PHOSPHATE SORPTION AS INFLUENCED BY ADDED UREA IN AN ACID SOIL UNDER LIMED AND UNLIMED CONDITIONS.

A THESIS SUBMITTED TO
THE ORISSA UNIVERSITY OF AGRICULTURE AND TECHNOLOGY, BHUBANESWAR
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE IN AGRICULTURE
(AGRICULTURAL CHEMISTRY, SOIL SCIENCE AND BIOCHEMISTRY)

BY

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Orissa University of Agriculture & Technology
BHUBANESWAR
1995

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DEDICATED TO

MY LATE FATHER

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Certified that the thesis entitled " **PHOSPHATE SORPTION AS INFLUENCED BY ADDED UREA IN AN ACID SOIL UNDER LIMED AND UNLIMED CONDITIONS.**", *submitted in partial fulfilment of the requirement for the award of the Degree of* "**MASTER OF SCIENCE IN AGRICULTURE**" (***Agricultural Chemistry, Soil Science & Biochemistry***) *of the Orissa University of Agriculture & Technology, Bhubaneswar is a faithful record of bonafied research work carried out by* **Sri Pramoda Kumar Sahoo** *under my guidance and supervision. No part of this thesis has been submitted for the award of any other degree or diploma. Assistance and help received during the course of investigation, have been duly acknowledged by him.*

(U.K. Misra.)

ACKNOWLEDGEMENT

I avail this unique opportunity to express my deepest sense of reverence and gratitude to **Dr. Uma Kanta Mishra** *, Grad. Dip,(New South Wales), Ph.D. (Missouri), Professor of Soil Science (IFFCO chair), the Chairman of my Advisory Committee, who had injected gallons of advice and suggestion into my circulatory system which scientifically instrumented me to carry out the problem and evolve this manuscript. It is a matter of pride and privilege on my part to have Dr. Misra, a scientist of international reputation as my guide.*

This thesis work would have been a farce, but for the inexplicable encouraging attitude and perspicacious guidance of members of my Advisory Committee, Dr. D.Sahu, Professor & HOD, Agril. Chemistry, Soil Science and Biochemistry. Dr. S.K. Pattanaik, Junior Soil Scientist (BNF Project), Dr. N.C. Sahoo , Reader , Dept. of Plant Physiology to whom I am extremely indebted.

I am also grateful to Dr. N.Acharyya, the then Professor & HOD for his inspiring guidance, constructive criticism throughout the course of my research work.

With a profound and unfading sense of gratitude I am eager to express my heartiest thanks to all the Professors, Readers and Lecturers of my department for their noble advice and immense help as and when required during my research work.

I am pleased to express my deep appreciation for Ashis Sir, Khitoo Bhai ,Dheera Bhai, Manoj Bhai, Jyostna, Alam, Manoj, Maharana Babu, Rabi Babu, Arun Babu, Mallick Babu , Mahana for their needful help and inspiration during my investigation.

I would not be exaggerated to acknowledge that I feel immensely grateful and indebted to Rabi , Sudhansu, Ram Bhai without whose painstaking efforts and immeasurable selfless assistance, this work would have been delayed to see the light

I am ever thankful to Pradeep, Deelip, Nanda, Ranjeeb, Subrat, Pandey, whose altruism and incessant help are envisaged during the reasearch work.

From the fathomless ocean of my heart rise waves upon waves of gratitude and reverence to my loving father in heaven whose love, affection, blessing and encouragement have brought me to this stage of life. I pray, may His soul rest in peace and bless me from heaven .

Last, but not least I express my indebtness to all my family members for their incessant support and constant encouragement that enabled me to develop my tiny personality.

Bhubaneswar
Date: 23. 12.96.

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PHOSPHATE SORPTION AS INFLUENCED BY ADDED UREA IN AN ACID SOIL UNDER LIMED AND UNLIMED CONDITIONS.

Student : **P. K. Sahoo.** Advisor: **Dr. U. K. Misra.**

ABSTRACT

The interaction of urea with phosphatic fertilizer in soil-fertilizer microsites may have an important bearing on P availability to crops. The effect of urea on P sorption and desorption in an acid soil (pH 4.8) under unlimed and limed (pH 6.2) condition was investigated. Soil incubated with urea at the rates of 0,50,100,200 and 400 mg N kg^{-1} for 3 days at room temperature were equilibrated for 24 h with 5 rates of P *viz.* 0,50,100,200 and 400 mg P kg^{-1} of soil taken in either 0.01 *M* $CaCl_2$ or 0.03 *M* KCl medium and P sorption was studied. Phosphate desorption was also evaluated by sequentially extracting the phosphate sorbed soil with 0.01 *M* $CaCl_2$ and 0.5 *M* $NaHCO_3$.

Urea application increased the soil pH (0.01 *M* $CaCl_2$) in the fertilizer microsites resulting in an increase in pH of the equilibrium extract from 4.8 to 6.8 in the unlimed soil and 6.1 to 7.1 in the limed soil. Similar increase in pH was also observed when KCl was used as background electrolyte. These pH changes had variable effects on soil P sorption characteristics, depending on soil and electrolyte. Phosphate sorption increased with increasing urea and pH when $CaCl_2$ was the background electrolyte. But the added urea and pH had little effect when KCl was used, indicating that the urea effect on P sorption was influenced by Ca content. But the sorption was more in $CaCl_2$ medium than in KCl medium. The effect of urea was not significant at P rates < 200 mg P kg^{-1} soil. The observed increase in P sorption and decrease in solution P with added urea was probably related to precipitation of Ca-P compounds and the shift from $H_2PO_4^-$ to $HPO_4^{=}$ at higher pH values . The different in solution P concentration due to N doses in limed soil were less compared to unlimed soil .

A urea treated soil though sorbed more P also contained a greater reserve of desorbable P (labile P) available for crop. Limed soil treated with urea had a larger reserve of labile P. Besides urea, the effect of N added through N containing phosphatic fertilizer on phosphate sorption and desorption studied in unlimed soil in $CaCl_2$ medium showed that their effect was not significant in influencing the distribution of added P in different P fractions like sorbed, desorbed, $NaHCO_3$-extractable and non-extractable P.

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INTRODUCTION

CHAPTER I

INTRODUCTION

Next to nitrogen (N), phosphorus (P) is the most critical essential plant nutrient in influencing growth and production. It plays an important role in energy transformation and metabolic processes of plants and acts as "energy currency" within the plant. Considering the importance of P in plant growth and metabolism, Thomson Green Clemson (1859), founder of Clemson University wrote, "There can be no civilization without population, no population without food, and no food without phosphoric acid."

In soil, P is found both in organic and inorganic form, and both are important to plants. But the relative amount in two forms vary greatly from soil to soil. The organic fraction generally constitutes 20 to 80 per cent of the total P in the soil. But the available form of P at any time in soil is very low, seldom exceeding about 0.01 per cent of total P in the soil. The crop recovery of added fertilizer P amounts to only 10 to 30 per cent . The remaining 70 to 90 per cent has been assumed to be consumed by microbes, precipitated by soluble cations in the soil solution or sorbed by soil complex. It is now generally accepted that the role of microbes in this context is relatively minor and the chemical precipitation and sorption plays the major role in converting the soluble phosphates which is available for crop growth to relatively unavailable form.The P fraction which has been rendered insoluble is defined as 'fixed'.

Soil solution containing 0.1 ppm of P has been regarded as minimum concentration for obtaining good crop yields, particularly paddy. But, P concentrations in soil solution required for optimum growth vary from crop to crop. For example, a concentration of 0.2 ppm has been recognized as optimum for groundnut.

Under field condition where P fertilizers are applied to soil, the adjacent soil is contacted by soil solution containing very high concentration of P and accompanying cations. Phosphorus retention reactions begins in this environment which often initially favours *in situ* precipitation of phosphatic compounds. A major problem often found in acid soils is P deficiency for crop production. Applying P fertilizer to acid soils often results in low fertilizer efficiency because of high P sorption capacity of these soils.Phosphorus sorption by soils is also influenced by pH and salt concentration and this effect can be highly variable.

Besides precipitation of phosphatic compounds, adsorption is an important phenomena in studying the chemistry of soil phosphorus. Phosphate is known to be adsorbed on the clay surfaces as well as on colloidal forms of iron and aluminium. Despite the fact, that the adsorption sites are localized but not uniformly distributed, a large number of studies have shown the P adsorption data to fit the Langmuir isotherm. Langmuir equation has been suggested by Gunary (1970) for better fit, which may also depend on equilibrium P concentration at lower levels. Therefore, eventhough P sorption in soil has been extensively studied, the subject continue to demand further investigation.

A good understanding of the nature of phosphate sorption and desorption characteristics of the soil is of great help, for efficient management of phosphates for crop production. Use of different combinations of nitrogenous and phosphatic fertilizers or complex fertilizers alone on the basis of field experiment and laboratory analysis is the key for profitable crop production.

Urea applied with single super phosphate (SSP) to a calcareous soil have been reported (Lu *et al*. 1987) to increase Olsen's P and P uptake by crop as compared with diammonium phosphate (DAP). Urea hydrolysis in soil increases the concentration of OH^- and HCO_3^{-1} ions, which is likely to reduce soil acidity and increase P availability in the soil. Urea phosphate has been reported to increase yield, grain P content, and total P uptake than ammonium pyrophosphate and DAP applied to a calcareous soil (Raun *et al*. 1987) .

However, little information is available on the the effect of added urea on P availability to crop in acid soils. No information on P sorption in soil of added P in form of complex fertilizer in which P is associated with varying amounts and form of N and K are available. Such informations are needed to develop effective fertilization practices.

So the present study was conducted with the following objectives

* The effect of added urea on P sorption and distribution in different fractions in an acid soil under limed and unlimed conditions.

* The effect of different complex fertilizers like DAP, IFFCO NPK 10:26:26, Gromor NPK 28:28:0, and straight fertilizer like SSP on P sorption and distribution in different fractions in an acid soil.

CHAPTER - II

REVIEW OF LITERATURE

CHAPTER II

REVIEW OF LITERATURE

Phosphorus is one of the most essential nutrient element required by all organisms. The importance of P is next only to N for plant growth. But availability of P in soil is limited owing to severe fixation of native and applied phosphates. Although quite a few research have been made in the field of chemistry of soil P and its availability to plants, the efficient utilisation of native and applied P by the crop plants and its bio- chemical reactions in plants as well as soil are yet to be understood clearly.

A pertinent review of some of the works in the field of chemistry of soil P is briefly presented in this chapter.

2.1. FACTORS AFFECTING THE AVAILABILITY OF SOIL PHOSPHORUS:

Although the quantity of total P in an average mineral soil is almost equal to that of N, but the fraction of P that is made available to crop is meager as compared to N. Even under most ideal conditions, application of soluble forms of phosphatic fertilizer to the soil, the availability of P to crops is limited due to fixation.

According to Lovis T. Kardos (1964), the phosphate fixation reactions are categorized into 3 types, viz.(i) Adsorption (ii) Isomorphous replacement (iii) Double decomposition reaction involving solubility product principles. Also the factors affecting phosphate fixation can be grouped under two heads i.e. (a) Physical factors, (b) Chemical factors.

2.1.a. PHYSICAL FACTORS:

2.1.a.1. Soil Texture:

Work of Perkins *et al.*(1942) revealed that with the decrease of the particle size of the soil, the SiO_2: R_2O_3 ratio decreases, resulting in decrease of phosphate fixation on the surface area basis, but increase on the weight basis.

Kanwar (1956) reported an increase in phosphate fixation with increase in particle size, but also observed the coarse and fine sand fraction showed high fixation which was attributed to the presence of sesquioxides. Work of Olsen and Watanabe (1963) showed that fertilizer P reacted to form less soluble P compounds in clay soils than in fine sandy loam soils for equal rate of P addition.

