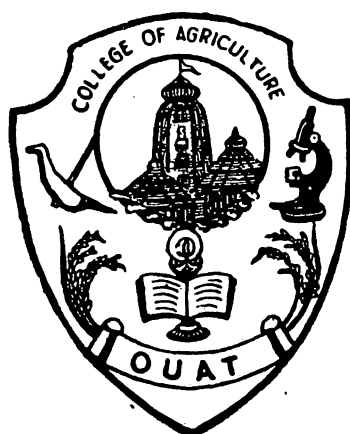# PHOSPHATE ROCK DISSOLUTION AND AVAILABILITY IN AN ACID SOIL

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 & Biochemistry)

By

Biswajit Nanda

Department of Agricultural Chemistry, Soil Science & Biochemistry
COLLEGE OF AGRICULTURE
Orissa University of Agriculture and Technology
BHUBANESWAR
1992

THESIS ADVISOR :   Dr. U. K. MISRA

Dedicated to
my
Beloved Parents

PHOSPHATE ROCK DISSOLUTION AND
AVAILABILITY IN AN ACID SOIL.

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)

1992

BY
BISWAJIT NANDA

APPROVED BY :   CHAIRMAN   DR.U.K.MISRA

MEMBERS   1. DR.S.K.SAHU

2.DR.N.C.SAHOO

EXTERNAL EXAMINER

Dr.U.K.MISRA
M.Sc.Ag.(OUAT),Grad. Dip.(New South Wales),Ph.D.(Missouri)
Reader, Department of Agricultural Chemistry,
Soil Science and Biochemistry
Orissa University of Agriculture & Technology
College of Agriculture, Bhubaneswar - 751 003.

Bhubaneswar
June 22, 1993.

C E R T I F I C A T E

Certified that the thesis entitled " PHOSPHATE ROCK DISSOLUTION AND AVAILABILTY IN AN ACID SOIL " submitted in partial fulfilment of the requirements for the award of the degree of MASTER OF SCIENCE IN AGRICULTURE (AGRICULTURAL CHEMISTRTY, SOIL SCIENCE AND BIOCHEMISTRY) submitted to the Orissa University of Agriculture and Technology, Bhubaneswar, is a faithful record of bona fide research work carried out by Sri Biswajit Nanda under my guidance and supervision during the academic year, 1992. No part of this thesis has been submitted for the award of any other degree or diploma. It is further certified that all possible help or sources of information availed during the course of investigation have been duly acknowledged by him.

(U.K.Misra)

A C K N O W L E D G E M E N T

Availing this unique opportunity, I wish to express my deep sense of gratitude and indebtedness to Dr.U.K.Misra, Reader, Deptt. of Agricultural Chemistry, Soil Science and Bio Chemistry, OUAT, Bhubaneswar, the Chairman of my advisory committee for his scholastic guidance, prudent suggestions, constructive criticism and ceaseless encouragement throughout the course of this investigation and preparation of this manuscript.

I owe a deep sense of reverence to the members of the advisory committee ; Dr.S.K.Sahu, Reader and Head, Deptt. of Agricultural Chemistry, Soil Science and Biochemistry and Dr.N.C.Sahoo, Lecturer, Deptt. of Plant Physiology for their precious advice and encouragement.

I wish to express my heartfelt thanks to Dr.C.Misra, Dr.G.N.Mitra, Dr.N.Acharya, Dr.G.C.Sahoo, Dr.D.Sahu, Mr.P.K.Das, Mr.R.K.Patro and Mr.S.K.Pattnayak for their noble advice and imense help as and when required during my investigation.

It is my great pleasure to thank Khitu Bhai, Birendra Bhai, Padhihari, Samal, Rabeya, Jitu, Vedabandhu, Nayak Babu, Chitta, Manoj and all my friends and well wishers who have helped me during preparation of this manuscript.

I express my heartful devotion and foremost indebtedness to my beloved parents whose blessings, inspiration, sacrifice and eternal benedictions have always a source of moral strength for me in developiung this tiny personality. I still pray their blessings to proceed on the way of life.

Last but not the least, I bow down my head before "The Almighty", whose blessings contributed solely to reach this point.

Bhubaneswar
June 22, 1993.

Biswajit Nanda
(BISWAJIT NANDA)

Phosphate Rock Dissolution and Availability in an acid soil

Student : B.Nanda   Chairman: Dr.U.K.Misra

A B S T R A C T

Dissolution and P release pattern of six Indian phosphate rocks namely Kasipatanam, Hirapur, Mussoorie, Udaipur, Maton and Purulia and two imported phosphate rocks from North Carolina and Jordan were studied in a laboratory incubation experiment and in a field trial laid on an acid soil treated with different P sources including SSP at the rate of 100kg P/ha and cropped with hybrid napier grass.

Dissolution of rock phosphates in unlimed (pH 5.6) and limed (pH 6.5) soil attained equilibrium at 45 days of incubation without complete dissolution, whereas in cropped field in presence of leaching and root uptake of Calcium and Phosphate from the site of the reaction higher dissolution was achieved. The dissolution of rock phosphates from Jordan and North Carolina was higher than all the Indian phosphate rocks. Although more P was released at pH 5.6 than at pH 6.5 from a given rock, the amount of P solubilised from NCRP and JRP at pH 6.5 was higher than the amount of P solubilised from any of the Indian phosphate rocks at pH 5.6. Among the Indian rock phosphates MRP(Mussoorie) and HRP(Hirapur) showed higher dissolution.

The availability of P from rock phosphates was related to their dissolution in soil which in turn was related to the crystal chemical parameters of the apatite. The relative agronomic efficiency of different P sources (rock phosphates & SSP) were Jordan(145) > North Carolina(125) > SSP(100) > Mussoorie(93) > Hirapur(76) > Purulia(59) = Maton(57) = Kasipatanam(52) > Udaipur(33).

The residual effect of rock phosphates increased and SSP decreased with time. Rock phosphates from Jordan and North Carolina proved to be better sources than SSP and all other Indian phosphate rocks.

Although Ca and P uptake by crop positively influenced crop yield, Ca uptake was not related to the total amount of Ca added through rock phosphates but to the dissolution of apatite in the rock.

The inorganic P forms to which applied P was transformed was mainly Al-P followed by occluded-P, Fe-P and Saloid-P. The major contribution to available P pool of soil determined by Bray's-I and Olsen's methods was from Al-P, Fe-P, Saloid-P. The crop yield was positively related to the available P determined by both the methods and hence any of the two methods can be used to predict the available P contect rock phosphate treated soil.

C O N T E N T S

APPENDIX

LIST OF TABLES

APPENDIX TABLES

LIST OF FIGURES

CHAPTER-I

INTRODUCTION

INTRODUCTION

Phosphorus plays a pivotal role in boosting and sustaining crop productivity particularly under intensive cropping systems. The dynamics of Phosphorus transformation in soil system and its availability to crops have been the subject of numerous research investigations. The work on phosphate nutrition of plants carried out in India and abroad suggest that about 15-25% of the applied phosphate is only utilised by the crops. The applied water soluble phosphatic fertilisers are likely to undergo transformation in the soil into relatively less available form. In this context, application of insoluble phosphatic fertiliser like Rock phosphate to acid soil provides greater scope to improve the efficiency of utilisation of applied phosphorus by crops.

Phosphatic rock and apatite are referred to microcrystalline calcium fluro apatite of sedimentary origin and macrocrystalline fluro apatite of igneous origin respectively. Both the forms of phosphatic rocks are chiefly composed of insoluble P, a part of which is citrate soluble. Rock phosphate of sedimentary origin are generally found to be more reactive and suitable for providing phosphorus directly to the plants when applied in powder form in soils with low pH.

In India nearly one third of the cultivated land is under acid soils. A large part of Orissa is also covered with acidic red and lateritic soil having low available phosphorus

1

content and very high phosphorus fixing capacity. Use of water soluble sources of phosphate in these soils is highly constrained because of high fixation and less availablity of P to crops. Consequently P becomes the chief limiting nutrient in acid soils. Powdered rock phosphate, however, can be effectively used to combat the problem of P fixation in acid soil and to increase P availability to crops. Plants derive phosphate from these relatively less soluble phosphate carriers after they undergo a process of dissolution or solublization in acid soil.

Minerological explorations by the Geological Survey of India have discovered extensive reserves of rock phosphate in various regions of India. India's present rock phosphate reserve is estimated at about 260 million tonnes of which only 30 million tones are rated as high grade. Benefication of low grade rock being expensive, direct use of ground rock phosphate in acid soil is desirable.

In the present agricultural scenario, hike in price of phosphatic fertilisers like SSP and DAP have severely curtailed the use of these costly phosphatic fertiliser. Thus these phosphatic fertilisers can be completely or partly substituted by rock phosphates which are cheap and easily available. Rock phosphates can serve as the most efficient phosphatic fertiliser for acid soils, particularly for long duration or perennial crops which can take full advantage of slow and continuous dissolution of rock phosphate for a longer period.

A large number of experiments conducted in India and

elsewhere have evidently proved the usefulness of ground rock phosphate as a direct fertiliser for acid soils.

In the present study attempts have been made to evalute the fertiliser value of two phosphate rocks imported from Jordan and North Carolina and six indegeneous rock phosphates collected from the mines at Mussoorie, Udaipur, Maton, Hirapur, Kasipatnam and Purulia as compared to single super phosphate.

The objectives of the present investigation were :

1. To determine the relative agronomic effectiveness of different sources of rock phosphates as compared to single super phosphate (SSP) for growing hybrid napier grass on an acid soil.

2. To compare the direct and residual effect of different rock phosphates with that of SSP.

3. To determine the percentage dissolution of rock phosphates both in laboratory incubation study (closed system) and in cropped field condition (open leaching system in presence of rhizosphere).

4. To study the transformation of P applied as rock phosphates and SSP into different inorganic phosphate^{o} fractions in soil and to relate these fraction to the available phosphate pool extracted by Bray's - 1, and Olsen's method.

CHAPTER-II

REVIEW OF LITERATURE

REVIEW OF LITERATURE

Phosphorus has been regarded as the principal cause for low productivity in acid soils of India. Due to high P fixing capacity of acid soils the efficiency of applied soluble P carriers is very low in these soils. Supply of P in adequate amount is essential for achieving higher yield in all crops. Due to the present hike in the price of phosphatic fertilisers, farmers cannot afford to use costly phosphatic fertilisers like SSP and DAP. Therefore low grade ground rock phosphate which is relatively less expensive can be profitably used in acidic soils. The rock phosphate deposits are estimated to be about 260 million tonnes in India. So it is for the soil scientists and fertiliser technologists to work out the ways and means for increasing the efficiency of rock phosphate in soil, by providing the soil conditions most conducive for maximum dissolution of rock phosphate in soil.

Fertiliser Value of Rock Phosphates and their Residual Effect in Soil

Raheja and Bains (1960) opined that in general the residual effect of P depends upon the factors, total amount of P applied, time and frequency of application, physical and chemical properties of soil, sources of phosphate used, weather conditions and the succeeding crop.

Motsara and Dutta (1971) reported that for all crops the rock phosphate had higher residual effect than · super

phosphate. Sanchez et al. (1978) in a field experiment in acidic soil, applying TSP, basic slag and rock phosphate for a ground nut crop taken for two successive years found that, superphosphate and basic slag provided higher yield in first year, but residual P concentration in soil two years after fetiliser application was greater from rock phosphate followed by basic slag and TSP.

Marwaha et al. (1981) in a two year field experiment with wheat and maize found that finely ground (100 mesh) Mussoorie rock phosphate was significantly inferior to superphosphate in its direct as well as residual effect, when compared on the basis of equal P. The efficiency of Mussoorie rock phosphate however improved greately at higher levels and when time of application was advanced. The residual effect of Mussoorie rock phosphate measured by yield and total P uptake on succeeding crop of maize, however was higher than direct effect.

Debnath and Basak (1984) in a two year field experiment in acid-laterite soil in rice-wheat-green gram, cropping found that neither Purulia rock phosphate nor Mussoorie rock phosphate was effective in increasing yield and P uptake by wetland rice grown as the first crop, but green gram responded favourably, which is the second crop. Mussoorie rock phosphate and Purulia rock phosphate were as effective as super phosphate.

Mitra and Misra (1991) conducting field trial for 3 years in paddy-groundnut cropping system for evaluation of Udaipur rock phosphate as a phosphatic fertiliser in soils of

Orissa, reported that the residual effect of (1:1) mixture of URP + SSP was significantly higher than SSP alone with respect to dry matter yield and P uptake. The difference in yield between rock phosphate treatment and SSP of the second crop is narrow as compared to the first crop indicating better residual effect of rock phosphate.

Singh et al. (1965) conducted experiments on a soil of pH 6.8 growing Lucern as fodder crop with Udaipur, Mussoorie rock phosphate and also super phosphate at application rates of 60, 120, 180 Kg P_2O_5 /ha. The percentage efficiencies of Mussoorie and Udaipur rock phosphates as compared to superphosphate were 78 and 54 respectively. The availability coefficient ratio (ACR) of these rock phosphates were 0.60 for Udaipur and 0.75 for Mussoorie rock phosphate. Taking ACR as a criterion, the residual effect of the two Indian rock phosphate was arranged in order of MRP > URP.

Marwaha (1986) in a 4 year study with wheat and soybean grown in rotation in a clay loam acid Alfisol found Mussoorie rock phosphate to be an efficient phosphate carrier. A single heavy dose of application through MRP once in 3 to 4 years to the first crop of the rotation was found to be superior to frequent application of smaller doses of P, when adjusted in terms of relative agronomic efficiency and total P uptake. Residual effect of rock phosphate was greater than super phosphate which become especially marked after 2-3 years of application.

In a three year field experiment Aspiolea et al. (1979)

compared single and triple super phosphates (100-300 Kg/ha/yr) and ground rock phosphate (200-600 Kg/ha/yr) as phosphatic fertiliser for irrigated _Digitaria_ _decumbens_ pasture. They found (i) highest dry matter yield and P uptake with SSP, (ii) increasing P application did not increase yield, (iii) the percentage recovery of fertiliser P was greatest in SSP treatments and rose with time. Soil reserves at the end of the experiment was greatest in rock phosphate treatment.

Alfanso et al. (1981) studying the effect of rock phosphate on the growth of _Panicum_ _maximum_ reported that greatest dry matter yield and P uptake were obtained with SSP and smallest with local rock phosphate until the sixth cut when differences between the phosphorus sources disappeared. Available phosphate reserves in the soil were raised as a result of local rock phosphate being most effective and super phosphate least.

Dash et al. (1988) have tried to evaluate crop factors by growing rice and Dhanicha on acid soils. In these studies the phosphate rocks were primed under moist aerobic soil condition before growing rice. They found that Indian phosphate rocks though gave slightly higher dry matter production than control, the yields were as poor as control compared to Jordan, Gafsa and North Carolina phosphate rocks, whose yields were comparable to that of super phosphate.

Experimemnt conducted by North Carolina State University (NCSU) in 1967-68 showed that under their field condition on an acid organic soil, North Carolina reactive

7

phosphate rock was as effective as super phosphate at the same rate of P application for both maize and soybean (Barnes and Kamprath, 1975). In 1970, NCSU again compared NCRP with superphosphate on a different acid soil and observed that the effectiveness was equal to that of super phosphate, when measured by wheat response (Barnes and Kamprath, 1975).

Sahu et al. (1974) evaluated the efficiency of six imported and one indigenous rock phosphate for rice crop in acid laterite soil in Kharif and summer seasons. They found that North Carolina rock phosphate (24.9% P_2O_5) and Udaipur rock phosphate (36.9% P_2O_5) were effective next to super phosphate. Super phosphate showed better residual effect than all forms of rock phosphates on second crop. However all the rock phosphates gave higher yield of second crop than no phosphate control.

Haundel et al. (1988) reported that Mussoorie rock phosphate was 50 and 61% as efficient as SSP for gram and Lentil respectively.

Mathur et al. (1989) reported that on unlimed soil Mussoorie rock phosphate performed significantly better than SSP. It increased crop yields of barley and soybean, raised soil pH and increased available P content. Mussoorie rock phosphate's residual effect increased with time while that of SSP decreased.

Dwivedi et al. (1989) reported that performance of MRP in an acid soil of U.P., Himalaya under maize-wheat and soybean-wheat cropping sequence was always superior to SSP regarding increased crop yield and phosphate availability irrespective of

lime in direct as well as residual effect.

Panda and Panda (1969) from the pot experiment raising 3 crops of paddy concluded that rock phosphate from United Arab Republic was more efficient than Mussoorie and much superior to Singhbhum rock phosphate in acid laterite soils of Orissa.

Mathur and Suresh Lal(1989) from a three years of field experiment laid out on acidic soils of Chotnagpur revealed that the yield of ground nut and gram at 50 Kg P_2O_5 ha^{-1} and soybean and pea at 150 Kg P_2O_5 ha^{-1} level as igneous rock phosphate (RP) were at part with 50 Kg P_2O_5 as single Super Phosphate (SSP). SSP was a better source of P for wheat, but RP was a better source of P for maize. P concentration in grains of crops at 150 and 50 Kg P_2O_5 ha^{-1} as RP and SSP was at par with each other. P utilisation from SSP and RP varied from 5.1 to 15.7% and 2.2 to 4.0% respectively. Ca concentration increased with increasing levels of Rock phosphate and was more in RP than in SSP treated soils thereby showing the superiority of RP over SSP in supplying Ca to the plants.

Sinclair, Johnstone, O'Connous and Smith (1989) through trials on grass or clover pasture reported that in terms of pasture dry matter production Sechura Phosphate Rock (SPR) was inferior to Triple Super Phosphate (TSP) initially. But averaged over all sites its relative performance continued to improve throughout a 6 year period. In 6th year SPR out yielded TSP in each application rate. Over the 6 year period, cumulative dry matter yield from SPR was generally as high as that of TSP. The

lime in direct as well as residual effect.

Panda and Panda (1969) from the pot experiment raising 3 crops of paddy concluded that rock phosphate from United Arab Republic was more efficient than Mussoorie and much superior to Singhbhum rock phosphate in acid laterite soils of Orissa.

Mathur and Suresh Lal(1989) from a three years of field experiment laid out on acidic soils of Chotnagpur revealed that the yield of ground nut and gram at 50 Kg P_2O_5 ha^{-1} and soybean and pea at 150 Kg P_2O_5 ha^{-1} level as igneous rock phosphate (RP) were at part with 50 Kg P_2O_5 as single Super Phosphate (SSP). SSP was a better source of P for wheat, but RP was a better source of P for maize. P concentration in grains of crops at 150 and 50 Kg P_2O_5 ha^{-1} as RP and SSP was at par with each other. P utilisation from SSP and RP varied from 5.1 to 15.7% and 2.2 to 4.0% respectively. Ca concentration increased with increasing levels of Rock phosphate and was more in RP than in SSP treated soils thereby showing the superiority of RP over SSP in supplying Ca to the plants.

Sinclair, Johnstone, O'Connous and Smith (1989) through trials on grass or clover pasture reported that in terms of pasture dry matter production Sechura Phosphate Rock (SPR) was inferior to Triple Super Phosphate (TSP) initially. But averaged over all sites its relative performance continued to improve throughout a 6 year period. In 6th year SPR out yielded TSP in each application rate. Over the 6 year period, cumulative dry matter yield from SPR was generally as high as that of TSP. The

excellent long term performance of SPR and relatively low cost of reactive rock phosphate could serve as an improved fertiliser for perennial pastures.

