Impact of Treated Rock Phosphate (TRP) on Phosphorus Availability and Growth of Mung Bean (*Vigna radiata).*

THESIS

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In partial fulfilment of the requirement for the degree of

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In

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by

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(2019)

CERTIFICATE – I

This is to certify that the thesis entitled "**Impact of Treated Rock Phosphate (TRP) on Phosphorus Availability and Growth of Mung Bean (*Vigna radiata*).**" submitted in partial fulfillment of the requirement for the **DEGREE OF MASTER OF SCIENCE in Agriculture (Soil Science and Agricultural Chemistry)** of the Rajmata Vijayaraje Scindia Krishi Vishwa Vidyalaya, Gwalior is a record of the benefited research work carried out by **Mahesh Patidar, ID No. 17111302** under our guidance and supervision. The subject of the thesis has been approved by the Student's Advisory Committee and the Director of Instruction.

No part of the thesis has been submitted for any degree or diploma (Certificate awarded etc.) or has been published. All the assistance and help received during the course of the investigation has been acknowledged by the scholar.

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CERTIFICATE –II

This is to certify the thesis entitled "**Impact of Treated Rock Phosphate (TRP) on Phosphorus Availability and Growth of Mung Bean (*Vigna radiata).*"** submitted **Mahesh Patidar, ID No. 17111302** to the Rajmata Vijayaraje Scindia Krishi Vishwa Vidyalaya, Gwalior in partial fulfillment of the requirements for the degree of Master **of Science in Agriculture (Soil Science and Agricultural Chemistry)** has been accepted after the evaluation by the External Examiner and by the Student's Advisory Committee after an oral examination on the same.

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Place: Gwalior

Date:

Mahesh Patidar

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Abbreviations and Acronyms

Abbreviations/ Acronyms	**Meaning**
"	Seconds
%	Per cent
&	And
@	At the rate of
Ag.	Agriculture
CD	Critical difference
Dist.	District
dSm^{-1}	Deci Siemens per meter
EC	Electrical conductivity
et al.	And co-workers
Fig.	Figure
Ha	Hectare
i.e.	In reference to; that is
K	Potassium
Kg	Kilogram
kg ha^{-1}	Kilogram per hectare
M	Meter
Max.	Maximum
mg kg^{-1}	Milli gram per kilogram
Min	Minimum
Mm	Milli meter
N	Nitrogen
No.	Number
^{o}C	Degree centigrade
OC	Organic carbon
P	Phosphorus
TRP	Treated Rock Phosphate
NRP	Normal Rock Phosphate
PC	Phosphocompost
pH	Soil reaction

ppm	Parts per million
R.V.S.K.V.V.	**Rajmata Vijayaraje Scindia Krishi Vishwa Vidhyalaya**
RP	Rock phosphate
S	Sulphur
SE (m)	Standard error of mean
SSP	Single Super Phosphate
t ha^{-1}	Tones per hectare
Temp.	Temperature
Viz	Namely
Vs	Verses
Zn	Zinc
ZnO	Zinc oxide
PROM	Phosphorus Rich Organic Matter

CHAPTER - I

INTRODUCTION

Phosphorus is a macronutrient that plays a number of important roles in plants and required for plant growth, yield and seed formation. Phosphorus is very reactive in soil. Although in many agricultural soils the total P concentration is large but it is not sufficiently available to plants due to its immobilization in different stable forms. Hence, very limited concentration of P is available to plant and soil becomes deficient in plant available P (Adesemoye and Kloepper, 2009). A survey of Indian soils revealed that 98% of soils were deficient in P, because the concentration of available P including in fertile soils was generally not higher than 10 µmol L^{-1} even at pH 6.5 where it is mostly soluble (Gyaneshwar et al., 2002). These low levels of P are due to high reactivity of soluble P with Ca, Fe or Al that leads to precipitation thus lowering the overall use efficiency. Generally the use efficiency of applied P fertilizers is 15-20%. Oberson et al. (2001) concluded that deficiency of P in soils decreased agricultural productivity on more than 2 billion hectares worldwide and therefore, agronomic treatments to improve P availability in the soil and to increase P utilization in agriculture are of special importance. To obtain the sufficient level of yield water soluble chemical fertilizers are applied. However, over use of fertilizers can not only cause unanticipated environmental impacts but also they are expensive, and have some harmful impacts on the soil structure, composition, micro flora and other properties of soil (Reddy et al., 2002; Koliaei et al., 2011). Increasing the high cost of chemical fertilizer has been a major emerging as an alternative and valuable source of P nutrition. The challenge is thus being faced not only of increasing productivity on sustainable basis, but also of the preserving and maintaining of soil fertility. Therefore, comprehensive account of planning of inherent resources like use of rock phosphate ascertaining its potential and problems towards low cost on sustainable basis is possible.

The total reserves/resources of rock phosphate as on 1.4.2015 have been placed at 312.67 million tonnes. Out of these, the reserves constitute 45.80 million tonnes while 266.87 million tonnes are under

Remaining Resources category. Of the total reserves/resources, 34% are in Jharkhand, 31% in Rajasthan, 19% in Madhya Pradesh, 8% in Uttar Pradesh & Uttarakhand each, respectively (India Minerals Year Book, 2017). In addition, sizable portions of RPs are imported. In 2016-17 imports of rock phosphate were 7.51 million tonnes, mainly from Jordan (37%) and Egypt (29%).

The effectiveness of rock phosphate (RP) relative to soluble P fertilizer varies from source to source depending upon mineralogy and chemistry of each rock as well as the influence of soil, crop, and environment and management practices. It has been well established that increasing substitution of CO_3^{2-} for PO_4^{3-} in the lattice structure increases the solubility of carbonate apatites. This occurs due to decreased a-dimension of the unit cell, and crystal instability on increased incorporation of planar CO_3^{2-} and F^{1-} for PO_4^{3-} tetrahedral (Lehr and Mc Clellan, 1972; Chien, 1977). As the rock phosphates are relatively insoluble materials, their geometric surface area have an important bearing on their rate of dissolution in soil. Bhagavati Ammal *et al.* (2000) reported that the finer particles of rock phosphate (100 mesh) resulted in higher values of dissolution than relatively coarser particles (60 mesh). Rajan *et al.* (1991), indicated that the amount of P dissolved from rock phosphate, decreases with increase in soil pH either exponentially or linearly. Rock phosphate (RP) is a raw material for all P containing fertilizers. It can be utilized as direct application fertilizer in acid soils because of low input cost and slow release of P to the soil (Sale and Mokwunye, 1993). However, this can be achieved if the dissolution of rock phosphate is continued in the soil system. Lower concentration of Ca in the soil solution favours the dissolution of rock phosphate according to law of mass action (Mackay and Syer, 1986). There are natural ways by which this can be achieved. For example, plants can influence the rate of rock phosphates dissolution by the secretion of acid or alkali, uptake of large quantity of Ca, production of chelating organic acids (citric, malic and 2- ketogluconic acid) which complex Ca and deplete P in the soil solution.

However, some artificial mechanisms have also been tried by various researchers to achieve the same. For example, zeolite and rock phosphate mixtures have been prepared and tested in the field. The objective was to bind the released calcium on high surface area (also high CEC) on zeolites so as to favour the dissolution of rock phosphates. However, zeolites are not ubiquitous in nature. We have attempted a new approach of preparing a mixture of high surface area and high CEC acid treated clay and rock phosphates to achieve the same.

The vertisols of Madhya Pradesh are rich in clay content. Moreover, the clay fraction is dominated by smectites which have high surface (internal and external) area and high CEC almost resembling the properties of zeolites. Our hypothesis was if rock phosphates are combined with acid treated smectitic clays then the released calcium would be adsorbed on clay surface and continuity in the release of rock phosphates would be maintained.

Hence, in this research work we have collected the soils from the vertisol region of Bhopal, Madhya Pradesh, separated the clay content, treated the isolated clay with acid and incubated the mixture with rock phosphates. I studied the release of phosphorus after regular time interval. Similarly, I also studied the bio-availability of phosphorus to mung bean crop by applying such treated rock phosphates. Hence, research work titled **"Impact of Treated Rock Phosphate (TRP) on Phosphorus Availability and Growth of Mung Bean (*Vigna radiata)*"** was started with following specific objectives:

Objectives:

The main objectives of this study are:

- To study the release of P from rock phosphate under different treatments
- To study the effect of application of rock phosphate on growth of mung bean in a pot experiment

CHAPTER-II

REVIEW OF LITERATURE

In this chapter, an attempt has been made to bring out review for the topic of interest **“Impact of Treated Rock Phosphate (TRP) on Phosphorus Availability and Growth of Mung Bean (*Vigna radiata)*”**. A brief resume of the work done in the past by various workers is reviewed under appropriate heads.