Coating of Fe and Al oxides on clay as well as exchangeable Al and Ca are known to affect P fixation in soil, but diffusion of P is related to clay content. At a given moisture tension the clay soil will have much higher moisture content than sandy soil, therefore large volume of diffusion with larger addition of fertilizer P. This means that the available P would become limiting more quickly in a sandy soil than in a clay soil.

2.1.a.2. Moisture:

Datta and Goswami (1962) observed that phosphate fixation was minimum at 60 per cent moisture level and maximum at 100 per cent moisture level. Khalid *et al.*(1977) reported that release of soil P is more favourable under reduced condition than oxidised condition.

Akbari *et al.*(1981) through an incubation study of soil with added P showed that Olsen's P increased with the increasing levels of P and moisture.

Working in a group of acid soils of Newzealand Haynes *et al.*(1985) opined that considerable hysteresis in P adsorption - desorption were observed for both moist and dry soil samples, indicating that the additional P adsorbed by the dried samples was held with the same strength as that held by the moist samples.

2.1.a.3. Temperature:

Comparative study on release of P by Mack (1959) revealed that P release was higher when the soil was incubated for 9 months at 20.5°C than at 27°C. Levesque (1967) has shown that Fe-P fraction on fertilized soil increased in expense of Al-P, when the soil was incubated at 26°C.

2.1.a.4. Time:

Ibrahim and Pratt (1982) conducted trials in southern California soils to study the effect of time on P sorption. They incubated the soils with different rates of P in 0.01 *M* $CaCl_2$ for studying the effect of incubation time up to 84 days at 25°C on P sorption and found that there were only small effects of incubation times beyond 3 days for low rates of P applications. At higher rate of application, those soils deficient in P gave increased P sorption with increase in incubation time beyond 3 days and attained equilibrium by 42nd day. Those soils well supplied with available P reached equilibrium in 3 days .

Work of Rajan and Fox(1972) reveals that P adsorption by several tropical soils was 85 per cent complete in 24 to 48 h, but reasonably stable levels of P in solution were attained only after 6 days of equilibration.

2.1.b. CHEMICAL FACTORS:

The chemical factors essentially responsible for P fixation and release in the soil are (i) Aluminium, Iron, and Manganese (ii) Type and amount of clay (iii) pH (iv) Liming (v) Organic matter content (vi) Phosphorus status of the soil (vii) Other associated ions.

2.1.b.1. Effect of Fe,Al and Mn:

The soluble form of Al,Fe and Mn are mostly found in acid mineral soils. When water soluble phosphate is added, the $H_2PO_4^-$ ions form, so-called hydroxy phosphates as presented below.

$$\underset{\text{(Soluble)}}{Al(OH)_3} + H_2PO_4^- \text{----->} \underset{\text{(Insoluble)}}{Al(OH)_2H_2PO_4} + OH^-$$

Laterite and Podzol soils have got higher proportion of sesquioxides which form a film over the individual phosphate particles. The hydrated oxides of these are insoluble in soil solution. Their colloidal nature and surface position on soil particles renders it very active to form insoluble complexes with phosphates when in contact.

Warrington (1953) was the first to detect the nature of reaction of hydrated oxides of Fe and Al with phosphates. Chang and Jackson (1957) found that at the same pH value activity of Fe is much less than the activity of Al in soil solution, since at the same pH value, solubility (pK) for $Fe(OH)_3$ and $Al(OH)_3$ are 37.00 and 37.72 respectively. Hence the precipitation of Al-P is more or less equal with that of Fe-P. In another experiment Blanchet (1959) concluded that both $Fe(OH)_3$ and $Al(OH)_3$ have greater capacities to fix phosphates than lime stone or clays.

Fractionation study of soil P by Yuan *et al.* (1960) revealed that 80 per cent of added P form complexes with Al and Fe and only 10 per cent or less remain in water soluble and rest in Ca-P form. It was also observed that highest per cent of inorganic P is recorded in soils where there is low concentration of Fe and Al and high concentration of Ca and Mg.

Study on interrelationship of P retention capacity of clay, organic matter, Fe and Al by Saini *et al.* (1965) revealed that Al had a dominant role in P fixation. They also observed that a significant relationship between P retention capacity and organic matter, but no relationship with clay and Fe.

Mandal and Das (1970) working with three acidic low land rice soils observed that added P remaining in equilibrium with soil solution declined and the rate of decline was influenced more by Fe_2O_3 and active Fe than by soil pH. Aluminium phosphate fraction increased over the untreated soil and appeared to ha been influenced by soil pH.

2.1.b.2. Effect of pH on P Retention and Release:

Among the different factors, the effect of pH on P sorption is probably the least understood (Barrow 1987; White 1983).While some reports have shown that P sorption decreased with increase in pH in the acidic pH range (Parfitt 1977; Friesen *et al*,1980),others have shown that P sorption increased with increase in pH (Amarasiri and Olsen 1973; Mokwunye 1975). There is also some evidence to show that P sorption decreased with increase in pH up to 5.0 to 6.0, beyond which it increased (Barrow 1987; Sims and Ellis 1983). The controversies on the effect of pH on P sorption were reported by White (1983) to be due largely to the difference in the exchangeable Al values of the soils.

Not only the applied phosphate but also the adsorbed phosphate is equally important in determining the concentration of P in the soil solution. Kanwar and Grewal (1960) working with the acid soils of Punjab have observed a decrease in P fixation with increase in pH.

According to Chiang (1963), most of the P fixation in acid soils is due to Fe-phosphate, but Ca-phosphate is important in neutral and basic soils especially in alluvial soils of clay-slate origin.

Experiment of Basu(1977) on P availability of submerged soils having different pH values concluded that P availability increased with increasing pH to neutrality.

Whenever an increase in P sorption was observed at high pH values,either Ca was used as liming material or was present in the background electrolyte.This led several authors (Fox *et al.* 1974;Barrow *et al.* 1980; Sanchez and Uehara,1980) to propose that the precipitation of calcium phosphate is responsible for the decrease in solution concentration at high pH values. Thus,using the method of Clark and Peech(1955),borrow *et al.*(1980) showed that the decrease in P concentration at high pH values during the sorption of P by goethite could be caused by the formation of insoluble Ca-P compounds. Helyar *et al.*(1976) related the increase in P sorption by gibbsite at high pH values to the presence of Ca and suggested that surface complex formation between sorbed P and solution Ca and P was responsible.However, Barrow (1984) found that sorption increased at high pH values even when the concentration of Ca was considered to be too low for precipitation to occur.

2.1.b.3.Effect of Liming:

Awn Abul Bari (1964) reported that liming of soil increased the release of applied P from organic compounds in acid soils. This was supported by Khan and Roy (1964) while conducting experiment on soils of east Pakistan.

It is commonly believed that extractable P concentration generally increases after liming an acid soil. When strengite and variscite are present, liming hydrolyses these compounds and releases phosphate ions to the soil solution (Lindsay and Moreno, 1960). Lime also reduces the concentration of Fe and Al ions which would have reacted with added soluble phosphates to form insoluble Fe and Al phosphates.

In addition to reducing Al toxicity, liming affects the amount of phosphate sorbed by acid soils. However, the effects can be highly variable. For example, liming of soils has been shown to decrease (Woodruff and Kamprath, 1965) increase (Amarasiri and Olsen, 1973) or not affect (Reeve and Sumner, 1970) the sorption of P by soils.

Various reasons have been advanced to explain these contrasting effects. For example, Haynes (1982) attributed the contrasting effects to inconsistencies in the soil incubation procedure used, suggesting that an intervening drying step between the addition of lime and P could have a significant effect on the P sorption characteristics of soils.

Barrow (1984) attributed the variable effects of liming on P sorption to four additional factors, viz. the pH over which P sorption was measured, the background electrolyte, the amount of desorbable P in the soil and the relationship between pH and the potential on the soil surface. From these studies it is apparent that the experimental conditions used can have a substantial influence on the results obtained.

Hall and Baker (1971) in their experiment found that effect of liming on P availability is not same for all the soils. They concluded that soils containing clays that react like vermiculite, addition of lime prior to addition of P will reduce the reactivity of Al through formation of stable interlayer Al-polymer which effectively reduces the specific surface of reactive Al and P adsorption sites, but reverse trend was found in soils containing clays that react like montmorillonite.

Lime requirement of acid soils ranges from 0.77 to 5.20 meq. (Ca + Mg) per 100gm soils (Cabala and Fassbender, 1971). They reported that liming increased the pH ,the exchangeable Ca and Mg, but decreased Al and had little effect on P fractions or on available P determined by Olsen, Troug, Egner-Riehonand Mehlich's method.

Greenhouse and laboratory experiment of Jotsymth and Pedro (1980) conducted on clay-kaolinite soils showed that $CaCO_3$, $CaSiO_3$ and previous P application decreased P fixation. Previous P application were more effective in decreasing P sorption than the amendments. Joint application of P and soil amendments increased the negative charge and decreased the positive charge to a greater extent than when applied separately.

Haynes *et al.* (1985) was of the view that P adsorption by moist limed soils can be increased, decreased or unaffected depending on the relative magnitudes of these two processes. They explained that after liming and/or air drying, crystallization of amorphous materials progressively decreases their surface area and adsorbing capacity. Thus liming tends to decrease phosphate adsorption when the soils are dried.

Naidu *et al.* (1990) opined that P sorption decreased with an increase in the rate of liming up to pH 5.5-6.0, above which sorption increased. The observed initial decrease in P sorption was probably related to the decrease in surface negative charge resulting from increased soil pH. Soils incubated with KOH and $Ca(OH)_2$ and using a variety of electrolyte concentrations, it was concluded that the presence of Ca was associated with the apparent increase in P sorption at high pH values. These results together with an observed decrease in exchangeable P at high pH, are consistent with the formation of insoluble Ca-P compounds.

2.1.b.4. Effect of Clay Minerals:

Fox and Searle (1978) reported that P sorption was strongly related to mineralogy, texture and intensity of desilication of colloids by weathering and leaching. From mineralogy aspect the order of increasing P sorption is quartz < organic material< 2:1 clays < 1:1 clays < crystalline oxides < desilicated volcanic ash minerals which strongly adsorb phosphate tend to dominate most tropical soils.

Motiramani *et al.* (1964) reported that with increase in percentage of clay in soil, P fixation increased. De Datt *et al.* (1966) opined that acid laterite soils containing Kaolinite type of minerals fix more P than soils rich in montmorillonite type of clay minerals. With increasing pH montmorillonite clays fix more P but reverse was observed in vermiculite (Hall and Baker,1971).

2.1.b.5 Effect of Organic Matter:

The primary phosphate minerals are dissolved by CO_2 and H_2CO_3, produced due to the decomposition of organic matter. The activity of P fixing agents Fe, Al in acid soils are deactivated by formation of stable chelating compounds with organic anions like malate, oxalate and citrate etc. produced due to organic decay.

Organic matter provides major sites for P adsorption (Sundarajan and Kothandaraman,1978). The role of organic matter in augmenting P sorption in soil has been attributed to the association with possible stabilization of the soil organic matter by the free sesquioxides (Sanyal and De Datta,1991).

According to Chakravarti and Ghosal (1969) the organic matter has got depressing effect on P availability.
Mandal and Khan (1972) reported that organic matter has no effect on availability of P in low land rice soils. Application of organic matter increased the solubility of soil P (Basu,1977). Mobility of P in laterite soil was greater in presence of applied organic matter (Bhart and Mohapatra,1978).

2.1.b.6. Effect of Phosphorus Status of the Soil:

Application of P to soils having high available P content, may not cause appreciable fixation. According to Basu and

Mukharjee (1972), incubating the soil with P solution for 5 days, the adsorption was gradual. But on prolonged contact, the adsorption reached a steady value at **higher** concentration. As the soil tended towards saturation with soluble P the availability was increased. Novais and Kamprath (1978) reported on some coastal plain soils of USA, heavily fertilized in the past that these soils could supply adequate amount of P for crop growth for several years without P fertilization.