Chien et al. (1987) in a long term field experiment observed that there was a a net loss of 20 to 30% of Ca dissolved from the PR, as dissolved calcium was susceptible to leaching. He also observed that amount of Ca remaining after a period of PR application was comparatively lower than that of P, which was attributed both to crop uptake and leaching losses of Ca from the soil.

DISSOLUTION OF ROCK PHOSPHATE IN ACID SOIL

Once a rock phosphate is applied to an acid soil, it undergo slow and continuous process of dissolution by the action of soil acidity, releasing available phosphate ions, which move directly through soil solution to the root of the crop plant, where it is absorbed. A portion of the phosphorus released from the phosphate rock may disappear temporarily into solid phase of the soil, reappearing in soilution at a later time to be absorbed by plants.

The insoluble P, in rock phosphate is solubilised by action of soil acidity. The hydrgen ions are furnished principally by the hydrolysis of Al^{+3}, the amount of Fe and Al phosphates formed would be expected to depend on the relative quantities of active Al and Fe present in the soil. In all the experiments a definite relationship exist between soil acidity and iron content in one hand and parent rock decomposed and Fe

phosphate : Al phosphate ratio in the other hand. Another factor is the increase Fe phosphate: Al phosphate ratio with time. This would be expected from relative solubilities of Fe and Al phosphates.

Ellis $\underline{et}$ $\underline{al.}$ (1955) suggested that soil acidity has a marked influence on availability of P from rock phosphate. The availability increases as the pH is lowered. Rock phosphate is decomposed by the action of acid to form monocalcium phosphate and other soluble compounds. Once $H_2PO_4^-$ ions are furnised their fate depend on soil environment.

$$Ca_3(PO_4)_2 + 4H^+ \longrightarrow 2 H_2PO_4^- + 3 Ca^{++}$$
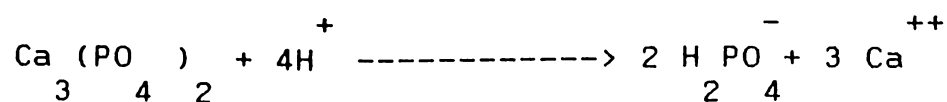
Hsu and Jackson (1960) have stressed the importance of pH in the formation of Fe and Al phosphates in acid soils. In acid soils, one would expect the reaction to be either of the following two.

$$H_2PO_4^- + 2 OH^- + Al^{+3} \longrightarrow Al(OH)_2 . H_2PO_4$$

$$H_2PO_4^- + 2 OH^- + Fe^{+3} \longrightarrow Fe(OH)_2 . H_2PO_4$$
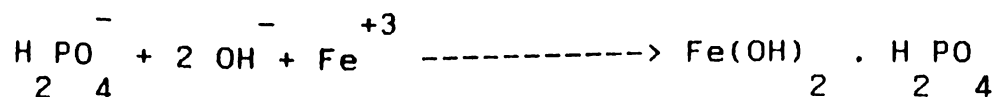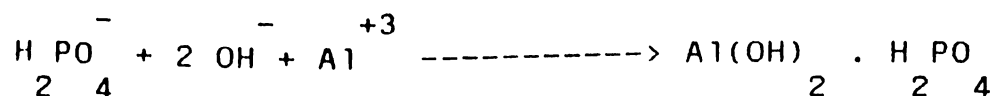
The above reaction may occur with Al^{+3} and Fe^{+3} in solution. They also may occur with adsorbed oxides or hydroxides of Al^{+3} and Fe^{+3}. In the first instance the $H_2PO_4^-$ ions are precipitated, while in the second case they may be regarded as adsorbed. Both types of reactions apparently occur in acid soils, but in more weathered soils the amounts of adsorbed Al and Fe

11

compounds are vastly higher than the quantities of Al^{+3} and Fe^{+3} in solution. Thus most phosphate is adsorbed in such soils. Jackson (1962) has suggested that the final product formed has about the same properties whether precipitated or adsorbed.

Soil pH has been identified as the most important soil factor influencing availability of P from rock phosphate (Ellis et al., 1955; Peaslee et al., 1962; Barnes and Kamprath, 1975). Availability of P from rock phosphate increases as the pH is lowered. Joos and Black (1951) reported that the availability of P from rock phosphate was considerable at a pH range of 4.6 to 5.6 but low at pH 6.6.

Chu et al. (1962) opined that transformation of rock phosphate both into Al and Fe phosphate fractions in soil decreased with increasing pH. The relationship between the pH and Al-phosphate was same for all soil studies, whereas the amount of Fe-phosphate formed varied both with pH and free iron content in soil. From these relationship it appearss that soils which respond well to rock phosphate application are those with low pH and relatively low iron content.

Wright et al. (1991) by conducting an incubation study on effect of dissolution of North Carolina Rock Phosphate on soil chemical properties and wheat seedling root elongation, reported that root length was significantly increased by RP treatment indicating that RP dissolution counteracted soil acidity, increase soil pH, exchangeable calcium and soil solution calcium, while lowering exchangeable aluminium by releasing aluminium

12

complexing ions into soil solution. Thus dissolution of NCRP changed the aluminium concentration from toxic to nontoxic form and contributed to ameliorate soil acidity.

Khasawneh and Doll (1978) reported that Ca is one of the products in phosphate rock dissolution in acid soils which is released in amount proportional to the rate of P released. The dissolved P undergo transformation while Ca remain as an exchangeable cation in soil solution, affecting the rate of dissolution of phosphate rocks. They observed that phosphate rock dissolution was greater when soil Ca level was low.

Sarangnath et al. (1977) studied ^{32}P tracer on the methods of increasing the efficiency of soluble and insoluble phosphates for rice in acid soils. They found that a considerable amount of applied phosphates even from DCP were converted to Al-P and Fe-P due to gradual dissolution by the H^+ ions of the system resulting in increased Olsen's and Bray's P. Dry matter production of rice and utilisation of applied P was found to be higher when the P carriers were applied to moist acid soils two weeks before flooding than when those were applied at flooding.

Rajan et al. (1991) from a field experiment evaluated the agronomic effectiveness of a reactive Peruvian phosphate rock relative to that of monocalcium phosphate (MCP) at different levels of soil pH and rates of fertiliser application. They found that in MCP plots P in soil solution decreased sharply with time especially at low pH and high rates of fertiliser application. In plots which received phosphate rocks, the concentration of P

either did not increase with time or increased slightly as compared to the P concentration observed one month after application. In both MCP and phosphate rock treated plots bicarbonate extractable P decreased with increasing pH. Bicarbonate extractable P was linearly related to MCP but not to phosphate rock applied. The rate of dissolution (calculated from the data on fractionation of inorganic P) and the proportion of PR dissolved decreased with increasing rates of PR application but the amount dissolved increased.

LABORATORY STUDY OF PHOSPHATE ROCK DISSOLUTION

Hanafi, Syers and Bolan (1992) studied the dissolution of two phosphate rocks, Gafsa(GPR) and Christmas Island (CIPR) in six Malayasian acidic soils by closed incubation and open leaching system and reported that in closed incubation system dissolution studied from increase in either 0.5M NaOH-extractable P ($\triangle$ P) or 1M BaCl$_2$ - TEA extractable Ca ($\triangle$ Ca) in rock phosphate treated soils, compared with the control soil, was higher (22-71%) in reactive GPR than that of (26-42%) in less reactive CIPR. Despite an adequate supply of protons the extent of dissolution of both PR materials was very negligible after 50 days. Calcium released from the PR occupied most of the -vely charged exchange sites and there was an insufficiently large Ca sink for dissolution to continue. Although the PR dissolution increased with increase in P retention capacity of the soil, in closed incubation system the size of sink for calcium determined the extent of PR dissolution in these high P sorbing soils. However the dissolution of PR materials was larger (56-94%) in the open

leaching systems. Continuous leaching resulted in removal of cations between 4.2 and 29.9 m.mol Kg^{-1} soil, thus providing new sites for the Ca released from PR. The renewal of Ca sink during leaching was the main reason for the continued dissolution of PR under leaching conditions.

Robinson et al. (1991) have observed in incubation studies that the dissolution of Gafsa PR in some UK soils stopped within 60 days, despite an adequate supply of H$^+$. They attributed this to saturation of calcium exchange sites in these soils. However dissolution could be increased with increasing addition of cation exchange resins, which act as a sink for the Ca released from PR.

A two fold increase in sink size in these soils caused an increase in PR dissolution of 44 - 120%.

Chien (1978) reported that incubation increased the amount of P extracted with Bray's-1 from soil treated with phosphate rock at the rate of 800 ppm P added, the amount of Bray's P derived from the unreacted phosphate rocks varied with sources of phosphate rocks ranging from 9.6 to 93.7 ppm. The amount of Bray'P, in the soil treated with phosphate rocks before and after incubation correlated very well with the citrate soluble P of the phosphate rock, the amounts of phosphate extracted from the unreacted phosphate rocks decreased as the application rate increased, conversely the contribution from the unreacted phosphate rock to the total Bray'sP in the samples incubated for 3 weeks increased as the application rate

increased.

Studying the dissolution pattern of phosphatic rock in an incubation study Kumar and Mishra(1986) stated that the rate of dissolution of each rock phosphate was rapid in the first week and decreased thereafter. Most of the dissolution occurred within six weeks of application. Increase in pH and Ca concentration in the solution due to dissolution of rock phosphate seem to have depressed the rate of dissolution at the later stage. They explained that the low rate of dissolution of Mussoorie rock phosphate is due to presence of high amount of calcite and dolomite which would lower the acidity and thereby decrease the rate of dissolution.

Basak and Debnath (1986) in an incubation experiment observed that, irrespective of moisture regimes none of the doses of (50 Kg and 100 Kg/ha) Purulia rock phosphate and only the higher dose (100 Kg/ha) of Mussoorie rock phosphate significantly increased the Bray's-1 extractable P. The two rock phosphates failed to show water soluble P.

From an incubation study extending over 90 days using contrasting soil and Sechura Phosphate Rock (SPR) and single super phosphate, Syers and Mackay (1986) reported that the rate and extent of dissolution of SRP, measured by single extraction with 0.5M NaOH increased as the phosphate (P) sorption capacity of the soil increased. In contrast the initial dissolution of SSP was independent of soil type, whereas the amounts of water and Olsen extractable P in soils to which SSP was added initially

increased with both P sources, the amounts of extractable P decreased as P-sorption capacity increased.

Using 30 contrasting soils, Mackay et al. (1986) found that the dissolution of Sechura phosphate rock (SPR) was measured by single extraction with 0.5M NaOH increased as exchangeable Ca decreased and P sorption capacity increased. This was because extraction with dilute NaOH removes non-occluded Al-P and Fe-P from a soil (Syer et al., 1972) and minerals of the apatite group do not dissolve significantly in this reagent, and any increase in NaOH extractable P in soil to which PR has been added provides an estimate of PR dissolution.

FACTORS AFFECTING DISSOLUTION OF ROCK PHOSPHATE

Crop response to phosphate rock (PR) applications is strongly dependent upon the rate of dissolution of the rock (Olsen, 1975; Chaverri and Black, 1976). The susceptibility of PR to protonation is one aspect controlling dissolution. Another aspect is the transport of reactant and product ions to and away from the PR particle surface. Researchers have noted that the rate of chemical breakdown of PR particles relates to particle porsity or density (Caro and Hill, 1956), apatite crystal size (Khasawhew and Doll, 1978), apatite solubility (McClellan and Lehr, 1969; Khasawneh and Doll, 1978) and rock phosphate size (Joos and Black, 1950; Caro and Hill,1956). However other work has shown that the degree of isomorphous substitution of CO_3^{-2} and PO_4^{-3} in the apatite lattice controls the dissolution rate of PR (Arminger and Fried, 1957; Lehr and McClellan, 1972). This is

logical because the degree of CO_3^{-2} substitution determines the crystal size (McClellan, 1978) which in turn controls the surface area and porosity (Khasawaneh and Doll, 1978). Specific surface area though considered to affect solubility, it appears to be of secondary importance since particle fineness can not completely compensate the low content of substituted CO_3^{-2} (Chien, 1978).

Several soil factors that influence PR dissolution have been identified. These include soil pH (Joos and Black, 1950; Graham, 1955; Ellis, 1955; Vander Paaw, 1965; McLean and Bolan, 1967; Choudhuri and Mishra, 1980) Soil pH buffering capacity (Graham, 1955), exchangeable Al (Cantarutti et al., Chien et al., 1980; Novais and Ribeiro, 1982), Calcium (Graham, 1955; Cabala et al., 1982) and phosphorus (Van Der Paauw, 1965; Juo and Kang, 1978; Smyth and Sanchez, 1982). Apatite solubility is strongly influenced by activities of reaction products in the surrounding soil solution. Hien, 1977 and Wier et al., 1971). Dissolution is therefore expected to be sensitive to changes in soil solution activities of Ca^{+2}, HPO_4^{-2} ions, as well as the soil P buffering power and exchangeable Ca.

COMPOSITION OF ROCK PHOSPHATES AND THEIR REACTIVITY

Indian rock phosphates are mostly tricalcium phosphate or Fluro apatite with some accessory minerals like calcite, dolomite, quartz, goethite, feldspar and iron oxide (Bhujabal and Mistry, 1984). Udaipur, Purulia and Jhabua apatites has essentially a fluroapatite composition with negligible amount of

18

substitution of CO_3 for PO_4 in apatite structure. Mussoorie, Durmala and Maldeota apatites are francolitess with small amount of substitution of CO_3 for PO_4. Kasipatnam phosphate rock had a fluorochlorapatite composition and is believed to be of igneous origin. A highly significant linear correlation was observed between citrate solubility of phosphate rocks with the mole ratio of $CO_3 : PO_4$ in the apatite structure and a value AOAC $NH_4 -$ Citrate extractable P is taken as a measure of rock phosphate reactivity (Khasawaneh and Doll, 1978). The presence of accessory minerals likee calcite, dolomite, gypsum etc. in phosphate rocks of sedimentary origin considerably influence NH_4 - Citrate extractable P in rocks (Lehr and McClellan, 1972). Crystallinity of apatite, total P content and the textural effect of apatite silica intermixing have a measured effect on solubility of P in NH_4 - Citrate solution (Chien and Hammond, 1978). The degree of $CO_3 + F$ substitution affect solubility of P from apatite in neutral ammonium citrate (Chien, 1977).

According to Caro and Hill (1956) physical compactness or surface area rather than particle size is associated with reactivity of rock. Presence of phosphate bound carbonates in apatites increases the solubility of phosphorus from rock phosphate whereas fluorine decrease it. $CaCO_3$ incorporated within apatite structure decreases crystallinity of rock (Howeller and Woodruff, 1968).

SOIL CHARACTERISTICS AFFECTING DISSOLUTION

Choudhury and Mishra (1980) found that the

transformation of rock phosphate in soil was mainly related to soil acidity and phosphate potential as these two soil parameters accounted for 94% variation in the dissolution of phosphate rock.

Mackay and Syers (1986) in a model to describe the dissolution of phosphate rocks in soil, identified percent Ca saturation, P sorption capacity and Ca exchange capacity of the soil were three most important parameters influencing dissolution. Percent Ca saturation is the single most important variable, accounting for 45% variability and the second most important factor P sorption capacity when combined with % Ca-saturation explained 65% of variation. The next two important variables in decreasing order of importance are Ca-exchange capacity and organic carbon. Their inclusion accounted for the variation upto 77% . Soil pH did not appear to be important even in combination with the other variables. Wilson and Ellis (1984) have in fact shown that an increase in the Ca^{+2} activity in solution at a constant pH results in a decrease in the rate of dissolution of phosphate rock.

Soils with high Ca-exchange capacity (Mackay et al., 1986) and organic matter content (Chien, 1979; Khasawneh and Doll, 1978) have been shown to provide a sink for Ca^{+2} , thereby promoting dissolution of phosphate rock. Similarly soils high in Fe and Al oxidess can sorb the P released from rock phosphate and induce dissolution (Mackay et al., 1986; Smyth and Sanchez, 1982).

Chien et al. (1980) found that P-sorption capacity of

soil was the most important soil factor controlling the extent of dissolution of North Carolina phosphate rock in 16 Colombian soils. As these soils were acidic, exchangeable Calcium was not highly correlated with dissolution.

Mackay et al. (1986) reported that as the dissolution of Sechura phosphate rock depends on the concentration of Ca^{+2} and $H_2PO_4^-$ in the soil solution, a decrease in moisture content in soil decreased the rate and extent of dissolution, because of the increase in concentration of Calcium and Phosphate in soil solution.

TRANSFORMATION OF PHOSPHORUS IN ACID SOILS

Inorganic phosphorus formed by fertiliser application is believed to exist as sparingly soluble orthophosphates of Al, Fe and Ca in soil. Calcium phosphate compounds such as apatites are of primary importance. Al-P and Fe-P such as variscite ($AlPO_4 . 2H_2O$) and Strengite ($FePO_4 . 2H_2O$) are believed to be the end products of inorganic P in soil, which are unavailable to crop.

According to Juo and Ellis (1968) when soluble P was applied to acid soils or when Ca-P was dissolved, the soluble P precipitated to form colloidal Al-P and Fe-P. Because of their smaller paritcle sizes, greater surface area and amorphous structure, these colloidal forms are readily available to plants. But these colloidal forms tend to crystallise to hydrated compounds such as variscite and Strengite, which are less available to crop. Since Fe-P crystallizes at a much faster rate than Al-P, so the native Al-P fraction seemed to be more

available to plants than Fe-P fractions.

Mandal and Chatterjee (1972) observed that soils having higher Bray's-I extractable P experiences greater transformation into Al-P. According to them transformation of added P to Fe-P and Al-P was directly related to total inorganic P already present in soil and the amount of native Fe and Al oxides in soil.

Biddappa and Perur (1978) working on Mysore laterite soils reported that application of P fertilisers increased Al-P and Fe-P fraction upto 60 days, but gradually decreased thereafter. Other forms showed slight change only.

Chu et al. (1962) showed that transformation of rock phosphate mainly resulted in an increase in Fe-P and Al-P fraction in soil. These two fractions decreased in soil with increase in pH. Amount of Al-P in soil varied with pH whereas the amount of Fe-P formed varied both with pH and free iron oxide content in soil.

Juo and Kang (1978) studied the availability and transformation of Morocco and North Carolina rock phohates and compared with concentrated super phosphate. A larger proportion of rock phosphate (Ca-P) applied to soils was transformed into Al-P and Fe-P from North Carolina rock than from Morocco rock after 90 days of incubation.

Pattnayak and Misra (1989) reported that about 53 to 90% of added P (200 ppm) as fertiliser was recovered as

inorganic-P, a large percentage of which was in Fe-P and Al-P forms. In Alfisol and Inceptisol Al-P was the dominant form, whereas in Entisol Fe-P was dominant. Bray's-P and Olsen's available P correlated positively with Al-P and Saloid-P fractions of the soil. Several workers like Verma, Singh and Srivastava, 1991; Biddapa and Sarkunan, 1981 and Mishra and Verma, 1979 reported that Olsen's-P was closely and positively related with Al-P and Fe-P fractions in all type of soils.