Effect of phosphorus on growth and yield of legumes

Availability of phosphorus from rock phosphates under different treatments/conditions

Efficiency of rock phosphate as P source to plant

Impact of rock phosphate on P uptake, nutrient content and soil fertility

Effect of acidulation of rock phosphate

Direct effect of rock phosphate in different soil

Release kinetics of P in different soil

Effect of phosphorus on growth and yield of legumes

The effect of phosphorus on growth and yield of crops is well known. However, in this section of review, give some quantitative estimates of the effect of phosphorus on growth and yield of legume crops primarily mung bean.

Ahmad *et al.* (2019) concluded that the RP was activated with HCl (APR-H), EDTA (APR-E) and oxalic acid (APR-O), and tested for their capabilities to release soil available P and lateral transport of P in soil under unsaturated conditions was investigated. The effects of the amendments are improved plant growth by enhancing lengths and dry matter production of shoot and root of wheat plants. The enhanced plant growth under APR-O and APR-E applications resulted in higher uptake of P, Fe, Mn, and Zn to the wheat plants.

Singh *et al.* (2018) concluded these studies show that a treatment combination of phosphorus Organo-Mineral Fertilizers (P-OMF), sulphur Organo-Mineral Fertilizers (S-OMF) and recommended doses of fertilizers (RDF) with (75%RDF + P-OMF@ 5.0 q ha^{-1} + S-OMF@5.0 q ha^{-1}) can enhance plant height, grain yield, stover yield, test weight, pod length, number of pods plant^{-1} , number of seeds pod^{-1}, total nodules plant^{-1}, and dry weight of nodules plant^{-1} in green gram. This fertilizer consortium may be used as efficient formulation for green gram production in farmers' fields.

Mohammad *et al.* (2017) concluded that the application of P up to 40 kg P_2O_5 ha^{-1} recorded significantly higher number of pods per plant, number of seeds per pod and seed and straw yield, nitrogen, phosphorus and potassium uptake in seed and straw, protein content in seed, microbial biomass carbon, nitrogen and phosphorus in soil as compared to absolute control and 20 kg P_2O_5 ha^{-1} but was at par with 60 kg P_2O_5 ha^{-1}. Application of 40 kg P_2O_5 ha^{-1} represented an increase of grain yield over control and 20 kg P_2O_5 ha^{-1} by 32.15 and 7.48 per cent, respectively. This might be due to excess assimilates stored in the leaves and later translocated into grains at the time of senescence, ultimately led to higher grain yield. It was noted that a unit increase in number of pods/plant, number of grains/pod, test weight and total N, P and K uptake increased grain yield of mung bean.

Patel *et al.* (2017) reported that P applied @ 40 kg ha^{-1} recorded significantly higher plant height at 60 DAS and at harvest, number of branches per plant, dry matter production per plant, number of pods per plant, number of seeds per pod and length of pod over control. Significantly the higher seed and haulm yields of 1168 and 2475 kg ha^{-1} as well as protein content (19.34%) and protein yield (226.20 kg ha^{-1}) of green gram were produced with the 40 kg P_2O_5 ha^{-1} over control, respectively.

Khan *et al*. (2017) reported that on growth parameters and yield attributes of mung bean were influenced by graded levels of P viz. P^0 (no P_2O_5), P^1 (15 kg P_2O_5 ha^{-1}), P^2 (30 kg P_2O_5 ha^{-1}), P^3 (45 kg P_2O_5 ha^{-1}), they

founded that application of 45 kg P_2O_5 ha^{-1} was found significantly superior and increased the dry weight of the crop at all stages, produced highest no. of branches over as recorded with 45 kg P_2O_5 ha^{-1} which was significantly superior to other treatments. The lowest grain yield (673.1 kg ha^{-1}) was recorded in the control (P^0).

Venkatarao *et al.* (2017) reported that the application of P @ 40 kg ha^{-1} and dual inoculation of biofertilizers (PSB + *Aspergillus awamori*) had significant effect in improving the growth attributes and yield (grain and straw) in comparison to other treatments of mung bean.

Yadav *et al.* (2015) conducted a field experiment to study the effect of different nutrient combination and sources on mung bean (*Vigna radiata* L. Wilczek) in sandy loam soil. Among the treatments, application of 50 kg P, 8 kg nitrogen as basal along with 1.0 ton of vermicompost ha^{-1} gave maximum plant height, number of active nodules, number of pods per plant and number of grains per pod in mung bean and seed and straw yield which were significantly higher than the other treatments.

Rathour *et al.* (2015) conducted a field experiment during summer season and found that the highest nodule dry weight (35 mg $plant^{-1}$) was obtained with the application of 20 kg P_2O_5 ha^{-1} through SSP + PSB in mung bean and application of 40 kg P_2O_5 ha^{-1} significantly increased the growth, yield attributes and seed yield over control.

Choudhary *et al.* (2015) conducted an experiment and reported that application of P up to 40 kg P_2O_5 ha^{-1} in mung bean under rainfed recorded significantly higher number of pods per plant, number of seeds per pod, number of total and effective root nodules, test weight, higher seed and straw yield as compared to absolute control and 20 kg P_2O_5 ha^{-1} but was at par with 60 kg P_2O_5 ha^{-1}.

Tiwari *et al.* (2015) conducted an experiment on green gram and result revealed that application of P @ 60 kg P_2O_5 ha^{-1} recorded significantly higher seed and straw yield as compared to other treatments.

Rathour *et al.* (2014) in a field experiment conducted during summer season to study the integrated P management in summer green gram (*Vigna radiata* L.) found that significantly highest pod length was recorded with the treatment 40 kg P_2O_5 ha^{-1} through DAP.

Bhatt *et al.* (2013) conducted an experiment and found that application of P @ 40 kg P_2O_5 ha^{-1} + PSB recorded significantly higher seed (1099 kg ha^{-1}) and straw yield (2301 kg ha^{-1}) in mung bean compared to other treatments.

Kumawat *et al.* (2013) in a field experiment was conducted at Udaipur concluded that application of full dose of P through DAP significantly increased the number of pods per plant, number of grains per pod, test weight and seed yield of black gram as compared to SSP and phosphorus rich organic manure (PROM).

Thenua and Kumar (2011) observed that uptake of N, P, K and S were increased with the application of P up to 60 kg P_2O_5 ha^{-1}, sulphur up to 80 kg S ha^{-1} and PSB inoculation in chickpea.

Zafar *et al.* (2011) reported that integrated application of mineral P, Poultry manure and PGPR (plant growth promoting rhizobacteria) in cowpea significantly increases shoot height, shoot fresh weight, shoot dry weight and leaf chlorophyll content by 67, 160, 51 and 106%, respectively while increase in root length, root fresh weight and root dry weight was 79, 161, and 187%, respectively over unfertilized control without PGPR application. Integrated use of different P sources and PGPR also increased number of nodules per plant, nodule fresh weight and nodule dry weight by 158, 107 and 168% over the control.

Ali *et al.* (2010) conducted an experiment and results revealed that all the levels of P fertilizer showed significant impact on mung bean compared to that of control plots. Application of P fertilizer @ 84 kg ha^{-1} gave the maximum yield components and grain yield compared to rest of the treatments.

Singh (2010) conducted a field experiment at Jobner and reported that application of P through PROM was recorded significantly higher number of pods per plant, seeds per pod, number of total and effective nodules and test weight of mung bean and significantly higher seed and straw yield of mungbean as compared to SSP, DAP and control.

Availability of phosphorus from rock phosphates under different treatments/conditions

Basak *et al.* (2019) measured the chemical reactivity of Indian rock phosphates (RPs) by five chemical extraction methods (i.e. water, neutral ammonium citrate (NCA), 2% citric acid (CA), 2% formic acid (FA) and absolute citrate solubility (ACS)). These measurements were assessed by agronomic response data obtained by growing ryegrass and palmarosa in two highly weathered acidic soils under pot culture experiment. The P solubility value of RP measured by different methods followed the order: ACS > 2% CA > 2% FA > NAC > water. Considering triple super phosphate (TSP) as a standard reference P fertilizer, the agronomic response of RPs followed the order Udaipur RP > Jhabua RP ≥ Purulia RP > Mussorie RP. Methods based on citrate solubility (i.e. NAC, 2% CA and ACS) were significantly and positively correlated with agronomic response irrespective of the plant species and soil types. The best correlation value obtained with NCA indicated that P solubility in NAC solution may offer better prediction of agronomic effectiveness of RP in terms of biomass yield, relative agronomic efficiency (RAE) and P recovery efficiency. So, the present investigation will help to predict the agronomic effectiveness of low-grade RP based on chemical methods.

Samreen *et al.* (2019) concluded that earlier the original source of P fertilizer was bones; as time passes, the supply of P fertilizer will get exhausted. Today, rock phosphate is the only raw material in the form of P fertilizers. There are two types of rock phosphates: igneous and sedimentary; both have the same P mineral, i.e., calcium phosphate of apatite group. The general formula for pure rock phosphate is $Ca_{10}(PO_4)_6(X)_2$, where X is F^-, OH^- or Cl^-. These minerals are called apatites. The most common rock phosphate mined is fluorapatite, which contains impurities like CO_3, Na and Mg. Carbonate-fluorapatite (francolite) is primary apatite mineral in the majority of rock phosphates. The high reactivity of some rock phosphates is due to the occurrence of francolite. The major deposits are found in the US followed by China, Morocco and Russia. The US produced about 33% of the world's rock phosphate, although nearly 50% of the world reserves are in Morocco. P fertilizers are produced from either acid-treated or heat-treated rock phosphate to break the apatite bond and to increase the water soluble P content. There are many commercially available P fertilizers like phosphoric acid, calcium orthophosphates, ammonium phosphates, ammonium polyphosphate and nitric phosphates.

