EFFECT OF FOUR SALTS ON THE TRANSPORT AND RETENTION

OF FERTILIZER P IN SOILS AND ITS AVAILABILITY TO PLANTS

BY

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A Thesis
submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the degree of

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Winnipeg, Manitoba

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ABSTRACT

Growth chamber and laboratory experiments were conducted to investigate the effect of mixing four salts, $(NH_4)_2SO_4$, urea, K_2SO_4 and $MgSO_4$ with ^{32}P-labelled MCP, on the uptake of fertilizer P by plants, and retention and diffusion of ^{32}P in soils.

A growth chamber experiment conducted using four chernozemic soils revealed that, although the total P uptake by buckwheat plants was not significantly affected by the salt treatments, the proportion of P taken up from the fertilizer source was substantially increased. Ammonium salts were more effective than non-ammonium salts in increasing fertilizer P uptake. Whether the enhancement of fertilizer P uptake was mainly due to a chemical or a physiological effect was not clear.

Laboratory incubation experiments were conducted with two soils, a neutral sandy loam and a calcareous loamy sand to investigate the effect of salts on diffusion of P. The addition of $(NH_4)_2SO_4$ and $MgSO_4$ with MCP, increased the extent of P diffusion in both soils. The addition of K_2SO_4 increased P diffusion in the neutral soil, but not in the calcareous soil, whereas urea had little or no effect on P diffusion in both soils.

An elution experiment was carried out to investigate the effect of mixing salts on the retention and movement of P from MCP during elution. The elution of surface-applied P was increased when $(NH_4)_2SO_4$, K_2SO_4 or $MgSO_4$ was mixed with MCP, indicating that less P was retained in the soil. Mixing urea with MCP had little or no effect on P elution. In all the treatments, the peak concentrations of Ca and P were observed together, indicating that P retention was associated with Ca retention.

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According to the mathematical model used to explain the results of the diffusion experiments, the retardation of P movement in soil is mainly due to precipitation of P with displaced Ca, when Ca is the dominant exchangeable species. The addition of sulphate salts increased P diffusion, as sulphate strongly competed with phosphate for precipitation with Ca, thus reducing the amounts precipitated as Ca phosphates. When urea was added with MCP, the pH was increased and carbonate was formed. The higher pH favoured the precipitation of Ca phosphates, however, the pH was not high enough to favour $CaCO_3$ precipitation. Therefore, carbonate, did not compete with phosphate for precipitation with Ca, thus, the addition of urea did not increase P diffusion.

ACKNOWLEDGEMENTS

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1. INTRODUCTION

It has been known that the availability of fertilizer P to plants is influenced by the presence of other non-phosphatic salts. This effect has been observed using many ammonium salts (Bouldin and Sample, 1958; Blanchar and Caldwell, 1966; Blair et al., 1970; Miller et al., 1970; Riley and Barber, 1971; Leikham et al., 1983; Kamprath, 1987; Sangakkara and Cho, 1987; Beever, 1987; Flaten, 1989), as well as some non-ammonium salts such as KNO_3 (Bouldin and Sample, 1958), K_2CO_3, $MgSO_4$ (Starotska and Hill, 1955) and K_2SO_4 (Starotska and Hill, 1958; Miller et al., 1970).

The influence of associated salts in increasing fertilizer P availability has been attributed to either chemical effects which alter the solubility and the availability of added fertilizer P (Rennie and Mitchell, 1954; Starotska and Hill, 1955; Bouldin and Sample, 1958; Miller et al., 1970) or physiological effects which change the uptake pattern of P by plants (Duncan and Ohlrogge, 1958; Miller and Ohlrogge, 1958; Rennie and Soper, 1958; Cole et al., 1963).

It is well established that diffusion is the main mechanism of movement of fertilizer P towards plant roots. Experiments conducted in Manitoba have shown that one dimensional diffusion of fertilizer P in soil columns could be increased by the addition of certain ammonium salts and decreased by others (Beever, 1987). However these salts did not show a consistent effect on P diffusion in all the soils tested. Many researchers have reported pH changes in soil as a result of addition of salts (Bouldin et al., 1960; Isensee and Walsh, 1971; Beever, 1987). Alteration in pH may affect the solubility of fertilizer P depending on

the pH. In addition, pH changes as well as changes in concentrations of ionic species in soil solution could affect the interactions of P with soil constituents and/or other ions i.e. adsorption and precipitation reactions. It is clear that these processes retard the movement of P since they convert P to less mobile forms. If addition of other salts make the soil conditions less favourable for precipitation and adsorption processes, this would lead to an increase in diffusion of P.

Addition of P to soil involves the simultaneous addition of a cation. In calcareous soils, the cation of the added compound would displace the exchangeable Ca of the soil (Sample et al., 1979). Similarly in acidic soils, Al or Fe would be displaced. This displacement would lead to precipitation of P as less soluble Ca, Al or Fe phosphates (Sample et al., 1979; Kim et al., 1983a,b). If another salt with different ion species is added with fertilizer P, the concentration of ionic species in the solution would be altered, which may affect the precipitation reactions and the forms of precipitates. It could be expected that the anion of the salt would compete with phosphate in adsorption and precipitation reactions.

Since diffusion, precipitation and adsorption of P take place simultaneously, it is not possible to find experimentally how these processes are affected by the addition of other salts. Mathematical models have been commonly used to describe the transport of P accompanied with adsorption and precipitation reactions. Such models have been often shown to predict the P reactions and transport reasonably well (Mansell et al., 1977; Hira and Singh, 1978; Enfield et al., 1981b).

A mathematical model was recently developed by Cho (1990), to explain the transport phenomenon of P in calcareous soils, considering the effect of exchangeable cations upon retardation of P transport. This model consisted of five simultaneous transport equations which included transport equations for P, the cation associated with P, displaced Ca, carbonate and H. In formulating the model Cho (1990) considered most of the interactions that would take place, interactions between different ions as well as interactions of ions with soil.

The objectives of this study were:

a) to investigate the effect of four salts, namely, $(NH_4)_2SO_4$, urea, K_2SO_4 and $MgSO_4$ on the plant uptake of fertilizer P,

b) to investigate the effect of the same salts on the solubility, diffusion and retention of fertilizer P in soils and

c) to explain the effects of these salts on P transport and transformations using the mathematical model developed by Cho (1990).

2. REVIEW OF LITERATURE

2.1. Phosphorus chemistry in soil

The importance of phosphorus as an essential plant nutrient has been established for a long time. Plants take up P exclusively from the soil. The total content of P in soil is in the range of 0.02 to 0.15 % (Mengel and Kirkby, 1982), however, only that fraction of P, which occurs in the soil solution, is immediately available to plants. The phosphorus in solution is mainly in the forms of $H_2PO_4^-$ or HPO_4^{2-}, at pH values normally encountered in soils. In unfertilized soil, the P concentration of the soil solution is commonly low, in the range of 0.02 - 0.08 μg mL^{-1} P (Barber et al., 1963). As plants take up P from the soil solution, it is replenished by other fractions of P that are in equilibrium with the solution P. These include the P held on the solid surfaces (adsorbed P), readily soluble forms of P precipitates, as well as sparingly soluble P precipitates which would release P slowly into soil solution.

Since the P concentration in soil solution is often very low, the P supplied to plants as a result of mass flow and root interception is not sufficient to meet the demand of plants for P. Therefore diffusion plays a major role in supplying P to plants. The diffusion coefficient of P in soil is about 10^{-7} cm^2 s^{-1}, whereas in water it is about 10^{-5} cm^2 s^{-1} (Olsen et al., 1962). One reason for this low value of diffusion coefficient of P in soil as compared with P in pure water, is the interaction of P with soil constituents as well as with other ions present in the soil solution, which results in less mobile forms of P. Therefore, from the viewpoint of plant nutrition, these reactions are

quite important, as they retard the movement of soil P as well as fertilizer P toward the plant roots.

2.1.1. Phosphorus retention in soils

The reactions of dissolved P with soil constituents and other ions, which remove P from the solution phase and convert it to less soluble forms are collectively known as retention or fixation of P. Adsorption and precipitation reactions have been considered as the two main mechanisms of P retention in soils. Since both these processes occur simultaneously, although usually at different rates, there is uncertainty regarding the main mechanism of P removal from the solution phase. Generally, at high solution P concentrations, precipitation reactions dominate over adsorption, whereas at low P concentrations, P retention is predominantly due to adsorption (Sample et al., 1980). Thus, when fertilizer P compounds are banded, one would expect precipitation to be the dominant mechanism of P retention in soil close to the band.

Adsorption of P has been categorized into more refined mechanisms during recent years, which includes chemisorption, physical adsorption and anion exchange. In chemisorption, the forces holding P to adsorbing soil particles are essentially of a chemical nature, they exhibit a strong bonding and therefore are anion specific (Taylor and Ellis, 1978). Thus, it is often referred to as specific P adsorption. Physical adsorption, on the other hand, involves adsorption of non-specific ions by electrostatic forces, when OH groups of P adsorbing soil particles are protonated or positively charged. This type of adsorption therefore exhibits pH dependency, as the protonation of surface OH groups in P

adsorbing minerals occur under low pH conditions. Since the adsorption is due to electrostatic forces, P adsorbed can be replaced by any other anion. At the same time, other adsorbed anions could be replaced by phosphates.

A number of soil minerals and amorphous soil colloids have been reported to be capable of adsorbing applied phosphorus (Parfitt, 1978; Sample et al., 1980). These include amorphous and crystalline hydrous oxides of Al and Fe (Wild, 1950; Saeki and Okamoto, 1957; Hsu and Rennie, 1962a,b; Hsu, 1964; Muljadi et al., 1966, Taylor and Schwertmann, 1974; Parfitt et al., 1975; Parfitt, 1977), Fe and Al organo complexes (Wild 1950; Appelt et al., 1975; Gunjigake and Wada, 1981), silicate clay minerals (Russell and Low, 1954; Ellis and Troug, 1955; Muljadi et al., 1966; Kuo and Lotse, 1972; Bar-yosef et al., 1988) and calcium carbonate particles (Cole et al., 1953; Kuo and Lotse, 1972).

The adsorption of P is often followed by a delayed precipitation reaction, specially at high P concentrations. Precipitation of P in soil could be either a surface precipitation (Russell and Low, 1954; Smillie et al., 1987) or precipitation in a separate solid phase (Lindsay and Stephensen, 1959b; Yuan et al. 1960). In acidic soils, precipitation of iron and aluminium phosphate is common (Rusell and Low, 1954; Yuan et al., 1960; Veith and Sposito, 1977b; Sanchez and Uehara, 1980), whereas in calcareous soils, precipitation as calcium phosphate predominates (Cole et al., 1953).

The involvement of exchangeable cations in P precipitation reactions have been reported by many researchers (Sample et al., 1979; Sanchez and Uehara, 1980; Kim et al., 1983a,b). Kim et al. (1983a) observed that in

Al-impregnated cation exchange resin, the addition of KH_2PO_4 resulted in the formation of tarnakite, whereas in Fe-impregnated resin, the addition of the same compound led to precipitation of potassium iron phosphate (Kim et al., 1983b). On addition of diammonium phosphate to soil, Sample et al. (1979) observed precipitation of calcium phosphate, following an ion exchange reaction that displaced exchangeable Ca^{2+} by the added NH_4^+. These results therefore indicate that in an exchange resin, as well as in soil, the forms of reaction products of P, are generally governed by the dominant exchangeable cation species.

Precipitation reactions of P, however, are not limited to solution and exchangeable cations. Lindsay and Stephensen (1959a,b) reported that reaction of soil with TSP (Triple Superphosphate) resulted in the dissolution of Fe, Al, Mn and Ca, which subsequently precipitated with the dissolved phosphate.

2.1.2. Phosphorus diffusion

As the concentration of P in the soil solution is very low, diffusion plays a major role in supplying P to plant roots. When mass flow plus intercepted P are not sufficient to meet the demand of the plants, the P concentration in the solution at the root surface would decrease, which would create a concentration gradient radiating perpendicularly to the root axis. P therefore would diffuse toward the root along this concentration gradient.

Diffusion is described by Fick's law which is mathematically expressed by the equation,

$$J = -D \ (\partial c/\partial x)$$

where J stands for the diffusive flux, c is the P concentration in solution, x is the distance and D is the diffusion coefficient.

When combined with the equation of continuity, which is,

$$(\partial c/\partial t) = -\nabla \cdot J$$

the equation becomes,

$$(\partial c/\partial t) = -\nabla (-D (\partial c/\partial x))$$

which can be simplified as

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

if we assume a constant D, and one-dimensional diffusion. This equation is commonly known as the diffusion equation.

Therefore the diffusive flux of P in soils depends on the diffusion coefficient, which is a property of the medium through which it diffuses, and the concentration gradient.

The diffusion coefficient of P in soil has been reported to be lower than in pure water. Nye (1968) proposed an equation for calculating the effective diffusion coefficient for diffusion of an ion in soil, assuming that it diffuses mainly in the solution, which is,

$$D_e = D\theta f(\partial c_i/\partial c)$$

where D_e is the effective diffusion coefficient, D is the diffusion coefficient in water, θ is the volumetric moisture content, f is the tortuosity factor and $(\partial c_i/\partial c)$ is the inverse of differential buffering capacity. Thus, the main factors influencing the effective diffusion coefficient are the volumetric moisture content, which determines the average fraction of cross sectional area through which P can diffuse, the tortuosity factor which in turn is a function of moisture content and bulk density, and the buffering capacity of P which determines the

proportion of added P that would remain in solution. Hira and Singh (1977) experimentally observed an increase in diffusion coefficient with an increase in bulk density and moisture content in the soil.

2.2. Effect of salts on P availability

An increase in fertilizer P availability as a result of mixing various salts with fertilizer P have been reported by many researchers (Bouldin and Sample, 1958; Rennie and Soper, 1958; Blanchar and Caldwell, 1966; Blair et al., 1970; Miller et al., 1970; Riley and Barber, 1971; Leikham et al., 1983; Sangakkara and Cho, 1987; Beever, 1987; Flaten 1985, 1989). Several factors are believed to be effective in increasing P availability ;

a) an increase in solubility of fertilizer P and its reaction products (Starotska and Hill, 1955; Bouldin and Sample, 1958; Miller et al., 1970; Riley and Barber, 1971; Soon and Miller, 1977),

b) an increase in root proliferation in the fertilizer band (Duncan and Ohlrogge, 1958; Miller and Ohlrogge, 1958) and

c) an effect on metabolic processes controlling P uptake (Cole et al., 1963; Leonce and Miller, 1966; Thein and McFee, 1970).

Some workers have found that certain salts decrease P availability (Starotska and Hill, 1955). This was mainly explained by the decrease in solubility of fertilizer P as a result of addition of these salts.

2.2.1. Chemical effects

The addition of salts to soil modifies the concentration of the ionic species in the soil solution. At the same time, pH changes may

occur. These changes would not only alter the solubilities of fertilizer P and its reaction products, but also would affect the interactions of P with soil constituents and other ions, which may result in an increased availability of fertilizer P.

A lower pH favours dissolution of Ca phosphate compounds. The presence of acidic salts such as $(NH_4)_2SO_4$ and $MgSO_4.7H_2O$ have been shown to increase the solubility of dicalcium phosphate (Starotska and Hill, 1955). Not only the acidic salts, but also certain alkaline salts were observed to increase the solubility of dicalcium phosphate by the same researchers. Thus, it is evident, that the decrease in pH is not the only reason for the increased solubility of P fertilizer compounds.

An increase in plant P uptake, upon addition of different ammonium and potassium salts mixed with concentrated super phosphate, was observed by Bouldin and Sample (1958). This was attributed to the higher amounts of water soluble phosphorus present in the volume of soil influenced by the addition of fertilizer. These results, therefore, suggest that the increased solubility of added fertilizer P and its reaction products, is at least partly responsible for the increased P uptake on addition of these salts.

In contrast to the conclusions of Bouldin and Sample, Caldwell and Blanchar (1965) and Blanchar and Caldwell (1966), observed that chemical solubility and distance of P movement was not significantly affected by the addition of NH_4Cl or KCl with MCP. They concluded that physiological effects play a more prominent role than chemical effects in increasing fertilizer P availability upon addition of salts. It is likely that both chemical and physiological factors are effective in increasing P uptake

on salt addition, and the degree to which each is responsible will depend on the soil characteristics and the type of plant.

Dissolution of P compounds added to soil is followed by precipitation reactions close to the site of application (Sample et al., 1980). Changes in concentrations of ionic species in the soil solution due to addition of salts may change the forms of reaction products. Miller and Vij (1962), observed increased diffusion of P when $(NH_4)_2SO_4$ was added with concentrated superphosphate, and they speculated that the sulphate ion increased the solubility of phosphate by precipitating Ca as calcium sulphate, which would reduce the conversion of phosphate to insoluble Ca phosphates. Isensee and Walsh (1972) observed a decrease in solution P concentration on addition of NH_4NO_3 or KCl with MCP. However, it is uncertain whether this was due to increased diffusion of P, or whether the formation of insoluble Ca and Mg phosphates, following dissolution of Ca and Mg compounds by the high ionic strength soil solution played a major role. The same researchers observed that combining urea with MCP also reduced the solution P concentration, which they reasoned is due to the high initial pH which favours the formation of insoluble Ca phosphates, and thereby removes P from solution.

Changes in pH and alterations in ionic concentrations in the soil solution associated with addition of salts, could affect the adsorption of P to soil particles. In soils containing high amounts of amorphous material, P adsorption is favoured at lower pH values, when the pH dependent charges are predominantly positive (Mengel, 1985). The addition of acidic salts therefore, may promote P adsorption in such soils.

Evans and Sorensen (1986) investigated the effect of different salts on P adsorption and observed that the reaction of P with soil constituents was not affected by the salt source. However, the increased ionic strength of the solution, when high salt concentrations were used, released various organic molecules into solution, which competed with P for adsorption sites, thus reducing the amounts of P retained in soils.

2.2.2. Physiological effects

During recent years much attention has been given to changes in pH and ionic environment that occur in the rhizosphere zone during the growth of the plant (Riley and Barber, 1969; Soon and Miller, 1977; Aguilar and Van Diest, 1981; Nye, 1981). Increases or decreases in pH values have been observed in nutrient culture (Kirkby, 1968) as well as in rhizosphere soil (Riley and Barber, 1969, 1971; Soon and Miller, 1977; Aguilar and Van Diest, 1981) depending on the relative rates of uptake of anions and cations. Riley and Barber (1969) observed an accumulation of HCO_3^- and an increase in pH in the root-soil interface environment of soybean roots as compared to the original soil. They further observed that the magnitude of HCO_3^- accumulation and pH increase was related to the NO_3^- concentration of the soil solution. They inferred that this effect is due to a greater uptake of anions than cations by the plant involving a release of HCO_3^- to maintain electrical neutrality. In a later publication, the same authors showed that when N was supplied in the form of NH_4^+, more cationic than anionic nutrients were absorbed, leading to a pH decrease in the rhizosphere soil, since H^+ ions were released to balance the charge (Riley and Barber, 1971). Similar results were

observed by Soon and Miller (1977).

According to Aguilar and Van Diest (1981), three groups of plants could be identified, considering their abilities to affect the pH of the growth medium. One group consists of plants that absorb approximately equivalent quantities of cationic and anionic nutrients. These plants exert no influence on the pH of the nutrient solution or the rhizosphere. The second group consists of plants that on an equivalence basis absorb more anions than cations as long as nitrate is the main source of N. These plants therefore would tend to raise the pH of the nutrient solution or the rhizosphere. The third group of plants are those that absorb more cations than anions even when nitrate is the main source. Buckwheat is one of the few cultivated crops that belongs to this group. It has been shown that the buckwheat crop exerts an acidifying effect on the soil, even when N is absorbed as nitrate (Ray and Van Diest, 1979).

It is to be expected that changes in rhizosphere pH would alter the availability of fertilizer P to plants. Increased mobilization and higher availability of rock phosphates to plants have been observed due to the acidification of soils as a result of the absorption of more cationic nutrients than anionic nutrients by legumes making use of symbiotically fixed N (Aguilar and Van Diest, 1981). Many other researchers (Miller et al., 1970; Riley and Barber, 1971; Soon and Miller, 1977), observed an increase in availability of fertilizer P when N was supplied in the form of NH_4^+, which resulted in a higher rate of cation uptake and acidification of the rhizosphere. Experiments conducted by Miller et al. (1970) using ^{32}P labelled MCP and an autoradiograph technique showed precipitation of P on the surface of roots when only MCP was applied and

less precipitation when either $(NH_4)_2SO_4$ or K_2SO_4 was added with MCP. They speculated that the precipitate was a calcium phosphate and attributed the difference to a reduced rhizosphere pH as measured, which was caused by the release of H^+ ions into the soil solution during NH_4^+ and K^+ uptake.

Acidification of the rhizosphere soil and increase in P uptake as a result of addition of ammonium salts could be due to nitrification of NH_4^+, which releases H^+ into soil solution (Rennie and Mitchell, 1954; Grunes et al., 1958). However, increased P absorption on NH_4^+ addition, has been observed even when nitrification was inhibited by using nitrification inhibitors (Leikham et al., 1983; Hanson and Westfall, 1985). Blair et al. (1970) documented evidence that the decrease in pH upon addition of NH_4^+ is not the main reason for increased P uptake. Even when the pH of the culture solution was maintained using a constant flow culture system, supply of N in the NH_4^+ form increased the uptake of phosphate. They believed it to be the result of stimulated anion uptake in response to cation (NH_4^+) uptake, as the plant would maintain an anion-cation balance.

The possibility of a specific effect of N on P uptake has been suggested by many researchers (Cole et al., 1963; Leonce and Miller, 1966; Thein and McFee, 1970). Leonce and Miller (1966) hypothesized that the ammonium ion has a specific effect in the transfer of P across the symplast into the xylem. Thein and McFee (1970) suggested the existence of a N requiring metabolite which might influence P uptake. However, the metabolic pathways actually involved are still not identified.

Experiments conducted by Franklin (1969, 1970) revealed that

pretreatment of roots with polyvalent cations increased the P absorption more than the pretreatment with di or monovalent cations. Their results supported the hypothesis that cell wall can act as a negatively charged membrane regulating P uptake by plants. Pretreatment with polyvalent cations reduced the electrical potential at the root surface or within the pores of the negatively charged cell wall more than monovalent cations, which resulted in a higher rate of P uptake by plants.

Duncan and Ohlrogge (1958) and Miller and Ohlrogge (1958) observed an increase in P uptake due to addition of NH_4^+, which they suggested is a result of increased root proliferation in the fertilizer zone. However, results of Miller (1965) and Leonce and Miller (1966) indicated that increased root growth is not a prerequisite for the increased P uptake.

2.3. Modelling P transport and reactions in soil

The commonly used one dimensional form of transport equation describing the simultaneous movement and retention of P through soil is given by

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} - \frac{\beta}{\theta}\frac{\partial s}{\partial t}$$

where c stands for the P concentration in solution, s stands for the solid phase P concentration, D is the hydraulic dispersion coefficient, v is the average pore water velocity, β is the bulk density of the soil, θ is the volumetric water content, t is the time and x is the distance.

To use this equation the rate of change of solid phase P concentration, s, with time must be defined. Two distinct approaches, based on the rates of reactions, are recognized in the literature: the

equilibrium approach and the kinetic approach (Mansell and Selim, 1981; Enfield, 1981; Sparks, 1986, 1989). The equilibrium approach which is based on thermodynamics assumes that the reaction is very rapid and is reversible. Therefore in analyzing such reactions, it is assumed that local equilibrium always exists at every point of the system considered. However, it is well known that in many cases, the reaction of P with soil minerals does not reach equilibrium (Enfield et al., 1976; 1981b; van Riemsdijk and De Haan, 1981). Many researchers have observed that P interactions with soils could be more appropriately described with a kinetic approach as opposed to an equilibrium approach (Kuo and Lotse, 1972; Enfield et al., 1981a; van Riemsdijk et al., 1984a).

Until recently, the models used for P transport were essentially single-ionic models, and most of the models were non mechanistic in describing P retention. It is important to note, however, that on addition of P to soil, a cation is also added to maintain electro neutrality, thus, the cation concentration in the solution too is altered. The direct and indirect effects of these added cations on P retention have been neglected in single-ionic models. Recently, Cho (1990) developed a multi-ionic model, which considered the altered concentrations of cations on addition of P to soil, and their direct as well as indirect effects on P retention and transport.

2.3.1. Single-ionic models assuming chemical equilibrium

Equilibrium methods have been widely used to characterize P adsorption, which generally is a rapid reaction when compared with precipitation and dissolution reactions. Several different adsorption

equations or modifications of these have been used. Langmuir (Olsen and

Watanabe, 1957), Freundlich (Rusell and Low, 1954) and Temkin (Bache and

Williams, 1971) are some of the commonly used equations.

The Langmuir equation was first applied to P adsorption in soil by

Olsen and Watanabe (1957). It is usually expressed as

$$q = abc \ / \ (1+ac)$$

where q stands for the weight of P adsorbed per unit weight of soil, c

is the equilibrium P concentration, b is the adsorption maximum and a is

the equilibrium constant.

This equation can be rearranged as,

$$c/q = 1/ab + c/b$$

Therefore, if the Langmuir equation applies, a plot of c/q vs. c

will be a straight line and a and b could be calculated using the slope

and the intercept of the plot. Thus, the Langmuir equation provides two

very useful parameters for P sorption in soil.

The equation implies that a) energy of adsorption is constant for

each increment of P adsorbed, b) the adsorption occurs on localized sites

and c) the maximum adsorption corresponds to a complete monomolecular

layer (Olsen and Khasawneh, 1980). However, it is unlikely that all these

conditions will hold for P adsorption in soil (Larson, 1967).

Although the Langmuir equation has been successfully used to

describe P adsorption by many researchers (Cole et al., 1953; Olsen and

Watanabe, 1957; Hsu and Rennie, 1962a; Hsu, 1964; Kuo and Lotse, 1972;

Syers et al., 1973; Mehadi and Taylor, 1988), its limitations in

describing P adsorption in soil are well documented in literature

(Larson, 1967; Vieth and Sposito, 1977a; Mansell and Selim, 1981). At

high P equilibrium concentrations, the Langmuir plot of the data has often been shown to deviate from linearity (Olsen and Watanabe, 1957; Hsu and Rennie, 1962; Syers et al., 1973; Blanchar and Stearman, 1985).

Another common isotherm is the Freundlich equation,

$$q = ac^b$$

where q is the weight of P adsorbed per unit weight of soil, c is the equilibrium P concentration and a and b are constants. This isotherm is empirical and the constants have no physical meaning. The constant b is usually less than 1, so that a plot of q vs. c is convex to the c axis.

The Freundlich equation has been shown to be equivalent to a multiple layer Langmuir equation (Enfield and Ellis, 1983). Unlike the Langmuir equation, the Freundlich equation implies neither a constant energy of adsorption nor an adsorption maximum corresponding to monolayer saturation. Confirmation of experimental adsorption data to the Freundlich equation indicates that the energy of adsorption decreases exponentially with increasing surface saturation (Mansell and Selim, 1981).

Freundlich isotherms have been successfully used to describe P adsorption in soil by many researchers (Russell and Low, 1954; Laverdiere and Karam, 1984). The applicability of this isotherm has been shown to be improved by a slight modification of the equation (Fitter and Sutton, 1975). This modification consists of subtracting the native labile P (isotopically exchangeable P) from the sorption data, such that the equation becomes,

$$q = ac^b - q_r$$

where q_r is the native labile P.

The Temkin equation proposed by Bache and Williams (1971) implies that the energy of adsorption decreases linearly with increasing surface saturation. This is expressed as

$$q/b = (RT/B)\ln Ac$$

where A and B are constants and q, c, b are as in the Langmuir equation.

All these isotherms apply when P reactions with soil are at equilibrium, which is never achieved during transport of P in soil. Thus, in many P transport models, P reactions are assumed to be at least locally at equilibrium.

Mathematical models for transport of P in soil assuming a linear, reversible sorption with local equilibrium have been developed by a number of researchers (Caguan et al., 1968; Mansell et al., 1977b). Caguan et al. (1968) tested such a model using P miscible displacement data of two clay soils from Hawaii. They found that the model predicted the experimental data reasonably well in one soil, but not in the other, which had much greater capacity to sorb P from soil solution.

Cho et al. (1970) investigated the convective transport of ^{32}P and ^{31}P in several Manitoba soils. They concluded that a local equilibrium theory cannot be applied to the convective transport of phosphate in soil. Mansell et al. (1977a) came to the same conclusion after comparing different models having a linear or nonlinear instantaneous reaction, or a kinetic reaction to describe P adsorption-desorption.

2.3.2. Single ionic models assuming chemical non-equilibrium

The retention of P from the soil solution occurs as a rapid initial reaction followed by a slower reaction that may not reach equilibrium

even after a contact time of several weeks (Mansell and Selim, 1981). It is believed that adsorption is the initial reaction while the precipitation and/or diffusion into the soil particles controls the slower reaction.

Several approaches have been proposed to describe the kinetic reaction of P with soil (Kuo and Lotse, 1972; Griffin and Jurinak, 1974; Enfield et al., 1981a; Enfield, 1981; Kim et al., 1983 a,b; van Riemsdijk et al., 1984a). Kuo and Lotse (1972) investigating the kinetics of P adsorption by $CaCO_3$ and Ca- kaolinite, assumed a second order kinetic model with equilibrium described by a Langmuir isotherm. The kinetic equation they used considers both the change in solution P concentration as well as the change in surface unsaturation of the adsorbent. Thus, the rate of P sorption was expressed by the equation

$$dx/dt = k_1 (Co-x)(m-x) - k_{-1} x$$

where k_1 is the rate constant for adsorption, k_{-1} is the rate constant for desorption, (Co-x) represents the P ions remaining in solution and (m-x) represents the surface unsaturation.

Since at equilibrium, dx/dt = 0, this equation becomes

$$k_1 (Co-x)_{eq} (m-x)_{eq} = k_{-1} x_{eq}$$

The Langmuir equation is obtained by rearranging this equation and expressing x and m in μg adsorbed/g of adsorbent:

$$1/k_m m = c_{eq}/x - c_{eq}/m$$

where K_m is the equilibrium constant and is equal to k_1/k_{-1}.

According to Griffin and Jurinak (1974) the kinetics of P adsorption on calcite could be described by two simultaneous reactions, a second order initial reaction accompanied by a pseudo-first order slower

reaction. The second order P adsorption on the surface of calcite is regulated by the P concentration in solution and the number of empty adsorbing sites as in the model proposed by Kuo and Lotse (1972). However, in this model, this reaction is accompanied by a slow first order reaction, which is ascribed to the surface rearrangement of amorphous phosphate ion clusters into calcium phosphate heteronuclei.

Enfield et al. (1976) compared five models to describe P sorption: an empirical model; a linearized first order model; a first order Freundlich model; a diffusion limited Langmuir model; and a diffusion limited Freundlich model. They showed that, of the models considered, the experimental data fitted best to a diffusion limited model combined with Langmuir or Freundlich equations. A similar model was proposed by van Riemsdijk et al. (1984a) to study the P reactions with metal oxides in soils. Phosphate diffusion through the surface coating of metal phosphate was taken as the rate limiting step. The experimentally observed sorption data using two top soils and one sub soil supported the model theory (van Riemsdijk and van der Linden, 1984, van Riemsdijk et al.,1984b).

Enfield et al. (1981a) proposed a model based on an instantaneous reversible adsorption theory plus a time-dependent solubility theory. They assumed that first order kinetics would adequately describe the formation or dissolution of phosphate minerals. The proposed theory is described by the equation,

$$S(t) = bac(t)/ [1+ac(t)] + \sum_{j=1}^{n} P_j$$

where a and b are as in the Langmuir equation, S(t) is the P sorption at

time t, $c(t)$ is the solution concentration at time t,

$$\text{and } P_j = \begin{cases} \int a_j \, [c(t)-cE_j] \ dt & \text{for } 0 <= P_j <= P_{mj} \\ P_{mj} & \text{for } p_j > P_{mj} \\ 0 & \text{for } p_j < 0 \end{cases}$$

where P_j stands for the solid phase concentration of a given species, a_j stands for the rate of precipitation or dissolution of a given species, cE_j represents the equilibrium solution concentration for a given species as a function of pH, P_{mj} is the maximum concentration of solid phase P which can be formed by a particular ionic species and j is the symbol indicating the species under consideration.

As indicated by the equation several compounds could be forming simultaneously, each following first order kinetics. As equilibrium solution concentration decreases, the number of compounds forming would decrease, with an associated dissociation of more soluble compounds.

Transport models assuming either reversible or irreversible kinetic reactions for applied P have been developed and tested during the past few years (Cho et al., 1970; Mansell et al., 1977b; Panda et al., 1978; Mansell et al., 1985). Cho et al. (1970) formulated a convective-dispersive P transport model considering P interaction with soil to be a first order irreversible reaction. They hypothesized that a reversible sorption reaction with a rapid forward reaction and a slower reverse reaction manifests itself like an irreversible reaction during a relatively short time interval. They developed an analytical mathematical solution for the transport equation combined with a sorption described by the equation,

$$Q = (k/\theta)c$$

where Q is the volumetric reaction rate, θ is the average rate of water movement, c is the P concentration in solution and k is a first order rate coefficient.

Their solution assuming a step-input boundary condition was:

$$c/c_o = 0.5 \exp (-kt/\rho) \, \text{erfc}[(x-vt)/\sqrt{(4Dt)}]$$

where c_o is the concentration introduced at the boundary and erfc is the complementary error function.

Panda et al. (1978) used the model developed by Cho et al. (1970) to describe P movement, and observed a poor agreement between calculated and experimental breakthrough curves for P concentrations in the effluent. They concluded that P sorption from the flowing soil solution did not obey a strictly irreversible first order reaction.

Mansell et al. (1977b) used a transport model with a reversible first order kinetic adsorption-desorption process. They observed that in both water saturated and water unsaturated soil, there was a good agreement between calculated and experimental data. Mansell et al. (1985) formulated a model assuming that P sorption occurs as two consecutive reactions, rapid physical adsorption followed by chemisorption. Both reactions were assumed to be first order and reversible. However the applicability of this model was not tested using experimental data.

2.3.3. Single-ionic models assuming both chemical equilibrium and non-equilibrium

Overman et al. (1976) obtained an analytical mathematical solution for convective-dispersive transport equations where P interactions were described by both reversible instantaneous reactions and irreversible

kinetic reactions. Sorption-desorption was assumed to be linear, reversible and instantaneous, combined with a kinetic irreversible removal of P from soil solution by a first order sink. This model was used to predict the movement of P through soil columns during steady water saturated flow. They also compared calculated and measured P concentrations in a field site that has been irrigated with municipal waste water for 5 years. The distribution of solution P concentration with soil depth was closely related with the distribution predicted from the mathematical model. Calculated values for the irreversible reaction rate constant also agreed with the experimentally obtained values.

Cameron and Klute (1977) formulated a one-dimensional convective-dispersive transport model where a combination of equilibrium and kinetic adsorption were hypothesized to describe the nature of the overall reaction. The kinetic and equilibrium reactions were considered to be independent of each other. The equilibrium reaction was expressed using a Freundlich isotherm, and the kinetic reaction was assumed to be first order and reversible. The applicability of this model was tested using the P breakthrough curves obtained by Cho et al. (1970) in a Wellwood clay loam soil, and the results clearly indicated that P retention in the soil could be represented by the model.

Camargo et al. (1979) developed a similar model assuming two groups of adsorption sites, where P adsorption in the first group reaches equilibrium instantaneously, while in the second group the reaction is time dependent. The model adequately described the P break-through curves for a range of soil aggregate sizes and pore water velocities.

2.3.4. Single-ionic mechanistic models for P transport

None of the above mentioned models considers the mechanisms by which P is removed from the solution phase. A single-ionic multiphase mechanistic model for describing transformations and transport of P was presented by Mansell et al. (1977a). Six kinetic reactions describing adsorption, desorption, mobilization, immobilization, precipitation and dissolution were considered to control P transformations among solution, adsorbed, immobilized (chemisorbed) and precipitated phases. The transport of P was described using convective-dispersive theory. Four simultaneous equations were used to describe the rate of P transfer among the four phases. When the convective flow is negligible, these equations could be expressed as:

$$\partial(\theta A)/\partial t = -\theta(K_a A^n + K_3 A) + \rho_B(K_d B + K_4 D)$$

$$\partial(\rho_B B)/\partial t = K_A \theta A^n - (K_d + K_1) \rho_B B + K_2 \rho_B C$$

$$\partial(\rho_B C)/\partial t = K_1 \rho_B B - K_2 \rho_B C$$

$$\partial(\rho_B D)/\partial t = K_3 \theta A - K_4 \rho_B D$$

where A stands for P concentration in solution, B, C, and D represent the amounts of P sorbed, immobilized, or precipitated per gram of soil, respectively, n stands for a constant representing the order of adsorption, and K_a, K_d, K_1, K_2, K_3 and K_4 stand for the rate constants for adsorption, desorption, immobilization, mobilization, precipitation and dissolution respectively.

Mansell et al. (1977a) presented simulated results for a range of rate coefficients. However, the applicability of this model was not tested with experimental results.

2.3.5. Multi-ionic mechanistic model for P transport

Cho (1990) developed a multi-ionic mechanistic model to describe P transport in soil. He emphasized that P transport is not only governed by P transformations in soil, but also by the transformations of other ions, which may in turn affect the P interactions. For example, cation added with phosphate may be involved in an ion exchange reaction, and if the soil is dominant in Ca, the displaced Ca may precipitate with phosphate. According to Cho (1990) to describe the P transport in a calcareous soil, a minimum of five simultaneous transport equations are required. These include transport equations for P, for the cation associated with P, for displaced Ca, for carbonate and for H. The main interactions considered were an ion exchange reaction which releases Ca into the soil solution, subsequent precipitation of Ca with phosphate or carbonate, adsorption of P on $CaCO_3$ particle surfaces and H production during precipitation of Ca phosphates and Ca carbonates. In addition, the conversion of $H_2PO_4^-$ to HPO_4^{2-} and vice versa with the changes in pH was taken into account.

The general forms of equations are:

$$\frac{\partial A}{\partial t} = D \frac{\partial^2 A}{\partial x^2} - \frac{\partial S_A}{\partial t}$$

$$\frac{\partial B}{\partial t} = D \frac{\partial^2 B}{\partial x^2} - \frac{\partial S_B}{\partial t} - \phi_c - \phi_q$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{\partial S_c}{\partial t} - \phi_c$$

$$\frac{\partial q}{\partial t} = D \frac{\partial^2 q}{\partial x^2} - \phi_q + \phi_E$$

$$\frac{\partial H}{\partial t} = D \frac{\partial^2 H}{\partial x^2} + \phi_{H1} + \phi_{H2} + \phi_{H3}$$

where A, B, C, q and H stand for the solution concentrations of the cation added with P, displaced Ca, phosphate, carbonate and H, respectively. S_A is the concentration of exchangeable cation, whereas S_B stands for the concentration of exchangeable Ca. S_c represents the concentration of adsorbed P on the surfaces of $CaCO_3$ particles. All these concentrations were expressed as solution concentrations. ϕ_c and ϕ_q represents the rates of precipitation of Ca phosphates and Ca carbonates and ϕ_{H1} and ϕ_{H2} stand for the rates of H^+ production due to precipitation of Ca phosphates and Ca carbonates respectively. ϕ_E stands for the rate of dissolution of atmospheric CO_2 and ϕ_{H3} stands for the rate of production of H^+ due to dissolution of atmospheric CO_2.

3. EXPERIMENTAL PROCEDURE AND RESULTS

3.1. Growth chamber experiment

As mentioned in the literature review, there is much evidence indicating that ammonium salts, when mixed with a P carrier, can increase P uptake by plants. However, the effectiveness of non-ammonium salts in enhancing P uptake is not yet very clear. A growth chamber experiment was conducted to investigate the effect of addition of two ammonium salts and two non-ammonium salts on the availability of fertilizer P.

Methods

Four soils were used for the experiment, Almasippi loamy sand, Stockton sandy loam, Red River clay and Firdale loam. Soil samples were taken from the A_p horizon, and prior to use, were air dried and passed through a 2 mm mesh sieve. The legal location and some of the physical and chemical properties of the soils are given in Table 1.

The $NaHCO_3$ extractable P contents were unusually high in Stockton sandy loam and Firdale loam soils when compared with the average value of 10-12 μg g^{-1} P obtained by the Provincial Soil Testing Laboratory in Manitoba. It is possible that these soils may have been fertilized prior to sampling.

^{32}P-labelled monocalcium phosphate ($Ca(H_2PO_4)_2.2H_2O$) was used as the P fertilizer in this experiment (Preparation of solid labelled MCP is given in Appendix A). The five treatments consisted of the addition of labelled MCP alone, or mixed with one of four salts, $(NH_4)_2SO_4$, urea, K_2SO_4 or $MgSO_4$. All the salts used were in the solid form. Each treatment was

Table 1. Chemical and physical properties of the soils used.

Soil series	Almasippi	Stockton	Red River	Firdale
Legal location	31-8-6E	SW29-11-14	28-8-3E	NW36-11-13
Soil classification	Gleyed Rego Black, carbonated	Orthic Black	Gleyed Rego Black	Orthic Dark Grey
Texture	Loamy sand	Sandy loam	Clay	Loam
pH (1:1, soil:water)	8.0	7.3	7.6	7.0
Organic matter (%) (Walkley-Black)	8.4	3.9	9.2	6.7
CEC (mmol(+) kg^{-1}) (Rhoades, 1982)	122	215	541	257
Available P (μg g^{-1}) (Olsen et al., 1954)	7.8	64.6	28.0	84.0
Carbonate content (%) (Bundy and Bremner, 1972)	4.9	very low	<1	very low
Field Capacity (%) (1/3 bar)	25.6	22.0	42.8	19.3

replicated three times. The pots were arranged in randomized complete blocks inside the growth chamber and rotated within the block weekly.

Buckwheat (Fagopyrum esculentum Moench. variety Mancan) was grown in cylindrical pots (20 cm diameter) lined with polyethylene bags. Each pot contained 5 kg soil. MCP was placed as a narrow band across the centre of the pot, 5 cm below the surface, with or without mixing with another salt, depending on the treatment. All salts were ground to a fine powder prior to mixing with MCP. P was added at the rate of 20 kg P ha^{-1} on an area basis, which corresponded to 62.8 mg P per pot.

In the treatment where $(NH_4)_2SO_4$ was banded with MCP, $(NH_4)_2SO_4$ was added to obtain a rate of 100 kg N ha^{-1} on an area basis, which corresponded to 314.2 mg N per pot, or 11.2 mmol of the salt per pot. In the other treatments, urea, K_2SO_4 or $MgSO_4$ were added at the rate of 11.2 mmol of the salt per pot, so that all the treatments had the same molar concentration of salts added.

In the treatments where N and/or K were not banded with MCP, NH_4NO_3 or K_2SO_4 at the same rates were applied, by uniformly mixing these fertilizers throughout the soil. In addition, Zn at the rate of 8 μg g^{-1} and Cu at the rate of 5 μg g^{-1} were added by uniformly mixing solid $ZnCl_2$ and $CuCl_2$ throughout the soils.