2.2. PHOSPHATE FIXATION IN SOILS:

Two separate approaches have been prominent in the interpretation of the mechanism of P fixation. One based upon theories of adsorption on the surface of clay minerals and hydrated Fe and Al oxides and the other postulating the formation of P compounds by precipitation. Both appear to explain many aspects of P fixation, but neither is adequate for comprehensive interpretation. Although surface adsorption theories may describe the way in which the P concentration in the soil solution responds to the amount present in the solid phase, they fail to account for the way in which the amount of adsorbed P accessible to isotopic exchange varies in respond to soil pH.

According to Hsu (1964) mechanism of fixation basically follows the solubility product principle, but the total activity of all forms of Al and Fe including amorphous Al-Oxides, and Fe-oxides, should be a concern of governing the concentration of P in solution.

More recently Quirk, Posner and several co-workers have elaborated the hydroxyl-exchange hypothesis of phosphate adsorption at the edge faces of Kaolinite crystals and the surfaces of gibbsite and goethite. However, their hypothesis (Hingston *et al.* 1967, 1972,1974) which has been referred to as P adsorption by ligand exchange or specific adsorption of phosphate, rests on assumptions and data that are at variance with other published results on clays and oxides and with observations on soils.

The assumption attributing P adsorption in soils solely to surfaces of variable charge, whereas it may be desorbed only if the pH is raised, or a competitive anion is introduced to increase the surface negative charge (Hingston *et al.* 1968), is contrary to the results of Aslyng (1954) who showed that the ion activity product 1/2 pCa + pH_2PO_4 was independent of the supporting electrolyte concentration. The implication of Aslyng's work is that the phosphate and Ca activities in solution were controlled by the electrical potential differences across the same diffuse double layer, or at least there was a constant potential difference between the sites at which phosphate and Ca ions were held. Adsorption of phosphate at discrete, positive sites would not give this result since the potential functions at surfaces of variable charge (clay mineral edge faces and sesquioxide surfaces) do not vary consonantly with change in ionic strength.

The ligand exchange hypothesis predicts that phosphate adsorption should attain a maximum at a pH = pK, for H_3PO_4 (~ 2) and fall with increase in pH. This was confirmed by Obihara and Russel (1972) who studied several acid soils at levels of phosphate addition close to maximum adsorption capacity.

Hsu (1964) treated a slightly acid soil with dilute phosphate solutions of pH 7 to study the mechanism of phosphate fixation . He recognised two reactions to operate at different rates. The one proceeded more rapidly is believed to be due to surface adsorption of phosphate on amorphous aluminium hydroxides and iron oxides already in the soil which were the native source . This reaction was completed within few hour. The other a much slower reaction was due to surface adsorption on similar amorphous hydroxide and oxides developed during the experiment.

Woodruff and Kamprath (1965) reported on a number of soils with a wide range of chemical properties that neutralization of exchangeable Al markedly reduced the P adsorption maximum. A high concentration of P was needed for the soils with a high saturation of exchangeable Al to give maximum yield. Sree Ramulu *et al.* (1967) studied the fixation of phosphate by 12 acid soils containing various amounts of free Fe_2O_3 and observed a significant correlation (r= 0.78) between P fixation and dithionite extractable Fe_2O_3.

Kar and Chakravarti (1969) working on five acid soils of West Bengal (pH 4.37 to 6.18) reported that the soil fixed 30-

50 % of added P.

Shukia *et al.* (1971) observed that non-calcareous sediments sorbed more of added P than calcareous sediments. Further more P sorption was inversely related to $CaCO_3$ content of calcareous sediments.

Parfitt (1977) studying P adsorption in A and B horizon of an oxisol of Paupa New Guinea reported that there existed high affinity for adsorption at low concentration of P. Adsorption of P increased with decrease in pH in the range of 3 to 8. They also reported that phosphate reacted with FeOH and $Fe(OH)_2$ groups on soil iron oxide surfaces to form a binuclear bridge $Fe\text{-}P(O_2)$ O Fe complex and with exposed $Al(OH)H_2O$ on Kaolinite edges and on hydroxy-aluminium species to form a binuclear phosphate complex. At higher P concentration adsorption increased by further reacting with hydroxy aluminium groups.

Imal (1981) studying the kinetics and heats of P adsorption in soil reported that when very large amount of P are added, new and very reactive surfaces are progressively exposed for adsorption. They further reported that adsorption increased with increase in soil acidity and in soils containing less of molybdenum (Mo).

Can (1982) reported that phosphate sorption in soils containing large amounts of free oxides that increased with increase in free Al and Fe compounds.

2.3. EFFECT OF ELECTROLYTE AND ITS STRENGTH ON PHOSPHATE SORPTION:

Ionic strength and cation species of supporting electrolyte is one of the important experimental variables which affects P sorption by soils (Bala *et al.* 1995). Generally a 0.01 M $CaCl_2$ solution has been widely used in adsorption studies on the premise that it provides a medium of constant ionic strength similar to composition of ambient soil solution under natural conditions without inducing any changes on the clay surface (Schofield 1955). But the assumption seems far from true due to the fact that Ca^{2+} ions have specific affinity for the colloidal surfaces as well as for the phosphates. Moreover, precipitation of basic Ca-phosphates may be enhanced by addition of Ca^{2+} ions (Lindsay *et al.*1989). Therefore some workers have used variable concentration of NaCl, KCl and even distilled water (Shapiro *et al.* 1959; Syers *et al.* 1970) for adsorption studies.

Phosphate sorption was higher at higher ionic strength and in the presence of higher valent cation (Ca^{2+} as opposed to Na^+ , K^+) (Eze *et al.* 1990; Rajan *et al.* 1972). AT a particular molarity, it was higher in the presence of $CaCl_2$ as compared with NaCl, KCl (Bala *et al.* 1995). Helyar *et al.* (1976 b) while studying the adsorption of phosphates by gibbsite at pH 5.5, reported increased P sorption in the presence of Ca^{2+} than in the presence of Na^+, K^+ and Mg^{2+} which was explained to be due to surface complex formation between a calcium ion and two phosphate ions. The same was observed by Stoop (1983) in the oxidic Hawaiin soils.

2.4 EFFECT OF ADDED N ON P SORPTION IN SOIL WITH SPECIAL REFERENCE TO ADDED UREA :

The reaction products of urea hydrolysis may cause soil pH changes. At soil pH < 8, most of the inorganic carbon released from the urea by hydrolysis will diffuse from the soil as CO_2 consuming, two H^+ in the overall process (Koelliker and Kissel 1988). Since two NH_4^+ ions are formed for each CO_2 lost, each NH_4^+ formed should result in one H^+ consumed from the soil. Such observation was also made by Izaurralde *et al.*(1987) in the process of anhydrous NH_3 adsorption by soil. Fenn *et al.*(1981) suggested that precipitation of $CaCO_3$ may occur during urea hydrolysis after the pH exceeds 7.

Blair *et al.*(1971) reported that a decreased rhizosphere pH and increased $H_2PO_4^-$ / $HPO_4^=$ ratio have been found when NH_3 and P are applied together. This effect is most pronounced in alkaline soils where slight reduction in pH alter greatly the concentration of $H_2PO_4^-$. Increased P absorption when it is applied with N is in part due to an enhanced physiological capacity of roots to absorb P brought about by greater root development in an N-P band.

The phosphoric acid component in urea phosphate (UP) has been found to retard the enzymatic hydrolysis of the urea by soil urease, thereby reducing gaseous losses of urea N as NH_3 (Fenn *et al.*1981). When P was applied in association with NH_4^+ as in DAP, more P was found concentrated within the application zone and more of the added P remained water soluble after 4 weeks as compared to ammonium polyphosphate (APP) (Khasawneh *et al.* 1974). Cations of Fe and Al were found to be complexed by APP, thereby delaying the precipitation of P in acid soils (Lindsay *et al.*1962).

In a laboratory study Fan *et al.*(1993) found that urea application in an acid soil increased the soil pH in the soil fertilizer microsites which had variable effects on soil P sorption characteristics, depending on electrolyte. Phosphate sorption increased with increasing urea and pH when using $CaCl_2$ as the electrolyte but, added urea and pH had little effect when KCl was used, indicating that urea effect on P sorption was influenced by Ca content. For soils with high Ca content, urea application with P fertilizer reduced P concentration in soil solution and P mobility because of the increase in P sorption and P buffer capacity, but increased available P as expressed by $NaHCO_3$-extractable P.

CHAPTER - III

MATERIALS AND METHODS

CHAPTER III

MATERIALS AND METHODS

A laboratory investigation was carried out to study the effect of added urea on P sorption and desorption in an acid soil under unlimed and limed conditions.The P sorption and desorption was also studied taking different fertilizers like SSP, DAP,IFFCO NPK 10:26:26 and Gromor NPK 28:28:0.

3.1. MATERIALS USED :

3.1.1. Soil Used in the Investigation:

The soil (Haplustult) used for laboratory study was collected from the orchard area,the central farm of O.U.A.T.,Bhubaneswar.The soil was collected from 0 to 15 cm depth and air dried, ground to pass through a 1mm sieve and stored in polyethylene bags for further investigation.

3.1.2. Nitrogen and Phosphate Sources Used:

Analytical grade urea, Potassium dihydrogen phosphate and fertilizer grade SSP,DAP, IFFCO NPK 10:26:26 and Gromor NPK 28:28:0 were used as and when needed.

3.2. EXPERIMENTAL METHODS:

3.2.1.Preparation of Limed Soil:

To 7kg soil taken in a pot 12.5g of paper mill sludge (PMS) having $CaCO_3$ equivalent of 75 per cent was added. The amount of lime was added (based on the lime requirement of the soil determined by Shoemaker buffer method) to raise the pH to 6.8. The soil was alternatively wetted and dried for two months. The soil was mixed thoroughly before each addition of water. At the end of the last wetting and drying cycle the pH was found to be 6.2 .

3.2.2.(a) Phosphate Sorption Study in Presence of Urea:

Two grams of soil (limed or unlimed) were treated with 0.4 cc of either urea containing one of the five N concentrations, *viz.* 0,250,500,1000 and 2000 mg N L^{-1} of solution in 50 mL centrifuge tube just to maintain near field capacity.The N concentrations were equivalent to 0,50,100,200, and 400 mg N Kg^{-1} soil respectively .The treated soil samples were incubated for 3 days at room temperature i.e. 30±2°C.Following incubation ,25 mL of either 0.01 *M* $CaCl_2$ or 0.03 *M* KCl containing one of five P (KH_2PO_4) concentrations (0,4,8,16, and 32 mg P L^{-1} solution) was added to each soil. These were equivalent to 0,50,100,200 and 400 mg P Kg^{-1} soil respectively. Each treatment was replicated twice. Soil-solution mixtures were shaken at room temperature for 24 h using a mechanical shaker. After shaking, the pH of the suspension was measured and then centrifuged at 3000 rpm for 10 min. Supernatant liquid was filtered through Whatman No.1 filter paper wherever needed and P concentrations in the extracts were determined colorimetrically following the ascorbic acid reduction method of Murphy and Riley (1962).

3.2.2.(b) Phosphate Sorption from Phosphatic Fertilizers Containing N :

Phosphate sorption by soil from solutions of fertilizers like DAP, IFFCO NPK 10:26:26, Gromor NPK 28:28:0 and SSP were also studied by equilibrating the soil with different P concentrations. The equilibration was carried out as per the procedure described above except that the P solution was prepared in water medium in stead of $CaCl_2$ medium. After addition of P to soil, $CaCl_2$ solution was added to maintain the strength of $CaCl_2$ at 0.01 *M* and the soil: solution ratio of 1:12.5.

3.2.3 Phosphate Desorption Study:

Residual soil in the centrifuge tube after sorption study was used to determine P desorption by sequentially extracting once with 25 mL of 0.01 *M* $CaCl_2$ solution followed by single extraction with 25 mL of 0.5 *M* $NaHCO_3$ (Olsen's extractant) solution. For each extraction, samples were shaken on a mechanical shaker for 20-h. Suspensions were centrifuged and filtered and P in the extract was determined as described above. Phosphorus retained in soil was determined by subtracting the desorbed P from the sorbed P.