Seshagiri et al. (1972) fractionated the black and red soils after treating them with super phosphates and ammonium phosphate and found Fe-P to dominate other forms in both the soils. Al-P was only found in super phosphate treated soil. Because strong acids produced during reaction of super phosphate with water, caused dissolution of Fe and Al from clay and formed Fe-P and Al-P.

Enwezor (1978) fractionated the soil after growing 3 crops of maize in soils treated with rock phosphate. They observed that bulk of applied phosphorus remaining in soil after cropping had reverted to Al-P and Fe-P and these two fractions highly correlated with phosphate sorption capacity of soil.

Batten, Blair and Lill(1979) reported to obtain positive linear relationship between fertiliser P applied and inorganic P pool. They also found that Al-P increased rapidly per unit of fertiliser phosphorus than other inorganic phosphorus pool.

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 phosphorus(225 kg P/ha). There was appreciable increase in Al-P,Fe-P and reductant soluble Fe-P fraction and lesser degree of occluded Al-Fe phosphates after 3 months of treatment. Ca-P was unaffected except in soil with pH 6.18.

Yuan, Robertson and Neller (1960) fractionated soil P and concluded that 80% of the added phosphorus formed complexes with Al and Fe and only 10% or less remain in water soluble or Ca-P form.

Direct methods for measuring dissolution of a phosphate rock in soil have invariably being based on the inorganic P fraction procedure of Chang and Jackson (1957) or one of its many modifications. Thus increase in Fe-P and Al-P fractions in a soil to which a phosphate rock is added are considered to provide and estimate of P that has dissolved from the rock whereas, increase in Ca-P are considered to indicate unreacted phosphate rock (Chu et al. 1962; Robertson et al., 1966; Cescar and Tyner,1976).

CHAPTER-III

MATERIALS AND METHODS

MATERIALS AND METHODS

PHOSPHATE SOURCES

Six indigenous phosphate rocks from Kasipatnam, Hirapur, Mussoorie, Maton, Purulia and Udaipur and two imported phosphate rocks from North Carolina and Jordan were used. All these rocks except North Carolina phosphate rock were finely ground to pass through a 100 mesh sieve. In case of North Carolina phosphate rock 95% of the rock passed through a 35 mesh sieve and 45% pass through a 60 mesh sieve. Single super phosphate (SSP) of local market was used in the experiment.

FIELD TRIAL (MICROPLOT EXPERIMENT)

To evaluate the effectiveness of rock phosphate as a source of P, a field experiment in randomised block design with ten treatments and three replications was laid during November, 1991 in the campus of College of Agriculture, Bhubaneswar. The test crop was hybrid napier grass (_Pennisetum Purpureum_.Schum). Soil of the experimental site was Haplustalf. The treatments consisted of a control, eight sources of rock phosphates as described above and SSP applied at the rate of 100 Kg/ha. All these plots received uniform dose of potassium as Muriate of Potash (40 Kg K_2O/ha) and Nitrogen as Urea (40 Kg N/ha) at the time of planting. The first cutting of the grass was taken after three months of planting and the subsequent cuttings were taken at one month intervals. After each cutting N at the rate of 20 Kg/ha was applied as Urea. The first two cuttings of grass were

25

taken, analysed as reported by earlier worker (Sahu, 1991). The experiment was continued by subsequent cuttings of grass from third cutting onwards upto nine cuttings.

Immediately after cutting, the fresh weight of fodder from each plot was recorded. About 150 to 200 gram of representative plant sample from each plot was separated and washed thoroughly with very dilute hydrochloric acid and then with sufficient deionised water. Then the samples were dried to constant weight in a hot air oven maintained at 75°C. The moisture percentage of each sample was calculated. The oven-dried samples were chopped into pieces and ground to powder form using a Wiley Drill and kept for further analysis.

The dry matter yield of grass has been recorded on oven dry basis. The relative agronomic efficiency (RAE) of different phosphate rocks was computed from yield data as follows.

$$RAE = \frac{Y_{treatment} - Y_{control}}{Y_{SSP} - Y_{control}} \times 100$$

where, Y is dry matter yield.

Before the start of experiment, soil samples from each plot and a bulk sample of the experimental site was collected. After taking the 9th cutting of grass, roots and stubbles from each plot were uprooted and the soil of each plot upto 15 cm depth was thoroughly mixed and samples from each plot were collected. After 60 days the plots were replanted with new

suckers of hybrid napier grass at the rate of 4 hills/plot and N and K_2O @ 40 Kg/ha each was applied to all the plots. First cutting from replanted plots was taken after 90 days of planting.

The soil samples collected were air dried and ground to pass through a 2mm sieve and stored for further analysis.

Analysis of Plant Sample

Di acid digestion (Blancher et al. (1965):-

One gram of powdered plant sample from each treatment was predigested with 15 ml concentrated nitric acid for 12 hours, following digestion with 5 ml of di acid mixture (HNO_3 : $HClO_4$ = 3:2). The volume was made to 100 ml with double distilled water. The digestion extract was analysed for P, Ca and Zn.

Phosphorous was determined by vanado-molybdate yellow colour method as described by Jackson (1973). Calcium in the extract was determined flame photometrically following the procedure suggested by Wells and Corey (1960). To 10 cc of extract taken in a 50 cc volumetric flask 2 to 3 drops of methyl red indicator and 2 cc of 2.5% Ferric chloride solution was added and dilute ammonia was added till all the iron precipitated. Then dilute HCl was added drop wise till the supernatant liquid was light pink. Then the volume was made up to the mark and Calcium was determined. Zinc in the plant extract was determined by atomic absorption spectroscopy using a Varian Atomic Absorption Spectroscope model - 1475.

All the results have been expressed on oven dry weight

27

basis.

Soil analysis

Soil pH was determined in a 1:2 soil water suspension using a ELICO digital pH meter. Available P was determined following Olsen's and Bray's - I method as described by Jackson (1973). Cation exchange capacity and exchangeable cations in bulk sample was determined by successive extraction with neutral normal ammonium acetate (Jackson, 1973). Phosphorous retention capacity of the soil was determined by shaking the soil with 1000 ppm solution of P (Soil: Solution = 1:25) as suggested by Saunders (1965). Exchange acidity and Exchangeable Al was determined by extraction with 1M KCl and titration with 0.1M NaOH as decribed by Jackson (1973).

Fractionation of inorganic phosphorus in soil

The amount of different fractions of inorganic phosphates in initial and final samples were estimated by modified Chang and Jackson procedure as outlined by Hesse (1971).

LABORATORY INCUBATION STUDY

The soil for incubation study was collected from a plot near the experimental site. The lime requirement of the soil was determined by new Woodruff's buffer method as suggested by Brown and Cisco (1984).

Five Kg of soil, was thoroughly mixed with pure $CaCO_3$ at the rate of 50% of lime requirement. The soil was alternately

wetted and dried at an interval of four days. This procedure was repeated for fifteen days. After that both the limed soil and unlimed soil were used for incubation experiment.

In order to study the dissolution of rock phosphate in soil, rock phosphate samples collected from eight sources as described earlier were applied @ 500 mg P per Kg of soil to 200 gram each of limed and unlimed soil taken in 500 ml beakers. A limed and unlimed control was also included. There were altogether 9 treatments each under limed and unlimed conditions, which were replicated twice.

After adding the phosphate sources the content of each beaker was thoroughly mixed and water was added to maintain the moisture at 50% of water holding capacity and incubated at room temperature. Required amount of water was added on each alternate day to compensate the loss of moisture on drying. Soil samples were collected at 15, 30, 45, 60 and 90 days of incubation after thorough mixing. Then the samples were dried and analysed for pH, phosphorus and calcium.

Phosphorus was extracted from soil sample by adding 25ml of 0.5M NaOH to 0.5 g of soil taken in 50 ml centrifuge tube and shaking it for 16 hours, following a pre wash with 1M NaCl for 1 hour (Mackay et al., 1986). Phosphorus in the extract was determined colorimetrically by ascorbic acid method (Murphy and Riley, 1962). Dissolution of rock phosphate was studied by calculating Δ P in mg/kg soil as the difference between 0.5M NaOH extractable P from different treatments in comparison to

respective control (Mackay et al.,1986).

Exchangeable calcium, in incubated sample was determined by the procedure described by Bascomb (1964). In this method 5g of soil was weighed into a perforated crucible with a small moistened filter paper disc. The sample was leached with 50 ml of 1M BaCl$_2$ - Tri ethanol amine (TEA) adjusted to pH 8.1, using a suction pump assembly. This was followed by a washing with 40 ml distilled water. The leachate was collected in a 100 ml volumetric flask and the volume was made upto the mark with distilled water. Calcium in the extract was determined flame-photometrically by pipetting 10 cc of extract into a 100 cc volumetric flask to which 5 cc of 1000 ppm K was added and volume made upto the mark with distilled water. Dissolution of rock phosphate was studied by calculating $\triangle$Ca in mg/Kg of soil as a difference between 1M BaCl$_2$ - TEA (pH 8.1) extractable Ca in treated sample as compared to respective control soils.

CHAPTER-IV

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

The rock pho-sphates used in the present investigation have been characterised in an earlier study (Sahu, 1991). The chemical composition and crystal chemical parameters of the apatite present in the rocks are listed in Appendix Table-1. Out of them six were Indian phosphate rocks (Udaipur, Kasipatnam, Mussoorie, Maton, Purulia and Hirapur) and two were imported rocks (North Carolina and Jordan). Only the phosphate rocks from Kasipatnam and Purulia were of igneous origin and the rest were of sedimentary origin. The low grade Indian phosphate rocks as compared to the imported rocks have low reactivity as shown by absolute citrate solubility (ACS).

The physical and chemical properties of the soil of the experimental site (Haplustalf) which was also used in the incubation experiment have been shown in Table-1. The soil was a sandy loam having pH 5.6 and CEC of 3.1 c mol (P^+) Kg^{-1}. The available P content of the soil was low (Olsen's P - 2.3 ppm) and P fixation capacity was high (1752 mg P/Kg of soil).

LABORATORY INCUBATION STUDY

The lime requirement of the soil determined by Woodruff's buffer method was found to be 2.5 MT/ha. The soil treated with pure $CaCO_3$ @ 50% of lime requirement raised the pH from 5.6 to about 6.5 and decreased the P retention capacity of the soil from 1752.5 mg/Kg of soil. The changes in pH, NaOH extractable P and exchangeable Ca content of the limed and

31

Table - 1   Physical and Chemical Properties of the soil of
             Experimental Site

	Results

Mechanical Analysis

    (a) Sand   75.54

    (b) Silt   8.20

    (c) Clay   16.26

Textural Class   Sandy Loam

Organic Carbon   0.66

pH   5.6

Cation exchange capacity
[CMol (P^+) Kg^{-1}]   3.1

Exchangeable acidity
[CMol (P^+) Kg^{-1}]   0.09

Exchangeable Al
[CMol (P^+) Kg^{-1}]   0.02

Availble P   Olsen's Method   2.3
(ppm)   Bray's-1 Method   3.4

P retention capacity
(mg P/kg of soil)   1752.5

---

unlimed soils treated with 500 ppm P as rock phosphates and incubated upto 90 days by maintaining moisture percentage at 50% of water holding capacity are given in Table 2 and 3.

The gradual increase in pH of the rock phopsphate treated soil (Fig.1 and Table-2) may be explained based on the consumption of H^+ ion for the dissolution of rock phosphate. The calcium released from the dissolution of phosphate rock also helped to raise pH by raising the percent base saturation of the soil. Hellums et al.,(1989) and Yeats and Allen (1987) have also recognised the contribution of above two factors towards the increase in pH of rock phosphate treated soil. The pH increased at a slow rate upto 30 days and the rate of increase was highest between 30 and 45 days which corresponded to the period of maximum dissolution of rock phosphate. After 45 days of incubation the increase in pH was negligible. Because of higher dissolution of rock phosphates in unlimed soil, increase in pH of rock phosphates treated samples over control was more in unlimed than in limed soil. The rock phosphates from Jordan and North Carolina showed the largest change in pH both in limed and unlimed soil indicating higher dissolution as compared to rock phosphates of Indian origin.

Since extracion of rock phosphate treated soil with dilute NaOH removed non occluded Al-P and Fe-P from soil (Syers et al., 1972) and the minerals of the apatite group do not dissolve to any significant extent in this reagent (Chang and Jackson, 1957) any increae in NaOH extractable P provide an estimate of P that has been dissolved from rock phosphate.

Table - 2   Variation of pH with incubation time

Source of Phosphorus	Days					
	0	15	30	45	60	90
UN LIMED SOIL						
NCRP	5.56	5.98	6.31	6.84	7.02	6.98
KRP	5.55	5.68	5.90	6.16	6.34	6.38
HRP	5.60	5.67	5.87	6.22	6.35	6.36
MRP	5.62	5.82	6.05	6.36	6.52	6.58
JRP	5.63	5.84	6.10	6.56	6.68	6.71
MNRP	5.63	5.78	5.89	6.24	6.38	6.41
PRP	5.61	5.79	5.93	6.21	6.36	6.41
URP	5.64	5.78	5.97	6.35	6.52	6.59
Control	5.60	5.61	5.54	5.64	5.72	5.76
LIMED SOIL ,						
NCRP	6.56	6.78	6.95	7.32	7.33	7.34
KRP	6.57	6.48	6.58	6.88	6.89	6.99
HRP	6.56	6.58	6.65	6.98	6.99	7.02
MRP	6.57	6.60	6.80	6.99	6.99	7.07
JRP	6.55	6.70	6.89	7.38	7.46	7.46
MNRP	6.55	6.60	6.62	6.86	7.04	7.09
PRP	6.58	6.62	6.70	6.98	7.15	7.23
URP	6.56	6.64	6.73	7.02	7.13	7.15
Control	6.57	6.50	6.50	6.65	6.70	6.72
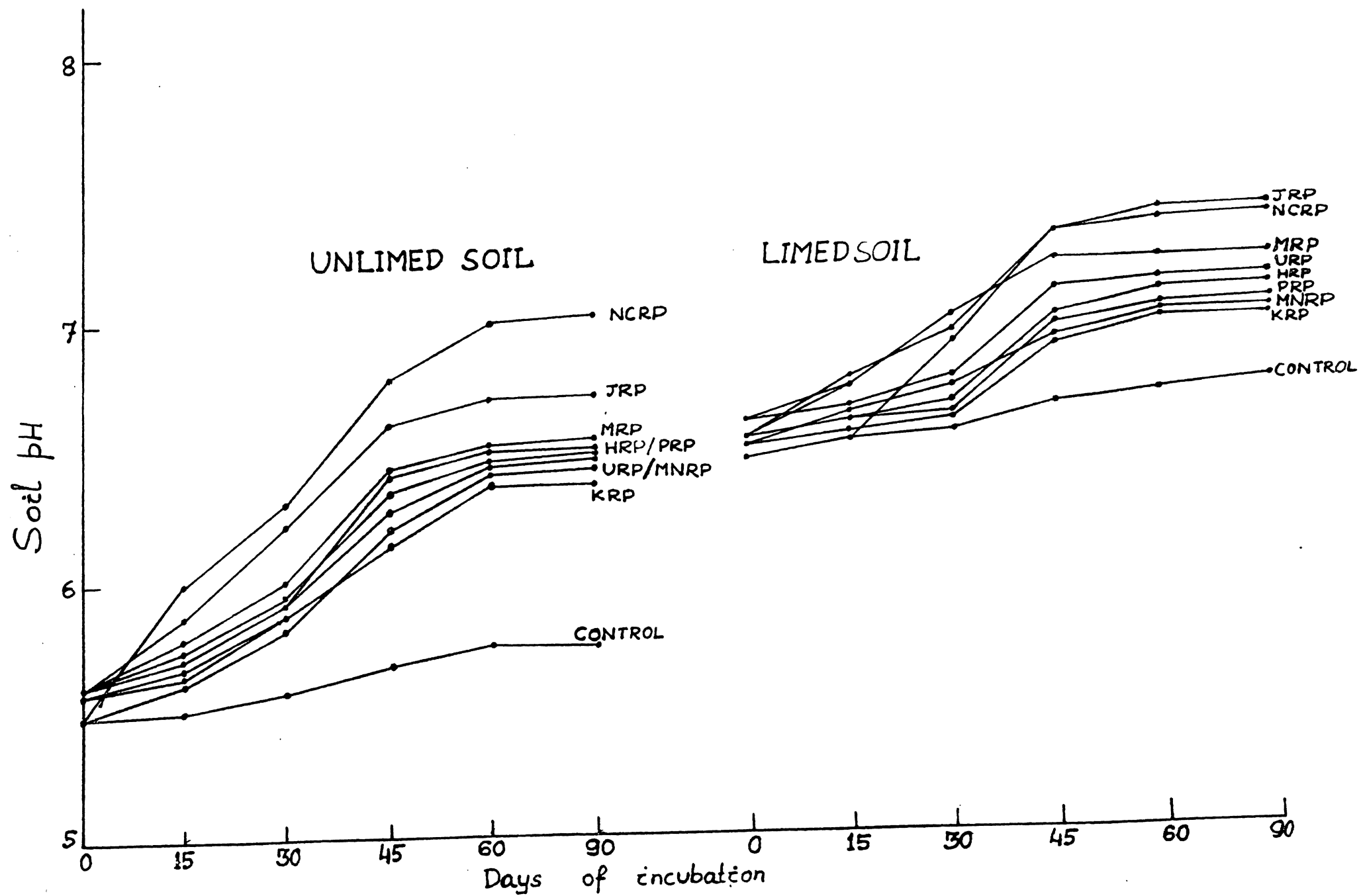
Fig - 1 Changes in pH of unlimed and limed soils incubated with rock phosphates

Dissolution of rock phosphate was studied by calculating ᐃP as the difference between 0.5M NaOH extractable P in rock phosphate treated soil and control soil. The change in NaOH extractable P for different rock phosphate treatments under unlimed and limed conditions calculated and reported in Table-3 and Fig.2 shows that during first 15 days dissolution was quite low and increased upto 45 days after which the increase was negligible. Rock phosphate dissolution was significantly higher in unlimed than in limed soil. The extent of dissolution of different rock phosphates were consistent to their reactivity as indicated by their ACS (r = 0.85**). Higher dissolution in unlimed than in limed soil may be explained on the basis of higher P retention capacity and lower exchangeable Ca content of the unlimed soil. A larger sink of P and Ca available in unlimed soil helped to remove the two products of dissolution of rock phosphate viz. P and Ca from the reaction site and increased dissolution. Comparision of dissolution (studied by ^P method) curves rock phosphates indicated higher dissolution and release of P from the rock phosphates imported from Jordan & North Carolina.