Soils were watered daily to maintain at field capacities. Ten seeds of buckwheat were sown 1 cm below the surface, in a row just above the fertilizer band. Seedlings were thinned to 5 plants per pot after emergence. The environmental conditions used were 20 C temperature and 50% relative humidity during the day, and 15 C temperature and 80 % relative humidity during the night, with a 16 hour day length. Lighting

was from a mixture of incandescent and fluorescent lamps giving an average intensity of 350 $\mu Ei\ s^{-2}$.

Plants were harvested at 39 days, which corresponded with the flowering stage. Plants were dried at 70 C for 48 hours and ground using a small Wiley mill. Plant samples were analyzed for total N using the Kjeldahl procedure and total P and K by nitrate-perchlorate digestion. Total P was determined colorimetrically by the molybdate blue-ascorbic acid method (Murphy and Riley, 1962) with a Baush and Lomb spectrophotometer at a wavelength of 885 nm. The radioactive P was measured by liquid scintillation counting. K was measured using a Perkin-Elmer 560 atomic absorption spectrophotometer.

Total uptake of N, P and K by plants were calculated. Phosphate derived from fertilizer (PDFF) was determined using the equation,

$$PDFF = \frac{\text{Specific activity of plants}}{\text{Specific activity of fertilizer}} \times 100$$

and the utilization of fertilizer phosphorus was calculated .

Results and Discussion

The dry matter yield, plant uptake of N, P and K, PDFF and per cent utilization of fertilizer P for all treatments are given in Appendix B.

The dry matter yield was not significantly affected by the addition of salts with MCP (Table 2), except in the Red River clay, where $MgSO_4$ treatment gave a significantly lower yield than the $(NH_4)_2SO_4$ or urea treatments. The corresponding plant P concentration in the $MgSO_4$ treatment was significantly greater than in the other treatments indicating a dilution effect in the other treatments. In all four soils tested, the

total P uptake values were not significantly affected by any of the treatments. A similar study conducted by Starotska and Hill (1955) using alfalfa and rye grass showed significant increases in plant P uptake in 3 of the 4 soils tested, when dicalcium phosphate was mixed with $(NH_4)_2SO_4$ or $MgSO_4$, as compared to adding dicalcium phosphate alone. In their study, mixing with K_2SO_4 significantly increased the P uptake in all the soils, whereas, urea decreased plant P uptake significantly in one soil, but had no significant effect on the other 3 soils. However, in this study, P uptake by buckwheat was not affected when P fertilizer was mixed with any of the salts tested, possibly due to the ability of buckwheat to utilize fertilizer P more efficiently compared to most other crops as reported by Strong and Soper (1974 a,b). Sangakkara and Cho (1987), also observed using four different crops, canola, lentil, soya bean and wheat, that the enhancement of P uptake on addition of P mixed with ammonium salts is less with crops having a higher efficiency of fertilizer P utilization.

The plant P concentrations were fairly low in Almasippi loamy sand which had a low content of available P (Table 2). The concentrations were lower than the critical P concentration values (0.20 - 0.24 %) published in the literature (Larsen et al., 1952; Andrew and Robins, 1971).

The PDFF and % fertilizer P utilization values were much higher in Almasippi loamy sand, when compared with the other soils (Table 3). Plants grown in Almasippi soil derived approximately 40 -60 % of their P from the fertilizer source, whereas in the other three soils less than 15 % of the P was derived from the fertilizer. The higher recovery of fertilizer P in the Almasippi soil suggests that the inadequacy of native labile soil P enhanced the plant uptake of P from the fertilizer source,

whereas, the high level of native soil P in the other soils had a negative effect on P uptake from the fertilizer.

PDFF as well as P utilization were affected by the addition of salts with MCP (Table 3). Mixing $(NH_4)_2SO_4$ with MCP, increased the PDFF significantly in three soils, while the increase in P utilization was statistically significant for all the four soils. Similar effects of $(NH_4)_2SO_4$ on P uptake have been reported in the literature (Miller et al., 1970; Beever, 1987; Sangakkara and Cho, 1987).

Addition of urea with MCP significantly increased the PDFF and P utilization consistently in all the soils. Urea appears to be superior to other salts tested in increasing the fertilizer P utilization, except in the calcareous Almasippi soil, having a low content of native soil P. Ammonia toxicity on addition of urea have often been reported (Toews and Soper, 1978; Flaten, 1989), and it is documented that the release of free ammonia is more likely when the soil is calcareous (Fenn and Kissel, 1973). Therefore, it is possible that in the calcareous Almasippi soil, the presence of free ammonia reduced the beneficial effect of mixing urea with MCP.

The increase in availability of P fertilizer associated with the addition of ammonium salts could possibly be a result of acidification of the rhizosphere as has been reported in the literature (Riley and Barber, 1970; Soon and Miller, 1977). Rhizosphere acidification may occur as a result of nitrification of NH_4^+ which releases H^+ (Rennie and Mitchell, 1954; Grunes et al.,1958), or it may occur due to the higher cation uptake by plants releasing H^+ into soil solution (Miller et al., 1970).

Table 2. The effect of associated salts on dry matter yield,
plant tissue P concentrations and total P uptake.

Treatment	Almasippi	Stockton	Red River	Firdale
Dry Matter Yield (g pot^{-1})				
MCP (only)	12.4 A	12.6 A	11.0 AB	11.0 A
MCP + $(NH_4)_2SO_4$	14.2 A	13.3 A	12.9 B	10.6 A
MCP + Urea	13.3 A	12.2 A	12.9 B	12.6 A
MCP + K_2SO_4	13.7 A	16.5 A	12.6 AB	13.1 A
MCP + $MgSO_4$	13.2 A	15.1 A	10.2 A	11.6 A
Plant tissue P concentration (%)				
MCP (only)	0.18 A	0.53 A	0.37 A	0.56 A
MCP + $(NH_4)_2SO_4$	0.16 A	0.48 A	0.36 A	0.60 A
MCP + Urea	0.19 A	0.47 A	0.33 A	0.55 A
MCP + K_2SO_4	0.18 A	0.51 A	0.33 A	0.56 A
MCP + $MgSO_4$	0.17 A	0.50 A	0.44 B	0.67 A
P uptake (mg P pot^{-1})				
MCP (only)	21.94 A	66.88 A	40.50 A	61.21 A
MCP + $(NH_4)_2SO_4$	22.34 A	64.19 A	46.20 A	62.52 A
MCP + Urea	23.63 A	57.57 A	42.93 A	70.01 A
MCP + K_2SO_4	24.47 A	83.44 A	40.96 A	72.26 A
MCP + $MgSO_4$	21.95 A	75.66 A	44.36 A	77.40 A

Numbers in the same column not designated by the same letter differ
significantly at 5% level (Duncan's Multiple Range Test)

Table 3. The effect of associated salts on PDFF and P utilization.

Treatment	Almasippi	Stockton	Red River	Firdale
		PDFF (%)		
MCP (only)	38.44 D	2.02 C	4.97 C	2.89 B
MCP + $(NH_4)_2SO_4$	58.57 A	6.77 AB	9.71 AB	4.01 B
MCP + Urea	51.50 B	8.21 A	13.11 A	6.75 A
MCP + K_2SO_4	48.98 B	2.75 C	9.98 AB	4.32 B
MCP + $MgSO_4$	44.33 C	4.04 BC	7.17 BC	3.27 B
		P utilization (%))		
MCP (only)	13.36 B	2.16 B	3.20 D	2.72 D
MCP + $(NH_4)_2SO_4$	20.80 A	6.78 A	7.15 B	3.98 C
MCP + Urea	19.33 A	7.19 A	8.86 A	7.31 A
MCP + K_2SO_4	19.09 A	3.65 B	6.15 BC	4.97 B
MCP + $MgSO_4$	15.51 B	3.84 B	5.06 C	4.02 C

Numbers in the same column not designated by the same letter differ significantly at 5 % level (Duncan's Multiple range test).

In both $(NH_4)_2SO_4$ and urea treatments, the fertilizer P uptake was increased without a significant increase in N uptake (Appendix B). Similar results have been reported in the literature (Soper and Nethsinghe, 1972). However, it should be noted that in the $(NH_4)_2SO_4$ and urea treatments, N was supplied only in NH_4^+ form, whereas in the other treatments, N was supplied in both NH_4^+ and NO_3^- forms, since NH_4NO_3 was added. Thus, it is possible that in the ammonium salt treatments, more N was taken up in the NH_4^+ form, which may lead to physiological acidification of the rhizosphere. Apart from the rhizosphere acidification, the increase in root proliferation near the band on addition of ammonium salts could have played a role in increasing fertilizer P uptake.

Not only the ammonium salts, but even the non-ammonium salts increased the PDFF and P utilization, but the effects were not always statistically significant. In the two soils with lower native soil P contents, Almasippi loamy sand and Red River clay, K_2SO_4 significantly increased the PDFF and P utilization, but $MgSO_4$ did not have a consistent significant effect. The increased availability of fertilizer P on addition of these non-ammonium salts could be through a chemical effect, possibly by forming P reaction products that are more soluble than those formed when MCP was added alone (Miller and Vij, 1962). When K_2SO_4 was added, an increase in K^+ uptake was observed (Appendix B), which may have increased the fertilizer P availability, through physiological acidification of the rhizosphere (Miller et al., 1970).

Conclusions

Neither ammonium nor non-ammonium salts affected the total P uptake by plants, but all the salts increased the proportion of P taken up from the fertilizer source. The utilization of fertilizer P was higher in the Almasippi soil, probably because it had a lower content of native available P.

Ammonium salts seem to have a more pronounced effect than non-ammonium salts in increasing the availability of MCP. In three of the soils, urea showed a superior effect over the other salts, however, in the calcareous Almasippi soil, $(NH_4)_2SO_4$ showed the greatest effect. This is probably due to the ammonia toxicity on addition of urea to this soil. Although no direct evidence of this effect was found, ammonia toxicity upon addition of urea to calcareous soils is well documented in the literature.

Experimental results did not give a clear indication as to the reason for the increased fertilizer P uptake on addition of salts. It is likely that both chemical and physiological effects played a role, in increasing the fertilizer P uptake.

3.2. Column experiment 1

The results of the growth chamber experiment did not show an enhancement of P uptake due to addition of salts with MCP (Table 2). However, the results indicated that an increased proportion of P was taken up from the fertilizer source, which could have been due to chemical changes that took place on addition of salts, or due to physiological effects that enhanced plant P uptake from the fertilizer source. To further investigate the salt effect on the chemical availability of MCP, laboratory studies were conducted using incubated soil columns.

Methods

A Stockton sandy loam was used in this experiment. The soil characteristics are given in Table 1. The soil was passed through a 1 mm mesh sieve prior to use. The salts used were the same as those in the growth chamber experiment.

Columns consisted of 20 acrylic rings (5.1 cm diameter, 5 mm height), stacked and taped to form a cylinder. The bottom ring was glued to an acrylic plate which had been drilled with approximately 15 holes (approx. 3 mm diameter) for aeration. Polyethylene mesh (Spectramesh, 150 μm opening) was glued between the bottom ring and the plate.

The soil was uniformly moistened to its field capacity before packing into the cylinders. The soil was packed to obtain a bulk density of 1.3 g mL^{-1} (air-dry basis).

Labelled MCP in the solid form was added to the surface, as uniformly as possible, with or without mixing with a salt depending on

the treatment. Rates applied were same as in the growth chamber experiment, which was equivalent to 40.87 mg P per column (166.28 mg MCP per column) and 8 mmol of salts per column.

Protective acrylic collars (3 cm height, 5.1 cm diameter) were taped to the top of the column. Then the columns were covered with parafilm which was punctured several times to allow air exchange. The columns in an upright position were incubated in a container at 100 % relative humidity and 20 C temperature. After periods of 1, 2, 4 and 6 weeks, two replicate columns for each treatment were sliced into 5 mm sections using a sharp knife. Soil samples from the replicates of each treatment were analyzed separately. Approximately half of the soil in one section was placed in a weighed moisture can for moisture content determination. The rest of the soil was used for chemical analyses.

Total inorganic P was determined using a method described by Hesse (1971). The method was slightly modified. A preliminary experiment conducted using soil samples with known amounts of added ^{32}P, showed that more than 95 % of the P could be recovered by this method. According to the method, approximately 1 g of soil was weighed into a centrifuge tube (15 mL), mixed with 10 mL of concentrated hydrochloric acid and heated on a steam bath for 10 minutes. The sample was then kept at room temperature for 1 hour and centrifuged at 3000- 4000 rpm for 5 minutes, and the solution was decanted into a 100 mL volumetric flask. Then 10 mL of deionized water was added to the remaining soil in the centrifuge tube, centrifuged again and the solution was decanted into the same volumetric flask. This step was repeated again, and made to 100 mL by adding deionized water. The total P in solution was measured by the

molybdate blue-ascorbic acid method (Murphy and Riley, 1962). ^{32}P was measured using a Beckman 7500 liquid scintillation counter.

Approximately 2 g of soil was leached with 30 mL of 2 mol L^{-1} NaCl using suction through a column with a diameter of 2 cm. The leachate was made to 100 mL by adding deionized water. The pH of the solution was measured using a Fisher Accumet 620 pH meter. Ca^{2+}, Mg^{2+} and K^+ of the leachate was measured using a Perkin-Elmer 560 atomic absorption spectrophotometer. Ammonium + ammonia was measured using an automated procedure modified from Svensson and Anfalt (1982), whereas nitrate + nitrite were measured using an automated procedure modified from Kamphake et al. (1967).

Results and Discussion

The moisture contents were generally uniform throughout the columns in all treatments. The concentration profiles of total labelled P, pH and exchangeable Ca^{2+} after 1 and 6 weeks were plotted using the mean data from duplicate soil columns (Fig. 1-6). Total labelled P, pH and exchangeable Ca^{2+} distribution after 2 and 4 weeks of incubation, as well as ammonium + ammonia, nitrate + nitrite, K and Mg distributions at all time periods are given in Appendix C.

The variation in duplicate soil columns was generally small, except for the labelled P concentration in the surface sample which had a high variability because of the presence of the solid residue. Due to this reason the area under the curve, ^{32}P concentration against the distance, (which gives the total labelled P) was not the same even though the same rates of P were applied to all the columns. The average error between the

replicates, when expressed as a percentage of the measured, was approximately 10 % for labelled P and often less than 2 and 5 % for pH and exchangeable Ca, respectively. However, it should be noted that in the labelled P measurement, the % error between replicates was higher at the diffusion front, where the labelled P activity was very low.

Labelled P distribution

Fig. 1 shows the distribution of labelled P after 1 week. The distance at which the extrapolated labelled P concentration is zero was considered as the distance of P diffusion. In the MCP (only) treatment P diffused to a distance of approximately 1.5 cm, which is somewhat less compared to the distance of P movement observed by other researchers using monoammonium and diammonium phosphates (Khasawneh et al. 1974; Beever, 1987; Flaten, 1989).

At 1 week of incubation, the addition of $(NH_4)_2SO_4$ and urea with MCP (Fig. 1a) did not affect the extent of P movement as compared to the MCP (only) treatment. But the addition of K_2SO_4 + MCP as well as $MgSO_4$ + MCP enhanced the movement of labelled P (Fig. 1b), and the extent of enhancement was greater with $MgSO_4$ than with K_2SO_4.

When the incubation time was extended to 6 weeks (Fig. 2), the effects of addition of salts with MCP upon phosphate transport become more apparent. The addition of $(NH_4)_2SO_4$ + MCP (Fig. 2a) substantially increased the distance of P movement as compared to the MCP (only) treatment. The addition of urea + MCP resulted in higher concentrations of labelled P close to the application site, to a distance of about 1.2 cm, but beyond that distance, the concentrations dropped sharply, and the
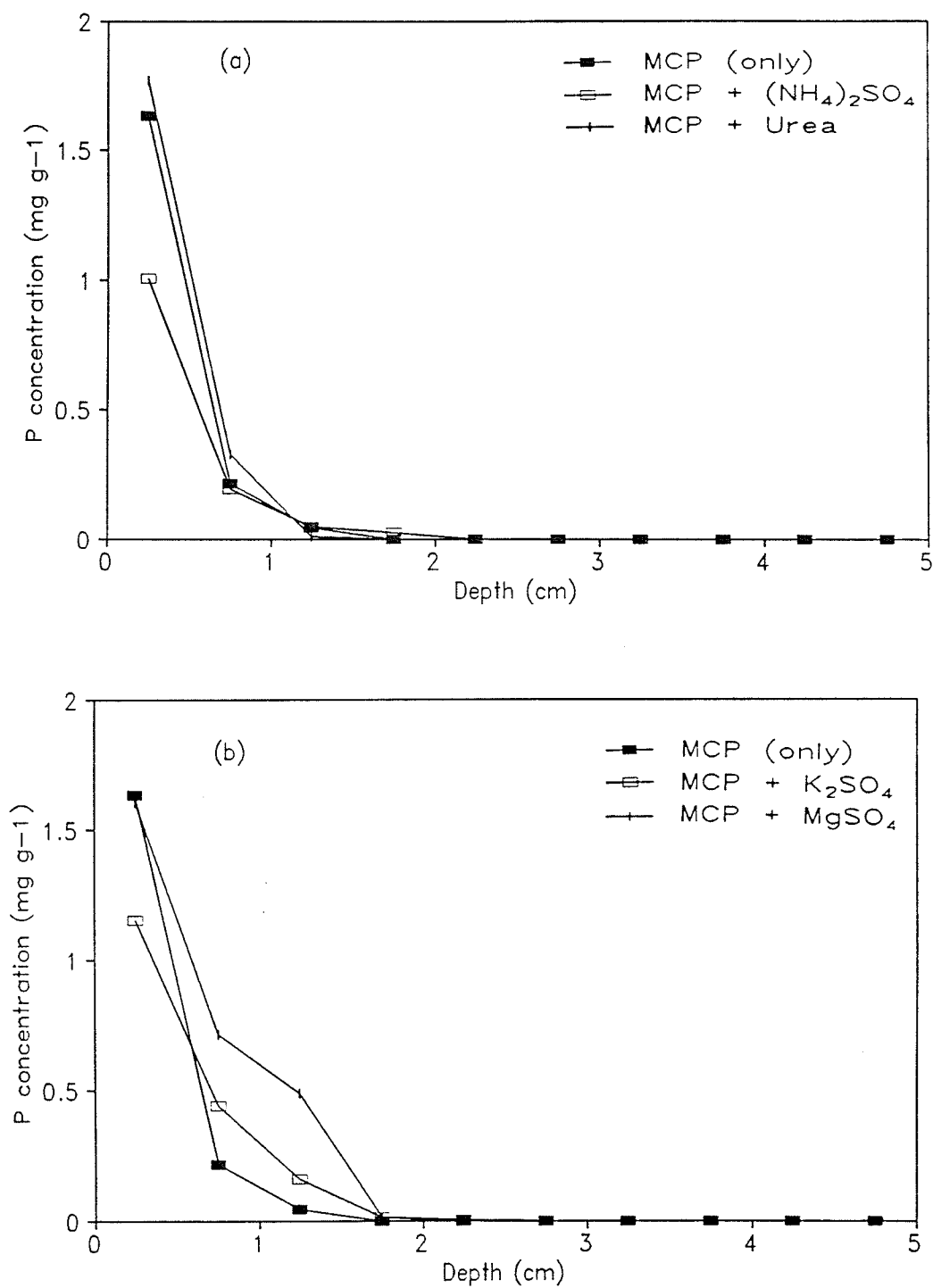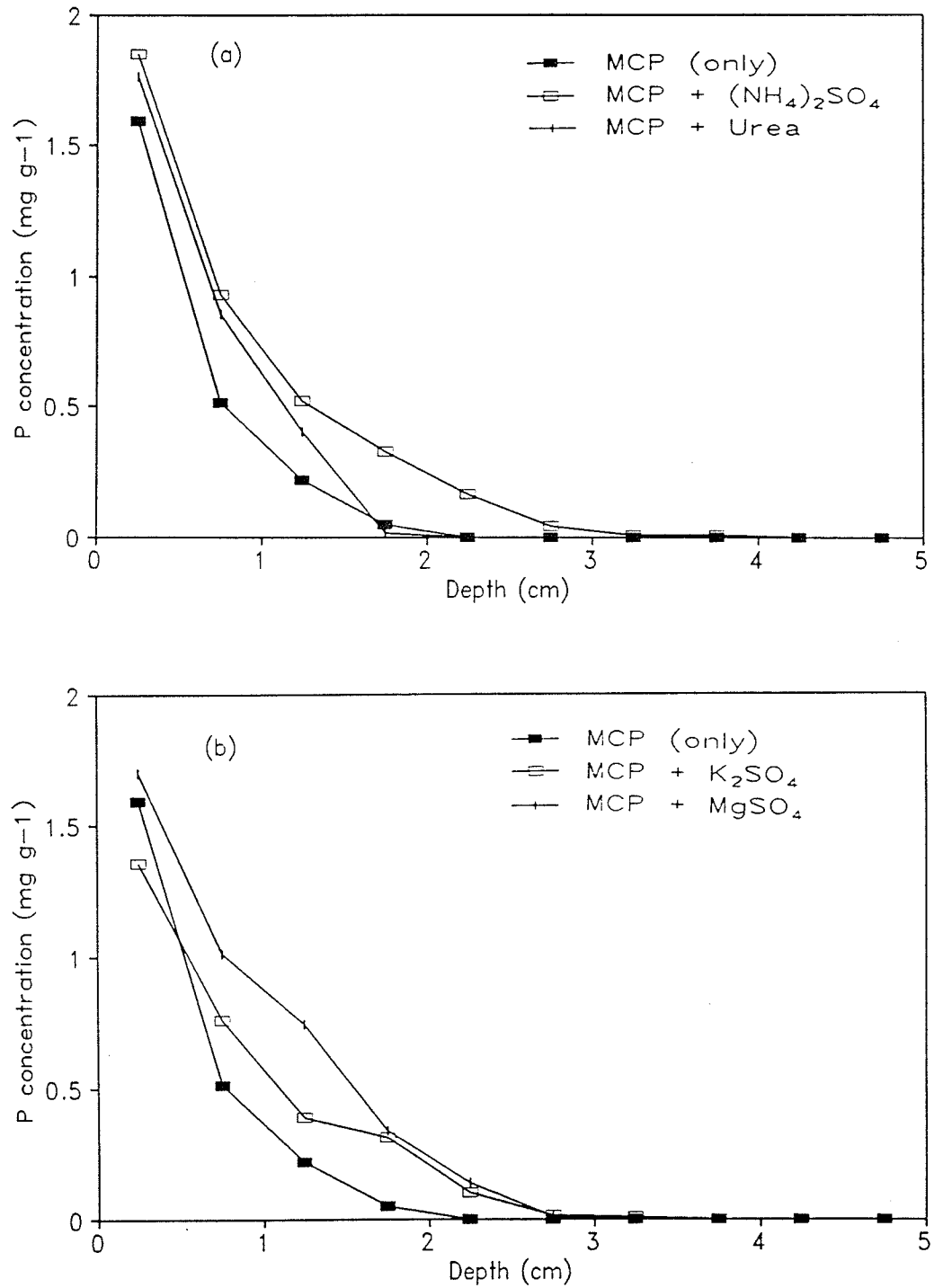
Fig.1. Effect of addition of salts upon total labelled P distribution
after 1 week of incubation in the Stockton sandy loam (a) $(NH_4)_2SO_4$
and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

Fig.2. Effect of addition of salts upon total labelled P distribution
after 6 weeks of incubation in the Stockton sandy loam
(a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

distance of P diffusion was slightly less than in the MCP (only) treatment. Similar results have been reported by Flaten (1989) on addition of urea with monoammonium phosphate.

The addition of both K_2SO_4 and $MgSO_4$ with MCP greatly enhanced the P movement at 6 weeks of incubation (Fig. 2b). The labelled P concentration in the MCP reaction zone was substantially higher when sulphate salts were added with MCP, and this effect was more pronounced when the salt was $MgSO_4$.

In the MCP (only) treatment, P distribution with time shows that the rate of P diffusion decreased with time. This retardation of P diffusion is mainly due to interactions of P with soil constituents and other ions, leading to the formation of less soluble P forms. Lindsay and Stephensen (1959a) reported that in slightly calcareous soils, the dissolved Ca was sufficient to cause DCPD (Dicalcium phosphate dihydrate) to precipitate, not only at the original placement site, but also throughout the soil contacted by the fertilizer solution. When $(NH_4)_2SO_4$, K_2SO_4 or $MgSO_4$ salts were added with MCP, the chemical availability and diffusion of P was increased, possibly due to the formation of P reaction products that are more soluble than those formed when MCP was added alone. It is likely that added sulphate would precipitate with Ca, thus reducing the effective concentration of Ca in soil solution and thereby reduce the formation of insoluble calcium phosphate compounds.

The addition of urea + MCP, only increased the labelled P concentration close to the surface, without affecting the distance of P movement, indicating that P diffusion is even more retarded than in the MCP (only) treatment. Urea, on hydrolysis, produces carbonates, but the

presence of a high concentration of carbonate, unlike sulphate, did not seem to increase the diffusion of P. The reason for the difference between carbonate and sulphate on their effect on diffusion of P is not very clear.

pH distribution

pH distribution in soil columns at 1 and 6 weeks of incubation are shown in Fig. 3 and 4. In the MCP (only) treatment, the measured pH was uniform throughout the column near 6.5. Thus, the pH measured was considerably lower than the pH measured in 1:1 soil:water mixture (Table 1), possibly because leaching with NaCl displaced more H^+ into solution. The activity of microorganisms during incubation also may have reduced the pH, due to release of CO_2.

The addition of slightly acidic $(NH_4)_2SO_4$ with MCP did not seem to modify the soil pH (Fig. 3a), and pH remained near 6.5 throughout the column. The addition of urea, however, raised the soil pH near the surface to a depth of about 4 cm. Similar observations on addition of urea to soil have been reported by other researchers (Isensee and Walsh, 1971; Beever, 1987, Flaten, 1989). The other sulphate salts (Fig. 3b) had little or no effect on soil pH at 1 week of incubation.

The effective depth of modification of soil pH due to the addition of urea was approximately 4 cm (Fig. 3a). On the other hand, the effective depth of labelled P movement with urea addition (Fig. 1a) was approximately 1 - 1.5 cm at 1 week of incubation. It is thus seen that the magnitude of OH^- movement was far greater than labelled P.

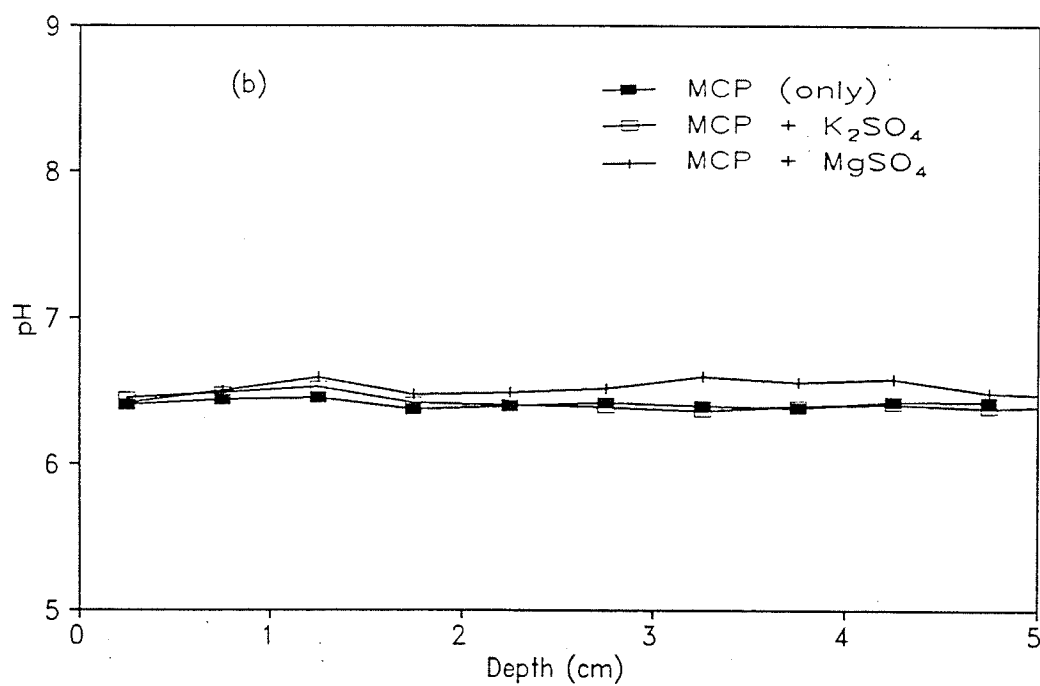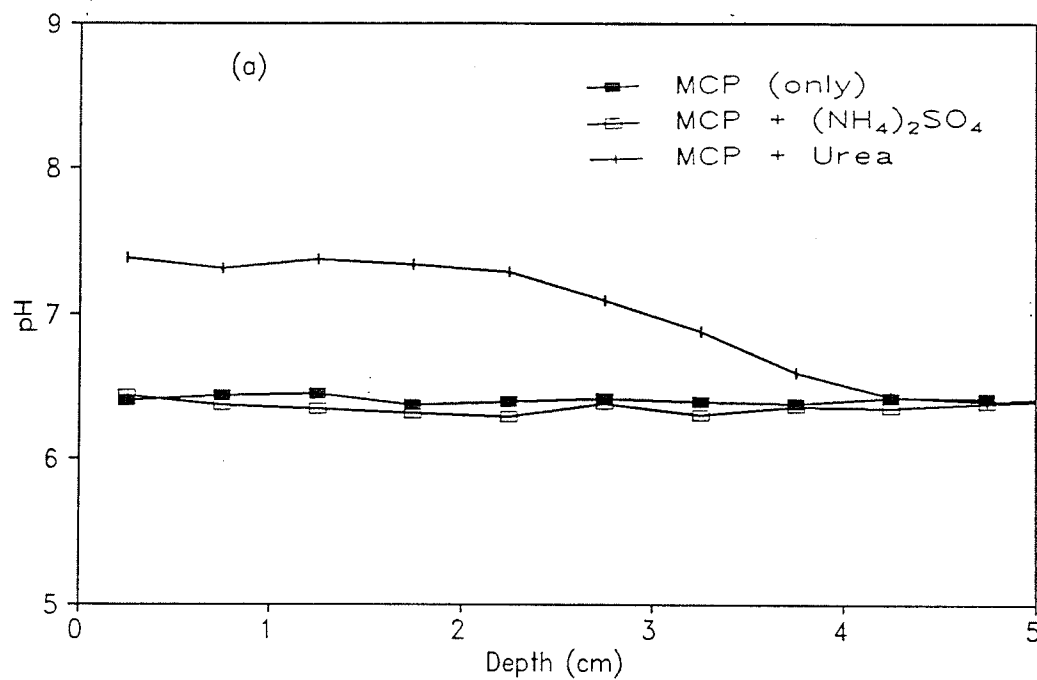At 6 weeks of incubation a low pH zone was observed in soil columns

Fig.3. Effect of addition of salts upon change in soil pH at various
distance after 1 week of incubation in the Stockton sandy loam
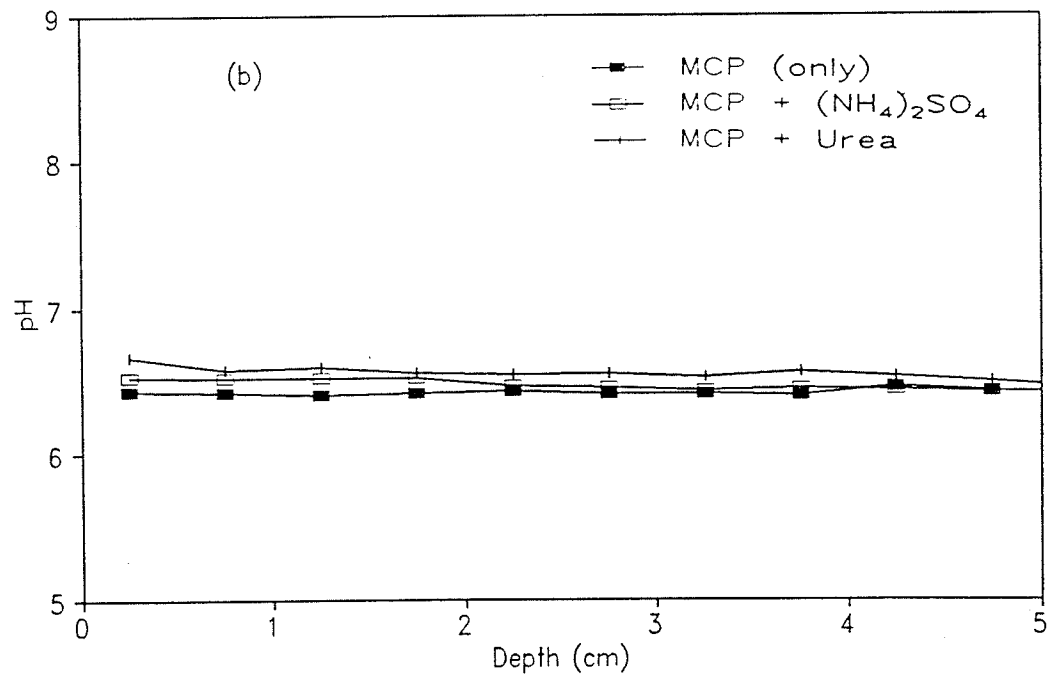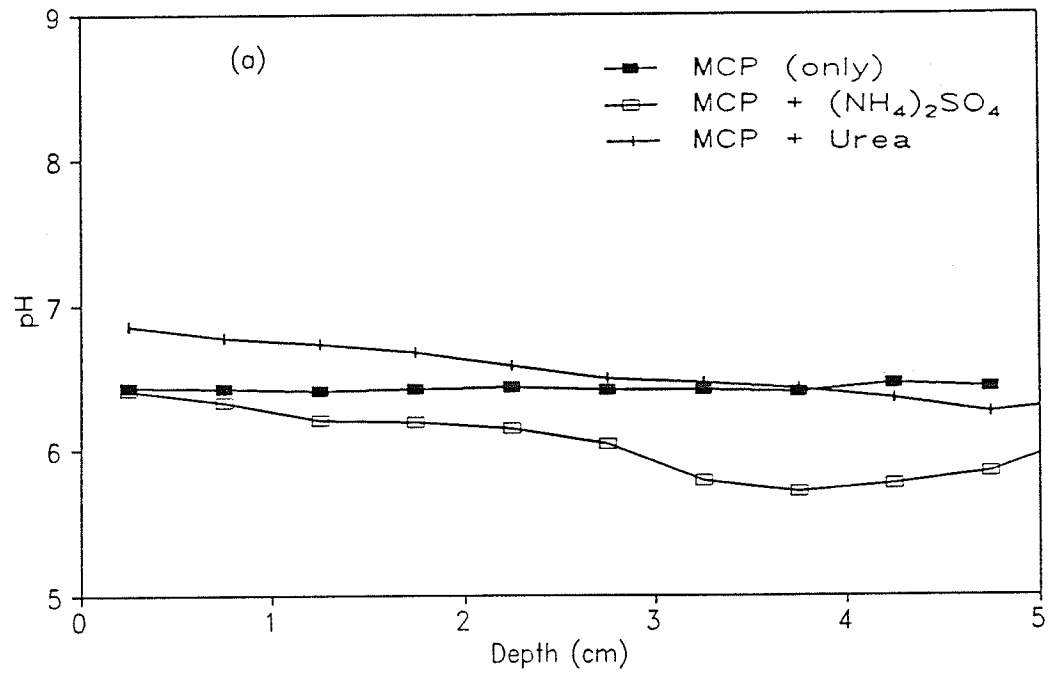(a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

Fig.4. Effect of addition of salts upon change in soil pH at various
distance after 6 weeks of incubation in the Stockton sandy loam
(a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

treated with $(NH_4)_2SO_4$ (Fig. 4a), approximately in the region of 2-5 cm below the surface. In the urea treatment, the high pH observed initially at the surface decreased with time, and at 6 weeks, pH values were much less than at 1 week of incubation (Fig. 3a), thus, the difference between the urea treatment and the control treatment was quite small (Fig. 4a). Even at 6 weeks of incubation K_2SO_4 and $MgSO_4$ did not seem to affect the pH of the soil (Fig. 4b).

Both hydrolysis of urea and subsequent nitrification of ammonium are responsible for the large pH changes observed in MCP + urea treatment with time. The initial hydrolysis reaction of urea occurs rapidly on addition of urea to soil, releasing NH_4^+ and OH^-, thus increasing the pH. With time, the NH_4^+ is oxidized to nitrates, releasing H^+ which lowers the pH. In the MCP + $(NH_4)_2SO_4$ treatment, only nitrification contributed to the pH changes. The nitrification process seems to be most active in the region 2-5 cm below the surface, where NH_4^+ is present to allow nitrification to occur, but not in high concentrations so as to inhibit the activity of nitrifying bacteria. At the surface, the high concentration of salts would inhibit the activity of bacteria which would limit the nitrification process. Similar findings were reported by Isensee and Walsh (1971). The concentrations of $NO_3^- + NO_2^-$ were greater at the low pH zone in the $(NH_4)_2SO_4$ treatment (Appendix C-7).

Since pH measured was that of the NaCl leachate, it may be different from soil solution pH. However, the data are still very useful for comparisons among treatments.

<u>Exchangeable calcium</u>

Addition of MCP increased the extractable Ca at the surface (Fig. 5). Mixing of the salts $(NH_4)_2SO_4$, K_2SO_4 and $MgSO_4$ with MCP had a small depressing effect on extractable Ca^{2+} concentration below 2 cm depth as compared to the addition of MCP alone (Fig. 5a,b). However, mixing urea with MCP substantially decreased the extractable Ca^{2+} concentration near the surface (Fig. 5a).

The depressing effect of sulphate salts upon NaCl extractable Ca^{2+} was not visible after 6 weeks of incubation (Fig. 6a,b). The effect of urea in depressing the extractable Ca^{2+} was still observed at 6 weeks of incubation (Fig. 6a).

The lower extractability of Ca^{2+} associated with the addition of urea was a result of an initial high pH close to the surface. High pH would favour the precipitation reactions of calcium with carbonates as well as with phosphates, thus reducing the extractable Ca^{2+}. Even when the pH decreased, with time, the Ca^{2+} extractability remained low, thus indicating that these reactions were not reversible with pH.

<u>Conclusions</u>

It was found that the addition of sulphates of NH_4^+, K^+ and Mg^{2+} increased the diffusion of P, $MgSO_4$ having the greatest effect. But when urea was added with MCP, the P diffusion was more retarded than in the MCP (only) treatment..

The high pH observed close to the surface in the urea treatment favours the formation of less soluble forms of Ca phosphates, thus
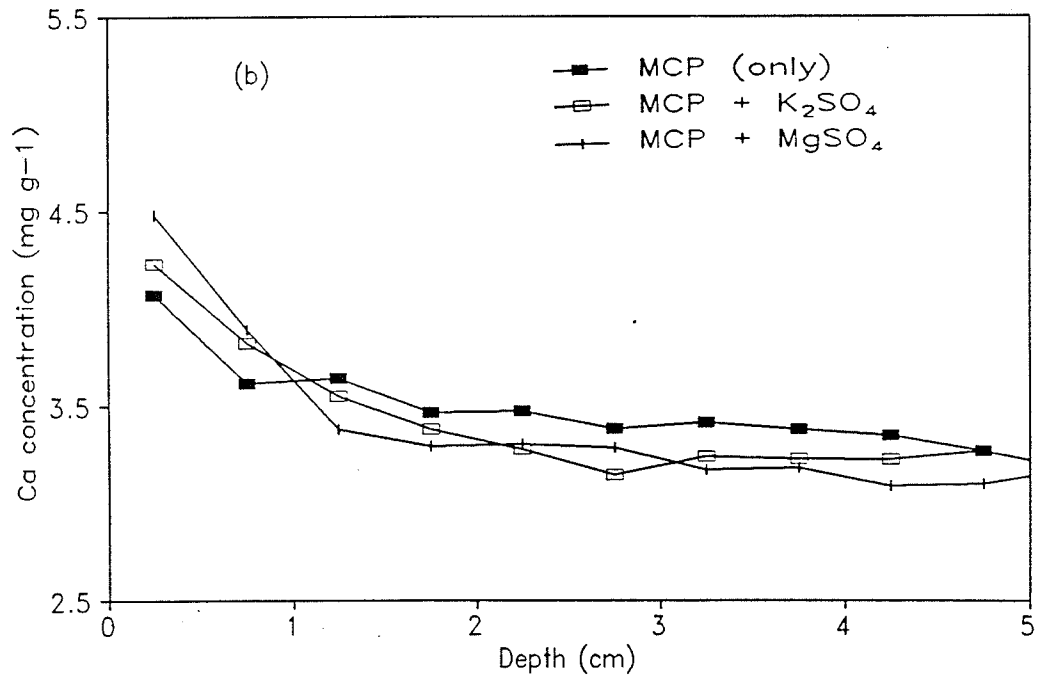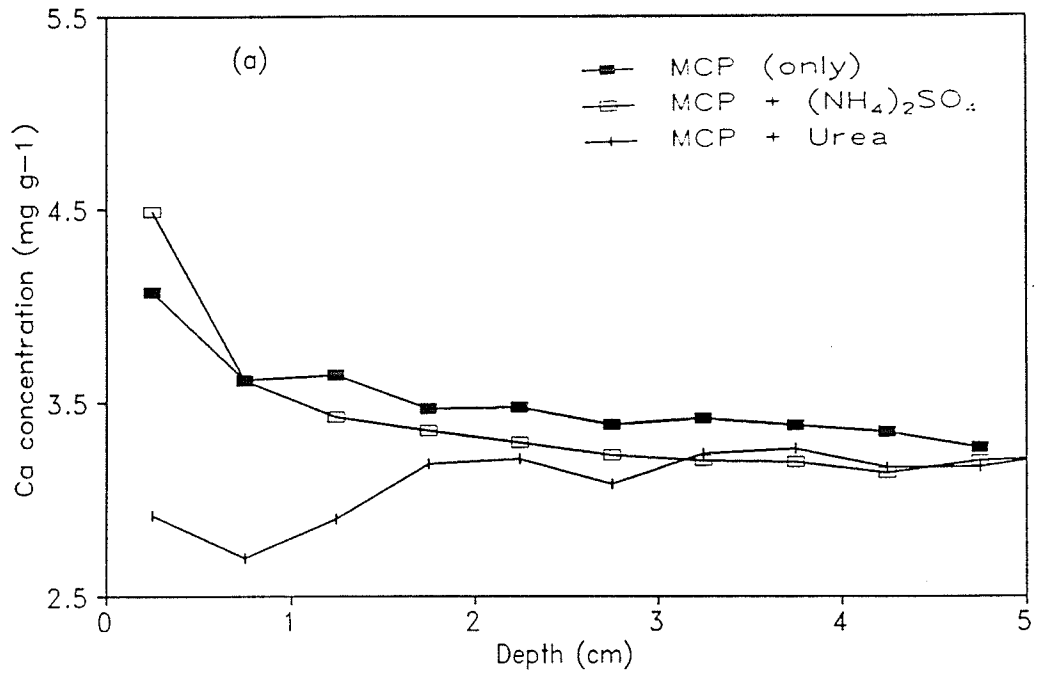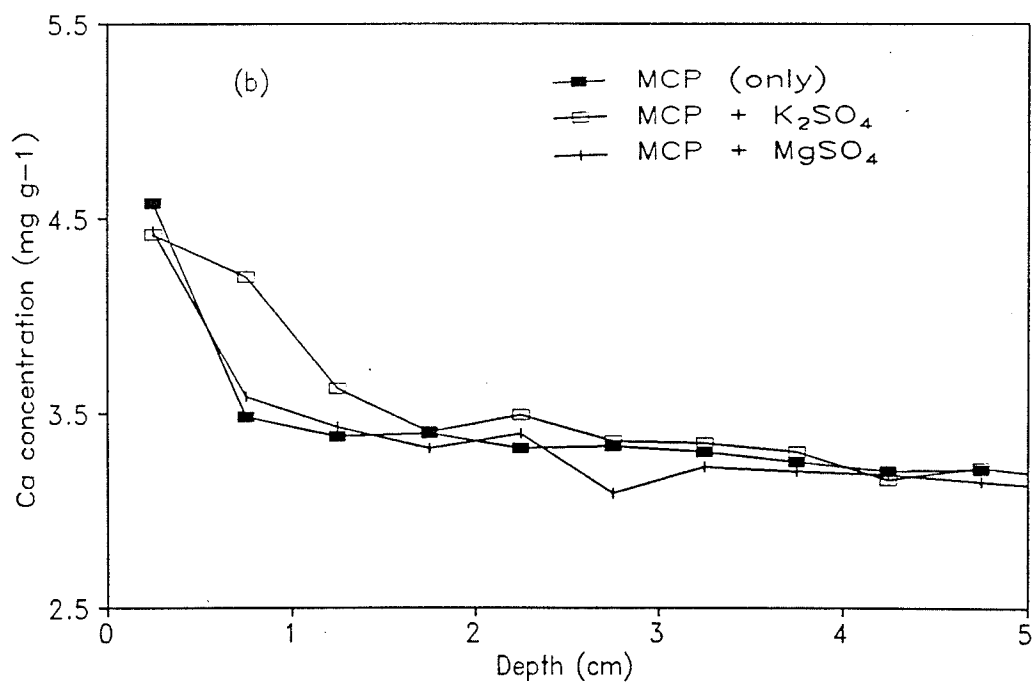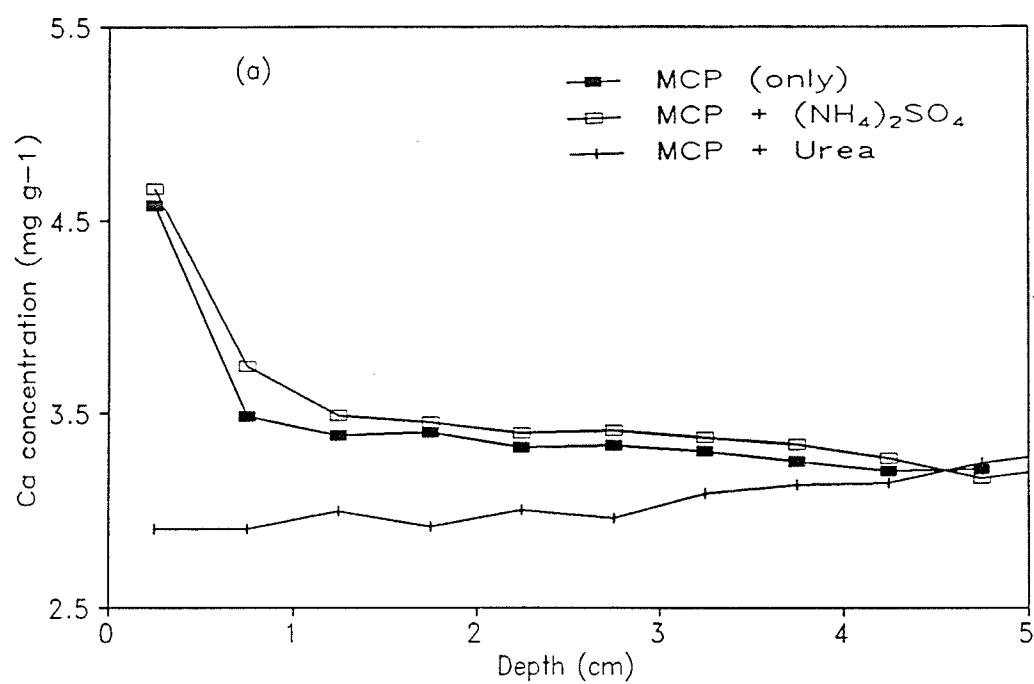
Fig.5. Effect of addition of salts upon distribution of exchangeable Ca^{2+} after 1 week of incubation in the Stockton sandy loam (a) (NH$_4$)$_2$SO$_4$ and urea addition (b) K$_2$SO$_4$ and MgSO$_4$ addition.

