeared to be neutralized by CO_3^{2-} associated with K^+, leaving the pH of the system unchanged.

Overall, the results showed that the maximum depth of H^+ ion penetration in the KH_2PO_4 ALONE treatment was about 5.1 cm, while H^+ ion moved throughout the entire 7.5 cm depth of the column on addition of either KCl, KNO_3 or K_2SO_4. The production

and transport of H^+ ion in the potassium system was greatest with the addition of the K_2SO_4 salt, suggesting that SO_4^{2-} produced more H^+ ion in addition to that from KH_2PO_4 alone. On the other hand, there was no net production or movement of H^+ ion in the column containing the K_2CO_3 salt, indicating that the CO_3^{2-} species neutralized the H^+ ion produced by the addition of KH_2PO_4, forming H_2O and CO_2; hence, the lack of changes in pH in the column containing K_2CO_3. These results imply that the level of Ca-P precipitation would be minimized in the $KH_2PO_4+K_2SO_4$ treatment to favour the solubility and transport of P, compared to $KH_2PO_4+K_2CO_3$ treatment.

Figure 3.2b illustrated the features of H^+ ion distribution in the ammonium system following two weeks of incubation. In the ammonium system, all treatments reduced the background pH of the mixture. However, at the point of salt application, the pH of the column containing $(NH_4)_2CO_3$ was higher compared to that of KH_2PO_4 (8.2 versus 7.1). While H^+ ion moved throughout the reaction zone with other salts, the maximum depth of H^+ ion penetration in the $KH_2PO_4+(NH_4)_2CO_3$ treatment was 4.2 cm; the depth at which the column pH (approximately 9.0) approached the background pH. On the other hand, the addition of other salts to KH_2PO_4 produced a pattern of H^+ ion distribution similar to that of KH_2PO_4 ALONE treatment in the top 5.1 cm depth. The depth of H^+ ion movement was limited to 5.1 cm in the column containing KH_2PO_4 ALONE treatment as the pH increased steeply beyond this depth, while H^+ ion continued to move in similar pattern into the remaining portion of the columns containing the NH_4Cl, NH_4NO_3 and $(NH_4)_2SO_4$ salt.

The pattern of H^+ ion distribution on addition of SO_4^{2-}, Cl^- and NO_3^- salts to the ammonium system were similar to those observed for these anionic species in the

potassium system (Figure 3.2a). The pH profile in Figure 3.2b clearly showed that $(NH_4)_2CO_3$ was not as effective in neutralizing H^+ ion produced by KH_2PO_4 compared to K_2CO_3. Therefore, it is possible that the level of Ca-P precipitation would be lower with $(NH_4)_2CO_3$ than with K_2CO_3. The results obtained from the pH profile of ammonium system suggest that the combination of the ammonium salts with KH_2PO_4 generally increased the concentration and transport of H^+ ion, compared to the combination of potassium salts with KH_2PO_4 in the potassium system.

Except for the $MgCO_3$ salt, the addition of other salts to KH_2PO_4 produced the same magnitude of pH reduction as KH_2PO_4 in the first 1.2 cm zone of the column (Figure 3.2c). Thereafter, the pH diverged in the $MgCl_2$ treatment as H^+ ion moved extensively into the column to produce the highest concentration and the deepest penetration of H^+ ion in the magnesium system. The pH profile showed that H^+ ion maintained a uniform trend in distribution throughout the entire section of the column with $MgCl_2$. Beyond 1.2 cm depth, H^+ ion continued to move in similar pattern in the columns containing $MgSO_4$, $Mg(NO_3)_2$ and KH_2PO_4 alone. At about 3.3 cm depth, there was a deeper penetration of H^+ ion in the $MgSO_4$ column compared to $Mg(NO_3)_2$ or KH_2PO_4 alone, while the pattern of H^+ ion movement beyond 4.2 cm depth of the column in $MgSO_4$ treatment was similar to that of $MgCl_2$ (Figure 3.2c).

Unlike the $MgCl_2$ or $MgSO_4$ treatment, the addition of $Mg(NO_3)_2$ to KH_2PO_4 maintained a similar trend in H^+ ion movement as that of KH_2PO_4 ALONE treatment to a depth of 5.1 cm before treatment differences occurred. Subsequently, H^+ ion moved deeper into the column with $Mg(NO_3)_2$ than it was in the KH_2PO_4 alone, however, with a slightly higher pH zone than either of $MgCl_2$ or $MgSO_4$ treatment.

The addition of $MgCO_3$ to KH_2PO_4 increased the column pH at the surface by 2.5 units compared to the pH observed on addition of KH_2PO_4 alone (Figure 3.2c). A steep decline in pH in the first 2.0 cm depth indicates that some of H^+ ion produced by KH_2PO_4 moved into the column and reduced the pH within the top 5.0 cm depth. The pH of $KH_2PO_4+MgCO_3$ treatment was higher than that of KH_2PO_4 ALONE treatment at every point in the entire portion of the column. This suggests that much of the protons produced by KH_2PO_4 were neutralized by $MgCO_3$, as the movement of H^+ ion was restricted to about 5.0 cm depth of the column.

In general, the addition of treatments containing the Cl^-, NO_3^- and SO_4^{2-} salts with KH_2PO_4 enhanced the concentration and transport of H^+ ion in the three cation systems compared to KH_2PO_4 alone. Conversely, the addition of the CO_3^{2-} salts to KH_2PO_4 resulted in a consumption and retardation of H^+ ion movement. Overall comparisons of the three pH profiles indicated that the combinations of the Mg^{2+}-based salts with KH_2PO_4 produced the greatest concentration and deepest penetration of H^+ ion compared to the other two cation systems (K^+ and NH_4^+, respectively). The marked effect of Mg^{2+} salts on the increased penetration of H^+ ion may be due to cation competition. It is possible that Mg^{2+}, a divalent cation, greatly out-competed H^+ ion, a monovalent cation, for exchange sites, thereby increasing the concentration and depth of H^+ ion transport in the columns.

The higher concentration and greater movement of H^+ ion in the magnesium system may also be attributed to the formation of weak hydroxide by Mg^{2+} following the hydrolysis of these Mg^{2+} salts. The acidifying effect due to the component anion dominates the alkaline effect produced by $Mg(OH)_2$, thereby producing a net reduction in

pH. On the other hand, the lesser effect of K^+ or NH_4^+ salts on H^+ ion movement may be attributed to the greater alkaline strength of KOH or NH_4OH, compared to $Mg(OH)_2$. Consequently, the stronger alkaline effect of K^+ or NH_4^+ tends to minimize the acidifying effect due to the component anion resulting in the production of a net neutral pH effect. As such, combinations of K^+ or NH_4^+ salts with KH_2PO_4 would result in a less acidifying effect compared to the effect of Mg^{2+} salts.

3.4.2.1 Extractable Phosphorus: Potassium System

Figure 3.3 showed the distribution of water- and acid-extractable P in the potassium system after two weeks of incubation. The combination of each potassium salt with KH_2PO_4 influenced the pattern of P movement and solubility of P in the soil column. In the first 3.0 cm depth (Figure 3.3a), the concentration of water-extractable P followed the order:

$KH_2PO_4 + K_2SO_4 > KH_2PO_4 + KNO_3 \geq KH_2PO_4$ ALONE $> KH_2PO_4 + KCl > KH_2PO_4 + K_2CO_3$
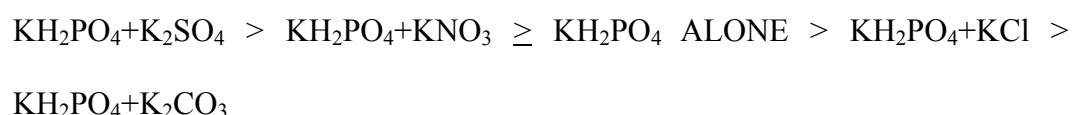
The water-extractable P profile showed that the addition of K_2CO_3 reduced the solubility of P in KH_2PO_4. Nevertheless, the depth of P movement was extended to approximately 4.0 cm, a little deeper than in the column containing KCl. The reduced solubility of P on addition of K_2CO_3 to KH_2PO_4 may be due to the consumption of H^+ ion by the CO_3^{2-} which promoted the precipitation of P.
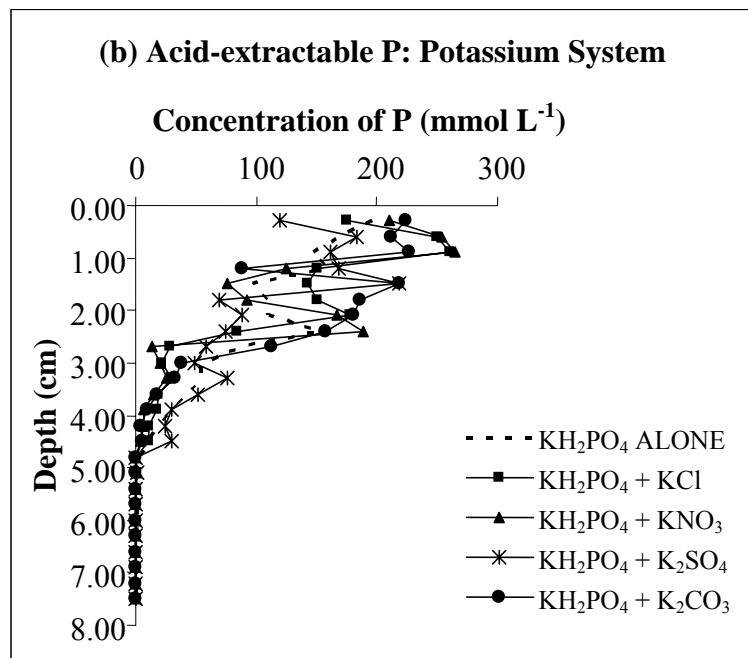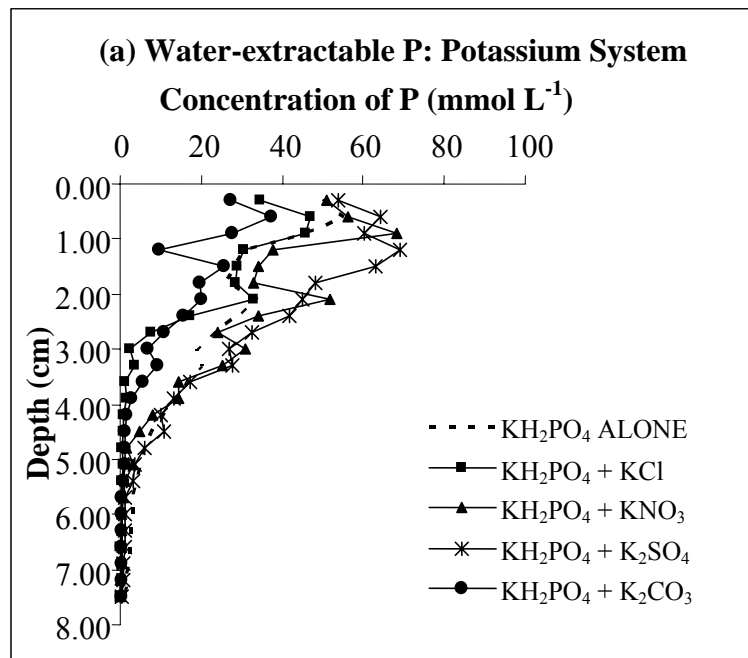
Figure 3.3 (a) Water- (b) Acid-extractable P in the potassium system after 2 weeks of incubation with dual band P.

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The ionization of monovalent phosphate ($H_2PO_4^-$) to produce divalent phosphate species (HPO_4^{2-}) is given by:

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad [3.1]$$

Any system that removes the H^+ ion produced by the above reaction would shift the reaction to the right side, thereby producing more divalent phosphate (HPO_4^{2-}) which is the candidate for Ca-P precipitation. As such, the level of Ca- P precipitation in such system would be promoted by the net consumption and retardation of H^+ ion movement.

Similar to the effect of K_2CO_3, the combination of KCl with KH_2PO_4 decreased the solubility of P and consequently increased the retardation of P transport in the soil column. The maximum depth travelled by P in KH_2PO_4+KCl treatment was limited to the top 3.6 cm depth, which was the smallest depth of all the treatments used in this study. Although pH was virtually identical between KH_2PO_4+KCl treatment and KH_2PO_4 ALONE in the first 5.0 cm of the column (Figure 3.2a), P was less soluble and strongly retarded when KCl was co-applied with KH_2PO_4. This implies that the addition of KCl to the resin-sand column promoted Ca-P precipitation reaction (Akinremi and Cho, 1993). Hence, the diffusion of P was greatly retarded due to the enhanced interactions of HPO_4^{2-} with Ca^{2+}.

Conversely, the addition of either KNO_3 or K_2SO_4 to KH_2PO_4 increased the solubility and transport of P in the reaction zone, compared to KH_2PO_4 alone; with the effect of K_2SO_4 being greater than that of KNO_3 (Figure 3.3a). Besides pH reduction, other reasons for the increased solubility of P by the NO_3^- species in the potassium system are not clear. However, the effect of SO_4^{2-} species on increased solubility and diffusion of P was probably due to both pH reduction and competition of SO_4^{2-} with

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HPO_4^{2-} for Ca^{2+} (Kumaragamage et al., 2004). Similarly, maximum depth of P penetration in the potassium system occurred in the K_2SO_4 treatment, in which P diffused to approximately 5.1 cm.

The concentration of acid-extractable P in the first 3 mm segment of the column in the potassium system (Figure 3.3b) was complementary to the concentration of P in the water-extractable fractions, i.e. the treatment with high water-extractable P had a low acid-extractable P. The least Ca-P precipitation occurred in $KH_2PO_4+K_2SO_4$ treatment, while the greatest concentration of solid phase P was observed in $KH_2PO_4+K_2CO_3$ treatment. The approximated ratios of the concentration of solution phase P to solid phase P at the surface of the resin-sand columns (the first 3 mm segment) were as follows:

1:2 ($KH_2PO_4+K_2SO_4$); 1:4 ($KH_2PO_4+KNO_3$); 1:4 (KH_2PO_4 ALONE);

1:5 (KH_2PO_4+KCl); 1:10 ($KH_2PO_4+K_2CO_3$)

This ratio indicates the magnitude of Ca-P precipitation at the site of salt application in each treatment.

Although SO_4^{2-} and CO_3^{2-} are both divalent, the effects of their interactions on the solubility and movement of P are quite different in the potassium system. These differences may be attributed to anionic competition. It is likely that the CO_3^{2-} species was less effective at competing against P (as HPO_4^{2-}) for precipitation with Ca^{2+} as compared to the SO_4^{2-} species. Coupled with the effect of anionic competition, the differences between K_2SO_4 and K_2CO_3 on the solubility and transport of P in solution may also be due to the effects of anion on the movement of H^+ ion in both treatments. The pH profile (Figure 3.2a) showed that the co-application of K_2SO_4 with KH_2PO_4

increased the concentration and depth of H^+ ion, while the co-application with K_2CO_3 increased soil pH in comparison to KH_2PO_4 alone. As such, the reaction zone of $KH_2PO_4+K_2CO_3$ treatment remained alkaline, which consequently promoted greater precipitation of P possibly as $Ca(HPO_4)_2 \cdot 2H_2O$ (DCPD). In the case of $KH_2PO_4+K_2SO_4$, the magnitude of Ca-P precipitation was smaller as a result of higher concentration of H^+ ion leading to pH reduction relative to KH_2PO_4 ALONE treatment.

In general, the zone of significant precipitation of P in the potassium system was limited to the top 5.0 cm depth of the column.

3.4.2.2 Extractable Phosphorus: Ammonium System

In the first 3.0 cm depth of the column (Figure 3.4a), the concentration of water-extractable P in the ammonium system was as follows:

$KH_2PO_4+NH_4Cl \leq KH_2PO_4+NH_4NO_3 \leq KH_2PO_4$ ALONE $< KH_2PO_4+(NH_4)_2SO_4$

$< KH_2PO_4+(NH_4)_2CO_3$
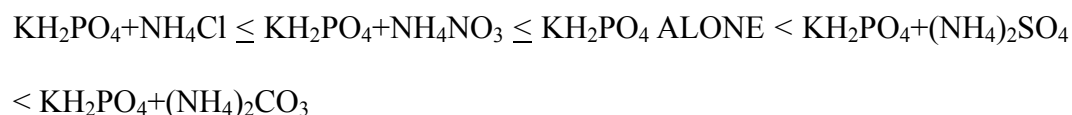
Within 3.0 cm segment from the surface, the addition of $(NH_4)_2CO_3$ increased the water solubility of P significantly. The increased concentration of P in soil solution enhanced the diffusion of phosphate ion to a depth of 4.5 cm. The addition of sulphate species increased the water solubility of P more than that of the carbonate; however, the concentration of water-extractable P within the top 3.0 cm depth in the $(NH_4)_2SO_4$ treatment was less than in the $(NH_4)_2CO_3$. Beyond this point, a higher concentration of water-extractable P was observed with $(NH_4)_2SO_4$ than with $(NH_4)_2CO_3$ and the depth of
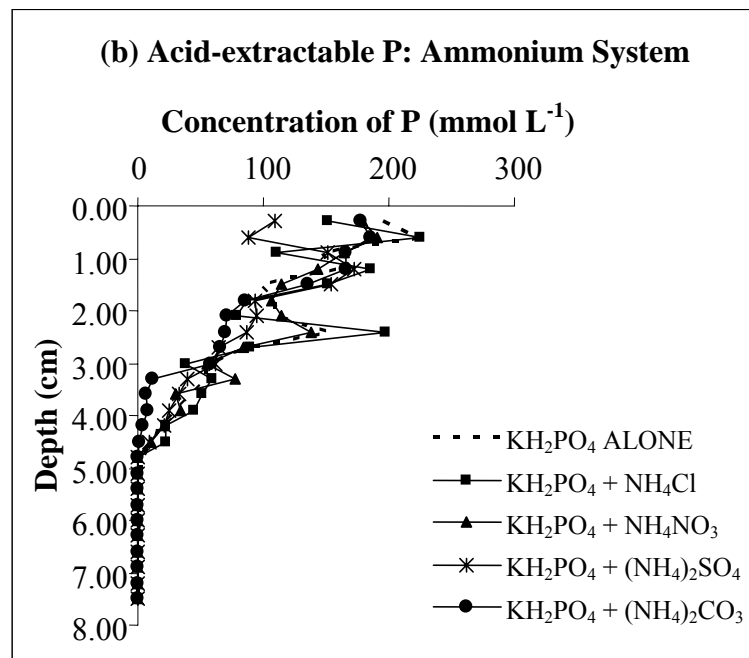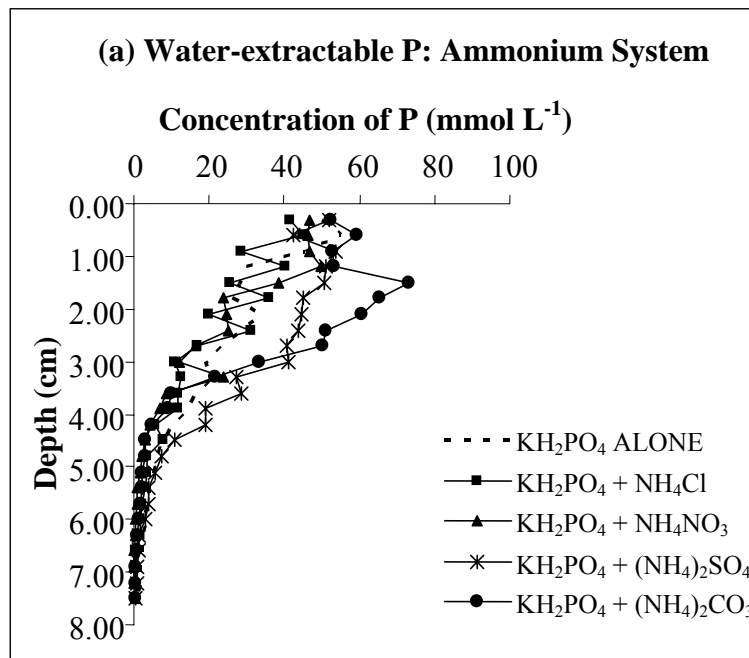
Figure 3.4 (a) Water- (b) Acid-extractable P in the ammonium system after 2 weeks of incubation with dual band P.

P penetration was about 6.0 cm in $(NH_4)_2SO_4$; which was 1.5 cm greater than that of $(NH_4)_2CO_3$. The addition of $(NH_4)_2SO_4$, thus, produced the maximum depth of P penetration in the ammonium system. While $(NH_4)_2CO_3$ enhanced the solubility of P especially close to the soil surface, $(NH_4)_2SO_4$ increased both the water solubility and diffusive movement of P, compared to the KH_2PO_4 ALONE treatment.

The co-application of either NH_4Cl or NH_4NO_3 salt with KH_2PO_4 did not produce a significant effect on the solubility and mobility of P in the ammonium system, as P behaved similarly in the columns containing these two salts and the KH_2PO_4 ALONE treatment (Figure 3.4a). In the region where these reactions took place (the first 5.0 cm) there was no difference in pH of the NH_4Cl and NH_4NO_3 salts when compared to that of KH_2PO_4 alone. Conversely, the addition of the ammonium salts containing the divalent anion species (SO_4^{2-} and CO_3^{2-}, respectively) with KH_2PO_4 increased the concentration of water-extractable P.