Sarangi *et al.* (2019) found that rock phosphate is a viable alternative to the high cost water soluble P fertilizers in increasing crop productivity in acid soil regions. Use of udaipur rock phosphate alone or with amendments increased soil pH, available P, Ca, biomass yield and P, Ca and S uptake by hybrid napier grass. Higher dose of URP (200% P) alone was as effective as URP: SSP mixture in 1:1 ratio for long duration napier grass as reflected by yield and RAE and can therefore be used as an affordable alternative to the more comprehensive water soluble SSP fertilizers. Effect of FYM or PSB on URP dissolution rate as reflected by soil pH, available P exchangeable Ca and biomass yield of hybrid napier grass was lower as compared to combined application of URP + SSP or URP + lime.

Ditta *et al.* (2018) reported that rock phosphate enriched compost (RP- EC) with a combination ratio of 50:50 (RP:Compost), applied before 7 days of sowing under pot culture conditions and at the rate of 800 kg ha^{-1} with phosphate solubilizing microorganisms under field conditions produced maximum nodulation, growth and yield parameters of chickpea in comparison to conventional chemical phosphatic fertilizers. Therefore, they concluded that RP-EC can be used as an alternate source of P for maximum production of leguminous crops.

Roy *et al.* (2018) found that non-renewable nature of rock phosphate (RP) reserves coupled with open ended nature of P cycle makes it imperative for maximum utilization of available P resources. In this context, use of Indian RPs from Purulia and Udaipur along with citric acid loaded nano clay polymer composite (CA-NCPC) as P source to costly di-ammonium phosphate (DAP) was investigated through an incubation experiment for 90 days followed by a greenhouse experiment with wheat-rice cropping sequence in a Luvisol (pH 5.14, available P 13.5 mg kg^{-1}). Soil available P, crop yield parameters and dynamics of soil P fractions were taken to judge the efficacy of CA-NCPC in solubilizing RPs. Application of CA-NCPC and DAP resulted in 82% and 69% increase in available P over control, respectively under incubation study. Direct effect of treatment receiving CA-NCPC + RP on yield and P uptake by wheat was comparable with DAP but residual impact of CA-NCPC + RP (16.7 g pot^{-1}) was better than DAP (13.8 g pot^{-1}) in rice. The changes in inorganic P fractions were also significant as inclusion of RP increased calcium-P from 16.1 to 61.5 mg kg^{-1}. Results indicated potentiality of RPs treated with CA- NCPC as an alternate P source which could prove promising amidst P scarcity.

Sarwar *et al.* (2018) studied the impact of de-waxed filter cake press mud (organic amendment) for the release of available P from insoluble rock phosphate (local Hazara rock phosphate) in normal soil (pH= 8.15, available P = 7.1 mg kg^{-1}, sandy clay loam). Results suggested application of recommended doses of NPK proved superior in terms of enhancing plant height, total biomass, biological yield, leaf area index and soil available P. However, soil organic matter and P content remained highest in treatments receiving organic amendments. The workers concluded that application of organic nutrition i.e. de waxed filter cake press mud (FCP) proved beneficial for the release of P from local red rock phosphate and also enhanced soil organic carbon fraction in similar growth environment.

Basak *et al.* (2017) concluded that composting of low-grade Indian RPs along with isabgol crop residue significantly improves P content as well as accelerates the mobilization of unavailable P from RP into its available form. The value added compost slowly but continuously released water soluble P during leaching experiment indicates its potentiality as slow release P fertilizer. Moreover, application of these composts in soil during incubation remarkably improves water soluble & available P, microbial biomass C and P as well as phosphatase activities which determine the P availability in soil. So, value added compost can be an effective alternative source of P fertilizer through efficient utilization of low grade RP which reduce the dependence on costly chemical fertilizer and huge amounts of foreign exchange.

Ganesapillai *et al.* (2016) prepared a novel fertilizer combination of two waste products: low-grade RP tailing and human urine. They demonstrated that the combined use of urine (nitrogen) and low-grade RP (phosphorous) can act as a substitute to synthetic inorganic fertilizers. Crop trials were carried out for *Cicer arietinum* using RP enriched urine at various application rates on a red loamy soil (pH 8.11). Direct application of this fertilizer combination resulted in plant growth performance equivalent to mineral fertilizer Di-Ammonium Phosphate added in the same ratio. The use of RP enriched urine thus holds a lot of promise for simultaneous waste minimization, waste utilization, and improved resource-use efficiency.

Osman (2015) concluded that acidulated rock phosphate was superior as compared to super phosphate in dry matter yield. Acidulation both of rock phosphate and super phosphate with sulfuric and fulvic acid was superior for increasing the nutrient uptake and yield components. Generally increasing the concentration of acids cause a significant increase in P use efficiency, the highest P use efficiency was obtained in presence of sulfuric and fulvic acid for both P- sources super phosphate and rock phosphate as compared to the other treatments, however, the opposite trend was obtained in presence of citric acid and compost extract.

Helmy *et al.* (2013) reported that rock phosphate can be considered as an environmental friendly alternative for P mineral fertilizers sources. This approach assists farmers to increase their income through reducing the potential hazardous contamination of surface and ground water which occurs when chemical fertilizer P is used. Utilization of P fertilizer decreased to 50% by integrating biological and organic phosphorus fertilizers with natural phosphorus fertilizer without yield loss. Also, environmental pollution is reduced by decreasing consumption of chemical fertilizers. Overall utilization of biological and organic phosphate fertilizers with rock phosphate fertilizer in addition to increased maize yield under saline conditions could be a strategy to achieve sustainable agriculture.

Liu *et al*. (2012) showed that the average amounts of P released by all the organic acids from the two RPs increased with the increase of concentrations of organic acids. The effectiveness of the organic acids in releasing P from RPs followed the order, i.e., oxalic acid > citric acid > tartaric acid > formic acid > malic acid > succinic acid > acetic acid. The P released from RPs was negatively correlated with the equilibrium solution pH. The types and concentrations of the acids, liquid/solid ratio and RP powder particle size had great impact on the P release from RPs. In addition, the amount of P released from RPs was related to the nature of the RPs, leaching time and temperature.

Akande (2011) reported that phosphate application significantly increased soil available P and exchangeable Ca. The percentage change in soil available P followed the order SSP > Crystallizer super > Ogun rock phosphate. Partially acidulated rock phosphates constitute both water soluble mono calcium phosphate and sparingly soluble unreacted RP.

Aria *et al.* (2010) found that the incubation of rock phosphate with elemental sulphur, vermicompost, *Thiobacillus, Thiooxidans* inoculation or different combinations of these treatments had increased the water soluble P of RPs significantly.

Kumari *et al.* (2008) founded that a high grade quality rock phosphate is an essential requirement for manufacturing of P fertilizers. In India, 15.3 MT of indigenous deposits of high grade rock phosphate could meet hardly 35% of the total demand and remaining demand is met through its import. In view of escalating cost of P fertilizers, it becomes necessary to generate technologies by which P from indigenous low grade rock phosphate can be solubilized and utilized as a source of P fertilizer. Various amendments which have been explored world over in order to increase the solubility and availability of low grade rock phosphate includes: composting with farm manure, green manuring, partial acidulation of rock phosphate, use of P solubilizing organisms, use of rock phosphate along with some chemicals etc. Rock phosphate is one of the basic raw materials needed in the manufacture of P fertilizers like single super phosphate, diammonium phosphate, nitro phosphates etc. Commercial rock phosphate occurs in nature as deposits of apatites (P-bearing minerals) along with other accessory minerals such as quartz, silicates, carbonates, sulphates, sesquioxides etc. Four types of rock phosphate minerals are: Carbonate apatite [$3Ca_3(PO_4)_2.CaCO_3$], Fluoro apatite [$3Ca_3 (PO_4)_2.CaF_2$], Hydroxy apatite [$3Ca_3(PO_4)_2.Ca(OH)_2$], Sulpho apatite [$3Ca_3 (PO_4)_2.CaSO_4$].

Odongo *et al.* (2007) conducted an experiment with the treatments of manure from steer supplemented with 113 g busunbu rock phosphate (BRP)/ day (FBRP), Manure from steers not supplemented with BRP, feces mixed with 113g BRP/day (MBRP) and Manure from steers not supplemented with BRP and feces not mixed with BRP (CONT). The sub-plots treatments were, mixed with 440g of wheat per kg fresh feces (WS) or without straw (WOS). The result shows that P enriched composting in the presence of wheat straw significantly increased P availability and increased plant growth. However, in terms of plant growth, there was no additional benefit of first feeding the RP to steers before composting the manure because most of the RP fed seem to have been utilized by the animal.