Fig.6. Effect of addition of salts upon distribution of exchangeable Ca^{2+}
after 6 weeks of incubation in the Stockton sandy loam
(a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

retarding the P movement. However, when sulphate salts were added there was no measurable pH change at the surface.

Both carbonate (the hydrolysis product of urea), and sulphate, under high concentrations, can form solid Ca compounds such as $CaCO_3$ and $CaSO_4$. The magnitude of formation is governed by the solubility product and relative concentrations of carbonate and sulphate. Thus, the increase in P diffusion in the presence of sulphate salts is possibly due to the competition between sulphates and phosphates for precipitation with Ca^{2+}. The reason why this effect was not observed with carbonate in the MCP + urea treatment is not clear. Apart from affecting P diffusion, all these salts seem to increase the P concentration in the MCP reaction zone, possibly by forming P reaction products that are more soluble than those formed when MCP was added alone.

3.3. Column experiment 2

In the previous column experiment, the concentration of ions were measured at every 5 mm distance from the site of application of MCP. Another column experiment was conducted using a calcareous soil, taking 2 mm sections for analysis, which would give a better picture of the concentration profiles.

Methods

Almasippi loamy sand was used for this experiment. The air dried soil was passed through a 1 mm mesh sieve prior to use. The important physical and chemical properties of the soil are given in Table 1. Treatments were same as in the previous column experiment.

Soil columns were prepared by packing dry soil to a bulk density of 1.3 g mL^{-1} in rectangular wax blocks having cylindrical cavities (5.1 cm diameter and 8 cm deep) at the centre. The blocks were prepared from a mixture of paraffin wax and petroleum jelly as described by Khasawneh and Soileau (1969). Soil was moistened to its field capacity after packing and equilibrated for 72 hours.

MCP was added at the rate of 200 mg MCP per column, whereas salts were added at the same rates as in the previous experiment. MCP, with or without salts were placed uniformly on the top of the soil column. Protective acrylic collars (3 cm height) were placed at the top of the columns and then covered with parafilm which was punctured several times. The columns were placed in an upright position in a humidified container at 20 C. After 1, 2, 3 and 4 weeks two replicate columns for each salt treatment were sliced using a meat slicer at 2 mm interval. The columns

were sliced only to a depth of 5 cm. Salts remaining at the surface were scraped off before slicing the columns. Soil samples from two replicates of each treatment were analyzed separately as in the previous experiment.

Total labelled P was measured using the same method described in the previous experiment. pH was measured in 1:1 soil: water extract to get a more accurate measure of soil solution pH. To measure the exchangeable ions, approximately 1 g of soil was leached with 15 mL of 2 mol L^{-1} NaCl using suction, and made to 100 mL by adding deionized water. Concentrations of P and other ions and pH were measured using the same methods as in the previous experiment.

Results and Discussion

The moisture content distribution was generally uniform throughout the soil column as observed with Stockton sandy loam. Fig. 7 - 12 shows the concentration profiles of total labelled P, pH and exchangeable Ca^{2+} after 1 and 4 weeks, by plotting mean data of duplicate samples. Concentration profiles of total labelled P, pH and exchangeable Ca^{2+} at 2 and 3 weeks of incubation, and $NO_3^- + NO_2^-$, $NH_4^+ + NH_3$, K^+ and Mg^{2+} for all the time periods are given in Appendix D.

Labelled P distribution

After 1 week of incubation, the phosphate applied on the surface has diffused downward. The P concentration was greater at the surface and it diffused to approximately 1 cm depth when only MCP was added (Fig. 7).

The addition of salts modified the phosphate distribution (Fig. 7), as observed with the Stockton sandy loam (Fig. 1). At 1 week of

incubation, the extent of movement of surface applied P was increased when $(NH_4)_2SO_4$ was added with MCP (Fig. 7a). However, the addition of urea with MCP, had little or no effect on the labelled P transport.

When K_2SO_4 was added with MCP (Fig. 7b), there was no obvious difference in the labelled P distribution as compared to the MCP (only) treatment. But the addition of $MgSO_4$ with MCP enhanced the P mobility, and the labelled P concentration was high throughout the MCP reaction zone.

At 4 weeks of incubation, the effect of salts on P diffusion was similar to that observed after 1 week, but the differences among the treatments were more apparent (Fig. 8). The extent of P diffusion was increased by the addition of $(NH_4)_2SO_4$ and $MgSO_4$ with MCP (Fig. 8a,b). Addition of MCP + urea increased the labelled P concentration to about 1 cm depth, but did not affect the distance of P movement (Fig. 8a). K_2SO_4 addition (Fig. 8b) had little or no effect on labelled P distribution even after 4 weeks of incubation.

At 1 week of incubation, the labelled P concentration at the surface was much higher in this soil (Fig. 7) than in Stockton sandy loam (Fig. 1), even though the residue remaining at the surface was removed in this experiment. It should be noted however, that in this experiment, a slightly higher rate of P was added, and at the same time, thinner sections were taken for analysis.

The extent of P diffusion after 1 week, in Almasippi loamy sand (Fig. 7), was slightly less than that of Stockton sandy loam (Fig. 1), when MCP was added alone. This is possibly due to the higher pH and higher $CaCO_3$ content of Almasippi loamy sand, which favour precipitation reactions of P. Similar differences in P movement have been observed
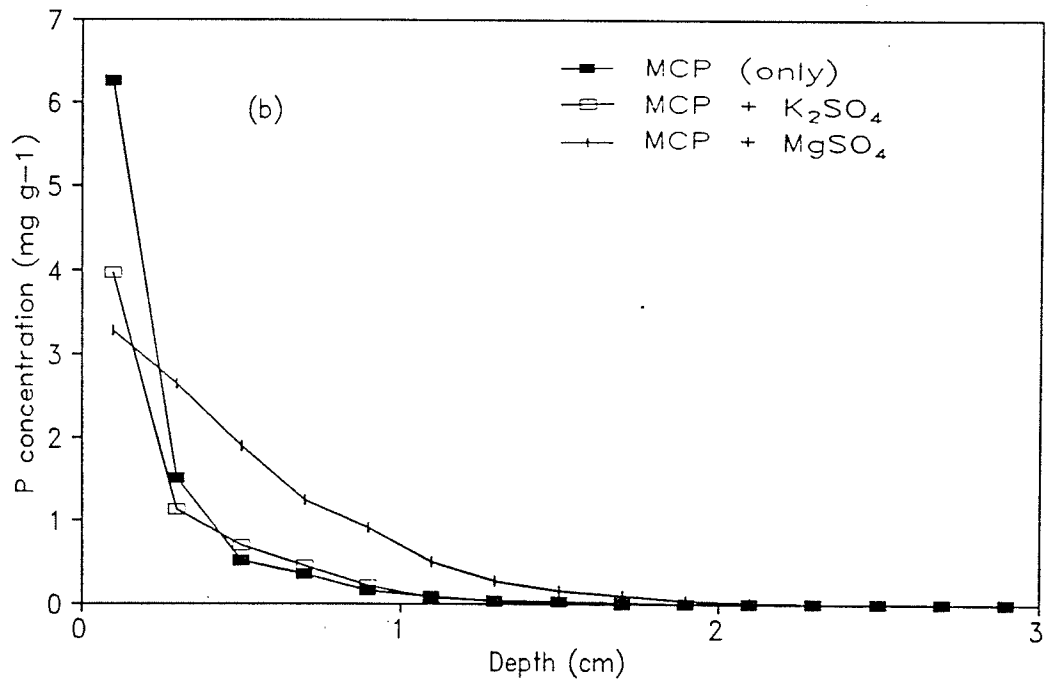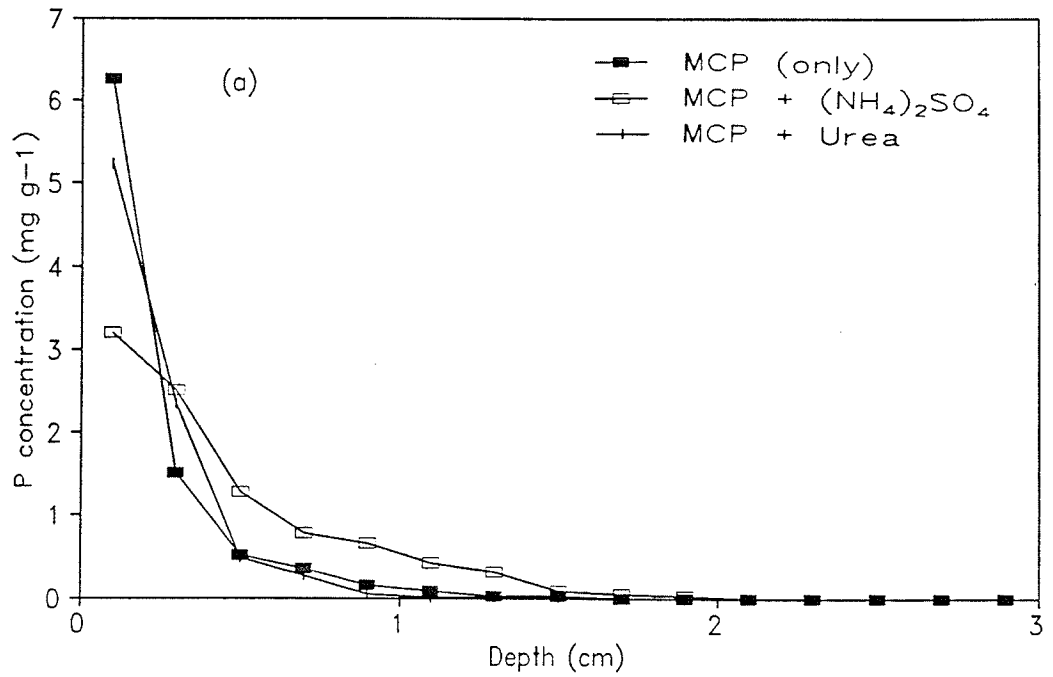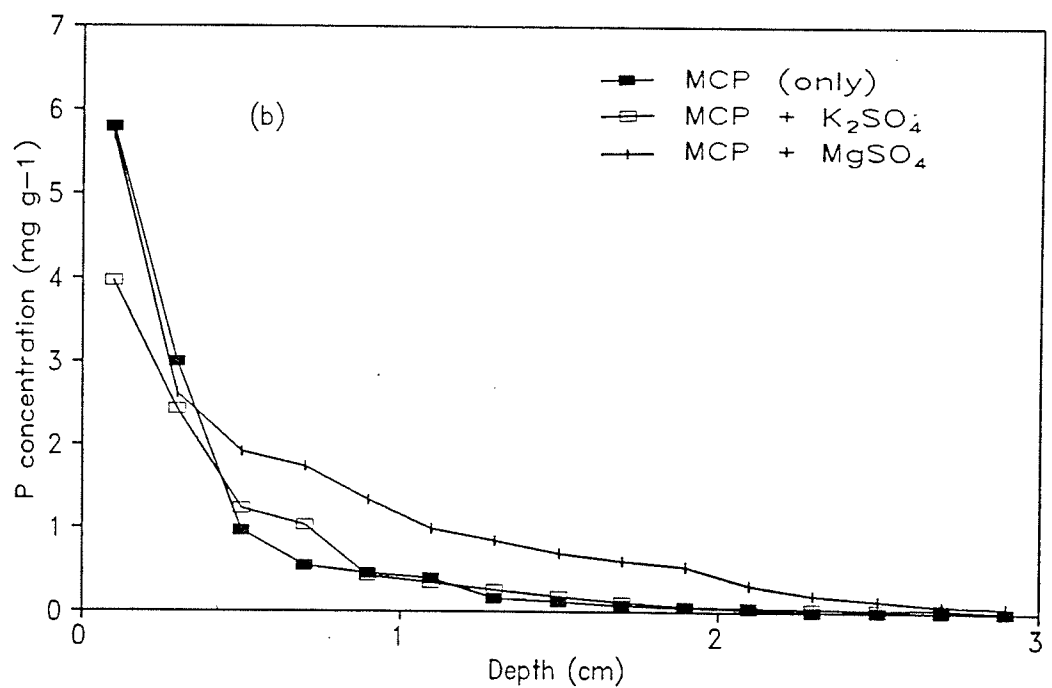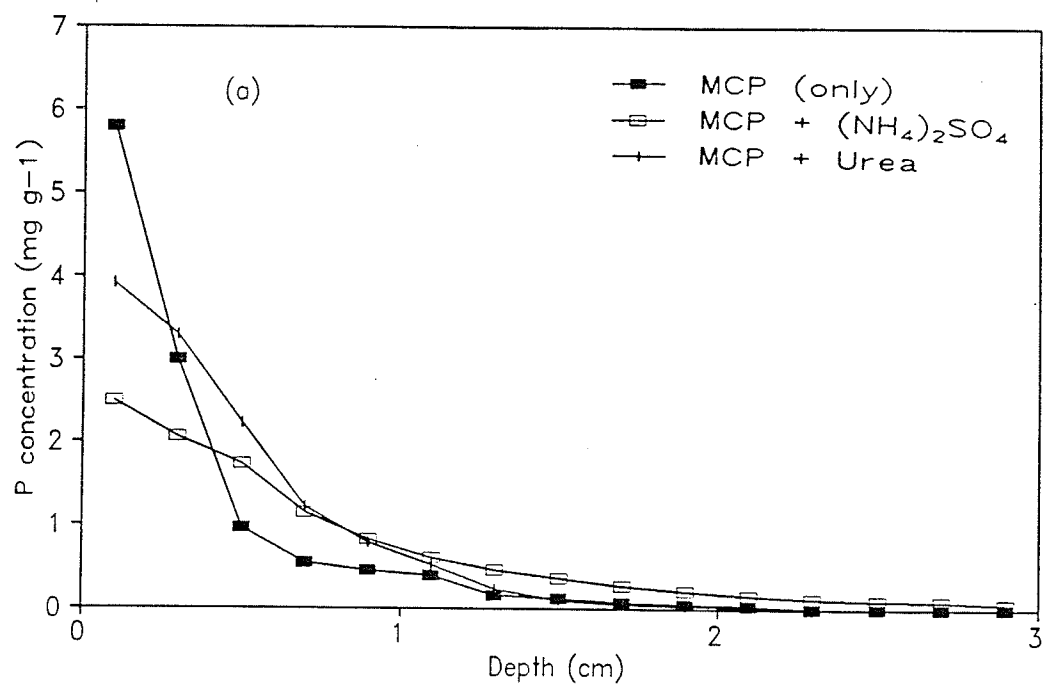
Fig.7. Effect of addition of salts upon total labelled P distribution
after 1 week of incubation in the Almasippi loamy sand
(a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition

Fig.8. Effect of addition of salts upon total labelled P distribution
      after 4 weeks of incubation in the Almasippi loamy sand
      (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition

by other researchers between calcareous and non-calcareous soils (Lindsay and Stephensen, 1959a; Lewis and Racz, 1969).

In the Stockton soil, the addition of K_2SO_4 increased the extent of P diffusion (Fig. 1b, 2b), whereas in Almasippi soil, there was no obvious effect (Fig. 7b, 8b). In both soils, the effects of $(NH_4)_2SO_4$, urea and $MgSO_4$ on P diffusion were similar.

pH distribution

Fig. 9 shows the pH changes due to addition of salts after 1 week of incubation. The addition of MCP decreased the pH at the surface (Fig. 9a). When $(NH_4)_2SO_4$ was added with MCP, a lower pH was observed to a depth of approximately 4 cm. As in the Stockton sandy loam (Fig. 3a), the addition of MCP + urea increased the pH to a depth of about 3 cm.

When K_2SO_4 was added with MCP, slightly higher values of pH were observed, approximately to a depth of 2 cm (Fig. 9b). On the other hand, the addition of MCP + $MgSO_4$ had slightly lower pH values to a depth of about 4 cm at 1 week of incubation.

The depressing effect of addition of MCP on soil pH as observed in this soil (Fig. 9a) has been reported by other researchers (Lindsay and Stephensen, 1959a; Isensee and Walsh, 1971). As the dissolution of MCP produces a solution pH as low as 1.5 (Isensee and Walsh, 1971), it is to be expected that diffusion of this acidic solution into the surrounding soil would reduce the soil pH. The reason why this effect was not observed in the previous experiment is not clear. It could be possibly due to the fact that pH was measured in the NaCl leachate in the previous experiment, while in the present study the pH of 1:1 soil: water mixture

was measured, which is quantitatively a better measure of the soil solution pH.

After 4 weeks of incubation, the pH at the surface was still low, in the treatment where MCP was added alone (Fig. 10a). The pH values were slightly lower in the MCP + $(NH_4)_2SO_4$ treatment than in the MCP (only) treatment, throughout the depth analyzed. In the MCP + urea treatment, the pH near the surface was much less than at 1 week of incubation, and below about 1.5 cm depth, the pH was even lower than in the MCP (only) treatment (Fig. 10a).

At 4 weeks of incubation, addition of K_2SO_4 with MCP increased the pH near the surface to a depth of about 2 cm (Fig. 10b) as compared to the MCP (only) treatment, whereas addition of MCP + $MgSO_4$ slightly increased the pH to about 1 cm depth and slightly depressed the pH approximately in the range of 1-3 cm below the surface.

The effects of addition of MCP + $(NH_4)_2SO_4$ and MCP + urea on pH were similar in the Almasippi loamy sand (Fig. 9a and 10a) and the Stockton sandy loam (Fig. 3a and 4a). However, in the Stockton sandy loam, a distinct low pH zone was observed in the MCP + $(NH_4)_2SO_4$ treatment at 6 weeks of incubation (Fig. 4a). But this was not observed in the Almasippi loamy sand (Fig. 10a), and the pH was lower throughout the soil column probably as a result of nitrification.

Exchangeable Calcium

The exchangeable Ca^{2+} concentration in the MCP (only) treatment after 1 week was nearly uniform to a depth of about 3 cm, and below that Ca^{2+}

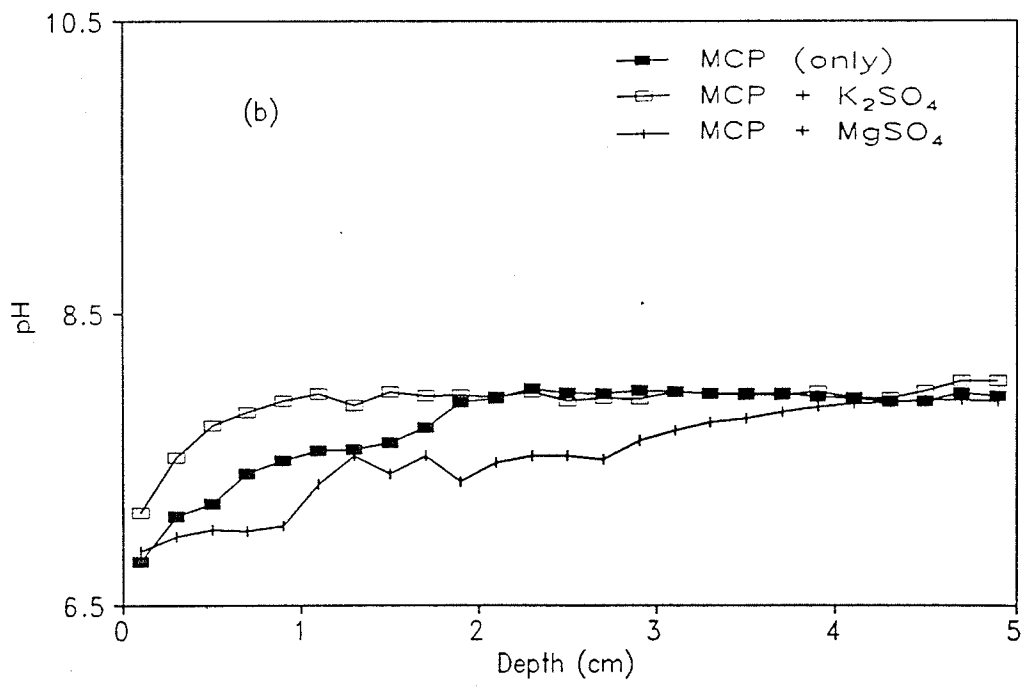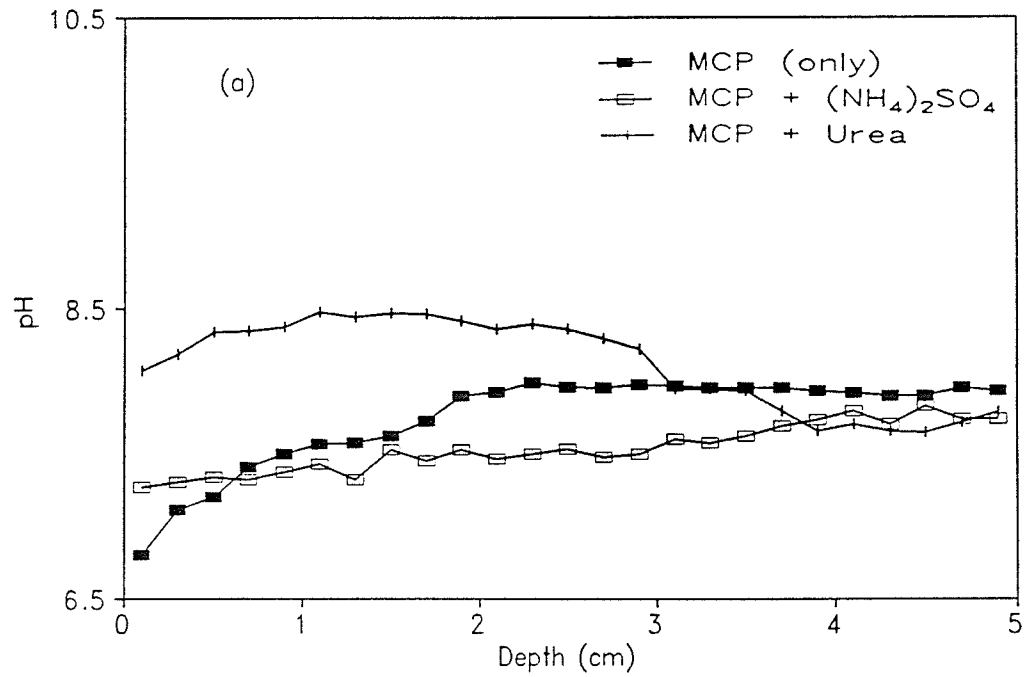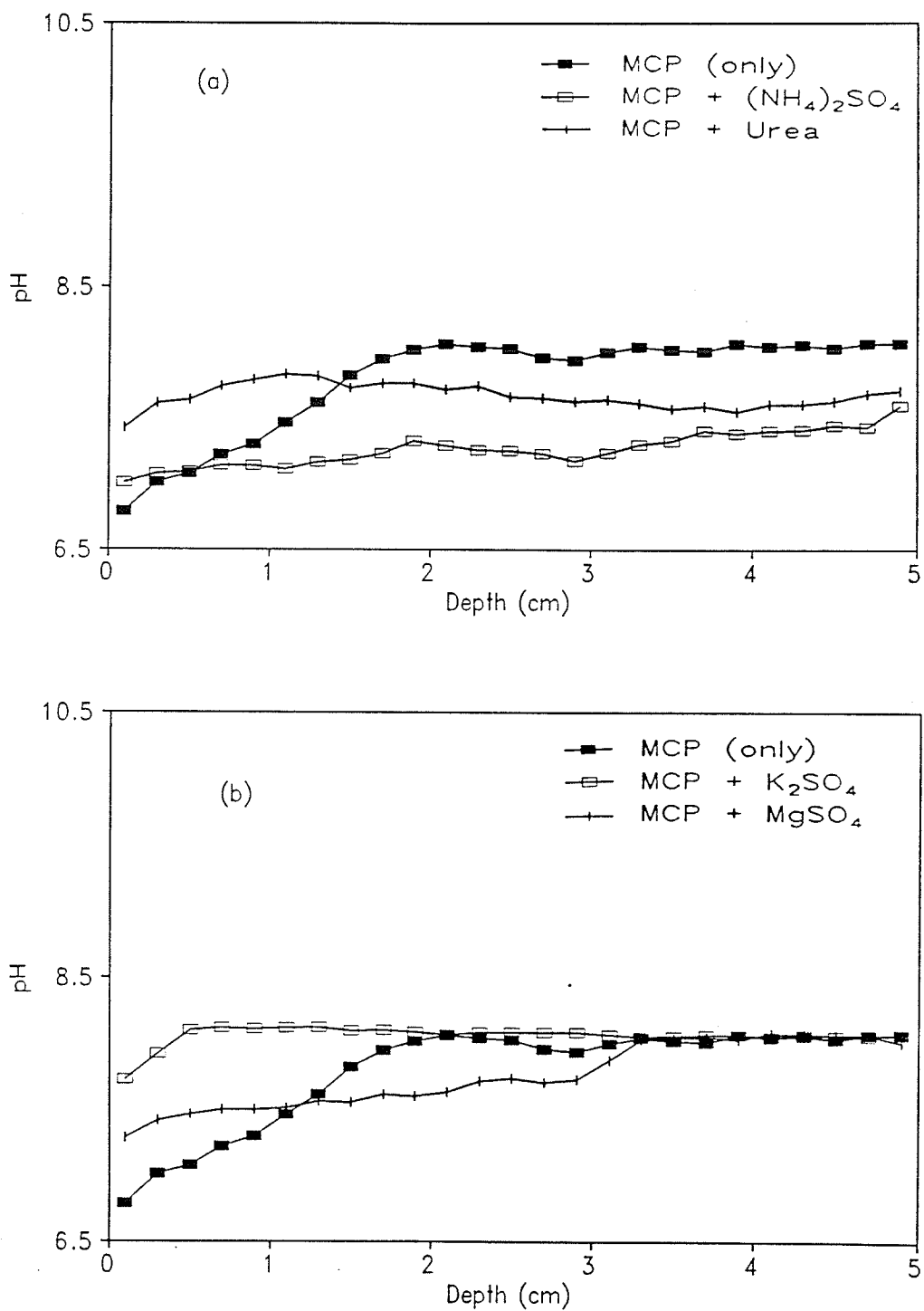Fig.9. Effect of addition of salts upon change in soil pH at various
distance after 1 week of incubation in the Almasippi loamy sand
(a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition

Fig.10. Effect of addition of salts upon change in soil pH at various
distance after 4 weeks of incubation in the Almasippi loamy sand
(a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition

concentration slightly decreased with depth (Fig. 11a). The addition of $(NH_4)_2SO_4$ with MCP (Fig. 11a) did not seem to modify the distribution of exchangeable Ca^{2+}. But the addition of urea with MCP had a depressing effect on the extractable Ca^{2+} to a depth of about 4 cm.

The addition of both K_2SO_4 and $MgSO_4$ (Fig. 11b) slightly depressed the extractable Ca^{2+} to a depth of about 3 cm, below which the concentrations were slightly higher than in the MCP (only) treatment.

At 4 weeks of incubation, the exchangeable Ca^{2+} concentration in MCP + $(NH_4)_2SO_4$ treatment was similar to that of the MCP (only) treatment to a depth of about 3 cm, but the concentrations below 3 cm were slightly higher (Fig. 12a). The addition of urea (Fig. 12a), K_2SO_4 as well as $MgSO_4$ (Fig. 12b), had an apparent depressing effect on extractable Ca^{2+} to a depth of about 3 cm.

Exchangeable Ca^{2+} in the MCP reaction zone was lower in the Almasippi loamy sand (Fig. 11, 12) than in the Stockton sandy loam (Fig, 5, 6). The addition of MCP increased the exchangeable Ca^{2+} close to the surface in the Stockton soil (Fig. 5), but not in the Almasippi soil (Fig. 11), probably due to the higher amounts of precipitation of Ca phosphates in the Almasippi soil.

As in the Stockton sandy loam, the high pH associated with addition of urea favoured precipitation reactions, and thus, the extractable Ca^{2+} content was lower. In the K_2SO_4 and $MgSO_4$ treatments, the decrease in exchangeable Ca^{2+} concentration close to the surface (Fig. 11b, 12b) is possibly due to the exchange and displacement of soil Ca^{2+} by added K^+ and Mg^{2+} ions. This effect, however, was not observed with the Stockton sandy loam.

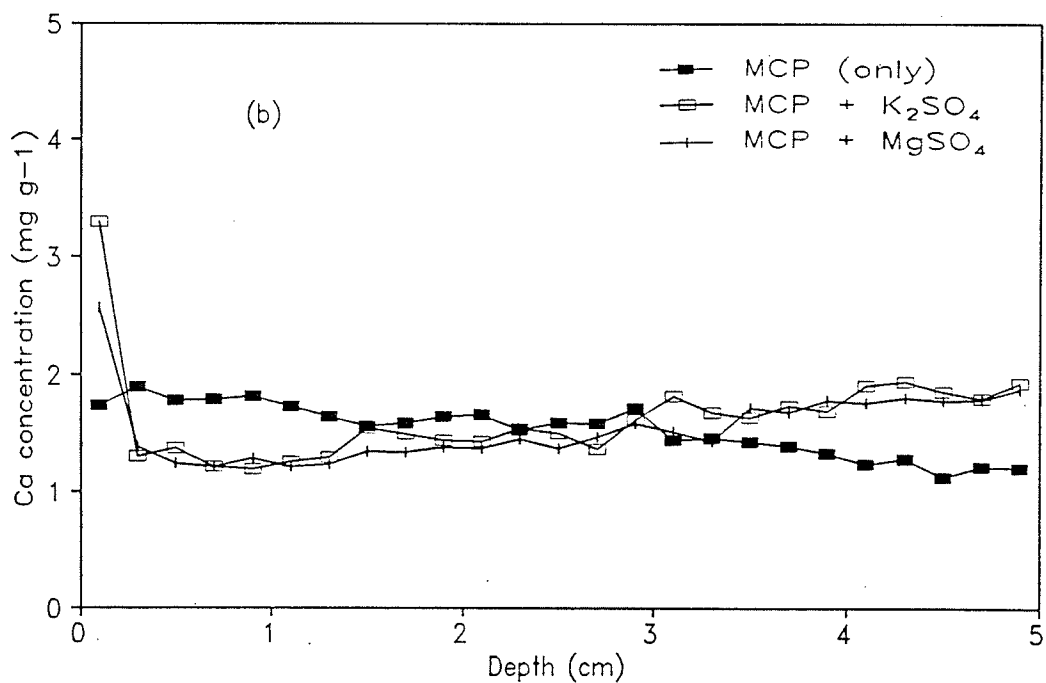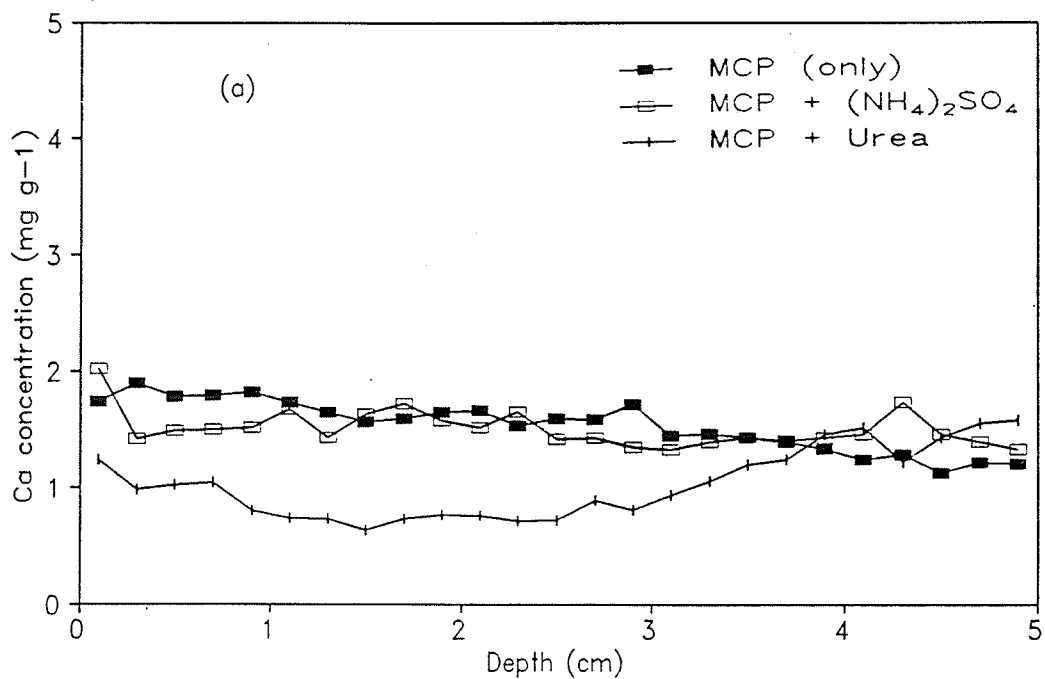Fig.11. Effect of addition of salts upon distribution of exchangeable
Ca^{2+} after 1 week of incubation in the Almasippi loamy sand
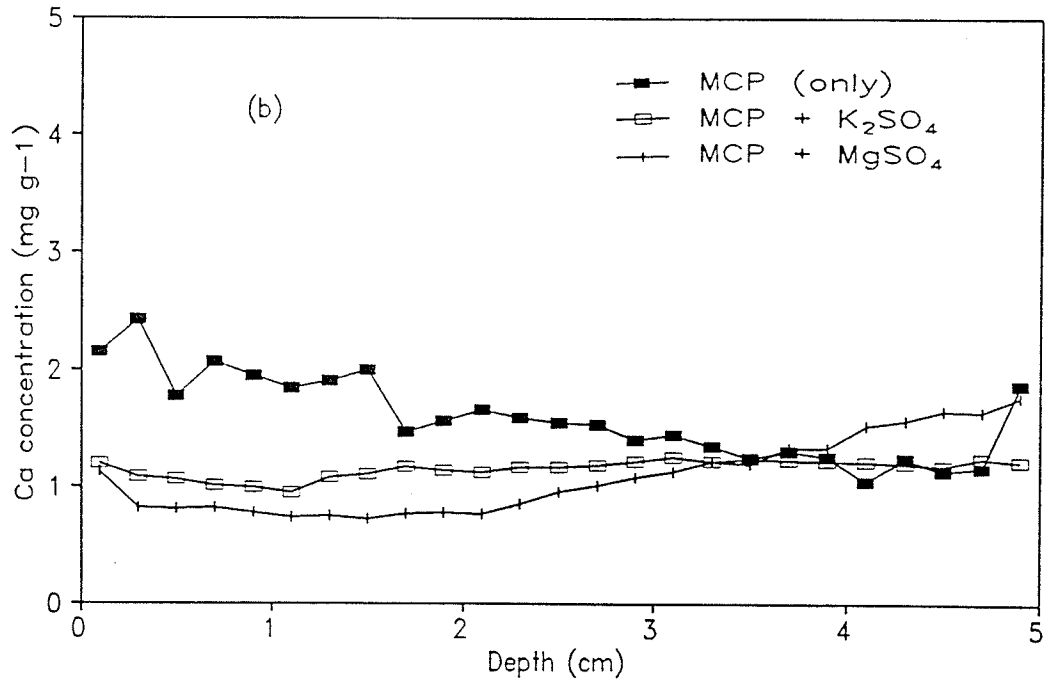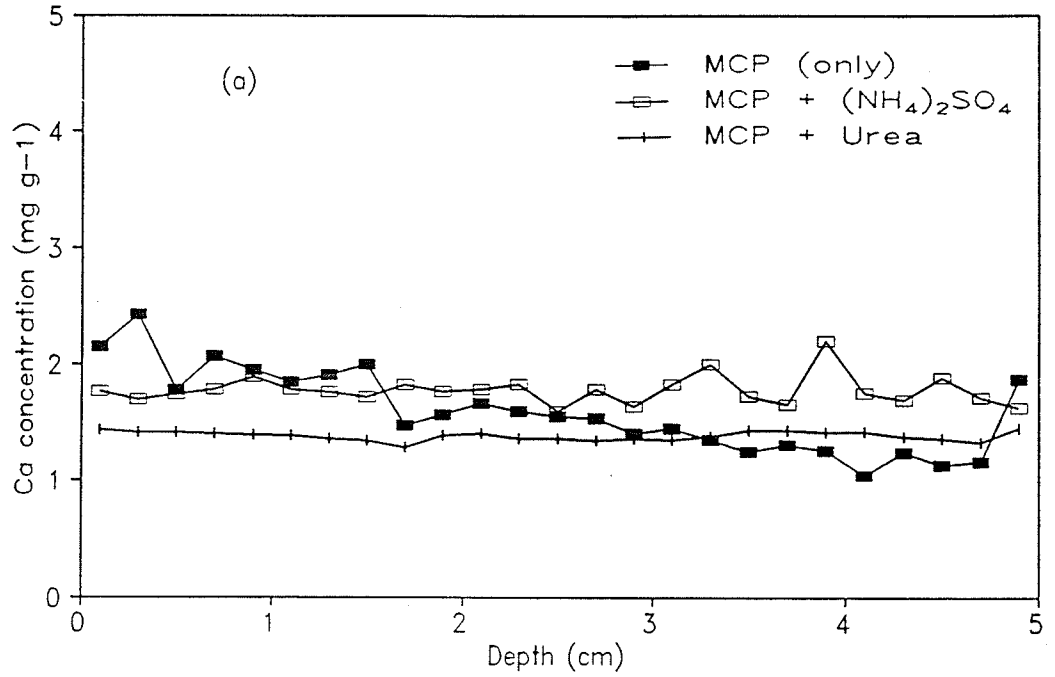(a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition

Fig.12. Effect of addition of salts upon distribution of exchangeable Ca^{2+} after 4 weeks of incubation in the Almasippi loamy sand (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition

Conclusions

As in the column experiment 1 using Stockton soil, $(NH_4)_2SO_4$ and $MgSO_4$, when added with MCP, increased the P concentrations and the extent of P diffusion, possibly due to the competition between sulphates and phosphates for precipitation with Ca^{2+}. However, in the Almasippi soil, K_2SO_4 did not seem to have this effect, although in the Stockton sandy loam, which had a near neutral pH, K_2SO_4 did increase the extent of P diffusion. The reason for the inconsistency in K_2SO_4 effect in these two soils is not clear. However, it should be noted that K_2SO_4 is less soluble than $MgSO_4$ and $(NH_4)_2SO_4$ (Handbook of Physics and Chemistry, 1972), and even though the same rates in terms of moles were applied in all the treatments, the sulphate concentration in the soil solution would be lower in the case of K_2SO_4 treatment. Apart from that, the changes in pH due to the addition of these salts could have affected the P mobility. The addition of both $(NH_4)_2SO_4$ and $MgSO_4$ decreased the soil pH unlike K_2SO_4.