To study the interaction of lime, P sources and time of incubation the data (ᐃ P in mg/kg of soil) were analysed and presented in Appendix Table 2. The statistical analysis indicated that there was significant increase in dissolution of rock phosphates upto 45 days. North Carolina and Jordan rock phosphates showed significantly higher dissolution than that of Indian rock phosphates. Among Indian rock phosphates there was no

Table - 3   Changes in NaOH extractable P (△ P) and exchangeable Calcium (△ Ca) in soils incubated with 500 ppm. P

Treatments	Unlimed Soil Days of Incubation					Limed Soil Days of Incubation				
	15	30	45	60	90	15	30	45	60	90

△ P (mg/Kg of soil)

Treatments	15	30	45	60	90	15	30	45	60	90
URP	16.75	118.65	173.11	180.0	175.0	8.5	94.72	160.05	165.0	168.48
JRP	50.13	223.17	314.65	318.0	317.39	30.13	217.75	274.37	259.0	256.53
HRP	10.5	65.3	160.05	175.0	164.13	9.26	62.62	151.32	149.0	142.39
MRP	5.88	67.95	146.98	156.0	150.0	4.63	64.25	129.28	133.0	138.04
MNRP	33.75	85.65	182.91	194.0	184.78	23.13	82.75	162.23	160.0	161.95
NCRP	88.00	223.41	297.23	307.0	296.74	80.00	214.5	264.57	249.0	251.09
KRP	5.25	65.3	148.08	158.0	151.08	3.88	64.25	126.3	130.0	134.78
PRP	22.5	109.05	205.77	217.0	206.52	9.26	106.7	180.74	172.0	175.0

△ Ca (mg/Kg of soil)

Treatments	15	30	45	60	90	15	30	45	60	90
URP	70	325	645	665	665	70	315	565	560	550
JRP	170	510	805	815	810	140	415	700	700	695
HRP	35	240	430	455	450	30	195	390	395	385
MRP	110	305	660	675	675	95	330	645	650	645
MNRP	50	270	505	570	565	50	220	445	440	430
NCRP	195	495	830	845	840	170	430	725	720	710
KRP	30	275	400	425	425	25	280	405	405	400
PRP	70	330	510	525	520	55	175	385	385	375

	15	30	45	60	90	15	30	45	60	90
Calcium in Control (mg/kg)	240	235	225	220	220	420	415	385	385	390
Phosphorus in control (mg/kg)	34.62	34.82	35.92	28.0	30.43	23.87	23.93	32.95	20.0	21.73
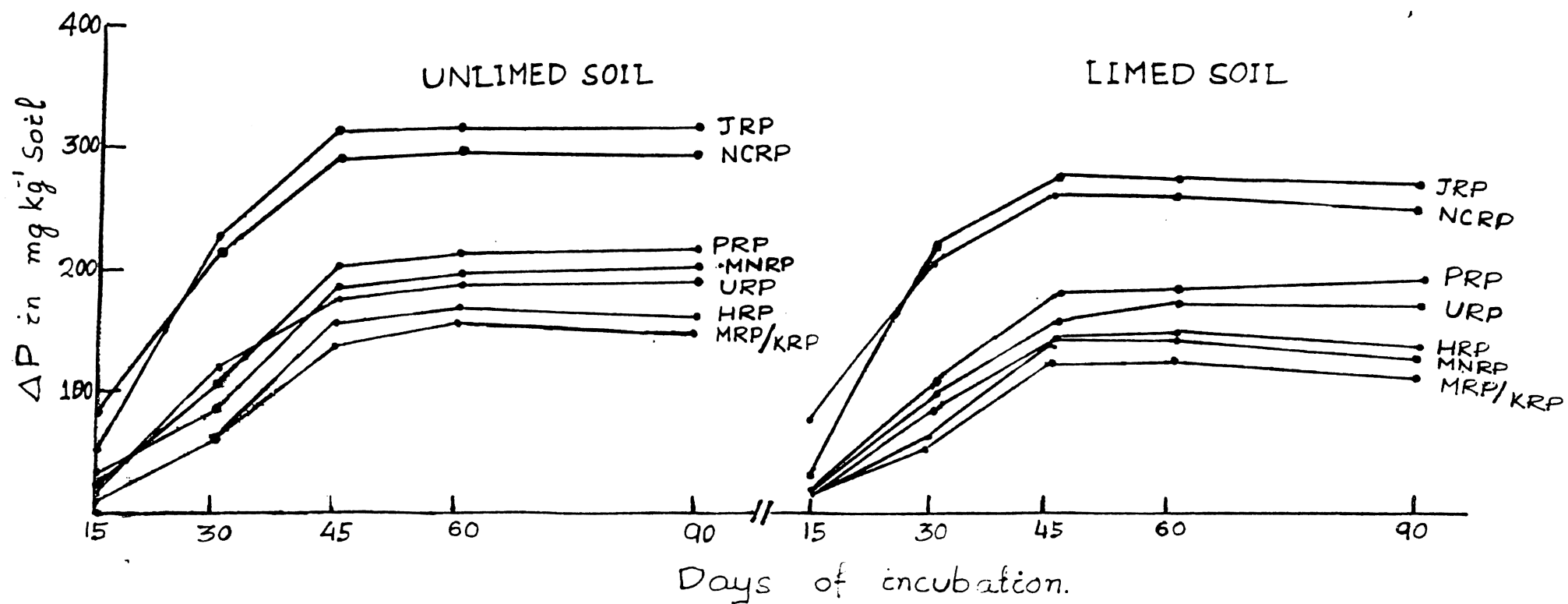
Fig 2. Changes in 0.5M NaOH extractable P (ΔP) in unlimed and limed soils incubated with rock phosphates.

significant difference in dissolution. Interaction between P sources and days of incubation was not significant. But the interaction between P sources and lime and between p sources and days of incubation were significant. Rock phosphates from North Carolina and Jordan showed significantly higher dissolution in limed soil as compared to the dissolution of Indian rock phosphates in unlimed soil, suggesting that the agronomic efficiency of NCRP and JRP is expected to be higher even in soils of higher pH as compared to Indian rock phosphates in soils of low pH.

Since calcium was one of the reaction products of rock phosphate dissolution in soil, any increase in exchangeable Ca in soil must have come from the dissolution of apatite in the rock and/or from the associated minerals like calcite, dolomite or gypsum present in the rock . Dissolution of rock phosphate was also studied by calculating Δ Ca as the difference between 1M BaCl$_2$ – TEA (pH 8.1) exctractable calcium in rock phosphate treated and control soil. Change in exchangeable calcium (^Ca) with the advancement of incubation time reported in Table-3 & Fig.3 for different rock phosphate treated soil with or without liming showed that the dissolution pattern followed the same trend as measured by the change in ^P method.

Maximum dissolution of each rock phosphate used in the incubation study as measurable by maximum percentage of applied dissolved and maximum percentage of a applied Ca dissolved have been calculated and reported in Table-4. In unlimed soil the maximum percentage of applied dissolved was highest for
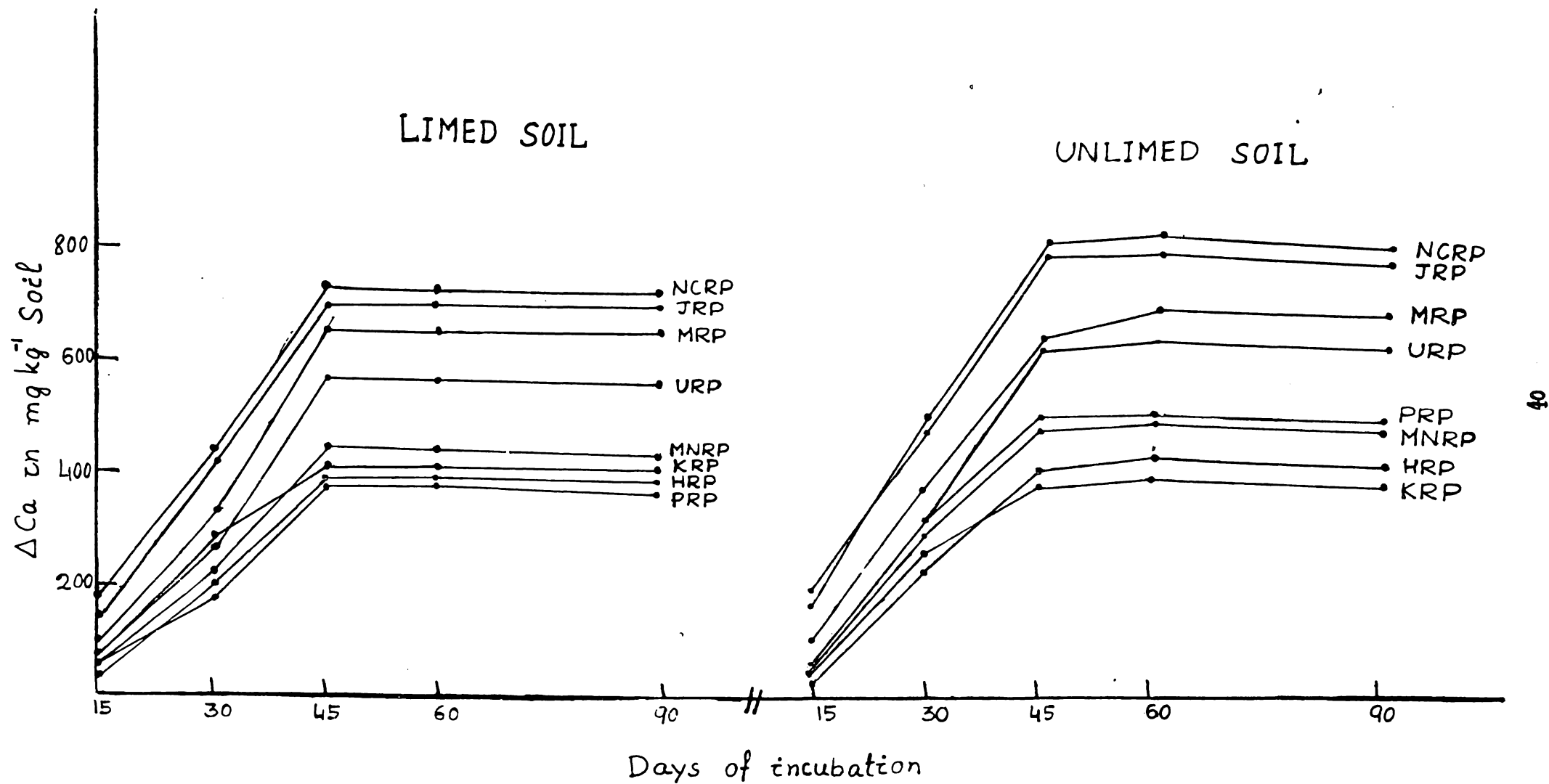
Fig 3: Changes in exchangeable calcium (ΔCa) in limed
and unlimed soils incubated with rock phosphates

Table - 4   Maximum dissolution of different rock phosphates by ΔP and ΔCa method in the incubation system.

Treatment	Maximum ΔP in ppm	Maximum ΔCa in ppm	Maximum dissolution of rock phosphate (%)	
			ΔP Method	ΔCa Method
UNLIMED SOIL				
NCRP	307.00	840	61.40	66.66
KRP	158.00	425	31.60	27.15
HRP	164.13	455	32.82	42.72
MRP	156.0	675	31.2	41.79
JRP	318.0	815	63.6	64.42
MNRP	194.0	570	38.8	45.96
PRP	217.0	525	43.4	40.46
URP	173.11	665	43.62	48.32
LIMED SOIL				
NCRP	264.57	725	52.91	57.53
KRP	134.78	405	26.95	25.87
HRP	151.32	395	30.26	37.08
MRP	138.04	650	27.6	38.01
JRP	274.37	700	54.87	55.31
MNRP	162.23	445	32.44	35.88
PRP	180.74	385	36.14	34.07
URP	168.48	565	33.69	37.56

JRP(63.6%) followed by NCPR (61.4%).

In limed soil the corresponding dissolution of the above two rock phosphates were 54.87% and 52.91% only. The dissolution of all the Indian phosphate rocks varied betwwen 31.2% to 43.6% in unlimed soil and between 27% and 33.7% in limed soil.

There was not much difference in maximum dissolution calculated by ΔP and ΔCa method in case of NCRP, JRP, KRP and PRP which do not contain appreciable amount of free calcite or dolomite. But, for HRP, MRP, URP and MNRP, a higher dissolution was indicated by ΔCa method than by ΔP method which may be related to the presence of appreciable amount of lime (free $CaCO_3$ /dolomite) in the rock phosphate sample. Since Ca in free $CaCO_3$ in preferentially extracted by 1M $BaCl_2$ - TEA, the $^\wedge Ca$ method over estimate the dissolution of rock phosphate containing free lime (Bolan et al., 1989).

The percent dissolution of phosphates rock by ΔP method showed a significant positive correlation (r = 0.92[**]) with the percent dissolution by ΔCa method. The regression line (Fig. 4) may be seen as slightly shifted from the equilibrium position towards the ΔCa method of dissolution suggestion that ΔCa method predicted slightly higher disolution. Since dissolution of rock Phosphate containing free lime is likely to be over estimated by ΔCa method, ΔP method appears be more reliable.

The dissolution of rock phosphate in soil as indicated
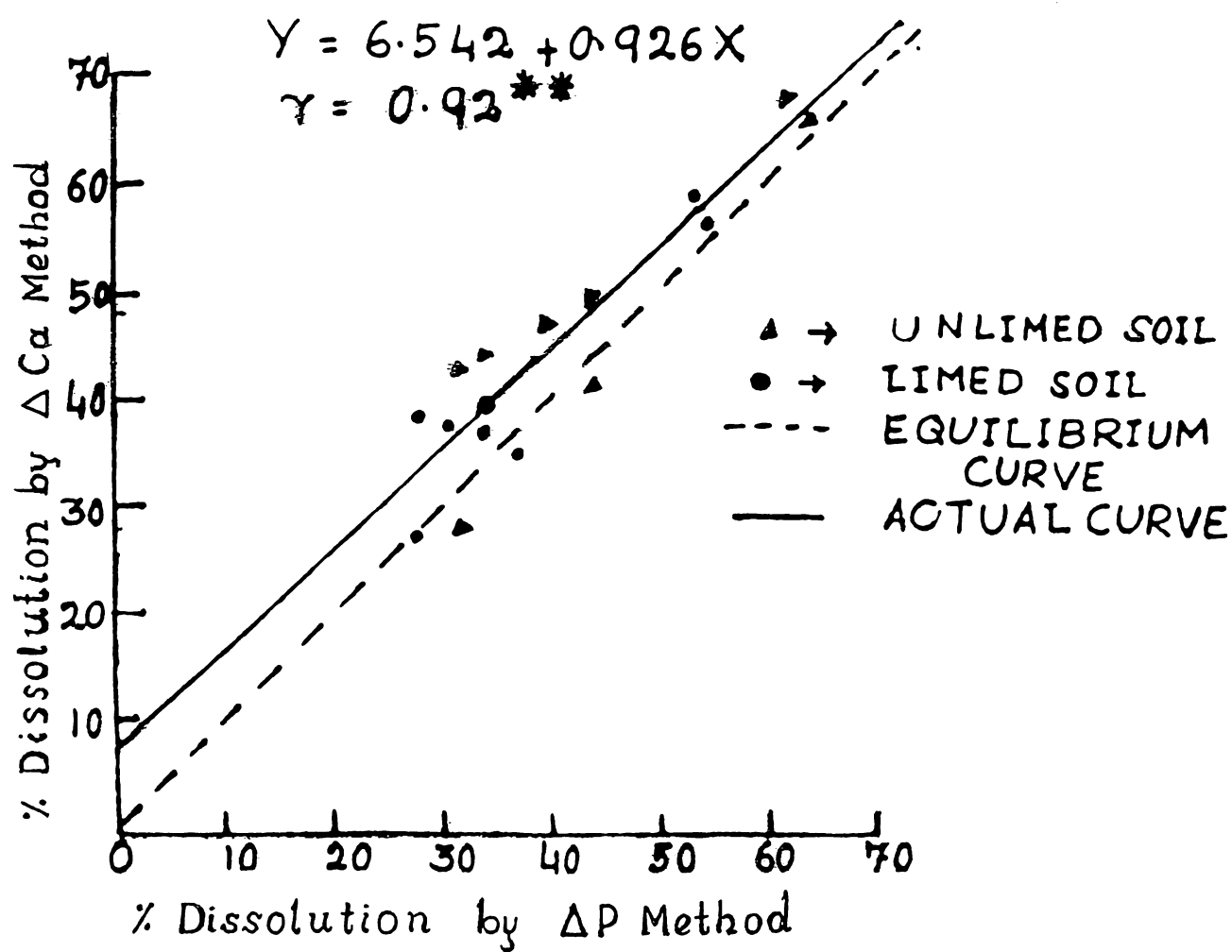
Fig - 4   Relationship between dissolution of rock phosphates
           estimated in a closed incubation system by ΔCa and ΔP
           methods.

by the change in soil pH. Δ P and Δ Ca appears to have reached an equilibrium at 45 days of incubation which may be attributed to the inadequate size of the sink for Ca^{++} and $H_2PO_4^-$.

The Phosphate and Calcium ions released due to dissolution of phosphate rock first enters into fixation and exchange sites respectively, in the soil. After these sites occuring in soil are saturated there is build up of Calcium and Phosphate ions in soil solution. When the product of these ions in soil solution exceeds the solubility product of the apatite, there is no further dissolution of the rock phosphate present (Hanafi et al.,1992). Therefore the dissolution of rock phosphate in unlimed soil having higher P retention capacity (1752.5 mg P/kg), lower calcium saturation (38%) and low pH (5.6) was greater than the dissolution in limed soil having P retention capacity of 1557.5 mg P/kg, calcium saturation of 67% and pH of 6.5.

Effectiveness of different rock Phosphates on growth and yeild of hybrid napier grass

The P supplying power of a rock phosphate for crop growth will be dependent upon its dissolution in soil. To evaluate the relative P supplying power of different rock phosphate, a field experiment growing a forage crop like hybrid napier grass in an acid soil treated with different rock phosphates and SSP was conducted. A perennial grass was choosen as test crop for facilitating the study of immediate and residual effect of rock phosphates by harvesting nine successive cuttings of grass over a period of nine months.

The dry matter yield of grass grown with 100 Kg P/ha applied as either SSP or as rock phosphates from different sources have been recorded along with their statistical analysis in Table-5. The cumulative dry matter of grass produced after each cuttings has been shown in Fig.5. The first harvest of grass taken after 90 days of planting showed that there was no significant difference in yeild due to SSP, NCRP and JRP treatments. All the Indian rock phosphate treatments recorded significantly higher yield than control but lower than SSP and two imported rock phosphates. From second cutting onwards the forage yield due to SSP was significantly lower than NCRP and JRP suggesting higher residual effect of rock phosphates than SSP. The yield of 6th and 7th cutting of grass showed that the residual effect of Indian rock phosphates were at par with that of SSP. A severe decline in yeild at the nineth harvest was due to senesence of the grass and there was no significant difference in yield between treatments.