Khalil *et al.* (2002) conducted an experiment to study the agronomic effectiveness of local rock phosphate with Biophos (PSM: Phosphorus Solubilizing Microorganisms) inoculation with organic and inorganic amendments on rice yield and P uptake. Rock phosphate, green manure, FYM, Ca and Al in soil as gypsum and aluminum sulfate were applied to pots. Rock phosphate with FYM produced 17% more yield than that of control (without PSM). With PSM inoculation, maximum P-uptake was observed where rock phosphate was applied with green manure followed by FYM. Sole application of rock phosphate with PSM inoculated treatment again performed better than that of gypsum and aluminum sulfate.

Baligar *et al.* (1997) conducted a pot experiment to examine the interaction between rock phosphate (RP), coal combustion by-product (BP), dolomite lime (DL), and cellulose (C) in an acidic soil and their effects on ryegrass growth. BP and RP application increased plant P content and dry matter yield (DMY) of shoots and roots by improving soil Ca availability and reducing Al toxicity. The addition of cellulose to the BP- and RP-amended soils reduced water-soluble Al and increased DMY. Plant growth increased RP dissolution by 2.4 to 243 % in a soil with low available P. Use of BP at moderate rates with RP and dolomites lime appears to be the best combination in increasing crop yields on infertile acidic soils.

Efficiency of rock phosphate as P source to plant

Kafle *et al*. (2019) described three major groups of microbes that participate in the cycling of P within the soil and that have the potential to enhance the plant P acquisition efficiency in agricultural and forestry ecosystems. However, the variability in responses after inoculation with different fungi or bacteria justifies the need to pursue additional research focused on identifying soil microbes that improve plant phosphate efficiency in cropping systems. More importantly, AM (Arbuscular Mycorrhiza) fungi, EcM (Ectomycorrhiza) fungi, and phosphate solubilizing bacteria do not act independently, but affect each others´ activities. These types of studies increase our understanding of the microbial systems that exist in nature and will likely facilitate the development of microbial inocula that are more efficient and optimized for the nutritional needs of plants.

Yadav *et al.* (2017) studied the effect of 'concentration of RP and compost showing maximum soluble P' on growth of plants. They found that 75:25 ratio of compost and rock phosphate showed maximum soluble P and found higher plant growth as compared to plants fertilized with normal compost and rock phosphate.

Heuer *et al.* (2017) reported that to access P from the soil, plants have evolved high and low affinity Pi transporters and the ability to induce root architectural changes to forage P. Also, adjustments of numerous cellular processes are triggered by the P starvation response, a tightly regulated process in plants. Given the high costs of fertilizers and in light of the fact that rock phosphate, the source of P fertilizer, is a finite natural resource, there is a need to enhance P fertilizer use efficiency in agricultural systems and develop plants with enhanced Pi uptake and internal P-use efficiency (PUE).

Al-Oud (2011) investigated phosphate-dissolution ability of rock phosphate (RP) in a calcareous soil as a function of either incubation period, or application of organic acids, elemental sulphur and /or organic manure. The results indicated that the availability of P from rock phosphate was increased by increasing incubation period regardless of the rate of applied RP. On the other hand, the solubility and/or availability of RP were increased by increasing the rate of applied elemental sulphur and/or organic manure. Furthermore, the oxalic acid solution at the rate of 0.2 mmol L^{-1} was superior to the other solution of either citric or EDTA. The applications of organic acids or organic manure and/or elemental sulphur could be successfully used for increasing P-availability from rock phosphate in calcareous soil.

Misra *et al.* (2002) reported that when Mussourie, Udaipur, Purulia and Jhabua rock phosphates modified by mixing either with iron pyrite or composting with paddy straw along with or without PSM inoculation (Phospho-compost) water soluble and citrate soluble P content of the original rocks was increased. A phosphate-deficient acid soil incubated with either of the modified products for 105 days increased the available (Olsen's) P content of soil after 60 days of incubation and the increase was more due to application of phospho-compost than RP + pyrite mixture. Results of pot culture study with rice as test crop revealed that application of modified RPs significantly increased dry matter yield and P uptake by the crop.

Impact of rock phosphate on P uptake, nutrient content and soil fertility

Ahmad *et al.* (2019) concluded that the RP was activated with HCl (APR-H), EDTA (APR-E) and oxalic acid (APR-O). They tested these amendments for their capabilities to release soil available P and lateral transport of P in soil under unsaturated conditions in a long term study. Results revealed that APR-O and APR-E were the most efficient amendments in releasing and transporting higher amounts of available P in the soil for longer time periods compared to pristine RP.

Venkatarao *et al.* (2018) conducted a field experiment on four levels of P (Control, 20, 40 and 60 kg P_2O_5 ha^{-1}) and four levels of biofertilizers (Control, PSB, *Aspergillus awamori* and PSB+*Aspergillus awamori*). Results indicated that N, P_2O_5 and K_2O content in grain and straw and their uptake after harvest were observed significantly maximum up to 40 kg P_2O_5 ha^{-1} level of phosphate application over control. Results further indicated that seed inoculation with the PSB and *Aspergillus awamori* significantly increased N,

P_2O_5 and K_2O content in grain and straw and their uptake after harvest over the rest of the treatments. The protein content was increased significantly with 40 kg P_2O_5 ha^{-1} level of phosphate application and seed inoculation with PSB and *Aspergillus awamori* over control.

Zafar *et al.* (2017) demonstrated that integrated use of poultry manure (PM) and composted rock phosphate (CRP) can act as P fertilizer and performed better than the sole SSP in terms of yield, P uptake and phosphorus use efficiency in wheat. The integrated use of PM and SSP with CRP and in the ratio of 50:50 resulted in i) yield equivalent or higher than the treatments receiving 100% SSP alone ii) increased plant total P uptake (grain

+ straw) and iii) increased PUE by 12-18%. Increased OC, total N and available P in integrated treatments compared with SSP alone indicated that the organic materials improved PUE from inorganic fertilizer. Further, to optimize the RP solubility and increased plant P uptake, it could be blended with compost at lower rates before its soil application.

Choudhary *et al.* (2015) conducted an experiment on mungbean and the results of the study indicated that application of P up to 40 kg P_2O_5 ha^{-1} recorded significantly higher nitrogen, phosphorus and potassium content and their uptake in seed and straw, protein content in seed and net return as compared to absolute control, 20 kg P_2O_5 ha^{-1} and 60 kg P_2O_5 ha^{-1}.

Rathour *et al.* (2015) conducted a field experiment during summer season and results revealed that the highest protein content in seed (24.20%) was obtained with the application of 20 kg P_2O_5 ha^{-1} through SSP + PSB in green gram.

Tiwari *et al.* (2015) conducted an experiment in green gram and results revealed that there was significant increase in the uptake of nitrogen and phosphorus by grain and straw and protein content up to 60 kg P_2O_5 ha^{-1}.

Kumar (2015) conducted an experiment on mung bean crop and reported that progressive increase in level of P up to 40 kg ha^{-1} significantly increased the available P content in soil but organic carbon content of soil remained unaffected due to increasing levels of phosphorus.

Rathour *et al.* (2014) conducted a field experiment during summer season to study the integrated P management in summer green gram (*Vigna radiate* L.) and revealed that protein content was significantly increased and the highest seed nitrogen content was recorded under the treatment of 20 kg P_2O_5 ha^{-1}. The maximum P content in seed was noticed under the treatment of 40 kg P_2O_5 ha^{-1} from DAP and 40 kg P_2O_5 ha^{-1} from DAP + 200 kg gypsum ha^{-1}.

Bhatt *et al.* (2013) conducted an experiment to investigate the effect of different levels of vermicompost and P with and without PSB on yield, quality, and nutrient content of summer green gram and soil fertility status after harvest of the crop. They reported that P application @ 40 kg P_2O_5 ha^{-1} + PSB performed equally as that of 40 kg P_2O_5 ha^{-1} without PSB, significantly improved the protein content, nutrients content and uptake and soil fertility status after harvest of the crop.

Yadav (2013) reported that organic carbon, available nitrogen, phosphorus, potassium content, dehydrogenase activity and alkaline phosphatase activity in soil after harvest of crop were significantly increased with the application of SSP+PROM in green gram.