The greater solubility of P in either $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ compared to NH_4Cl, NH_4NO_3 or KH_2PO_4 alone may be due to the ability of the associated divalent anion species to form precipitate with Ca^{2+}. However, this was not the case with the addition of K_2CO_3 to KH_2PO_4. It is possible that the initial pH in the $(NH_4)_2CO_3$ column was high enough to make CO_3^{2-} competitive with P for Ca^{2+}, thereby enhancing the water solubility of P. A time series experiment may be needed to verify this hypothesis.

Unlike the potassium system, the co-application of CO_3^{2-} species with KH_2PO_4 increased the concentration of water-extractable P in the ammonium system, possibly due to the differences in the reaction of K_2CO_3 compared to $(NH_4)_2CO_3$. Conversely, effects of sulphate species on water-extractable P and the depth of P penetration in the

ammonium system were consistent with that observed in the potassium system. The positive influence of SO_4^{2-} on P movement may be attributed to the ability of SO_4^{2-} ion to move with K^+ or NH_4^+ as ion pairs ahead of P in the solution phase (Lefroy et al., 1995). As such, the SO_4^{2-} ions present in the region beyond the soil-P reaction zone subsequently formed precipitate with the displaced Ca^{2+}, thereby preventing the backward diffusion of the displaced Ca^{2+} into the soil-P reaction zone. However, the magnitude of this process is a function of the concentration of SO_4^{2-} species in solution.

The features of acid-extractable P distribution in the ammonium system were slightly complementary to the water-extractable fractions (Figure 3.4b). Estimation of the extent of Ca-P precipitation indicated that the greatest magnitude of precipitation occurred on co-application of NH_4Cl with KH_2PO_4, while $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ minimized the amount of P concentration in the solid phase. At the site of application, the ratio of the concentration of solution phase P to the solid phase P was approximately 1:2 in $KH_2PO_4+(NH_4)_2SO_4$ treatment and 1:4 in other treatments.

Also, unlike the relatively smooth distribution of water-extractable P, the distribution of acid-extractable P was complex. The pattern of acid-extractable P in either NH_4Cl or NH_4NO_3 was similar to that of KH_2PO_4 alone, as the region of Ca-P precipitation extended over the entire reaction zone (5.0 cm). As such, the distribution of acid-extractable P on addition of NH_4Cl or NH_4NO_3 to KH_2PO_4 was similar to the water-extractable fraction. On the other hand, the addition of $(NH_4)_2SO_4$ reduced the amount of solid phase P in the first 1.0 cm by 38% of the concentration of P in the KH_2PO_4 alone while $(NH_4)_2CO_3$ reduced the concentration of P by 6%. Nevertheless, the region of Ca-P precipitation was restricted to 3.3 cm depth of the column containing $(NH_4)_2CO_3$ while

Ca-P precipitation extended to 4.5 cm with $(NH_4)_2SO_4$. Overall, the depth of P penetration in either $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ (Figure 3.4a) was greater than the region of Ca-P precipitation (Figure 3.4b). Hence, the addition of $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ to KH_2PO_4 reduced the concentration of acid-extractable P compared to KH_2PO_4 alone.

3.4.2.3 Extractable Phosphorus: Magnesium System

In the magnesium system, maximum concentration of soluble P occurred at the surface of the column containing the $MgCO_3$ salt (Figure 3.5a). However, the concentration of solution P declined markedly and its movement was strongly retarded as P diffused beyond 1.2 cm depth. The co-application of $MgSO_4$ with KH_2PO_4 reduced the solubility of P near the site of application. Nevertheless, P travelled extensively throughout the entire portion of the column sectioned (7.5 cm) in the $KH_2PO_4+MgSO_4$ treatment. Of all the treatments examined in this study, $MgSO_4$ promoted the deepest penetration of P into the soil column.

The effects of carbonate and sulphate on the solubility of P in the magnesium system were similar to their performance in the ammonium system. While the addition of $MgCO_3$ apparently increased the concentration of water-extractable P close to the surface, the $MgSO_4$ salt enhanced both the water solubility and mobility of P, compared to any other treatment in the magnesium system. The pattern of phosphate distribution in the column was similar for both salts containing the monovalent anion species (Cl^- and NO_3^-, respectively). The concentration of water-extractable P was lower in both monovalent anion treatments compared to KH_2PO_4 alone, while the diffusive transport of
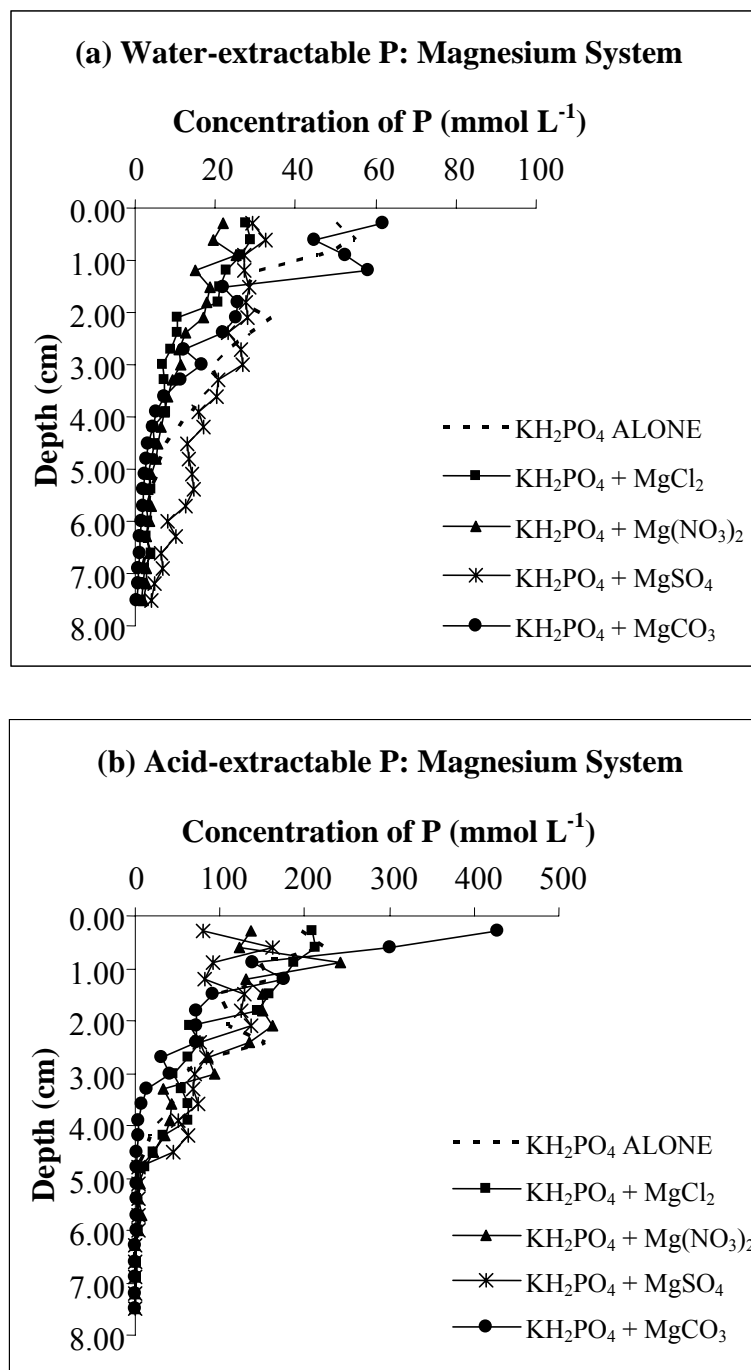
Figure 3.5 (a) Water- (b) Acid-extractable P in the magnesium system after 2 weeks of incubation with dual band P.

P was consequently restricted in the reaction zone of the column containing $MgCl_2$ or $Mg(NO_3)_2$.

The differences between the effect of the monovalent and divalent anions on P solubility in the magnesium system were further demonstrated by comparing the effects of chloride and sulphate salts. Although the addition of $MgCl_2$ or $MgSO_4$ to KH_2PO_4 produced a greater concentration and depth of H^+ ion penetration than that of the KH_2PO_4 alone, the SO_4^{2-} treatment enhanced the water solubility of P and depth of P penetration while P transport was retarded and the solubility reduced in the Cl^- treatment. Therefore, factors other than pH reduction controlled the chemical availability of P in the resin-sand columns.

Except for the $MgSO_4$, the addition of other salts to KH_2PO_4 produced the same depth of P penetration (5.1 cm) as KH_2PO_4 alone while the total distance travelled by P increased significantly to 7.5 cm in the column containing the $MgSO_4$ treatment. In general, the concentration of water-extractable P in the magnesium system was smaller than those observed for the other cation systems. The reduced water solubility of P in the magnesium system may be attributed to two mechanisms. First, the higher replacing power of Mg^{2+} on the exchange sites compared to that of K^+ or NH_4^+ resulted in substantial displacement of Ca^{2+} into solution, which consequently precipitated with P, thereby reducing the water solubility of P. Secondly, it is possible that part of the free Mg^{2+} produced from the dissolution of the magnesium salts reacted with P to form reaction products such as dimagnesium phosphate trihydrate ($MgHPO_4 \cdot 3H_2O$) (Sample et al., 1980).

The portion of the applied P not obtainable in the water-extracts of the magnesium system was recovered in the acid-extractable fraction (Figure 3.5b). In the column that contained $MgCO_3$, copious precipitation of P occurred within the first 1.0 cm depth of the column and the magnitude of precipitated P ranged from 420 to 150 mmol P L^{-1} an order of magnitude higher than the solution P. The concentration of acid-extractable P in $KH_2PO_4+MgCO_3$ treatment, which was initially high at the site of application, declined steeply beyond 1.2 cm depth.

It is interesting to note that the shape of the acid-extractable P profile of the carbonate treatment followed the same pattern as its H^+ ion distribution particularly at the region close to the surface of the column (Figure 3.2c). This suggests that the resulting higher pH at the site of salt application due to the neutralization of H^+ ion by CO_3^{2-} favoured the marked precipitation observed at the surface of the column containing $MgCO_3$. Hence, there was a copious precipitation of P on addition of $MgCO_3$ to KH_2PO_4, particularly in the first 1.0 cm segment of the column, compared to the magnitude of acid-extractable P observed on addition of K_2CO_3 to KH_2PO_4 in the potassium system.

Effect of the interactions of the reactive Ca^{2+} and Mg^{2+} with P was more prominent on the precipitation of P in the presence of salts containing the monovalent anions, compared to those containing the divalent anions (Figure 3.2c). Past studies showed that these monovalent anions did not undergo precipitation reactions with Ca^{2+} (Parfitt 1978; Rajan 1978; Satnam et al., 1996). Conversely, combinations of Mg^{2+} with the divalent anions (SO_4^{2-} and CO_3^{2-}, respectively) reduced the overall precipitation of P within the reaction zone, compared to either Cl^- or NO_3^- treatment (Figure 3.5b).

Although the addition of $MgCO_3$ to KH_2PO_4 increased the amount of precipitated P in the first 1.0 cm depth compared to other treatments, the concentration of acid-extractable P in $MgCO_3$ treatment declined steeply beyond 1.2 cm depth and smaller than any other treatment throughout the remaining portion of the column.

Conversely, the lowest concentration of acid-extractable P occurred in the first 1.2 cm depth on addition of $MgSO_4$ due to anionic competition of SO_4^{2-} with P for Ca^{2+} and Mg^{2+}. As such, the concentration of acid-extractable P over the entire reaction zone in the magnesium system (Figure 3.5b) produced the following trend:

$$KH_2PO_4 + MgSO_4 < KH_2PO_4 \; ALONE < KH_2PO_4 + MgCO_3 < KH_2PO_4 + Mg(NO_3)_2$$

$$< KH_2PO_4 + MgCl_2$$
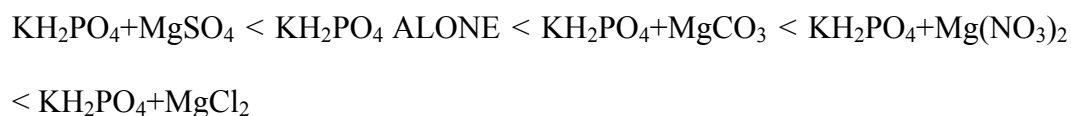
Similarly, comparison of the ratios of solution:solid phase P at the surface of the columns in the magnesium system indicated that the extent of Ca-P precipitation was significantly minimized in the sulphate treatment (ratio 1:3), while the ratio for other anions was approximately 1:7, respectively.

The acid-extractable fraction approximates the solid phase P, which probably comprised $CaHPO_4 \cdot 2H_2O$ (DCPD) and $MgHPO_4 \cdot 3H_2O$ (DMPT). This suggestion is supported by Racz and Soper (1967), who found DCPD and DMPT to be initial reaction products of pelleted MKP added to neutral and calcareous soils. Considering the positions of K^+, NH_4^+, Mg^{2+} and Ca^{2+} on the lyotropic series, it is evident that the preference of the exchange resin for Mg^{2+} was greater than for K^+ or NH_4^+ but similar to that of Ca^{2+}; both Mg^{2+} and Ca^{2+} being divalent species. Therefore, the amount of exchangeable Ca^{2+} displaced into solution would be higher in the magnesium system compared to either of potassium or ammonium system. Consequently, the soil solution

phase of the magnesium system would have higher concentration of Ca^{2+}, thereby increasing the potential for Ca-P precipitation. In addition to Ca-P precipitation, the interaction of Mg^{2+} with HPO_4^{2-} following the dissolution of the magnesium salts might also enhance the precipitation of P in the magnesium system. Therefore, the combination of interactions of Ca^{2+} and Mg^{2+} with P reduced the water solubility of P, accompanied by greater precipitation of P in the magnesium system, compared to the potassium or ammonium system.

3.4.3 Effect of Ionic Interactions on Extractable Phosphorus

The main effects of cations and anions were significant on the water-extractable and acid-extractable P (Table 3.2). As well, there was a significant cation by anion interaction on water-extractable and acid-extractable P. The significant interaction between the cations and the anions on the extractable P indicated that the effect of at least one cation varies across the anions types and also, the effect of at least one anion varies depending on the accompanying cation.

Figure 3.6 showed the effects of ionic interactions on water-extractable P. From this graphical illustration, KNO_3 and K_2CO_3 were the cause of the cation-anion interaction on water solubility of P in the resin-sand system. Effect of NH_4^+ was consistent at enhancing the highest concentration of water-extractable P with Cl^-, SO_4^{2-} or CO_3^{2-}, as compared to other cations. Conversely, the water solubility of P was consistently low with the interaction of Mg^{2+} with Cl^-, NO_3^- or CO_3^{2-}. While NH_4^+ and Mg^{2+} maintained a consistent trend in water solubility of P with three out of

Table 3.2 General linear models (GLM) analysis on water- and acid-extractable P in resin-sand columns after 2 weeks of incubation with dual band P

Source of variation	d.f.	Water-extractable P	Acid-extractable P
		mean square values	
Cations	2	197.46 [*]	188.67 [*]
Anions	3	242.55 [*]	218.60 [*]
Anions x Cations	6	88.67 [*]	109.41 [*]
Error	24	2.32	10.67

[*] Significant at $P < 0.05$.

four anions, the interaction of K^+ and NO_3^- produced the highest concentration of water-extractable P and least concentration with the interaction of K^+ and CO_3^{2-}, compared to the interaction of NO_3^- or CO_3^{2-} with NH_4^+ or Mg^{2+}, respectively. This implies that the effect of the interaction of K^+ and NO_3^- on water solubility of P was significantly different to that of K^+ and CO_3^{2-}; hence, the source of significant interaction between cations and anions on the water-extractable P, and possibly on the acid-extractable P as well (Table 3.2).

Besides pH effect due to salt addition, other reasons for the contrast effect of K^+ and NO_3^- interaction to that of K^+ and CO_3^{2-} are not clear. However, it was shown earlier that the addition of KNO_3 to KH_2PO_4 produced a greater reduction in pH with greater depth of H^+ ion movement compared to the addition of K_2CO_3 to KH_2PO_4; which resulted in marked neutralization and retardation of H^+ ion movement. Therefore, the
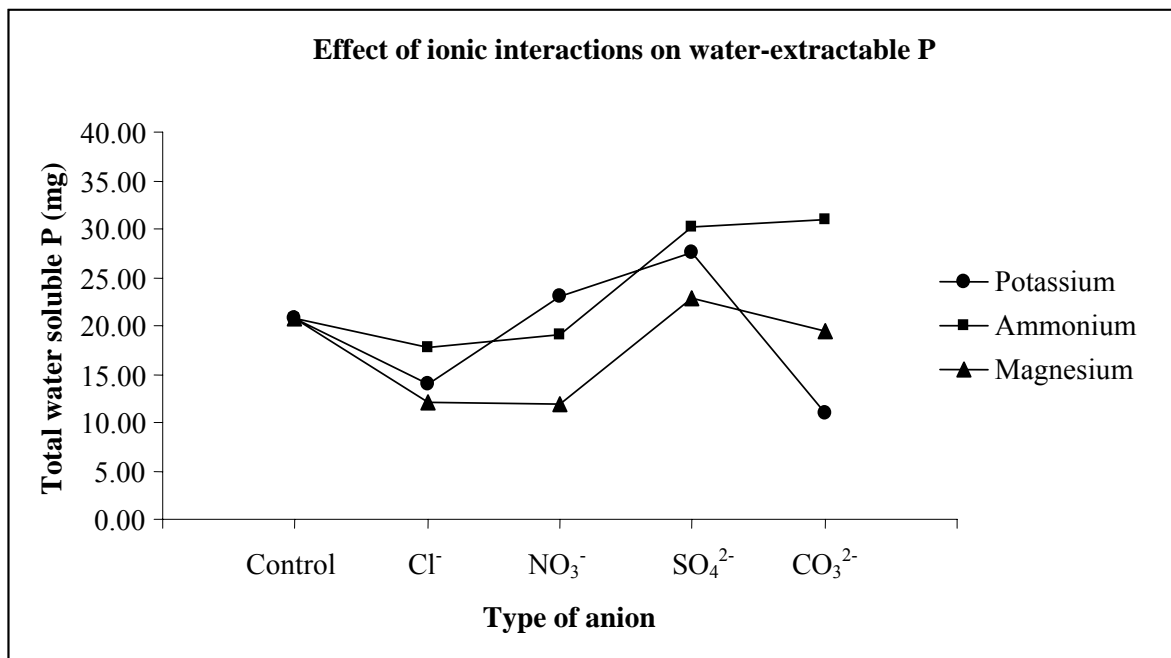
Figure 3.6 Effect of cationic and anionic interactions on water-extractable phosphorus.

prevailing high pH with K_2CO_3 treatment favoured Ca-P precipitation in the resin-sand column, which reduced the water-extractable P compared to KNO_3 treatment.

3.4.4 Mass Balance of Extractable Phosphorus

Table 3.3 provides information on the mass balance of the applied P. The mass balance described the quantitative recovery of P through the extraction procedure, as well as the degree of error involved in the column sectioning and measurements of P content in the extracts (Akinremi and Cho, 1991*a*). The values shown on the table represent the summation of the ionic mass of P extracted from each 3 mm segment, over the entire 7.5 cm depth of the column sectioned. This was done separately for the water and acid extractable fractions. Recovery of the added P was generally complete in all treatments.

A greater portion of added P was recovered from the acid extractable fraction probably as solid DCPD. These results indicated that P was significantly precipitated in the buffered resin-sand system as the magnitude of precipitated P ranged between 66-90% of the added P. The mass balance was also presented based on the statistical analysis of the effect of treatment means. The results showed that P content was complementary between the two extractable fractions, i.e. the treatment with high water-extractable P had a low acid-extractable P.

Addition of $(NH_4)_2CO_3$ or $(NH_4)_2SO_4$ to KH_2PO_4 produced the greatest amount of water-extractable P, followed by the addition K_2SO_4 while none of the Mg^{2+} salt increased the water solubility of P compared to KH_2PO_4 alone ($P < 0.05$). It appeared that the NH_4^+ salts were generally more effective at enhancing the solubility of P in the

Table 3.3 Mass balance of P in resin-sand columns after 2 weeks of incubation with dual band P

Treatment	[‡]Water P (mg)	[ℓ]Acid P (mg)	Total P (mg)	Input P (mg)	% Recovery
KH$_2$PO$_4$ ALONE	20.8 *cd*	70.9 *de*	91.8	91.2	101
KH$_2$PO$_4$ + KCl	13.9 *f*	74.5 *cd*	88.4	91.2	97
KH$_2$PO$_4$ + KNO$_3$	23.0 *c*	68.0 *ef*	91.0	91.2	100
KH$_2$PO$_4$ + K$_2$SO$_4$	27.5 *b*	63.9 *fg*	91.4	91.2	100
KH$_2$PO$_4$ + K$_2$CO$_3$	10.9 *g*	82.2 *a*	93.0	91.2	102
KH$_2$PO$_4$ + (NH$_4$)Cl	17.7 *e*	73.9 *cd*	91.7	91.2	101
KH$_2$PO$_4$ + (NH$_4$)NO$_3$	19.1 *de*	73.0 *de*	92.1	91.2	101
KH$_2$PO$_4$ + (NH$_4$)$_2$SO$_4$	30.2 *a*	61.4 *g*	91.6	91.2	100
KH$_2$PO$_4$ + (NH$_4$)$_2$CO$_3$	30.9 *a*	60.4 *g*	91.4	91.2	100
KH$_2$PO$_4$ + MgCl$_2$	12.1 *fg*	78.7 *abc*	90.8	91.2	100
KH$_2$PO$_4$ + Mg(NO$_3$)$_2$	11.9 *fg*	79.8 *ab*	91.7	91.2	101
KH$_2$PO$_4$ + MgSO$_4$	22.9 *c*	67.9 *ef*	90.8	91.2	100
KH$_2$PO$_4$ + MgCO$_3$	19.5 *de*	73.7 *cd*	93.2	91.2	102

[‡]Water-extractable P. The data represent average of three columns.
[ℓ]Acid-extractable P. The data represent average of three columns.
Means with the same letter are not statistically different according to Least Significant Difference (LSD) test ($P < 0.05$).

water-extractable fraction, compared to K^+ or Mg^{2+} salts. These differences may be due to the differences in the preference of the exchange complex for the accompanying cations in these salts.