When urea was added with MCP, P movement was more retarded due to the increased pH leading to higher rates of P precipitation. This effect was consistent in both Almasippi and Stockton soils.

Retardation of P movement seems to be slightly greater in the Almasippi loamy sand than in the Stockton sandy loam, possibly because of the higher pH in the Almasippi loamy sand which favours precipitation of calcium and magnesium phosphates.

3.4. Elution experiment

In the two column experiments conducted, the P movement within the columns were brought about mainly by a diffusion process, as the columns had uniform moisture distributions which kept mass flow to a minimum. It is important to know how different salts, when mixed with P fertilizers, would affect the retention and movement of P, when mass flow is the main mechanism of P movement. Such knowledge would give an insight as to how the downward movement of P in the field is affected by the addition of salts. An elution experiment was conducted using soil columns, to investigate the effect of salts on the retention and movement of P when mass flow is the main mechanism of P movement.

Methods

A Stockton sandy loam and an Almasippi loamy sand were used for this experiment (Table 1). Soils were passed through a 1 mm mesh sieve prior to use. Dry soils were packed in chromatography columns with an internal diameter of 16 mm and length of 20 cm. Soils were packed to 10 cm and packing was done to get a bulk density of 1.3 g mL^{-1} (air-dry basis), which gave a total pore volume of about 10 mL.

Approximately 10 mL of water was added to the soil surface and the columns were equilibrated for 24 hours in a humidified container at 20 C before adding the fertilizers.

Labelled MCP was used as the P fertilizer as in the other experiments. The salts added were similar in terms of mol per unit surface area. MCP alone or mixed with a salt depending on the treatment, was placed at the surface of the soil column. Each treatment had two

replicates. Deionized water was then supplied continuously to the top of the column and eluate samples were extracted from the soil column using a Masterflex 7553-10 pump. Two columns, duplicates of one treatment were eluted at a time, using the same pump. Suction was controlled so as to extract about 10 mL per hour. At each 10 minutes eluate fractions were collected into culture tubes using a fraction collector. The volume of eluate fractions varied between columns, but within a column, eluate volume was fairly constant with time. When the steady state flow was established, the volume of the eluate fractions in each column was measured and the average of duplicate columns were taken. Approximately 8 pore volumes were collected for each column.

Each eluate sample was measured for ^{32}P concentration using a liquid scintillation counter and total P concentration using the molybdate blue-ascorbic acid method (Murphy and Riley, 1962). Ca^{2+} concentration was measured using an atomic absorption spectrophotometer. Mg^{2+} and K^+ concentrations were measured in $MgSO_4$ and K_2SO_4 treatments respectively. However, the NH_{4+} concentration could not be measured in the $(NH_4)_2SO_4$ and the urea treatments as the volume of samples was limited. Total amount of ^{32}P eluted in each column was calculated.

After the elution, water supply was discontinued and the columns in upright position were left for one day. Then the columns were opened from both ends, and the soil was pushed very slowly from one end to get the soil out without breaking. Soil columns were sectioned to approximately 6 mm slices and each section was analyzed separately. Approximately 1 g of sample was extracted with 10 mL of 2 mol L^{-1} KCl solution by shaking for 30 minutes and centrifuging at 3000 rpm for 5 minutes. The labelled

P concentration in each sample was then measured using a liquid scintillation counter. The moisture content was also measured using a soil sample from the middle of the column.

Results

Elution of P

In the elution experiment, conditions were quite different to those of the column experiments. As there was a continuous water flow through the soil column during elution, the displaced ions following ion exchange reactions are pushed out of the column, thus minimizing reactions involving displaced ions. Apart from that, the higher moisture contents maintained would increase the rates of dissolution of the added salts, MCP as well as the precipitates formed. Therefore, these differences should be taken into account when comparing the results of elution experiment with the results of the diffusion experiments.

Fig. 13 and 14 shows the ^{32}P concentration in eluted samples in the Stockton and Almasippi soils respectively. The concentrations plotted were the average concentrations of duplicate samples. The elution profiles for P varied substantially for the various salt treatments in both soils.

In the Stockton sandy loam, when MCP was added alone, the labelled P elution started after eluting about 1 pore volume of water (Fig. 13a). The ^{32}P concentration in eluted samples rapidly increased thereafter and reached a maximum of about 45 mg P L^{-1}, when approximately 3 pore volumes have been eluted, and then slowly declined with further elution. The addition of $(NH_4)_2SO_4$ with MCP (Fig. 13a), increased the peak ^{32}P

concentration to about 90 mg P L^{-1}. As in the MCP (only) treatment, the peak was observed when about 3 pore volumes were eluted, and further elution gave samples with higher ^{32}P concentrations than in the MCP (only) treatment. The addition of urea (Fig. 13a) did not seem to modify the ^{32}P elution profile. When K_2SO_4 was added with MCP (Fig. 13b), the peak ^{32}P concentration increased to about 85 mg P L^{-1}, but the position of the peak was not modified. In the MCP + $MgSO_4$ treatment, the ^{32}P elution was delayed, and the peak ^{32}P concentration of about 50 mg P L^{-1} was observed when about 3.5 pore volumes had been eluted.

In the Almasippi soil, when MCP (only) was added, the labelled P elution started approximately after 1 pore volume of water was eluted (Fig. 14a), as in the Stockton soil. Further elution increased the labelled P concentration very rapidly in eluted samples, and the peak concentration of about 65 mg P L^{-1} was observed when about 1.2 pore volumes of water was eluted, whereas in the Stockton sandy loam (Fig. 13a), the peak concentration was observed after about 3 pore volumes of elution. Therefore, the results show that elution of surface applied P was faster in the Almasippi soil than in the Stockton soil. The addition of both $(NH_4)_2SO_4$ and urea (Fig. 14a), delayed the elution of ^{32}P when compared to the MCP (only) treatment. In the MCP + $(NH_4)_2SO_4$ treatment (Fig. 14a), the peak ^{32}P concentration of about 110 mg P L^{-1}, was observed when about 2.5 pore volumes have been eluted, which is about twice of that of the MCP (only) treatment. The addition of urea decreased the peak concentration slightly to about 50 mg P L^{-1}, and the peak was observed after about 1.5 pore volumes were eluted (Fig. 14a). The addition of K_2SO_4 increased the peak ^{32}P concentration to about 90 mg P L^{-1}, but the

position of the peak was not greatly affected (Fig. 14b). As in the Stockton sandy loam, the addition of $MgSO_4$ with MCP delayed the ^{32}P elution, and the peak was observed approximately after 3 pore volumes had been eluted (Fig. 14b).

In both the Stockton and Almasippi soils, the peak ^{32}P concentrations observed when MCP (only) was added, were comparable to P concentrations in a saturated solution of dicalcium phosphate dihydrate (Handbook of Physics and Chemistry, 1972), which has been reported to be the dominant initial reaction product of MCP in alkaline soils (Bell and Black, 1970; Olsen and Flowerday, 1971), as well as in slightly acidic soils (Bell and Black, 1970). The addition of $(NH_4)_2SO_4$ and K_2SO_4 with MCP, in both soils, markedly increased the peak ^{32}P concentration, indicating that the reaction products formed were more soluble than DCPD. However, the addition of urea and $MgSO_4$ with MCP, did not have a pronounced effect on the peak ^{32}P concentration.

The ^{32}P concentration, when expressed as a per cent of total P concentration in the eluate samples, was zero in both soils during the elution of first pore volume of water, since only soil P was eluted during this period. ^{32}P elution was initially retarded due to the exchange of ^{32}P with ^{31}P in the soil. However, with further elution, the ratio of labelled P concentration to total P concentration in eluate samples rapidly increased, and reached to about 95 % when the peak ^{32}P concentration was observed, indicating that most of the soil P was eluted, during the elution of first 2-3 pore volumes.
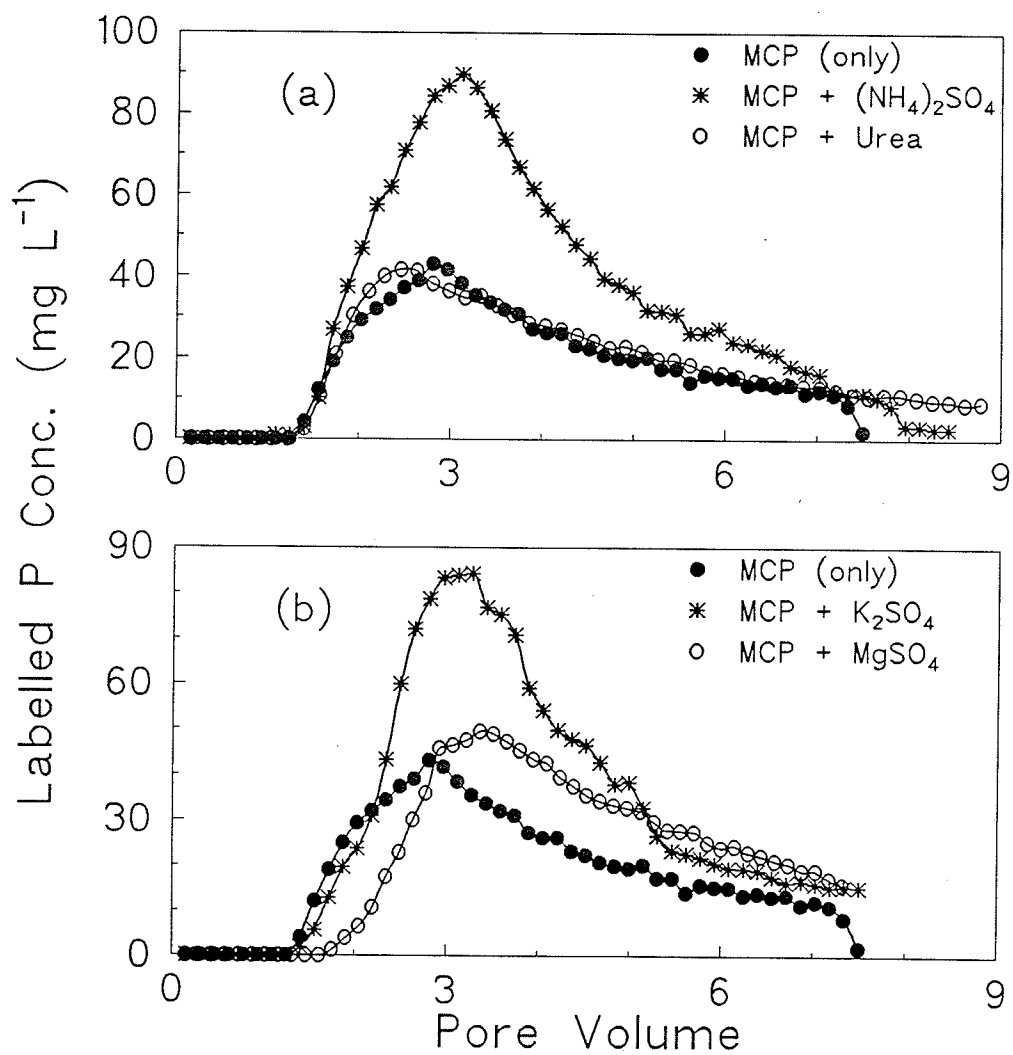
Fig. 13. Elution of surface-applied labelled P in the Stockton sandy loam
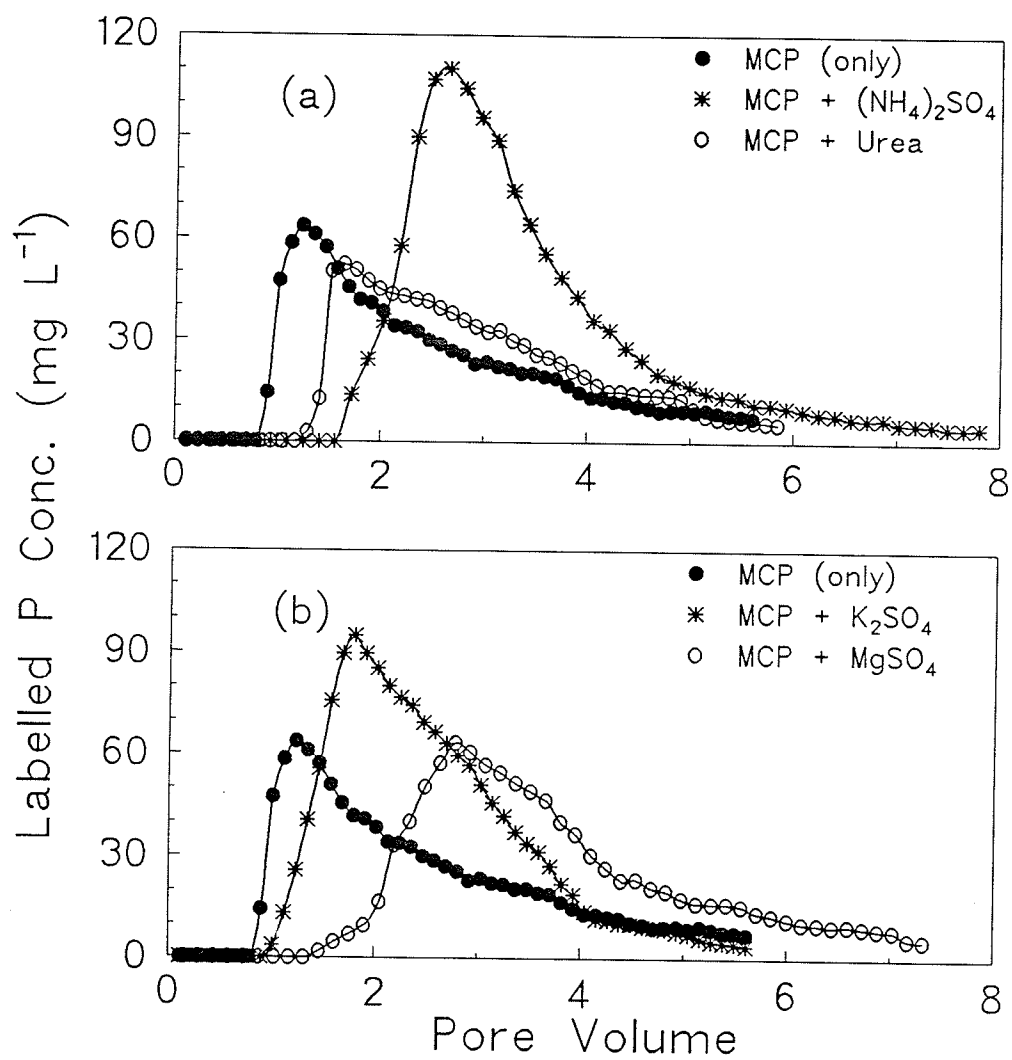columns as affected by addition of salts.

Fig. 14. Elution of surface-applied labelled P in Almasippi loamy sand columns as affected by addition of salts.

<u>Distribution of P in columns</u>

Distribution of KCl extractable labelled P after elution for the Stockton sandy loam and Almasippi loamy sand are shown in Fig. 15 and 16 respectively. In almost all the treatments in both soils, extractable P in the columns increased with depth. Similar results have been observed by Evans and Sorensen (1986) using 50 cm deep soil columns. In the Stockton sandy loam, the concentration of labelled P extracted in the $(NH_4)_2SO_4$ treatment was much less than in the MCP (only) treatment throughout the soil column (Fig. 15a). However, the addition of urea with MCP had little or no effect on the extractable ^{32}P concentrations after elution.

When K_2SO_4 or $MgSO_4$ were added (Fig. 15b), the ^{32}P extracted at the surface after elution was similar to that of the MCP (only) treatment. But with increasing depth, the ^{32}P concentration became gradually less than in the MCP (only) treatment in both K_2SO_4 and $MgSO_4$ treatments, K_2SO_4 having a greater effect.

Labelled P extracted in the Almasippi loamy sand after elution are shown in Fig. 16. The MCP + $(NH_4)_2SO_4$ treatment had lower extractable ^{32}P throughout the column (Fig. 16a) as in the Stockton sandy loam (Fig. 15a), whereas the MCP + urea treatment had slightly higher concentrations than in the MCP (only) treatment.

The addition of K_2SO_4 decreased the extractable labelled P after elution in the region 2-6 cm below the surface (Fig. 16b). But the addition of $MgSO_4$ in the Almasippi soil did not appreciably change the extractable ^{32}P concentration after elution.
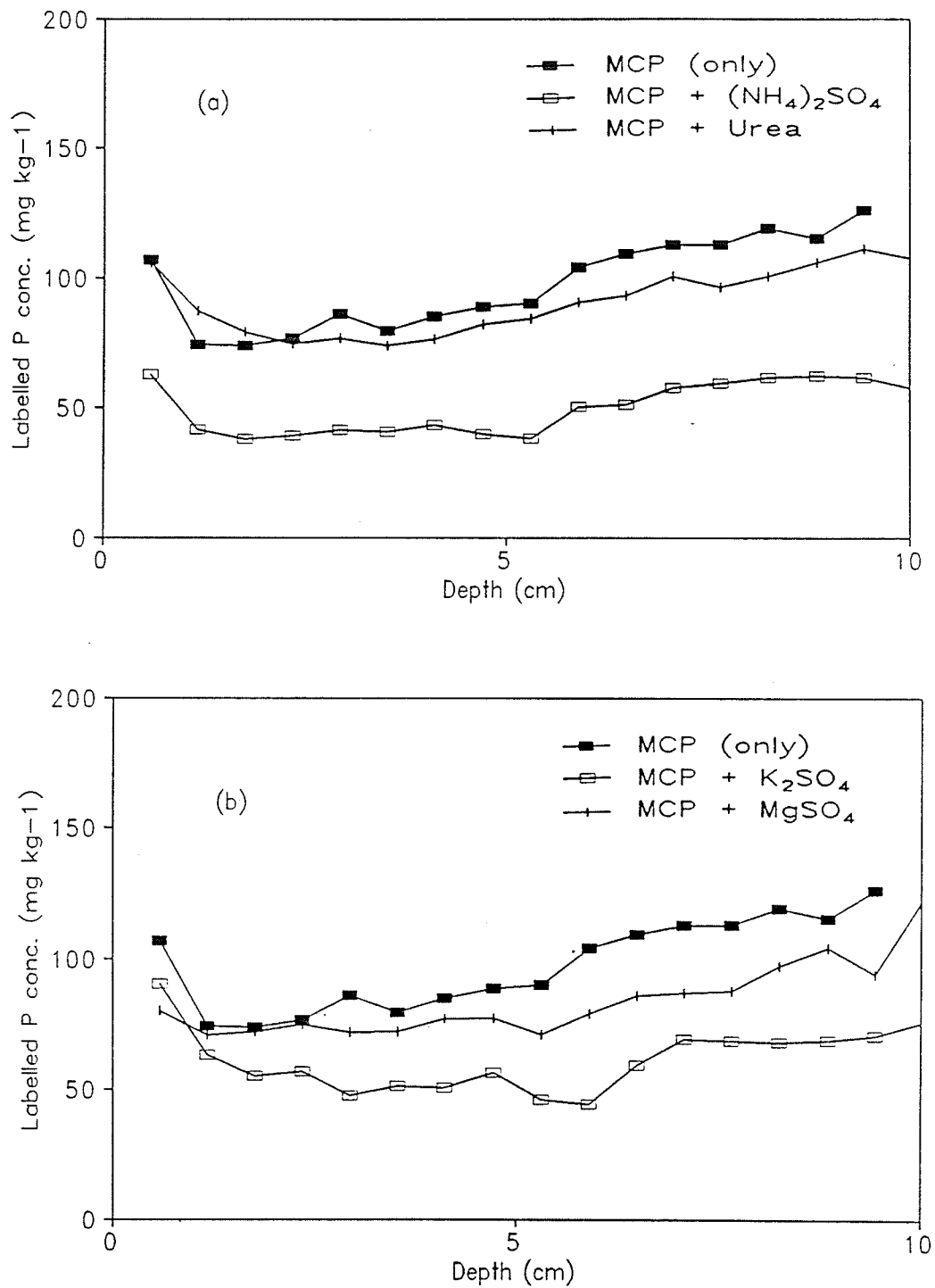
Fig. 15. Distribution of KCl extractable labelled P after elution in the Stockton sandy loam. (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition
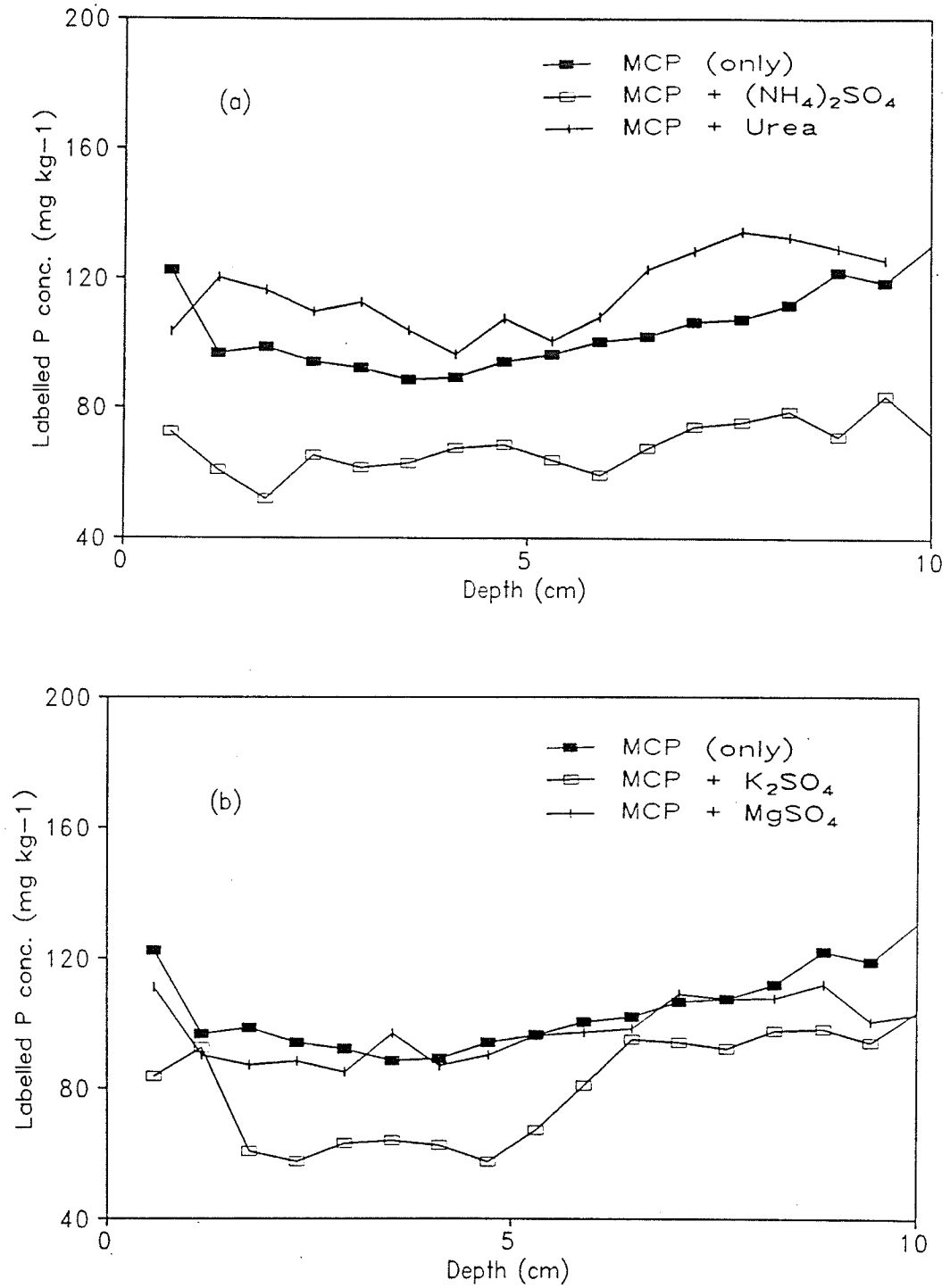
Fig. 16. Distribution of KCl extractable labelled P after elution in
the Almasippi loamy sand. (a) $(NH_4)_2SO_4$ and urea addition
(b) K_2SO_4 and $MgSO_4$ addition

The total amount of ^{32}P eluted and ^{32}P extracted from each column are given in Table 4. The variation in values between the replicate columns was generally small. However, there was a substantial variation between the treatments.

In the MCP (only) treatment, approximately 30-35 % of the added P was eluted. The amounts eluted were slightly greater in the Stockton soil than in the Almasippi soil. This is to be expected as the Almasippi soil had a higher pH which favours precipitation of insoluble calcium and magnesium phosphates.

The addition of sulphate salts in the Stockton soil enhanced the movement of ^{32}P applied to the surface. The effect of the sulphate addition on ^{32}P movement was, however, less obvious in the calcareous Almasippi soil with a pH of 8.0 as opposed to 7.3 in the Stockton soil. In both soils, the addition of urea with labelled MCP applied on the surface, did not appreciably affect the elution of ^{32}P.

There could be a number of possible causes for the increase in ^{32}P elution on addition of sulphates in the neutral Stockton soil. One possible cause would be the precipitation of Ca^{2+} by sulphate, thus reducing the effective concentration of Ca^{2+}, which may, otherwise combine with ^{32}P to form more insoluble phosphates. Apart from this effect, the addition of $(NH_4)_2SO_4$ or $MgSO_4$ makes the solution acidic, which does not favour precipitation of insoluble calcium and magnesium phosphates. Sulphates also may play a role by competing for adsorption sites. When urea was added, on the other hand, the higher solution pH as a result of urea hydrolysis would favour the precipitation reactions of phosphate with Ca and Mg, thus reducing the amount of ^{32}P eluted.

Table 4. Effect of addition of different salts on the elution of
fertilizer P* from soil columns

Treatment	^{32}P eluted (mg)	^{32}P extracted (mg)
Stockton sandy loam		
MCP (only)	1.45 ± 0.07	2.57 ± 0.09
MCP + $(NH_4)_2SO_4$	2.75 ± 0.01	1.30 ± 0.04
MCP + Urea	1.63 ± 0.00	2.39 ± 0.00
MCP + K_2SO_4	2.43 ± 0.03	1.61 ± 0.03
MCP + $MgSO_4$	1.70 ± 0.03	2.32 ± 0.05
Almasippi loamy sand		
MCP (only)	1.25 ± 0.03	2.73 ± 0.05
MCP + $(NH_4)_2SO_4$	2.14 ± 0.01	1.88 ± 0.01
MCP + Urea	1.19 ± 0.02	2.85 ± 0.04
MCP + K_2SO_4	1.79 ± 0.01	2.23 ± 0.00
MCP + $MgSO_4$	1.53 ± 0.03	2.49 ± 0.02

*All columns received 4.18 mg of P as MCP.

An inverse relationship was observed between the total amount of labelled P eluted and the total amount of labelled P extracted with KCl. When the amounts eluted and the amounts extracted were summed up the total accounted for about 95 % of the P added.

Elution of Ca

The elution curves for Ca^{2+} from the experimental soils (Fig. 17, 18) show that the patterns of distribution are quite different from that of ^{32}P. In the case of Ca^{2+}, another peak was observed before the main Ca^{2+} peak (Fig. 17, 18), which was absent in ^{32}P elution (Fig. 13, 14). This was apparent in the Stockton sandy loam (Fig. 17), but less obvious in the Almasippi loamy sand (Fig. 18). The first peak was observed at the
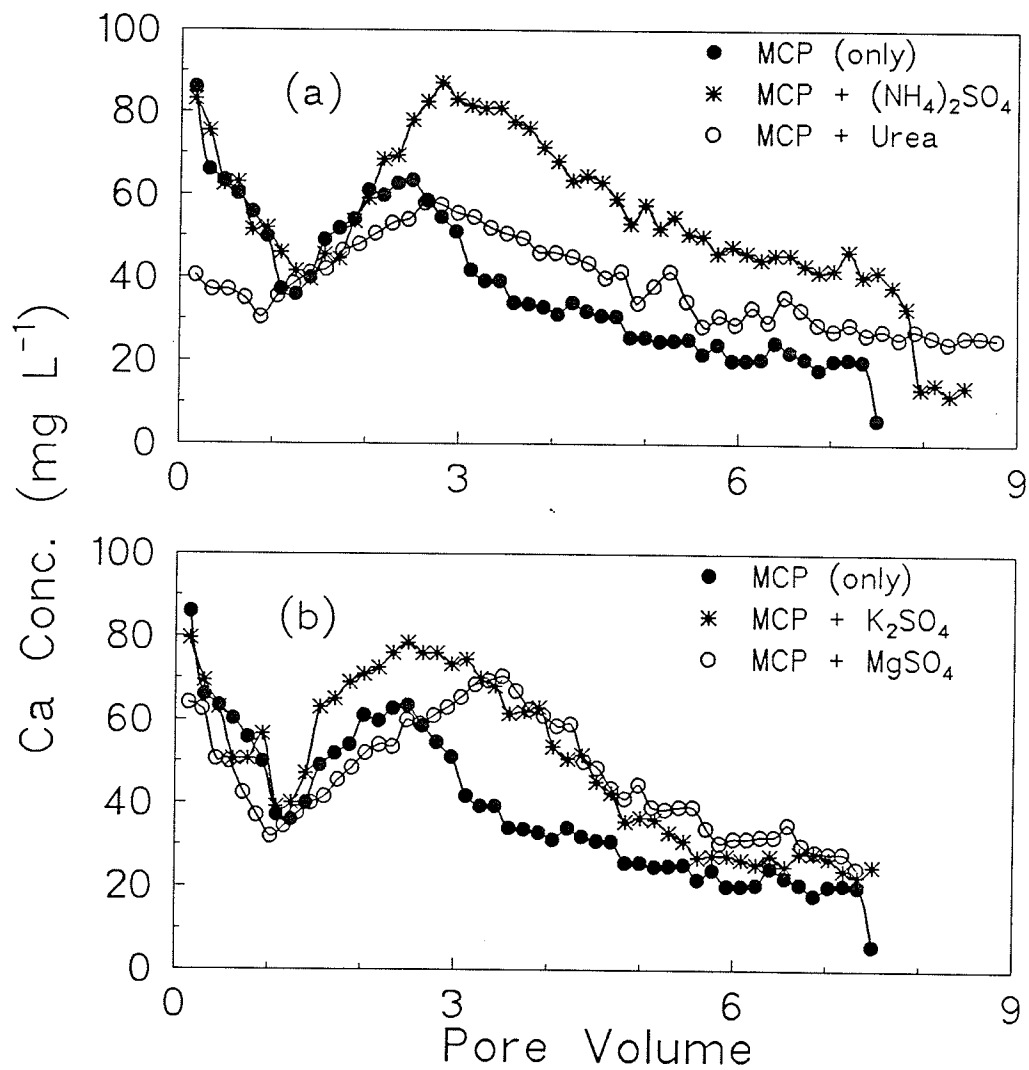
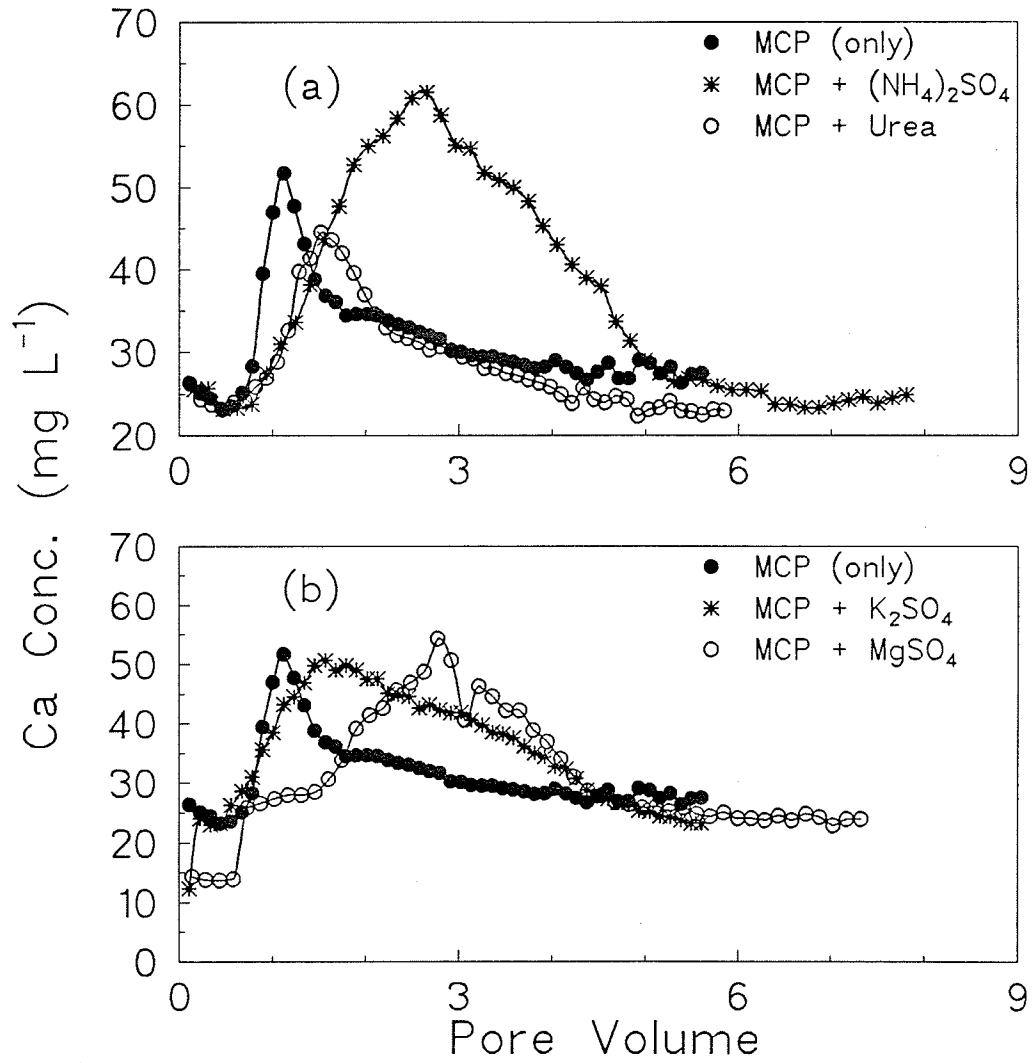Fig. 17. Elution curve of Ca^{2+} in the Stockton sandy loam as affected by the addition of salts.

Fig. 18. Elution curve of Ca^{2+} in Almasippi loamy sand as affected by the addition of salts.

beginning of elution, and Ca^{2+} concentration decreased almost linearly with further elution, until about 0.5 - 1 pore volumes had been eluted, after which the second peak was eluted. Thus, it is obvious that the first peak must be due to the soluble Ca^{2+} present in soil columns which was displaced by eluting solutions.

In the Stockton sandy loam, when MCP (only) was added, the second peak in Ca^{2+} was observed when nearly 3 pore volumes had been eluted (Fig. 17a). The addition of $(NH_4)_2SO_4$ with MCP increased the peak Ca^{2+} concentration, whereas the addition of urea with MCP slightly decreased the peak concentration. But both these salts did not seem to affect the position of peak Ca^{2+} concentration. Further elution in $(NH_4)_2SO_4$ and urea treatments gave eluted samples with higher concentrations of Ca^{2+} than in the MCP (only) treatment.

The addition of both K_2SO_4 and $MgSO_4$, increased the second peak Ca^{2+} concentration in the Stockton sandy loam (Fig. 17b). The peak was delayed in the $MgSO_4$ treatment, but not in the K_2SO_4 treatment.

In the Almasippi loamy sand when MCP was added alone (Fig. 18), the second peak in Ca^{2+} concentration was observed when about 1 pore volume was eluted. The addition of both $(NH_4)_2SO_4$ and urea with MCP (Fig. 18a) delayed the elution of Ca^{2+}, $(NH_4)_2SO_4$ having a greater effect. The peak Ca^{2+} concentration was much higher in the $(NH_4)_2SO_4$ treatment, and was observed when about 3 pore volumes had been eluted. Further elution gave samples with much higher Ca^{2+} concentration than in the MCP (only) treatment. The addition of urea decreased the peak Ca^{2+} concentration slightly.

The addition of both K_2SO_4 and $MgSO_4$ had no apparent effect on peak Ca^{2+} concentration, in the Almasippi loamy sand (Fig. 18b). The addition of $MgSO_4$ delayed the elution of Ca^{2+}, and the peak was observed only after about 3 pore volumes have been eluted.

The total Ca^{2+} eluted in the Almasippi loamy sand (Fig. 18) was much less than with the corresponding treatments in Stockton sandy loam (Fig. 17), since CEC and exchangeable Ca content was higher in the latter.

Generally, in all the treatments in both soils, the second peak of Ca^{2+} (Fig. 17, 18) and the peak in labelled P (Fig. 13, 14) were observed together, indicating that P retention is closely related to the retention of Ca^{2+}, possibly due to formation of less soluble Ca phosphates.

Elution of K or Mg

Elution profiles of K^+ and Mg^{2+} in the Stockton and Almasippi soils are shown in Fig. 19 and 20, respectively. K^+ in both soils was eluted fast, and reached a peak even before 1 pore volume was eluted, and with further elution, K^+ concentration in eluted samples decreased. Comparatively, Mg^{2+} elution was much slower, and reached a peak after about 3 pore volumes were eluted, and peak concentration was about 10 times less than for K^+.

The total amounts of K eluted in both soils were much higher than that of Mg. Since K_2SO_4 and $MgSO_4$ were added at the same rates, in terms of mmol per column, K^+ concentration added would be twice the concentration of Mg^{2+} added. At the same time, K, having a higher atomic weight than that of Mg, would have higher concentrations when expressed in mg L^{-1}. Still, a lower proportion of added Mg was eluted when compared
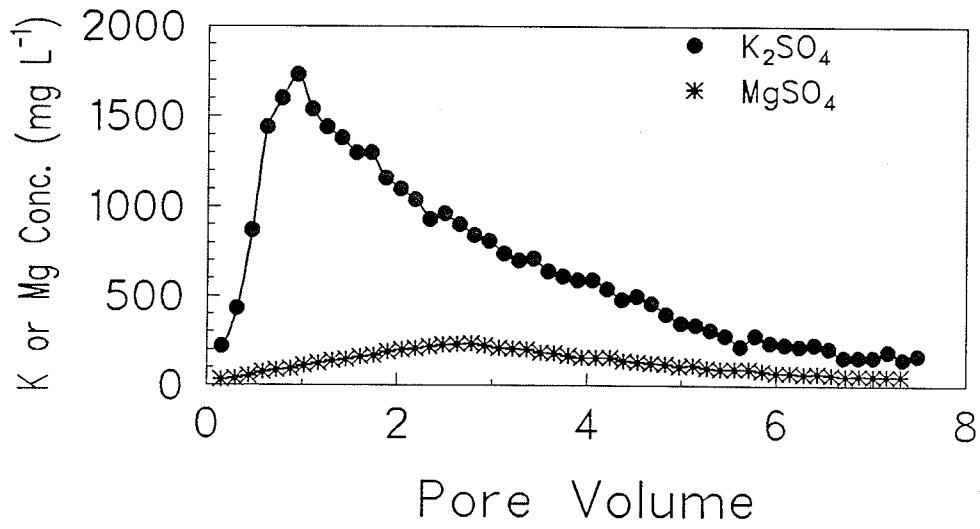
Fig. 19. Elution curve of K and Mg (added as sulphates) in the Stockton
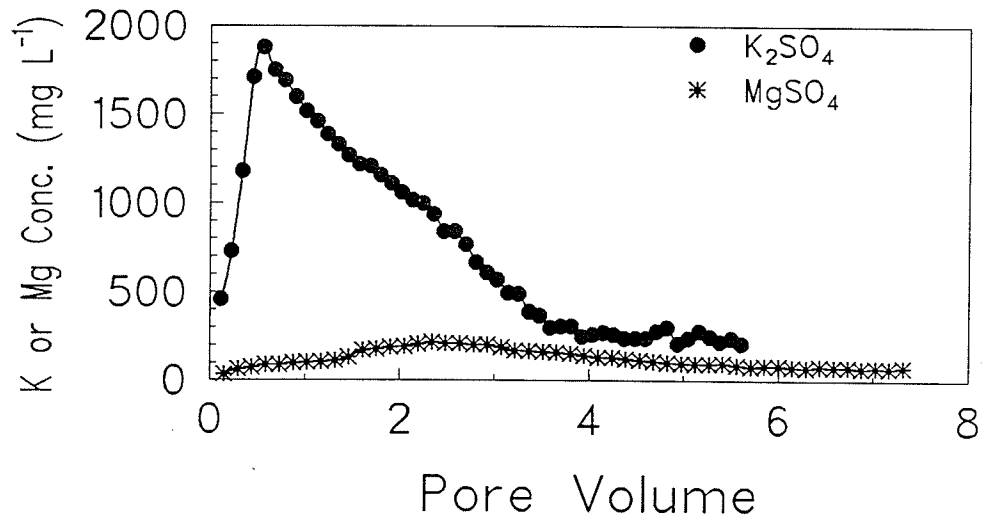sandy loam.

Fig. 20. Elution curve of K and Mg (added as sulphates) in the Almasippi
loamy sand.

with K, possibly because of the retention of Mg due to precipitation reactions.

Conclusions

Salts such as ammonium, K and Mg sulphates increased the elution of fertilizer P. Results of this experiment and previous column experiments indicated that these salts increased P movement whether the main mechanism of P transport was mass flow or diffusion. However, the relative magnitude of the effects were not consistent in all the experiments. In the elution experiment, $(NH_4)_2SO_4$ had a larger effect on P movement than the other two sulphate salts, whereas in the column experiments $MgSO_4$ had the greatest effect. In both these studies urea had little or no effect on P movement.

Generally, the peak Ca^{2+} concentration coincided with the peak concentration of labelled P, which suggests that P retention is associated with Ca retention, possibly due to precipitation of Ca phosphates.

Total amount of extractable P after elution was influenced by different salt treatments. When amounts of eluted and extracted P were summed up, it accounted for about 95 % of the added P, indicating that the major proportion of retained P is extractable. The results of this experiment suggest that P retention is mainly due to precipitation with Ca^{2+} in the two soils tested, and the precipitates are fairly soluble thus easily extracted.

3.5. Mathematical model

Column experiments and elution experiment previously discussed showed the effect of salts on P movement. Since diffusion, precipitation and adsorption of phosphate takes place simultaneously, the effect of salts on each of these processes cannot be evaluated experimentally. Transport of P accompanied with adsorption and precipitation reactions have been often described using mathematical models (Mansell and Selim, 1981; Enfield, 1981; Sparks, 1986, 1989). A recently developed model by Cho (1990) to describe the transport of phosphate in calcareous soils emphasized the importance of exchangeable Ca^{2+} upon retardation of P transport. This model was used to describe and explain the results obtained in column experiment 2, using the Almasippi loamy sand.

Theory

The mathematical model developed by Cho (1990) is made up of five transport equations for cation associated with P, exchangeable Ca^{2+}, phosphate ion, hydrogen ion and carbonate ions. In this study, the model of Cho (1990) was modified so that the sulphate transport equation replaced the carbonate transport equation when sulphate salts were used. Only when urea was mixed with phosphate, was the original formulations of Cho (1990) used.