Ghosal *et al.* (2012) showed that the ability of the RPs to release P in the plant available forms depends on the particle size and chemical and mineralogical characteristics of the RPs as well as the properties of the soil in which they are applied. So an experiment was conducted with four sources of phosphatic fertilizers namely Triple super phosphate (TSP – 21.75%P), Partially acidulated rock phosphate (PARP – 12.97%P), Morocco rock phosphate (MORP – 14.87%P) and Mussoorie rock phosphate (MRP – 8.12%P) whose solubility were tested in six different extractants namely 2% Citric acid, 0.002 N Hydrochloric acid, N-Ammonium citrate, Bray-2 P extractant, Olsen’s extractant and Morgan’s reagent under seven periods of incubation (1, 2, 3, 7, 10, 15 and 30 days), with and without soil. The results revealed that release of P were increased on addition of soil irrespective of fertilizers or extractants used. TSP released maximum P (3.05% - 3.27% with soil, 2.11% - 2.22% without soil) by the 7th day of incubation. The partially acidulated source was found to release P, higher than rock phosphates but lower than TSP, for the initial periods of incubation (1-3 days) (1.31%-1.34% with soil, 0.46% without soil) with an increase in the later periods (7th day onward) (1.27%-1.92% with soil, 0.55%-0.66% without soil). The RPs released maximum P after the 7th day of incubation. Among the different solvents, maximum release of phosphorus was observed by 2% citric acid followed by Bray 2 P and Olsen's extractants.

Effect of acidulation on rock phosphate

Ahmad *et al.* (2019) concluded that activation of raw RP with EDTA or low molecular organic acids such as oxalic acid could release higher amounts of P and some trace metals over a longer period of time compared to raw RP, resulting in higher crop production when applied directly to soil as amendments.

Xie *et al.* (2019) studied the viability of enriching P_2O_5 from low-grade rock phosphates through organic acid leaching. The organic acids removed the carbonaceous part from rock phosphates. The authors opine that these experimental results provide an essential scientific support for further upgradation of the technology to commercial scale utilization.

Basak (2018) reported that low molecular weight organic acids (LMWOAs) are naturally occurring in soil, particularly in the rhizosphere due to microbial metabolites and secretion of root exudates. Various functional groups present in LMWOAs can play an effective role in P dissolution. In their study, potentiality of LMWOAs for P release from low-grade Indian rock phosphates (RPs) collected from Udaipur, Jhabua and Purulia was investigated under laboratory conditions. The characteristic of P release and the factors influencing P release from selected low-grade RPs by using seven LMWOAs along with two inorganic acids were also investigated. The amount of P release from RPs with different acids at various concentrations and equilibrium pH as well as the different factors of P release was also compared. Results showed that the average amounts of P released by all the organic acids from the three RPs increased with the concentration of organic acids. The amount of P release by the organic acids from the RPs followed the order, i.e. oxalic acid > citric acid > tartaric acid > formic acid > malic acid > succinic acid > acetic acid. A negative correlation was observed between P released from RPs and an equilibrium solution pH. The average amounts of P released from RP ranged from 12 to 81 mmol P kg^{-1} by acetic acid and citric acid, respectively. In addition, the nature of RPs, RP/acid solution ratio, leaching time and temperature significantly influenced the P release from RPs by organic acids. Thus, the LMWOAs could be a potential amendment for improving bio availability of P from RP.

Kumar *et al.* (2018) conducted a field experiment from 2009–2012 at the Norman E. Borlaug Crop Research Center at Pantnagar, Uttarakhand, to find out the efficiency of rock phosphate (RP) with different organic [farmyard manure (FYM), press mud and phosphate solubilizing bacteria (PSB)] and inorganic [single superphosphate (SSP) and gypsum] acidulating materials. Rainy season (*kharif*) crops, namely rice (*Oryza sativa* L.), soybean [*Glycine max* (L.) Merr.], maize (*Zea mays* L.) and winter season (*rabi*) crops, namely Indian mustard [*Brassica juncea* (L.) Czernj & Cosson], *rabi* maize, chickpea (*Cicer arietinum* L.) and lentil (*Lens culinaris* Medik.), were selected for the study. The experiment carried out in a randomized block design with 8 treatment combinations of different acidulates with rock phosphate and replicated 3 times. Treatments include control, SSP + RP, RP + gypsum, RP

+ PSB, RP + FYM, RP + PM, RP + FYM + PSB and RP + PM + PSB. The

maximum grain yield (5.18 t ha^{-1}) and straw yield (10.87 t ha^{-1}) in rice were observed when press mud and gypsum was used for acidulation respectively. *Kharif* maize and *rabi* maize gave the maximum grain yield when rock phosphate was acidulated with SSP. However, treatment effects were non-significant. Soybean, Indian mustard and lentil gave the maximum grain yield in gypsum acidulation of rock phosphate, but the effect due to treatments was significant in Indian mustard only. In chickpea, significantly higher grain yield (2.38 t ha^{-1}) was recorded in FYM + PSB acidulation than the other treatments which was found on a par with FYM and PM + PSB acidulation treatment.

Rahman *et al.* (2018) investigated the effect of different levels of acidulated rock phosphate (RP), liquid or solid and application methods on phosphorus use efficiency and wheat yield under calcareous soils of Peshawar during 2015-16. Treatments included acidulation of 100 kg RP with 7.5, 15, 30 and 45 kg H_2SO_4 equivalent to 25, 50, 100 and 150 % acidulation, applied in the form of either liquid or solid as single (no split) or two equal splits at sowing and knee height stage. The rate of P in all treatment was equal to 90 kg P_2O_5 ha^{-1}. Our results showed that acidulation levels significantly increased wheat yield, post-harvest soil and plant tissue P optimum at 100 % acidulation level. Solid form of the acidulated RP was more effective than liquid revealing that lesser the contact of soil, could improve P availability from the source. It was further affirmed by the split application where it significantly increased the crop yield and P availability over no split irrespective of solid and liquid form. Our results suggest that solid RP with 100

% acidulation applied in two splits improved the crop yield, P use efficiency and could substitute commercial fertilizers under the prevailing soil and agro- climactic conditions.

Hamadi *et al.* (2012) reported that the acidulation reaction is more rapid with hydrochloric acid than with sulphuric acid, and yields soluble products from both the calcium and phosphate. Thus, there is neither a need to heat the mixture to speed up the reaction, nor are there any crystal form problems requiring temperature stabilization.

Mahendran *et al*. (2005) prepared partially acidulated rocks phosphate from Purulia and Udaipur rocks phosphate at three level (20, 40 and 60%) with sulphuric acid under different methods (a) treated the rock phosphate directly with concentrated acid alone (b) wetted the rock phosphate with water first followed by acid (c) treated the rock phosphate with acid first followed by water (d) treated the rock phosphate with acid first allowed half an hour and added after with water (e) treated the rock phosphate with pre-diluted acid with water. The results showed that no significant effect of the acidulation methods on total P content of PARPs, whereas the highest water soluble and citrate soluble P obtained when pre-diluted acid method was used at 60% acidulation.

Direct effect of rock phosphate in different soil

Hellal *et al.* (2019) concluded that biological solubilization of rock phosphate is more environmentally friendly than acidulation. Fungi are widely used as producers of organic acids, and particularly, some *Aspergillus* and *Penicillium* species have been directly introduced into the soil in order to solubilize the rock phosphate. Biological solubilization will make P available for plant use with minimum pollution to the environment. Rock phosphate inoculated with bacteria and *Mycrrohizae* proved to be a suitable approach to use RP for continuous crop production.

Zhang *et al.* (2019) reported that P is one of the most important nutrients for increasing crop yield; the increase in effective P ratio directly from raw rock phosphate (RP) powder by mechanical grinding to increase its microcrystallinity is believed to be the best choice for this purpose. This study reports the improvement in the activation property of PR powder with different lignite ratios (1%, 2%, 3%, and 5%), particularly the relationship between particle-size distribution, specific surface area, granule morphology, and the citric acid-soluble P. It was found that a 3% lignite addition was the optimal treatment for increasing the release of citric acid-soluble P. The maximum total amount of dry matter from rapeseed cultivation and the available P after the test increased by 56.1% and 89.6%, respectively, with direct use of PR and microcrystallized RP powder (RP2), compared with the control test without any addition of phosphate minerals.

Husnain *et al.* (2014) evaluated direct application of reactive rock phosphate (RRP) for Maize, and its combination with manure and agronomic effectiveness. Reactive rock phosphate improved soil fertility and maize crop productivity. Moroccan RRP contained the highest citric acid extractable P_2O_5 among other rock phosphate tested and also the most effective in improving maize yield. In addition, the residual effect of rock phosphate in supplying plant with P for up to six cultivation years was demonstrated. However, although rock phosphate is cheaper than SP-36, farmers did not adopt this technology yet.

Khalil (2013) evaluated the best combination of rock phosphate (RP), sulphur (S), organic manure, and phosphate dissolving bacteria (PDB) inoculation to enhance the availability of phosphorous from rock phosphate and their effects on yield of broad bean plants. It was found that either sulphur application or PDB inoculation with RP had a significant effect on broad bean yield and its quality. Application of RP and different soil amendments individually or together increased N, P, and K contents in straw and seeds of broad bean plant. The highest contents of the studied nutrients were found when the plants were fertilized by a mixture of RP and different soil amendments (RP, S and OM or RP, PDB, S and OM). Results also showed the important role of organic matter, sulphur, and PDB for releasing phosphorus from rock phosphate. The combination of soil amendments with RP as a natural P-source has the possibility of saving significant quantities of industrialized inorganic phosphate fertilizers.