The effectiveness of the cation associated with the individual salt to displace the exchangeable Ca^{2+} into solution had a significant implication on the precipitation of P. It is likely that NH_4^+ was less preferred by the exchange complex, as compared to K^+ or Mg^{2+}. It is also possible that the accompanying NH_4^+ coexisted with NH_3, which consequently reduced the effective concentration of NH_4^+, more so under the high pH (above 7.0) prevailing in the columns (Havlin et al., 1999). Hence, the amount of Ca^{2+} displaced into solution in NH_4^+ treatments would be smaller, and this may explain the greatest water solubility of P observed with some NH_4^+ salts, compared to other salts associated with K^+ or Mg^{2+}. Although the lowest pH was measured in the Mg^{2+} system, the overall water solubility of P was greatly reduced with the co-application of Mg^{2+} species with KH_2PO_4 (Table 3.3). These results suggest that the effect of cation competition had a greater influence on the water solubility of P compared to the effect of pH reduction in the resin-sand system.

It was also shown that the addition of sulphate salts to KH_2PO_4 enhanced the water-extractable P in the potassium and ammonium system but similar in magnitude to that of KH_2PO_4 alone in the magnesium system ($P < 0.05$). Similar to the influence of sulphate species, the addition of carbonate salt enhanced the water-extractable P in the ammonium system, compared to KH_2PO_4 alone. In contrast, the interaction of carbonate species in the potassium system reduced the water solubility of P, accompanied by marked precipitation of P, compared to KH_2PO_4 alone. On the other hand, the addition of

chloride or nitrate salts to KH_2PO_4 did not increase the water-extractable P in any of the cation system, compared to KH_2PO_4 alone ($P < 0.05$).

While the differences between the effects of K_2CO_3 and $(NH_4)_2CO_3$ on water-extractable P may be attributed to pH effect; as K_2CO_3 was more effective at neutralizing H^+ ion, the differences between the individual anionic species was probably due to anionic competition. It appeared that the SO_4^{2-} species in K_2SO_4 and $(NH_4)_2SO_4$ and the CO_3^{2-} in $(NH_4)_2CO_3$, were more effective at competing with P for precipitation with Ca^{2+}, compared to Cl^- or NO_3^- species (Parfitt 1978; Rajan 1978; Satnam et al., 1996; Kumaragamage, 2004). The results showed that the concentration of water-extractable P on addition of Cl^- or NO_3^- salts was consistently lower or similar to that of KH_2PO_4 alone (Table 3.3). In contrast, SO_4^{2-} salts were consistent at enhancing the water solubility of P compared to KH_2PO_4 alone, while the effect of CO_3^{2-} on water-extractable P changes depending on the accompanying cation.

3.4.5 Chemical Retardation of Added Phosphorus

The retardation of phosphate movement in the treatments was estimated by calculating the apparent diffusion coefficient of P for each treatment. The diffusion coefficient of P simply controls the diffusive transport of phosphate ion through the bulk solution to the root surface (Nye and Barber, 1977; Bhadoria et al., 1991a). The apparent diffusion coefficient of P was estimated by considering the interactions of P with soil particles (adsorption process) and with soil chemical components (precipitation reactions).

According to Bhadoria et al. (1991*b*), the diffusion coefficient of P is inversely related to P buffering capacity, a parameter that describes the ability of P in the solid phase to maintain the concentration of P in soil solution as P is being depleted. Therefore, an increase in the buffering capacity of P decreases both the solution-P concentration and the extent of P movement to the plant roots. Similarly, the apparent P diffusion coefficient derived for each treatment in the present study is considered as the controlling-factor that governs the depth of P penetration in such treatment. As such, this coefficient is inversely related to the chemical retardation of P movement in the soil solution. In this study, retardation of P movement was assumed to be mainly due to the precipitation reaction of P with the displaced Ca^{2+}. Hence, a higher value of apparent diffusion coefficient in a treatment implies a lower magnitude of P retardation.

Konstantinos et al. (2004) calculated a maximum value of 4×10^{-15} cm^2 s^{-1} for the apparent diffusion coefficient of P in water treatment residuals at room temperature. The chemical retardation of P movement in each treatment for this experiment was illustrated by a mathematical model that measured the apparent diffusion coefficient of P in the soil column. The underlying assumption to this model is that, the diffusion curve obtained from the water extractable P profile of each treatment was described by the equation of a normal distribution curve. The apparent diffusion coefficient was then determined by a relationship stated below:

$$D_a = \sigma^2 / 2t \qquad\qquad\qquad [3.1]$$

Equation [3.1] was derived by considering a solute transport exclusively under transient state diffusion mechanism, as described by Fick's second law of diffusion:

$$\frac{\partial C}{\partial t} = \frac{D \partial^2 C}{\partial x^2} \qquad\qquad\qquad [3.2]$$

The analytical solution of the above equation is given as;

$$C = \frac{1}{(\sqrt{4 \pi D t})} \, e^{\,-x2/4Dt} \qquad\qquad [3.3]$$

In a Standardized Normal Distribution Curve, the peak height is expressed as;

$$\text{Peak height} = \frac{1}{(\sqrt{2} \pi) \sigma} \qquad\qquad [3.4]$$

Given that x = 0 in equation [3.3], the concentration term, C, is synonymous to the peak height in equation [3.4]. Therefore;

$$\frac{1}{(\sqrt{4 \pi D t})} = \frac{1}{(\sqrt{2} \pi) \sigma} \qquad\qquad [3.5]$$

$$\frac{(\sqrt{4 \pi D t})}{(\sqrt{2} \pi)} = \sigma \qquad\qquad [3.6]$$

Squaring both sides, equation [3.6] becomes;

$$\sigma^2 = \frac{4\pi D t}{2\pi} \qquad\qquad [3.7]$$

$$\sigma^2 = 2 D t \qquad\qquad [3.8]$$

$$D = \sigma^2 / 2 t \qquad\qquad [3.9]$$

In equation [3.9], D is the diffusion coefficient of the solute, σ is the standard deviation of mean of the idealized distribution; which constitutes 68% of the observations measured on the distribution curve (Moore, 1994). The term t stands for time expressed in seconds. Equation [3.9] is related to equation [3.1]; the term D is equivalent to the apparent diffusion coefficient, D_a, of phosphate ion in the soil column. Also, σ represents the depth of the column on the water extractable P profile, which produced a magnitude of unit area that is equal to 68% of the total area of the diffusion curve on the

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water extractable P profile. The term t denotes the time taken for the diffusion of phosphate ion in the column, which is equal to the two-week incubation period.

The total area of the diffusion curve on the water extractable P profile was calculated by an analytical solution of the definite integral equation of the polynomial function for each curve. The lower limit of the integral equation (0.3 cm) is common to all the treatments. On the other hand, the upper limit represents the maximum depth traversed by P in each profile, and the value varies between treatments.

Figure 3.7 summarized the apparent diffusion coefficients as calculated using the above approach. The values of these coefficients vary between treatments. Contrasting each treatment with KH_2PO_4 ALONE treatment, Figure 3.7 showed that the apparent diffusion coefficients of some treatments are smaller than the D_a measured in KH_2PO_4 ALONE treatment. A number of these treatments appeared to enhance the water solubility of P at the region close to the surface of the column, but the diffusive transport of P was consequently restricted in the columns. Such treatments include $(NH_4)_2CO_3$ and $MgCO_3$. On the other hand, some treatments resulted in lower solubility of P with marked retardation of P movement. These include KCl and K_2CO_3.

Other treatments with lower concentration of soluble P increased the depth of P penetration extensively in the soil column. This result was most noticeable in the $MgSO_4$ treatment, which had the highest value of apparent diffusion coefficient. While some treatments enhanced the solubility of P, the depth of P transport was also increased in the columns. The apparent diffusion coefficients of these treatments were also greater than that obtained for KH_2PO_4 ALONE. Such treatments are K_2SO_4 and $(NH_4)_2SO_4$.
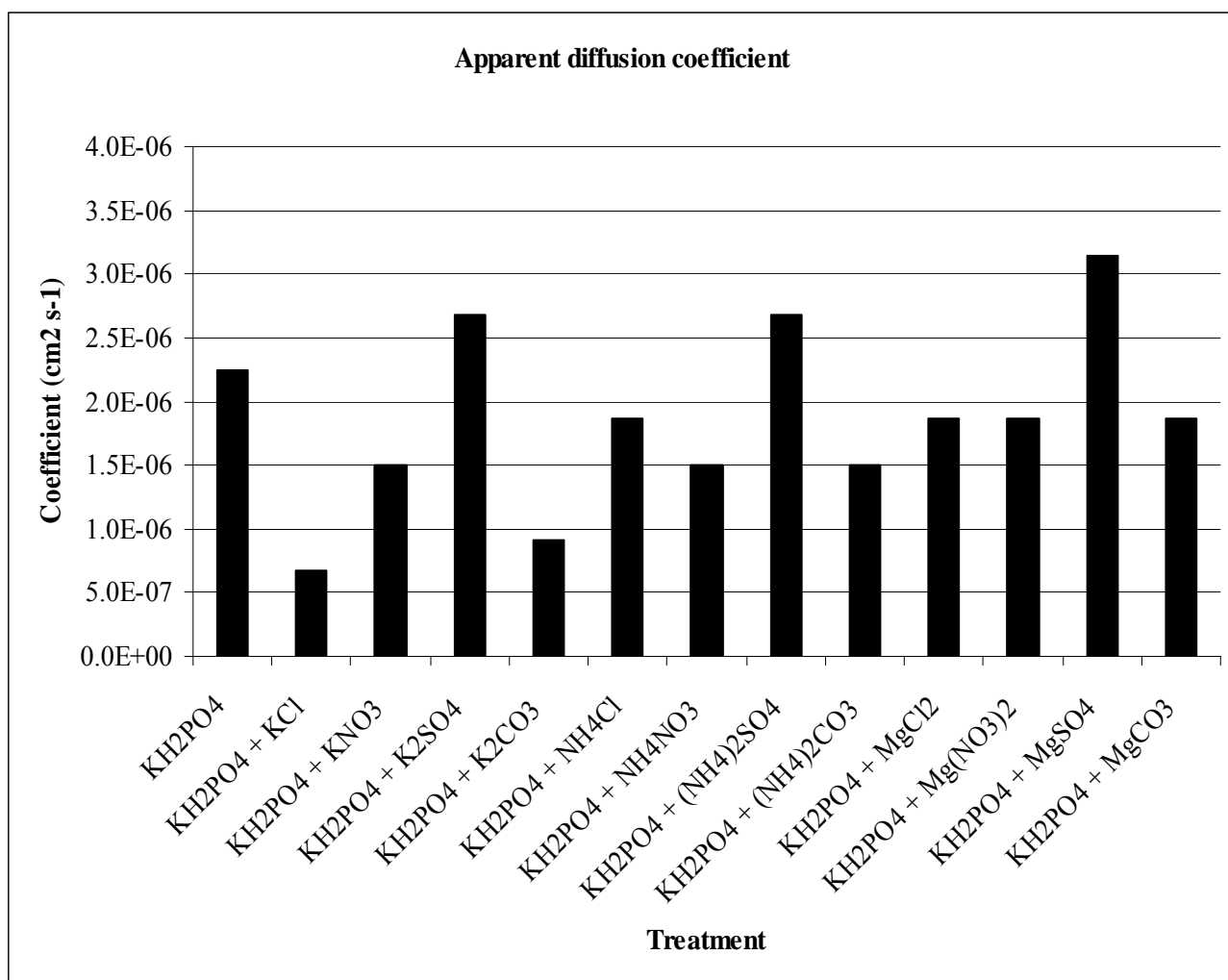
Figure 3.7 Apparent diffusion coefficient of P in the dual band treatments after 2 weeks of incubation.

These results suggest that increase in the water solubility of P did not always enhance the depth of P penetration in some treatments. However, other treatments such as K_2SO_4 and $(NH_4)_2SO_4$ were able to increase both the solubility of P in the reaction zone and the mobility of phosphate ion in the column. Therefore, the co-application of the ionic components of these treatments with P fertilizer compound would be considered to favour the transport of P to the plant roots and its consequent uptake.

3.5 Summary and Conclusions

This study characterized the effects of various cationic and anionic compositions in the P dual bands, on H^+ ion movement and the transformation of the applied phosphate. While the combination of $MgCl_2$ or $MgSO_4$ with KH_2PO_4 produced the greatest concentration and transport of H^+ ion from KH_2PO_4, the addition of K_2CO_3 to KH_2PO_4 increased the column pH compared to that of KH_2PO_4 alone as a result of significant consumption of H^+ ion. Addition of NO_3^- or Cl^- salts did not increase the water solubility and transport of P, compared to KH_2PO_4 alone in all cases. The co-application of SO_4^{2-} salts, however, increased the water solubility and mobility of P more consistently than any other salts. Such effects are attributed to the combined roles of significant pH reduction and anionic competition of SO_4^{2-} ion with P for precipitation with the reactive Ca^{2+}.

The cation effects were related to the effectiveness of the individual cation associated with each salt to replace the exchangeable Ca^{2+}. The results indicated that

NH_4^+ had the greatest effect in increasing the water solubility and movement of P, while Mg^{2+} resulted in marked precipitation of P through the combined effect of the displaced Ca^{2+} and the interactions of HPO_4^{2-} with Mg^{2+}. We conclude that the combination of significant pH reduction, cation effect of NH_4^+ ion and anionic competition of SO_4^{2-} species, enhanced the water solubility and depth of P penetration in the resin-sand columns following two weeks of incubation. Therefore, we suggest that the dual application of $(NH_4)_2SO_4$ with P fertilizer would enhance the solubility and mobility of P in calcareous soils.

The results of the previous study showed that the addition of $(NH_4)_2SO_4$ or K_2SO_4 to $NH_4H_2PO_4$ or KH_2PO_4 increased the water-extractable P and the transport of P in soil solution, compared to adding either of the phosphate salts alone. The present study also revealed that the addition of $(NH_4)_2SO_4$ or K_2SO_4 to KH_2PO_4 was consistent with the results obtained in the first study. The co-application of $(NH_4)_2CO_3$ with KH_2PO_4 also increased the water solubility of P compared to KH_2PO_4 alone in the present study, while the addition of K_2CO_3 to KH_2PO_4 resulted in a significant reduction of the solubility and movement of P compared to KH_2PO_4. Therefore, it will be interesting to verify the effects of the interactions of $(NH_4)_2SO_4$, K_2SO_4, $(NH_4)_2CO_3$ or K_2CO_3 with KH_2PO_4 on the solubility and diffusion of phosphate in real soil columns.

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4. CHEMICAL DIFFUSION AND SOLUBILITY OF PHOSPHATE IN SOIL COLUMNS

4.1 Abstract

Conversion of P into less soluble forms minimizes fertilizer P recovery and crop utilization of P. Measures to rectify this problem include the modification of the chemical environment of soil-P fertilizer reaction zone through co-application of non-phosphatic salts with fertilizer P. In this study, we tested the effects of various combinations of salts selected from the previous experiments on the chemical diffusion and solubility of phosphate ion in two soils. This experiment was established as a factorial design. One factor was five types of salt combinations namely: KH_2PO_4; $KH_2PO_4+(NH_4)_2SO_4$; $KH_2PO_4+(NH_4)_2CO_3$; $KH_2PO_4+K_2SO_4$ and $KH_2PO_4+K_2CO_3$, denoted as MKP ALONE, MKP+ASU, MKP+ACB, MKP+KSU and MKP+KCB, respectively. The second factor consisted of two soil types: Ramada loam and Dezwood loam. The treated soil columns were incubated for a period of two weeks after which samples were obtained by sectioning the columns at 3 mm interval to a depth of 6.0 cm. Each sample was extracted with water at 1:5 soil to solution ratio and subsequently with 1 M HCl, which were both analysed for inorganic P. Prior to treatment application, the original pH of the Ramada soil was 6.2 while that of Dezwood was 7.3. The addition of MKP ALONE treatment reduced the soil pH at the site of application to 5.4 and 6.0 in

Ramada and Dezwood soil, respectively. The addition of MKP+ASU treatment to Ramada or Dezwood soil column produced the lowest pH compared to the addition of other treatments, while the addition of MKP+KCB treatment increased the column pH at the surface by 2.0 and 1.6 units compared to that observed with MKP ALONE in Ramada and Dezwood soil, respectively. While MKP ALONE treatment reduced the soil pH compared to the control in the Ramada soil, the magnitude of pH reduction was similar for MKP ALONE and MKP+KSU treatment in the Dezwood soil column. The addition of MKP+ACB treatment slightly increased the soil pH in the first 0.6 cm depth compared to MKP ALONE, below which the pH dropped significantly in the MKP+ACB treatment. The main effect due to soil type, salt combination, as well as the interaction of soil type with salt was significant on the water-extractable P ($P < 0.05$). The depth of P penetration was restricted to the top 2.0 cm in all treatments in the Ramada soil. In contrast, the greatest depth of P penetration occurred on addition of MKP+ASU to the Dezwood soil as P travelled to 2.7 cm in the column. Statistical analysis of treatment means also indicated that co-application of all salts with MKP reduced the water-extractable P in the Ramada soil compared to MKP ALONE, while the highest concentration of soluble P was observed on addition of MKP+ASU to the Dezwood soil ($P < 0.05$). Although MKP+ASU treatment caused a decrease in the water solubility of P compared to MKP ALONE in the Ramada soil, the increase in water solubility and movement of P from adding ASU to MKP in the Dezwood soil was consistent with the results obtained in the buffered resin-sand system.

4.2 Introduction

The reduced efficiency of phosphate fertilizer in high pH soils is primarily due to the retardation of P movement in the soil-P fertilizer reaction zone. This retarded movement is caused by rapid reactivity and affinity of the applied P with soil particles and chemical components. The reactivity of the applied P with soil chemical components in alkaline to calcareous soils is mainly by the interactions of P with the exchangeable calcium and magnesium displaced into soil solution. These soil components form a series of reaction products with P, with varying degree of solubility (Lindsay et al., 1962; Sample et al., 1980; Akinremi and Cho, 1991). On the other hand, the retention of P by soil particles involves the adsorption of P to the surfaces of clay minerals (Olsen and Watanabe, 1963), organic matter (Bhatti et al., 1998), as well as $CaCO_3$ and $MgCO_3$ in calcareous soils (Holford, 1983; Andrade et al., 2002).

The resulting slow-releasing P fractions following the reactions of P with soil constituents, therefore, impede early season plant nutrition of P (Grant et al., 2001) by lowering the availability of applied P. The accumulation of these less soluble P forms in soil consequently intensify the risk of P loss to adjacent water bodies through surface and sub-surface pathways (Sharpley et al., 2000). Researchers in the past have shown that the retardation of P movement following its reactivity with soil components consequently reduced the solution concentration of P (de Camargo et al., 1979; Eghball and Sander, 1989; Eghball et al., 1990). As such, the equilibrium concentration of P in the soil solution phase is one of the dominant factors controlling the mobility of P in soil (Silberbush and Barber, 1984).

The present study is established on the findings gathered from the two previous studies conducted using columns containing a mixture of Ca^{2+}-saturated cation exchange resin and $CaCO_3$-coated sand. The first study showed that the addition of either $(NH_4)_2SO_4$ or K_2SO_4 to $NH_4H_2PO_4$ or KH_2PO_4 increased the solubility and transport of P in soil solution compared to the phosphate salts alone. Similarly, the second study revealed that the addition of $(NH_4)_2SO_4$ or K_2SO_4 to P (KH_2PO_4 in this case) was consistent with the results obtained in the first study, while the co-application of $(NH_4)_2CO_3$ with KH_2PO_4 also increased the solubility of P compared to KH_2PO_4 alone. In contrast, however, the addition of K_2CO_3 to KH_2PO_4 resulted in a significant reduction of the solubility and movement of P compared to adding KH_2PO_4 alone.

The resin-sand mixture was a simplified model system that eliminates various interferences encountered in natural soils. However, it is necessary to verify and validate the findings made earlier in the resin-sand system with the aid of soil columns, to extend knowledge of the behaviour of P in soil into a practical environment. The objective of this study was to investigate the effects of the various combinations of salts selected from the previous experiments, on the chemical diffusion and solubility of phosphate ion in two natural soils.