The relative P supplying power of a rock phosphate can be judged from their immediate and residual effect on yield. Therefore, the increase in cumulative dry matter yields recorded for different rock phosphate treatments over control have been used to calculate the relative agronomic efficiency (RAE), taking the yeild increase due to SSP to be 100. In terms of their RAE the rock phosphates can be arranged in the following descending order: JRP(145) > NCRP(125) > MRP(93) > HRP(76) > MNRP (59) = PRP(57) = KRP(52) > URP(33). The cumulative dry matter yeild showed a significant positive correlation between crystal

Table - 5 Effect of different rock phosphates on dry matter yield of grass (quintal/ha)

| Sources of Phosphorus | No. of Cuttings | | | | | | | | | Total | RAE |
	1	2	3	4	5	6	7	8	9		
NCRP	56.50	40.73	36.60	35.38	39.51	36.12	32.27	29.69	16.68	323.98	124.50
KRP	35.96	35.90	24.10	25.81	35.21	28.41	29.56	26.34	15.36	256.68	51.76
HRP	48.03	38.80	29.70	27.18	34.88	30.70	29.62	25.39	14.67	278.97	75.86
MRP	42.56	37.76	34.30	35.71	38.39	35.22	29.51	25.60	16.10	294.94	93.12
JRP	56.43	41.56	38.40	41.54	41.94	37.24	35.26	32.60	18.24	343.21	145.30
MNRP	38.30	33.13	23.70	24.88	32.98	33.57	30.89	29.53	16.06	263.03	58.63
PRP	42.66	37.43	27.40	26.00	30.53	29.15	29.03	23.58	15.56	261.55	57.03
URP	37.46	33.70	23.10	23.32	29.00	28.16	27.52	23.68	13.73	239.67	33.38
SSP	55.56	33.46	32.80	31.18	38.32	30.69	28.54	28.26	14.86	301.30	100.00
Control	33.16	30.70	22.00	22.08	25.63	24.00	18.85	20.84	11.53	208.79	-
	**	**	**	**	**	**	**	**		**	
SE(M)±	1.75	0.63	1.56	1.82	2.25	2.45	2.47	2.26	NS	18.26	
CD 0.05	5.22	1.87	4.65	5.42	6.6	7.28	7.40	6.78		54.26	

* Different Rock phosphates are abreviated as

NCRP - North Carolina Rock Phosphate,   KRP - Kasipatnam Rock Phosphate
HRP - Hirapur Rock Phosphate,   MRP - Mussoorie Rock Phosphate
MNRP - Maton Rock Phosphate,   JRP - Jordan Rock Phosphate,
URP - Udaipur Rock Phosphate,   PRP - Purulia Rock Phosphate,
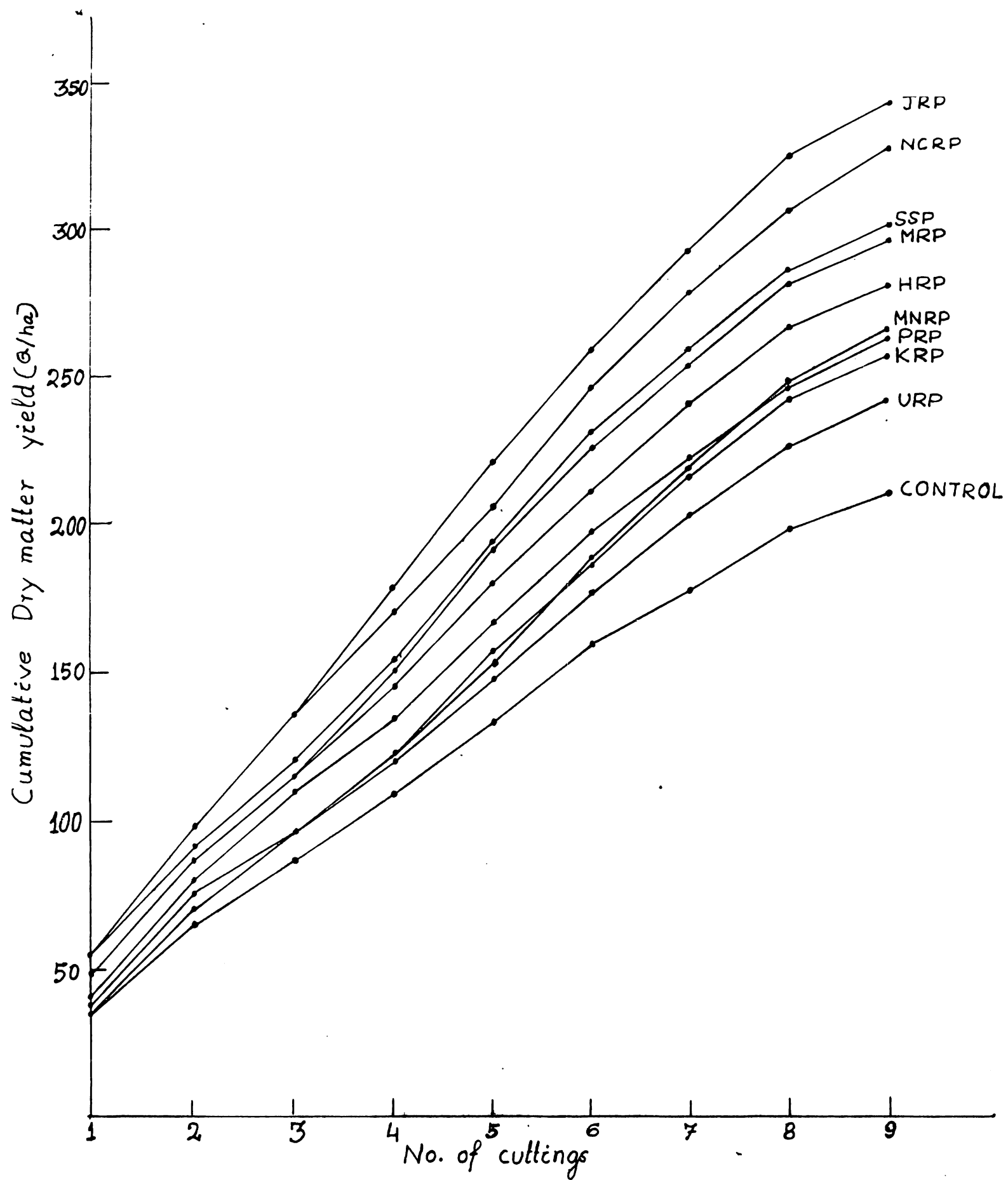
Fig 5: Effect of P sources on dry matter yield (quintal/ha)
of hybrid napier grass.

Table - 6   Relationship of different P availability indices of Rock phosphates with cumulative dry matter yield of grass, P uptake and RAE.

Variable correlated		Regression Equation	Correlation Coefficient (r)	No. of Data Pairs (n)
Y	X			
Dry matter	AOAC - NH_4 Citrate Soluble P	Y = 223.385 + 90.638X	0.87 **	8
	ACS	Y = 221.158 + 8.208X	0.83 **	8
	a_0	Y = 26654.17 - 2819.345X	- 0.83 **	8
	$CO_3 : PO_4$ molar ratio	Y = 236.446 + 509.573X	0.83 **	8
	F / P_2O_5 weight ratio	Y = -142.858 + 4058.277X	0.83 **	8
P-uptake	AOAC - NH_4 Citrate Soluble P	Y = 51.04 + 46.456X	0.89 **	8
	ACS	Y = 50.937 + 4.068X	0.82 **	8
	a_0	Y = 13057.17 - 1387.18X	- 0.82 **	8
	$CO_3 : PO_4$ molar ratio	Y = 58.504 + 252.715X	0.82 **	8
	F / P_2O_5 weight ratio	Y = -132.726 + 2039.32X	0.82 **	8
RAE	a_0	Y = 27991.46 - 2983.85X	- 0.82 **	8

NB   * Significant (P=0.05)
     ** Significant (P=0.01)
     ACS :- Absolute Citrate Solubility

47

chemical parameters of apatite Viz. citrate soluble P(r=0.87**),

ACS (r = 0.83**), CO_3 / PO_4 molar ratio (r = 0.83**), F /P_2O_5

weight ratio (r = 0.83**) and negative correlation with a

(r = -0.83**). The regression equations of the above

relationships have been given in Table-6.

The cumulative dry matter yeild and P uptake from

treatments receiving different sources of rock phosphate arranged

in increasing order of ACS are shown in Fig.6. Which indicated

that higher the ACS value greater is the dry matter yield and P

uptake.

Phosphorus,Calcium and Zinc uptake by crop

The P uptake by grass (Table-7) reflected the dry mater

yield (r=0.98**) and the cumulative amounts of P removed by grass

after each cutting plotted in Fig. 7 showed more or less similar

trend as that of dry matter yield. Uptake of P was also

significantly related to different crystal chemical parameters of

apatite in the rock (Table-6).

The uptake of Ca by crop (Table-8) and the cumulative

uptake of Ca at different stages of harvest showed that highest

amount of Ca was removed from JRP treated plot followed by NCRP

treated plot. The dry matter yield was positively related to

calcium uptake by the grass (r=0.93**). Inspite of application of

different amounts of Ca in different treatments the uptake of Ca

(Fig.8) showed similar trend as that of P. The amount of Ca added

in different treatments in Kg/ha were NCRP-252, KRP-313, HRP-213,
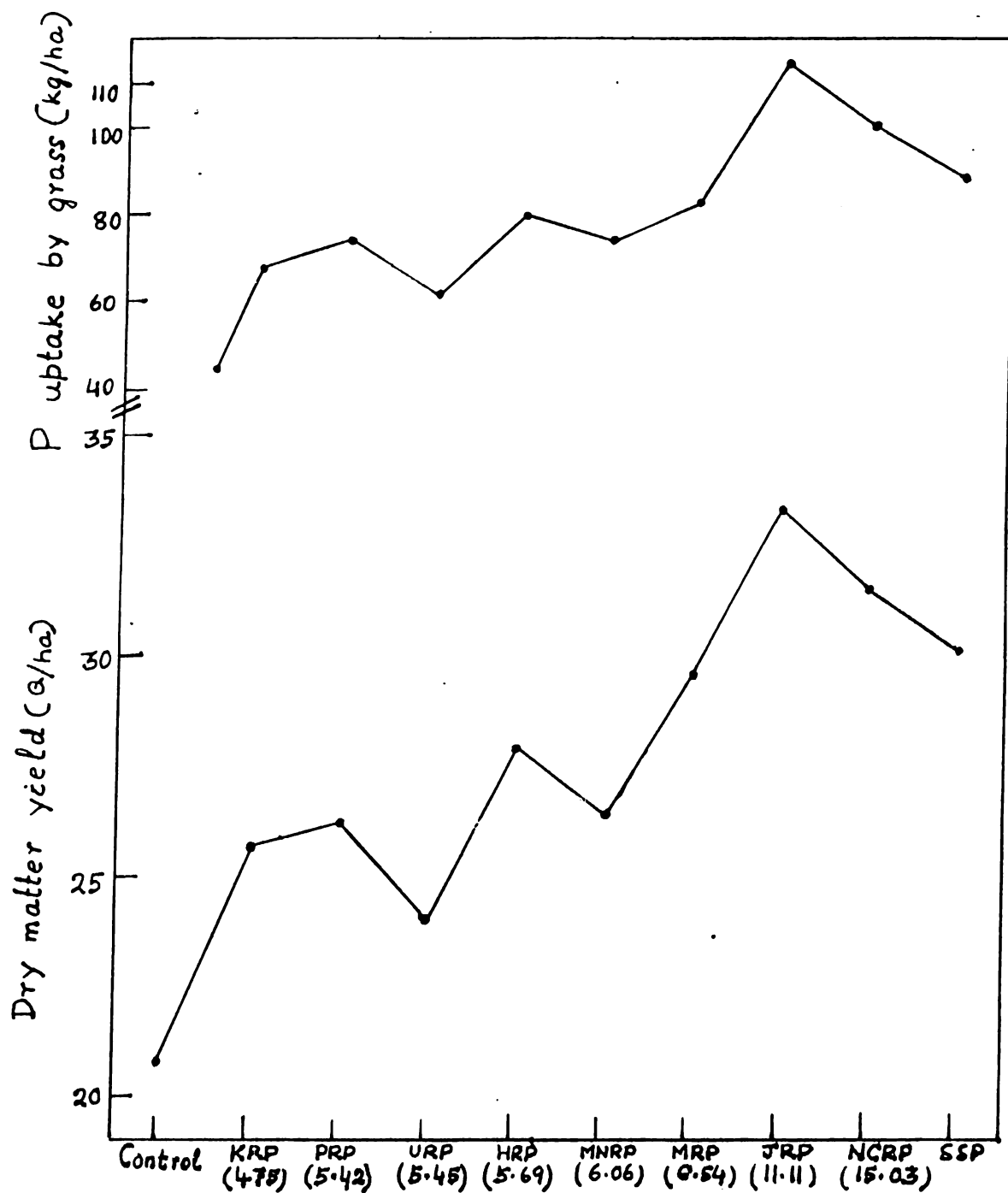
Fig 6 : Dry matter production and P uptake by napier
grass grown with different phosphate rocks
arranged in ascending order of ACS.(Figures
in parentheses indicate ACS values).

Table - 7   Mean Uptake of Phosphorus (kg/ha) by hybrid napier grass

| Sources Phosphorus | No. of Cuttings | | | | | | | | | Total |
	1	2	3	4	5	6	7	8	9	
NCRP	14.29	10.98	8.99	8.89	13.49	13.29	12.14	11.32	6.66	100.05
KRP	8.19	8.77	4.57	5.23	9.68	8.19	8.74	8.17	4.97	66.51
HRP	11.33	10.29	6.01	6.72	10.49	10.32	10.35	8.68	4.97	79.66
MRP	10.05	9.07	7.81	7.55	11.25	10.84	9.50	8.58	5.5	81.59
JRP	14.26	11.54	9.44	9.33	17.75	15.58	15.09	14.25	8.08	115.28
MNRP	9.50	8.77	5.60	6.12	9.59	10.01	9.71	9.09	5.03	73.47
PRP	10.05	9.15	6.14	5.95	9.16	9.77	9.96	8.08	5.52	73.70
URP	7.96	7.93	4.41	4.60	8.28	8.56	8.20	7.18	4.39	61.50
SSP	15.43	11.91	9.51	7.65	13.01	9.36	9.31	8.57	4.55	89.30
Control	6.8	6.76	4.02	3.78	5.79	5.50	5.40	4.60	2.59	45.04
SE(M)±	0.60**	0.36**	0.74**	0.82**	0.69**	0.64**	0.90**	1.07**	NS	9.41**
CD 0.05	1.79	1.09	2.2	2.42	2.07	1.93	2.67	3.2		27.95
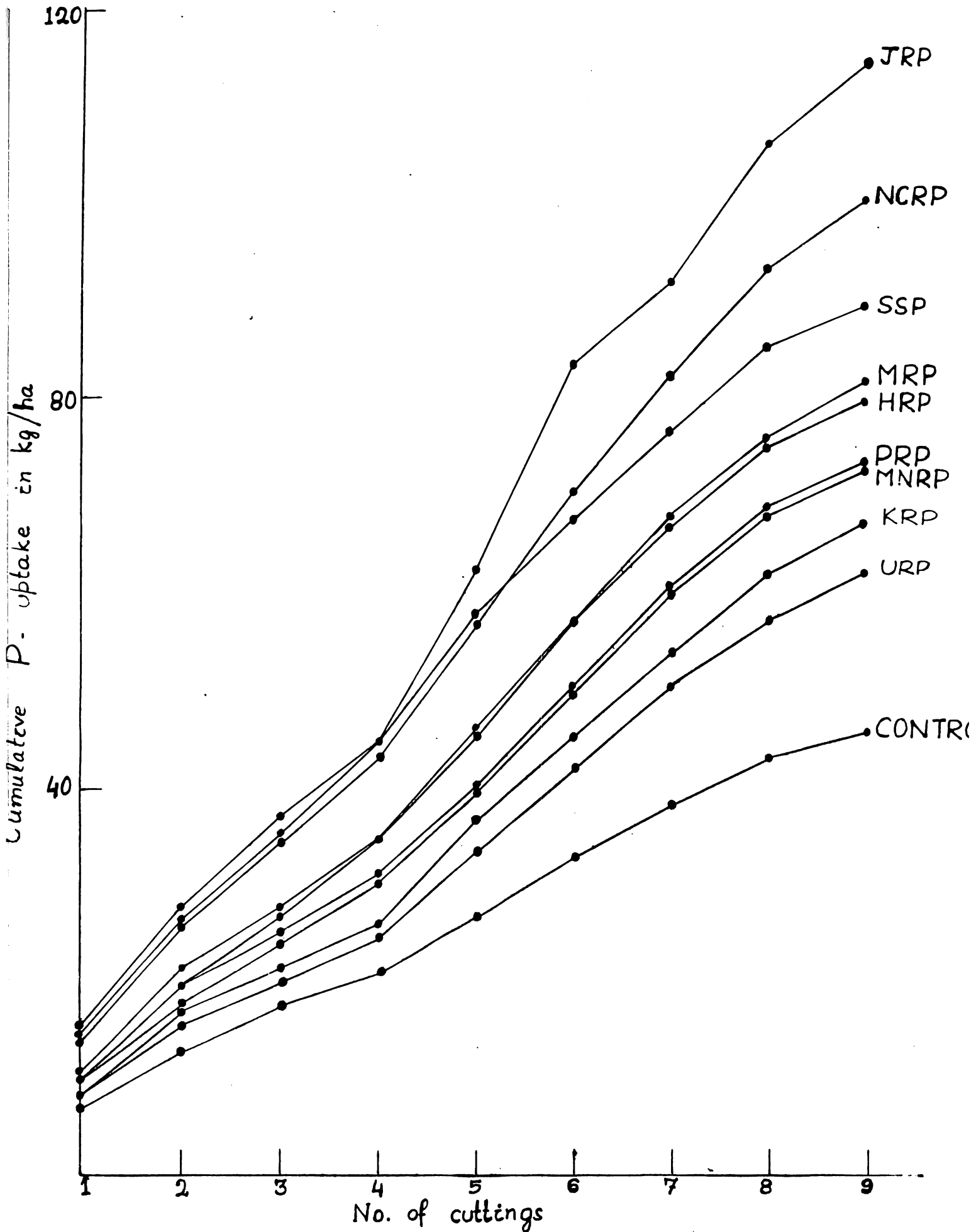
Fig 7 : Effect of different P sources on phosphorus uptake (kg/ha) by grass.

MRP-342, JRP-253, MNRP-248,PPR- 226, URP-347. Inspite of addition of relatively large amount of Ca through URP, MRP and KRP the uptake was highest in case of JRP followed by NCRP. It is observed that that Ca uptake was positively related (r=0.85**) to the percent dissolution of P in the rock (Fig. 9) but not with the total calcium added (which include Ca from apatite and other associated minerals like dolomite, calcite and gypsum present in the rock). Hellum et al. (1989) have also made such observation that Ca uptake was related to rock phosphate reactivity.

Addition of large quantity of rock phosphate to soil is likely to increase pH and reduce Zinc availability to crop. Zn uptake (Table-9) was related to yeild. Although dry matter yield was positively related (r=0.60) with Zn uptake, the correlation coeffecient was not significant.

The concentration of Zn in plant at different growth stages varied between 23 and 65 ppm (Fig.10). The concentration of zinc in plant in most cases gradually decreased after the second harvest, the decrease being greater in P treatments than in control. But in none of the treatments zinc defficiency was observed. Though not significant a negative relationship (r = -0.56) was observed between yield and average zinc concentration in plant. The cereals and grasses are considered to be defficient if the concentration in plant is below 20 ppm (Yashida, S.(1968). Therefore, in the present study yield of crop was not limited by Zn but rather governed by availability of P.