3.2.4. Analytical Methods Followed :

The pH of 1:2 soil : water suspension, water holding capacity and field capacity were determined following the standard methods . The mechanical analysis of soil was done following the Bouyoucos hydrometer method as described by Piper

(1950). The cation exchange capacity (Neutral Normal NH_4OAc exchangeable) of soil was determined following the procedure as outlined by Jackson (1973). The exchange acidity of soil (1 *M* KCl extractable) and total acidity of soil (extracted with $BaCl_2$ -Triethanol amine) was determined following the procedure of coleman *et al.* (1959) and Mehlich (1953) respectively as outlined by Page *et al.* (1982). Organic carbon in the soil was estimated by Walkley and Black rapid titration method as described by Jackson (1973). Exchangeable sodium and potassium from the ammonium acetate extract of the soil was determined flame photometrically, exchangeable calcium and magnesium were determined by EDTA (Versenate) complexometric titration as outlined by Hesse (1971). The water soluble P content of fertilizers collected from market was determined by Vanado Molybdate yellow colour method (Jackson, 1973) after dissolving the fertilizer in water. Then fertilizer solutions containing 100 ppm P were prepared and used as per requirement.

3.2.5 Analysis of Data:

The P sorbed on the solid phase (P_s) was calculated from the difference between added P (P_a) and increase in solution P (dP_1). The value of P_s was divided into 0.01 *M* $CaCl_2$ desorbed P (P_d), $NaHCO_3$ - extractable P (P_e) and non-extractable P (P_n). The distribution of added P in soil was computed as

$$Pa= dP_1+dP_d+dP_e+dP_n \qquad [1]$$

where $dP_1 = P_1 - P_{1(0)}$, $dP_d = P_d - P_{d(0)}$ and $dP_e = P_e - P_{e(o)}$; subscript o refers to the value obtained at each urea level from a soil suspension without added P. The non-extractable P(dP_n) , was computed as follows:

$$dP_n = P_a - (P_1 - P_{1(0)}) - (P_d - P_{d(0)}) - (P_e - P_{e(0)}) \quad [2]$$

Rearranging Eq.[2] yields

$$dP_n = P_a + (P_{1(0)} + P_{d(0)} + P_{e(0)}) - (P_1 + P_d + P_e) \quad [3]$$

For the relation of sorbed P with soil solution P after 24 h shaking, results obtained from the P sorption were fitted to the Langmuir equation $Q=kbC/(1+kC)$, which can be rearranged to $C/Q=(C/b) + (1/kb)$, where Q is the amount of P sorbed per unit weight of soil, C is the P concentration in soil solution (P_1); k is bonding energy constant and b is P adsorption maximum (Sample *et al.* 1980).The PBC (maximum P buffering capacity) was calculated from kb (Olsen and Khasawneh,1980).Finally the effects of urea, DAP,SSP,IFFCO NPK 10:26:26,Gromor NPK 28:28:0 on equilibrium solution pH, P sorption, buffer capacity and P distribution of added P into various fractions as determined were statistically analysed.

CHAPTER - IV

RESULTS AND DISCUSSION

CHAPTER IV

RESULTS AND DISCUSSION

Urea is a widely used nitrogenous fertilizer for most crops. Its application is likely to increase the soil pH temporarily in the rhizosphere and the soil pH is known to affect P availability. Hence the effect of added urea on phosphate sorption and desorption was investigated taking an acid soil (Haplustult) under limed (pH 6.2) and unlimed (pH 4.8) conditions. Some of the physico-chemical properties of the soil are recorded in Table-1. The soil was a sandy loam containing organic carbon of 4.8 g kg^{-1}, having field capacity 190 g kg^{-1} soil, CEC 11.02 c $mol(p^+)kg^{-1}$

It is known that addition of urea increases the soil pH due to its hydrolysis in soil as per the following mechanism :

$$NH_2CONH_2 + 2\,H_2O + H^+ \xrightarrow{\text{urease}} 2NH_4^+ + HCO_3^- \text{ ---------[1]}$$

Further reaction of HCO_3^- with H^+ in soil results in CO_2

$$HCO_3^- + H^+ \longleftrightarrow CO_2\ (g) + H_2O \text{ ----------------[2]}$$

Both the reactions consume H^+ and hence, raise soil pH. If hydrolysis of urea is complete and all the urea-C diffuses from the soil as CO_2, the net result is that $2H^+$ ions are consumed from the soil and $2NH_4^+$ ions are formed or a net of one H^+ ion is consumed for each NH_4^+ formed. Izaurralde *et al.*(1987) observed that the adsorption of one NH_3 (g) molecule by soil also consume one H^+, even at pH values approaching 9. Above pH 8.2, where Eq.[1] is dominant and Eq.[2] becomes relatively insignificant, the net result is that one H^+ is consumed for 2 NH_4^+ ions formed or a ratio of 0.5 H^+ ion per NH_{4+} formed.

In order to determine the time required to attain the maximum pH after addition of urea, a preliminary investigation was carried out by incubating 2 g soil with 100 mg N kg^{-1} of soil in separate beakers for different time period after which the pH was measured. The effect of incubation time on soil pH is recorded in Table-2. It is observed that the highest pH of 5.55 was attained on the 4th day of incubation or after 72 h of urea addition. Hence to study the effect of urea on phosphate sorption, the soil was first incubated with added urea for 3 days and then P sorption by soil was studied.

4.1. PHOSPHATE SORPTION:

Phosphate solutions of different concentrations, *viz.*0,4,8,16 and 32 mg P L^{-1} as KH_2PO_4 in 0.01 *M* $CaCl_2$ or 0.3 *M* KCl medium were used in the sorption study. The strength of calcium chloride was chosen on the premise that it provides a medium of constant ionic strength similar to composition of ambient soil solution under natural conditions without inducing any changes on the clay surface (Schofield 1955). In an attempt to separate the effect of pH from that of calcium, P sorption was also studied using KCl solution as background electrolyte of 0.03 *M* strength which was equivalent in ionic strength to that of 0.01 *M* $CaCl_2$.

4.1.1. Effects of Urea:

The phosphate concentration and pH of equilibrium extracts

Table 1 : Selected Physico-chemical properties of the soil used in the investigation.

Particle size distribution (g kg^{-1})	
Sand	706.2
Silt	118.2
Clay	175.6
Texture	Sandy loam
Water holding capacity (g kg^{-1})	357
Field Capacity (g kg^{-1})	190
pH$_w$ (1:2)	4.8
Organic Carbon (g kg^{-1})	4.8
CEC (c mol(p^{+}) kg^{-1})	11.02
Exchangable Ca(c mol (p^{+}) kg^{-1})	6.02
Mg (c mol (p^{+}) kg^{-1})	1.90
K (c mol (p^{+}) kg^{-1})	0.21
Na (c mol (p^{+}) kg^{-1})	0.49
Al (c mol (p^{+}) kg^{-1})	0.28
Total Acidity (c mol (p^{+}) kg^{-1})	0.45

Table 2 Effect of incubation time of added urea on soil pH

Days ofincubation with urea	Soil pH
1	5.13
2	5.39
3	5.55
4	5.45
5	5.40

of soils treated with different N and P (as KH_2PO_4) doses are recorded in table-3. Soil incubated for 3 days with different amounts of urea had pH varying from 4.8 to 6.8 in unlimed soil and from 6.1 to 7.1 in limed soil in $CaCl_2$ medium. The corresponding pH in KCl medium were 4.9 to 6.9 in unlimed and 6.4 to 7.3 in limed soil. The pH measured in KCl medium was more or less similar to that measured in $CaCl_2$ medium.

The equilibrium phosphate concentration as a function of added P and varying dose of urea is depicted in fig. 1 and 2. The equilibrium P concentration increased with increasing P doses, but decreased with increasing dose of urea in unlimed soil, fig.1 The difference in solution P concentrations due to N doses in limed soil were less compared to unlimed soil as may be seen from spread of the graph due to N doses.These effects upto a P dose of 200 mg kg^{-1} are similar for both limed and unlimed soils. When soil was suspended in KCl medium the equilibrium P concentration was higher at most of the levels of P and N addition as compared to the soil suspended in $CaCl_2$ medium (fig.2). These results were similar to those reported by Eze et *al*. (1990) and Rajan *et al*. (1972) that phosphate sorption was higher at higher ionic strength and in the presence of higher valent cation.

The relation of sorbed P to equilibrium P concentration (C) in most cases followed the Langmuir sorption isotherm (fig.3 and 4).The regression equations for the Langmuir isotherms shown in

Fig 1: **Effect of added P and urea-N on P concentration in (a) unlimed (b) limed soils suspended in 0.01 *M* $CaCl_2$ solution**

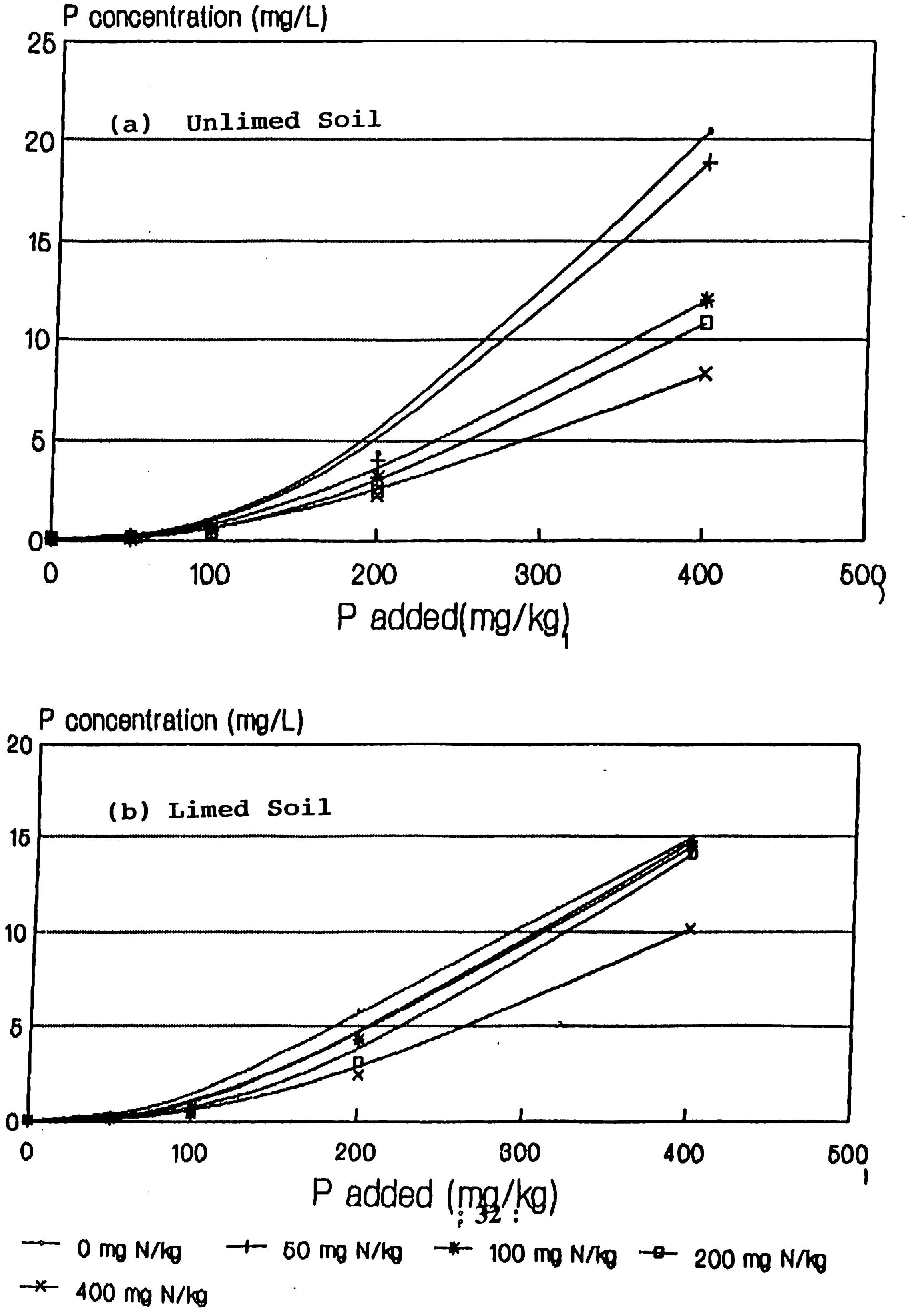

Fig 2: **Effect of added P and urea-N on P concentration in (a) unlimed (b) limed soils suspended in 0.03 *M* KCl solution**