4.3 Materials and Methods

The soils used in this study are Ramada loam and Dezwood loam that were collected from a depth of 0 – 15 cm. The legal description and location, as well as the pertinent properties of these soils are given on Table 4.1. Each soil was air dried and passed through a 2 mm mesh sieve prior to use. Wax columns, similar to those used in the previous studies, were used with the exception that these columns were packed with natural soil, rather than the buffered resin-sand mixture. The soil was packed into the column at a bulk density of 1.2 Mg m^{-3} and wetted at the surface to their respective field capacity (Table 4.1). The wetted soils were allowed to equilibrate for 72 hours before treatment application.

The treatment combinations for this experiment are described on Table 4.2. To maintain consistency with the previous study, the P source used for this study was monopotassium phosphate salt (KH_2PO_4). The preference of KH_2PO_4 to $NH_4H_2PO_4$ in the present experiment was necessary to avoid the complications due to microbial nitrification of the component NH_4^+ in $NH_4H_2PO_4$ in the soil columns. This was added at a concentration of 45.6 mg P per column, exactly one-half of what was used in the previous study. Following the application of treatments, the columns were set into an incubator as described in the previous studies at 20 ℃ for a period of two weeks. Duplicate columns were prepared for each soil, and columns were segmented at 3 mm intervals to a total depth of 6.0 cm.

The H$^+$ ion concentration in the soil sample was measured at 1:1 soil to solution ratio with an Accument Model AR50 digital pH meter (Fisher Scientific Ltd., Winnipeg, MB, Canada) fitted with a combination electrode. The extraction procedure was

Table 4.1 Selected properties of the soils used for the soil column study

Property	Ramada loam	Dezwood loam
Legal description	Orthic Black Chernozerm	Orthic Dark Gray Luvisol
Legal location	8-Tp11-Rge14-W1	6-Tp5-Rge7-W1
$CaCO_3$ (% Eq.)	0.30	0.42
Dolomite (% Eq.)	0.17	0.27
CEC ($cmol_c$ Kg^{-1})	30.5	24.7
[1]Field Capacity (%)	26.3	24.3
[2]% sand	29	41
% silt	40	34
% clay	31	25
pH (1:1in water)	6.2	7.3
[3]Exch Ca^{2+} ($cmol_c$ Kg^{-1})	16.6	18.9
Exch Mg^{2+} ($cmol_c$ Kg^{-1})	5.04	3.97
Exch K^+ ($cmol_c$ Kg^{-1})	0.66	0.68
Exch Na^+ ($cmol_c$ Kg^{-1})	0.12	0.05
Exch Al^{3+} ($cmol_c$ Kg^{-1})	0	0
Exch Fe^{3+} ($cmol_c$ Kg^{-1})	0	0
[4]Water-P (μg P g^{-1} soil)	4.10	1.94
[5]Acid-P (μg P g^{-1} soil)	297.0	223.5
[6]$NaHCO_3$-P (μg P g^{-1} soil)	55.4	31.6

[1]Moisture content at field capacity on weight basis.
[2] Source: Manitoba Soil Survey Report.
[3]Exchangeable Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+} and Fe^{3+} in $cmol_c$ Kg^{-1}.
[4]Water extractable P at soil to water ratio of 1:5 in μg P g^{-1} soil.
[5]Acid (1 *M* HCl) extractable P fraction of the soil following water extraction in μg P g^{-1} soil.
[6]$NaHCO_3$ extraction method (pH 8.5) in μg P g^{-1} soil.

Table 4.2 Treatment combinations and mass of salts applied per column

Treatment	Salt	Mass of salt per column (mg)	mmol P per column	[1]mmol cation per column	[2]mmol anion per column
MKP	KH_2PO_4	200	1.47	1.47	None
MKP+ASU	KH_2PO_4 +	200	1.47	1.47	None
	$(NH_4)_2SO_4$	97		1.47	0.73
MKP+ACB	KH_2PO_4 +	200	1.47	1.47	None
	$(NH_4)_2CO_3$	71		1.48	0.74
MKP+KSU	KH_2PO_4 +	200	1.47	1.47	None
	K_2SO_4	128		1.47	0.74
MKP+KCB	KH_2PO_4 +	200	1.47	1.47	None
	K_2CO_3	102		1.48	0.74

Equivalent mass of P (45.6 mg P per column) was applied in all the treatments.
[1]Amount of cation present in the salt, in mmol (+) per column.
[2]Amount of anion present in the salt, in mmol (-) per column.

performed in a similar fashion to the two previous experiments, except that the soil sample was shaken for 1 hour during the water-extraction procedure, instead of the 15 minutes shaking used in the resin-sand experiments.

Inorganic phosphate in both extracts (water and 1 M HCl), was determined by the ascorbic acid-ammonium molybdate method of Murphy and Riley (1962). The concentration of P measured in the water-extracts represents the amount of P in the mobile phase and that of acid-extracts approximates the solid phase P. The concentration of inorganic P in each segment was plotted against distance to provide the distribution of phosphate ions in the soil columns.

Effect of treatments means on P solubility and retention was compared using the Least Significant Difference (LSD) test at 0.05 level of significance. Also, the main effects due to soil types and salts, and the interactions between the two factors were analyzed by two-factor analysis of variance (ANOVA), using the General Linear Models (GLM) procedure of SAS software for Windows, version 9.1 (SAS Institute, Inc., Cary, NC).

4.4 Results and Discussion

Although the two soils contained equivalent amount of exchangeable cations and small amounts of $CaCO_3$ (0.2-0.5%), the contrasting chemical properties of the two soils pertinent to this study are basically the cation exchange capacity (CEC) and pH status (Table 4.1). Comparison of the physical properties of both soils indicates that the proportion of sand particles in the Ramada soil was smaller than that of Dezwood. However, the clay content of both soils was quite similar and this probably accounts for the similarity in their gravimetric moisture content at field capacity.

The water content of both soils is shown on Figure 4.1. The moisture distribution in these soils was slightly different from those observed in the resin-sand columns. Figure 4.1 showed that the soil water content was slightly higher in the first 1.2 cm and 1.0 cm depth of the Ramada and Dezwood soil columns, respectively. It appeared that the surface layer held onto more water than other portion of the columns. This may be due to variability in pore size distribution of the real soils, unlike the resin-sand mixture which comprised a uniform pore size distribution. However, beyond the top 1.5 cm depth in both soil columns, there was a complete uniformity in moisture profile. Overall, the water content can be said to be relatively uniform within the column, as there was no sign of significant evaporation and upward movement of water. These profiles also confirmed that the mode of ion transport was mainly by chemical diffusion.
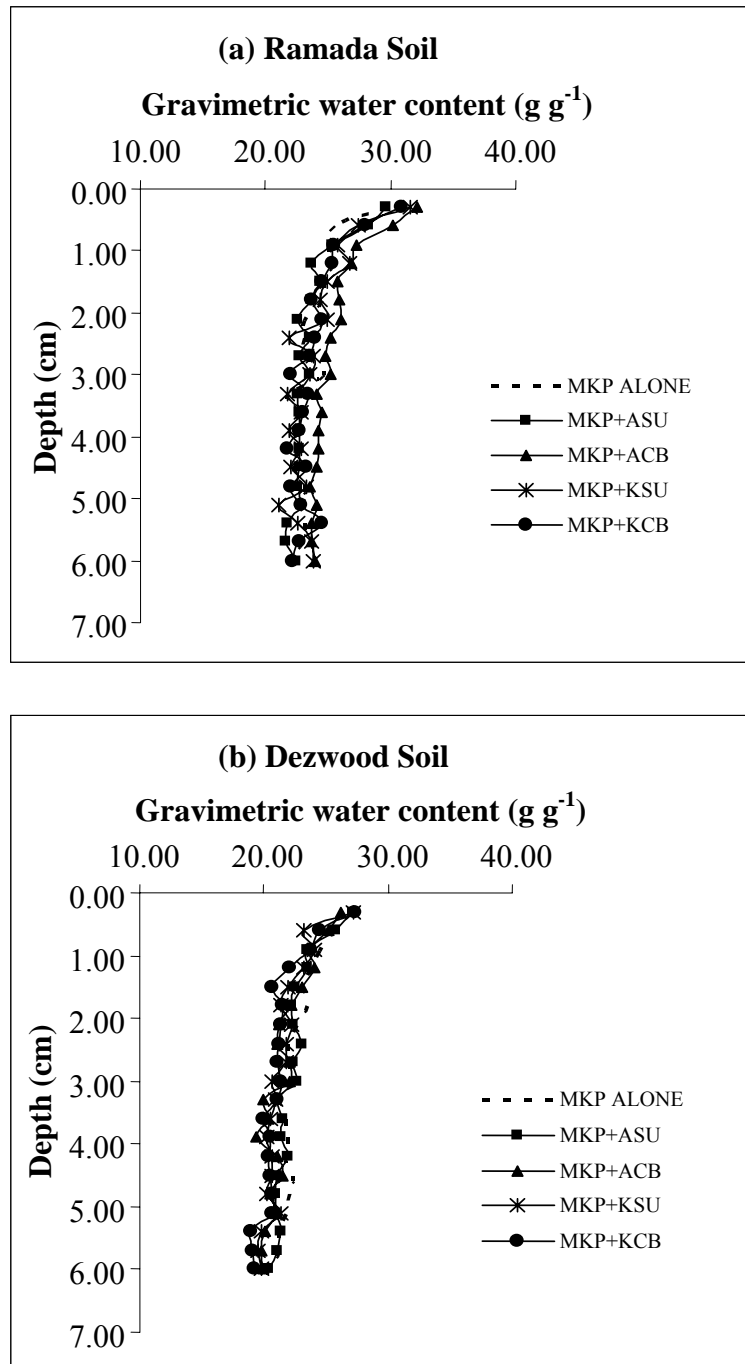
Figure 4.1 Gravimetric water content after 2 weeks of incubation in (a) Ramada and (b) Dezwood soil treated with dual band P.

4.4.1 The pH Profile

The pH profile of Ramada soil is illustrated in Figure 4.2a. At the site of salt application, the addition of MKP+ASU treatment significantly reduced soil pH in comparison to MKP ALONE. The diffusion of H^+ ions from the dissolution of MKP+ASU treatment reduced the column pH within the top 3.0 cm portion of the soil column, as indicated by the region of lower pH compared to MKP ALONE. The effect of MKP+KSU and MKP ALONE treatment on column pH was similar at the surface of the column, while MKP+ACB slightly increased the soil pH at the surface compared to MKP ALONE. However, beyond 1.2 cm depth from the surface, a lower pH zone was observed in the column treated with MKP+ACB, compared to MKP+KSU or MKP ALONE. Thereafter, the pH pattern in MKP+ACB treatment was similar to that in the MKP+ASU column.

In soil, unlike in the resin system, microbial oxidation of NH_4-N to NO_3-N along the diffusion front produced H^+ ions which contributed to the greater pH reduction observed in MKP+ASU and MKP+ACB treatment, respectively. The production of H^+ ion in dual N-P bands through biological oxidation of NH_4^+ in soil had been reported by other authors (Isensee and Walsh, 1971; Flaten, 1989; Fan and MacKezie, 1993; Kumaragamage et al., 2004).

In contrast, the addition of MKP+KCB treatment to Ramada soil column did not decrease pH, as the pH was slightly increased at the surface by 2.0 units of the pH observed with MKP ALONE. The distribution of H^+ ion in the column containing MKP+KCB treatment followed the same pattern as the background soil throughout the remaining portion of the column. Beyond 3.0 cm depth from the surface, hydrogen ion
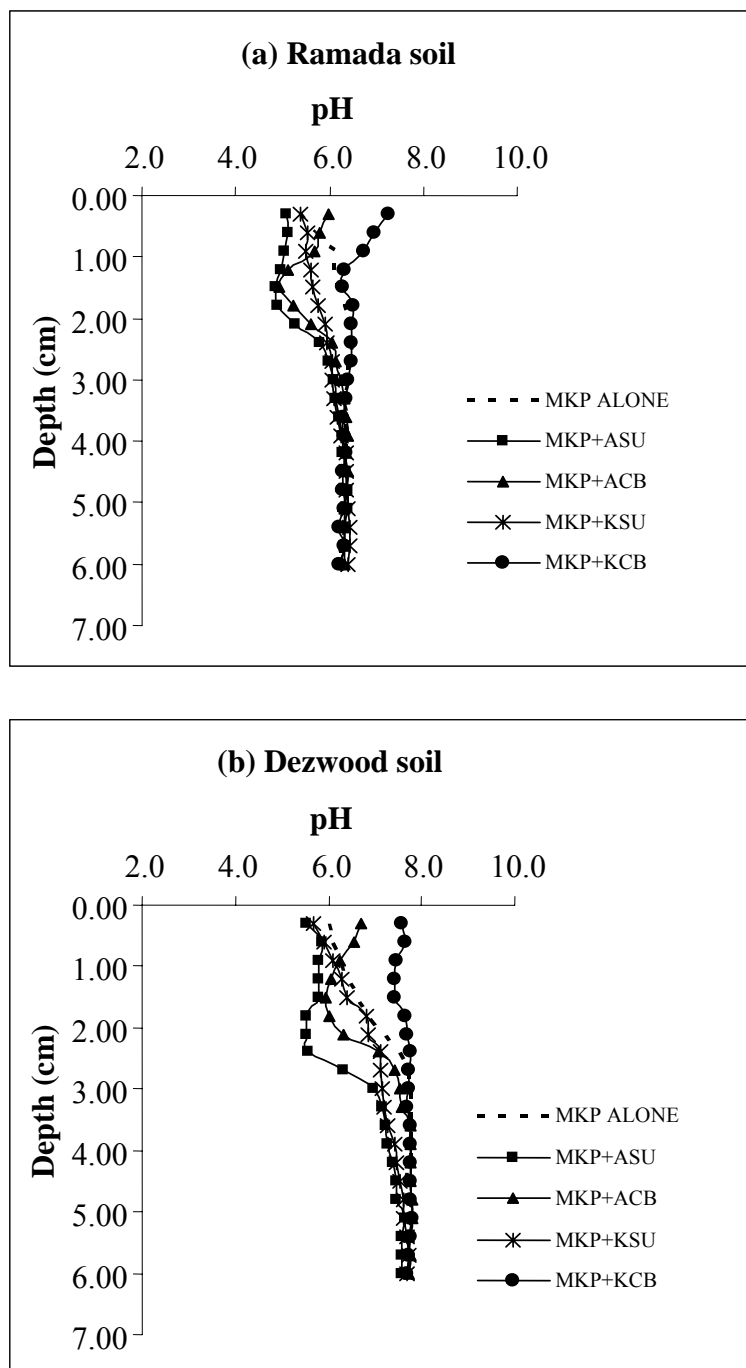
Figure 4.2 Hydrogen ion distribution after 2 weeks of incubation in (a) Ramada and (b) Dezwood soil treated with dual band P.

distribution was uniform in all treatments in the Ramada soil and similar to that of the background soil. This uniformity in pH level is an evidence for the consumption of H^+ ion by the buffering action of the Ramada soil components.

Nearly all treatments applied to the Dezwood soil columns exhibited similar features of H^+ ion distribution as those observed in the Ramada soil columns. However, there was a greater reduction in pH in the Dezwood soil columns, indicating a smaller buffering capacity than the Ramada soil. Other distinguishing features of pH profiles in the Dezwood soil system include the similarity in H^+ ion distribution between MKP+ASU and MKP+KSU treatments within the first 6 mm depth. Afterwards, however, H^+ ion moved deeper into the column in MKP+ASU treatment while the column pH increased slightly with depth in MKP+KSU treatment. Similar to the Ramada soil, the addition of MKP+KCB treatment to Dezwood soil increased the column pH at the surface by 1.6 units of the pH observed with MKP ALONE. The pH profile of MKP+KCB treatment in the Dezwood soil was similar to that observed on addition of K_2CO_3 salt to KH_2PO_4 in the resin-sand column.

In general, the maximum depth of H^+ ion movement in Ramada soil columns was restricted to 3.0 cm, while the depth of penetration of H^+ ion extended to approximately 4.0 cm in the Dezwood soil. It is evident that the Dezwood soil was less buffered against pH changes as compared to Ramada soil, although the original pH of the Dezwood soil was higher than that of the Ramada soil. These results suggest that the effect of pH reduction due to salt addition was more significant in the Dezwood soil system. As such, it is expected that P would be more soluble in the Dezwood soil columns in the form of $H_2PO_4^-$. Moreover, Table 4.1 showed that the exchange sites of both soils did not contain

any trace of Al^{3+} and Fe^{3+}, which are known to precipitate the monovalent phosphate species under a low soil pH condition (pH < 6.0) (Sample et al., 1980; Hinsinger, 2001).

We found, from the two previous studies, that pH may not be the only important factor influencing the fate of P as other factors such as cationic and anionic competition can override the pH effect. However, the pH of the system also affected the solubility and transport of P in some treatments particularly in the differences between the effects of adding the CO_3^{2-} species to each cation system. The dissolution of KH_2PO_4 salt and speciation of phosphate ion are described below as:

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

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad\qquad [4.2]$$
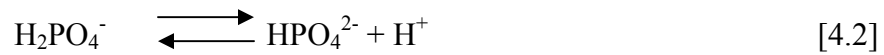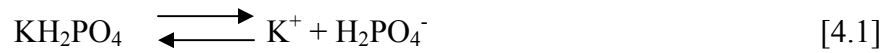
The equilibrium relation in equation [4.1] is governed by the solubility of KH_2PO_4 while that of [4.2], which is a dissociation reaction of $H_2PO_4^-$, is governed by the second dissociation constant (K_2) of phosphoric acid (H_3PO_4). At pH 7.2, there is equal amount of HPO_4^{2-} and $H_2PO_4^-$ in solution.

$$\frac{(H^+) \times (HPO_4^{2-})}{(H_2PO_4^-)} = K_2 = 10^{-7.2} \qquad\qquad [4.3]$$

Below 7.2 $H_2PO_4^-$ predominates, and at pH greater than 7.2 HPO_4^{2-} predominates. At pH 7.2 there is equal quantity of HPO_4^{2-} and $H_2PO_4^-$. This is by virtue of equation [4.3]. At pH 7.2 the equation [4.3] becomes:

$$\frac{(10^{-7.2}) (HPO_4^{2-})}{(H_2PO_4^-)} = K_2 = 10^{-7.2} \qquad\qquad [4.4]$$

Rearranging, we have:

$$\frac{(HPO_4^{2-})}{(H_2PO_4^-)} = \frac{10^{-7.2}}{10^{-7.2}} = 1.0 \qquad\qquad [4.5]$$

If pH = 5.0, equation [4.5] becomes:

$$\frac{(HPO_4^{2-})}{(H_2PO_4^-)} = \frac{10^{-7.2}}{10^{-5.0}} = \frac{1}{100} \qquad\qquad [4.6]$$

Thus, there are 100 times $H_2PO_4^-$ compared to HPO_4^{2-} in the soil solution at pH of 5.0.

According to Lindsay et al. (1962), the pH of a solution in equilibrium with KH_2PO_4 salt is approximately 4.0. This indicates that the addition of KH_2PO_4 alone as a treatment has an acidifying effect on soil pH, and such was the case in both soils (Figure 4.2). Apparently, the ratio of (HPO_4^{2-}) / $(H_2PO_4^-)$ stated in equation [4.5] above would be less than 1.0 on addition of KH_2PO_4 salt. This implies that the $H_2PO_4^-$ species would be dominant in soil solution. As such, the extent of Ca-P precipitation reactions would be minimized. However, the acidifying effect associated with the dissolution of KH_2PO_4 salt was diminished by the buffering action of the soil components (Figure 4.2).

Past works (Isensee and Walsh, 1971; Teng and Timmer, 1995; Kumaragamage et al., 2004) have shown that mixing non-phosphatic salts with P had a significant effect on soil solution pH. In view of this, the pH profiles shown on Figure 4.2 support the evidence reported by these past authors. This observation was also confirmed by the results obtained in our previous studies with resin-sand system. Unlike the resin-sand system, however, there were more sinks in the soil for the protons produced from the dissolution of the added salts. These sinks include soil organic compounds and clay particles with negatively charged sites, and the dissolution of various soil solid components such as $CaCO_3$ and $(CaHPO_4)_2.2H_2O$ (Xie and Mackenzie, 1990; Cho, 1991).

4.4.2 Effect of Dual Banding on Water-Extractable Phosphorus

The main effect of soil type was significant on the water-extractable and acid-extractable P ($P < 0.05$). In contrast, effect due to salt addition significantly influenced the solubility of P but no significant effect on phosphate retention (Table 4.3). The statistical analysis also showed that significant interaction exists between the effect of soil type and salt addition on P solubility and retention. This significant interaction indicates that effect of salt was not consistent across soils. The curve obtained for each treatment represents the mean of two replicates. The water-extractable P profile showed that the addition of non-phosphatic salts to MKP modified the distribution of phosphate ion in both soils (Figure 4.3).