The concentration of Ca and P in plant at different

Table - 8   Mean Calcium uptake (Kg/ha) by hybrid napier grass

Sources of Phosphorus	No. of Cuttings									Total
	1	2	3	4	5	6	7	8	9	
NCRP	28.07	26.38	25.57	25.48	29.33	27.57	26.22	25.16	14.23	227.83
KRP	17.99	19.67	10.79	13.45	19.07	15.71	16.87	16.06	9.53	139.14
HRP	27.07	22.38	14.58	14.76	19.31	18.20	18.08	18.89	9.64	160.22
MRP	24.25	25.17	17.10	15.78	19.02	17.76	19.46	16.37	11.16	166.48
JRP	30.11	26.76	24.85	27.97	29.61	27.38	25.84	24.87	14.34	232.56
MNRP	23.44	23.89	18.19	18.67	24.10	22.61	23.22	22.24	12.09	188.45
PRP	22.82	20.11	20.66	21.68	23.26	21.11	19.81	17.71	11.53	179.60
URP	20.72	18.87	13.21	13.06	17.08	16.90	17.01	15.49	9.3	141.75
SSP	27.75	25.98	26.19	22.08	27.16	21.27	18.84	17.10	9.08	188.26
Control	15.12	18.18	11.88	11.64	13.16	11.60	11.35	9.16	4.68	107.86
	**	**	**	**	**	**	**	**	**	**
SE(M)±	2.33	1.28	1.58	1.78	2.6	2.37	2.47	2.09	1.73	5.98
CD 0.05	6.92	3.8	4.71	5.34	7.73	7.11	7.34	6.21	5.19	17.8
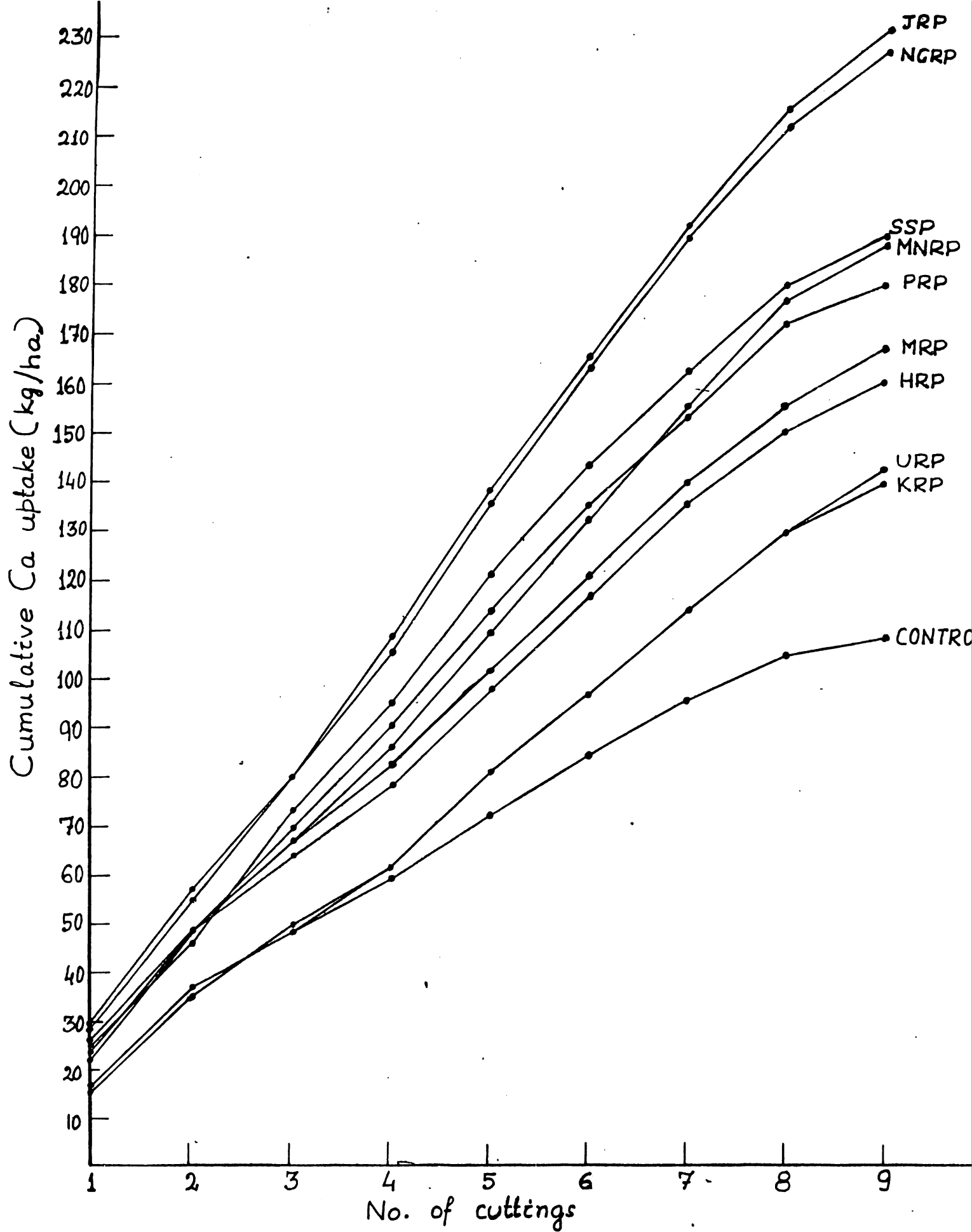
Fig 8 : Effect of different P sources on calcium
uptake (kg/ha) by grass.
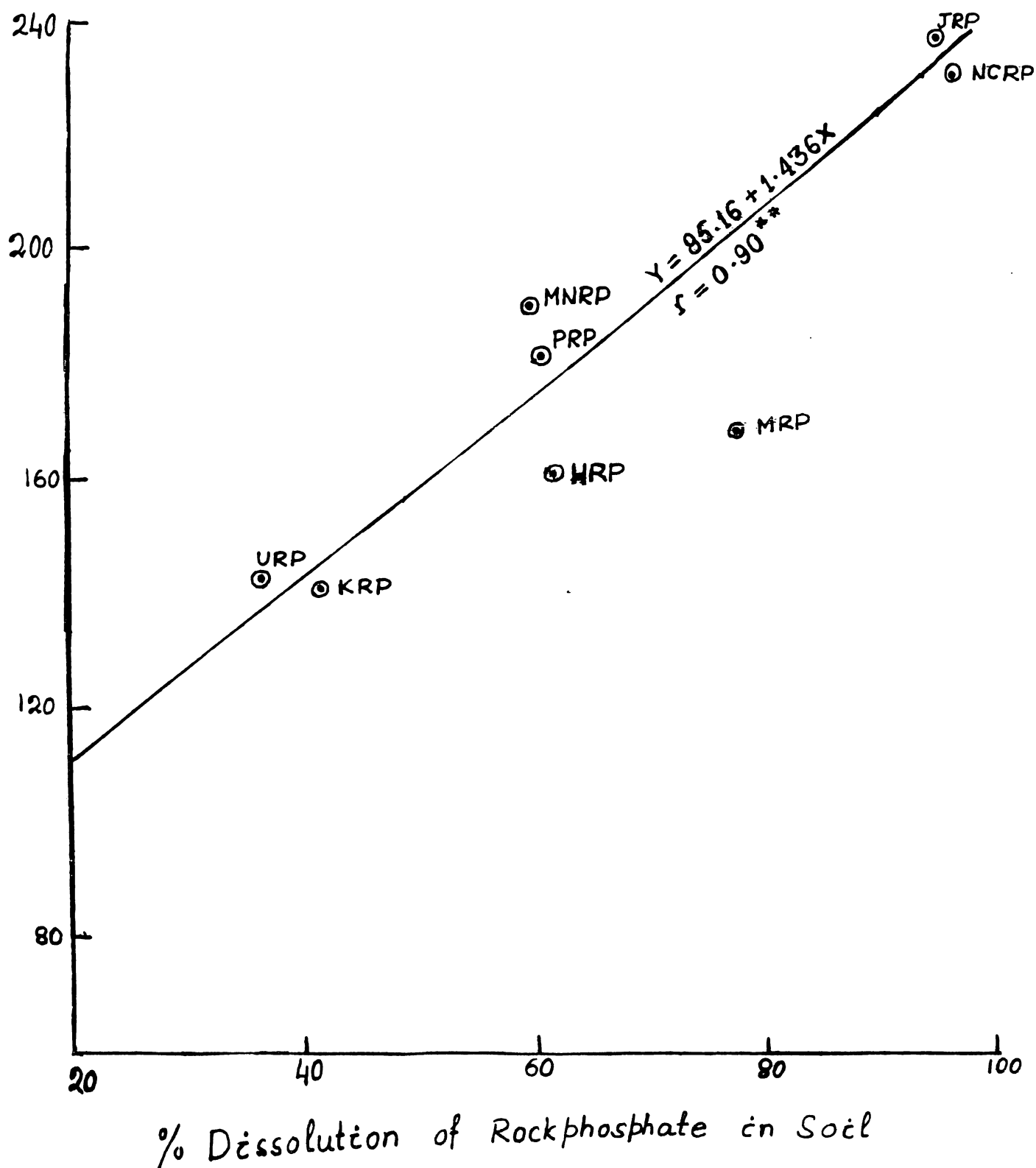
Fig 9 : Relationship between percentage dissolution of rock phosphates in field experiment and Calcium uptake by grass.

55

Table - 9   Mean uptake of Zinc (Kg/ha) by hybrid napier grass.

Sources of Phosphorus	No. of Cuttings									
	1	2	3	4	5	6	7	8	9	Total
NCRP	0.28	0.18	0.15	0.14	0.15	0.12	0.10	0.08	0.03	1.23
KRP	0.18	0.19	0.13	0.15	0.19	0.15	0.14	0.12	0.06	1.31
HRP	0.19	0.20	0.16	0.15	0.19	0.16	0.15	0.12	0.06	1.38
MRP	0.22	0.23	0.22	0.23	0.24	0.21	0.17	0.13	0.08	1.73
JRP	0.28	0.18	0.16	0.17	0.15	0.12	0.10	0.09	0.04	1.29
MNRP	0.17	0.15	0.09	0.09	0.11	0.11	0.09	0.08	0.04	0.93
PRP	0.23	0.19	0.12	0.11	0.12	0.11	0.10	0.08	0.04	1.10
URP	0.16	0.17	0.11	0.12	0.14	0.13	0.12	0.10	0.05	1.05
SSP	0.27	0.23	0.18	0.17	0.18	0.14	0.13	0.14	0.08	1.52
Control	0.15	0.13	0.08	0.08	0.09	0.09	0.09	0.07	0.04	0.82
	**	**	**	**	**	*	*			**
SE(M)±	0.02	0.02	0.02	0.02	0.02	0.03	0.03	NS	NS	0.11
CD 0.05	0.07	0.06	0.06	0.07	0.05	0.08	0.09			0.33

stages of growth shown in Fig.10 indicated that the concentration of Ca in control and SSP treated plots significantly decreased after 2nd and 4th cutting respectively, whereas in other treatments there was a slight increase. Phosphorus concentration in a given treatment was more or less same upto fourth cutting which slightly increased at fifth cutting of grass and remained more or less same there after. The cumulative dry matter yield showed a significant positive correlation with average % P ($r = 0.94^{**}$) and average % Ca in plant ($r = 0.74^{**}$).

Phosphorus transformation in rock phosphate treated soil

The soil sample collected from each plot before fertilization and after harvesting nine cutting of grass was analysed for different inorganic P fraction and reported in Table-10. The data reported are average of three replications. The variation of different P fractions of different plots were negligible indicating that the experimental site was fairly uniform and contained an average amount of 135 ppm of inorganic P. The fractionation of post harvest soil showed a decrease of 8.57 ppm of total inorganic P in control and an increase of 12 to 25 ppm in rock phosphate treated plots as compared to the soil before cropping. In the post harvest soil, there was highest increase in Al-P fraction followed by Occlued-P and Fe-P fractions and there was a decrease in Ca-P and reductant soluble P fractions. Amongst different inorganic P fractions reductant soluble P was dominant both in initial and final samples. The dominance of this fraction may be attributed to the presence of large amount of iron oxide in the soil which may precipitate and

57

Table - 10 Inorganic P fractions (ppm) in soil before fertilisation and after harvesting nine cuttings of grass.

P Sources	Saloid-P	Al-P	Fe-P	Ca-P	Reductant soluble P	Occluded P	Total inorganic P
				Before Fertilisation			
NCRP	3.40	12.25	9.81	50.02	65.02	0	134.5
KRP	3.33	12.08	9.63	51.04	64.00	0	134.0
HRP	3.36	12.28	9.84	50.00	65.02	0	134.5
MRP	3.46	12.51	9.88	50.09	65.06	0	133.5
JRP	3.50	12.12	9.81	51.00	66.05	0	136.0
MNRP	3.40	12.44	9.76	50.00	66.00	0	134.5
PRP	3.43	12.52	9.85	50.05	65.15	0	134.0
URP	3.46	12.49	9.88	50.07	65.10	0	135.0
SSP	3.50	12.62	9.91	50.22	63.75	0	133.0
Control	3.45	12.45	9.85	50.00	65.02	0	134.0
			After harvesting nine cuttings of grass				
NCRP	8.9	32.39	13.28	43.24	55.36	4.24	154.96
KRP	7.29	23.03	12.10	44.20	55.40	3.78	144.80
HRP	7.45	23.82	12.27	44.84	56.54	3.24	148.16
MRP	8.09	26.73	12.13	44.70	58.57	4.03	153.75
JRP	8.76	32.35	13.45	37.77	57.61	3.21	148.20
MNRP	7.82	23.60	12.54	46.74	56.36	3.50	149.56
PRP	7.83	25.39	12.94	46.82	59.61	3.98	150.57
URP	6.90	22.43	11.93	45.02	56.09	3.47	145.87
SSP	10.60	33.66	13.92	46.13	59.67	4.22	158.00
Control	2.26	8.50	6.23	45.13	63.04	0.27	125.43

Table - 10 Inorganic P fractions (ppm) in soil before fertilisation and after harvesting nine cuttings of grass.

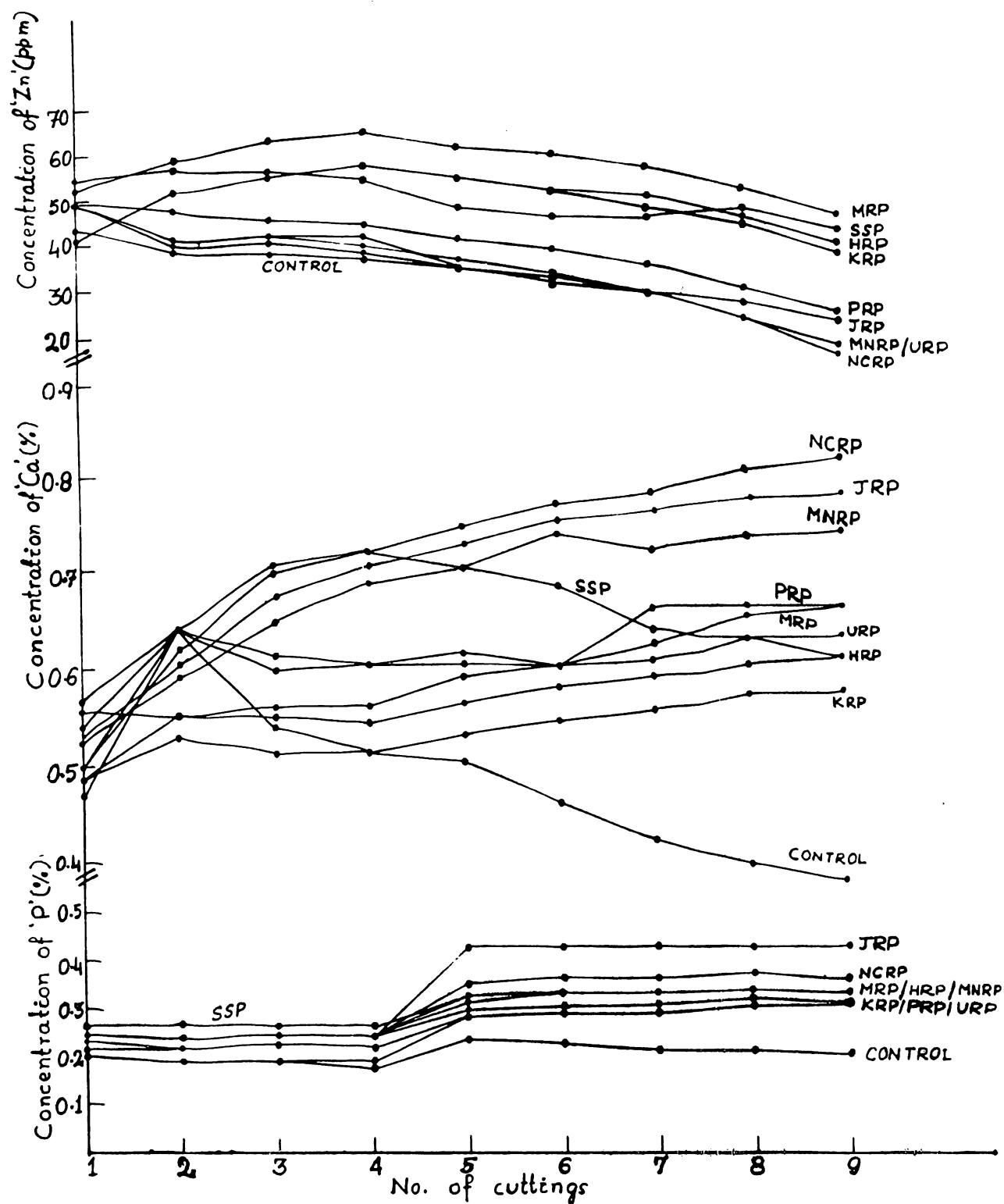| P Sources	Saloid-P	Al-P	Fe-P	Ca-P	Reductant soluble P	Occluded P	Total inorganic P
				Before Fertilisation			
NCRP	3.40	12.25	9.81	50.02	65.02	0	134.5
KRP	3.33	12.08	9.63	51.04	64.00	0	134.0
HRP	3.36	12.28	9.84	50.00	65.02	0	134.5
MRP	3.46	12.51	9.88	50.09	65.06	0	133.5
JRP	3.50	12.12	9.81	51.00	66.05	0	136.0
MNRP	3.40	12.44	9.76	50.00	66.00	0	134.5
PRP	3.43	12.52	9.85	50.05	65.15	0	134.0
URP	3.46	12.49	9.88	50.07	65.10	0	135.0
SSP	3.50	12.62	9.91	50.22	63.75	0	133.0
Control	3.45	12.45	9.85	50.00	65.02	0	134.0
				After harvesting nine cuttings of grass			
NCRP	8.9	32.39	13.28	43.24	55.36	4.24	154.96
KRP	7.29	23.03	12.10	44.20	55.40	3.78	144.80
HRP	7.45	23.82	12.27	44.84	56.54	3.24	148.16
MRP	8.09	26.73	12.13	44.70	58.57	4.03	153.75
JRP	8.76	32.35	13.45	37.77	57.61	3.21	148.20
MNRP	7.82	23.60	12.54	46.74	56.36	3.50	149.56
PRP	7.83	25.39	12.94	46.82	59.61	3.98	150.57
URP	6.90	22.43	11.93	45.02	56.09	3.47	145.87
SSP	10.60	33.66	13.92	46.13	59.67	4.22	158.00
Control	2.26	8.50	6.23	45.13	63.04	0.27	125.43

Fig 10 : Change in concentration of phosphorus, calcium
and zinc in grass at different stages of growth
indicated by number of cuttings.

cover the surface of Fe-P and Al-P particles to form reductant soluble P (Chang & Jackson, 1973).