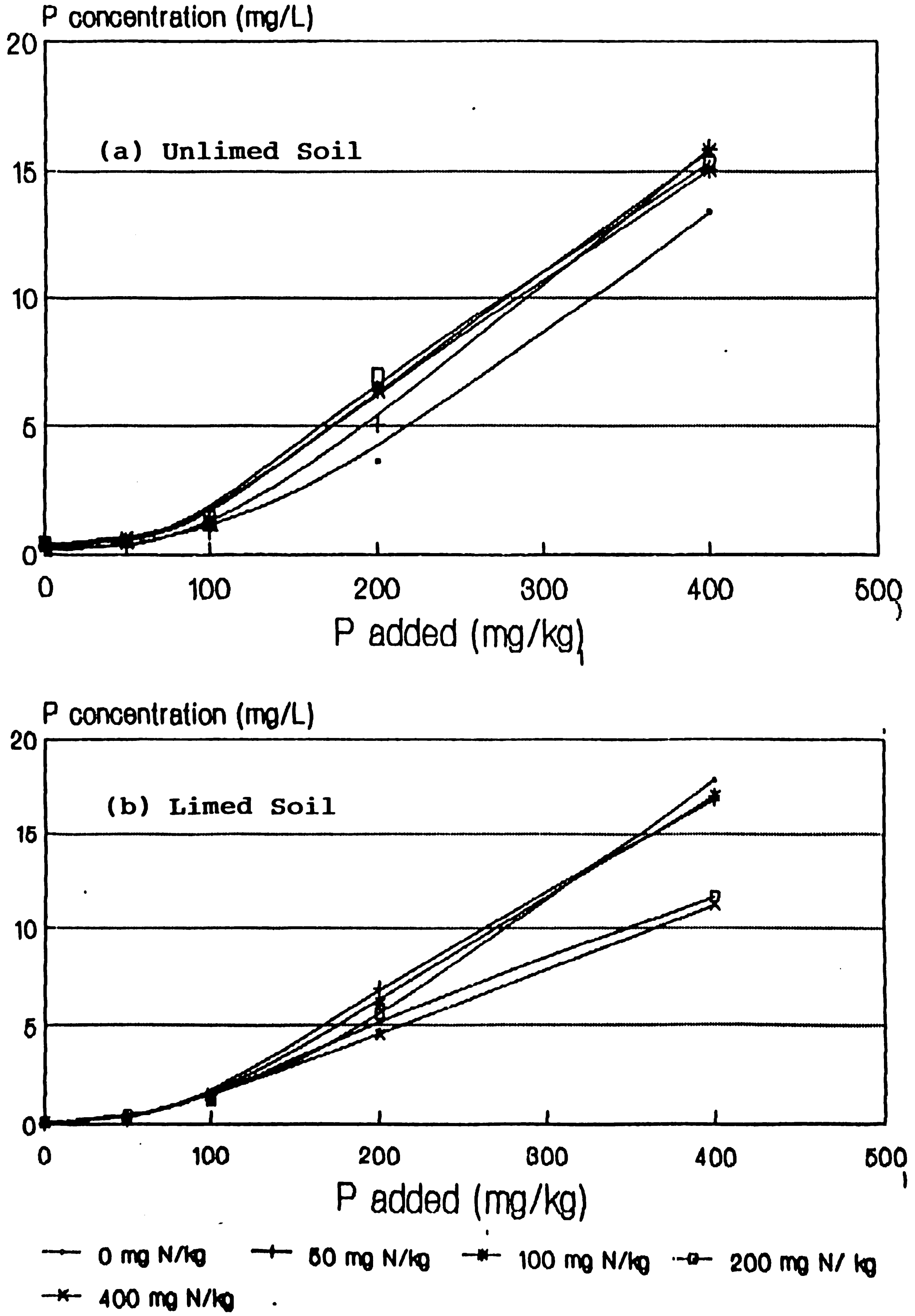

Fig 3. **Phosphate sorption ($CaCl_2$ medium) data of (a) unlimed (b) limed soils treated with urea fitted to Langmuir adsorption isotherm.**

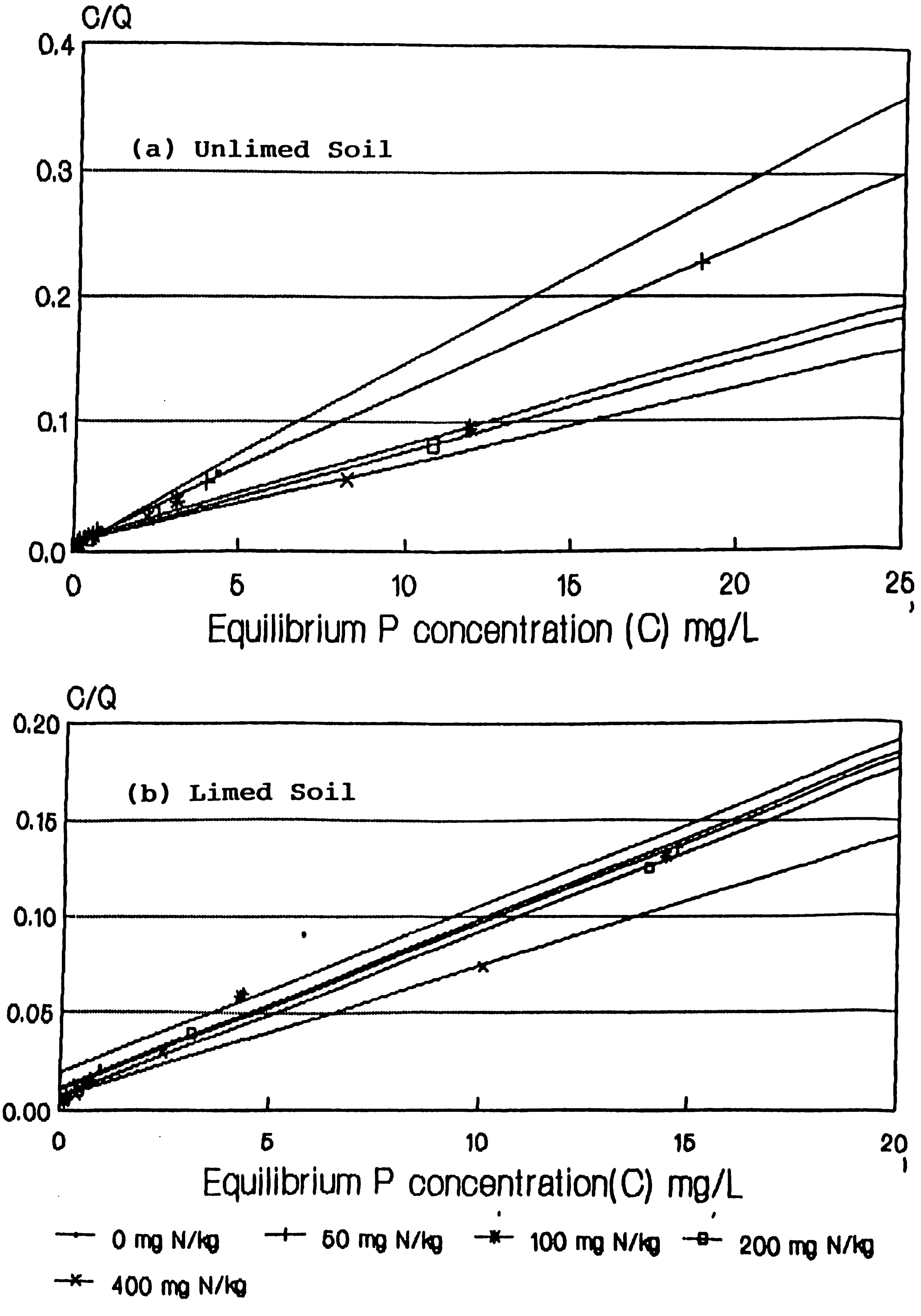

Fig 4. **Phosphate sorption (KCl medium) data of (a) unlimed (b) limed soils treated with urea fitted to Langmuir adsorption isotherm.**

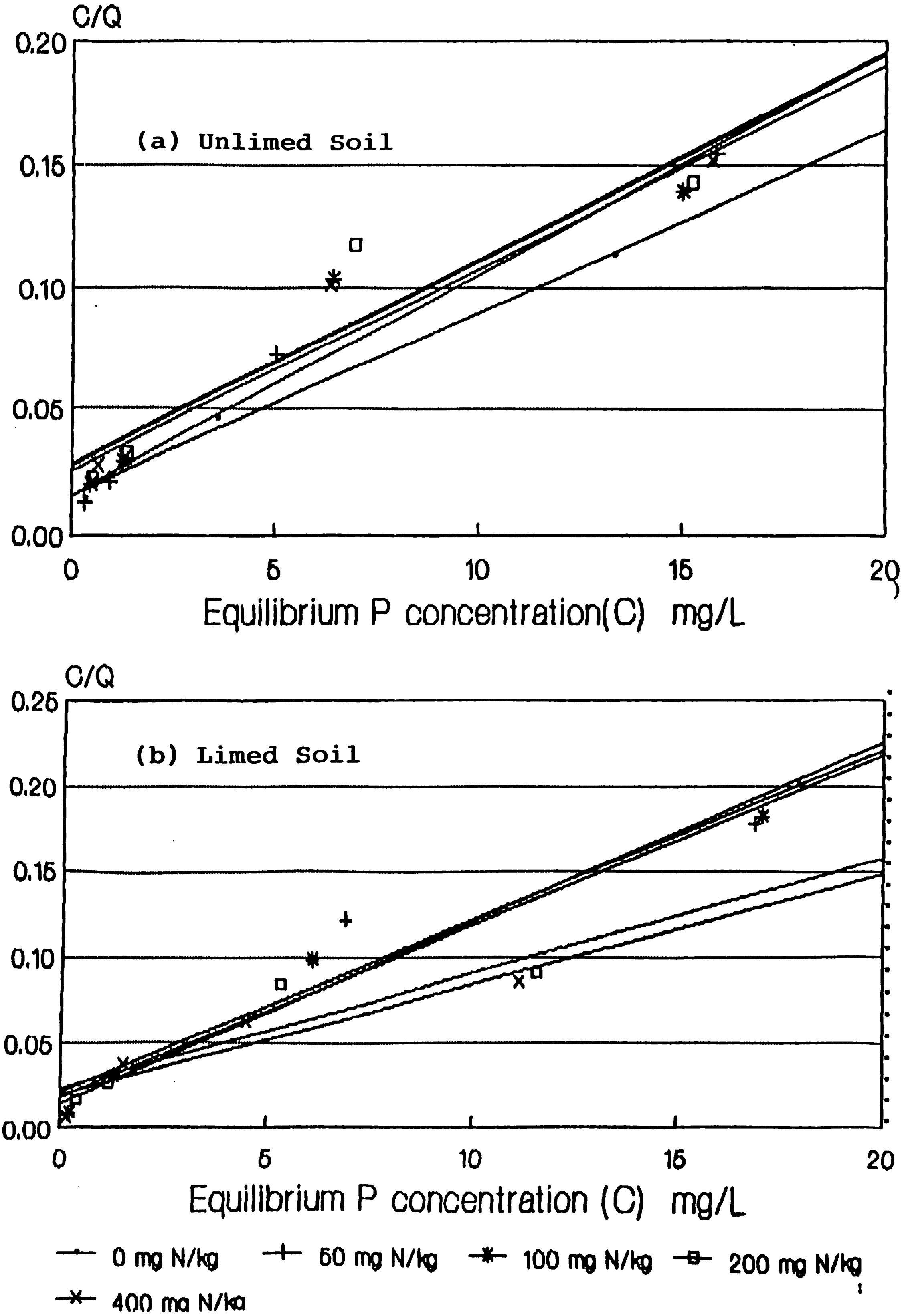

fig.3 and 4 are presented in table 4. The goodness of fit, as assessed by the coefficient of determination for the Langmuir linear plots was highly significant. The Langmuir constants, adsorption maximum (b) and bonding energy constant (k) calculated from the regression equation are given in table-5.