Table 4.3 The GLM analysis on the water- and acid-extractable P in soil columns after 2 weeks of incubation

Source of variation	d.f.	Water-extractable P	Acid-extractable P
		Mean square value	
Soil	1	8.42 *	19.25 *
Salt	4	1.00 *	3.73 *ns*
Soil x Salt	4	7.72 *	48.61 *
Error	10	0.19	3.43

 * Significant at $P < 0.05$. *ns* indicates not significant at $P < 0.05$.
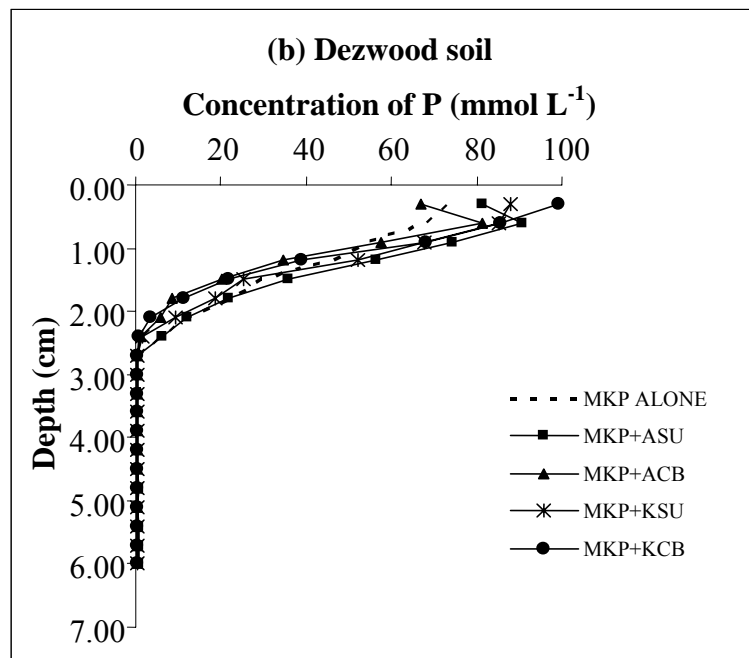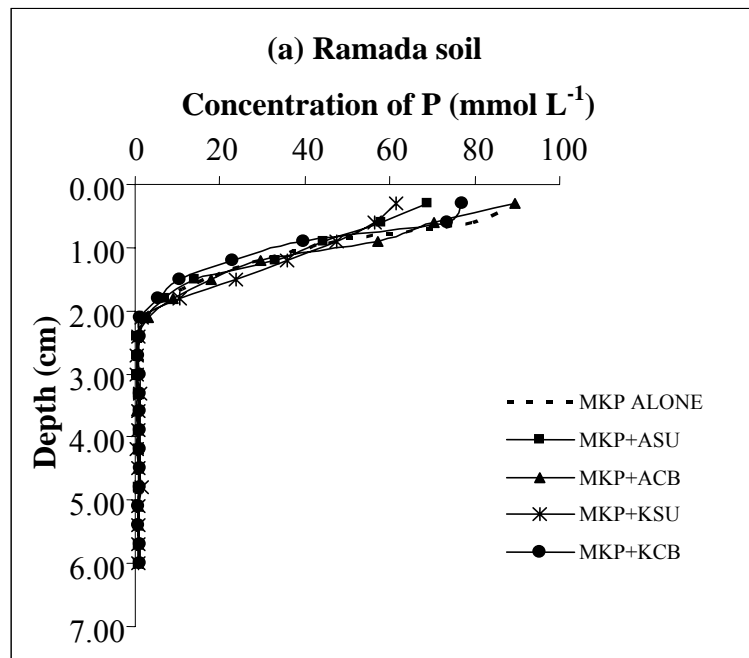
Figure 4.3 Distribution of water-extractable P after 2 weeks of incubation in (a) Ramada and (b) Dezwood soil treated with dual band P.

In the Ramada soil columns, maximum concentration of water soluble P occurred at the point of salt application and the magnitude of P in soil solution decreased considerably with depth as P diffused into the column (Figure 4.3a). Except for MKP+ACB treatment, the addition of other dual band treatments generally reduced the solubility of P at the point of salt application, compared to MKP ALONE. On the other hand, the magnitude of water-extractable P was similar between MKP+ACB and MKP ALONE treatment close to the surface of the column.

The least water soluble P was found in MKP+KSU and MKP+ASU treatment within the top 1.0 cm depth. Beyond this zone, however, the movement of P increased slightly in the reaction zone of MKP+KSU treatment, while the greatest retardation of P movement occurred in MKP+KCB. Figure 4.3a also indicated that the addition of MKP+ACB treatment produced a greater solubility of P, compared to other dual bands, in the first 1.0 cm depth and subsequently enhanced the diffusion of P in the reaction zone of Ramada soil. Overall, the maximum depth traversed by P in all treatments in the Ramada soil was restricted to the top 2.0 cm zone of the column.

The effect of MKP+ASU (KH_2PO_4+$(NH_4)_2SO_4$) treatment on P solubility and movement in Ramada soil was not consistent with that obtained in the resin-sand experiments. In the Ramada soil, the application of MKP+KCB (KH_2PO_4+K_2CO_3) treatment increased the water solubility of P, compared to adding $(NH_4)_2SO_4$ or K_2SO_4 to KH_2PO_4, whereas both $(NH_4)_2SO_4$ and K_2SO_4 enhanced the water solubility of P in the resin-sand system. Although both treatments (MKP+ASU and MKP+KSU) depressed the soil pH more than by MKP ALONE, it is obvious that the reduced concentration of water-extractable P on addition of ASU or KSU to MKP in Ramada soil was not due to

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pH reduction. More so, the addition of MKP+ACB treatment also depressed the column pH more than it was with MKP ALONE, particularly beyond 1.0 cm depth of the column.

According to the results obtained from the resin-sand studies, the SO_4^{2-} component of these treatments (MKP+ASU and MKP+KSU) was expected to reduce Ca/Mg-P precipitation, but results of the Ramada soil indicate the opposite. Although neither Al nor Fe was shown to be present on the exchange site of both soils, the Ramada soil, however, had a higher CEC compared to the Dezwood soil (Table 4.1). Therefore, it is possible that the addition of these SO_4^{2-} salts to Ramada soil, coupled with the high CEC of Ramada soil, promoted substantial levels of P retention processes such as immobilization of P by soil microbes and the adsorption of P to soil particles, in addition to precipitation of P by Ca and Mg in the Ramada soil column. However, the fundamental mechanisms by which the combination of the effects due to the SO_4^{2-} salts and high CEC of Ramada soil caused the marked retention of P in the Ramada soil are not clear.

At the site of salt application (the first 3 mm segment of the column) in the Dezwood soil (Figure 4.3b), the concentration of water-extractable P followed the order:

MKP+KCB > MKP+KSU > MKP+ASU > MKP ALONE > MKP+ACB

The concentration of water soluble P in MKP+ASU and MKP+ACB treatment increased in the second depth increment below the column surface. The lower water solubility of P observed at the surface of MKP+ACB and MKP+ASU columns may be due to substantial displacement of the exchangeable Ca^{2+} and Mg^{2+} as a result of the high concentration of NH_4^+ and K^+ at the site of salt application. Thereafter, the overall movement of P in the reaction zone of MKP+ACB treatment was retarded relative to

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other treatments. Phosphorus diffused to approximately 2.7 cm depth in MKP+ASU treatment; the maximum depth of P penetration observed in the Dezwood soil column, a little deeper than the movement of P in the Ramada soil.

Except for the MKP+ACB treatment, the co-application of other non-phosphatic salts with MKP increased the overall water solubility of P in the Dezwood soil system, while the greatest solubility occurred in the column treated with MKP+ASU. The addition of MKP+KSU treatment also increased the concentration of water-extractable P than that of MKP ALONE. Unlike MKP+ASU, the overall movement of P in MKP+KSU treatment was retarded in the reaction zone. The sulphate component of MKP+ASU and MKP+KSU treatment probably precipitated with Ca^{2+}/Mg^{2+} in the Dezwood soil column (Kumaragamage et al., 2004). Therefore, the effective concentration of the displaced Ca^{2+}/Mg^{2+} in soil solution was reduced, allowing the concentration of water-extractable P to increase. Similar to the Ramada soil, the addition of MKP+KCB to Dezwood soil enhanced the solubility of P near the point of salt application. However, diffusive movement of P was subsequently retarded in the soil column.

Unlike in the resin-sand system, treatment differences were small in the soil columns. This may be due to smaller amount of P added to the soil columns (45.6 mg P) which was one-half of the amounts of P applied to the resin-sand columns (91.2 mg P). The absence of large treatment differences in the soil columns may also be due to the occurrence of various additional retention processes such as immobilization and adsorption of P by soil organic matter and clay surfaces, as opposed to the retention of P in the resin-sand system which was exclusively due to precipitation reaction between Ca

and P. In addition, the high buffering capacity of the soil against chemical changes as a result of heterogeneous nature of the soil matrix may mask or minimize the effect of treatment differences in the soil columns.

4.4.3. Effect of Dual Banding on Acid-Extractable Phosphorus

Similar to the resin-sand system, higher concentration of acid-extractable P occurred in the zone near the site of salt application in each soil column (Figure 4.4). The concentration of acid-extractable P, however, declined considerably with depth. Although one-half of the P used in the resin-sand columns was added to the soil columns (45.6 versus 91.2 mg P), the proportion of acid-extractable P was the same or higher in the soil compared to that of the resin-sand system (Figure 4.4a and 4.4b). This shows that the confinement of P movement to 2.0-3.0 cm depth was due to copious precipitation of P and retention of the added P by soil constituents.

Moody et al. (1995) also observed the precipitation of P in soil columns under a high solution concentration of applied P. In the column treated with diammonium phosphate (DAP), they observed that the retention process of P due to precipitation reactions with soil Ca or Mg, governed the extent of P movement from the fertilizer band as well as the magnitude of inorganic P in soil solution.

At the surface of Ramada soil columns (Figure 4.4a), the concentration of acid-extractable P ranged from 246 to 293 mmol P L^{-1} as observed in MKP+ASU and MKP+ACB treatment, respectively. Similarly, the range of P concentration in the acid
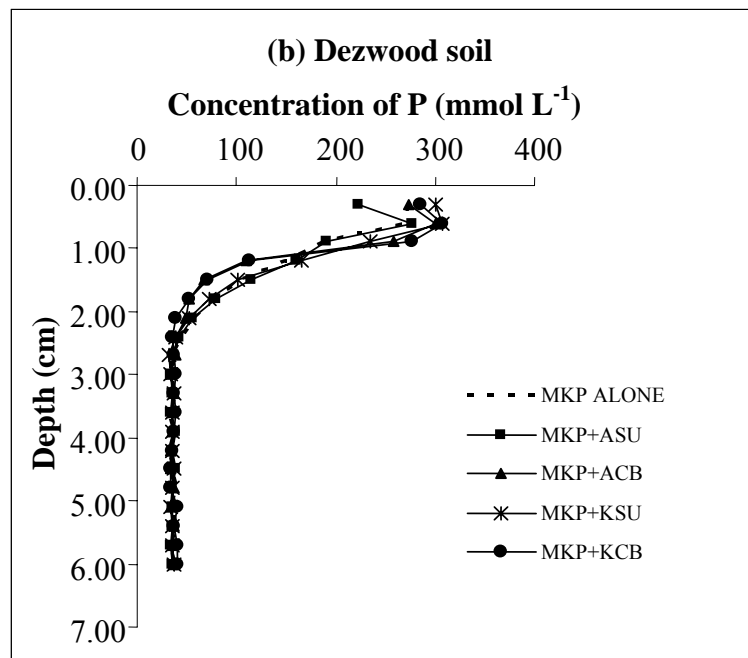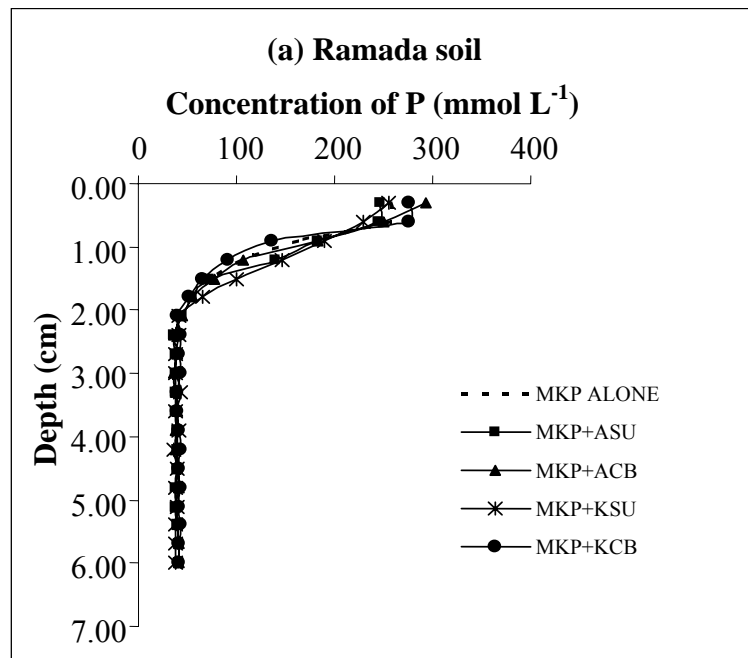
Figure 4.4 Distribution of acid-extractable P after 2 weeks of incubation in
(a) Ramada and (b) Dezwood soil treated with dual band P.

extracts measured at the surface of Dezwood soil columns (Figure 4.4b) was between 222 and 301 mmol P L^{-1} as observed in MKP+ASU and MKP+KSU treatments, respectively.

The concentration of acid-extractable P increased slightly as P diffused from the site of salt application in the Dezwood soil columns, suggesting that further retention occurred as P moved away from the surface of the column. Unlike the resin-sand system, there were little treatment differences in the distribution curves of acid extractable P in this experiment. Generally, the concentration of acid-extractable P in the columns of both soils dropped steeply from the peak to the background level. Subsequently, the zone of significant P retention was limited to the first 2.0 and 2.4 cm depth of the column in Ramada and Dezwood soils, respectively.

One of the reasons for the different observation in the soils versus resin-sand system is that, the cation compositions on the exchange sites of the soil system are more complex than those of the resin-sand mixture. The exchange complex of the resin-sand system was homo-ionic with Ca^{2+} (Akinremi, 1990), while the soil exchange sites consist of multi-ionic phases. The variety of cations on the soil exchange sites, coupled with the presence of other P retention sites, probably contributed to the smaller treatment differences in P distribution observed in the acid extractions (Figure 4.4a and 4.4b). Based on the concentration range of the applied P, it was assumed that the predominant form of P retention in this experiment was precipitation of the added P with soil Ca/Mg, (Sample et al., 1980). However, it is possible that adsorption process due to the soil clay content (Olsen and Watanabe, 1963) and soil organic matter components (Bhatti et al., 1998) occurred concurrently with precipitation reactions of the added P.

4.4.4 Mass Balance of Extractable Phosphorus

The mass balance accounted for the quantitative recovery of P through the extraction procedure as well as the degree of error involved in the column sectioning and other chemical analyses (Table 4.4). The values shown on the table represent the summation of the ionic mass of P in each 3 mm segment over the entire 6.0 cm depth of the column. These values have been corrected for the amount of both water and acid extractable native P after two weeks of incubation of the control columns of both soils.

In nearly all treatments, the percentage of P recovered in the columns of both soils was considerably higher than the amount of P added to the soil. Based on the information obtained from the acid-extractable P profile, it is possible that this over-recovery emanates from the amount of P measured in the acid extract. A possible explanation to this over-recovery is that, the combination of the effect of salt addition to the soil columns and the effect of acid extraction procedure on the column segments probably resulted in the solubilization of native P compounds. For example, the percentage recovery of extractable P was closer to 100% in the treatments where the concentration of water-extractable P was lowest i.e. MKP+KSU in Ramada and MKP+ACB in Dezwood soil.

Except for the addition of ACB treatment, the co-application of other non-phosphatic salts with MKP reduced the water solubility of P in the Ramada soil ($P < 0.05$), while the water-extractable P in MKP+ACB was not statistically different from that of MKP ALONE. Conversely, dual banding increased the water solubility of P in the Dezwood soil system, with the exception of MKP+ACB treatment. Overall, the water solubility of P was greatest on addition of MKP+ASU treatment to the Dezwood

Table 4.4 Mass balance of net P in soil columns after 2 weeks of incubation

Soil type	Treatment	[1]P added	[2]Water P	[3]Acid P	% Recovery
Ramada	MKP	45.6	13.5 *bc*	42.5 *ab*	123
	MKP+ASU	45.6	11.1 *e*	43.9 *a*	121
	MKP+ACB	45.6	13.1 *cd*	45.1 *a*	128
	MKP+KSU	45.6	10.0 *f*	35.3 *c*	99
	MKP+KCB	45.6	12.2 *d*	42.5 *ab*	120
Dezwood	MKP	45.6	12.3 *d*	39.1 *bc*	113
	MKP+ASU	45.6	14.8 *a*	37.6 *c*	115
	MKP+ACB	45.6	11.1 *e*	36.1 *c*	104
	MKP+KSU	45.6	14.1 *ab*	44.3 *a*	128
	MKP+KCB	45.6	14.0 *abc*	42.4 *ab*	124

[1] Amount of P added (mg).
[2] Net value of water-extractable P (mg) after correcting for the native P (0.9 and 0.4 mg in Ramada and Dezwood soil, respectively); the data represent average of two columns.
[3] Net value of acid-extractable P (mg) after correcting for the native P (28.3 and 25.1 mg in Ramada and Dezwood soil, respectively); the data represent average of two columns.
Means with the same letter are not statistically different according to Least Significant Difference (LSD) test ($P < 0.05$).

soil column but statistically similar to that of MKP+KSU or MKP+KCB ($P < 0.05$), while the least occurred with the application of MKP+KSU to Ramada soil.

Unlike in the resin-sand system and the Ramada soil, the addition of MKP+KCB ($KH_2PO_4+K_2CO_3$) to the Dezwood soil produced a concentration of water-extractable P similar to that of MKP+ASU or MKP+KSU ($P < 0.05$). Similar to the resin-sand system, the greatest portion of the added P was recovered with the acid extraction. This indicates that substantial magnitude of phosphate retention occurred in the soil columns.

4.5 Summary and Conclusions

This study revealed that mixing the non-phosphatic salts with KH_2PO_4 modified the chemical interactions of P in the soil-P reaction zone of both soil types. The application of MKP+ASU, MKP+ACB or MKP+KSU treatment to both soil systems reduced pH more than MKP ALONE. Conversely, the addition of MKP+KCB treatment had no significant effect on pH in either soil column.

The co-application of the non-phosphatic salts with KH_2PO_4 reduced the water solubility of P in the Ramada soil, while the dual banding increased the water-extractable P in the Dezwood soil columns, with the exception of $(NH_4)_2CO_3$ treatment. The positive influence of $(NH_4)_2SO_4$ on P solubility and movement in the Dezwood soil column indicated that a combination of certain factors have the potential to optimize the availability of fertilizer P in alkaline soils. These factors include: (1) significant pH reduction, (2) the characteristic cation exchange reaction of NH_4^+ with soil exchangeable

Ca^{2+}/Mg^{2+}, and more importantly, (3) anionic competition of SO_4^{2-} with P for Ca^{2+}/Mg^{2+} precipitation reactions. However, none of these factors accounts for the solubility and movement of P in the Ramada soil, as the addition of all the dual band treatments reduced the concentration of solution P compared to MKP ALONE treatment.

The contrasting behaviour of these dual bands in both soils suggests that, the lower cation exchange capacity (CEC) and greater magnitude of pH reduction in the Dezwood soil generally enhanced the solubility and mobility of P in the soil columns, as compared to the extent of P solubility and movement in Ramada soil columns. Overall, the salt effect observed in these soils was of smaller magnitude compared to what was reported from the resin study. This study showed that: (1) results from the resin-sand system can not be extrapolated directly to soil systems, (2) effect of salt on P mobility and solubility was soil specific and more studies are needed to identify factors that make one soil respond positively and the other not.

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5. OVERALL SYNTHESIS

Low phosphate fertilizer efficiency in high pH soils is primarily due to the retardation of P transport in the soil-P fertilizer reaction zone. This retarded movement is caused by various interactions of the applied P with soil components. Such interactions include the precipitation of P with reactive Ca^{2+} and Mg^{2+} in the soil solution. These soil cations form a series of reaction products with P, with varying degrees of solubility. Measures that have been taken to rectify this problem include the modification of the chemical environment of soil-P fertilizer reaction zone through the co-application of non-phosphatic salts with fertilizer P. Mixing various salts with fertilizer P induces changes in the pH status and in the reactions of P with soil components and other ions. These multi-ionic interactions consequently affect the concentration and movement of phosphate species in the soil solution.

In this study, we obtained fundamental information on the roles of cationic and anionic interactions on the solubility, diffusion and retention of P in various columns packed with Ca^{2+}-saturated resin-sand mixture and two soil types. The broad objective of this research study was accomplished in three experiments. In the first experiment, we investigated the chemical interactions and diffusive transport characteristics of P in the resin-sand model system, as influenced by dual application of various sulphate salts with KH_2PO_4 or $NH_4H_2PO_4$. The results showed that the addition of SO_4^{2-} salts to either a KH_2PO_4 or $NH_4H_2PO_4$ system increased the water solubility of P ($P < 0.05$) and its

movement in the reaction zone, compared to the phosphate salts alone. The enhanced water solubility and movement of P with the sulphate salts may be due to anionic competition of SO_4^{2-} with HPO_4^{2-} for precipitation with Ca^{2+}. As such, the co-application of SO_4^{2-} salts with P fertilizer might enhance the availability of P for crop uptake in calcareous soils.