The equations were,

$$\frac{\partial A}{\partial t} = D_A \frac{\partial^2 A}{\partial x^2} - \frac{\partial S_A}{\partial t}$$

$$\frac{\partial B}{\partial t} = D\frac{\partial^2 B}{\partial x^2} - \frac{\partial S_B}{\partial t} - \phi_c - \phi_q$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - \frac{\partial S_C}{\partial t} - \phi_c$$

$$\frac{\partial q}{\partial t} = D\frac{\partial^2 q}{\partial x^2} - \phi_q + \phi_E$$

$$\frac{\partial H}{\partial t} = D\frac{\partial^2 H}{\partial x^2} + \phi_{H1} + \phi_{H2} + \phi_{H3}$$

where A, B, C, q and H stand for the solution concentrations of the cation (associated with the salt), Ca^{2+}, phosphate, carbonate (or sulphate) and H^+, respectively. S_A stands for the concentration of exchangeable A and S_B stands for the concentration of exchangeable B. S_c is the adsorbed P on the surfaces of $CaCO_3$ particles. All concentrations were expressed in terms of solution concentration units, including the exchangeable ions. This is obtained by multiplying the adsorbed P concentration (mmol g^{-1}) by the ratio of bulk density to volumetric moisture content. ϕ_c and ϕ_q stand for rates of precipitation of $CaHPO_4$ and $CaSO_4$ (or $CaCO_3$) respectively. ϕ_E stands for the rate of production of carbonate due to dissolution of atmospheric CO_2. The rate of H^+ production from precipitation of $CaHPO_4$ and $CaCO_3$ is expressed as ϕ_{H1} and ϕ_{H2} respectively, and the rate of H^+ production due to dissolution of CO_2 is expressed by ϕ_{H3}.

Ion exchange

In his model Cho (1990) considered both divalent-divalent exchange and monovalent-divalent exchange. The chosen selectivity coefficient for divalent-divalent exchange was,

$$K = BS_A / (AS_B)$$

where K is the selectivity coefficient.

If the CEC of the soil is R, where R is expressed in mmol L^{-1}, then,

$$S_A + S_B = R$$

which gives,

$$S_A = KRA / (B + KA)$$

Therefore,

$$\frac{\partial S_A}{\partial t} = KR \left(\frac{\partial A}{\partial t} - A \frac{\partial B}{\partial t} \right) / (B + KA)^2$$

If $KRB / (B + KA)^2 = \phi_1$ and $KRA / (B + KA)^2 = \phi_2$ then,

$$\frac{\partial S_A}{\partial t} = \phi_1 \frac{\partial A}{\partial t} - \phi_2 \frac{\partial B}{\partial t}$$

and

$$\frac{\partial S_B}{\partial t} = \phi_2 \frac{\partial B}{\partial t} - \phi_1 \frac{\partial A}{\partial t}$$

For monovalent - divalent cation exchange, Cho (1985, 1990) derived the relationship,

$$S_A = (y^2 + 2Ry)^{1/2} - y$$

where $y = KA^2/4B$. The terms $\partial S_A/\partial t$ and $\partial S_B/\partial t$ were obtained by differentiating this equation (Cho, 1985).

When using the model to fit the experimental data of column

experiment 2, divalent-divalent formulation was used when $MgSO_4$ was the added salt and monovalent-divalent form was used for the other salt treatments.

P adsorption

Since P adsorption to $CaCO_3$ surfaces is a rapid reaction, a local equilibrium condition was chosen by Cho (1990), describing P adsorption using the Langmuir adsorption isotherm, which is expressed as,

$$S_C = K_r R_r C / (1+K_r C)$$

where K_r is the equilibrium constant and R_r is the adsorption maximum.

This equation was differentiated to get the $\partial S_C / \partial t$, which is then substituted in the P transport equation. Cho (1990) assumed that the surface Ca^{2+} is responsible for adsorption of P, and R_r was chosen to be 1% of $CaCO_3$ content.

Precipitation

Precipitation of $CaHPO_4$, $CaSO_4$ (or $CaCO_3$) were all chosen to be second order reactions. It should be noted however that in $CaHPO_4$ and $CaCO_3$ precipitation reactions, Cho (1990) considered the HPO_4^{2-} and CO_3^{2-} concentrations and not the total P concentration (C) and carbonate concentration (q). As the P concentration (C) is the sum of $H_2PO_4^-$ and HPO_4^{2-} concentrations, the fraction of HPO_4^{2-} in C was expressed as a function of pH and total P concentration (C), as follows:

$$f_c = K_c / (K_c + (H^+))$$

where K_c is the second dissociation constant of phosphoric acid and f_c is the fraction of C in HPO_4^{2-} form.

Similar relationship was derived for carbonates assuming that $q = (HCO_3^{2-}) + (CO_3^{2-})$, which gives,

$$f_q = K_q / (K_q + (H^+))$$

where f_q is the fraction of CO_3^{2-} in q, and K_q is the second dissociation constant of carbonic acid.

The equilibrium concentration of Ca^{2+} due to solubility of $CaHPO_4$, B_c is incorporated into the rate equation so that the reaction will not proceed any further when Ca^{2+} concentration has reached its equilibrium concentration. The equation Cho (1990) used was,

$$\phi_c = r_c(HPO_4^{2-})(B-B_c)$$

where r_c is the rate constant for $CaHPO_4$ precipitation.

Similarly for $CaCO_3$ precipitation the equation used was

$$\phi_q = r_q(CO_3^{2-})(B-B_q)$$

where r_q is the rate constant for $CaCO_3$ precipitation.

CO_2 dissolution from atmosphere

Cho (1990) assumed that the rate of dissolution of CO_2 is directly proportional to the deficit quantity $q_{eq}-q$ (where q is carbonate). Thus,

$$\phi_E = r_E(q_{eq} - q)$$

where r_E is the rate constant.

H^+ production terms

Removal of HPO_4^{2-} and CO_3^{2-} from the solution, during precipitation of $CaHPO_4$ and $CaCO_3$ respectively, would result in the dissociation reactions,

$$H_2PO_4^- \quad = \quad H^+ + HPO_4^{2-} \quad \text{and}$$

$$HCO_3^- \quad = \quad H^+ + CO_3^{2-}$$
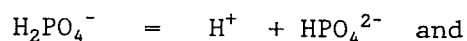
which release H^+ into solution.

Cho (1990) derived the equations for the rate of H^+ production as $(1-f_c)\phi_c$ and $(1-f_q)\phi_q$ due to precipitation of HPO_4^{2-} and CO_3^{2-} respectively.

As H^+ produced is buffered in soils, it was assumed that above pH 6.0, there is a buffering effect described by the relation,

$$\text{buff} = \exp (-2.0 (\text{pH} - 6.0))$$

However, for this study, the equation was modified as,

$$\text{buff} = \exp (-\text{buffl} (\text{pH} - \text{eph}))$$

which allows buffl and eph to be changed until a good prediction is observed.

The magnitude of net rate of H^+ production due to precipitation reactions were given by the equations,

$$\phi_{H1} \quad = \quad \text{buff} (1-f_c) \ \phi_c$$

$$\phi_{H2} \quad = \quad \text{buff} (1-f_q) \ \phi_q$$

As implied by the equations, H^+ production is rather small and negligible at very low and very high pH values.

ϕ_{H3}, the rate of production of H^+ due to dissolution of atmospheric CO_2 was considered to be proportional to ϕ_E, the rate of dissolution of CO_2, where the proportionality constant is pH dependent. The fraction HCO_3^- is $(1-f_q)$ with H^+ production coefficient of 1, while CO_3^{2-} with a fraction of f_q has a production coefficient of 2, resulting in a proportionality coefficient of $(1+f_q)$ between ϕ_{H3} and ϕ_E.

Initial and boundary conditions

Equations for the interaction terms were substituted to the original set of 5 transport equations and the equations were solved using the following initial and boundary conditions.

1) $t \leq t_{Ch1}$, t_{Ch2} and $x = 0$

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

2) $t = 0$ and $0 < x \leq L$

$A = A_i$, $B = B_i$, $C = C_i$, $q = q_i$, $H = H_i$

3) $t_{Ch1} \geq t > t_{Ch2}$ and $x = 0$

No flux for A and q. $B = B_o$, $C = C_o$, $H = H_o$

4) $t > t_{Ch1}$ and $x = 0$

No flux for every species

5) $t \geq 0$ and $x = L$

No flux for every species

where t_{Ch1} and t_{Ch2} stand for the change over time from constant boundary to no flux boundary condition for MCP and salts respectively. Since all the salts used were more soluble than MCP, always the condition $t_{Ch2} < t_{Ch1}$ was met. Subscripts o and i in the equations stand for boundary and initial values respectively. A_i and B_i were chosen so that the exchange complex was initially saturated with Ca^{2+}.

As the set of transport equations cannot be solved analytically, Crank-Nicholson method was used to approximate the equations considering the boundary conditions (Appendix E). Thomas algorithm combined with iteration was used to solve the dependent variables at fixed time and position. Distribution of adsorbed and precipitated P were also obtained.

Assumptions

The model assumes that the movement of P as well as other ions are only through diffusion, and the contribution of mass flow is negligible. As this model was originally formulated to describe P transport in calcareous soils, it assumes that the exchangeable complex is saturated with Ca^{2+}. Phosphorus is assumed to be in three phases, in the solution, adsorbed or precipitated, and the immobilization of P which converts inorganic P to organic P has not been considered, as the model prediction is considered for a short period of time. Precipitation of P is assumed to be only as $CaHPO_4$ and other forms of precipitates are assumed to be negligible.

A local equilibrium condition has been assumed for ion exchange reactions as well as for adsorption of P, whereas precipitation reactions were assumed to be slower, described by rate equations. The rate constants, equilibrium constants and diffusion coefficients of ions were assumed to be constant with time.

Model predictions

The parameters needed for the calculation were varied until a predicted distribution was in good agreement with the experimentally observed distribution, while the parameters used were physically sound. Once the diffusion coefficient, rate constants for precipitation (for $CaHPO_4$, $CaSO_4$ and/or $CaCO_3$) and equilibrium constant for adsorption were obtained from the prediction of P distribution in the MCP (only) treatment, these values were used in all the other treatments, as they would not change among the treatments. As such, the diffusion coefficient

of P used was 0.0025 cm^2 h^{-1} which is equivalent to 6.94 x 10^{-7} cm^2 sec^{-1}.
This is much lower than the diffusion coefficient of P in water mainly
because of the tortuosity of the diffusion path. The same value was used
for the diffusion coefficient of K and Mg, but a slightly higher value
was used for the ammonium diffusion as it can move in the gaseous phase
(as ammonia gas), as well. Thus, the diffusion coefficient used for NH_4^+
was 0.003 cm^2 h^{-1}. In all the treatments, the rate constant for
precipitation of both $CaHPO_4$ and $CaSO_4$ (or $CaCO_3$) was 0.0015, and the
equilibrium constant used for P adsorption was 0.01.

The only parameters that were varied in predictions among treatments
were the boundary concentrations for cation, anion, P, Ca^{2+} and pH, and
the change-over times for MCP and the salt at which a constant boundary
condition changes to a no-flux boundary condition. The cation and anion
concentrations, and the change-over time for the added salt, were
selected considering the solubilities of the salts. Thus, the salts with
higher solubilities had higher cation and anion concentrations with lower
values of change-over time.

As some of the salts affected the solubility of MCP, boundary
concentrations of P and Ca^{2+} and change-over time for MCP would not be the
same in all the treatments. Treatments having salts that increase the
solubility of MCP would have a higher P and Ca^{2+} boundary concentrations
and a lower change-over time.

The boundary pH was also varied among the treatments depending on
the acidity or the alkalinity of the salt added. In all the treatments
except the urea treatment, the boundary pH was considered to be lower
than the initial pH, as MCP itself was acidic.

The constant parameters used for the treatments were,

$R = 120$ mmol kg^{-1}, $K = 2$, $R_r = 5$ %

$pK_c = 7.2$, $pK_q = 10.33$

$pK_{Sc} = 6.9$, $pK_{eq} = 18.1$

pK_{sq} (for $CaCO_3$) = 8.41 , pK_{sq} (for $CaSO_4$) = 4.52

buffl = 4, eph = 5.0

$dx = 0.2$ cm, $dt = 0.1$ hours

$D = 0.0025$ cm^2 h^{-1}, D_a (when A is NH_{4+}) = 0.003 cm^2 h^{-1}

$K_c = 0.0015$, $K_q = 0.0015$, $K_r = 0.01$

Since total P was measured in the experiment, the predicted P in solution, adsorbed P and precipitated P were summed before comparisons were made. The concentration of the first sample (surface sample) was not considered, as it had a high variation in P concentration.

The variable parameters used in different treatments are given in Table 5. In $MgSO_4$, $(NH_4)_2SO_4$ and urea treatments, higher values for boundary concentration of P and Ca^{2+} had to be used to get a good prediction, which indicated that the solubility of MCP was increased by these salts.

Predicted and observed P concentration distributions for the five treatments are shown in Fig. 21-25. In the MCP (only) treatment (Fig.21), predicted P and observed P distributions are in good agreement at all time periods considered. In the $(NH_4)_2SO_4$ treatment (Fig. 22), the model predicted the P distribution reasonably well at 1 and 3 weeks of incubation (Fig. 22a, 22c), but at 2 and 4 weeks of incubation (Fig. 22b, 22d), the observed concentration at some depths slightly deviated from those predicted. When urea was added with MCP (Fig. 23), the predicted

Table 5. Parameters used for model predictions

	MCP (only)	MCP + $(NH_4)_2SO_4$	MCP + urea	MCP + K_2SO_4	MCP + $MgSO_4$
A_o (mmol L^{-1})	-	5000	5000	1300	2160
B_o (mmol L^{-1})	90	200	110	90	225
C_o (mmol L^{-1})	180	400	220	180	450
q_o (mmol L^{-1})	-	2500	2500	650	2160
pH_o	6.8	6.5	8.5	7.8	6.0
t_{Ch1} (hours)	500	192	450	500	300
t_{Ch2} (hours)	-	12	12	72	24

P distribution is in close agreement with the observed distribution at all time periods, whereas, in the K_2SO_4 treatment, the model predicted the P distribution reasonably well at 1 and 2 weeks (Fig. 24a, 24b) but not at 3 and 4 weeks of incubation (Fig. 24c, 24d). When $MgSO_4$ was added with MCP, the prediction was fairly good for the first three weeks of incubation (Fig. 25a, 25b, 25c), but at 4 weeks of incubation (Fig. 25d), the observed concentrations at 5-8 mm depth deviated from those predicted.

The calculated phosphate concentration distribution in soil solution at various times of incubation for the different treatments are shown in Fig. 26. At 1 week of incubation (Fig. 26a), the predicted P concentration is high at the surface and decreased with depth. In the MCP + $(NH_4)_2SO_4$ and MCP + $MgSO_4$ treatments, the predicted P concentrations at
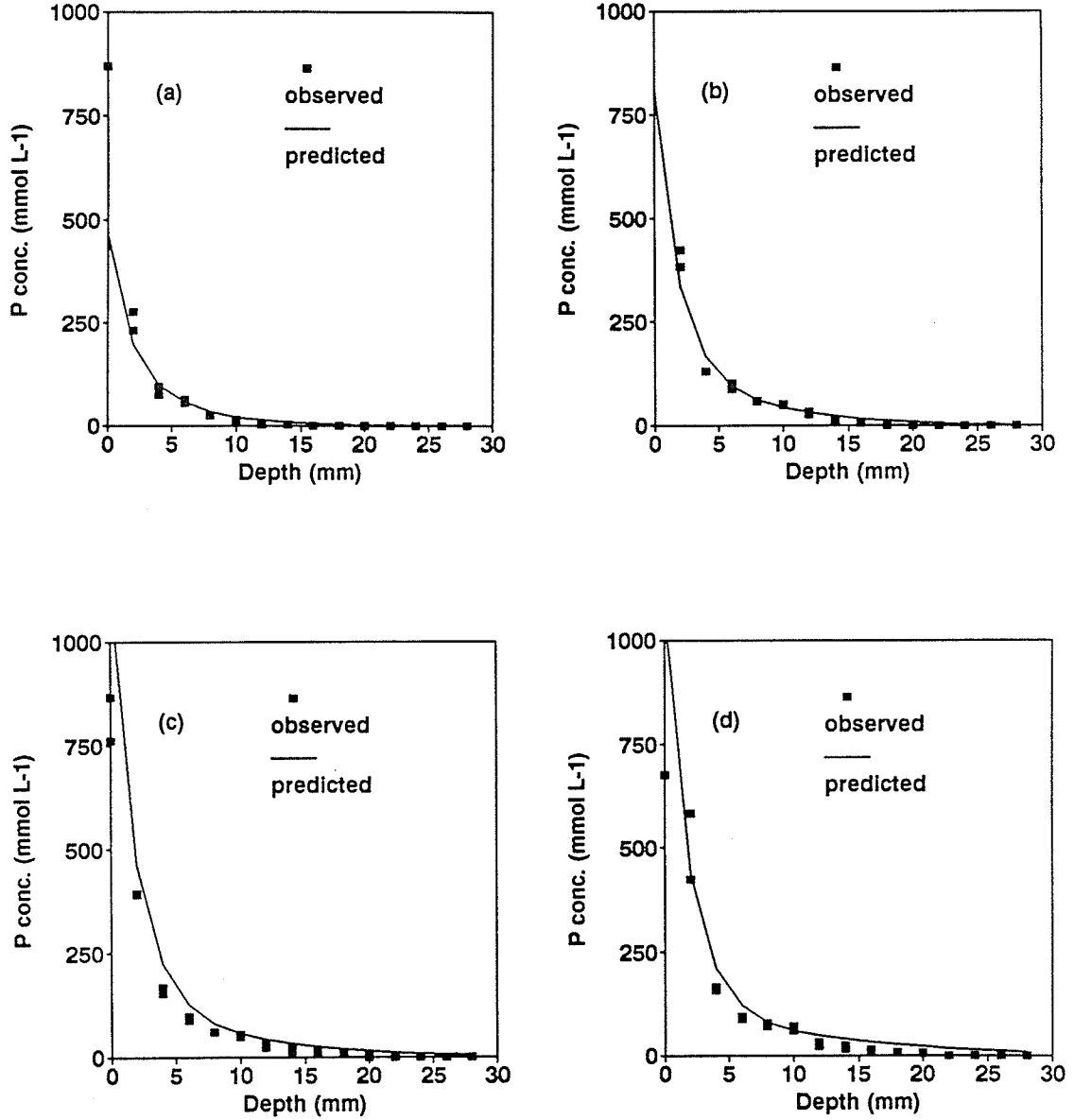
Fig. 21. Predicted and observed total labelled P distribution in the MCP (only) treatment at different times of incubation (a) 1 week (b) 2 weeks (c) 3 weeks (d) 4 weeks.
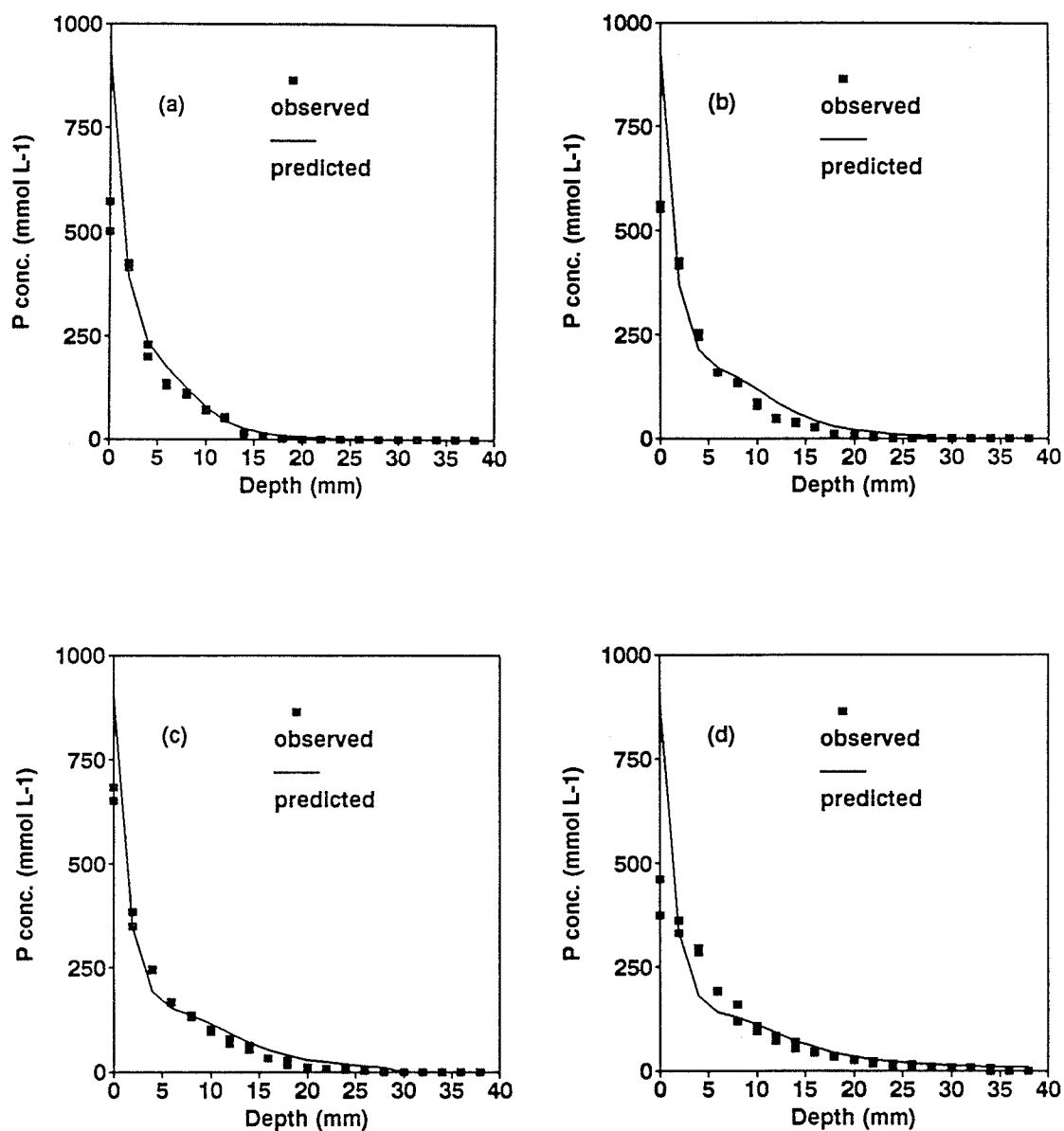
Fig. 22. Predicted and observed total labelled P distribution in the
MCP + $(NH_4)_2SO_4$ treatment at different times of incubation
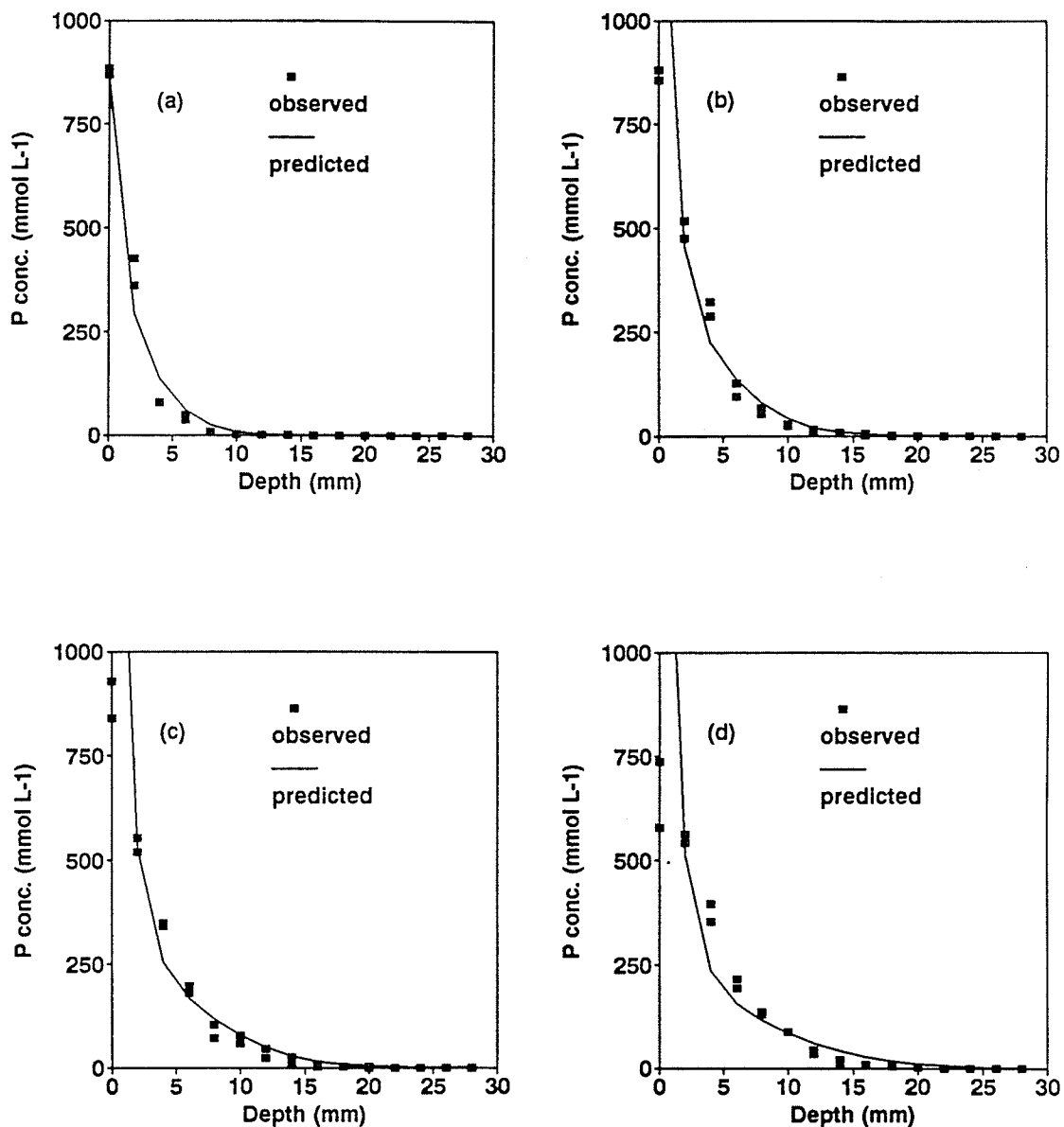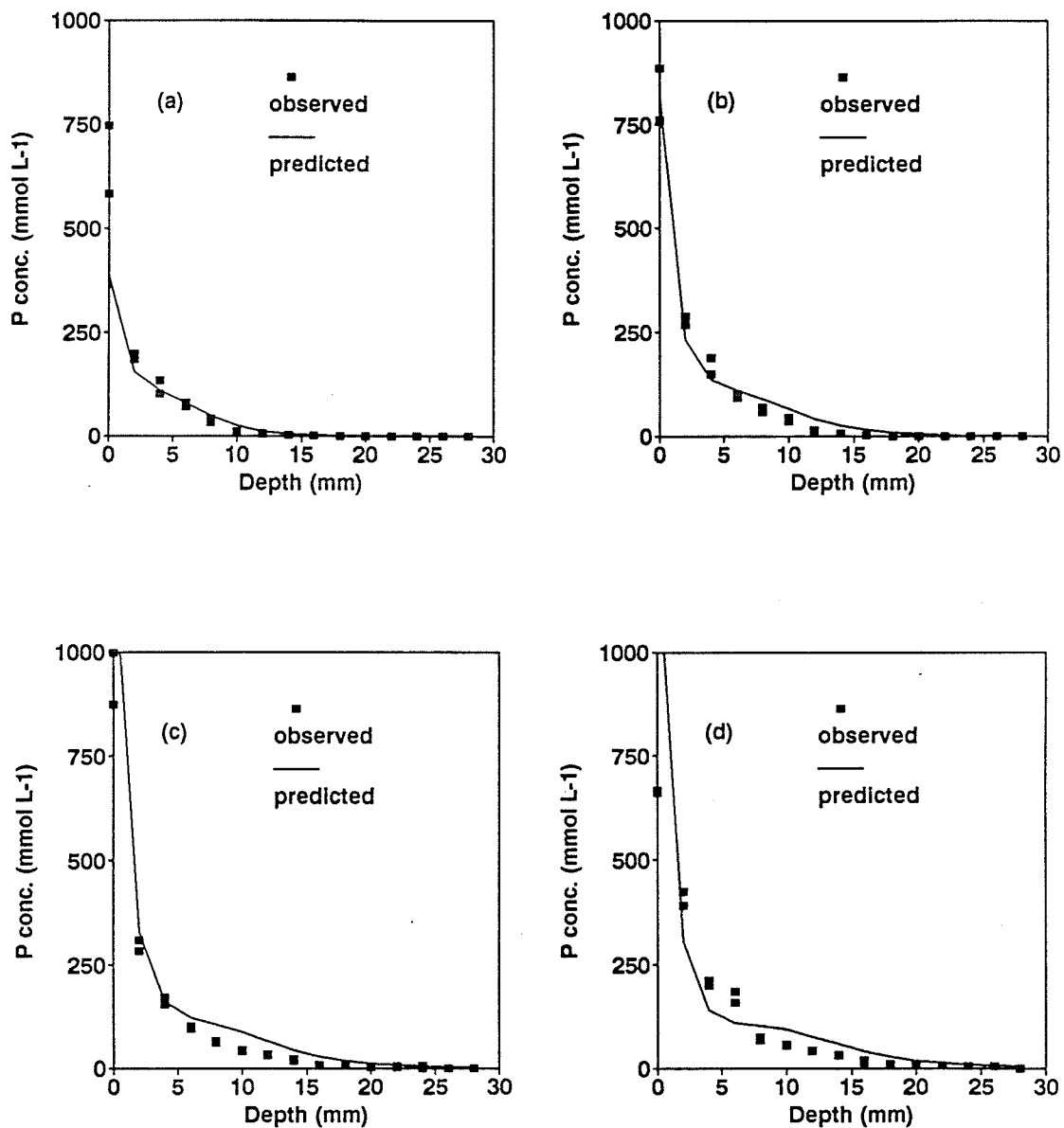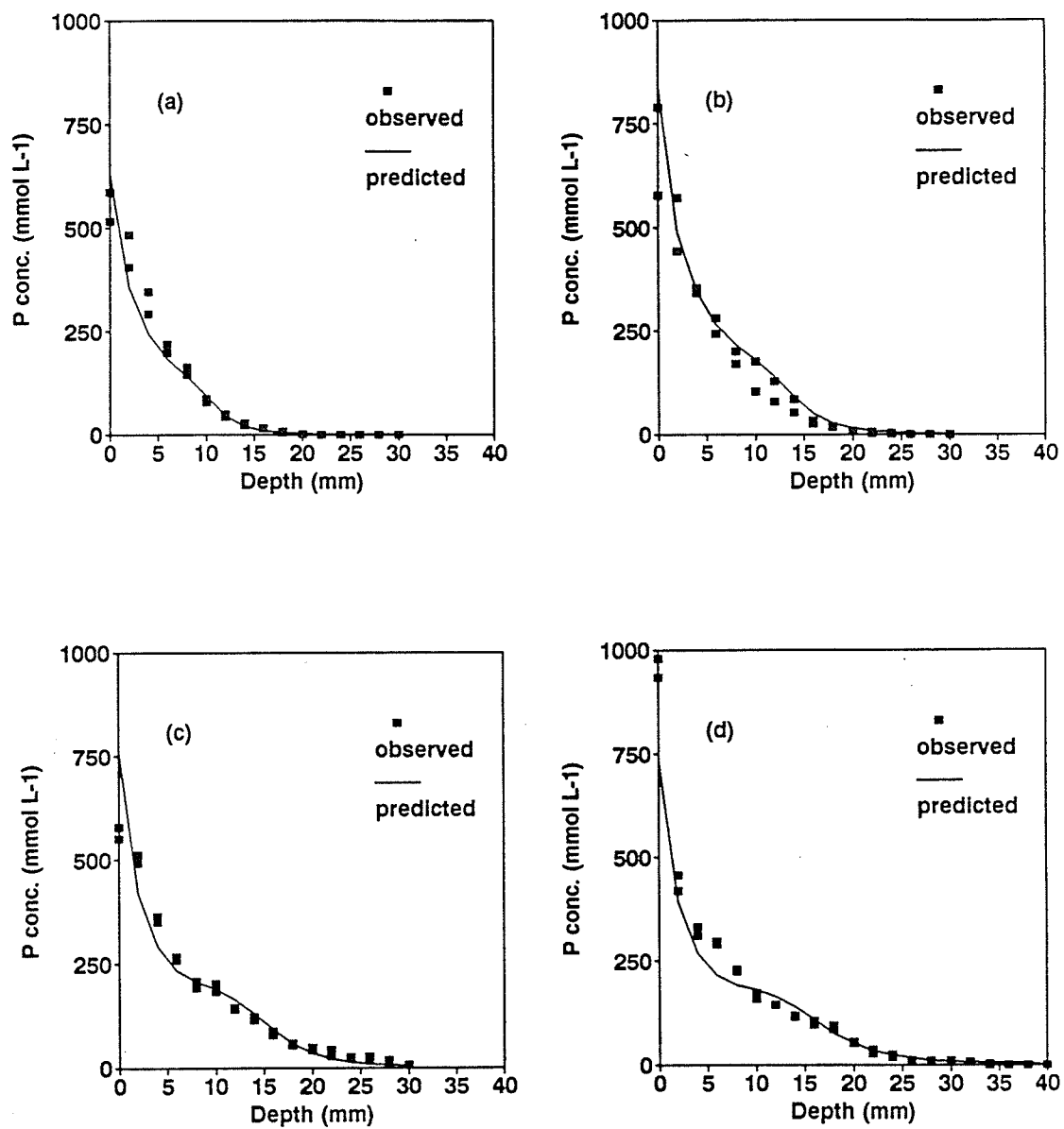(a) 1 week (b) 2 weeks (c) 3 weeks (d) 4 weeks.

Fig. 23. Predicted and observed total labelled P distribution in the
MCP + urea treatment at different times of incubation
(a) 1 week (b) 2 weeks (c) 3 weeks (d) 4 weeks.

Fig. 24. Predicted and observed total labelled P distribution in the
MCP + K_2SO_4 treatment at different times of incubation
(a) 1 week (b) 2 weeks (c) 3 weeks (d) 4 weeks.

Fig. 25. Predicted and observed total labelled P distribution in the
MCP + MgSO₄ treatment at different times of incubation
(a) 1 week (b) 2 weeks (c) 3 weeks (d) 4 weeks.

the surface were more than twice that of other treatments. At 2 weeks of incubation (Fig. 26b), P had diffused down the column, and the concentrations at the surface were much lower. After 3 weeks of incubation (Fig. 26c) the concentrations predicted at the surface were even less, and at the same time, the total amounts of P in the solution phase had decreased considerably due to adsorption and precipitation reactions. At 4 weeks of incubation (Fig. 26d), the predicted differences in P concentrations among the treatments were considerably less, and in all the treatments, the total amount of P in solution predicted, was very low.

At all time periods, MCP + $MgSO_4$ treatment had the highest predicted P concentrations that extended deeper into the soil column than in the other treatments, whereas the lowest concentrations were predicted for the urea treatment.

The adsorbed P on the $CaCO_3$ surfaces predicted by the model are shown in Fig. 27. The concentration distribution of adsorbed P (Fig. 27) in all the treatments were similar to those of solution P (Fig. 26) as those two fractions were considered to be at equilibrium. At 1 week of incubation (Fig. 27a), predicted amounts of P sorbed were much higher at the surface, and decreased with depth. The amounts sorbed were much higher in the MCP + $(NH_4)_2SO_4$ and MCP + $MgSO_4$ treatments, whereas in the MCP + urea treatment, the predicted amounts of P adsorbed were much lower than for the MCP (only) treatment.

The amounts of P adsorbed at the surface, as well as the total amount of P adsorbed in all the treatments, decreased with increasing incubation time, according to the model prediction. At 4 weeks, the

predicted adsorbed concentration at the surface was about half of that at 1 week of incubation, for all the treatments.

The precipitated $CaHPO_4$ distributions according to the model are shown in Fig. 28. The amounts precipitated in all the treatments were higher at the surface and decreased with depth. At 1 week of incubation, the predicted concentrations of precipitated P at the surface in the MCP + urea and MCP + $(NH_4)_2SO_4$ treatments were much higher (Fig. 28a) than for the other treatments. Increasing incubation time increased the precipitated P concentrations at the surface and extended deeper in the column (Fig. 28b, 28c). In all the treatments except MCP + $MgSO_4$ treatment, the precipitated P concentrations decreased exponentially with depth, but in the MCP + $MgSO_4$ treatment, P precipitation was nearly constant within the range 5 - 15 mm depth.

At all time periods, the precipitated P concentrations predicted were higher in the MCP + urea treatment to a depth of about 5 mm, and below that, the MCP + $MgSO_4$ treatment had the highest precipitated P concentrations predicted.

The predicted and observed pH distribution for the different treatments are shown in Fig. 29 - 33. In the control treatment (Fig. 29), the model predicted the pH distribution reasonably well at all time periods.

In the MCP + $(NH_4)_2SO_4$ and MCP + urea treatments (Fig. 30, 31), the predicted pH was not in good agreement with the observed distribution at all time periods. One reason for this could be the pH decrease due to the nitrification reaction, which was not considered in the model. At the same time, the buffering effect of pH considered in the model may not
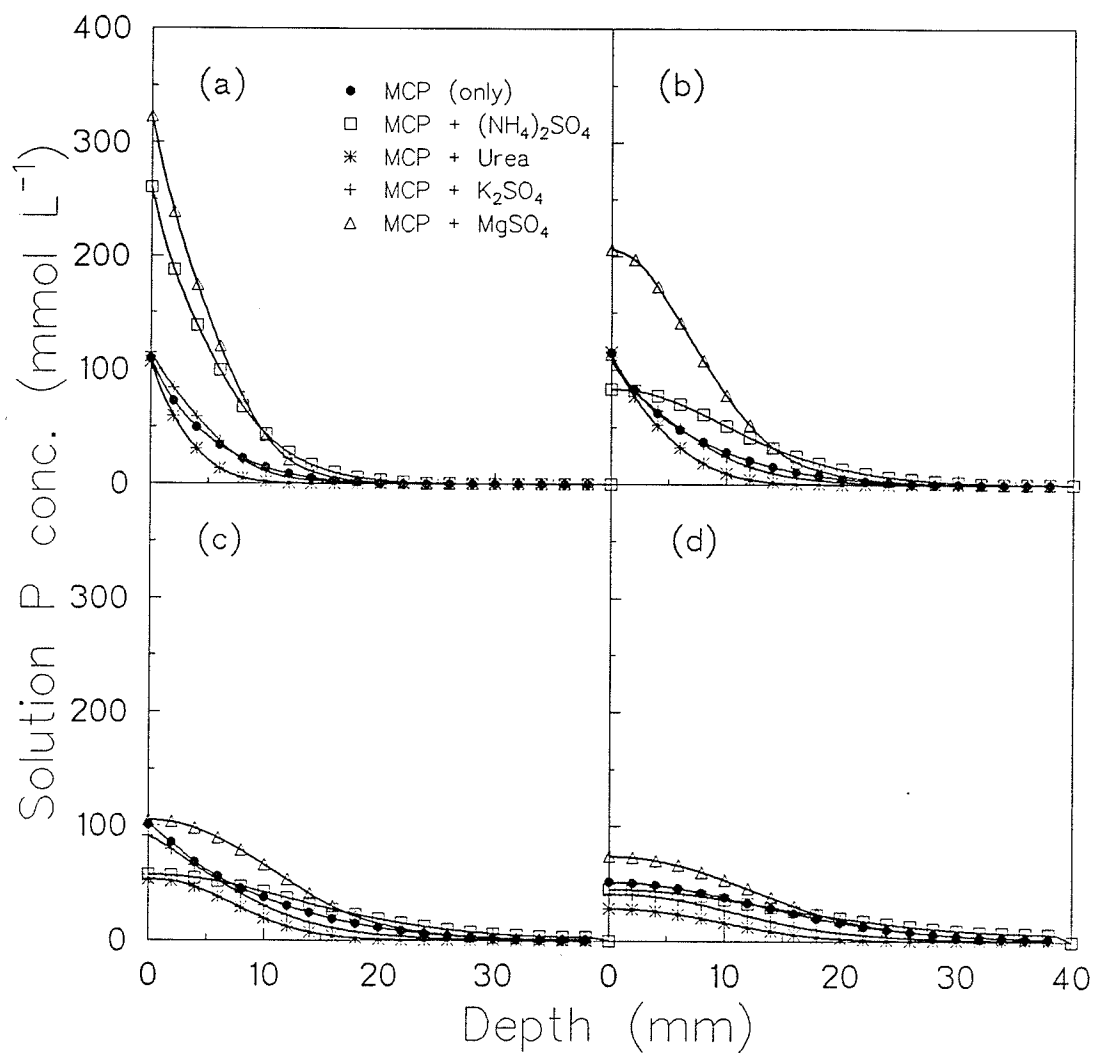
Fig. 26. Predicted distribution of solution P concentration at various
times of incubation (a) 1 week (b) 2 weeks (c) 3 weeks
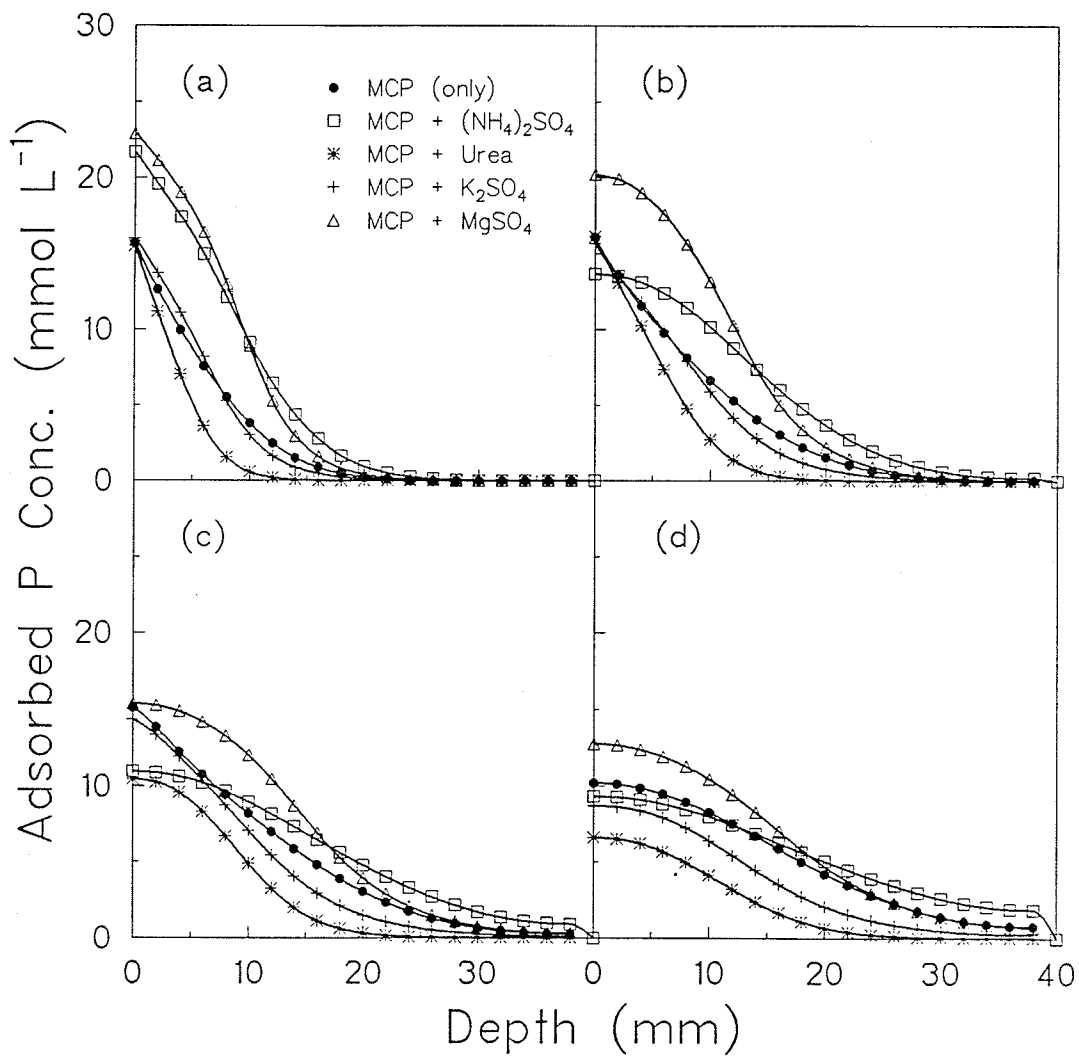(d) 4 weeks.