Nakamura *et al*. (2013) reported that direct application of Burkina faso rock phosphate has an effect on rice grain yield comparable to that of chemical water-soluble phosphate fertilizer.

Ghosal *et al.* (2013) compared the direct and residual effects of rock phosphate with triple super phosphate. The results revealed that while water soluble triple super phosphate gave the best performance by direct application in rainfed rice, insoluble but slowly available rock phosphate particularly partially acidulated one and Morocco rock phosphate showed good promise by their residual effects in the following seasons and was found even better than water soluble P-source. Rock phosphates (PARP and MORP) also left higher P-balance in soil applied once in three years under acid soil condition.

Ibrahim *et al.* (2010) founded that the direct application of rock phosphate seems to offer a better alternative in terms of low cost, least energy-intensive and sophistication of processing of the phosphate ore to produce soluble fertilizers. On the other hand, lower sensitivity to the ore quality offers a big advantage and the presence of impurities, which may play a positive significant role in the process in addition to the technique flexibility in utilizing of some useful elements needed for plant growth. All these factors can be expressed in terms of the economic advantage of the mechanical activation technique. In their study, Red Sea phosphate ore was subjected to the mechanical activation treatment with and without the beneficiation. Various products before and after activation were compared in terms of solubility and the process economy. The results showed that the mechanical activation is economically preferable.

Gholizadeh *et al.* (2010) evaluated the relative agronomic effectiveness (RAE) of asfordi rock phosphate (PR) partially acidulated at five levels (0, 40, 60, 80, and 100 %) in two calcareous and non-calcareous soils. The partially acidulated rock phosphate (PARP) was compared vs. triple superphosphate, using canola as the test crop. They found that the relative effectiveness of fertilizers as based on dry mater and P uptake significantly increased with an increase in acidity level. In 100% acidulated RP (in match with single super phosphate) the relative dry matter and P uptake were low as compared to standard fertilizer application but very high against no PR application. The relative dry matter yield in calcareous soil (with low free Fe_2O_3) was significantly higher than that in non-calcareous soil (with high free Fe_2O_3). Also, the relative dry matter yield and P uptake increased with increasing the rate of applied P.

Dib *et al.* (2006) studied the behavior of natural Syrian rock phosphate in acidic soil and its effect on plant. Powdered or dust natural rock phosphate added to the soil at different rates and compared with triple super phosphate (TSP) as control, using ray grass as the test plant. The results revealed that phosphorus absorbed by ray grass plants was maximum in case of natural rock phosphate compared with dust phosphate and control. Moreover, the available amounts of residual P_2O_5 in the soil after harvest gave enough stock to the following crop. The addition of natural rock phosphate increased the soil pH with different values depending on the type and rate of added phosphate, while TSP reduced it.

Begum *et al.* (2004) reported from greenhouse experiment on an alkaline soil conducted in order to assess the phosphate P supplying capacity of eight sources of phosphatic fertilizers, at three levels of P (25, 50 and 75 mg P kg^{-1} soil), using wheat as the test crop, that grain and straw yield of wheat increased with increasing the dose of applied fertilizer P, as did the application of compacted RPs when compared to non-compacted RPs. Apparent P recovery and phosphorus content were found to be maximum in treatments receiving RP+MAP+S°, the efficiency of which in terms of grain yield was found to be 80.5% in comparison to DAP.

Release kinetics of P in different soil

Yang *et al.* (2019) P fertilizers are added to improve the soil P fertility, but the rate of P release can greatly influence its availability. Organic acids are effective in the release of inorganic P (Pi), but the contribution of each Pi fraction is not well understood. This study reported the transformation rate of P and solubility of Pi fractions induced by organic acids. Path analysis was utilized to explore the direct and indirect effects of Pi fractions on the amount of total Pi (TPi) solubilized. Results showed that the P release was initially rapid, followed by a slower release that lasted up to 2160 hour, and the Elovich equation was the best-fitted kinetic equation to estimate the transformation rate of available P. The amount of TPi-solubilized by oxalic and citric acids tended to increase with increasing organic acid concentrations. Oxalic acid exhibited a lower TPi-solubility capability than citric acid when the organic acid concentration was ≤1 mmol L^{-1}, whereas citric acid was higher at

≥1.5 mmol L^{-1}. The Al-P-solubilized had the highest content of studied fractions, and path analysis revealed that the Al-P-solubilized exhibited a significant direct effect on TPi-solubilized. Thus, Al-P is a potential P source in black soil.

Kherbawy *et al.* (2014) analyzed different Egiptian rock phosphates for P release. By studying the variations in kinetic parameters in different types they concluded that phosphate is retained in raw materials with different forces which represent variation in P bioavailability.

Jalali and Ranjbar (2010) studied the transformation rate and fractionations of P in 20 calcareous soils of varying properties. The samples were incubated for 3, 24, 168, 336, 504, 720, 1440, and 2160 hrs at 25 °C and Olsen-P was determined after each incubation period. The transformation rate of Olsen-P for soils was estimated by best fitted kinetic equation (parabolic) for above incubation periods. The results showed a sharp decrease in Olsen-P within 3 hrs after P addition. There were changes in the proportional distribution of P in all the soils during 2160 hrs of incubation with amended P. In general the proportions of P associated with the most weakly bound fraction (KCl-P) tended to decrease with corresponding increases in the NaOH-P and HCl-P fractions during the incubation. The principal component analysis showed that the first four components explained 77.1 % of the overall variation.

Shariatmadari *et al.* (2006) studied the Kinetics of P release from Iranian calcareous soils at upper-, mid-, and lower-slope positions of two arid and two semiarid landscapes were determined and relations between the P release rate parameters and P uptake by wheat were investigated. The kinetic data was best described by simple Elovich equation as evidenced by the relatively higher values of determination coefficient (r^2) and the relatively lower values of the standard error of estimate. Power function, parabolic diffusion and first order equations also well fitted the time-dependent P release data. The rate parameters showed positive significant relationships with clay, active calcium carbonate and citrate-bicarbonate-dithionate (CBD) extractable Al contents of the soils. The soil properties promoting the P release rate and the P release kinetic parameters increased from the upper-slope to the lower- slope positions of the arid top sequences.

Ahroni *et al.* (1991) reported that the kinetics of phosphate sorption /release can be describe by an expression that is approximated it at beginning time by a fractional - power equation, it intermediated time by the evolich equation, and it long times by an apparent first - order equation such kinetics, which can be characterized by a sigmoidal Z (F plot of the reciprocal of the rate against time (dq/dt)-vs.t)), are consistent with theoretical homogenous, hetrogenous models based on diffusion of the sorbate in the soild phase or at the solid / liquid interface these models were applied to data from the published literature on sorption and release of phosphate by soil. The experimental results were accounted for by assuming a constant diffusion coefficient. For other soils it was assumed that diffusion process with various diffusion coefficients takes place simultaneously. Using these models, diffusing parameters can be estimated.

Barrow (1984) studied from six soil samples which was incubated at 60°C for 24 hrs with several levels of either calcium carbonate or hydrochloric acid. An interpolation method was used to give points on the three- dimensional surface relating the final pH of the suspensions to sorption of phosphate at specified solution concentrations of phosphate. Result revealed that the differences between the soils were ascribed to differences in two soil properties. One was the rate at which the electrostatic potential in the plane of adsorption decreased as pH increased. The electrostatic potential decreased more quickly in solutions of a sodium salt than in solutions of calcium salt and this explained the observed differences between these media. The other soil property that affected observed sorption was the release of phosphate from the soil. The amount released was largest at low pH. Consequently, for fertilized soils, measured sorption increased with pH.

CHAPTER-III

MATERIALS AND METHODS

The present investigation **"Impact of Treated Rock Phosphate (TRP) on Phosphorus Availability and Growth of Mung Bean (*Vigna radiata*)"** was carried out during summer season of 2018-19 at the research farm, ICAR- Indian Institute of Soil Science, Bhopal, Madhya Pradesh. The present chapter deals with a brief description of the methods followed and materials used during the investigation.

Detailed description of experimental site

Location and climate

The pot experiment was conducted during summer season of 2018-19 at the research farm, ICAR-Indian Institute of Soil Science, Bhopal, Madhya Pradesh. The study area falls under semi-arid and sub-tropical zone characterized by hot summer and cold winter. Mean annual precipitation is about 650 mm, most of which is received during the monsoon period of July to September. The average maximum temperature during summer is 35°C, while the average minimum temperature during winter is 4°C.

Geographical situation

Indian Institute of Soil Science Bhopal is situated in Madhya Pradesh.
Its geographical coordinates are 23°18'29"N 77°24'23"E.

Experimental details:

The experiment was conducted at the Laboratories of Indian Institute of Soil Science, Bhopal (M.P.). All the important facilities to conduct the research work were available in the laboratory.

Collection and preparation of soil sample:

To achieve the objectives of the present investigation, surface (0-15 cm) soil samples were collected from research farm of the ICAR- Indian Institute of Soil Science Bhopal. The collected soil samples were air-dried, ground and passed through 2 mm sieve. The processed soil samples mixed thoroughly for ensuring homogenization. The processed soil samples were used for laboratory incubation study and for pot culture experiment.