The summation of increase or decrease in different inorganic P fractions plus the amount of P removed by crop from rock phosphate treated plot over control expressed as the percent of applied P provides an estimate for the dissolution of rock phosphates in cropped field. The percent of applied P appearing in different inorganic P fractions in soil and removed by crop are shown in Table-11.

The data presented in the Table-11 showed that amongst the rock phosphates dissolution was highest for NCRP(96%) and JRP (95%). Although dissolution of the above two rock phosphates are same, only 55% of applied P was taken up by crop from NCRP as against 70% from JRP. Amongst the Indian rock phosphates highest dissolution was observed for MRP (77%) followed by HRP (61%), PRP (60%), MNRP (59%), KRP (41%) and URP (36%). The dissolution of rock phosphate reflected P uptake by crop.

Comparison of dissolution of rock phosphates in closed incubation system and open leaching system in presence of rhizosphere

The dissolution of rock phophate in the laboratory incubution study representing closed system where the dissolution products of rock phosphate do not get a chance to be removed from site by leaching has been discussed earlier. In the cropped field in addition to P fixing sites in soil and cation exchange sites to retain Ca which act as sink for these two ions, and removal of phosphates and Ca from soil solution by plant root and by

Table - 11   Percent dissolution of rock phosphate in cropped field

| P Sources	Change in inorganic P fractions of soil after fertilisation and copping expressed as % of applied P							Cumulative uptake of P by grass from fertilised plot over control expressed as % of applied P (B)	Percent Dissolution of applied P (A + B)
	Saloid-P	Al-P	Fe-P	Ca-P	Red. Sol. P	Occluded P	Total (A)		
NCRP	11.11	40.28	6.94	-15.6	-10.2	8.48	41.01	55.01	96.02
KRP	7.92	21.90	4.94	-11.68	-11.00	7.56	19.64	21.47	41.11
HRP	8.18	23.22	4.86	- 8.32	- 7.92	6.48	26.50	34.62	61.12
NRP	9.26	28.44	5.50	- 5.39	- 5.49	8.06	40.35	36.55	76.90
JRP	10.52	40.46	7.28	-16.46	-23.48	6.41	24.71	70.24	94.95
MNRP	8.84	24.32	5.56	- 6.52	- 8.00	7.00	30.14	28.43	58.57
PRP	8.80	25.74	6.10	- 6.46	-11.0	8.00	31.18	28.66	59.84
URP	6.88	19.62	4.10	-10.10	- 8.0	6.94	19.44	16.46	35.90
SSP	14.50	43.08	8.00	-10.18	- 8.16	8.44	55.68	44.26	99.94
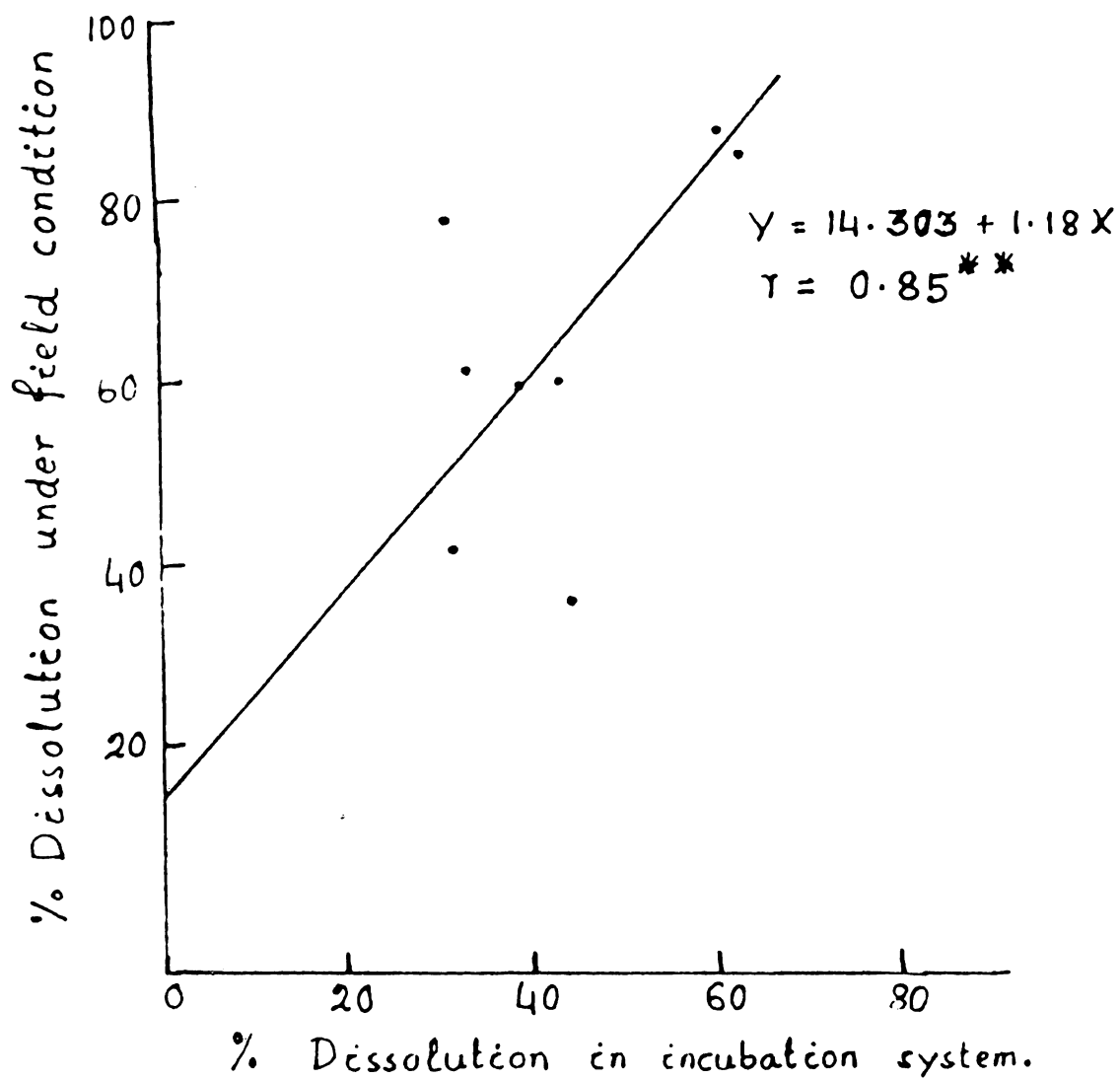
Fig 11 : Relationship between dissolution of rock phosphates
in closed incubation system and open leaching
system in field experiment.

leaching enhances the dissolution of rock phosphates. The dissolution which was always higher in crop field showed a significant positive correlation (Fig.11, r = 0.68*) with the dissolution in incubation experiment.

pH and available P content of soil

The pH and available P content of soil determined by Bray's - I and Olsen's method reported in Table-12 showed an increase in pH of post harvest soil as compared to the initial soil. The soil pH increased by to 0.5 to 0.7 unit in case of rock phosphate treated samples whereas the increase was only 0.2 in case of control P. The availabe P determined by Bray's - I method was always higher than Olsen's Method. All the treated soils showed an increase in available P which was consistent with their dissolution in soil. The available P determined by both the methods showed significant positive correlation with dry matter yeild (Bray's-P, r = 0.93** , Olsen's-P r = 0.92**) and P uptake Bray's-P, r = 0.91** , Olsen's P, r = 0.90**).

A multiple correlation analysis of available P with inorganic P fractions along with their regression coefficent and regression equation are reported in Table-13. Olsen's-P showed a significant positive correlation with Al-P (r = 0.93**), Fe-P (r=0.77**) and with Saloil-P (r=0.84**). The relationship was negative with Ca-P (r=-0.96**) and non significant with reductant soluble-P. Similar relationship was also observed for Bray's-P. The multiple regression coefficient was significant and found to be 0.98** for both Olsen's & Bray's-P. Path analysis

Table - 12   pH and available P content before fertilisation and after harvesting
               nine cuttings of grass.

| Treatments | Soil before fertilisation | | | Post Harvest soil | | |
	pH	Bray's-I P	Olsen's P	pH	Bray's-I P	Olsen's P
NCRP	5.56	3.42	2.36	6.23	26.3	15.5
KRP	5.48	3.36	2.33	6.01	15.1	8.9
HRP	5.59	3.45	2.38	6.16	19.1	11.3
MRP	5.61	3.34	2.25	6.19	20.6	12.1
JRP	5.49	3.42	2.28	6.27	29.8	16.4
MNRP	5.62	3.43	2.29	6.09	12.5	7.3
PRP	5.58	3.37	2.27	6.14	16.4	8.3
URP	5.55	3.44	2.32	6.05	13.7	8.13
SSP	5.47	3.39	2.35	6.07	29.3	17.3
Control	5.59	3.45	2.39	5.73	4.8	2.8

Table - 13   Relationship of available P with cumulative dry matter yield and P uptake by grass.

Variables correlated	Regression equation	r	n
Olsen's P Vs cumulative dry matter yield	Y = 189.903 + 8.079X	0.92 **	10
Bray's P Vs cumulative dry matter yield	Y = 188.00 + 4.839X	0.93 **	10
Olsen's P Vs cumulative P uptake	Y = 36.316 + 3.915X	0.90 **	10
Bray's P Vs cumulative P uptake	Y = 34.779 + 2.361X	0.91 **	10

Table - 14   Correlation of available P with different inorganic phosphate fractions in soil

	Saloid-P(X_1)	Al-P(X_2)	Fe-P(X_3)	Ca-P(X_4)	Reductant soluble-P(X_5)	Multiple R
Olsen's P (Y_1)	0.84 **	0.93 **	0.77 **	- 0.96 **	- 0.14	0.98 **
Bray's P (Y_2)	0.86 **	0.95 **	0.79 **	- 0.95 **	- 0.15	0.98 **

Multiple Regression Equations :-

Olsen's $P(Y_1)$ = 27.814 + 0.284 X_1 + 0.568 X_2 - 1.017 X_3 - 0.401 X_4 - 0.063 X_5

Bray's $P(Y_2)$ = 5.168 - 0.431 X_1 + 1.403 X_2 - 1.338 X_3 - 0.237 X_4 + 0.141X_5

of these data showed that Al-P had the greatest contribution(45%) followed by Fe-P(32%) and Saloid-P(12%) to available P pool determined by Olsen's method and 52%, 30% and 10%, respectively to available P determined by Bray's-I method.

Although there was quantitative differences in the amount of P extracted by both the method any one can be employed to predict the available P status of soil treated with rock phosphate.

CHAPTER-V

SUMMARY AND CONCLUSION

SUMMARY AND CONCLUSION

The dissolution and availability of phosphorus from six Indian phosphate rocks from Kasipatnam, Hirapur, Mussoorie, Maton, Purulia and Udaipur and two imported rock phosphates from North Carolina and Jordan were studied through laboratory incubation experiment and their P supplying power was compared with SSP by growing hybrid napier grass in a field experiment laid on an acid soil (Haplustalf) having pH-5.6, CEC-3.1 cmol (p^+) kg^{-1} low in available P (Bray's-I - 3.4 ppm and Olsen's - 2.3 ppm) and lime requirement of 2.5 tonnes/ha.

Dissolution of rock phosphates as affected by soil properties and period of incubation

The soil from the site of the field experiment was limed to 0 and 50% of lime requirement (pH 6.5). Both the limed and unlimed soils treated with 500 ppm of P as rock phosphates were incubated upto 90 days at room temperature. During the incubation the moisture content of the soil was maintained at 50% of water holding capacity. Soil samples were drawn at regular interval of 15days and monitered for changes in their pH, 0.5.M NaOH extractable P and exchangeable Ca extracted by 1M $Bacl_2$ - TEA (pH 8.1).

The dissolution of rock phosphate consumed protons and released P and Ca to soil as a result soil pH rose slowly upto 30 days and the highest rise was observed between 30 to 45 days which corresponded to the period of maximum dissolution of rock

phosphates. The pH increase was negligible after 45 days of incubation. Increase in pH was more in unlimed than in limed soil indicating higher dissolution of rock phosphates in the former.

. NCRP and JRP showed largest change in pH in both the soils indicating higher dissolution in comparison to Indian rock phosphates.

The dissolution of rock phosphates calculated as $\triangle$ P (the difference of 0.5 M NaOH extractable P in rock phosphate treated soil and control soil) was quiet low upto 15 days, increased upto 45 days after which the change was negligible. Higher dissolution of imported rock phosphates viz. NCRP and JRP in comparison to Indian phosphate rocks were consistent with their reactivity (ACS).

A higher sink for P and Ca in unlimed soil as indicated by higher P retention capacity (1752.5mg P/kg of soil as against 1557.5 mg P/kg for limed soil) and lower exchangeable calcium (1.2 ppm as against 2.1 ppm for limed soil) produced higher dissolution of rock phosphates.

The dissolution of rock phosphates was also studied by calculating $\triangle$ Ca as the difference between exchangeable Ca in rock phosphate treated and control soil. The pattern of dissolution indicated by ^ Ca method followed the same trend as measured by ^ P method.

Maximum percentage of applied P dissolved was highest for JRP (63.6%) followed by NCRP (61.4%)in unlimed soil as

against the corresponding dissolution of 57.87% and 52.91% in limed soil. The dissolution of all Indian rock phosphates varied between 31.2% to 43.6% in unlimed soil and between 27% and 33.7% in limed soil.

Rock phosphates viz. HRP, MRP, URP and MNRP indicated a higher dissolution in $\triangle$Ca method than in the $\triangle$P method as the Ca present in $CaCO_3$ or dolomite occuring as associated minerals in the rock was preferentially extracted by 1 M $BaCl_2$ — TEA. So the $\triangle$Ca method over estimated the dissolution of rock phosphates containing free lime, where as the $\triangle$P method appeared to be more reliable as the mineral of the apatite group present in rock phosphates was not likely to dissolve appreciably in dilute NaOH. The percent dissolution by $\triangle$P method showed a significant positive correlation (r=0.92[**]) with percent dissolution by $\triangle$Ca method, but the regression line was shifted from equilibrium position towards $\triangle$Ca method of dissolution suggesting higher dissolution.

The dissolution of different rock phosphates in soil as indicated by change in soil pH, $\triangle$P and $\triangle$Ca appeared to have reached equilibrium at 45 days of incubation which may be attributed to the build up of calcium and phosphate ions released from rock phosphate in soil solution due to inadequate size of sink for these two ions in soil. When the concentration of these two ions in soil solution exceeded the solubility product of apatite, there was no further dissolution of rock phosphates.

Effectiveness of different rock phosphates on growth and yield of hybrid napier grass

To evaluate the P availability from different rock phosphates as compared to SSP a microplot trial was conducted in randomised block design to which P was applied @ 100 kg/ha as rock phosphates or SSP. Hybrid napier grass was the test crop.

The first harvest was done after 90 days of planting and successive cuttings were taken at regular interval of 30 days and analysed for P, Ca and Zn.

Though the dry matter yields of NCRP and JRP treatments were at par with SSP for the first two cuttings, their yields were significantly higher than SSP from second cutting onwards indicating higher residual effect of rock phosphates. All the Indian rock phosphate treatments produced significantly higher yield as compared to control but the yields were lower than SSP and imported rock phosphates. The relative agronomic efficiency (RAE) of different rock phosphates calculated by taking the increase in yield due to SSP to be 100 percent followed the order : JRP(145) > NCRP(125) > MRP(93) > HRP(76) > MNRP(59) = PRP(57) = KRP(52) > URP(33). Phosphorus uptake by grass followed more or less similar trend as that of dry matter yield.

Cumulative dry matter yield and P uptake showed a significant positive correlation with crystal chemical parameters of apatite viz. citrate soluble P, ACS, CO_3 / PO_4 molar ratio, F / P_2O_5 weight ratio and a significant negative correlation with a_0 value.

Inspite of application of different amount of calcium in different treatments the uptake of Ca showed a similar trend as that of P, suggesting that Ca - uptake was positively related to the dissolution of P in the rock but not with the total Ca added.

Addition of large quantity of rock phosphate to the soil is likely to increase pH and thus reduced Zn availability to crops. The concentration of Zn in plant gradually decreased after second cutting. The decrease was not to the extent of attaining the critical level of Zn in plant to cause deficiency.

Concentration of Ca in control and SSP treated plots decreased after 2nd and 4th cutting respectively where as in other treatments it showed a slight increase. Phosphorus concentration in plant was more or less same upto 4th cutting, which slightly increased in fifth cutting and again remained more or less constant thereafter. Correlations of P, Ca and Zn uptake with yield showed that the grass yield was limited by availability of P and Ca which in turn was governed by dissolution of rock phosphate.

Phosphorus transformation in rock phosphate treated soil

The inorganic P fractionation of soil samples collected from each plot before fertilization and after harvesting nine cutting of grass showed that in post harvest soil there was a decrease of 8.57 ppm of total inorganic P in control and an increase of 12 to 25 ppm in rock phosphate treated plots as compared to the samples collected before fertilization. In the

71

post harvest soil there was highest increase in Al-P fraction, followed by occluded P and Fe-P fraction, and there was a decrease in Ca-P and reductant soluble P. Amongst different inorganic P fractions reductant soluble P was dominant in both initial and final samples.

Percent dissolution of rock phosphate and SSP in cropped field was calculated by summing up the increase or decrease in different inorganic P fraction in post harvest soil and P uptake by crop from phosphate source and expressing it as percentage of applied P. Rock phosphates arranged in descending order of their dissolution in soil and listed below

SSP(99%) > NCRP(96%) > JRP(95%) > MRP(77%) > HRP (61%) = PRP(60%) = MNRP(59%) > KRP(41%) > URP(36%) indicate their relative effectiveness as a source of P.

Comparision of dissolution of rock phosphates in closed incubation system and open leaching system in presence of rhizosphere

The disolution of rock phosphates were always higher in an open leaching system in cropped field where in addition to presence of P fixing sites and Ca exchange sites in soil, uptake of phosphate and calcium by crop and leaching of these ions from the reaction site provide a higher sink for these ions. But, the dissolution was of correspondingly reduced magnitude in closed system of incubation, where the dissolution products of rock phosphate did not get a chance to be removed sufficiently from the reaction site because of lesser size of sink for Ca and P.

pH and available P status of post harvest soil

The available P content (Olsen's and Bray's-I P) and pH of post harvest soil were higher than the initial samples. Increase in available P was in consistent with dissolution of rock phosphates. Available P determined both by Olsen's and Bray's-I method showed a significant positive correlation with Al-P, Fe-P and Saloid-P, a significant negative correlation with Ca-P and a non significant negative correlation with reductant soluble P. Path analysis of multiple regression data showed Al-P had the greater contribution (45%), followed by Fe-P (32%) and Saloid-P (12%) to Olsen's P and 52%, 30%, 10% respectively to Bray's P. Although the P extracted by Brays-I method was higher than Olsen's method, any one of them can be employed for determination of available P status of soil as yield and P uptake were significantly correlated with available P determined by both the methods.