Fig. 27. Predicted distribution of adsorbed P concentration at various
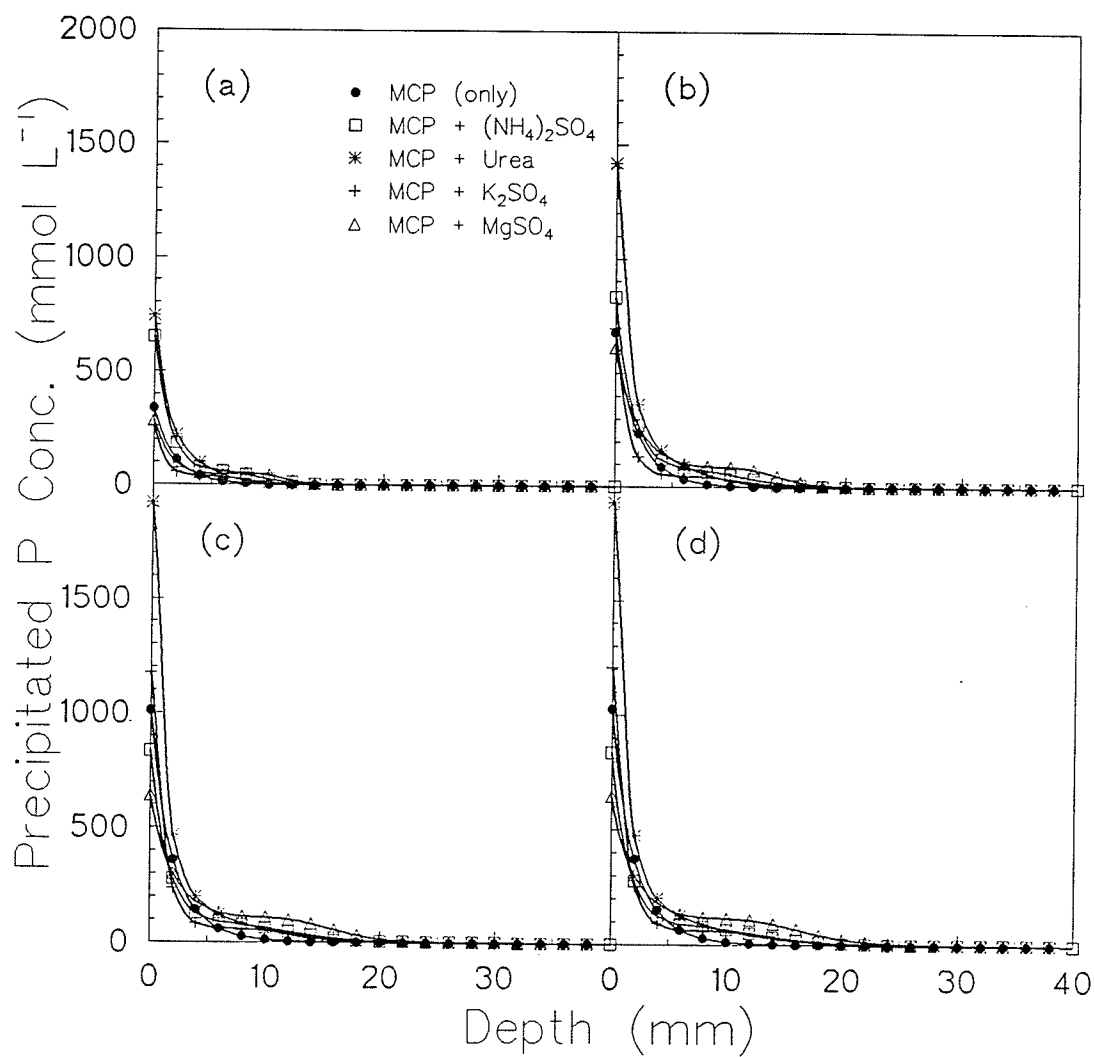   times of incubation (a) 1 week (b) 2 weeks (c) 3 weeks
        (d) 4 weeks.

Fig. 28. Predicted distribution of precipitated P concentration at various times of incubation (a) 1 week (b) 2 weeks (c) 3 weeks (d) 4 weeks.

have adequately described the buffering effect of pH in these treatments.

In the MCP + K_2SO_4 treatment (Fig. 32), the pH distribution predicted for 1 week of incubation, reasonably agreed with the observed values (Fig. 32a). However, at 2, 3 and 4 weeks of incubation, the model predicted slightly lower pH values than those observed.

In the MCP + $MgSO_4$ treatment, a poor agreement was observed between observed and predicted pH distribution at all times of incubation (Fig. 33). The model predicted a lower pH close to the surface, which was not observed experimentally. Thus, the prediction of pH using this model seems to be unsatisfactory, except in the MCP (only) treatment. This is because, in this model, pH changes due to addition of salts as well as the buffering effect of pH due to the presence of $CaCO_3$ was not considered.

The predicted cation distributions in treatments with salt addition are shown in Fig. 34. At 1 week of incubation (Fig. 34a), the concentrations were higher at the surface and decreased with depth. At 2 weeks of incubation (Fig. 34b), the concentrations at the surface decreased and cations moved deeper in the columns. The total amount of cations in solution in all the treatments decreased with time due to ion exchange reactions that removed cations from the solution phase to the exchangeable phase. At 3 weeks of incubation (Fig. 34c), cation concentrations at the surface and the total concentration of cations in solution further decreased. The differences among treatments in predicted cation distribution were quite small after 4 weeks of incubation (Fig. 34d).
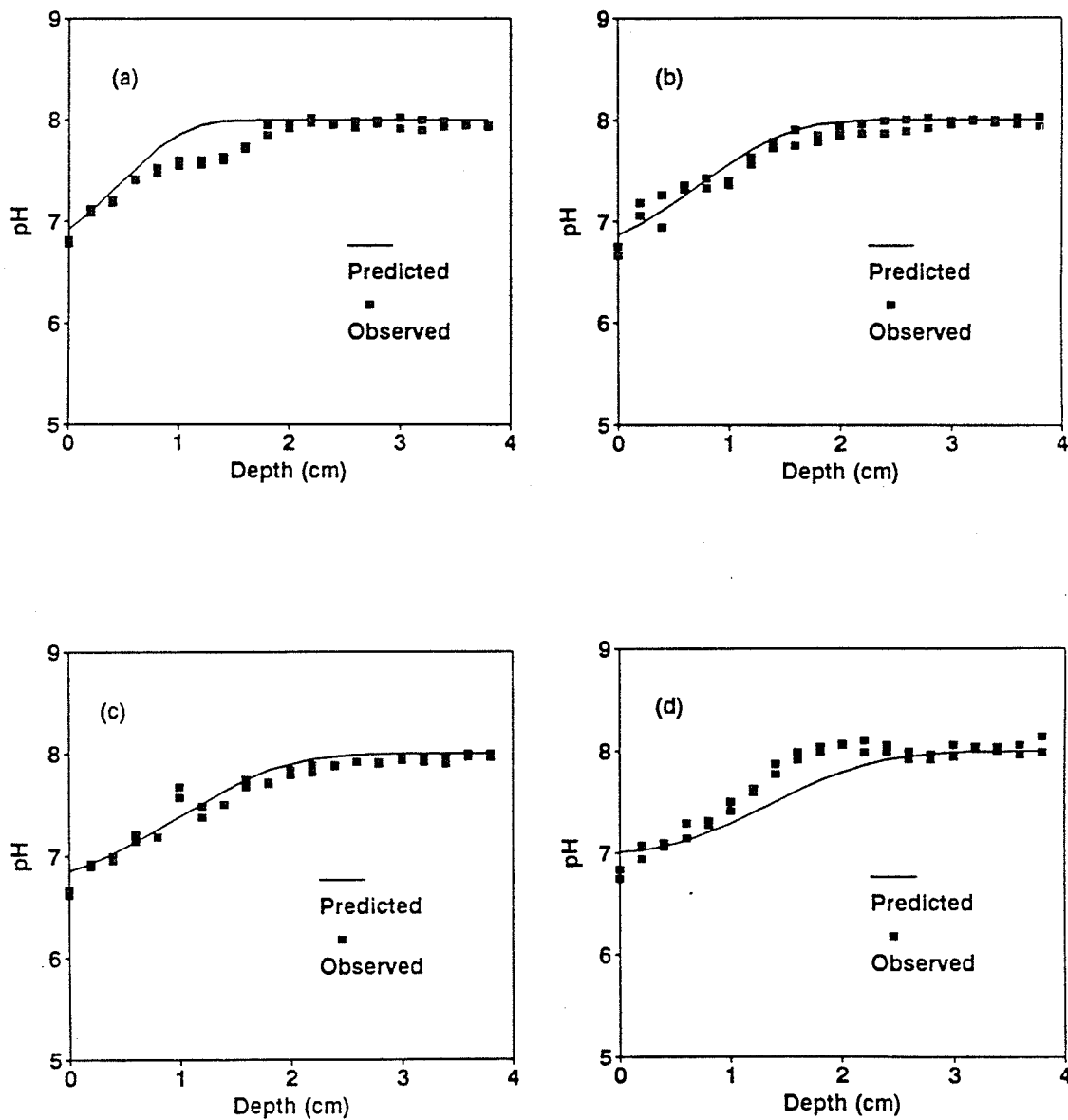
Fig. 29. Predicted and observed pH distribution in the MCP (only)
treatment at different times of incubation (a) 1 week
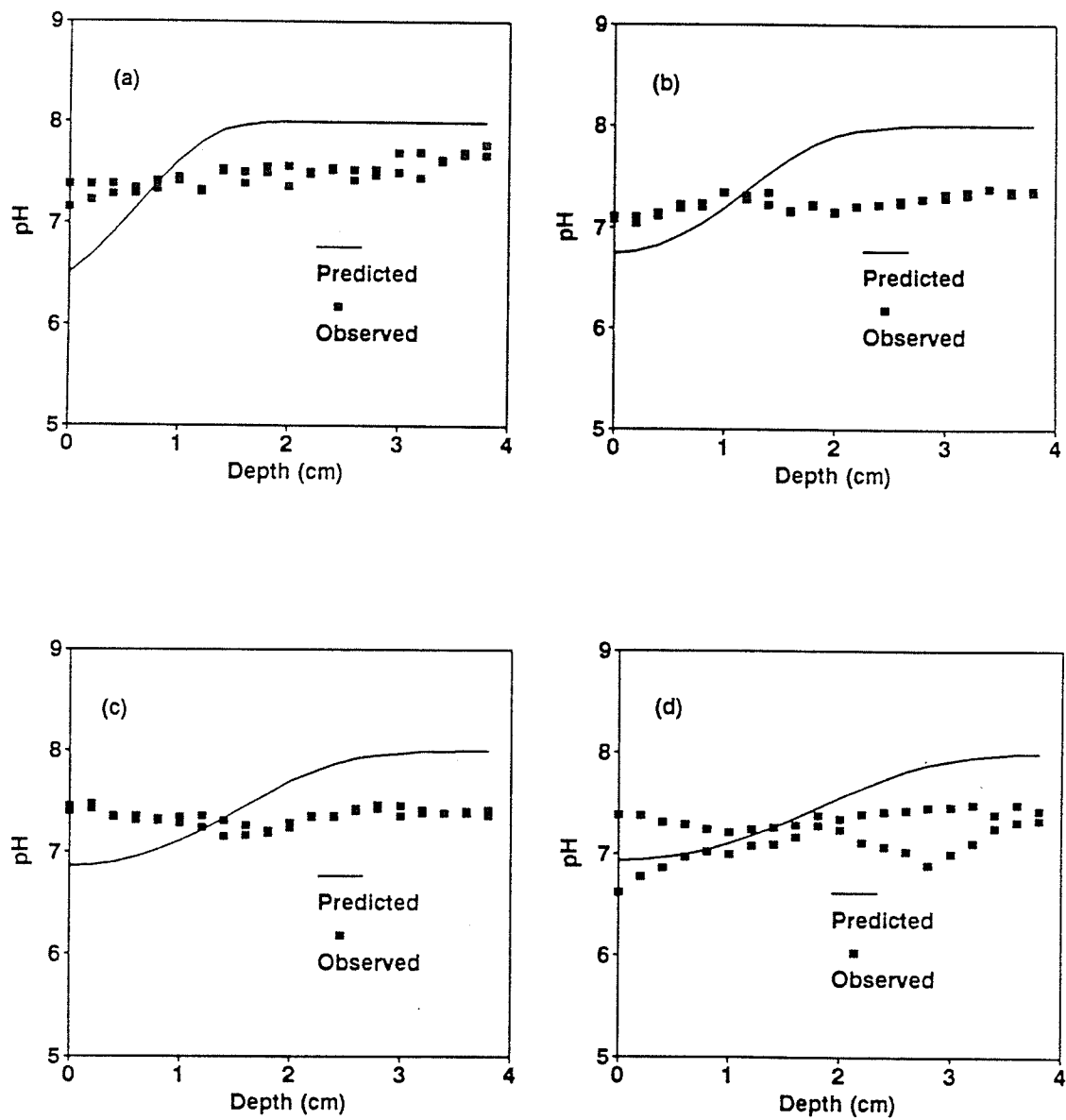(b) 2 weeks (c) 3 weeks (d) 4 weeks.

Fig. 30. Predicted and observed pH distribution in the MCP + $(NH_4)_2SO_4$ treatment at different times of incubation (a) 1 week (b) 2 weeks (c) 3 weeks (d) 4 weeks.
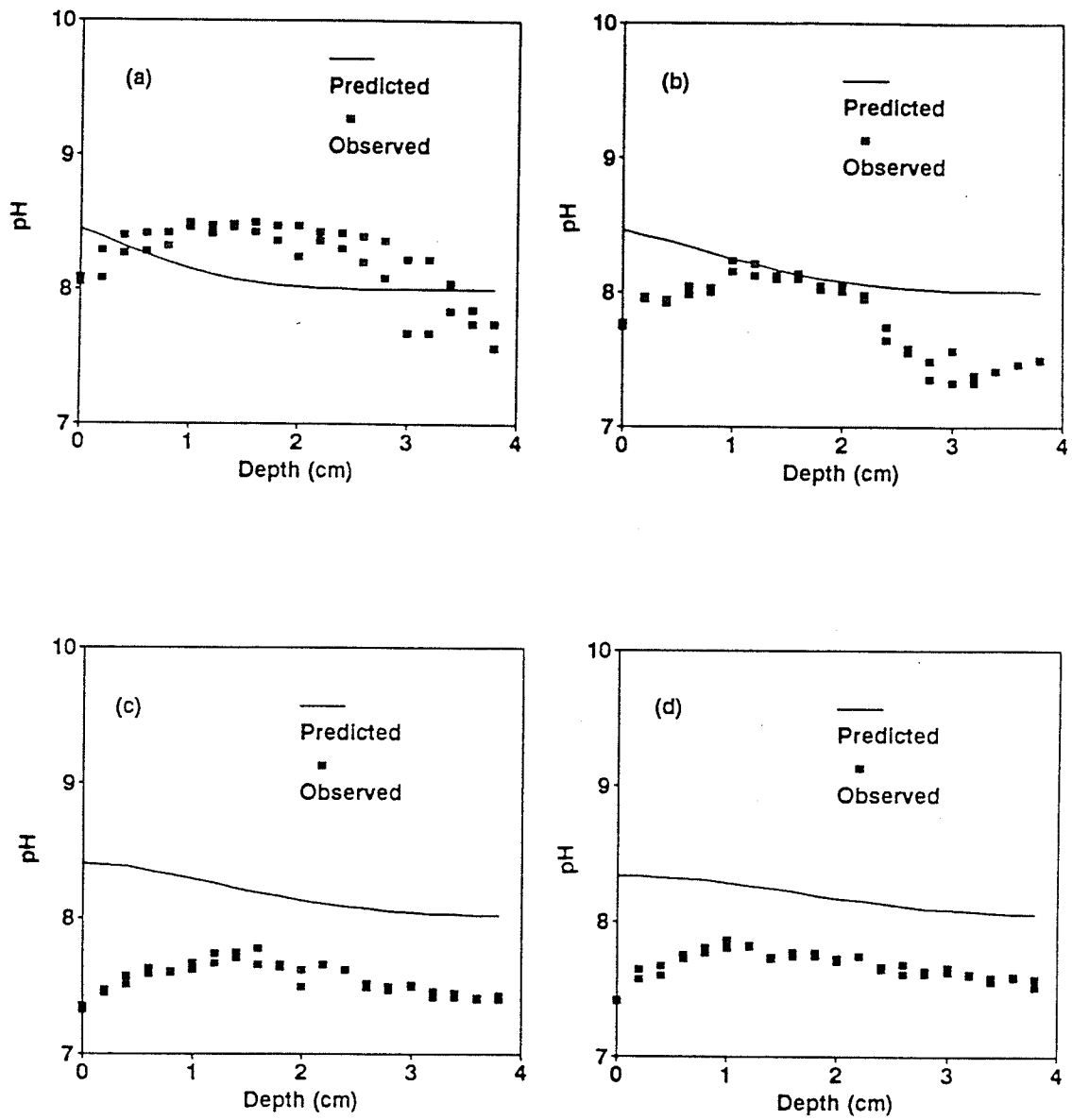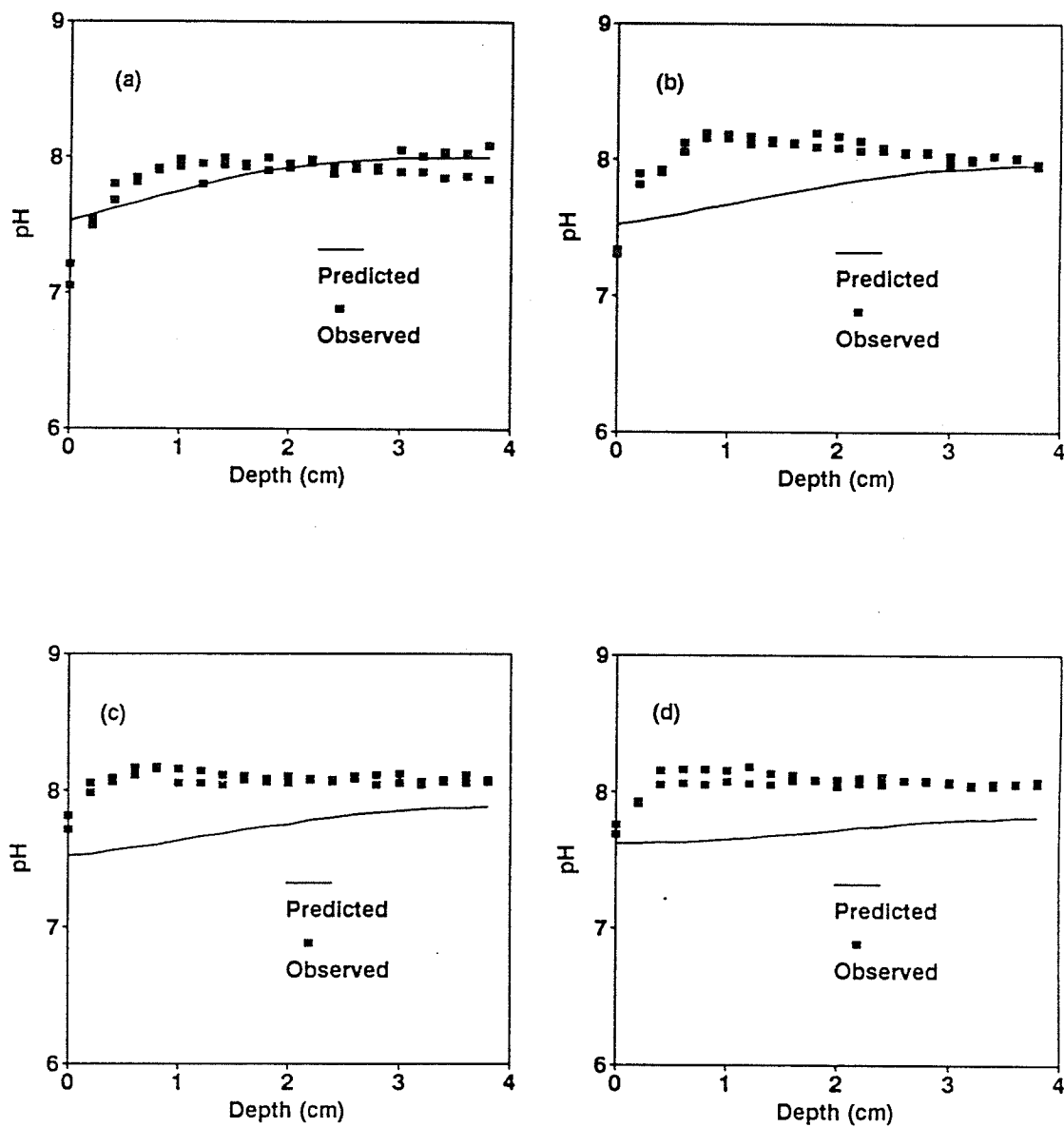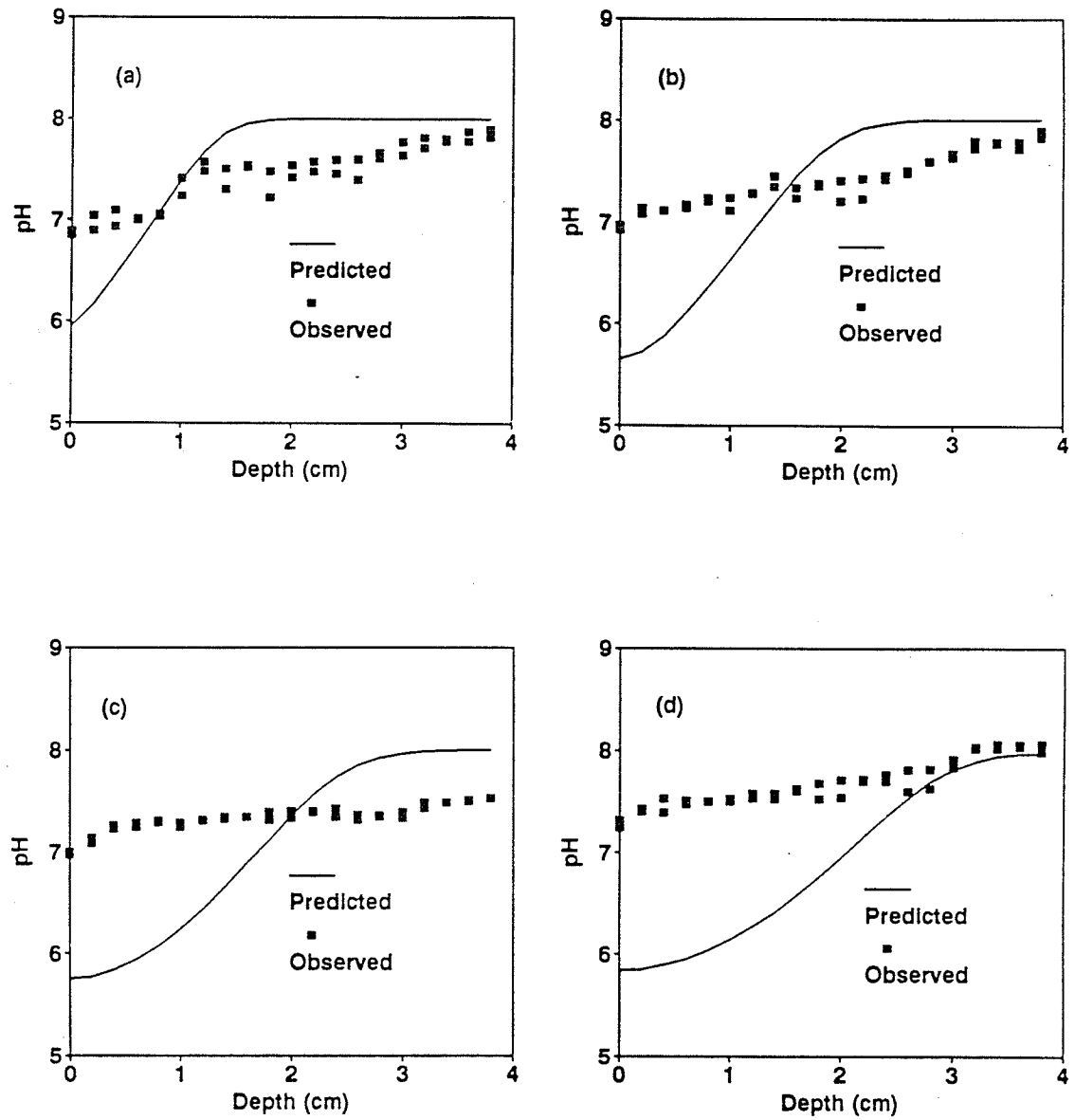
Fig. 31. Predicted and observed pH distribution in the MCP + urea
treatment at different times of incubation (a) 1 week
(b) 2 weeks (c) 3 weeks (d) 4 weeks.

Fig. 32. Predicted and observed pH distribution in the MCP + K_2SO_4
treatment at different times of incubation (a) 1 week
(b) 2 weeks (c) 3 weeks (d) 4 weeks.

Fig. 33. Predicted and observed pH distribution in the MCP + MgSO$_4$
treatment at different times of incubation (a) 1 week
(b) 2 weeks (c) 3 weeks (d) 4 weeks.

The Ca^{2+} concentration distributions predicted by the model after 1 week (Fig. 35) show a high Ca^{2+} concentration at the surface in all the treatments (Fig. 35a), which decreased with depth to about 5 mm. In treatments where a salt was added, a second peak of Ca^{2+} was predicted by the model, approximately at 10-15 mm depth. This peak, which is due to the displacement of exchangeable Ca^{2+} was more apparent in the MCP + urea and MCP + $MgSO_4$ treatments, MCP + urea treatment having a predicted peak Ca^{2+} concentration of about twice as much as that of MCP + $MgSO_4$ treatment. At 2 weeks (Fig. 35b), the surface concentration of Ca^{2+} as well as peak Ca^{2+} concentration in salt treatments decreased as precipitation took place. After 3 and 4 weeks of incubation (Fig. 35c, 35d), solution Ca^{2+} concentrations were much lower and the predicted differences between the treatments were slight.

In the treatments where $(NH_4)_2SO_4$, K_2SO_4 or $MgSO_4$ were added, sulphate would react with Ca^{2+} desorbed from the exchange phase. At any position, the rate of formation was assumed to be second order reaction, i.e. directly proportional to the product of sulphate and Ca^{2+} concentrations. In the case of urea addition, however, sulphate was not added. Instead the hydrolysis of urea give rise to carbonate formation. Consequently the desorbed Ca^{2+} would combine with CO_3^{2-} to form $CaCO_3$. The predicted distribution pattern of $CaCO_3$ and $CaSO_4$ are shown in Fig. 36.

At 1 week of incubation, the predicted concentrations of $CaSO_4$ precipitated were high at the surface in sulphate salt treatments, and decreased with the depth (Fig. 36a). The differences between MCP + $(NH_4)_2SO_4$, MCP + K_2SO_4 and MCP + $MgSO_4$ treatments were slight. In contrast, predicted concentration of $CaCO_3$ precipitated in the MCP + urea treatment
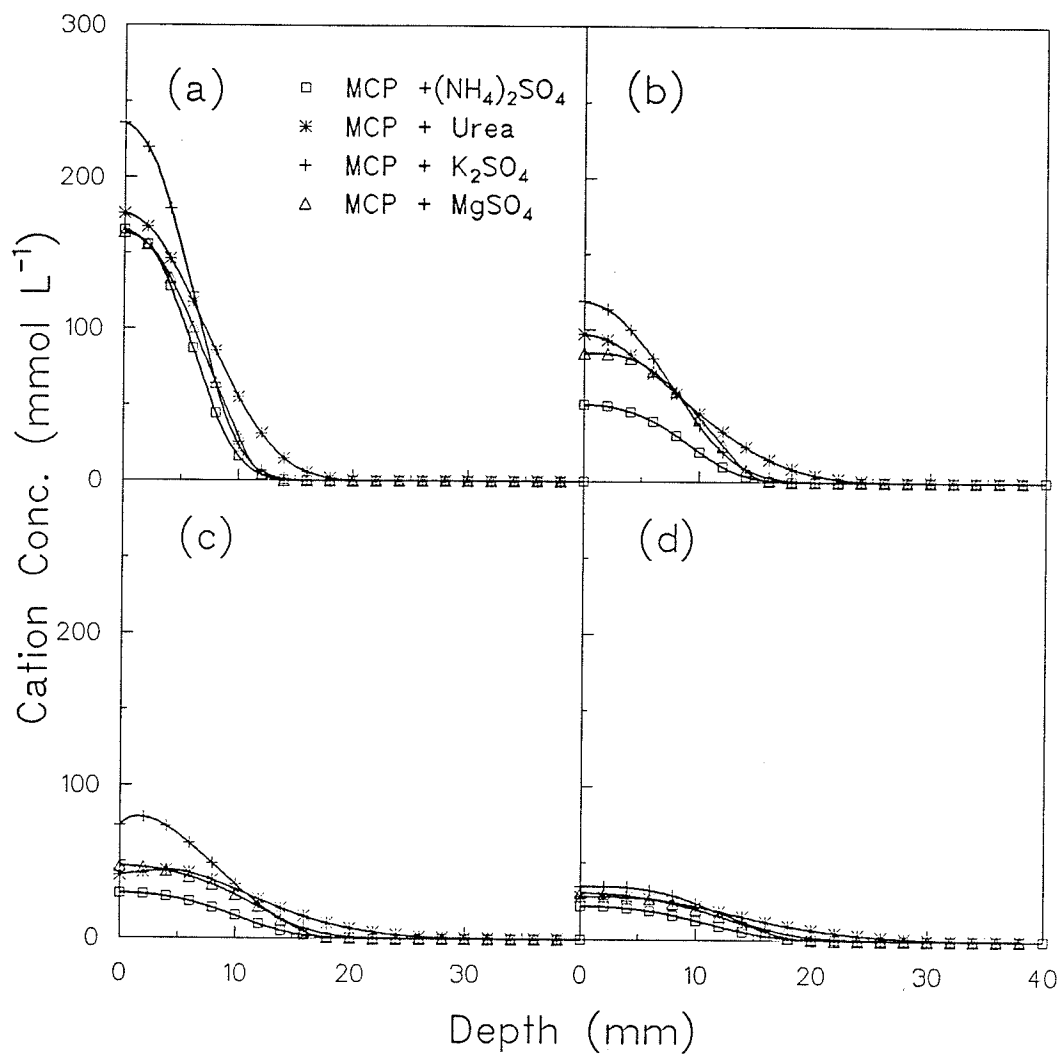
Fig. 34. Predicted distribution of cation (NH_4^+, K^+ or Mg^{2+}) concentration in solution at various times of incubation (a) 1 week (b) 2 weeks (c) 3 weeks (d) 4 weeks.
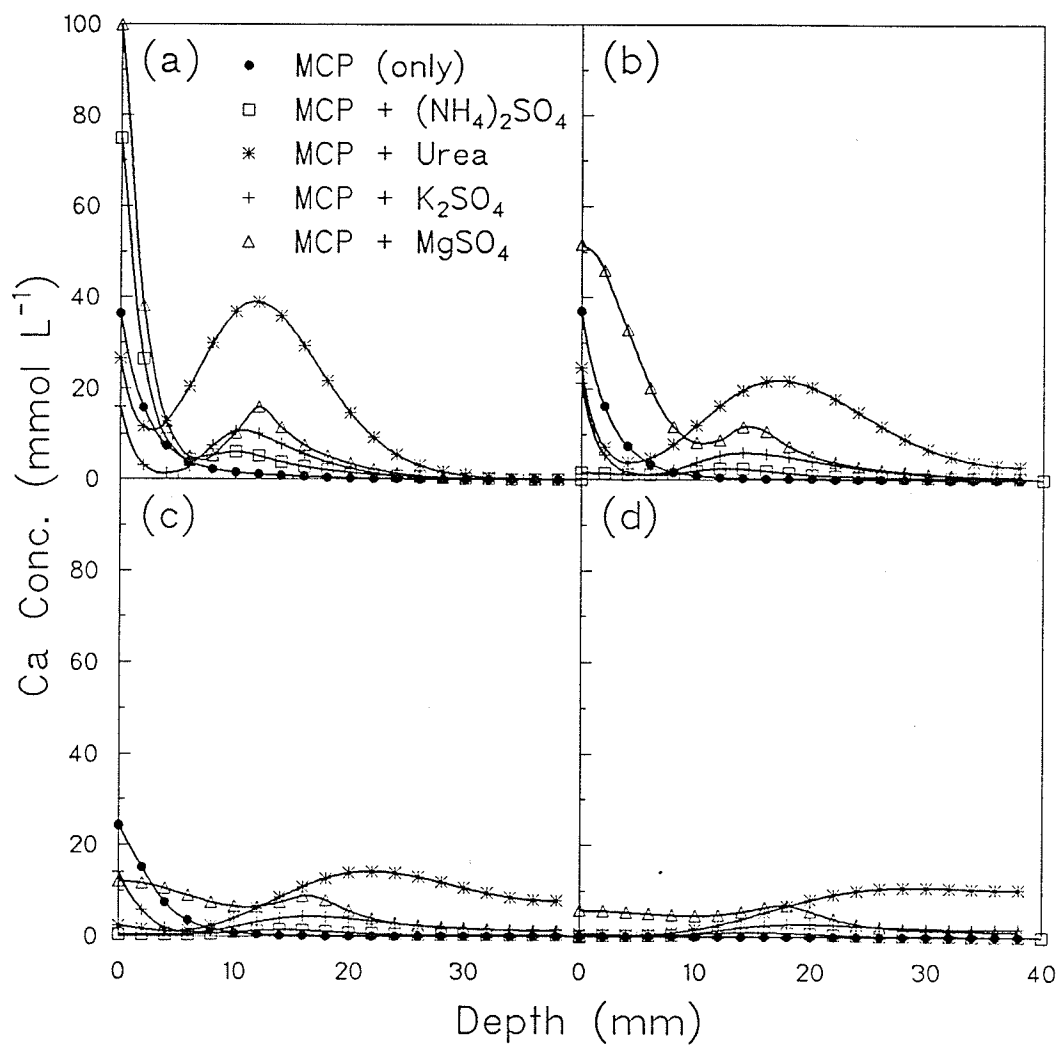
Fig. 35. Predicted distribution of Ca^{2+} concentration in solution at various times of incubation (a) 1 week (b) 2 weeks (c) 3 weeks (d) 4 weeks.
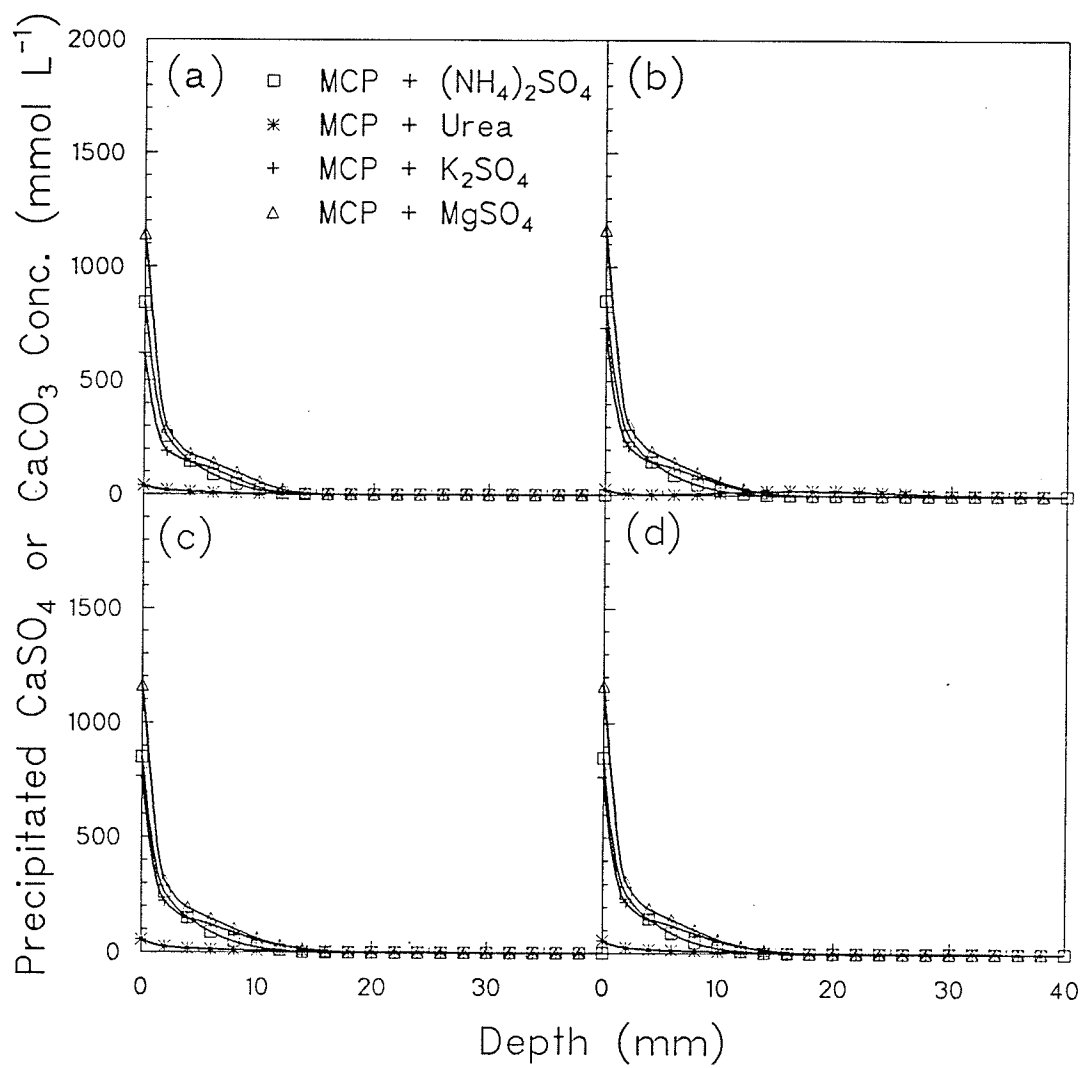
Fig. 36. Predicted distribution of precipitated $CaSO_4$ or $CaCO_3$ concentration at various times of incubation (a) 1 week (b) 2 weeks (c) 3 weeks (d) 4 weeks.

was much less. An increase in incubation time did not change much the concentration distribution of precipitated $CaSO_4$ and $CaCO_3$.

Lower amounts of $CaCO_3$ precipitation in the MCP + urea treatment could be due to the sensitivity of $CaCO_3$ precipitation reaction to pH. Precipitation of $CaCO_3$ only occur under very high pH conditions, where CO_3^{2-} dominates over HCO_3^-. When both phosphates and carbonates are present in high concentrations, the competition between the two anion species for precipitation with Ca occurs only if the pH is above 9.0 (Cho, 1990). At the pH conditions observed in this experiment, the pH was high, so as to favour precipitation of $CaHPO_4$, but not high enough to favour precipitation of $CaCO_3$. Thus, the low amounts of $CaCO_3$ precipitation in the urea treatment maintained a higher Ca^{2+} concentration in the solution, leading to high amounts of $CaHPO_4$ precipitation, thus, reducing the P concentration in solution. On the other hand, when sulphate salts were added, the solution Ca^{2+} concentration is reduced due to precipitation of $CaSO_4$, which results in lower rates of $CaHPO_4$ precipitation. Therefore, the main difference between sulphate salts and urea in affecting P diffusion in this soil was that SO_4^{2-}, in sulphate salts competed with phosphate for precipitation, whereas CO_3^{2-} in urea treatment did not compete, as the pH was not very high.

4.SUMMARY AND CONCLUSIONS

The effect of mixing various salts with MCP on the solubility, diffusion, retention and plant uptake of fertilizer P was investigated using 4 different salts, namely, $(NH_4)_2SO_4$, urea, K_2SO_4 and $MgSO_4$.

A growth chamber experiment conducted with four chernozemic soils using labelled MCP revealed that although the total P uptake by buckwheat plants was not significantly affected, the proportion of P taken up from the fertilizer source was significantly increased by most salt treatments. Whether the enhancement of fertilizer P uptake is mainly due to a chemical effect or a physiological effect is not clear. The ammonium salts appeared to be more effective than the non-ammonium salts in increasing fertilizer P availability to plants, urea having the greatest effect in most soils.

Laboratory incubation experiments conducted using soil columns to investigate the effect of the same salts on P diffusion, revealed that addition of $(NH_4)_2SO_4$ and $MgSO_4$ increased the extent of P diffusion in both soils tested. The addition of K_2SO_4 increased the extent of P diffusion in one soil, but not in the other, whereas, addition of urea had little or no effect on P diffusion in both soils. However, urea addition did increase the concentration of P close to the application site. Therefore these results suggest that fertilizer P uptake by buckwheat plants was more influenced by the P concentration near the band rather than the extent of P movement.

The increase in P diffusion associated with the addition of sulphate salts, is possibly due to the precipitation of $CaSO_4$, which reduces the Ca^{2+} concentration in solution, and thereby reduces the rate of

precipitation of $CaHPO_4$, resulting in a higher P concentration in soil solution. In the calcareous Almasippi soil, the addition of K_2SO_4 with MCP did not increase P diffusion, possibly because K_2SO_4 is less soluble than $(NH_4)_2SO_4$ and $MgSO_4$, and therefore would yield a lower SO_4^{2-} concentration in solution. It was also observed that addition of $(NH_4)_2SO_4$ and $MgSO_4$ decreased the pH of this soil, but K_2SO_4 did not have such an effect.

The extent of P diffusion was not affected by the addition of urea, but higher P concentrations close to the site of application indicate a higher retardation of P movement than in the control treatment. This is possibly due to the increase in pH as a result of urea hydrolysis, which favours precipitation of $CaHPO_4$.