Maximum P sorption capacities (b) in 0.01 *M* $CaCl_2$ electrolyte increased with pH for both soils (Table-5).But in KCl medium only in limed soil the b value increased with increasing pH and N doses, but reverse was the case in unlimed soil. The range of phosphate adsorption maximum (b) observed in unlimed soil were 69.9 to 169.5 in $CaCl_2$ 133.3 to 117.6 in KCl medium. The respective ranges for limed soil were 113.6 to 147.1 and 94.3 to 156.3. The bonding energy constant (k) decreased from 4.3 to 0.7 in unlimed and increased from 0.52 to 1.21 in limed soil with increasing pH under $CaCl_2$ medium. But no such systematic trend was observed in KCl medium.

The effect of urea on solution P as a function of added P (fig.1) was significantly higher (Table-3) only for P rates of 200 mg kg^{-1} or more in both soils when $CaCl_2$ was used as electrolyte. At high dose of urea the P concentration was significantly lower as compared with the lower dose, which may be due to precipitation of phosphorus as calcium phosphate when $CaCl_2$ electrolyte was used and the soil pH was also high due to hydrolysis of urea. It is supported by the observation of White and Taylor (1977) that dicalcium phosphate precipitated at

Table :3 **Phosphate concentration (mg L^{-1}) in equilibrium extract of soil.**

P dose mg kg^{-1} soil	unlimed soil					limed soil				
N dose mg kg^{-1} soil	0	50	100	200	400	0	50	100	200	400
					($CaCl_2$ medium)					
0	0.09	0.21	0.79	4.37	20.42	0.00	0.18	0.95	5.78	14.93
50	0.08	0.18	0.70	4.04	18.85	0.00	0.16	0.71	4.36	14.71
100	0.07	0.13	0.58	3.15	11.92	0.00	0.12	0.65	4.30	13.96
200	0.07	0.10	0.45	2.46	10.80	0.00	0.13	0.44	3.13	14.02
400	0.06	0.14	0.49	2.25	8.22	0.00	0.10	0.38	2.42	10.06
	SE(m) = + 0.77 CD (0.05) = 1.53					SE(m) = + 0.45 CD(0.05) = 1.31				
					(KCl medium)					
0	0.17	0.34	1.01	3.63	13.35	0.02	0.30	1.36	4.72	17.92
50	0.25	0.32	0.95	5.04	15.85	0.02	0.20	1.29	6.90	16.87
100	0.30	0.47	1.26	6.40	15.01	0.02	0.21	1.28	6.10	17.06
200	0.41	0.52	1.39	6.94	15.26	0.03	0.38	1.14	5.53	15.43
400	0.39	0.63	1.32	6.34	15.74	0.03	0.15	1.51	4.50	16.84
	SE(m) = + (0.47) CD(0.05) = 1.37					not significant.				

Table : 4 Relationship between equilibrium P concentration (C) and C/Q where Q is the is the amount of P fixed per unit weight of soil.

N added as urea mg kg^{-1}	Unlimed Langmuir linear equation	r	Limed Langmuir linear equation	r
	$CaCl_2$ as electrolyte.			
0	$C/Q=(14.3C + 3.3)10^{-3}$	0.99*	$C/Q =(8.8C + 16.9)10^{-3}$	0.97*
50	$C/Q= (11.8C+ 6.1)10^{-3}$	0.99*	$C/Q =(8.7C + 11.2)10^{-3}$	0.99*
100	$C/Q= (7.3C + 8.9)10^{-3}$	0.99*	$C/Q= (8.6C + 10.3)10^{-3}$	0.99*
200	$C/Q = (7.0C + 6.7)10^{-3}$	0.99*	$C/Q = (8.5C + 7.0)10^{-3}$	0.99*
400	$C/Q = (5.9C +8.0)10^{-3}$	0.99*	$C/Q = (6.8C + 6.5)10^{-3}$	0.99*
	KCl	as electrolyte		
.0	$C/Q= (7.5C + 15)10^{-3}$	0.99*	$C/Q = (10.6C + 14.7)10^{-3}$	0.99*
50	$C/Q= (9.0C+ 15.2)10^{-3}$	0.99*	$C/Q= (10.0C + 21.4)10^{-3}$	0.96*
100	$C/Q= (8.3C +24.7)10^{-3}$	0.96*	$C/Q= (10.0C + 8.3)10^{-3}$	0.98*
200	$C/Q= (8.4C +27.6)10^{-3}$	0.94	$C/Q=(6.8C+ 23.1)10^{-3}$	0.91
400	$C/Q = (8.5C + 25.1)10^{-3}$	0.98*	$C/Q=(6.4C+19.9)10^{-3}$	0.93

Table: 5 Effect of added Urea on suspension pH and Langmuir parameters for unlimed and limed soil under different electrolyte medium.

		Urea as N source				
Soil	Added N	Suspension pH	Langmuir Parameters b	k	R^2	PBC(k
	mg N kg-1		mg P kg-1			mg P kg-
			0.01 *M* $CaCl_2$ as electrolyte.			
Unlimed	0	4.8	69.9	4.30	0.99*	300.6
	50	5.0	84.7	1.90	0.99*	160.9
	100	5.5	136.9	0.80	0.99*	109.5
	200	6.2	142.9	1.00	0.99*	142.9
	400	6.8	169.5	0.70	0.98*	118.6
limed	0	6.1	113.6	0.52	0.94*	59.07
	50	6.5	114.9	0.78	0.98*	89.62
	100	6.9	116.3	0.83	0.98*	96.53
	200	7.1	117.6	1.21	0.99*	142.3
	400	7.1	147.1	1.05	0.99*	154.4
			0.03 *M* KCl as electrolyte			
unlimed	0	4.9	133.3	0.50	0.99*	66.65
	50	5.6	111.1	0.59	0.99*	65.55
	100	5.8	120.5	0.34	0.91*	40.97
	200	6.0	119.0	0.30	0.88	35.70
	400	6.9	117.6	0.34	0.95*	39.98
limed	0	6.4	94.3	0.72	0.99*	67.90
	50	6.6	100.0	0.47	0.93*	47.00
	100	6.8	100.0	0.55	0.97*	55.00
	200	7.0	147.10	0.29	0.82	42.66
	400	7.3	156.30	0.32	0.86	50.00

* significant at P (0.05) level of t- test

solution P concentration of 1 m*M* in $CaCl_2$ medium and at pH less than 5.5.

The presence of calcium was associated with the apparent decrease in P concentration or increase in P sorption at high pH values, probably due to the formation of insoluble Ca-P compounds and the affinity of Ca for adsorption surfaces (Barrow 1985). Thus, Ca^{2+} concentration tend to modify the effect of added urea and pH on P sorption.

These results were similar to those reported by several workers (Fox 1986, Barrow 1979 and Naidu and Syers 1990) that precipitation of Ca-P compounds was responsible for the increase of P sorption at higher pH values, when either Ca was added in liming materials or was present in the background electrolyte. Helyar *et al.* (1976) and Smillie *et al.* (1987) suggested that Ca may play an important role in the formation of surface complexes with P.

The effect of urea on soil PBC (maximum P buffering capacity) (Table-5), calculated from P sorption isotherms (PBC= kb), also varied with soil and electrolytes. The maximum PBC of the unlimed soil decreased from 300.6 to 118.6 with pH changes from 4.8 to 6.8 in $CaCl_2$, but the decrement was not as much in KCl medium (66.65 to 35.70). In contrast, the PBC of limed soil increased from 59.07 to 154.45 in $CaCl_2$ medium whereas in KCl medium the change was not significant.

The effect of urea on P sorption was related to changes of pH and salt concentration in the soils. Regarding the effect of pH on P sorption, it is usually considered that increasing pH in acid soils may reduce the concentration of soluble and exchangeable Fe and Al ions, which otherwise could react with added P to form the sparingly soluble Fe and Al phosphates. Surface charge would become more negative with the pH changes, thus decreasing the number of P-sorption sites and reducing the strength of P sorption (Sanchez and Uehera 1980).

The increased P sorption with added urea and higher pH observed in this study may have been caused by one or more of the following reasons.

(1) As pH is increased, the concentration of $HPO_4^=$ increases at the expense of $H_2PO_4^-$. Because $HPO_4^=$ is sorbed more readily on soil surfaces, Bowden *et al.*(1980) suggested that increase in concentration of $HPO_4^=$ is sufficient to offset the decrease in electrostatic potential.

(2) Another possible explanation is precipitation of relatively insoluble Ca-P compounds, which are often formed in slightly acid to alkaline condition (White and Taylor 1977).

(3) Finally, the addition of large rates of urea can increase salt concentration in the sorption medium. At high pH, a high concentration of cations in the outer planes of adsorption can decrease the negative potential on the surface, resulting in increased P sorption (Barrow 1984).

4.1.2. Effect of N Containing Phosphatic Fertilizers:

The results of the investigation on the effect of added urea on phosphate sorption discussed above have shown that phosphate sorption increased with increasing dose of urea.

Since most of the phosphatic fertilizers available in the market are associated with some amount of N, the sorption of phosphate from the solutions of some of these fertilizers (*viz.* SSP, DAP,Gromor NPK 28:28:0, IFFCO NPK 10:26:26) were studied and compared with phosphate sorption in soil when urea was used as N source. DAP contains NH_4^+ form of N whereas, both Gromor NPK 28:28:0 and IFFCO NPK 10:26:26 contain both NH_2- and NH_4^+ form of N .

This investigation was conducted only in unlimed soil and using 0.01 *M* $CaCl_2$ electrolyte. The equilibrium P concentration as a function of added P from SSP, Gromor NPK 28:28:0, DAP and IFFCO NPK 10:26:26 (Phosphate content reported in table-6) are graphically illustrated in fig.6(a) and data presented in table-7. The difference in equilibrium P concentration due to differnt P sources were negligible and was not affected by the N present in the fertilizer.The sorption data fitted well to the Langmuir isotherm and the equations describing these isotherms and the Langmuir parameters b and k are given in table-8 and 9 respectively. The phosphate adsorption maxima(b) varied between 85.5 and 99 mg P kg^{-1} and the bonding energy constant (k) varied between 0.57 to 0.90 for all the fertilizers except Gromor. The

Table : 6 Phosphate content of the collected fertilizer samples

Fertilizer	% P_2O_5
DAP	39.6
SSP	16.0
Gromor(28:28:0)	19.6
IFFCO(10:26:26:)	22.4

Table : 7 **Phosphate concentration (mg L^{-1}) in equilibrium extract of unlimed soil treated with N containing phosphatic fertilizer and suspended in $CaCl_2$ medium.**

	P dose (mg kg^{-1} soil)				
P source	0	50	100	200	400
DAP	0.03	0.20	1.36	5.91	17.29
SSP	0.03	0.16	1.26	5.73	18.64
Gromor(28.28.0)	0.03	0.20	0.88	5.77	18.64
IFFCO (10: 26:26)	0.03	0.21	1.46	6.33	17.94

SE(m) = + 0.20
CD (0.05) = 0.59

Table: 8 Relationship between equilibrium P concentration (C) and C/Q where Q is the amount of P fixed per unit weight of soil.