Properties of phosphate rock

Jhamarkotra, Rajsthan rock phosphate was used for the experiment having 31.5% P_2O_5. Rock phosphate was ground and passed through 0.125 mm sieve and used in the experiment.Rock phosphate is a natural mineral found as a geological deposit on a large scale in the form of sedimentary rocks containing various amounts of calcium phosphates. Once ground, it is used as a phosphatic fertilizer, called phosphorite or mineral phosphate, or as a primary source of phosphorus. The properties of the rock phosphate used in the experiment are given below (Chandraprabha, 2017):

Table 3.1: Chemical properties of experimental rock phosphate

Constituent	Jhamarkotra (weight %)
P_2O_5	31.5
CaO	45
SiO_2	6.1
F	2.8
Fe_2O_3	2.1
MgO	2
Organic Matter	0.14
Cl (ppm)	97
CO_2 as ($CaCO_3$)	1.2
SO_3	14
Na_2O+ K_2O	0.6
Loss on ignition (LOI)	5.1

Preparation of acid treated clay

First, cementing agents will be removed. Organic matter was removed by treating the soil with hydrogen peroxide (6 per cent). The soil, after decomposition of organic matter, was treated with enough hydrochloric acid (0.2 N) to decompose the carbonates, as well as remove the iron and aluminium oxide. Sand fraction was separated through wet sieving. The clay fractions (<0.002 mm) was isolated by gravity settling in water using stokes law. The steps are described below:

1. Removal of organic matter with hydrogen peroxide

Soil was placed in beaker and 100 ml of dilute hydrogen peroxide was added. The beaker was stirred with a glass rod to suspend the sample. The glass rod was rinsed between each sample and dried with a lab tissue. Another 50-100 ml of dilute hydrogen peroxide was added after the bubbling was stopped and the procedure was repeated till the bubbling stopped. When the addition of hydrogen peroxide to the samples no longer causes bubbling, the organics have been removed.

2. HCL Treatment and removal of sand

The soil, after decomposition of organic matter, was treated with enough hydrochloric acid (0.2 N) to decompose the carbonates, as well as remove the iron and aluminium oxide. Sand fraction was separated through wet sieving.

3. Separation of silt and clay by decantation

The clay silt suspension was filled in long jars and the clay was removed after settlement of silt. Long jars were taken and labelled at 0 (top) and 5-cm depths (bottom). Then the suspension to be separated was added in jars, up to the 0-cm water-depth line. A small amount of dispersant was added with the spatula. The jars were sealed and shaken vigorously to homogenize the suspension. After the elapse of appropriate time when the silt has settled past the 5 cm mark clay suspension was withdrawn by using a syringe (Poppe, *et al.* 2001).

4. Acid clay

Sufficient quantity of clay was recovered and treated with HCl to make acid clay. This clay was treated with 1N HCl (1:1 soil: solution) thrice. After acid treatment the clay was washed with ethanol 4 times and air dried.

Photo 3.1: Clay separation from silt+clay solution

Details of experiment

The details of the incubation and pot experiments are given in table below:

Table 3.2: Experimental details

S. No.	**Experimental details**	
1	Location	ICAR-IISS, Bhopal
2	Design	Completely Randomized Design (CRD) Lab incubation & Pot culture
3	Treatments	Incubation treatments- 7
		Pot experiment treatments- 7
4	Replications	3
5	Crop	Mung bean
6	Variety	Narmada-139
7	Date of sowing	19/02/2019 (pot culture)
8	Date of harvesting	03/05/2019
9	Seed rate	10 eed per pots

Incubation experiment:

A laboratory incubation study was conducted to assess the release of P from the soil as influenced by different treatments. Soil and clay samples was thoroughly mixed with rock phosphate and/ or vermicompost as per treatment in plastic beakers in a completely randomized design. Moisture content in each beaker was maintained at 50% of field capacity. Each treatment was replicated thrice. The soils in beakers were incubated at room temperature for different periods i.e. 10, 20, 30, 40, 50, 60, 70, 80, 90, 100,

110 and 120 days. After completion of incubation period for estimation of available phosphorus, soil was extracted with 0.5*M* $NaHCO_3$ (Olsen *etal.*,

1954). Phosphorus (P) content in the extracts was determined by ascorbic acidblue colour method (Watanabe and Olsen, 1965). The details of the treatment are given in table below:

Table 3.3: Treatment details of incubation experiment

Treatments	Incubation experiment (Black soil/Alluvial soil)
T1	Control (soil)
T2	Soil + TRP (2%)
T3	Soil + TRP (5%)
T4	Soil + NRP (2%)
T5	Soil + NRP (5%)
T6	Soil + NRP (2%) +Phosphocompost (@20 kg P/ha)
T7	Soil + NRP (5%) +Phosphocompost (@ 20 kg P/ha)

Note: TRP= Treated Rock Phosphate, NRP= Normal Rock Phosphate

Photo 3.2: Incubation experimental setup

i. Pot culture experiment

A pot experiment in greenhouse was conducted to assess the impact of rock phosphate application on biomass yield and P uptake by mung bean grown on Black soil and Alluvial soilunder different treatments. For conducting the greenhouse study, plastic pots of 10 kg capacity were filled with 7 kg of soil. Rock phosphate was mixed thoroughly then filled into pots. Pots were watered to take the soil into sufficient moisture for germination. 10 seeds of mung bean were sown in each pot, after germination 5 plants were maintained in each pot. After completion of the experiment whole plant were harvested and dried. The treatment details of pot culture experiment are given in table below:

Table 3.4: Treatment details of pot culture experiment

Treatments	Pot Culture experiment (Black soil/Alluvial soil)
T1	Control (soil)
T2	Soil + TRP (2%)
T3	Soil + TRP (5%)
T4	Soil + NRP (2%)
T5	Soil + NRP (5%)
T6	Soil + NRP (2%) +Phosphocompost (@20 kg P/ha)
T7	Soil + NRP (5%) +Phosphocompost (@ 20 kg P/ha)

N and K were applied in all the treatments.

b. Plant analysis

Plant samples (grain and straw) were collected and dried in oven at 70°C, then dried samples were ground in an electric grinder to 0.5 mm size. These samples were used for the analysis for available P.

Determination of phosphorus

One g oven dried ground plant sample was taken in 100 ml conical flask and was digested using 10 ml of di-acid mixture consisting of AR grade concentrated HNO_3 and $HClO_4$in the 9:4 ratios and the volume of digested material was made-up 100 mL volumetric flask and was filtered through What man No. 42 filter paper and filtrate was used for estimation of available phosphorus.

Estimation of phosphorus

10 ml of aliquot from the colorless filtrate was taken into 25 mL volumetric flask for determination and then 5 mL of ammonium molybdate vanadate mixture was added to it and volume was made up to 25 mL after shaking well. It was kept for 30 minutes for development of yellow color and color intensity was measured in spectrometer (model CE 2031) at 470 nm after setting the instrument to zero with blank as described by Jackson (1973).

c. Soil Analysis

All the individual soil samples were analyzed for the following chemical properties.

i. Soil pH

The pH of soil was determined by using pH meter with glass electrode (model, 420A)using 1:2.5 ratio soil water suspensionsafter stirring it for 30 minutes as described by(Jackson, 1973).

ii. Electrical conductivity (dSm^{-1})

The supernatant liquid of the soil suspension formerly used for pH determination was used for the determination of electrical conductivity by conductivity meter (model-105 A plus) (Jackson, 1973).

iii. Organic carbon

Organic carbon content of the soil sample was determined following the wet digestion method (Walkley and Black, 1934; Walkley, 1947). One- gram soil was digested with 10 ml potassium dichromate ($K_2Cr_2O_7$) and 20 ml conc. H_2SO_4 in dark condition for 30 min. Then excess dichromate was determined by titration with ferrous ammonium sulphate [$Fe(NH_4)$ $(SO_4)_2.6H_2O$] after adding 10 ml conc. H_3PO_4 using diphenyl amine indicator. The same procedure was repeated by taking blank sample (without soil) and amount of dichromate used for digestion of carbon was measured which indirectly tells the amount of carbon in soil. Organic carbon percentage was calculated from the following formula:

$$SOC\% = \underline{\begin{array}{c} 10(B - S)\ X\ 0.003\ X\ 100 \\ B\ X\ W \end{array}}$$

Where, B= blank reading; S= sample reading; W= weight of the soil sample

iv. Available Nitrogen

Available nitrogen was estimated by alkaline $KMnO_4$ method where the organic matter in the soil was oxidized with hot alkaline $KMnO_4$ solution. The ammonia (NH_3) evolved during oxidation was distilled and trapped in boric acid and mixed indicator solution. The amount of NH_3 trapped was estimated by titrating with standard acid (Subbiah and Asija, 1956).