Elution of P was found to be influenced by the addition of salts. When P is being eluted, the main mechanism of P movement is not diffusion, but mass flow, and the conditions are quite different to that of the diffusion experiments. Continuous water flow through the soil column during elution removes the displaced ions out of the soil column, thereby minimizing any reactions involving displaced cations and anions. In addition, all the salts and MCP as well as the precipitates formed during elution, would be more easily dissolved as there is a continuous flow of water. Differences in effect of salts in the diffusion and elution experiments were likely due to these two reasons. Total amount of P eluted was substantially increased by the addition of $(NH_4)_2SO_4$ and K_2SO_4, and these treatments also had much higher peak P concentrations in eluate samples. The addition of $MgSO_4$ slightly increased the total amount of P eluted, but had little or no effect on the peak P concentration.

The addition of urea, on the other hand, did not seem to affect the P elution in both soils.

The elution of surface-applied Ca^{2+} was also increased by the addition of $(NH_4)_2SO_4$, K_2SO_4 and to some extent by $MgSO_4$. Again, urea had little or no effect on the elution of Ca^{2+}. The peak Ca^{2+} concentration in all the treatments coincided with the peak P concentration, indicating that P retention is associated with Ca^{2+} retention.

In both column experiments and the elution experiment, the addition of urea did not increase the P movement, whether by diffusion or mass flow. Thus, more P remained at the site of application than in the sulphate salt treatments. It is possible that in the urea treatment, the initial high pH that favoured the precipitation reactions of phosphate which reduced the movement of P away from the rhizosphere zone, and the subsequent decrease in pH during nitrification which made the P more available to the plants could have increased the fertilizer P uptake, as observed in the growth chamber experiment.

To describe the effects of salts on P diffusion, a mathematical model developed by Cho (1990) was used. The model predictions were made to fit the observed P distribution, by changing the various parameters used in the model. In most of the treatments a close fit in terms of total P concentrations were obtained. According to the model prediction, solubility of MCP was increased by $(NH_4)_2SO_4$, $MgSO_4$ and to some extent by urea. The main difference between sulphate salts and urea in affecting P diffusion was found to be the competition between anions for precipitation with Ca^{2+}, where SO_4^{2-} competes with P under any pH condition, whereas CO_3^{2-} only competes with P under high pH. Under the pH

conditions observed in this soil, CO_3^{2-} did not compete with P for precipitation, which increased $CaHPO_4$ precipitation, thus retarding the diffusion of P.

This study, therefore, emphasizes the importance of other cations and anions in soil, in affecting P transport and transformations, by directly or indirectly interacting with P.

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6.APPENDIX

APPENDIX A

Preparation of labelled MCP $(Ca(H_2PO_4)_2 \cdot 2H_2O)$

Labelled MCP was used as the P fertilizer in most of the experiments. To obtain labelled MCP, solid MCP was mixed with distilled water at the ratio of 1:2 and to this mixture carrier-free ^{32}P in the form of H_3PO_4 was added to get a specific activity of approximately 1.5×10^{-2} MBq mg^{-1} P . The mixture was then mixed thoroughly, dried and ground.

APPENDIX B

Growth chamber experiment

Soil	Treatment	Dry wt. (g)	N uptk mg/pot	P uptk mg/pot	K uptk mg/pot	PDFF %	P utilization %
Almasippi							
	MCP (only)	12.95	211.30	22.030	341.34	39.214	13.76
		11.64	205.63	18.976	297.80	40.388	12.20
		12.66	236.04	24.816	356.03	35.715	14.11
	MCP + $(NH_4)_2SO_4$	11.98	242.93	20.368	346.01	57.371	18.61
		13.50	283.59	20.936	363.20	61.269	20.43
		17.02	371.17	25.709	415.26	57.068	23.36
	MCP + urea	15.31	361.95	21.895	472.34	53.499	18.65
		14.02	278.58	22.161	358.79	51.339	18.12
		10.56	214.30	26.840	336.88	49.665	21.23
	MCP + K_2SO_4	10.64	232.00	24.583	254.34	50.047	19.59
		15.15	323.12	24.703	370.09	49.184	19.35
		15.36	350.64	24.118	406.17	47.697	18.32
	MCP + $MgSO_4$	14.20	289.60	23.156	331.57	45.362	16.73
		12.10	223.37	20.585	279.35	43.250	14.18
		13.30	288.98	22.093	354.02	44.378	15.61
Stockton							
	MCP (only)	14.77	336.98	70.639	484.72	2.044	2.30
		10.46	247.39	54.627	301.92	1.937	1.69
		12.64	315.32	75.376	435.44	2.081	2.50
	MCP + $(NH_4)_2SO_4$	13.67	341.47	71.236	490.31	4.668	5.30
		13.68	335.47	68.161	374.48	7.585	8.23
		12.45	297.30	53.183	322.34	8.051	6.82
	MCP + Urea	9.31	204.20	43.864	256.95	10.948	7.65
		13.89	346.45	58.089	505.71	7.354	6.80
		13.42	317.44	70.766	508.12	6.319	7.12
	MCP + K_2SO_4	14.37	328.11	75.022	569.85	2.774	3.31
		16.68	398.20	88.581	632.92	2.627	3.71
		18.32	350.28	86.485	717.35	2.850	3.92
	MCP + $MgSO_4$	19.60	496.94	106.450	587.73	2.896	4.91
		12.87	282.24	54.183	466.15	3.705	3.20
		12.70	299.68	66.336	451.77	3.757	3.97

(Continued)

Soil	Treatment	Dry wt. (g)	N uptk mg/pot	P uptk mg/pot	K uptk mg/pot	PDFF %	P utilization %
Red River							
	MCP (only)	9.77	173.07	38.905	221.21	5.521	3.42
		11.63	226.74	45.024	236.64	4.867	3.49
		11.70	218.14	37.563	250.89	4.520	2.70
	MCP + $(NH_4)_2SO_4$	12.59	255.04	42.939	282.06	9.577	6.55
		13.35	260.20	51.668	274.63	9.905	8.15
		12.75	277.12	43.991	285.62	9.653	6.76
	MCP + Urea	13.82	275.89	40.913	268.84	12.248	7.18
		13.27	246.96	51.386	278.17	12.033	9.85
		11.69	218.51	36.495	244.94	15.035	8.74
	MCP + K_2SO_4	10.02	186.95	29.686	257.95	13.951	6.59
		12.53	235.33	49.247	308.39	8.033	6.30
		15.31	299.19	43.951	402.91	7.965	5.57
	MCP + $MgSO_4$	10.24	171.91	47.844	228.05	7.413	5.65
		9.53	189.40	41.274	220.95	7.615	5.00
		10.61	197.92	43.959	244.96	6.480	4.54
Firdale							
	MCP (only)	10.47	229.06	50.280	298.12	4.103	3.29
		11.89	288.50	63.141	352.45	1.999	2.01
		10.73	251.80	70.194	335.08	2.560	2.86
	MCP + $(NH_4)_2SO_4$	10.74	256.39	71.750	404.94	3.843	4.39
		11.13	258.43	51.537	380.79	4.155	3.41
		9.99	218.53	64.281	408.18	4.045	4.14
	MCP + Urea	14.61	341.88	88.573	432.78	5.514	7.78
		11.17	258.64	64.603	348.28	6.500	6.69
		11.89	278.24	56.858	340.55	8.244	7.46
	MCP + K_2SO_4	10.96	233.93	75.419	432.01	4.457	5.35
		15.08	338.75	79.347	615.92	4.224	5.34
		13.22	322.00	62.021	574.45	4.276	4.22
	MCP + $MgSO_4$	10.60	233.76	71.378	395.07	3.539	4.02
		12.46	307.64	81.147	454.22	3.129	4.04
		11.71	283.50	79.662	467.08	3.151	4.00

(Concluded)

Appendix C-1
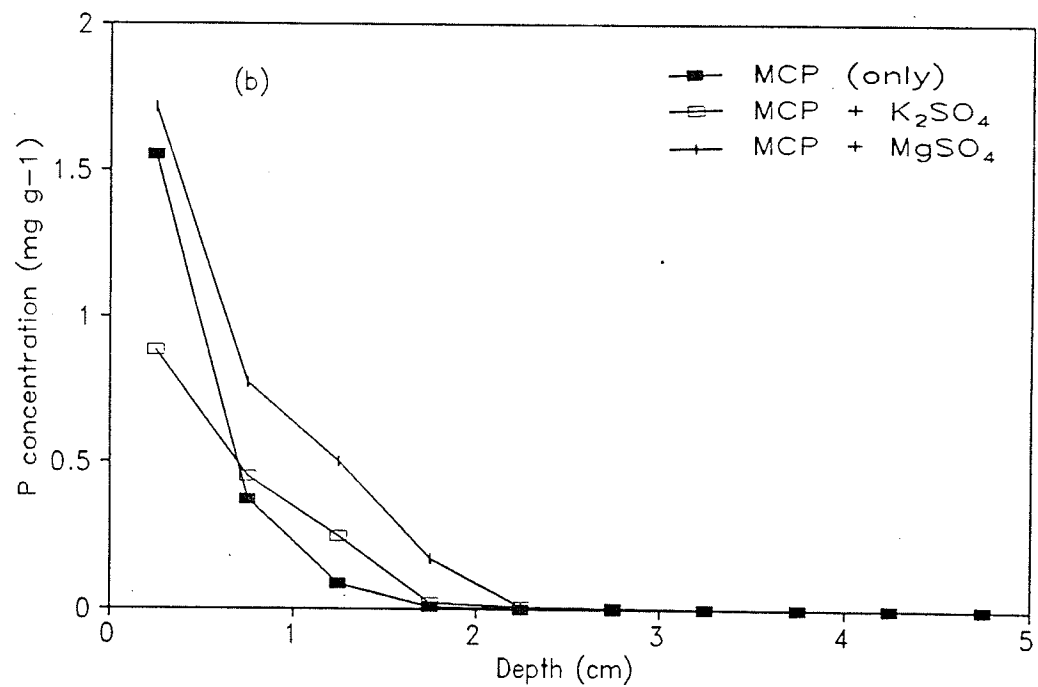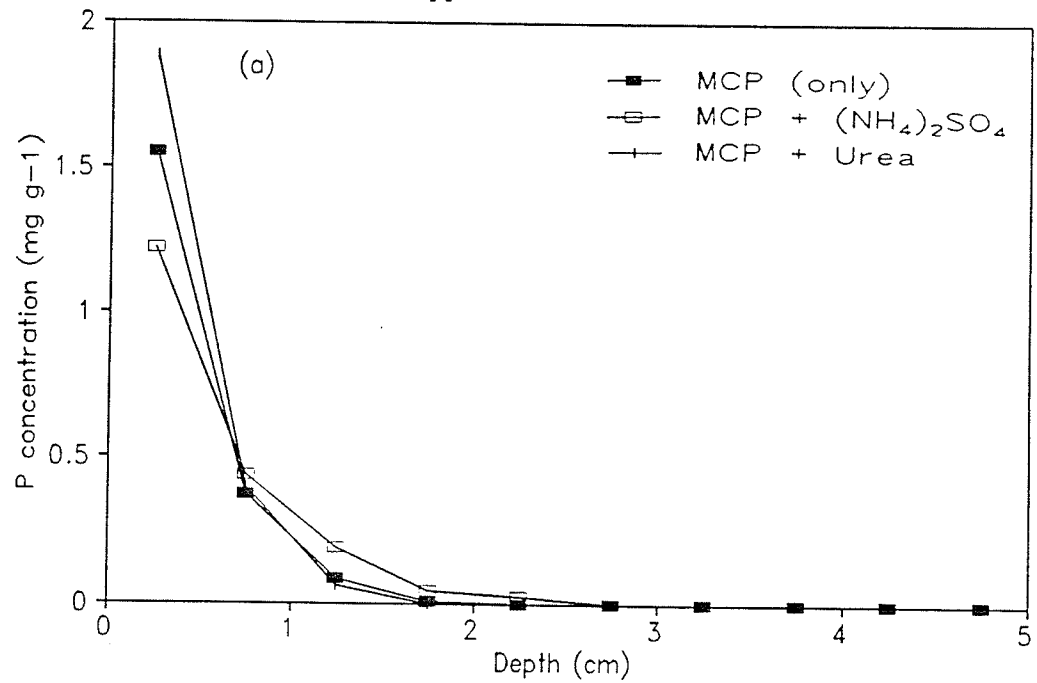
Effect of addition of salts upon total labelled P distribution after 2 weeks of incubation in the Stockton sandy loam (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.
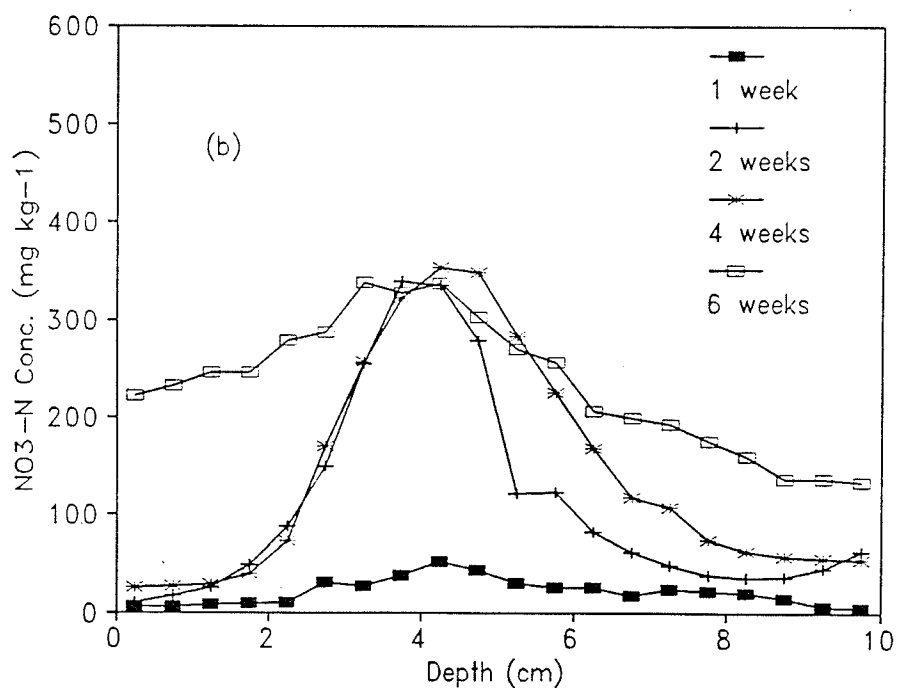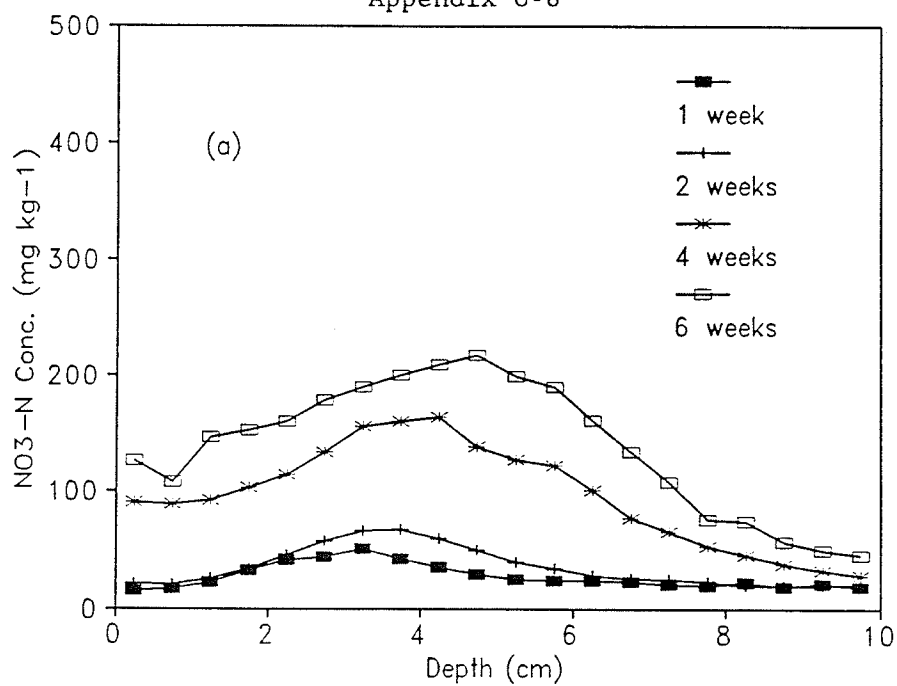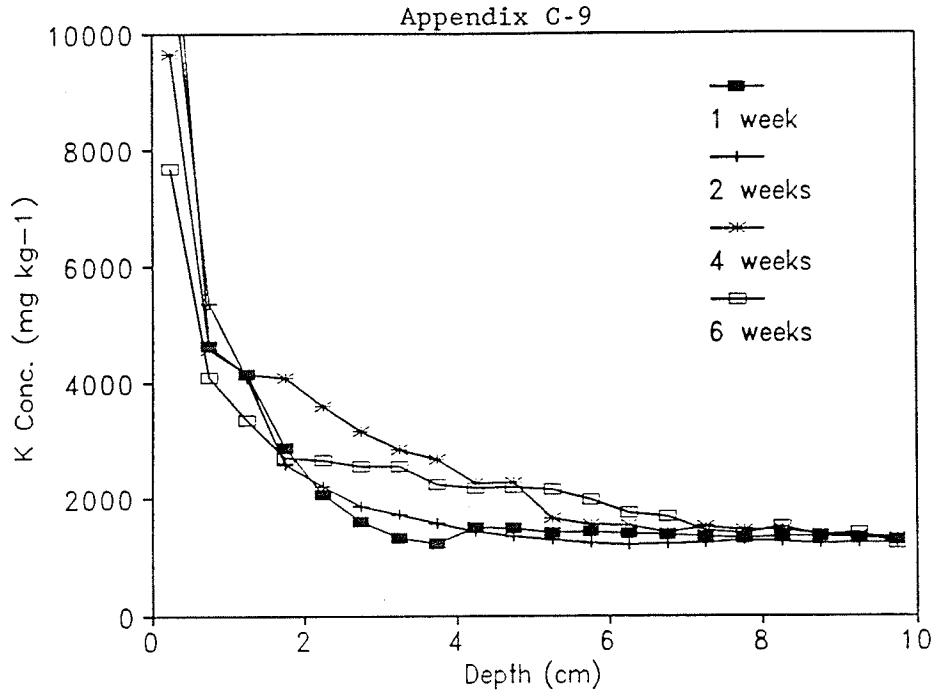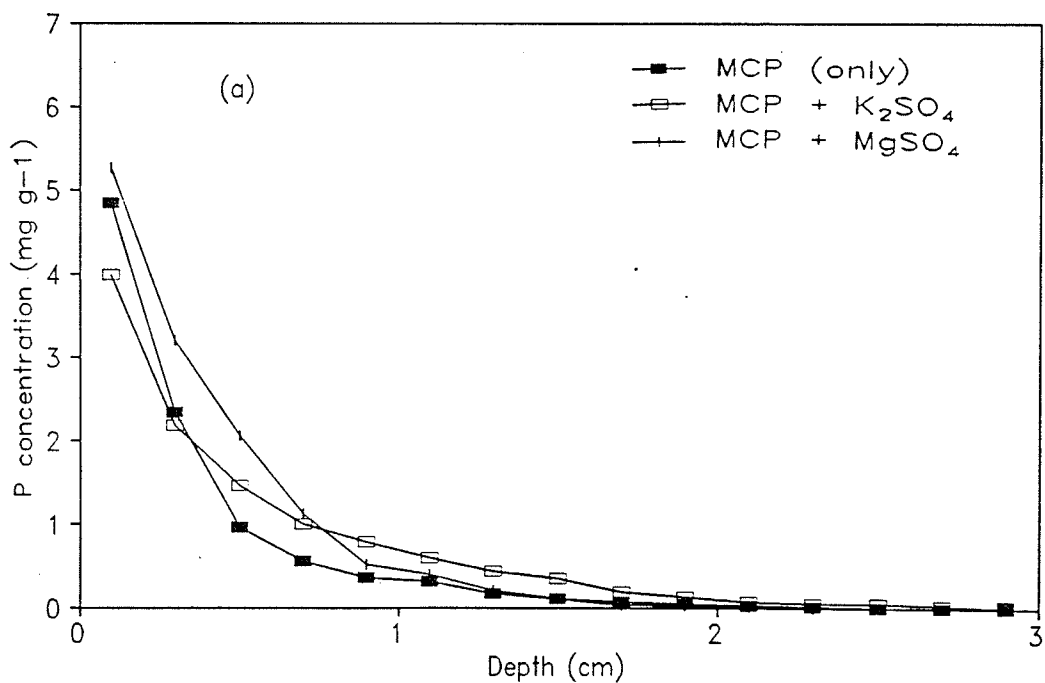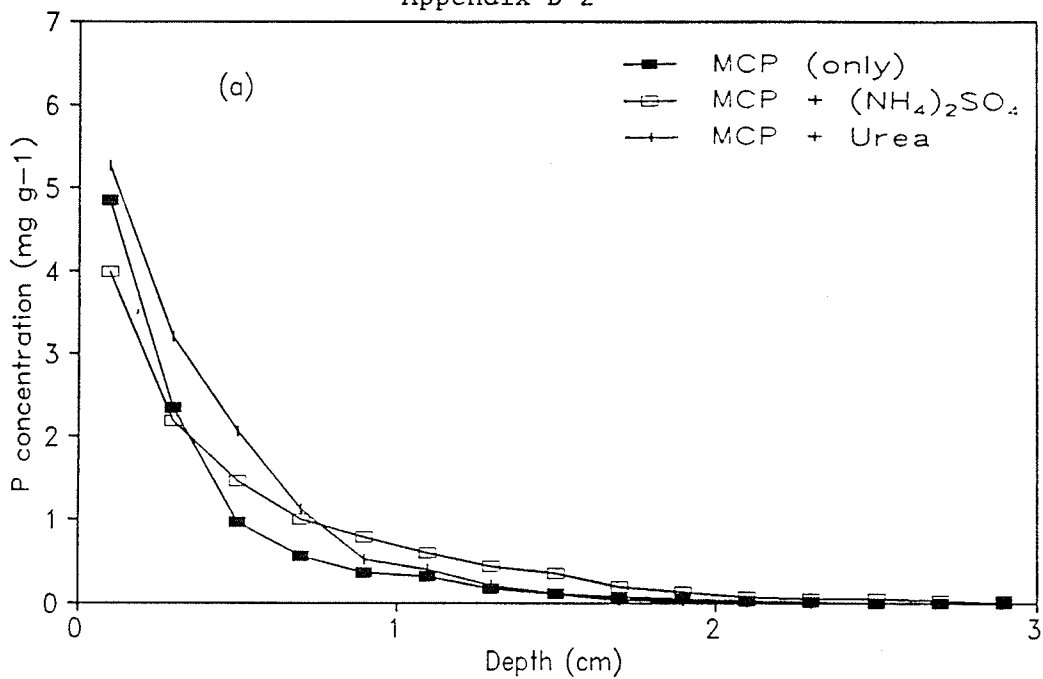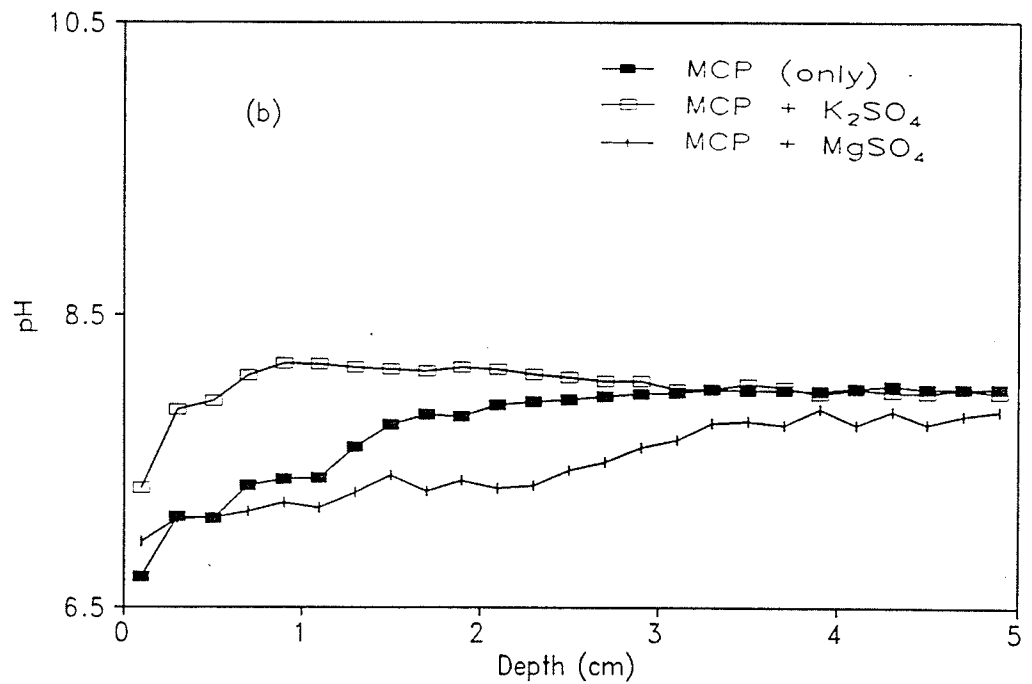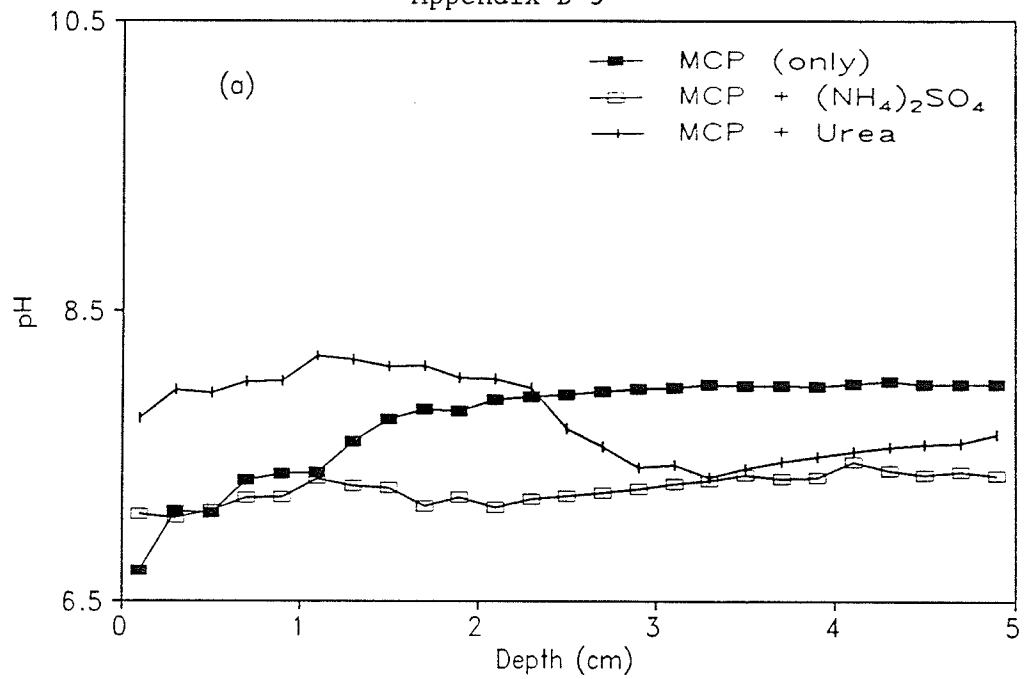
Appendix C-2
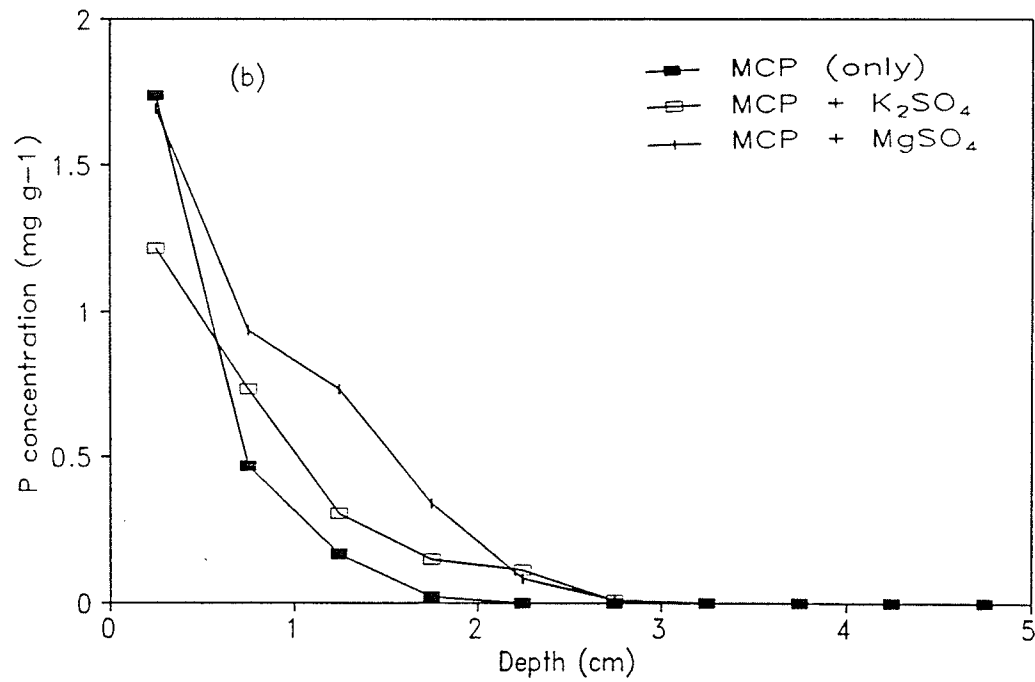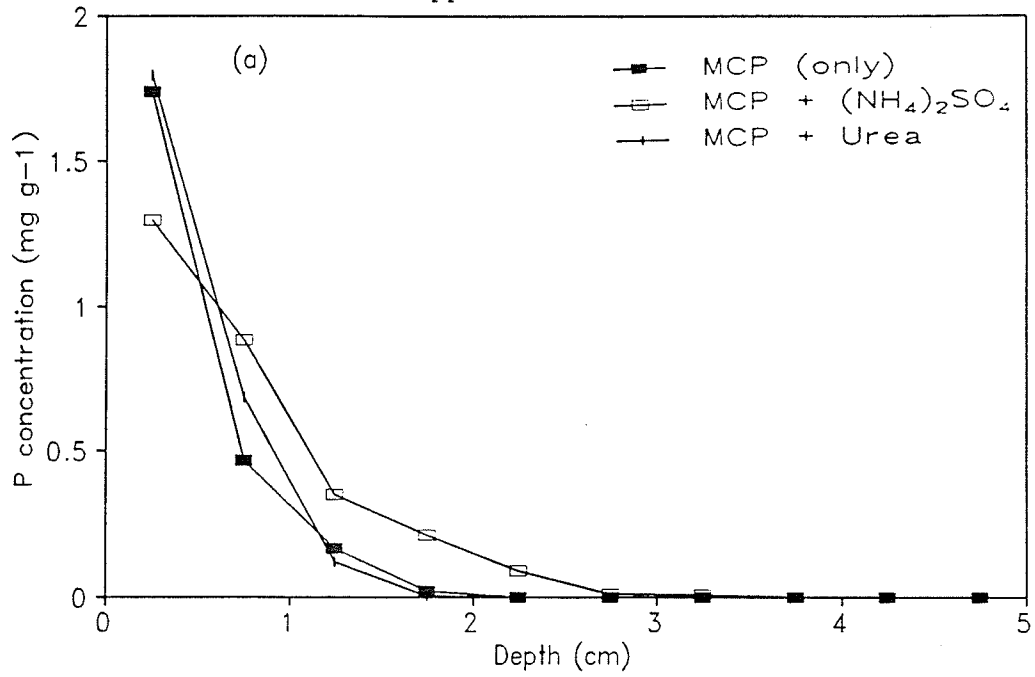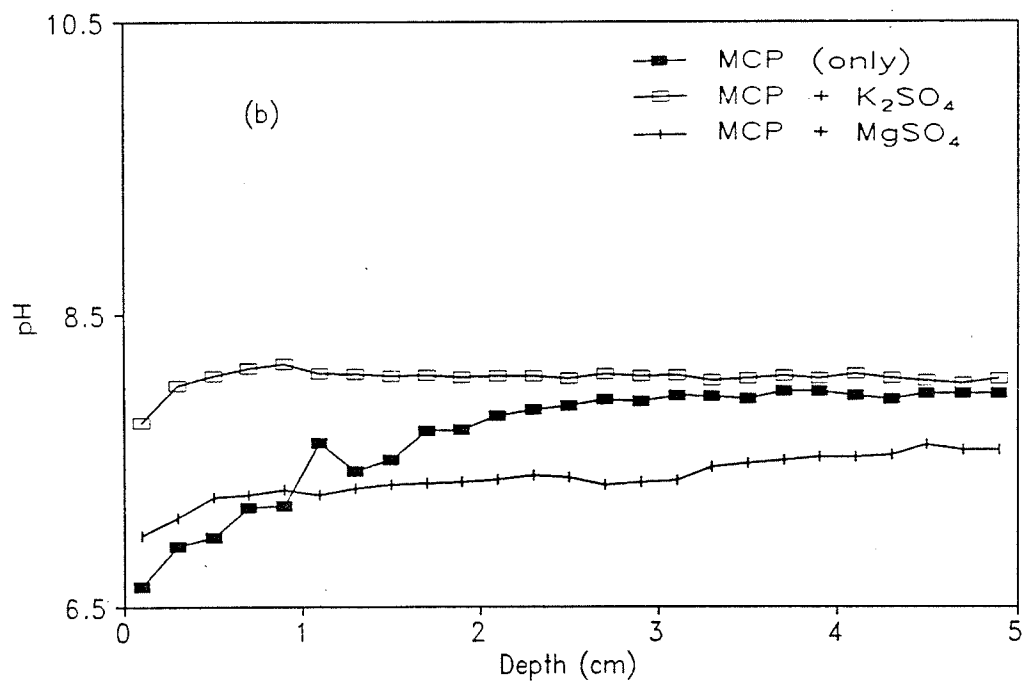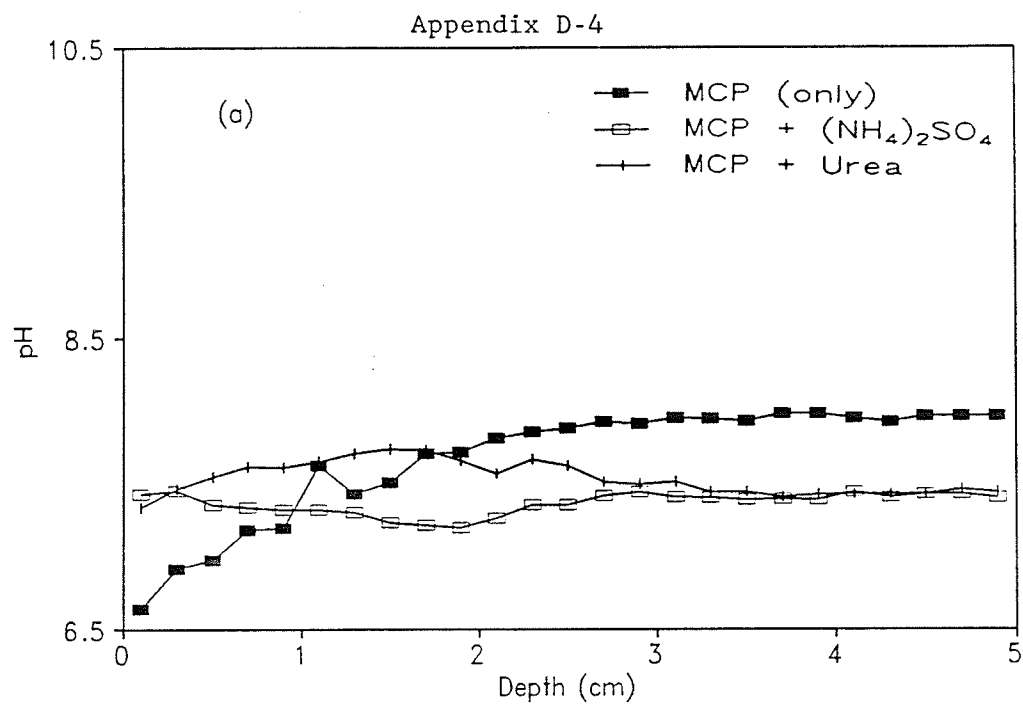

Effect of addition of salts upon total labelled P distribution after 4 weeks of incubation in the Stockton sandy loam (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

Appendix C-3
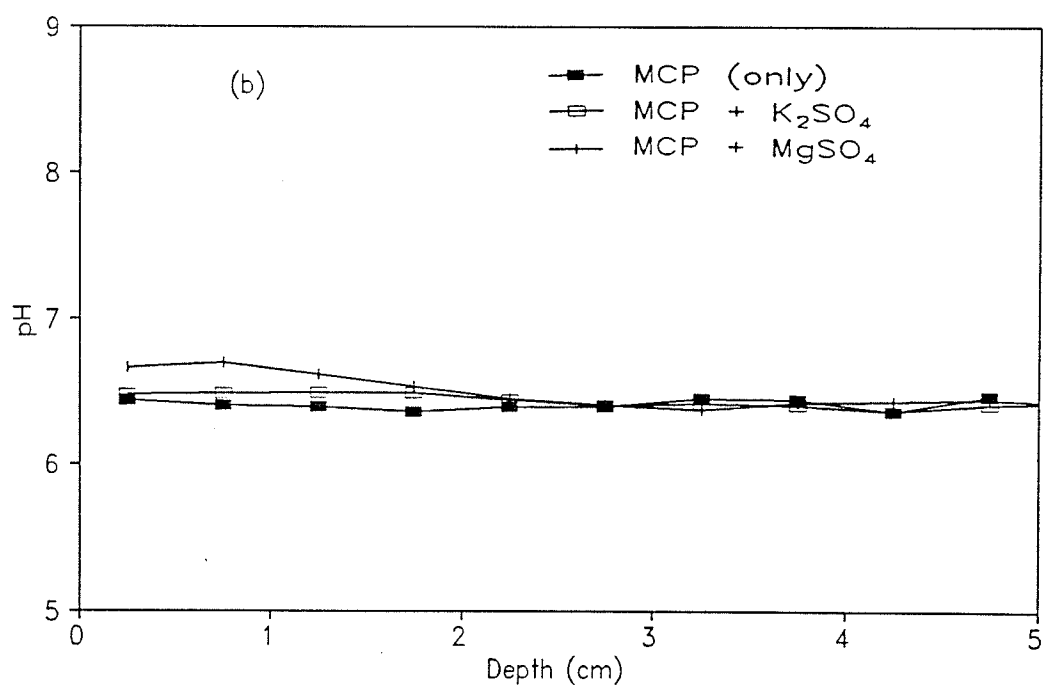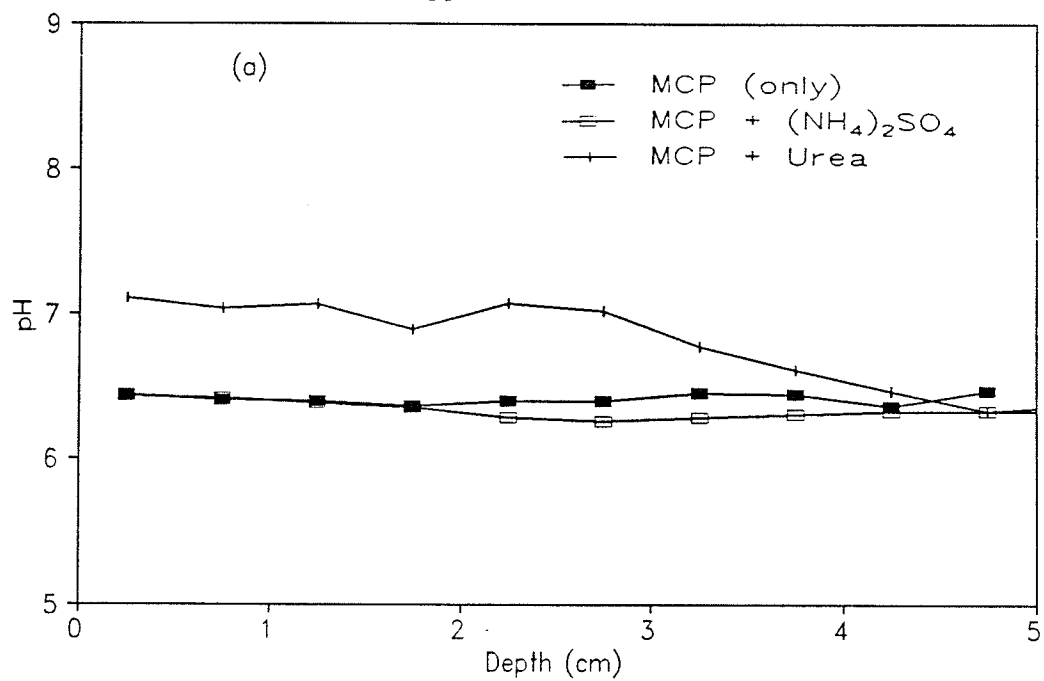
Effect of addition of salts upon change in soil pH at various distance after 2 weeks of incubation in the Stockton sandy loam (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.
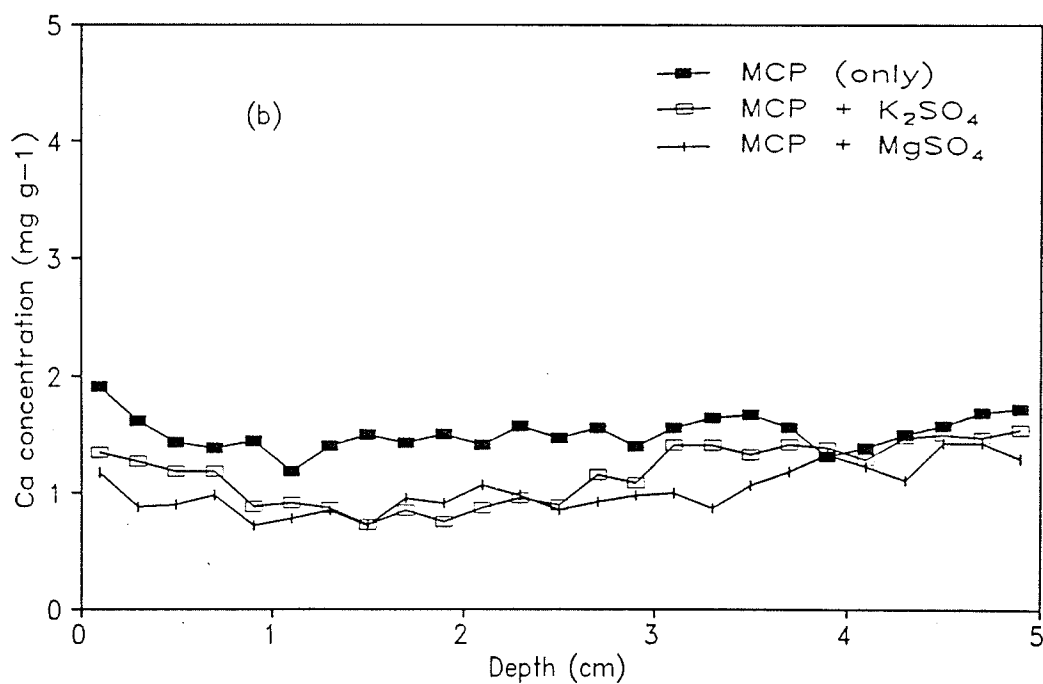
Appendix C-4
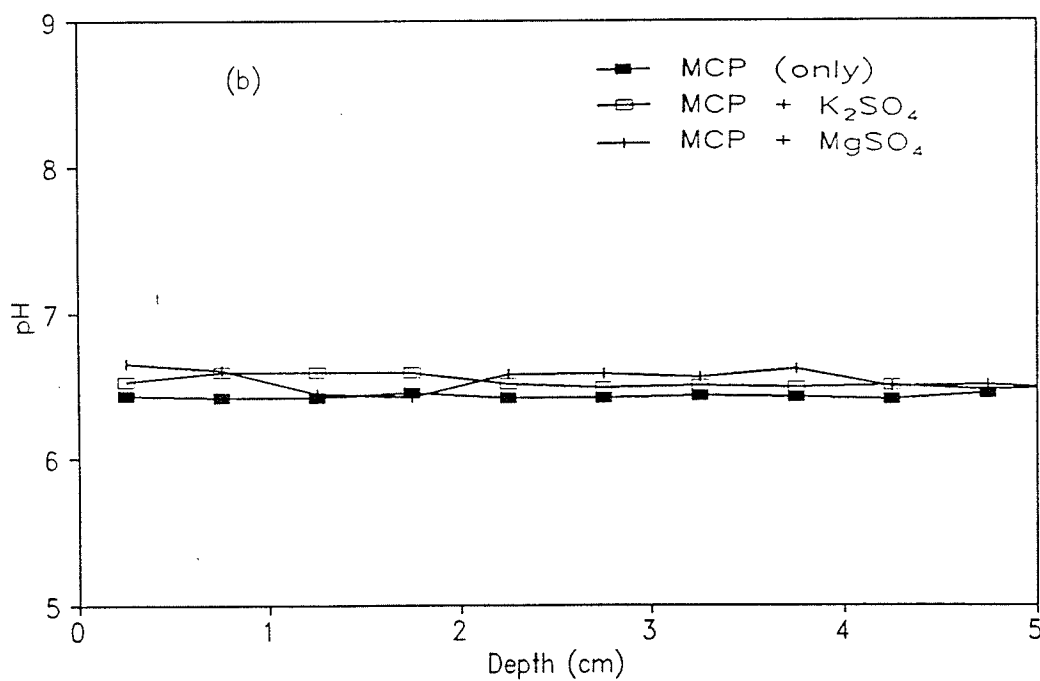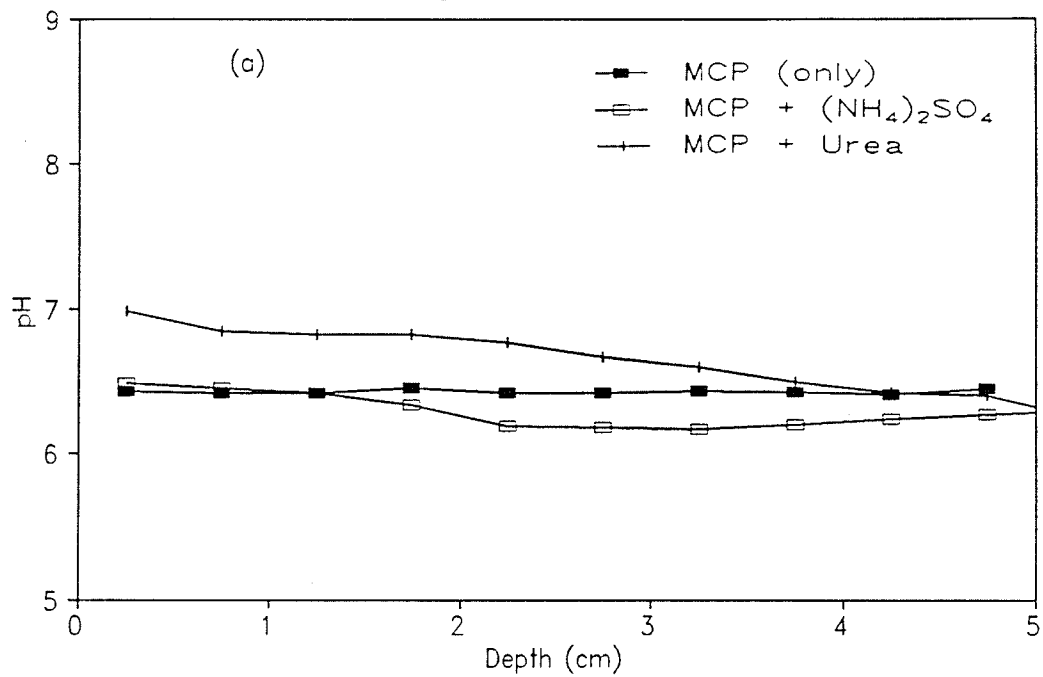
Effect of addition of salts upon change in soil pH at various distance after 4 weeks of incubation in the Stockton sandy loam (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