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

CONCLUSION

1. The dissolution of NCRP and JRP was higher than all the Indian phosphate rocks. Although more P was solubilised at pH 5.6 than at pH 6.5 from a given rock phosphate, the amount of P released from NCRP and JRP at pH 6.5 was higher than the amount of P released from any of the Indian phosphate rocks at pH 5.6. Amongst the Indian rock phosphates MRP & HRP showed higher release of P.

2.   The dissolution of rock phosphate attained an equilibrium after 45 days of incubation without complete dissolution because of the saturation of P fixation and Ca exchange sites of soil and the resulting concentration of P and Ca in soil solution exceeded the solubility product of apatite. A greater percentage of applied P was dissolved under field condition than in laboratory condition due to renewation of sink for P and Ca in former condition by crop uptake and leaching.

3.   Calcium uptake by crop was not related to the total amount of calcium added by rock phosphate but to the dissolution of apatite in the rock.

4.   The availability of P from rock phosphates was related to their dissolution which in turn was related to the crystal chemical parameters of the apatite. The relative agromonic efficency of different P sources were:
JRP (145) > NCRP (125) > SSP (100) > MRP (93) > HRP (76) > PRP (59) = MNRP (57) = KRP (52) > URP (33).

5.   The residual effects of rock phosphate increased and SSP decreased with time. Rock phosphate from Jordan and North Carolina proved to better sources of P than SSP.

6.   The inorganic P forms to which applied P was transformed was mainly Al-P followed by occluded-P, Fe-P and Saloid-P. The major contribution to avilable P pool in soil determined by Bray's-I or Olsen's method was from Al-P, Fe-P and Saloid-P. The crop yield was positively related to the

available P determined by both the methods and hence any of
the two methods can be used to predict the available P
content of rock phosphate treated soil.

BIBLIOGRAPHY

B I B L I O G R A P H Y

* Alfanso,C.A., Battle,J. and Rodriguez,R. (1979). A comparative study of rock phosphates as phosphorus fertilisers for guinea grass. Suelos Y Agroquimica. 2 (11):37-56.

Armiger, W.H. and Fried, M.(1957). The Plant availabilty of various sources of Phosphate rock. Soil Sci. Soc. Am. Proc. 21:183-188.

. Aspiolea, J.C., Avila, A., Valdes, M. and Portieles, M.(1979). A comparision of phosphate sources for Pangola grass, established under irrigated condition. Seuls Y. Agroquimica. 2(2):5-16.

*Barnes, J.S. and Kamprath, E.J.(1975). Availability of North Carolina rock phosphate applied to soils. North Carolina Agric Exp. Station Tech. Bull. No. 229.

Basak, R.K. and Debnath, N.C. (1986). Dissolution of rock phosphates and basic slag in an acid soil as influenced by their rate of application and moisture regimes. Environment and Ecology. 4(4):625-629.

Bascomb, C.L.(1964). Rapid method of determination exchange capacity of calcareous and noncalcareous soil. J. Sc. Food Agric. 15:821-823.

Batten, G.D.; Blair, A.C.; and Lill, W.J.(1979). Changes in soil phosphorus and pH in red earth soil during build up and residual phase of wheat clover by farming systems. Austra. J. Sci. 17(1):163-175.

Bhujbal, B.M., and Ministry, K.B.(1984). Characterisation of major indian phosphate rocks and assessment of their reactivity. Fertilizer News 29(9):26-32.

Biddapa, C.C. and Perur, N.G.(1978). Dynamics of phosphorus transformation in laterite soils of Mysore. Mysor. J. Agril. Sc. 12:91-94.

Biddappa,C.C. and Sarkunam, V.(1981). Realtionship of Olsen'S P with Fe-P and Al-P fractions in soil. J. Indian Soc. Soil Sc. 29:281.

Blancher, R.W.; Rehm, George and Cold well, A.C.(1965). Determination of sulphur in plant material by digestion with nitric acid and perchloric acid. Soil Sc. Soc. Am. Proc. 29:71-72.

Brown, J.R. & Cisco, J.R. (1984). An improved wood ruff buffer for estimation of lime requirement. Soil Sc. Soc. Am. J. 48:587-590.

Caro, J.H. and Hill, W.L.(1956). Characteristics and fertiliser value of phosphate rock from different fields. J. Agric. Food Chem. 4:684-687.

Cescar, M.P., and Tyner, E.H.(1976). Rate of rock phosphate disappearance from the Morrow plots. Adv. Agron. 27:891-924.

Chang, S.C and Jackson, M.L.(1957). A detailed procedure of soil phosphorus fractionation. Soil Sci. 84:133-144.

*Chaverri, J.G. and Black C.A.(1976). Theory of solubility of phosphate rock. IOWA. St. J. Sci. 41:77-95.

Chien, S.H. and Hammond,L.L. (1978). A Comparision of various laborotory methods for predicting agronomic potential of phosphate rocks for direct application. Soil Sci. Soc. Am. J. 44:1267-1271.

Chien, S.H (1977). Dissolution rates of phosphate rock. Soil Sc. Soc. Amer. J. 41:656-657.

Chien, S.H. and Hammond, L.L.(1978). A simple chemical method for evaluating the agronomic potential for granulated phosphate rock. Soil Sci. Soc. Am. J. 42:615-617.

Chien, S.H. (1979). Dissolution of phosphate rocks in acid soils as influenced by nitrogen and potassium fertilizers. Soil Sci. 127:371-376.

Chien, S.H., Leon, L.A. and Tadeja, H.R.(1980). Dissolution of North Carolina phosphate rock in acid colombian soils as related to soil properties. Soil Sci. Soc. Am. J. 44:1267-1271.

Chien, S.H., Hammond, L.L.and Leon, L.A.(1987). Long term reactions of phosphate rocks with an oxisol of Columbia. Soil Sci. 144:257-265.

Chu, C.R., Moschler, W.W. and Thomas, G.W.(1962). Rock phosphate transformations in acid soils. Soil Sci. Soc. Amer. Proc. 26:476-478.

Dash, R.N., Mohanty, S.K. and Patnaik, S.(1988). Influence on phosphorus utilisation by Dhanicha (Sesbania aculeata). J. Indian Soc. Soil Sci. Vol. 36:375-378.

Debnath, N.C. amd Basak, R.K.(1984). Efficiencies of some RP and basic slag for rice, wheat and green gram in acid lateritre soil of W.B. Indian J. of Agril. Sc. 54:722-726.

Dwivedi, G.K., Dwivedi, M. and Pal, S.C.(1989). Relative efficiency of Mussoorie rock phosphate and single super phosphate with lime on yield and phosphorus availability in maize-wheat and soybean-wheat rotations in an inceptisol. Soil Sci.. 37(1):61-65.

Ellis, R.M.; Quader, M.A. and Truog, E.(1955). Rock phosphate availablility as influenced by soil pH. Soil Sci. Soc. Am. Proc. 19:484-487.

Enwezor, W.O.(1978). The effect of aging phosphorus in some soils of south eastern Nigeria on residual phosphate fractions in soil after cropping. Soil Sci. 126(6):353-359.

Graham, E.R. (1955). Availability of natural phosphates according to energy changes. Soil Sci. Soc. Amer. Proc. 19:26-29.

Haundes, H.S. and Arora, B.R.(1988). Efficiency of Mussoorie rock phosphate as a source of fertiliser phosphorus for gram and lentil. Indian Journal of Ecology. 15(2):133-136.

Hanfi, M.M.; Syers, J.K. and Bolan, N.S.(1992). Leaching Effect on the dissolution of two phosphate rocks in acid soils. Soil Sc. Soc. Am. J. Vol. 56:1325-1330.

Hellums, D.T.; Chien, S.H. and Touchton, J.T.(1989). Potential agronomic value of calcium in some phosphate rocks from South America and West Africa. Soil Sci. Soc. Am.J. 53:459-462.

Howeller, H.H. and Wood ruff, C.M.(1968). Dissolution and availability to plants of rock phosphates of igneous and sedimentary origins. Soil Sci. Soc. Amer. Proc. 32:79-82.

Hsu, P.H. and Jackson, M.L.(1960). Inorganic phosphate transformation by chemical weathering in soils as influenced by pH. Soil Sci. 90:16-24.

Jackson, M.L. (1973). soil chemical analysis, Prentice Hall of India Pvt. Ltd., New Delhi.

Joos,L.L. and Black, C.A. (1950). Availability of phosphate rock as affected by particle size and contact with soil of different pH value. Soil Sc. Soc. Amer. Proc. 15:69-75.

Juo, Anthony S.R. and Ellis and Boyd, G. (1968). Chemical and physical properties of iron and aluminium phosphates and their reaction to phosphorus availability. Soil Sci Soc. Am. Proc. 32(2):216-224.

Kar, A.K.. and Chakravarti, S.N. (1969). Availability and fixation of applied phosphate in some Indian soils. J. Ind. Soc. Soil Sci. 7(1).

Khasawneh, F.E. and Poll, E.C. (1978). The use of phosphate rock for direct application to soils. Advances in Agronomy 30:159-206.

Kumar, P. and Mishra, B.(1986). Dissolution pattern of Indian rock phosphates in acid soils. J. Indian Soc. Soil Sci. 34:611-613.

*Lehr, J.R. and Mcclellan, G.H.(1972). A revised laboratory reactivity scale for evaluating phosphate rocks for direct application. Bulletin y-34, Tennessee Valley Authority, Muscle shoals, Alabama, U.S.A.

Mandal, L.N. and Chatterjee, G.N. (1972). Transformation of applied water soluble phosphate materials in acidic low land rice soils. J. Ind. Soc. Soil Sci. 20(4):343-353.

Marwaha, B.C., Kanwar, B.S., Tripathy, B.R. (1981). Direct and residual effect of Mussoorie rock phosphate in wheat maize rotation. Ind. J. Agril. Sci. 51(12) 870-74.

Marwaha, B.C. (1986). Direct and residual effect of Mussoorie rock phosphate on soybean growing sequence with wheat in acid alfisol. Ind. J. Agril. Sci. 56(3) 101-106.

*Mathur, B.S. and Lal, S. (1989). Effect of residual P of rock phosphate on soil properties and crop yield in an Alfisol. Journal of Research, Birsa Agril. Unversity 1(2):127-130.

*McClellan, G.H. and Lehr, J.R.(1969). Crystal chemical investigation of natural apatites. Am. Min. 54:1374-1391.

*Mclean, E.O. and Balam, B.S.(1967). Partially acidulated rock phosphates as a source of phosphorus to plants; Ca uptake by corn from soils of different calcium status. Soil Sci. Soc. Amer. Proc. 31:811-814.

Mishra, B. & Verma, L.P. (1979). Contribution of different P fraction to available phosphorus in soil. Ann. Arid Zone, 18(3).153.

* Mitra,G.N and Mishra, U.K(1991). Evaluation of Udaipur rock phosphate as a phosphatic fertiliser in the soils of Orissa. Research Bulletin 1/91, O.U.A.T.

Motsara,M.R. and Dutta, N.P (1971). Rock phosphate as a fertiliser for direct application to acid soils. J. Ind. Soc. Soil Sci. 19(1) 107-113.

*Murphy,J. and Riley, J.P. (1962). A modified single solution method for determination of phosphorus in natural waters. Anal. Chim. Acta. 27:31-36.

Olsen, R.A. (1975). Rate of dissolution of phosphates from minerals and soils. Soil Sci. Soc. Am. Proc. 39 : 634-639.

Panda,N. and Panda,D. (1969). Evalution of mixtures of ground raw rock phosphate and super phosphate in lateritic paddy soil. J. Agric. O.U.A.T., Vol-I, December.

Pattanayak, S.K. and Mishra, U.K.(1989). Transformation of phosphorus in some acid soils of Orissa. J. Ind. Soc. Soil Sc. 37:455-460.

Raheja, P.C. and Bains, S.S.(1960). Effect of residual phosphorus on crop production. I.C.A.R. Review Series Bulletin No.30.

Robertson, W.K.; Thompson, L.G. and Hutton, C.E. (1966). Availability and fractionation of residual phosphorus in soils high with iron and aluminium. Soil Sci. Soc. Am. Proc. 30:446-450.

Robinson, J.S. and Syers, J.K. (1991). Effect of solution calcium and calcium sink size on dissolution of Gafsa phosphate rock in soil. J. Soil Sci. 42:389-397.

Sahu, B.N, Maity, K. and Mishra, S.N. (1977). Comparative effciencies of rock phosphate and superphosphate for rice in a laterite soil. Fertiliser News 19(11):23-25.

Sanchez, S.L.F., Ownen, B.E.J. (1978). Comparison of phosphate sources in an oxisol in the eastern plains of Columbia. Inst. Colomb. Agro. Pec. 13(4)641-648.

Saunders, W.M.H.(1965). Phosphate retention by New Zealand soils and its relationship to free sesquioxides, organic materials and other soil properties. N.Z.L. Agril. Res. 8:30-57.

Seshagiri Rao, T., Ahmed N., Gopinath Rao, H.K.,(1972) Fractionation of residual phosphorus compounds in black and red soils treated with p-fertilizer. J. Ind. Soc. Soil Sc. 20(4):325-326.

Sinclair, A.G.; Johnstone, P.D.; O'Connours, M.B. and Smith, R.J. (1989). Comparison of sechura phosphate rock and Triple super phosphate rock and Triple super phosphate as phosphate fertilisers for pastures in Newsland. Proc. of fert. Asia Conference, Phillpines (1989). 269-278.

Singh, B.P; Das, M. and Dwivedi, B.S. (1965). Efficiency of some Indian rock phosphates for fodder crop. J. Indian Soc. Soil Sc. 3(1).

Smyth,T.J. and Sanchez,P.A.(1982). Phosphate rock dissolution and availability in cerrado soils as affected by phosphate sorption capacity. Soil Sc. Soc. Am. J. 46:339-345.

Syers, J.K. and Mackay, A.D. (1986). Reactions of Sechura phosphate rock and single super phosphate in soil. <u>Soil</u> <u>Sci.</u> <u>Soc.</u> <u>Am.</u> <u>J.</u> 50:480-485.

Van Der Paauw, F. (1965). Factors Coutrolling the efficiency of rock phosphates for potatoes and rye on humic sandy soils. Plant Soil. 22:81-98.

Verma, L.P., Singh, A.P. and Srivastava, M.K.(1991). Relationship between Olsen's P and inorganic P fractions in soil. <u>J.</u> <u>Ind.</u> <u>Soc.</u> <u>Soil</u> <u>Sci.</u> 39:361-362.

Wells, C.G, Corey R.B (1960). Elimanation of interference of P and other elements in flame photometric determinations of Ca and Mg in plant tissue. <u>Soil</u> <u>Sci.</u> <u>Soc.</u> <u>Am.</u> <u>Proc.</u> 24:189-192.

*Wier, D.R., Chien, S.H. and Black, A.(1971). Solubility of hydroxy-apatite. <u>Soil</u> <u>Sci.</u> 111:1077-1112.

Wilson, M.A., and B.G. Elllis.(1984). Influence of Calcium solution activity and surface area on the solubility of selected rock phosphates. <u>Soil</u> <u>Sci.</u> 138:354-359.

Wright, R.J. and Baligar, V.C.(1991). Effect of phosphate rock dissolution on soil chemical properties and wheat seedling root elongation. Plant and soil, 134(1) 21-30.

Yoshida, S.(1968). Occurance, causes and cure of Zn deficiency of rice plant i calcareous soils. Water and fertiliser practices, Kandy, Ceylone, p.11.

Yuan, T.L.,Robertson, W.K. and Neller, J.R.(1960). Forms of newly fixed phosphorus in the three acid sandy soils. <u>Soil</u> <u>Sci.</u> <u>Soc.</u> <u>Amer.</u> <u>Proc.</u> 24:447-450.

---

* Originals not seen

APPENDIX

Appendix - 1

Crystal chemical parameters and chemical composition of diferent rock phosphates

Rock Phosphates	Ammonium Citrate soluble P	Citric Acid soluble P	ACS	a_0	$CO_3 : PO_4$	$F : PO_2 5$	P in percent	Ca in percent	Ca/P Weight Ratio	Fe in percent	Zn in ppm
NCRP	1.25	3.22	15.03	9.3319	0.212	0.120	13.71	34.57	2.52	0.64	278
KRP	0.44	0.15	4.73	9.3621	0.046	0.099	10.21	31.99	3.13	0.55	90
HRP	0.66	1.70	5.69	9.3593	0.062	0.101	14.23	30.54	2.14	1.67	235
MRP	0.43	0.15	6.54	9.3568	0.075	0.103	8.20	28.07	3.43	4.19	163
JRP	1.14	3.04	11.11	9.3434	0.149	0.112	14.36	36.32	2.52	0.32	283
MHRP	0.44	1.52	6.06	9.3582	0.068	0.102	10.69	26.52	2.48	0.88	83
PRP	0.44	1.20	5.42	9.3601	0.057	0.101	7.73	17.64	2.28	23.75	325
URP	0.44	1.20	5.45	9.3600	0.058	0.101	7.64	26.52	2.47	0.99	88

Source: (Sahu, 1991)

Appendix - 2

Interaction of lime, P sources and time of incubation on $\triangle$P in mg per kg of soil

(A) Mean values for two way interaction between treatments and days of incubation

Days	T-1	T-2	T-3	T-4	T-5	T-6	T-7	T-8	$\overline{D}$
D-1	12.62	40.13	9.88	5.25	14.21	84.0	4.56	15.88	23.31
D-2	106.68	220.46	63.96	66.10	84.20	214	64.77	112.87	117.25
D-3	166.58	294.52	155.53	138.13	172.57	280.8	137.2	193.25	192.33
D-4	172.5	288.5	162.0	144.5	177.0	248.0	144.0	194.5	195.12
D-5	171.75	286.96	153.3	144.02	173.1	243.9	142.9	190.75	192.12
$\overline{T}$	126.02	226.11	108.52	99.6	124.27	226.15	98.7	141.45	

CD (T) = 62.28,   CD(D) = 49.24

(B) Mean values for two way interaction between treatments and liming

Liming	T-1	T-2	T-3	T-4	T-5	T-6	T-7	T-8	$\overline{L}$
L-0	132.7	244.66	114.19	105.36	136.21	222.47	105.54	152.16	308.33
L-1	119.35	207.55	102.92	93.84	118.0	211.83	91.84	128.74	268.52

CD (L) = 31.14,   CD (T X L) = 52.64

(C) Mean values for two way interaction between liming and days of incubation

Liming	D-1	D-2	D-3	D-4	D-5
L-0	29.02	119.81	203.53	213.12	205.7
L-1	21.02	113.44	181.10	198.62	178.53

CD (D X L) = 69.64,

Symbols Used :

Treatments :

T-1 - URP; T-2 - JRP; T-3 - HRP; T-4 - MRP; T-5 - MMRP; T-6 - NCRP; T-7 - KRP; T-8 - PRP.
Days of Incubation : D-1 - 15; D-2 - 30; D-3 - 45; D-4 - 60; D-5 - 90.
L-0 Unlimed Soils; L-1 Limed Soil