Overall, there was a higher concentration of water-extractable P and the diffusive movement of P was also greater on addition of $(NH_4)_2SO_4$ to P, compared to K_2SO_4 in the first experiment. We observed that the differences in the effect of $(NH_4)_2SO_4$ and K_2SO_4 on P solubility and movement may be attributed to the role of the associated cation in each SO_4^{2-} salt. It appeared that K^+ from K_2SO_4 was more efficient than NH_4^+ from $(NH_4)_2SO_4$ in displacing Ca^{2+} from the exchange sites; which consequently caused a lower concentration of water-extractable P with a greater retardation of P movement with K_2SO_4, compared to $(NH_4)_2SO_4$. These results further suggest that the banding of $(NH_4)_2SO_4$ with fertilizer P might enhance the movement and crop uptake of P in calcareous soils, due to the lower replacing power or preference of NH_4^+ in $(NH_4)_2SO_4$ on the exchange sites, compared to that of K^+ from K_2SO_4.

Effect of ionic competition between K^+ and NH_4^+ on the distribution of each of these cations in the water-extractable and acid-extractable fraction was also observed. It was shown that K^+ associated with K_2SO_4 enhanced the water-extractability of NH_4^+ in $NH_4H_2PO_4+K_2SO_4$ treatment compared to $NH_4H_2PO_4$ alone by competing with NH_4^+ for the exchange sites. Similar trends were observed for the effect of NH_4^+ associated with $(NH_4)_2SO_4$ on the greater water-extractability of K^+ in $KH_2PO_4+(NH_4)_2SO_4$, compared to KH_2PO_4 alone. With these results, it is possible to influence the fate of a cation in the

soil through proper fertilizer management. For example, in situations where we want to limit the extent of movement of K^+ in MKP fertilizer, it is suggested that MKP be added alone to ensure the separation of K^+ from other cations. Alternatively, if we want to enhance the movement of K^+ in MKP fertilizer, this can be accomplished by banding other cations such as NH_4^+ through a dual band containing MKP and $(NH_4)_2SO_4$. The $(NH_4)_2SO_4$ compound will introduce NH_4^+ into the reaction zone to undergo cationic competition with K^+ for the exchange sites. Consequently, the solubility and movement of K^+ will increase as was shown in this study.

The same technique described above can be adopted for P fertilizer management depending on the type of crop under consideration. We suggest that banding P fertilizer alone, in isolation from other salts, would enhance the efficiency of P uptake for crops that can best utilize P when P is localized at a region close to the root surface. Conversely for other crops that are better at utilizing P from a distance within the root zone, the co-application of P with salts such as $(NH_4)_2SO_4$ would enhance P transport from the band and the availability of P for crop uptake.

We conducted the second experiment to see how the effects of the sulphate salts in the first experiment stand out among other non-phosphatic salts. The objective of the second experiment was to examine the effect of cationic and anionic interactions on the solubility and diffusive movement of P in the resin-sand column. We observed that the solubility of phosphate in the water extract was greatest and similar on addition of $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ to KH_2PO_4 compared to other treatments. However, the depth of P movement was greater in the $(NH_4)_2SO_4$ treatment than in the $(NH_4)_2CO_3$. The addition of K_2SO_4 to KH_2PO_4 also increased the concentration of water-extractable P

compared to KH$_2$PO$_4$ alone, while the addition of K$_2$CO$_3$ resulted in the least water-extractable P. Conversely, the concentration of water-extractable P was generally low in the Mg^{2+} treatments; however, maximum depth of P transport occurred in this system. Overall, the addition of (NH$_4$)$_2$SO$_4$ to P had the greatest enhancement on water-extractable P and depth of P penetration in the resin-sand column.

Even though we did not analyse for the accompanying ions in the second experiment, we observed that the interactions of SO$_4$$^{2-}$, NH$_4$$^+$ and K$^+$ were consistent at enhancing the water solubility of P in the second experiment, as observed in the first experiment. Of all the treatments used in the second experiment, only three of them ((NH$_4$)$_2$SO$_4$, (NH$_4$)$_2$CO$_3$ and K$_2$SO$_4$) increased the water-extractable P compared to KH$_2$PO$_4$ alone. Therefore, we selected these novel treatments, together with K$_2$CO$_3$ which had the least water-extractable P, to extrapolate the findings obtained from the resin-sand system to natural soils. Hence, the combinations of these salts with KH$_2$PO$_4$ set the basis for the third experiment.

The objective of the third experiment was to demonstrate the effects of the combinations of various salts selected from the previous experiments, on the chemical diffusion and solubility of P in two soils (Ramada and Dezwood) with contrasting pH and cation exchange capacity (CEC). Nearly all the non-phosphatic salts reduced the water-extractable P compared to KH$_2$PO$_4$ alone in the Ramada soil which had a low pH and high CEC, while the water solubility of P in (NH$_4$)$_2$CO$_3$ treatment was similar to that of KH$_2$PO$_4$ alone. Conversely, the addition of (NH$_4$)$_2$SO$_4$ salt enhanced the diffusive movement of P in the Dezwood soil which had a high pH and low CEC, compared to

other salts. However, the water solubility of P in $(NH_4)_2SO_4$ was statistically similar to that of K_2SO_4 or K_2CO_3 but greater than that of KH_2PO_4 alone in the Dezwood soil.

Analysis of variance (ANOVA) showed that interaction exists between soil and salts on the water-extractable and acid-extractable P in the third experiment. These results indicated that the effect of each salt on the water solubility and retention of P depends on the soil type. Therefore, we could not extrapolate the results of the resin-sand experiments directly to soil column study.

From the broad perspective of this study, we were able to identify several possible mechanisms that influence the interactions of P in multi-ionic environment by using the resin-sand system. Such factors are pH reduction due to salt effect, cation exchange reactions between the accompanying cations and the exchangeable Ca^{2+}, and anionic competition against P for precipitation reactions with the displaced Ca^{2+}. The information gathered from the first two experiments showed that the co-application of $(NH_4)_2SO_4$ with P enhanced the water solubility and depth of P movement significantly in the buffered resin-sand system, and consistent in the slightly alkaline Dezwood soil. Conversely, substantial retention and retardation of P movement occurred on addition of $(NH_4)_2SO_4$ to the slightly acidic Ramada soil column.

The practical implication of these results is that dual band application of P with ammonium sulphate has the potential to improve P uptake and crop utilization in alkaline to calcareous soils of Manitoba. This effect was attributed to the combination of various mechanistic factors associated with $(NH_4)_2SO_4$ compound. Such factors are significant pH reduction, cation exchange reaction of NH_4^+ with the exchangeable Ca^{2+}, and anionic competition of SO_4^{2-} with P for precipitation with Ca^{2+}. As such, smaller quantity of P

fertilizer compound co-applied with ammonium sulphate at a time will be sufficient to improve the efficiency of starter P fertilizer. This practice will also facilitate an adequate supply of P nutrient early in the season to meet seedling requirements, and simultaneously prevents excessive P build-up in the soil during the growing season. Consequently, lowering the rate of P loading in the soil will minimize the risk of P loss to the adjacent water bodies.

Besides the practical implications stated above, this study also calls for further studies to shed more light on the fate of P and accompanying cation. The resin-sand experiments presented in this study only characterized the diffusion of P spatially for one time period; two weeks of incubation. It may be necessary to perform the incubation procedure at various time intervals, in order to investigate how the effects of salt combination on P transport in the resin system change with time. This is most crucial with treatments containing CO_3^{2-}. In order to increase P solubility in water, it appeared that the initial pH of the band must be high enough to make CO_3^{2-} compete with P for Ca^{2+}. Conducting the study at a single time did not provide us with the opportunity to follow pH changes in the system.

The results obtained from the third experiment (on soil columns) suggested that effect of salt on P solubility and transport was soil specific. As such, further studies with several soils with contrasting chemical properties are needed in order to extrapolate the results of the model system directly to natural soils. Similarly, a longer period of incubation with the soil experiment is required to examine the effect of the dissolution of the dicalcium phosphate dihydrate (DCPD) that probably formed by the individual salt combination, on the chemical availability of P. A long term incubation study would also

help to investigate the impact of microbial activities on the multi-ionic interactions occurring in the soil columns. In addition, the determination of other ions of interest such as NH_4^+ and SO_4^{2-} in both soil systems would also provide better information on the behaviour of these ions on the solubility and diffusion of P in the soil columns.

Nevertheless, the results gathered from the three studies contributed some useful information to the objectives of Cargill Ltd. on the chemical characterization and agronomic evaluation of the newly formulated NPS fertilizer. Although this information was generated from laboratory experiments, it explained the possible fundamental chemical mechanisms that are likely to be encountered following the application of Cargill's homogeneous co-granulated NPS fertilizer or dual banded phosphate fertilizer placement.

The combination of the information gathered from these column studies with the earlier findings reported from other research studies conducted with the: (1) batch incubation studies, (2) growth chamber experiment and (3) field scale experimentation, would be sufficient to provide a better understanding of the chemistry of P fertilizer band in a multi-ionic environment and scientific recommendations to Cargill Ltd. This information will also enable Cargill Ltd. to optimize the potential uptake of P from the homogeneous NPS granules. Hence, the overall goal targeted at improving the crop nutrition of N, P and S by canola and wheat, and reduction of the export of P from Manitoba agricultural landscapes will be accomplished.

6. APPENDICES

Appendix A

EXPERIMENTAL DATA[‡] ON COLUMN SEGMENTATION AND EXTRACTION OF THE RESIN-SAND SYSTEM IN EXPERIMENT I

[‡] Data represent average of two columns

Gravimetric water content (%) – MAP System

DEPTH (cm)	MAP ALONE	MAP+AS	MAP+KS
0.30	24.21	24.36	24.36
0.60	25.01	22.55	24.85
0.90	24.36	24.58	23.03
1.20	24.29	23.85	23.10
1.50	24.29	23.68	24.47
1.80	24.55	23.09	25.50
2.10	23.79	22.44	24.73
2.40	24.30	23.42	23.17
2.70	24.64	25.87	22.63
3.00	23.99	26.60	25.01
3.30	22.62	24.89	23.05
3.60	23.75	24.98	23.78
3.90	23.04	21.66	22.56
4.20	23.60	22.16	24.02
4.50	24.53	23.75	24.08
4.80	24.13	24.01	24.40
5.10	24.03	25.65	24.34
5.40	23.76	27.18	23.14
5.70	23.72	25.63	22.98
6.00	23.20	25.37	23.38
6.30	21.98	23.59	23.39
6.60	23.45	24.88	23.03
6.90	21.10	25.29	23.17
7.20	21.21	24.46	22.38
7.50	19.43	23.29	21.23

Gravimetric water content (%) - MKP System

DEPTH (cm)	MKP ALONE	MKP+AS	MKP+KS
0.30	24.15	24.19	25.52
0.60	22.94	22.58	24.64
0.90	23.02	24.98	25.19
1.20	23.69	22.71	25.16
1.50	24.03	22.68	24.28
1.80	23.99	23.74	23.91
2.10	25.82	23.25	24.16
2.40	24.36	24.01	24.83
2.70	23.34	22.81	25.14
3.00	24.05	23.50	24.94
3.30	22.58	22.46	22.78
3.60	22.82	24.68	25.08
3.90	22.85	24.29	25.02
4.20	23.02	23.59	22.47
4.50	23.43	23.94	24.73
4.80	22.75	24.41	24.90
5.10	24.21	24.33	25.08
5.40	25.18	24.88	27.57
5.70	23.59	23.16	25.87
6.00	23.03	23.56	24.73
6.30	23.65	23.05	23.09
6.60	23.51	23.96	24.60
6.90	21.91	22.32	24.21
7.20	22.04	22.06	23.35
7.50	21.92	23.58	24.43

pH - MAP System

DEPTH (cm)	MAP ALONE	MAP+AS	MAP+KS
0.30	7.30	7.28	7.35
0.60	7.40	7.37	7.51
0.90	7.39	7.41	7.40
1.20	7.39	7.42	7.37
1.50	7.36	7.51	7.31
1.80	7.18	7.54	7.19
2.10	7.29	7.53	7.18
2.40	7.30	7.57	7.14
2.70	7.25	7.64	7.38
3.00	7.41	7.55	7.43
3.30	7.30	7.62	7.19
3.60	7.41	7.58	7.39
3.90	7.76	7.91	7.68
4.20	7.83	7.96	7.90
4.50	7.97	8.13	8.18
4.80	8.00	8.04	8.24
5.10	8.26	8.28	8.22
5.40	8.46	8.21	8.41
5.70	8.55	8.32	8.38
6.00	8.64	8.35	8.43
6.30	8.69	8.40	8.49
6.60	8.81	8.45	8.51
6.90	8.85	8.48	8.57
7.20	8.85	8.49	8.55
7.50	8.82	8.48	8.60

pH - MKP System

DEPTH (cm)	MKP ALONE	MKP+AS	MKP+KS
0.30	7.62	7.29	7.37
0.60	7.69	7.36	7.56
0.90	7.85	7.48	7.55
1.20	7.74	7.42	7.50
1.50	7.74	7.42	7.53
1.80	7.61	7.33	7.48
2.10	7.72	7.35	7.46
2.40	7.85	7.36	7.49
2.70	7.71	7.41	7.41
3.00	7.85	7.46	7.68
3.30	7.96	7.54	7.50
3.60	8.14	7.84	7.64
3.90	8.32	7.91	7.76
4.20	8.42	8.03	7.83
4.50	8.57	8.11	7.97
4.80	8.59	8.08	8.10
5.10	8.66	8.09	8.16
5.40	8.77	8.25	8.27
5.70	8.81	8.30	8.36
6.00	8.76	8.33	8.41
6.30	8.76	8.37	8.47
6.60	8.86	8.42	8.48
6.90	8.87	8.43	8.50
7.20	8.88	8.47	8.50
7.50	8.87	8.49	8.55

Water-extractable P (mmol L^{-1}) - MAP System

Depth (cm)	MAP ALONE	MAP+AS	MAP+KS
0.30	28.24	31.41	29.04
0.60	27.11	30.84	39.11
0.90	25.63	33.13	31.31
1.20	18.83	33.93	36.81
1.50	15.42	25.32	19.07
1.80	12.61	24.50	12.78
2.10	7.61	21.15	8.88
2.40	9.51	14.63	11.15
2.70	8.53	10.87	7.83
3.00	5.14	9.43	4.10
3.30	2.22	7.29	6.44
3.60	2.46	7.28	2.17
3.90	1.82	1.58	2.22
4.20	2.40	1.41	0.65
4.50	2.39	0.49	0.42
4.80	1.35	0.45	0.34
5.10	1.26	0.22	0.30
5.40	0.79	0.23	0.20
5.70	0.55	0.21	0.12
6.00	0.41	0.12	0.14
6.30	0.33	0.05	0.05
6.60	0.07	0.10	0.06
6.90	0.05	0.04	0.08
7.20	0.02	0.04	0.20
7.50	0.19	0.06	0.12

Water-extractable P (mmol L^{-1}) - MKP System

Depth (cm)	MKP ALONE	MKP+AS	MKP+KS
0.30	38.73	36.80	28.98
0.60	30.17	39.93	41.18
0.90	24.75	39.31	36.51
1.20	22.00	36.61	39.96
1.50	15.99	34.67	34.05
1.80	13.80	21.59	21.70
2.10	9.18	25.12	19.80
2.40	5.32	16.25	9.52
2.70	7.60	12.80	6.65
3.00	5.34	6.51	4.00
3.30	3.62	4.14	2.41
3.60	2.53	1.28	2.54
3.90	1.70	0.69	1.08
4.20	1.47	0.57	0.94
4.50	1.25	0.35	0.74
4.80	0.77	0.52	0.51
5.10	0.85	0.36	0.58
5.40	0.61	0.18	0.38
5.70	0.52	0.29	0.28
6.00	0.46	0.14	0.08
6.30	0.48	0.17	0.09
6.60	0.21	0.09	0.08
6.90	0.09	0.04	0.08
7.20	0.13	0.03	0.11
7.50	0.16	0.21	0.13

Acid-extractable P (mmol L^{-1}) - MAP System

Depth (cm)	MAP ALONE	MAP+AS	MAP+KS
0.30	113.96	61.89	95.01
0.60	131.40	149.68	122.07
0.90	107.17	127.48	87.96
1.20	66.69	123.57	73.65
1.50	59.09	83.43	50.83
1.80	41.46	27.39	41.18
2.10	34.53	26.83	31.66
2.40	35.59	19.77	46.05
2.70	32.36	19.59	31.71
3.00	24.17	18.80	15.88
3.30	9.07	10.83	17.25
3.60	7.15	11.40	15.98
3.90	3.03	8.15	7.89
4.20	2.39	6.73	8.43
4.50	1.33	3.03	3.76
4.80	0.07	0.08	0.13
5.10	0.05	0.05	0.10
5.40	0.33	0.06	0.09
5.70	0.06	0.07	0.10
6.00	0.06	0.02	0.10
6.30	0.08	0.03	0.08
6.60	0.07	0.04	0.12
6.90	0.05	0.05	0.08
7.20	0.07	0.04	0.10
7.50	0.07	0.06	0.07

Acid-extractable P (mmol L^{-1}) - MKP System

Depth (cm)	MKP ALONE	MKP+AS	MKP+KS
0.30	152.26	95.73	134.67
0.60	135.59	147.92	126.94
0.90	107.66	127.48	124.71
1.20	95.65	55.36	53.45
1.50	70.88	43.62	45.50
1.80	34.61	38.35	39.92
2.10	26.24	64.63	31.81
2.40	20.24	34.16	26.09
2.70	23.02	34.15	23.35
3.00	19.49	22.97	18.88
3.30	11.59	13.13	13.48
3.60	9.19	7.56	7.17
3.90	3.24	5.73	8.58
4.20	2.40	6.09	2.56
4.50	1.84	3.59	1.21
4.80	0.15	0.09	0.01
5.10	0.11	0.05	0.03
5.40	0.31	0.06	0.03
5.70	0.03	0.01	0.04
6.00	0.04	0.00	0.07
6.30	0.04	0.02	0.05
6.60	0.02	0.01	0.06
6.90	0.08	0.10	0.07
7.20	0.19	0.05	0.03
7.50	0.03	0.03	0.02

Water-extractable K (mmol L^{-1}) - MKP System

Depth (cm)	MKP ALONE	MKP+AS	MKP+KS	MAP+KS
0.30	71.58	68.91	183.74	104.91
0.60	55.63	63.05	174.05	105.65
0.90	45.99	64.08	164.89	98.28
1.20	42.63	53.80	164.98	108.82
1.50	37.61	53.22	149.16	80.43
1.80	18.87	43.36	109.25	59.69
2.10	16.23	45.99	96.91	51.76
2.40	12.53	32.68	73.77	54.35
2.70	13.74	29.36	65.36	44.32
3.00	8.47	22.61	31.06	31.90
3.30	6.58	18.76	41.66	31.04
3.60	4.46	14.54	33.66	24.08
3.90	0.00	10.00	28.39	20.14
4.20	0.00	9.45	26.07	17.03
4.50	0.00	6.87	35.31	10.15
4.80	0.00	7.15	14.92	12.51
5.10	0.00	2.86	12.86	7.89
5.40	0.00	1.07	9.15	4.32
5.70	0.00	0.00	6.29	3.08
6.00	0.00	0.00	5.22	0.00
6.30	0.00	0.00	0.00	0.00
6.60	0.00	0.00	0.00	0.00
6.90	0.00	0.00	0.00	0.00
7.20	0.00	0.00	0.00	0.00
7.50	0.00	0.00	0.00	0.00

Acid-extractable K (mmol L^{-1}) - MKP System

Depth (cm)	MKP ALONE	MKP+AS	MKP+KS	MAP+KS
0.30	115.31	50.96	139.08	101.18
0.60	99.67	51.05	142.87	82.23
0.90	97.80	45.91	159.59	88.26
1.20	77.04	43.47	116.50	96.55
1.50	54.31	41.04	114.91	75.82
1.80	39.75	39.15	102.41	64.27
2.10	22.11	34.27	95.71	61.93
2.40	21.48	25.59	84.39	60.19
2.70	17.57	24.09	71.34	39.93
3.00	20.23	18.71	59.21	32.01
3.30	16.61	14.27	52.30	32.87
3.60	11.96	11.24	39.80	26.96
3.90	6.58	9.23	31.69	20.00
4.20	4.69	7.64	29.14	13.93
4.50	2.25	5.69	21.48	9.35
4.80	4.10	7.06	18.35	9.91
5.10	0.00	2.82	13.99	4.07
5.40	0.00	0.00	8.85	2.99
5.70	0.00	0.00	6.31	1.88
6.00	0.00	0.00	4.70	1.78
6.30	0.00	0.00	2.41	0.00
6.60	0.00	0.00	0.00	0.00
6.90	0.00	0.00	0.00	0.00
7.20	0.00	0.00	0.00	0.00
7.50	0.00	0.00	0.00	0.00

Water-extractable NH$_4$-N (mmol L^{-1})