Appendix C-5
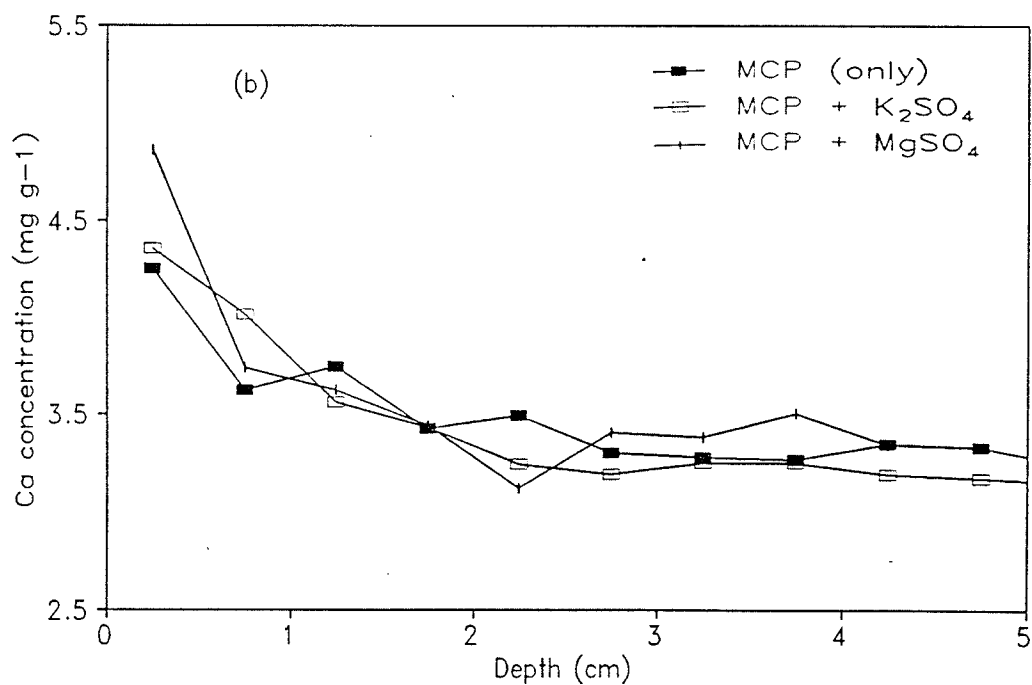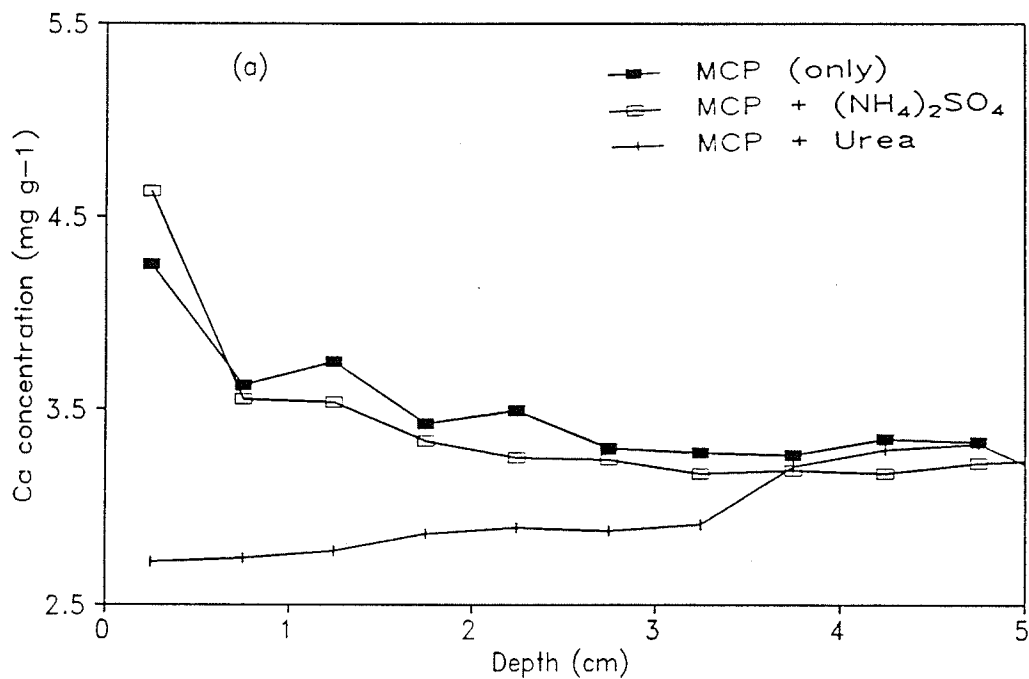
Effect of addition of salts upon distribution of exchangeable Ca^{2+} after 2 weeks of incubation in the Stockton sandy loam (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

Appendix C-6
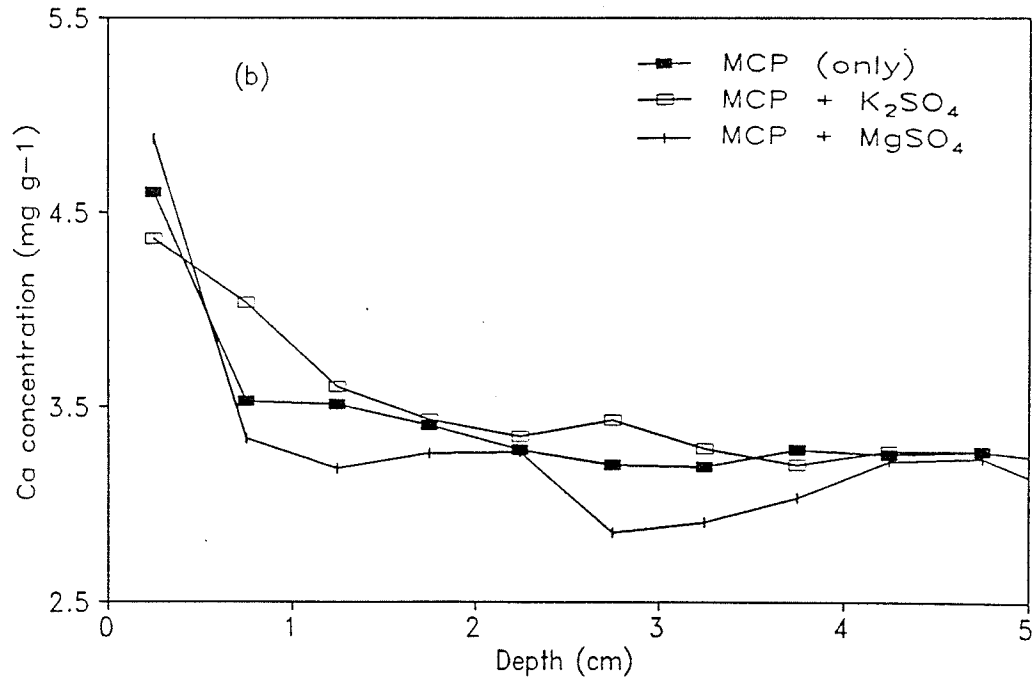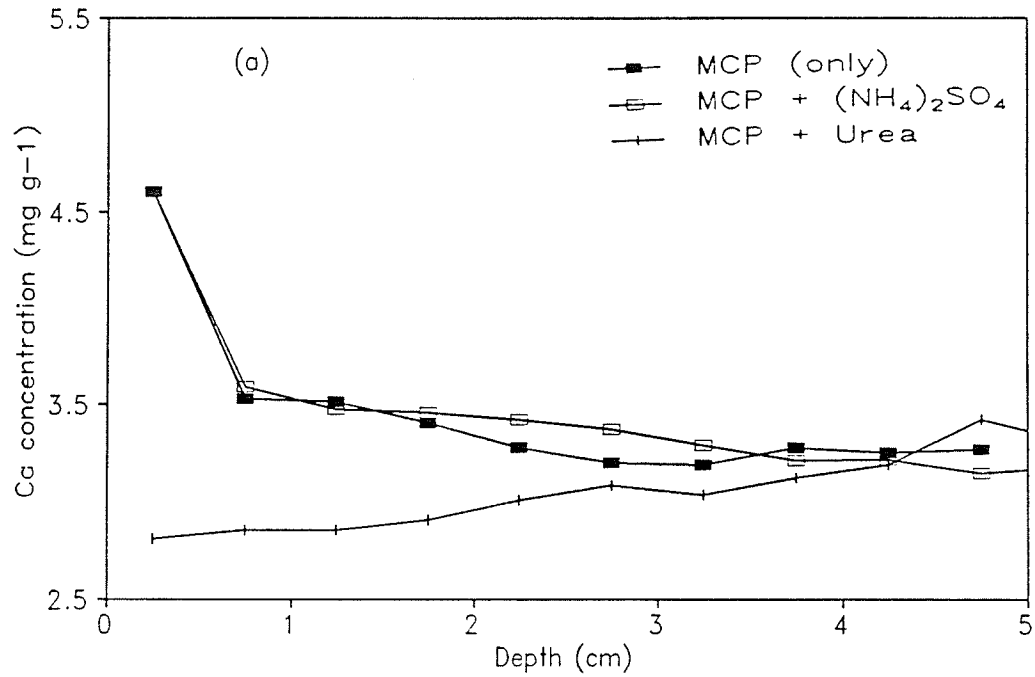
Effect of addition of salts upon distribution of exchangeable Ca^{2+} after 4 weeks of incubation in the Stockton sandy loam (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

Appendix C-7
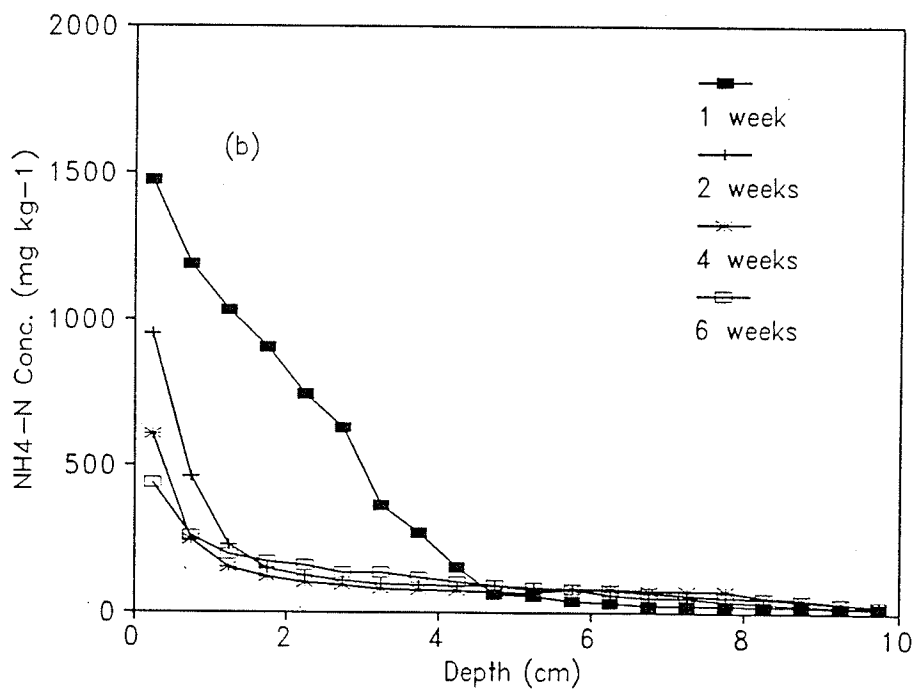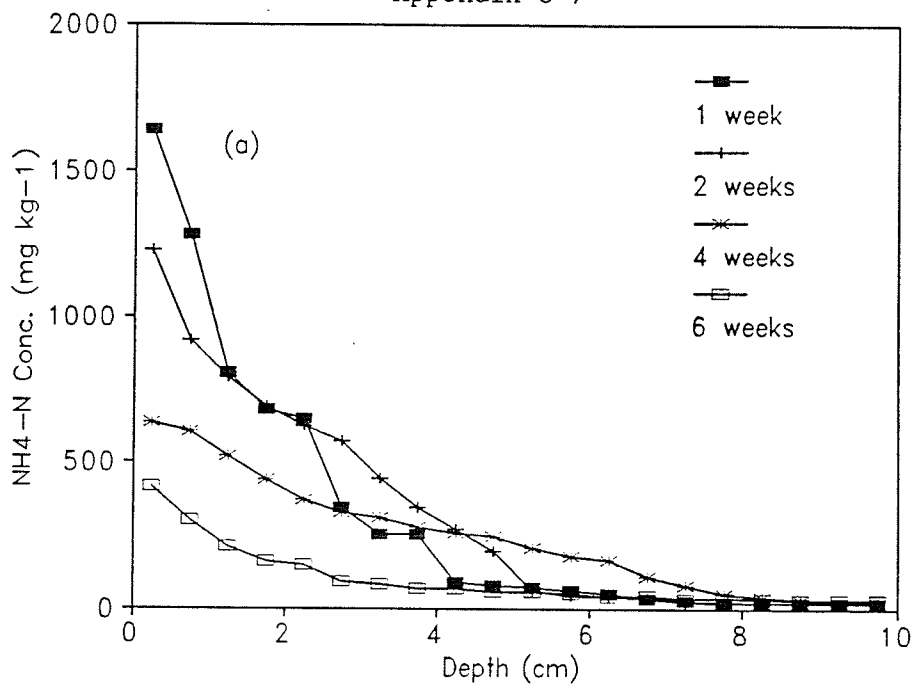
Distribution of extractable NO_3^- + NO_2^- at various times of incubation in the Stockton sandy loam (a) $(NH_4)_2SO_4$ treatment (b) urea treatment.

Appendix C-8

Distribution of extractable NH_4^+ + NH_3 at various times of incubation in the Stockton sandy loam (a) $(NH_4)_2SO_4$ treatment (b) urea treatment.

Appendix C-9

Distribution of extractable K$^+$ at various times of incubation in K$_2$SO$_4$ treatment in the Stockton sandy loam.

Appendix C-10

Distribution of extractable Mg$^+$ at various times of incubation in MgSO$_4$ treatment in the Stockton sandy loam.

Appendix D-1

Effect of addition of salts upon total labelled P distribution after 2 weeks of incubation in the Almasippi loamy sand (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.
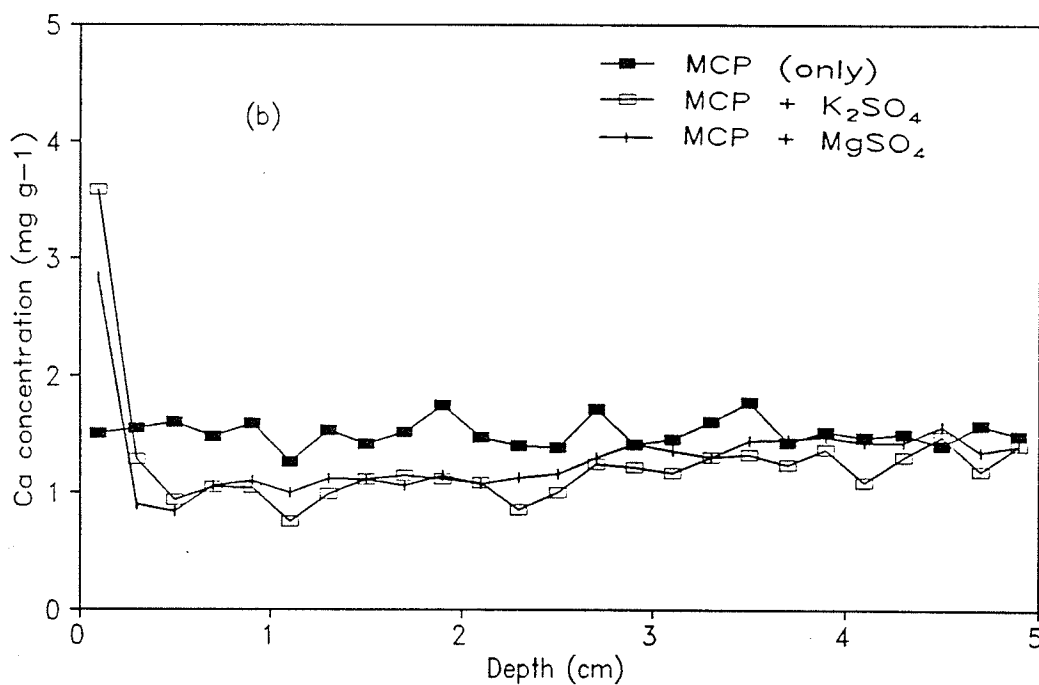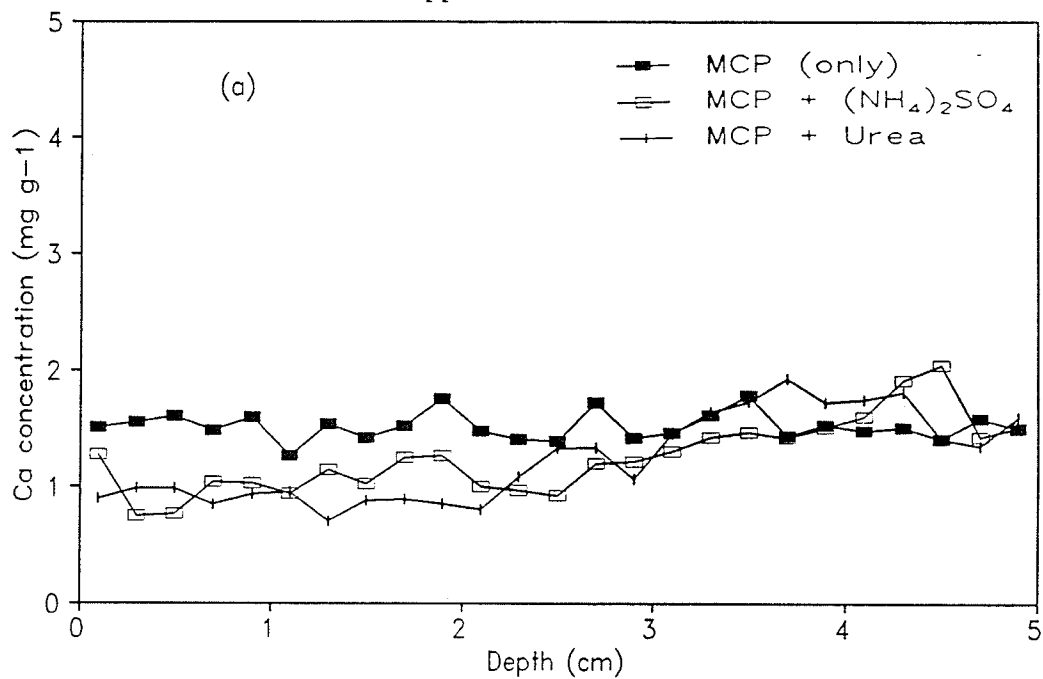
Appendix D-2

Effect of addition of salts upon total labelled P distribution after 3 weeks of incubation in the Almasippi loamy sand (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

Appendix D-3

Effect of addition of salts upon change in soil pH at various distance after 2 weeks of incubation in the Almasippi loamy sand (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

Effect of addition of salts upon change in soil pH at various distance after 3 weeks of incubation in the Almasippi loamy sand (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

Appendix D-5
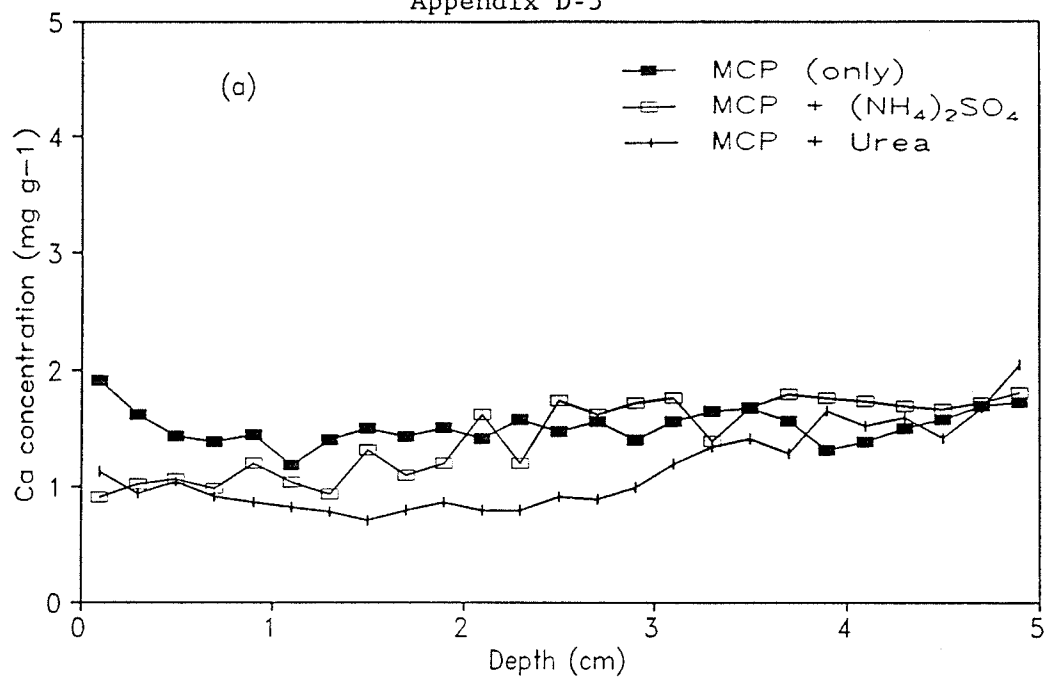
Effect of addition of salts upon distribution of exchangeable Ca^{2+} after 2 weeks of incubation in the Almasippi loamy sand (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.

Appendix D-6

Effect of addition of salts upon distribution of exchangeable Ca^{2+} after 3 weeks of incubation in the Almasippi loamy sand (a) $(NH_4)_2SO_4$ and urea addition (b) K_2SO_4 and $MgSO_4$ addition.
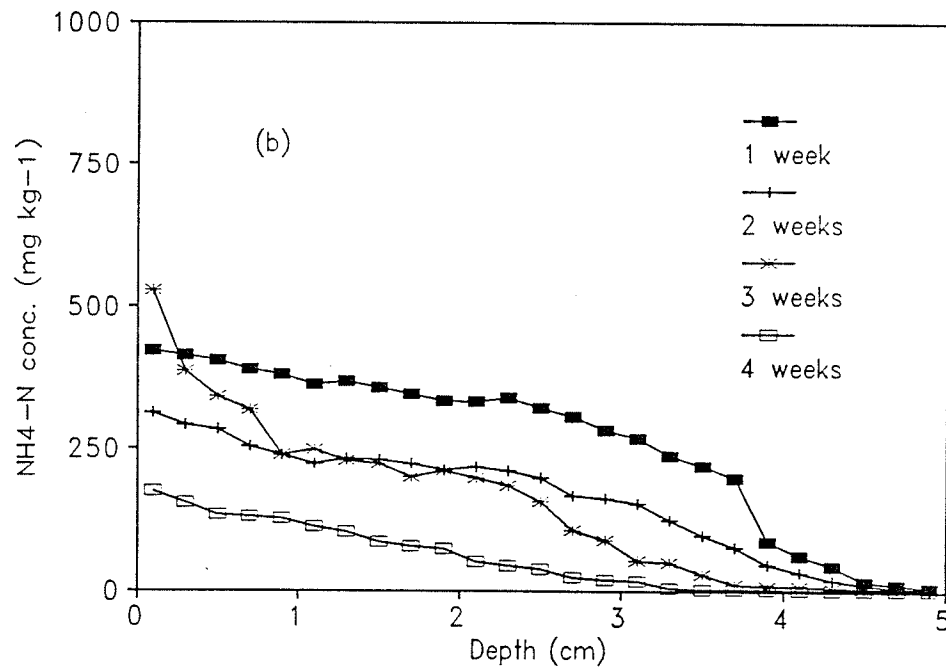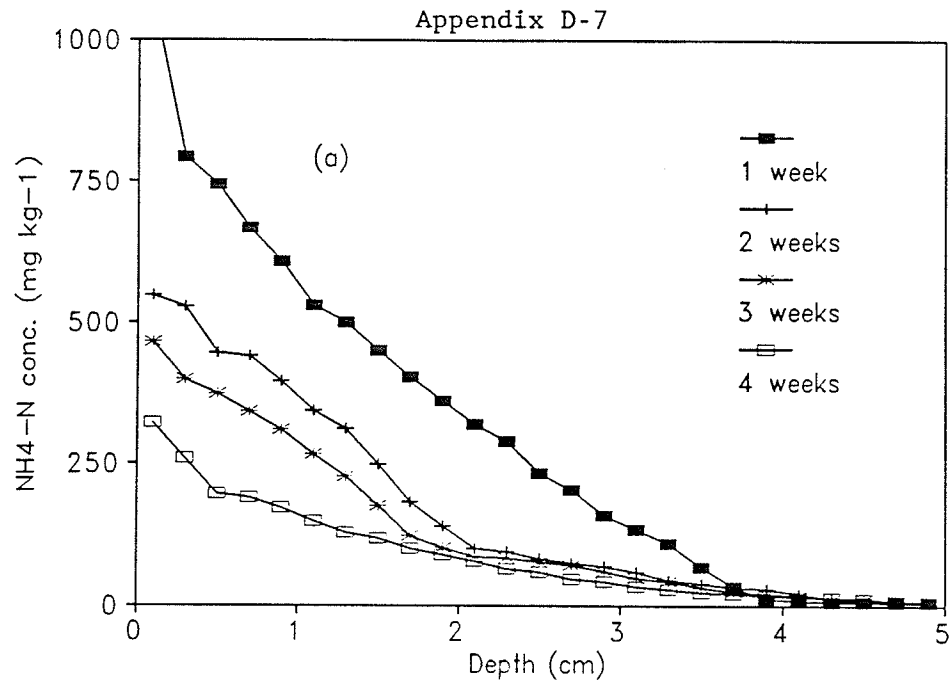
Appendix D-7
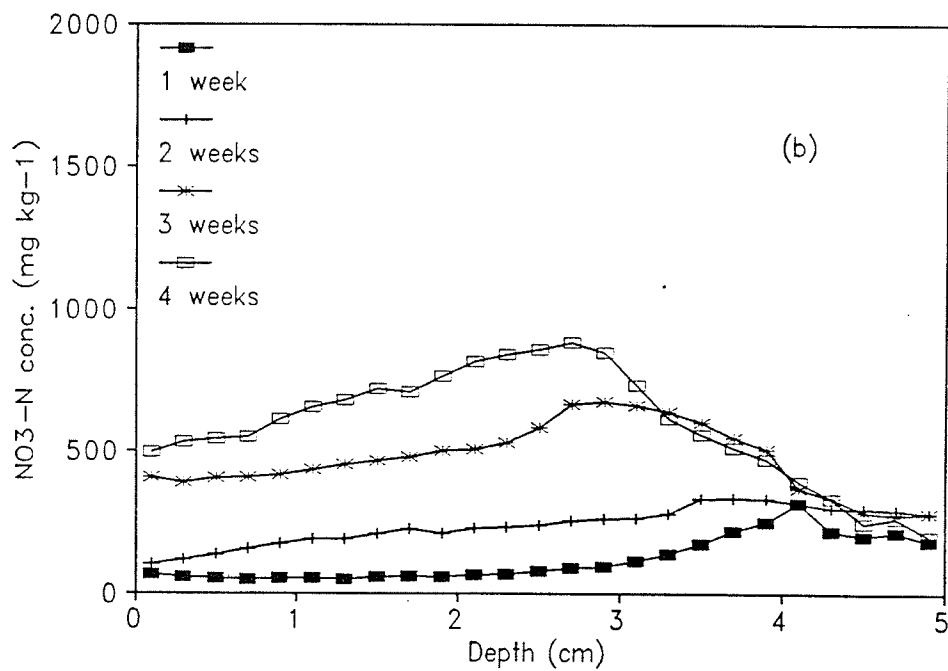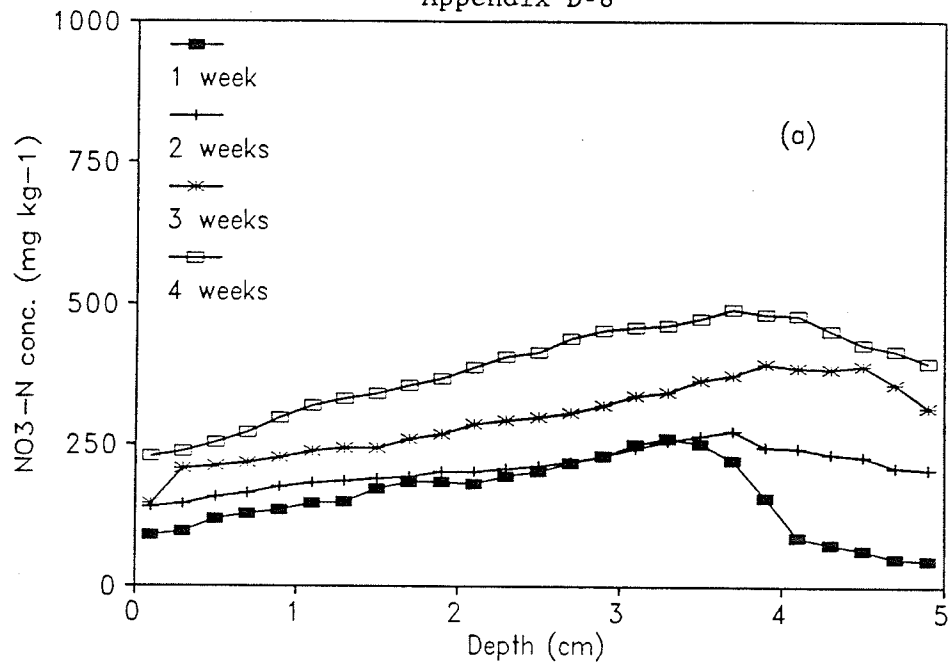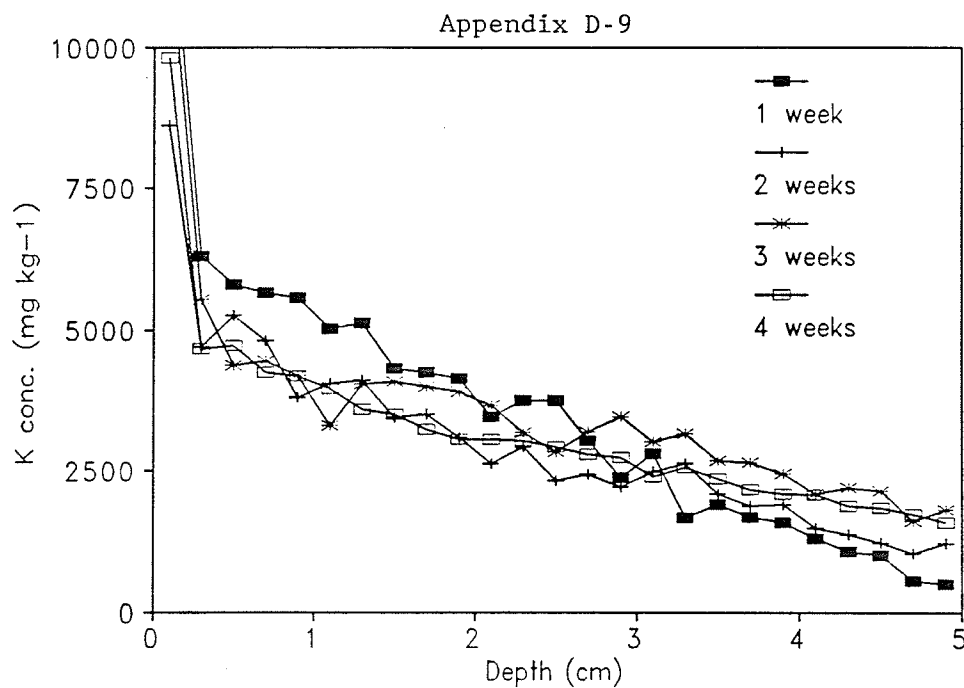
Distribution of extractable $NH_4^+ + NH_3$ at various times of incubation in the Almasippi loamy sand (a) $(NH_4)_2SO_4$ treatment (b) urea treatment.

Distribution of extractable NO_3^- + NO_2^- at various times of incubation in the Almasippi loamy sand (a) $(NH_4)_2SO_4$ treatment (b) urea treatment.
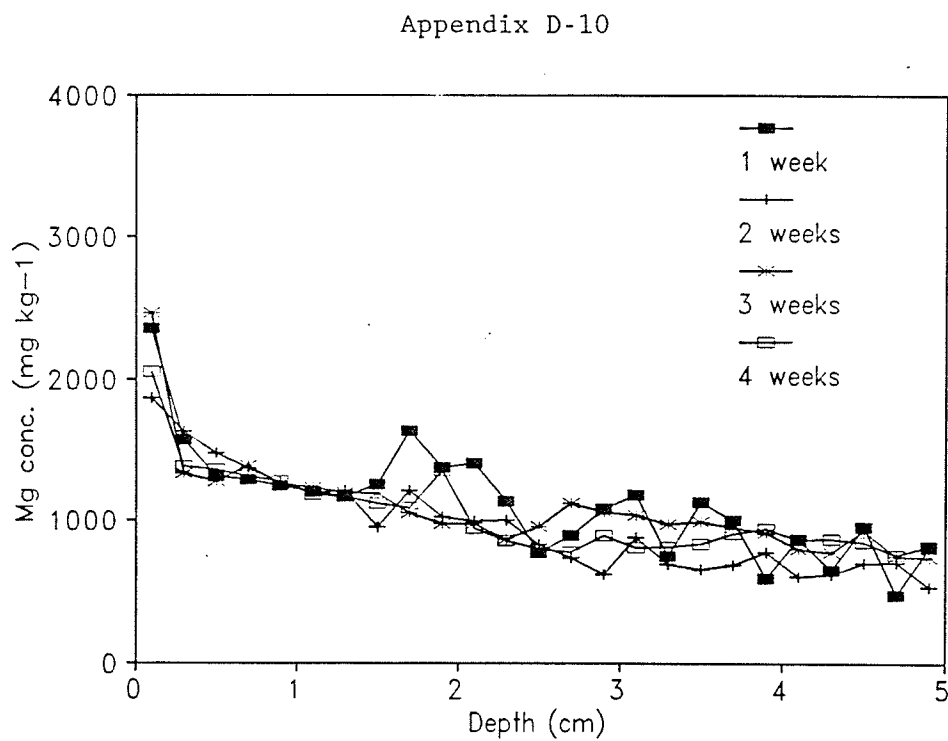
Appendix D-9

Distribution of extractable K⁺ at various times of incubation in K₂SO₄ treatment in the Almasippi loamy sand.

Appendix D-10

Distribution of extractable Mg⁺ at various times of incubation in MgSO₄ treatment in the Almasippi loamy sand

Appendix E

Solution of equations (Crank Nicholson method)

$$\frac{\partial A}{\partial t} = D_A \frac{\partial^2 A}{\partial x^2} - \frac{\partial S_A}{\partial t}$$

since

$$\frac{\partial S_A}{\partial t} = \phi_1 \frac{\partial A}{\partial t} - \phi_2 \frac{\partial B}{\partial t}$$

$$\frac{\partial A}{\partial t} = D_A \frac{\partial^2 A}{\partial x^2} - \phi_1 \frac{\partial A}{\partial t} + \phi_2 \frac{\partial B}{\partial t}$$

This could be rearranged as,

$$\frac{\partial A}{\partial t} = \frac{D_A}{1+\phi_1} \frac{\partial^2 A}{\partial x^2} + \frac{\phi_2}{1+\phi_1} \frac{\partial B}{\partial t}$$

According to the Crank- Nicholson method,

$$\frac{A_i^{j+1} - A_i^j}{\Delta t} = \frac{D}{2(\Delta x)^2 (1+\phi_1)} (A_{i+1}^{j+1} - 2A_i^{j+1} + A_{i-1}^{j+1} + A_{i+1}^j - 2A_i^j + A_{i-1}^j)$$
$$+ \frac{\phi_2}{1+\phi_2} \frac{B_i^{j+1} - B_i^j}{\Delta t}$$

where superscript j indicates the time and subscript i indicates the position. If $2(\Delta x)^2/D_A \Delta t = P_1$ then,

$$P_1(1+\phi_1) A_{i+1}^{j+1} - P_1 (1+\phi_1)A_i^j = A_{i+1}^{j+1} -2A_i^{j+1} +A_{i-1}^{j+1} +A_{i+1}^j -2A_i^j +A_{i-1}^j + P_1\phi_2(B_i^{j+1}+B_i^j)$$

This could be rearranged as,

$$A_{i+1}^{j+1} - (2+(P_1(1+\phi_1))A_i^{j+1} + A_{i-1}^{j+1} = -A_{i+1}^j + (2-P_1(1+\phi_1))A_i^j -A_{i-1}^j - P_1\phi_2(B_i^{j+1}-B_i^j)$$

If $-(2+P_1(1+\phi_1)) = bl[n]$ and $(2-P_1(1+\phi_2)) = br[n]$ then,

$$A^{j+1}_{i+1} - bl[n]A^{j+1}_i + A^{j+1}_{i-1} = -A^j_{i+1} + br[n]A^j_i - A^j_{i-1} - P_1\phi_2(B^{j+1}_i - B^j_i)$$

If the upper boundary is constant, then $A^{j+1}_{i+1} = A^j_{i+1} = A_o$. Thus,

$$bl[n]A^{j+1}_i + A^{j+1}_{i-1} = -2A_0 + br[n]A^j_i - A^j_{i-1} - P_1\phi_2(B^{j+1}_i - B^j_i)$$

If the upper boundary is no-flux then $A^{j+1}_{i+1} = A^{j+1}_{i-1}$ and $A^j_{i+1} = A^j_{i-1}$. Thus,

$$2A^{j+1}_{i+1} - bl[n]A^{j+1}_i = -2A^j_{i+1} + br[n]A^j_i - P_1\phi_2(B^{j+1}_i - B^j_i)$$

Lower boundary is always no-flux, therefore,

$$2A^{j+1}_{n-1} - bl[n]A^{j+1}_n = -2A^j_{n-1} + br[n]A^j_n - P_1\phi_2(B^{j+1}_n - B^j_n)$$

where n stands for the last position.

This method gives a tridiagonal matrix of algebraic equations that can be solved.