Fertilizer	**Langmuir linear equation**	**r**
DAP	$C/Q = (10.1C + 17.8)\ 10^{-3}$	0.99*
SSP	$C/Q =(11.7C+13.0)10^{-3}$	0.99*
Gromor (28:28:0:)	$C/Q = (5.6C + 17.9)10^{-3}$	0.90
IFFCO (10:26:26)	$C/Q= (10.6C + 19.2)10^{-3}$	0.99*

Table- 9 : Effect of N contaning phosphatic fertilizers on Langmuir parameters in acid soil.

Added fertilizer	Langmuir Parameters b(mgPkg^{-1})	k	PBC(kb) mgPkg^{-1}
SSP	85.5	0.90	84.7
IFFCO (10:26:26)	94.3	0.55	51.9
DAP	99.0	0.57	56.4
Gromor (28:28:0)	178.6	0.31	55.4

adsorption maxima for Gromor was as high as 178.6 mg P kg^{-1} but, the bonding energy constant was 0.31 only.

4.2. PHOSPHATE DESORPTION:

As soil solution P is usually very low (0.003 to 0.5 mg L^{-1}; Sample *et al.* 1980), crops depend on the release of solid-phase P into the soil solution. Therefore, P dissolution or desorption capacities and the distribution of added P in P fractions are important.

Desorption study was conducted only on soil suspended in $CaCl_2$ medium.

4.2.1. DISTRIBUTIONS OF ADDED PHOSPHATE IN DIFFERENT P FRACTIONS:

4.2.1.1. Effect of Added Urea:

Urea application increased P sorption in both limed and unlimed soil (fig.5 and table-10). Most of the increase in sorbed P, averaged across five P rates was accounted for by increased P extracted with 0.5 *M* $NaHCO_3$ in case of limed soil. Whereas, in case of unlimed soil it was accounted for increased non-extractable P. Phosphorus extracted with 0.5 $NaHCO_3$ increased with added urea from 26.4 to 40.9 per cent of added P in case of limed soil, and in case of unlimed soil it decreased from 29.57 to 27.25 per cent.The percentage of added P which was non-extractable increased with added urea from 41.04 to 56.44 in unlimed soil, but in limed soil it was only 48.69 for N dose of 50 mg kg^{-1}, 42.09 for 400 mg kg^{-1}.

Fig5. **Effect of added urea on (a) unlimed (b) limed soil P fractions**

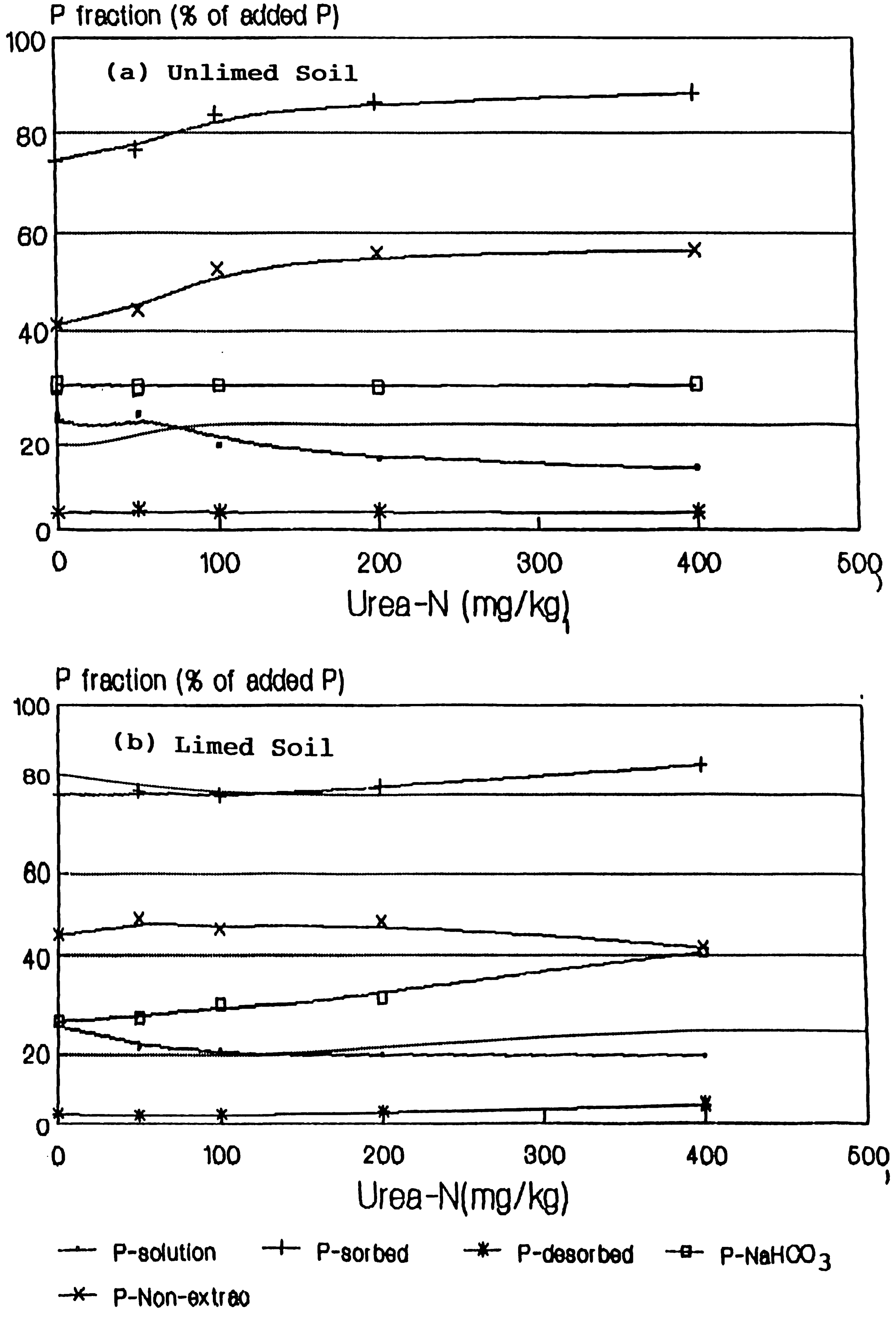

Fig6. **Equilibrium P concentration as affected by different P fertilizers added to unlimed soil suspended in 0.01 *M* $CaCl_2$ solution .**

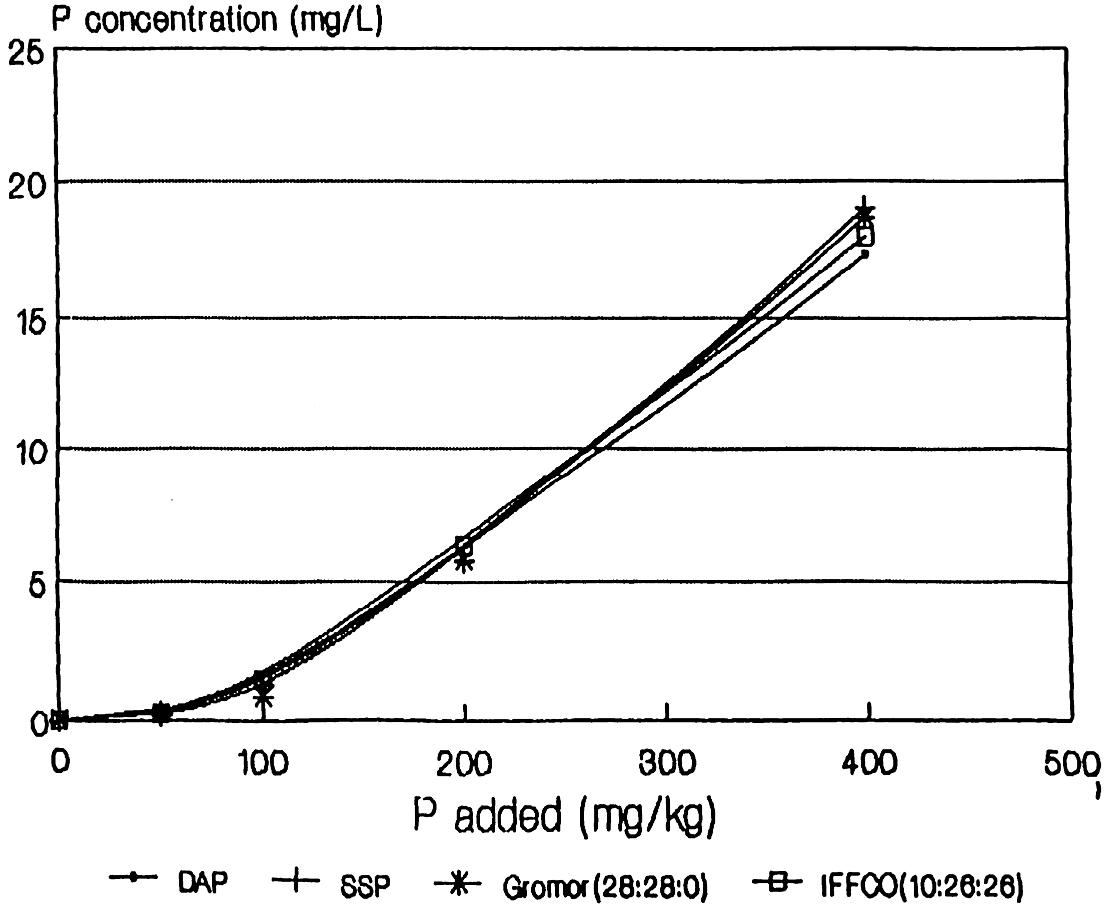

Table 10 : Average percentage of added P distributed among different P fractions.

N added (mg kg^{-1} soil)	Urea as source of N			
	CaCl$_2$ medium		KCl medium	
	unlimed	limed	unlimed	limed
a) Solution P(dP$_1$)				
0	25.51	25.70	19.40	27.27
50	23.41	21.50	22.30	29.01
100	16.04	20.80	25.09	27.94
200	13.50	18.03	25.56	23.27
400	11.64	13.30	25.70	21.04
b) Sorbed P (Ps)				
0	74.49	74.30	80.60	72.73
50	76.59	78.50	77.70	70.99
100	83.96	79.20	74.91	72.06
200	86.50	81.97	74.44	76.33
400	88.36	86.70	74.30	78.96
c) Desorbed P(dP$_d$)				
0	3.87	3.00		
50	4.91	2.56		
100	3.78	2.79		
200	3.60	3.14		
400	3.10	3.71		
d) NaHCO$_3$ - ext. P (dP$_e$)				
0	29.57	26.50		
50	27.68	27.20		
100	27.61	30.00		
200	27.25	30.50		
400	28.83	40.90		
e) Non -ext P (dP$_n$)				
0	41.04	44.81		
50	43.99	48.69		
100	52.56	46.43		
200	55.64	48.33		
400	56.44	42.09		

The P extracted by 0.5 *M* $NaHCO_3$ can be considered as labile P in soil. Although sorption increases due to urea addition, a large portion of this is extractable by $NaHCO_3$ and therefore shall be available for crop growth. But a bigger fraction of this is rendered non-extractable in acid soil under unlimed condition than limed condition. Hence, liming is beneficial.

Precipitation of Ca-P at higher pH values with more urea may have been in an amorphous form which can be more easily extracted by $NaHCO_3$. Increased extractable P with increased urea might also be related to some organic materials disslved through pH increases. In a recent study Fan *et al.* (1993) have reported that addition of urea increased the dissolution of soil organic matter which could inhibit the formation of stable Ca-phosphates, such as dicalcium phosphate and hydroxyapatite, by blocking sites for a new crystal grwoth (Grossl and Inskeep 1991).

When P fractions are averaged across both N and P doses it was found that limed soil gave more $NaHCO_3$- extractable P and retained less non-extractable P (Table-12).