Depth (cm)	MAP ALONE	MAP+AS	MAP+KS	MKP+AS
0.30	52.59	168.11	51.86	125.63
0.60	50.22	177.13	51.56	122.04
0.90	46.46	156.38	43.63	114.32
1.20	38.30	148.12	49.30	101.93
1.50	31.14	130.07	41.78	98.33
1.80	25.22	114.45	33.88	80.39
2.10	15.51	130.78	30.41	92.14
2.40	14.36	94.84	33.17	67.14
2.70	14.42	76.32	25.83	64.71
3.00	12.04	81.07	22.81	48.15
3.30	9.89	62.63	23.50	45.25
3.60	7.81	55.09	19.37	32.32
3.90	7.68	42.48	17.95	27.82
4.20	3.47	35.07	11.29	26.95
4.50	3.51	26.56	10.50	21.50
4.80	2.87	26.85	10.58	20.03
5.10	2.29	20.47	9.38	17.51
5.40	2.33	18.10	9.90	13.33
5.70	3.69	15.98	8.74	12.76
6.00	3.34	15.53	8.72	10.21
6.30	3.78	13.68	6.32	8.75
6.60	3.75	10.32	4.63	6.52
6.90	4.76	8.81	3.93	5.55
7.20	3.85	8.21	3.56	4.49
7.50	3.54	6.56	2.55	3.18

Acid-extractable NH$_4$-N (mmol L^{-1})

Depth (cm)	MAP ALONE	MAP+AS	MAP+KS	MKP+AS
0.30	113.65	89.47	40.52	73.40
0.60	84.27	94.37	34.39	74.52
0.90	83.63	80.72	36.05	73.03
1.20	64.70	83.86	39.64	71.45
1.50	53.05	85.44	32.24	66.35
1.80	40.53	85.66	29.15	60.17
2.10	20.08	88.87	26.77	62.39
2.40	25.12	70.10	27.84	50.70
2.70	19.16	54.85	19.17	48.39
3.00	11.70	57.79	17.74	42.86
3.30	9.31	52.91	19.91	37.19
3.60	7.24	46.25	15.82	29.88
3.90	4.27	38.69	11.73	24.15
4.20	3.39	31.50	10.58	21.20
4.50	3.20	21.67	6.20	16.80
4.80	5.40	21.44	2.04	16.69
5.10	4.47	16.90	1.65	14.30
5.40	3.70	12.47	1.71	12.18
5.70	3.56	13.16	1.51	10.47
6.00	3.56	9.95	1.42	8.66
6.30	2.49	6.94	1.25	7.46
6.60	2.31	6.00	1.33	6.14
6.90	2.27	4.69	1.20	5.59
7.20	2.13	3.78	1.42	5.35
7.50	1.98	3.33	1.75	3.26

Water-extractable SO$_4$ (mmol L^{-1}) - MAP System

Depth (cm)	MAP+AS	MAP+KS
0.30	36.22	23.11
0.60	34.35	23.06
0.90	26.07	27.71
1.20	27.37	28.40
1.50	23.79	18.59
1.80	21.01	18.34
2.10	25.53	16.39
2.40	23.73	18.87
2.70	18.96	18.03
3.00	21.23	16.84
3.30	18.64	17.80
3.60	19.11	15.82
3.90	16.00	16.73
4.20	17.74	15.01
4.50	14.27	15.87
4.80	15.44	13.00
5.10	12.23	15.50
5.40	13.36	12.58
5.70	12.26	10.82
6.00	12.69	10.75
6.30	13.66	10.13
6.60	10.92	9.14
6.90	9.72	11.09
7.20	9.37	9.55
7.50	7.72	9.05

Water-extractable SO$_4$ (mmol L^{-1}) - MKP System

Depth (cm)	MKP+AS	MKP+KS
0.30	27.32	27.40
0.60	24.51	21.54
0.90	24.74	29.90
1.20	20.87	22.08
1.50	20.93	19.87
1.80	18.54	18.43
2.10	18.85	18.29
2.40	16.48	16.03
2.70	16.24	15.07
3.00	14.61	12.13
3.30	14.67	11.40
3.60	11.87	8.69
3.90	10.39	10.14
4.20	9.56	9.95
4.50	8.25	8.04
4.80	9.02	8.85
5.10	9.32	9.08
5.40	9.24	8.48
5.70	7.92	7.28
6.00	8.40	8.09
6.30	8.04	8.04
6.60	7.21	7.07
6.90	8.62	8.06
7.20	7.51	7.18
7.50	7.52	7.30

Acid-extractable SO$_4$ (mmol L^{-1}) - MAP System

Depth (cm)	MAP+AS	MAP+KS
0.30	11.10	16.16
0.60	13.40	15.75
0.90	10.00	10.37
1.20	8.46	11.12
1.50	9.75	12.24
1.80	8.45	9.08
2.10	10.28	10.77
2.40	7.64	6.87
2.70	8.40	7.09
3.00	7.38	8.90
3.30	8.30	8.08
3.60	7.40	7.03
3.90	7.30	7.23
4.20	6.35	7.31
4.50	6.66	7.30
4.80	6.61	6.38
5.10	6.89	6.69
5.40	5.83	6.71
5.70	5.84	6.40
6.00	5.79	6.32
6.30	6.53	6.34
6.60	6.05	5.75
6.90	6.15	5.06
7.20	6.73	6.00
7.50	6.39	6.31

Acid-extractable SO$_4$ (mmol L^{-1}) - MKP System

Depth (cm)	MKP+AS	MKP+KS
0.30	8.78	9.30
0.60	12.05	9.63
0.90	9.41	12.39
1.20	10.46	14.10
1.50	11.82	10.14
1.80	9.00	8.83
2.10	10.78	8.68
2.40	9.43	9.30
2.70	7.56	9.37
3.00	8.58	7.68
3.30	8.23	7.73
3.60	8.37	8.19
3.90	8.44	7.78
4.20	8.76	7.67
4.50	7.69	6.07
4.80	8.16	6.96
5.10	6.56	6.13
5.40	5.51	6.12
5.70	6.94	6.49
6.00	7.12	6.21
6.30	7.58	6.56
6.60	6.57	6.24
6.90	6.31	6.69
7.20	5.81	5.16
7.50	5.62	5.62

Water-extractable Ca (mmol L^{-1}) – MAP System

Depth (cm)	MAP ALONE	MAP+AS	MAP+KS
0.30	2.60	22.77	25.42
0.60	9.08	37.23	25.97
0.90	2.10	25.42	18.65
1.20	4.38	21.55	16.21
1.50	5.60	26.75	22.17
1.80	5.74	12.71	15.36
2.10	3.31	20.74	15.03
2.40	3.97	19.78	10.26
2.70	4.57	12.87	20.51
3.00	9.57	13.84	22.78
3.30	5.56	14.83	18.76
3.60	3.77	10.99	16.54
3.90	5.53	14.02	19.18
4.20	6.31	10.67	12.74
4.50	5.98	10.87	16.00
4.80	6.57	13.15	21.08
5.10	6.35	12.16	11.97
5.40	4.95	10.44	13.55
5.70	4.19	10.17	10.39
6.00	5.47	10.86	9.28
6.30	5.41	14.89	8.78
6.60	5.55	9.95	18.34
6.90	5.16	9.71	8.01
7.20	11.26	13.09	8.05
7.50	5.98	15.58	8.97

Water-extractable Ca (mmol L^{-1}) – MKP System

Depth (cm)	MKP ALONE	MKP+AS	MKP+KS
0.30	5.74	30.74	24.21
0.60	17.61	26.33	22.32
0.90	3.88	19.21	20.16
1.20	50.86	20.21	22.53
1.50	14.13	34.71	20.60
1.80	3.47	14.15	10.50
2.10	3.06	20.52	15.39
2.40	6.53	15.96	8.17
2.70	18.39	15.86	18.53
3.00	5.01	17.65	14.56
3.30	3.62	14.01	7.63
3.60	12.98	9.29	7.90
3.90	8.19	13.28	10.88
4.20	8.48	11.66	10.48
4.50	4.80	12.13	9.40
4.80	4.15	17.98	17.47
5.10	5.95	14.11	15.75
5.40	4.63	12.21	11.03
5.70	14.71	17.06	11.22
6.00	8.32	11.46	17.71
6.30	4.58	11.22	9.51
6.60	4.08	9.43	7.93
6.90	5.90	9.84	8.56
7.20	15.92	11.57	7.23
7.50	16.87	9.79	10.79

Appendix B

EXPERIMENTAL DATA[‡] ON COLUMN SEGMENTATION AND EXTRACTION OF
THE RESIN-SAND SYSTEM IN EXPERIMENT II

[‡] Data represent average of three columns

Gravimetric water content (%) of Potassium System

Depth (cm)	KH_2PO_4	KH_2PO_4+KCl	$KH_2PO_4+KNO_3$	$KH_2PO_4+K_2SO_4$	$KH_2PO_4+K_2CO_3$
0.30	22.40	23.55	22.37	21.96	22.29
0.60	22.69	23.29	22.39	21.75	22.21
0.90	23.05	23.88	21.80	22.33	23.26
1.20	23.45	23.45	23.65	21.41	24.33
1.50	22.08	23.56	22.88	22.56	23.88
1.80	23.64	24.38	22.37	22.94	23.48
2.10	23.09	23.02	22.28	22.05	24.13
2.40	23.18	23.98	22.41	22.41	23.66
2.70	22.57	23.72	22.86	21.66	23.02
3.00	24.56	23.48	22.72	22.12	23.17
3.30	23.17	23.93	21.78	22.53	23.14
3.60	22.94	23.38	22.57	22.58	23.23
3.90	23.30	23.55	23.39	22.75	24.15
4.20	23.81	23.60	23.12	22.61	23.19
4.50	23.97	24.07	23.38	22.98	24.85
4.80	24.37	24.01	23.12	22.72	24.66
5.10	23.78	24.47	23.36	22.61	23.09
5.40	24.26	24.38	21.91	23.81	25.57
5.70	25.65	24.03	22.70	23.01	24.73
6.00	24.48	22.72	23.04	22.11	23.79
6.30	23.62	23.51	23.44	21.35	23.58
6.60	23.68	22.76	22.44	21.89	22.71
6.90	24.26	21.95	23.73	21.88	23.73
7.20	23.50	21.44	23.08	22.35	23.67
7.50	23.20	22.11	22.60	22.40	22.91

Gravimetric water content (%) of Ammonium System

Depth (cm)	KH$_2$PO$_4$	KH$_2$PO$_4$+NH4Cl	KH$_2$PO$_4$+NH$_4$NO$_3$	KH$_2$PO$_4$+(NH$_4$)$_2$SO$_4$	KH$_2$PO$_4$+(NH$_4$)$_2$CO$_3$
0.30	22.40	22.81	23.89	22.96	23.26
0.60	22.69	22.74	23.04	24.07	23.30
0.90	23.05	23.34	24.72	25.23	24.21
1.20	23.45	24.04	25.06	25.53	23.59
1.50	22.08	24.67	25.06	24.95	25.59
1.80	23.64	24.14	23.56	24.99	24.68
2.10	23.09	23.76	24.42	25.26	25.50
2.40	23.18	23.77	23.89	24.76	24.68
2.70	22.57	23.18	24.70	24.49	24.54
3.00	24.56	25.54	24.23	24.51	25.48
3.30	23.17	23.49	23.70	23.76	24.98
3.60	22.94	25.03	24.53	24.36	26.37
3.90	23.30	24.09	23.70	23.59	24.97
4.20	23.81	24.56	23.06	23.91	24.75
4.50	23.97	24.01	24.11	24.21	24.59
4.80	24.37	23.58	23.83	24.28	24.19
5.10	23.78	24.10	23.86	24.09	24.81
5.40	24.26	23.65	24.52	24.75	22.98
5.70	25.65	23.30	25.37	24.29	24.47
6.00	24.48	22.72	23.28	24.54	24.83
6.30	23.62	23.49	24.43	25.45	23.40
6.60	23.68	23.75	24.51	25.05	24.07
6.90	24.26	22.39	22.36	25.21	22.91
7.20	23.50	23.33	24.18	24.45	24.26
7.50	23.20	22.45	23.06	23.70	24.23

Gravimetric water content (%) of Magnesium System

Depth (cm)	KH_2PO_4	$KH_2PO_4+MgCl_2$	$KH_2PO_4+Mg(NO_3)_2$	$KH_2PO_4+MgSO_4$	$KH_2PO_4+MgCO_3$
0.30	22.40	22.86	23.54	23.43	24.03
0.60	22.69	23.02	23.75	23.91	24.70
0.90	23.05	23.69	24.83	24.66	24.34
1.20	23.45	24.56	24.45	24.71	23.88
1.50	22.08	24.05	23.69	25.02	24.62
1.80	23.64	24.46	23.67	25.09	24.94
2.10	23.09	24.04	24.66	24.83	25.17
2.40	23.18	24.97	24.26	24.86	24.85
2.70	22.57	24.20	23.97	24.26	25.10
3.00	24.56	25.10	23.68	24.35	25.15
3.30	23.17	24.20	23.54	23.61	24.80
3.60	22.94	23.72	23.18	23.42	25.13
3.90	23.30	23.50	22.90	23.70	24.45
4.20	23.81	23.39	23.20	23.01	24.39
4.50	23.97	23.95	23.27	23.87	24.71
4.80	24.37	23.41	22.99	23.42	24.90
5.10	23.78	23.67	23.63	24.13	24.47
5.40	24.26	23.18	23.59	24.60	24.73
5.70	25.65	24.40	23.17	24.24	24.91
6.00	24.48	24.47	22.55	23.64	24.78
6.30	23.62	23.84	23.36	24.51	23.73
6.60	23.68	23.56	23.74	23.87	25.01
6.90	24.26	23.67	24.21	23.40	23.88
7.20	23.50	23.55	24.40	23.10	23.81
7.50	23.20	23.40	23.13	23.66	23.26

pH of Potassium System

Depth (cm)	KH_2PO_4	KH_2PO_4+KCl	$KH_2PO_4+KNO_3$	$KH_2PO_4+K_2SO_4$	$KH_2PO_4+K_2CO_3$
0.30	7.05	6.99	7.22	7.12	9.05
0.60	7.22	6.97	7.26	7.30	9.16
0.90	7.23	7.13	7.32	7.33	8.95
1.20	7.25	7.25	7.34	7.31	9.38
1.50	7.29	7.26	7.32	7.28	9.04
1.80	7.32	7.18	7.31	7.22	9.03
2.10	7.21	7.22	7.35	7.27	9.00
2.40	7.24	7.41	7.34	7.31	9.11
2.70	7.25	7.49	7.40	7.21	9.22
3.00	7.33	7.48	7.50	7.28	9.18
3.30	7.25	7.38	7.43	7.14	8.99
3.60	7.38	7.66	7.53	7.12	9.03
3.90	7.39	7.69	7.65	7.18	9.03
4.20	7.49	7.73	7.74	7.14	8.92
4.50	7.72	7.75	7.84	7.14	8.91
4.80	7.68	7.76	7.89	7.25	8.90
5.10	7.94	7.80	7.91	7.23	8.97
5.40	8.26	7.82	8.00	7.52	9.02
5.70	8.53	7.92	8.04	7.80	9.04
6.00	8.77	7.95	8.06	7.86	9.09
6.30	8.82	7.97	8.11	8.05	9.11
6.60	8.92	8.06	8.18	8.09	9.15
6.90	8.99	8.05	8.19	8.23	9.16
7.20	9.00	8.09	8.21	8.31	9.17
7.50	9.05	8.13	8.25	8.47	9.19

pH of Ammonium System

Depth (cm)	KH_2PO_4	$KH_2PO_4+NH4Cl$	$KH_2PO_4+NH_4NO_3$	$KH_2PO_4+(NH_4)_2SO_4$	$KH_2PO_4+(NH_4)_2CO_3$
0.30	7.05	7.29	7.15	7.19	8.22
0.60	7.22	7.35	7.33	7.34	8.25
0.90	7.23	7.43	7.35	7.31	8.47
1.20	7.25	7.44	7.43	7.30	8.26
1.50	7.29	7.41	7.46	7.31	8.14
1.80	7.32	7.32	7.27	7.25	8.27
2.10	7.21	7.36	7.32	7.27	8.20
2.40	7.24	7.31	7.39	7.30	8.28
2.70	7.25	7.38	7.39	7.30	8.24
3.00	7.33	7.30	7.40	7.35	8.31
3.30	7.25	7.24	7.26	7.37	8.52
3.60	7.38	7.31	7.42	7.38	8.68
3.90	7.39	7.27	7.54	7.43	8.66
4.20	7.49	7.50	7.57	7.41	8.87
4.50	7.72	7.52	7.69	7.52	8.90
4.80	7.68	7.53	7.69	7.54	8.88
5.10	7.94	7.62	7.85	7.59	8.98
5.40	8.26	7.76	7.93	7.80	9.02
5.70	8.53	7.90	7.96	7.81	9.04
6.00	8.77	7.94	8.02	7.96	9.06
6.30	8.82	7.94	8.03	8.05	9.12
6.60	8.92	8.08	8.13	8.13	9.19
6.90	8.99	8.13	8.14	8.19	9.22
7.20	9.00	8.19	8.18	8.35	9.24
7.50	9.05	8.27	8.19	8.47	9.24

pH of Magnesium System

Depth (cm)	KH_2PO_4	$KH_2PO_4+MgCl_2$	$KH_2PO_4+Mg(NO_3)_2$	$KH_2PO_4+MgSO_4$	$KH_2PO_4+MgCO_3$
0.30	7.05	7.05	7.30	7.41	9.59
0.60	7.22	7.16	7.28	7.40	9.38
0.90	7.23	7.21	7.28	7.40	8.34
1.20	7.25	7.20	7.35	7.38	8.27
1.50	7.29	7.11	7.37	7.40	8.20
1.80	7.32	6.91	7.32	7.33	7.95
2.10	7.21	6.95	7.35	7.33	8.02
2.40	7.24	7.01	7.34	7.34	8.03
2.70	7.25	7.00	7.37	7.33	8.09
3.00	7.33	6.99	7.37	7.31	8.13
3.30	7.25	6.82	7.38	7.19	8.07
3.60	7.38	6.88	7.47	7.17	8.21
3.90	7.39	6.93	7.55	7.16	8.52
4.20	7.49	7.07	7.58	7.17	8.65
4.50	7.72	7.05	7.72	7.13	8.68
4.80	7.68	7.05	7.65	7.04	8.93
5.10	7.94	7.09	7.79	7.03	9.03
5.40	8.26	7.17	7.93	7.09	9.08
5.70	8.53	7.18	7.94	7.10	9.13
6.00	8.77	7.15	8.03	7.19	9.19
6.30	8.82	7.11	8.05	7.00	9.21
6.60	8.92	7.08	8.16	7.12	9.29
6.90	8.99	7.27	8.16	7.26	9.32
7.20	9.00	7.33	8.15	7.49	9.34
7.50	9.05	7.50	8.29	7.52	9.35

Water-extractable P (mmol L^{-1}) of Potassium System

Depth (cm)	KH$_2$PO$_4$	KH$_2$PO$_4$+KCl	KH$_2$PO$_4$+KNO$_3$	KH$_2$PO$_4$+K$_2$SO$_4$	KH$_2$PO$_4$+K$_2$CO$_3$
0.30	49.99	34.68	51.01	53.68	27.12
0.60	55.07	46.94	56.11	64.32	37.35
0.90	45.35	45.70	68.36	60.32	27.52
1.20	30.00	30.55	37.57	69.16	9.67
1.50	28.15	29.02	34.23	62.96	25.81
1.80	26.09	28.63	32.97	48.22	19.56
2.10	33.55	32.81	51.78	44.78	20.03
2.40	28.60	17.15	34.30	41.85	15.53
2.70	22.86	7.51	24.14	32.67	10.74
3.00	19.05	2.40	31.08	26.95	6.81
3.30	20.27	3.47	25.22	27.76	9.14
3.60	16.33	1.03	14.41	17.46	5.57
3.90	13.72	1.54	14.47	13.10	2.95
4.20	10.37	0.81	8.14	9.84	1.60
4.50	7.46	0.75	4.89	10.95	1.35
4.80	5.95	0.27	1.73	6.01	1.12
5.10	5.10	0.71	3.04	3.45	1.17
5.40	4.05	0.52	1.01	3.01	0.73
5.70	3.34	0.33	0.64	1.35	0.60
6.00	3.03	0.32	0.54	1.39	0.51
6.30	2.64	0.34	0.33	1.34	0.58
6.60	2.30	0.12	0.23	1.19	0.38
6.90	1.83	0.22	0.25	0.91	0.27
7.20	1.64	0.22	0.16	0.85	0.28
7.50	1.10	0.14	0.08	0.58	0.22

Acid-extractable P (mmol L^{-1}) of Potassium System

Depth (cm)	KH_2PO_4	KH_2PO_4+KCl	$KH_2PO_4+KNO_3$	$KH_2PO_4+K_2SO_4$	$KH_2PO_4+K_2CO_3$
0.30	195.34	175.21	210.13	119.62	224.43
0.60	168.03	249.99	253.83	183.58	211.94
0.90	145.86	260.87	264.44	162.00	226.08
1.20	157.54	150.65	125.15	167.75	88.55
1.50	96.94	142.37	75.73	218.94	218.32
1.80	108.74	151.03	91.68	69.32	186.65
2.10	109.67	177.70	166.38	87.58	180.01
2.40	152.26	84.44	188.76	74.55	156.96
2.70	87.62	29.00	13.53	58.97	113.00
3.00	54.02	22.21	19.82	49.30	37.39
3.30	53.89	30.34	25.71	75.57	32.03
3.60	40.62	18.61	14.82	51.10	17.36
3.90	28.03	17.33	6.18	29.83	9.44
4.20	17.35	11.07	7.35	24.24	3.59
4.50	11.53	10.23	3.65	29.82	5.90
4.80	2.88	0.48	0.61	0.48	0.31
5.10	2.72	0.32	1.29	1.06	0.27
5.40	2.45	0.44	0.66	0.44	0.30
5.70	1.33	0.39	0.52	0.57	0.19
6.00	1.35	0.46	0.47	0.44	0.21
6.30	0.11	0.06	0.00	0.04	0.06
6.60	0.21	0.03	0.00	0.01	0.11
6.90	0.12	0.03	0.00	0.03	0.05
7.20	0.11	0.01	0.02	0.02	0.06
7.50	0.08	0.01	0.02	0.02	0.05

Water-extractable-P (mmol L^{-1}) of Ammonium System

Depth (cm)	KH$_2$PO$_4$	KH$_2$PO$_4$+NH4Cl	KH$_2$PO$_4$+NH$_4$NO$_3$	KH$_2$PO$_4$+(NH$_4$)$_2$SO$_4$	KH$_2$PO$_4$+(NH$_4$)$_2$CO$_3$
0.30	49.99	41.63	46.58	51.91	52.34
0.60	55.07	44.98	46.25	42.49	59.16
0.90	45.35	28.45	46.77	53.78	52.89
1.20	30.00	40.38	49.69	51.08	53.45
1.50	28.15	25.48	38.45	50.61	73.19
1.80	26.09	36.06	23.93	45.19	65.25
2.10	33.55	19.73	24.88	44.63	60.60
2.40	28.60	31.32	25.03	43.54	50.95
2.70	22.86	17.05	16.63	40.91	50.08
3.00	19.05	10.79	12.11	41.07	33.29
3.30	20.27	12.64	23.64	27.09	21.53
3.60	16.33	11.54	8.81	28.37	9.76
3.90	13.72	11.74	7.09	19.22	8.97
4.20	10.37	5.46	4.13	19.14	4.74
4.50	7.46	7.75	3.00	11.02	3.18
4.80	5.95	3.68	1.96	7.34	2.87
5.10	5.10	3.41	1.62	5.80	2.22
5.40	4.05	3.10	0.68	3.84	2.03
5.70	3.34	1.98	0.69	3.79	1.57
6.00	3.03	1.75	0.47	3.11	1.19
6.30	2.64	1.65	0.23	1.44	0.97
6.60	2.30	0.47	0.18	1.22	0.73
6.90	1.83	0.47	0.20	0.94	0.54
7.20	1.64	0.35	0.11	0.68	0.32
7.50	1.10	0.25	0.31	0.58	0.30

Acid-extractable P (mmol L^{-1}) of Ammonium System

Depth (cm)	KH$_2$PO$_4$	KH$_2$PO$_4$+NH4Cl	KH$_2$PO$_4$+NH$_4$NO$_3$	KH$_2$PO$_4$+(NH$_4$)$_2$SO$_4$	KH$_2$PO$_4$+(NH$_4$)$_2$CO$_3$
0.30	195.34	151.74	179.02	109.18	177.11
0.60	223.85	225.64	190.69	88.19	186.01
0.90	145.86	110.01	164.54	151.69	165.91
1.20	157.54	185.33	143.73	172.69	166.25
1.50	96.94	151.20	114.58	153.61	135.56
1.80	108.74	87.02	106.81	93.90	85.83
2.10	109.67	79.25	114.91	95.17	71.59
2.40	152.26	197.86	138.58	86.79	69.32
2.70	87.62	89.78	84.72	64.34	66.29
3.00	54.02	38.67	55.54	61.62	57.25
3.30	53.89	59.03	77.69	39.51	12.20
3.60	40.62	51.18	30.03	33.39	6.25
3.90	28.03	44.17	33.79	25.33	7.38
4.20	17.35	22.81	21.61	20.42	3.33
4.50	11.53	22.23	9.98	9.66	1.67
4.80	2.88	0.18	0.12	0.34	0.05
5.10	2.72	0.17	0.16	0.36	0.06
5.40	2.45	0.10	0.06	0.20	0.04
5.70	1.33	0.05	0.06	0.18	0.03
6.00	1.35	0.07	0.07	0.22	0.07
6.30	0.11	0.10	0.03	0.12	0.02
6.60	0.21	0.09	0.01	0.13	0.07
6.90	0.12	0.05	0.01	0.08	0.04
7.20	0.11	0.05	0.01	0.08	0.03
7.50	0.08	0.03	0.07	0.05	0.02

Water-extractable P (mmol L^{-1}) of Magnesium System

Depth (cm)	KH$_2$PO$_4$	KH$_2$PO$_4$+MgCl$_2$	KH$_2$PO$_4$+Mg(NO$_3$)$_2$	KH$_2$PO$_4$+MgSO$_4$	KH$_2$PO$_4$+MgCO$_3$
0.30	49.99	27.60	21.82	29.11	61.77
0.60	55.07	28.88	19.49	32.66	44.70
0.90	45.35	26.24	25.40	27.35	52.49
1.20	30.00	22.85	15.24	27.20	57.93
1.50	28.15	21.30	18.90	28.64	21.82
1.80	26.09	20.81	17.85	27.56	25.77
2.10	33.55	10.62	17.07	28.16	25.09
2.40	28.60	10.70	12.64	23.19	22.06
2.70	22.86	9.02	11.16	26.44	12.35
3.00	19.05	7.07	11.35	26.67	16.69
3.30	20.27	7.41	9.39	20.59	11.30
3.60	16.33	7.18	8.07	20.30	7.20
3.90	13.72	7.65	7.31	15.93	5.32
4.20	10.37	4.36	6.35	16.89	4.30
4.50	7.46	4.74	5.52	12.98	3.42
4.80	5.95	3.91	5.37	13.56	2.66
5.10	5.10	3.40	3.89	14.10	2.43
5.40	4.05	3.97	3.30	14.78	2.12
5.70	3.34	2.72	3.92	12.65	1.83
6.00	3.03	3.45	3.65	8.08	1.53
6.30	2.64	2.80	2.86	10.32	1.37
6.60	2.30	3.93	3.74	6.55	1.04
6.90	1.83	2.25	2.66	6.97	0.82
7.20	1.64	2.00	2.82	4.74	0.64
7.50	1.10	1.61	2.05	4.15	0.52

Acid-extractable P (mmol L^{-1}) of Magnesium System

Depth (cm)	KH$_2$PO$_4$	KH$_2$PO$_4$+MgCl$_2$	KH$_2$PO$_4$+Mg(NO$_3$)$_2$	KH$_2$PO$_4$+MgSO$_4$	KH$_2$PO$_4$+MgCO$_3$
0.30	195.34	209.17	136.28	79.69	428.12
0.60	223.85	213.66	122.55	161.19	301.50
0.90	145.86	186.69	242.50	91.07	138.23
1.20	157.54	173.26	131.32	82.15	176.32
1.50	96.94	157.79	149.89	128.86	92.22
1.80	108.74	144.46	149.67	125.18	71.52
2.10	109.67	65.14	162.69	137.05	72.72
2.40	152.26	75.86	134.03	76.18	72.74
2.70	87.62	62.73	85.64	84.25	30.86
3.00	54.02	45.00	92.91	69.55	40.38
3.30	53.89	55.54	32.98	68.41	12.74
3.60	40.62	61.91	42.78	73.57	7.73
3.90	28.03	62.27	41.74	51.68	4.82
4.20	17.35	33.76	35.76	61.67	3.01
4.50	11.53	20.64	20.84	45.52	2.48
4.80	2.88	11.34	5.69	3.86	2.90
5.10	2.72	3.84	5.20	3.55	2.16
5.40	2.45	2.78	4.12	3.18	1.55
5.70	1.33	3.47	7.00	3.11	1.58
6.00	1.35	3.32	4.04	3.13	1.28
6.30	0.11	0.40	0.26	0.70	0.06
6.60	0.21	1.08	0.51	0.68	0.04
6.90	0.12	1.42	0.20	0.56	0.07
7.20	0.11	0.43	0.17	0.34	0.05
7.50	0.08	0.47	0.14	0.72	0.06

Apparent Diffusion coefficient, D_a (cm^2 s^{-1})

Treatment	σ (cm)	$D_a = \sigma^2 / 2t$
KH_2PO_4 ALONE	3.3	2.25E-06
KH_2PO_4 + KCl	1.8	6.7E-07
KH_2PO_4 + KNO3	2.7	1.51E-06
KH_2PO_4 + K_2SO_4	3.6	2.68E-06
KH_2PO_4 + K_2CO_3	2.1	9.11E-07
KH_2PO_4 + NH_4Cl	3.0	1.86E-06
KH_2PO_4 + NH_4NO_3	2.7	1.51E-06
KH_2PO_4 + $(NH_4)_2SO_4$	3.6	2.68E-06
KH_2PO_4 + $(NH_4)_2CO_3$	2.7	1.51E-06
KH_2PO_4 + $MgCl_2$	3.0	1.86E-06
KH_2PO_4 + $Mg(NO_3)_2$	3.0	1.86E-06
KH_2PO_4 + $MgSO_4$	3.9	3.14E-06
KH_2PO_4 + $MgCO_3$	3.0	1.86E-06

Time, t = 2 weeks = 2419200 secs

Appendix C

EXPERIMENTAL DATA[‡] ON COLUMN SEGMENTATION AND EXTRACTION OF
THE TWO SOIL TYPES IN EXPERIMENT III

[‡] Data represent average of two columns

Gravimetric water content (%) - Ramada soil

Depth (cm)	MKP ALONE	MKP+ASU	MKP+ACB	MKP+KSU	MKP+KCB
0.30	29.85	29.62	32.12	31.54	30.82
0.60	25.47	28.19	30.19	27.37	27.94
0.90	25.01	25.29	27.26	25.81	25.50
1.20	25.31	23.75	26.82	26.69	25.35
1.50	24.72	24.38	25.77	24.86	24.52
1.80	24.46	23.69	25.85	24.38	23.72
2.10	23.19	22.59	25.98	24.89	24.52
2.40	23.19	23.60	25.19	21.94	23.95
2.70	23.10	22.78	24.76	23.89	23.59
3.00	24.67	23.57	25.22	23.50	22.07
3.30	21.94	22.63	24.04	21.69	23.46
3.60	22.47	22.78	24.51	22.91	22.99
3.90	22.63	22.68	24.19	21.90	22.76
4.20	22.53	22.76	24.27	22.88	21.72
4.50	22.20	22.77	24.16	22.06	23.32
4.80	23.16	22.56	23.61	23.34	22.07
5.10	22.62	22.90	24.17	21.13	22.86
5.40	23.08	21.69	23.63	22.64	24.50
5.70	22.97	21.65	23.68	23.65	22.72
6.00	21.78	22.45	23.90	23.86	22.11

Gravimetric water content (%) - Dezwood soil

Depth (cm)	MKP ALONE	MKP+ASU	MKP+ACB	MKP+KSU	MKP+KCB
0.30	26.22	27.16	26.17	27.23	27.38
0.60	25.61	25.77	25.18	23.25	24.55
0.90	24.52	23.51	23.71	24.03	23.73
1.20	23.78	23.56	24.06	23.19	22.02
1.50	23.14	22.45	23.04	21.98	20.60
1.80	23.54	22.27	22.25	21.42	21.55
2.10	22.63	22.33	21.30	22.23	21.38
2.40	21.96	23.04	21.06	21.84	21.29
2.70	22.06	22.30	22.04	21.83	21.13
3.00	22.03	22.69	22.13	20.72	21.33
3.30	21.27	21.03	19.98	20.94	21.13
3.60	21.83	21.56	20.33	20.58	19.94
3.90	21.90	21.31	19.39	20.24	20.52
4.20	21.66	21.89	21.08	20.63	20.38
4.50	22.34	21.14	21.47	20.63	20.50
4.80	22.10	20.88	20.48	20.17	20.63
5.10	21.78	20.91	21.06	21.44	20.65
5.40	21.21	21.31	20.08	19.77	18.92
5.70	21.19	21.14	19.80	19.50	19.12
6.00	20.28	20.45	20.00	19.81	19.27

pH - Ramada soil

Depth (cm)	MKP ALONE	MKP+ASU	MKP+ACB	MKP+KSU	MKP+KCB	CONTROL
0.30	5.37	5.10	5.98	5.39	7.25	6.44
0.60	5.67	5.13	5.79	5.52	6.95	6.62
0.90	6.13	5.05	5.67	5.50	6.74	6.60
1.20	6.11	4.96	5.12	5.62	6.32	6.61
1.50	6.16	4.86	4.94	5.65	6.29	6.62
1.80	6.32	4.89	5.22	5.77	6.50	6.59
2.10	6.50	5.28	5.61	5.91	6.49	6.58
2.40	6.50	5.80	6.06	5.94	6.47	6.44
2.70	6.40	5.99	6.12	6.04	6.46	6.56
3.00	6.44	6.09	6.23	6.08	6.39	6.55
3.30	6.34	6.13	6.31	6.10	6.37	6.49
3.60	6.38	6.19	6.38	6.17	6.29	6.56
3.90	6.36	6.27	6.39	6.23	6.33	6.40
4.20	6.36	6.30	6.36	6.34	6.35	6.49
4.50	6.27	6.36	6.38	6.36	6.30	6.44
4.80	6.16	6.39	6.36	6.36	6.27	6.37
5.10	6.20	6.38	6.33	6.40	6.33	6.36
5.40	6.26	6.32	6.31	6.42	6.23	6.39
5.70	6.24	6.33	6.31	6.43	6.31	6.30
6.00	6.22	6.26	6.33	6.41	6.19	6.29

pH - Dezwood soil

Depth (cm)	MKP ALONE	MKP+ASU	MKP+ACB	MKP+KSU	MKP+KCB	CONTROL
0.30	6.03	5.55	6.69	5.67	7.56	7.65
0.60	6.08	5.87	6.57	5.89	7.66	7.66
0.90	6.25	5.80	6.23	6.11	7.48	7.71
1.20	6.39	5.80	6.06	6.28	7.43	7.73
1.50	6.64	5.79	5.93	6.38	7.43	7.68
1.80	6.83	5.51	6.03	6.82	7.66	7.55
2.10	7.20	5.53	6.33	6.84	7.71	7.72
2.40	7.50	5.58	7.07	7.12	7.75	7.67
2.70	7.74	6.31	7.43	7.11	7.74	7.75
3.00	7.75	6.99	7.54	7.14	7.74	7.74
3.30	7.75	7.14	7.59	7.20	7.69	7.63
3.60	7.76	7.25	7.75	7.27	7.75	7.54
3.90	7.75	7.27	7.75	7.41	7.77	7.57
4.20	7.77	7.40	7.75	7.45	7.78	7.43
4.50	7.67	7.47	7.76	7.55	7.75	7.63
4.80	7.74	7.46	7.79	7.61	7.76	7.62
5.10	7.75	7.66	7.81	7.63	7.79	7.62
5.40	7.76	7.57	7.73	7.69	7.78	7.65
5.70	7.78	7.59	7.77	7.73	7.72	7.61
6.00	7.81	7.58	7.74	7.67	7.68	7.61

Water-extractable P (mmol L^{-1}) - Ramada soil

Depth (cm)	MKP ALONE	MKP+ASU	MKP+ACB	MKP+KSU	MKP+KCB	CONTROL
0.30	89.97	68.89	89.34	61.55	77.23	0.79
0.60	79.41	58.00	70.35	56.55	73.73	1.02
0.90	46.91	44.32	57.12	47.62	39.66	1.05
1.20	29.11	32.90	29.74	35.96	22.80	1.12
1.50	15.87	13.99	17.93	23.77	10.40	1.34
1.80	6.96	6.81	9.07	10.41	5.49	1.28
2.10	1.80	2.51	3.30	1.70	1.10	1.44
2.40	1.07	0.42	0.60	0.85	1.06	1.35
2.70	1.03	0.47	0.73	0.46	0.95	1.53
3.00	0.85	0.49	0.49	0.56	0.99	1.44
3.30	1.08	0.67	0.82	1.10	1.14	1.46
3.60	1.04	0.72	0.49	0.65	1.11	1.46
3.90	0.77	0.83	0.70	0.77	0.98	1.39
4.20	0.91	0.82	0.78	0.35	1.13	1.44
4.50	0.92	1.16	0.76	0.72	1.14	1.43
4.80	0.91	0.66	0.89	1.60	1.11	1.33
5.10	0.80	0.71	0.96	0.82	0.95	1.27
5.40	0.81	0.84	0.87	0.74	0.92	1.07
5.70	0.86	0.80	0.77	0.77	1.06	1.09
6.00	0.83	0.73	0.71	0.90	1.13	1.15

Water-extractable P (mmol L^{-1}) - Dezwood soil

Depth (cm)	MKP ALONE	MKP+ASU	MKP+ACB	MKP+KSU	MKP+KCB	CONTROL
0.30	72.60	81.33	67.04	88.11	99.19	0.48
0.60	67.67	90.58	81.44	85.39	85.74	0.51
0.90	53.98	74.42	57.70	67.74	68.20	0.63
1.20	45.81	56.27	34.64	52.06	39.01	0.71
1.50	29.14	35.91	20.35	25.18	21.83	0.64
1.80	22.38	21.81	8.64	18.51	11.28	0.55
2.10	11.86	12.20	5.95	9.35	3.38	0.56
2.40	5.44	6.41	1.20	1.39	0.91	0.63
2.70	0.49	0.50	0.40	0.21	0.55	0.56
3.00	0.42	0.26	0.43	0.23	0.49	0.67
3.30	0.59	0.42	0.51	0.37	0.31	0.60
3.60	0.50	0.37	0.46	0.40	0.32	0.71
3.90	0.65	0.50	0.51	0.39	0.34	0.66
4.20	0.46	0.53	0.49	0.44	0.28	0.52
4.50	0.62	0.54	0.44	0.52	0.40	0.72
4.80	0.53	0.61	0.48	0.56	0.30	0.67
5.10	0.50	0.57	0.46	0.54	0.31	0.72
5.40	0.53	0.73	0.54	0.56	0.35	0.58
5.70	0.47	0.70	0.50	0.53	0.32	0.63
6.00	0.45	0.83	0.55	0.57	0.37	0.61

Acid-extractable P (mmol L^{-1}) - Ramada soil

Depth (cm)	MKP ALONE	MKP+ASU	MKP+ACB	MKP+KSU	MKP+KCB	CONTROL
0.30	256.19	246.01	292.94	254.73	275.12	31.66
0.60	257.04	244.66	249.64	229.23	276.26	37.05
0.90	164.25	182.00	183.15	189.17	136.05	32.47
1.20	104.85	139.26	107.00	146.00	90.66	37.52
1.50	72.51	73.05	76.81	100.78	65.79	36.20
1.80	53.87	55.26	55.58	65.09	51.27	36.71
2.10	40.82	45.43	44.20	41.39	40.26	43.25
2.40	38.24	35.74	37.07	42.08	42.44	42.91
2.70	39.08	38.23	38.94	37.86	40.63	40.36
3.00	36.66	37.18	36.68	38.52	43.17	44.07
3.30	42.19	38.75	37.48	42.91	39.39	42.76
3.60	41.62	38.78	40.27	38.74	39.85	45.26
3.90	39.75	39.19	37.15	41.08	41.78	44.35
4.20	40.08	39.31	38.31	36.82	42.98	45.34
4.50	40.91	39.09	39.22	39.99	40.54	42.92
4.80	40.43	37.46	40.81	37.87	42.97	42.06
5.10	40.24	38.26	38.15	40.22	41.58	42.60
5.40	40.12	40.11	40.01	38.43	43.42	43.81
5.70	39.02	40.86	41.26	37.17	41.44	43.52
6.00	42.85	40.74	41.89	38.23	41.87	40.48

Acid-extractable P (mmol L^{-1}) - Dezwood soil

Depth (cm)	MKP ALONE	MKP+ASU	MKP+ACB	MKP+KSU	MKP+KCB	CONTROL
0.30	273.87	222.36	272.60	300.84	285.61	31.68
0.60	266.65	276.77	299.61	307.56	306.80	31.65
0.90	187.84	191.03	258.05	235.15	277.60	34.83
1.20	147.92	160.47	110.12	164.61	113.58	34.52
1.50	102.47	115.24	68.19	101.40	70.99	33.47
1.80	75.29	79.37	51.69	73.21	52.77	36.00
2.10	55.12	55.92	48.68	52.96	39.24	37.51
2.40	44.83	42.90	38.07	37.98	35.74	31.87
2.70	34.45	37.18	39.17	32.72	36.40	31.90
3.00	34.00	33.21	33.73	34.43	38.57	37.85
3.30	38.64	35.92	36.71	37.89	36.64	35.65
3.60	34.14	34.21	34.81	35.68	38.92	29.45
3.90	35.80	39.59	35.26	35.07	36.89	34.35
4.20	33.73	34.99	33.36	34.83	36.15	34.36
4.50	35.35	38.46	33.56	36.73	34.13	36.22
4.80	38.28	35.48	37.76	36.20	33.56	33.84
5.10	35.09	35.26	32.92	34.47	40.19	37.29
5.40	38.78	36.01	36.92	35.36	37.47	40.44
5.70	34.88	34.50	35.31	36.28	39.95	39.75
6.00	36.43	36.19	36.63	36.94	40.00	39.75