Desorbed P accounted for about 3.5 per cent of the added P (Table-10, fig.5.) and was not affected by added urea. The effects of pH increase on surface charge of the sorption plane may have been offset by either the increased salt effect from urea hydrolysis or the shift of $H_2PO_4^-$ to $HPO_4^=$ thus nullifying any effects on easily desorbed P.

Table: 11 Average percentage of added P distributed among different P fractions in fertilizer treated acid soil.

P fractions	P Sources			
	Gromor (28:28:0)	DAP	SSP	IFFCO (10:26:26)
Solution P(dP_1)	27.23	27.90	28.34	29.43
Sorbed P (Ps)	72.77	72.10	71.66	70.57
Desorbed P (dP_d)	2.89	2.83	2.95	3.27
$NaHCO_3$ extractableP(dP_e)	29.81	31.96	30.66	32.38
Non extractable P(dP_n)	39.78	37.33	38.06`	34.92

Table: 12 Percentage of added P (averaged over P dose and N dose) distributed among different P fractions.

Urea as N Source

P fractions	$CaCl_2$ medium		KCl medium	
	Unlimed	limed	Unlimed	limed
Solution P (dP_1)	18.02	19.87	23.61	25.71
Sorbed P (Ps)	81.98	80.13	76.39	74.29
Desorbed P (dP_d)	3.85	3.04		
$NaHCO_3$ extractableP(dP_e)	28.19	31.02		
Non extractable P (dP_n)	49.93	46.07		

4.2.1.2. Effect of Added N in Phosphate Fertilizers:

The average percentage of added P sorbed (Table-11 and fig.7) from the four phosphatic fertilizers remained almost same (70.57 to 72.77). But 81.98 per cent of added P (as KH_2PO_4) was sorbed when urea was added as the source of N (Table-12). Percentage of added P which appeared in each of the P fractions *viz.* sorbed, desorbed, $NaHCO_3$- extractable and non-extractable remained almost same in soil treated with different P fertilizers. The available P ($NaHCO_3$- extractable) fraction was 29.81 to 32.38 per cent for phosphatic fertilizers, the highest being for IFFCO NPK 10:26:26. The corresponding recovery of available P in urea and KH_2PO_4 treated soil was 28.19 per cent only. However, this value increased to 31.02 per cent when the soil was limed.

4.3. GENERAL DISCUSSION:

The availability of P is a function of P concentration in soil solution, mobility and ability of soil to replenish the solution P as it is removed through uptake of P by crops and is significantly affected by both the amount of labile P and PBC.

The pH increase from urea hydrolysis reduced solution P and increased phosphate sorption, but also increased labile P and PBC in limed soil. Thus, at equal amounts of P extracted in soil solution, a urea treated soil would contain a greater reserve of desorbable P and thus a greater supplier of P for crops.

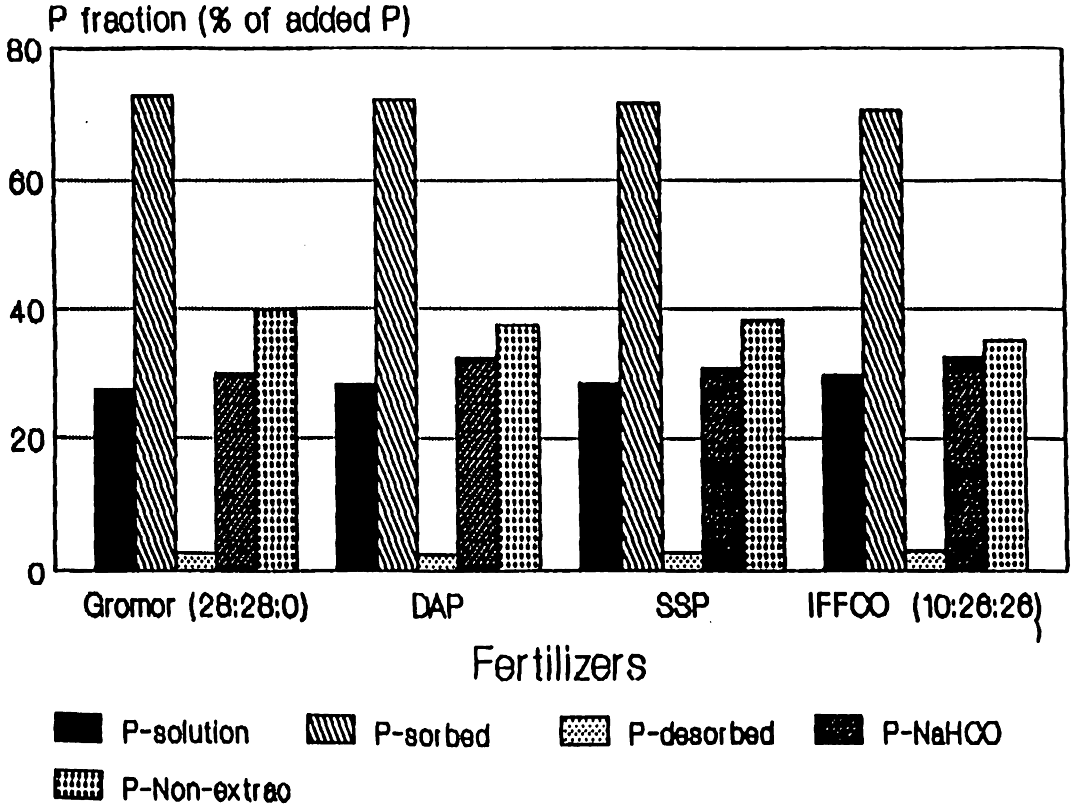

Fig.7.P fraction % of added P in fertilizer treated unlimed soil.

This also suggests that, when urea is applied with P fertilizers the pH and Ca content of soil should be considered to avoid a significant decrease in solution P. Such a decrease could be due to the increase in pH,Ca-P precipitation and any salt effect resulting from urea hydrolysis.

Like urea, addition of N through phosphatic fertilizers did not significantly influenced distribution of added P in different P fractions.

CHAPTER - V

SUMMARY AND CONCLUSION

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Among all nitrogenous fertilizers, urea is the most popular throughout the world for almost all crops. The hydrolysis of urea in soil produces temporary alkaline environment in soil which is likely to influence the sorption behaviour of added phosphate and thus influence the P availability to crop. The present investigation was aimed to study the effect of added urea on phosphate sorption and desorption in an acid soil both under limed and unlimed conditions. An acid soil of pH 4.8 collected from central farm of O.U.A.T., Bhubaneswar was limed to pH 6.2 with paper mill sludge. The soil was a sandy loam containing 4.8 g kg^{-1} organic carbon, CEC 11.02 c $mol(p^{+})$ kg^{-1}.

A preliminary investigation was carried out to find out the time required after addition of urea to attain the highest pH . It was observed that the highest pH was attained after 72 h of urea addition.

Phosphate sorption was studied by incubating both the soil with various dose of urea-N (0,50,100,200,400, mg kg^{-1}) for 3 days at field capacity and equilibrating the soil with phosphate solution suspended in 0.01 *M* $CaCl_2$ or 0.03 *M* KCl. Different background electrolyte was used to know whether there is any effect of Ca^{2+} and K^{+} on the sorption or not.

Four fertilizer samples as DAP, SSP, IFFCO NPK 10:26:26, Gromor NPK 28:28:0 collected from the market were also used in phosphate sorption study. These P fertilizers except SSP, also contain N in varying amounts and forms. To know the effect of N content of these fertilizers on P availability, P sorption was also conducted only in acid soil with background electrolyte being $CaCl_2$

The residual soil after phosphate sorption was used for desorption study. Phosphate desorption study was carried out in both soils, but only in $CaCl_2$ medium for urea incubated soil. The residual soil from sorption study was sequentially extracted, first by 0.01 *M* $CaCl_2$ (which was recorded as desorbed P) and then by 0.5 *M* $NaHCO_3$ ($NaHCO_3$ - extractable P, otherwise available P). The non-extractable P fraction of the sorbed P was calculated from the difference.

The equilibrium phosphate concentration and pH of the extract, as a function of added P at various urea-N levels have been recorded. The pH increased from 4.8 to 6.8 at 0 mg N kg^{-1} and 400 mg N kg^{-1} in unlimed soil and from 6.1 to 7.1 in limed soil in $CaCl_2$ medium. Similar increase in pH was also observed when KCl was used as background electrolyte.

The equilibrium P concentrations increased with increasing P doses, but decreased with increasing dose of urea in unlimed soil. Upto 200 mg N kg^{-1} the effects were same for both limed and unlimed soil. The phosphate sorption was higher in $CaCl_2$ medium than in KCl medium.

In most of the cases the relation of sorbed P to equilibrium P concentration followed Langmuir isotherm.The adsorption maximum (b) in 0.01 *M* $CaCl_2$ increased with pH for both soils .But in KCl medium only in limed soil the b value increased with increasing pH and N doses, but reverse was the case in unlimed soil.

THe bonding energy constant (k) decreased in unlimed soil and increased in limed soil with increasing pH under $CaCl_2$ medium. But no such systematic trend was observed in KCl medium. At high dose of urea the P concentration was significantly lower as compared to the lower dose, which may be due to precipitation of phosphorus as calcium phosphate when $CaCl_2$ electrolyte was the background electrolyte.

The maximum P buffering capacity (PBC) in unlimed soil decreased with increasing pH in $CaCl_2$,but the decrement was not as much in KCl medium.In contrast, the PBC of limed soil increased in $CaCl_2$ medium whereas in KCl medium the change was not significant.

The increased P sorption with added urea and high pH observed may have been caused by one or more of the following reasons.

a) With increase in pH the concentration of $HPO_4^=$ increases at the expense of $H_2PO_4^-$ and $HPO_4^=$ is more readily sorbed on soil surfaces.

b) Precipitation of relatively insoluble Ca-P compounds favoured by presence of $CaCl_2$ background electrolyte and increased pH due to urea hydrolysis.

c) Addition of large rates of urea can increase salt concentration in sorption medium. At high pH, a high concentration of cations in the outer planes of adsorption can decrease the negative potential on the surface,resulting in increased P sorption.

The difference in equililibrium P concentration due to different P fertilizer sources were negligible and was not affected by the varying amount and form of N present in them. The sorption data fitted well to the Langmuir isotherm. Adsorption maximum (b) varied between 85.5 and 99 mg P kg^{-1} and bonding energy constant (k) varied between 0.57 to 0.90 for all the fertilizer except Gromor for which the b value was 178.6 and K was 0.31 only.

The increased P sorption due to urea application was accounted for by increased $NaHCO_3$-extractable P in limed soil whereas in unlimed soil it was accounted for by increased non-extractable P.

The $NaHCO_3$-extractable P can be considered as labile P in soil. Although sorption increases due to urea addition, a large portion of this is extractable by $NaHCO_3$ and therefore shall be available for crop growth.But a bigger fraction of this is rendered non-extractable in acid soil under unlimed condition than limed condition. Hence liming is beneficial.

The phosphate sorption was higher in presence of urea than the N present in P fertilizers used in the study. The P-sorbed, P-desorbed, P-$NaHCO_3$ extractable, P-non-extractable remained more or less same in soil treated with different P fertilizers. Among the four fertilizers taken, IFFCO NPK 10:26:26: showed highest value of $NaHCO_3$-extractable P. Even this value is also low in case of urea and KH_2PO_4 treated soil.

From the results of the investigation summarised above, the following conclusions may be drawn.

CONCLUSIONS

1. The pH increase from urea hydrolysis reduced solution P and increased phosphate sorption. A urea treated soil contained a greater reserve of desorbable P (labile P) available for crop. Limed soil treated with urea had a larger reserve of labile P.
2. When urea is applied with P fertilizers the pH and Ca content of the soil be considered to avoid a significant decrease in solution P. Such a decrease could be due to the increase in pH, Ca-P precipitation and any salt effect resulting from urea hydrolysis.
3. Like urea, addition of N through phosphatic fertilizers did not significantly influenced distribution of added P in different P fractions.

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