$$N\ (kg\ ha^{-1}) = \underline{\begin{array}{c} (S - B)\ X\ \text{Normality of}\ H_2SO_4 X\ 14\ X\ 2.24\ X\ 10^6\ 1000 \\ X\ W \end{array}}$$

Where, B= blank reading; S= sample reading; W= weight of the soil sample

v. Available Phosphorus

The available phosphorus of soil was extracted with 0.5 *M* $NaHCO_3$ (pH 8.5) (Olsen *et al.,* 1954). The content of phosphorus in the extract was determined using ammonium molybdate and ascorbic acid reduction method by developing blue colour and intensity of blue colour was measured using spectrophotometer (model-CE2031) at 660 nm wave length (Jackson, 1973)**.**

$$\text{P (mg kg}^{-1}\text{)} = \frac{\text{C X Final volume (mL)X olsen reagent (mL)}}{\text{aliquot (mL)X W}}$$

Where, C= concentration of P; W= weight of the soil sample

vi. Available Potassium

The potassium in soil was extracted with neutral normal ammonium acetate and the content of potassium in the extract was estimated by flame photometer (model, CL 378) (Jackson, 1973).

$$\text{K (mg kg}^{-1}\text{)} = \frac{\text{R X F X volume of ammonium acitate (mL)}}{\text{Weight of the soil}}$$

Where, R= reading; F= unit factor; W= weight of the soil sample

d. Modeling P release in incubation experiment

Kinetics of P release for different treatment combinations were studied with time and the data was fitted employing 2 mathematical equations:

Elovich: $P_t = a + b \ln t$

First-order reaction: $\ln (P_0 - P_t) = a - bt$

Where, P_t and P_0 are the P released at time t and maximum P release. ‘a’, ‘b’, and P_0 are parameters of the model. The parameters were computed by nonlinear regression procedure in SPSS software.

The standard error of the estimate (SE) was calculated for each equation. SE = $[\Sigma(P_t - P_t^*)^2/(n-2)]^{1/2}$

Where, P_t and P_t^* are the measured and calculated concentrations of P released at time ‘t’ and ‘n’ is the number of measurements

e. Economics

Cost of treatments and expected return were calculated for each treatment.

i. Cost of Treatment

For different treatments total cost was calculated on the basis of prevailing market rate of fertilizer, field preparation, sowing of seeds, labour charges, culture and intercultural operations etc.

ii. Gross return

For different treatments gross returns was calculated on the basis of prevailing market rate of produce.

iii. Net Return

It was calculated treatment wise. The total cost of cultivation per hectare was subtracted from the gross income for computing net returns from each treatment.

$$\text{Net Return (Rs ha}^{-1}) = \text{Gross return (Rs ha}^{-1}) - \text{Cost of cultivation (Rs ha}^{-1})$$

iv. Benefit Cost Ratio (BCR)

It was calculated treatment wise. The gross income per hectare of each treatment was divided by the cost of cultivation of respective treatment

$$\text{Benefit Cost Ratio (BCR)} = \frac{\text{Gross return}}{\text{Cost of cultivation}}$$

f. Statistical analysis

Both incubation and pot culture experimentswere laid out in Complete Randomized Design (CRD). The data obtained from various characters under study were analyzed by the method of analysis of variance as described by Gomez and Gomez (1984). The level of significance used in “F” test was given at 5 per cent. Critical difference (CD) values are given in the table at 5 per cent level of significance, wherever the “F” test was significant at 5 per cent level. The skeleton of analysis of variance and formula used for various estimations are given below:

Table 3.5: The skeleton of the analysis of variance

Source of variance	**DF**	**SS**	**MSS**	**Fcal**	**Ftab**	**SEM+**	**CD 5%**
Treatment	(t-1)	TrSS	TrMS				
Error	(n-t)	ESS	EMS				
Total	(n-1)	TSS					

The following formula was used for standard error, critical difference and coefficient of variance estimation.

(a) S. Em± = $\frac{EMS}{r}$

(b) C. D. = S. Em ±× √2 × t7 D. F. . at 5%

(c) CV(%) = $\frac{EMS}{GM} \times 100$

Where,

R = Number of replication, D.F. = Degree of freedom,

T = Number of treatment, S.S. = Sum of square,

C.D. =Critical difference, C.V. = Coefficient of variance,

MSS = Mean sum of square, EMS = Error mean square, SEm

± = Standard error of mean, n = No of observations,

CHAPTER - IV
RESULTS

The results of the present investigation “**Impact of Treated Rock Phosphate (TRP) on Phosphorus Availability and Growth of Mung Bean (*Vigna radiata*)**” related to the study of P release from treated rock phosphate, availability & uptake of P by mung bean from treated rock phosphate and the yield of mung bean and residual fertility status of experimental soil are displayed and explained in this chapter. The data of the final observations of the various parameters were subjected to statistical analysis and the results have, therefore, been presented through tables. All the findings of the experiments have been described in the following paragraphs under suitable heads:

: Results of incubation experiments

The results of the incubation experiment carried out with two soils are presented. The incubation experiment was carried out at room temperature and continued upto 120 days with samples drawn for analysis after every ten days.

Properties of soils used for incubation experiment

Two soils, one black soil collected from ICAR-IISS farm and another alluvial soil collected from Indo Gangetic plains of Ludhiana, Punjab were used for the study.

Some properties of the soils used in the incubation experiment are presented in table 4.1.1. Both the soils were alkaline. The black soil was having considerable high clay content and CEC compared to alluvial soil. The available N status was almost similar in two soils. However, available P status was considerable high in alluvial soils. Similarly, available K was high in black soil due to high CEC. In general, black soil was having higher overall fertility as reflected in high organic C content.

Table 4.1.1 Some properties of soils used in incubation experiment

Soil Property	Black Soil	Alluvial Soil
pH	7.9	7.7
EC (dS m^{-1})	0.33	0.18
OC (%)	0.64	0.41
N (kg ha^{-1})	239	226
P (kg ha^{-1})	10.7	25.8
K (kg ha^{-1})	503	205
CEC (cmole (p+) per Kg)	44	8.6
Clay (%)	41	12
CEC (Acid Treated Clay) (cmole (p+) per Kg)	103	-

Phosphorus release in incubation experiment

The release of P under different treatments is given in alluvial and black soils are given in table 4.1.2.1 and 4.1.2.2, respectively. The P release was higher in alluvial soil as compared to black soil in all the treatments. Among the treatments, the treatment T3 and T7 showed considerably higher P release at the end of incubation period. The release of P from acid treated clay rock phosphate incubated treatments (T2 and T3) was higher than normal soil+rock phosphate treated treatment. Also, there was no perceptible difference in cumulative P release in control (T1), T4 and T5.

Kinetics of P release in incubation experiment

The release of P was also fitted with two kinetic models Elovich and First order. The coefficient of determination (R^2) and release rate constants are depicted in tables 4.1.3.1 and 4.1.3.2. The standard error of estimates are given in table 4.1.3.3.The goodness of fit (R^2) ranged between 0.948 and 0.983 and between 0.948 and 0.984 in case of alluvial and black soil, respectively for Elovich model. And, it ranged between 0.995 and 0.998 and between 0.997 and 0.999 in case of alluvial and black soil, respectively for First order model. Similarly, standard error of estimate (s.e.) ranged between 0.16 to 0.46 and between 0.85 to 2.40 in black and alluvial soils, respectively when fitted to Elovich model. The values were between 0.06 to 0.30 and between 0.20 and 0.93 in black and alluvial soils, respectively when fitted to First order model. Hence, First order equation fits the P release best in both the soils as evidenced with high R^2 values and low standard error of estimate.

Rate of P release in incubation experiment

The rate constants of P release are shown in tables 4.1.3.1 and 4.1.3.2. Highest rate of release was observed in treatment 3 followed by treatments 2, 6 and 7 in black soils from Elovich model. However, First order equation (black soil) showed highest rate of release in treatment 6 and 7 followed by treatments 2 and 3. The lower values of P release were observed in control and treatment numbers 4 and 5. Almost similar trend of P release was observed in alluvial soils also. First order which describes the rate of release best has shown highest rate of release in the treatments where phosphocompost has been applied. However, rate of P release is higher (compared to control, T4 band T5) in treatments where acid clay treated rock phosphate has been incubated with soil.

Table 4.1.2.1: Release of P (mg/kg) in black soil

Treatment	No. of Days												
	0	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**	**100**	**110**	**120**
T1: Soil (Control)	2.1	2.9	3.9	4.9	5.9	6.8	7.5	8.3	9.0	9.6	10.2	10.7	11.0
T2: Soil + TRP (2%)	3.4	6.8	10.0	13.4	16.6	19.7	22.6	25.3	27.5	29.0	30.6	31.9	32.7
T3: Soil + TRP (5%)	4.8	9.4	13.5	18.7	23.1	27.5	31.0	35.0	38.0	40.3	42.2	44.0	45.1
T4: Soil + NRP (2%)	2.1	3.2	4.2	5.1	6.3	7.0	7.6	8.7	9.5	10.0	10.6	11.1	11.4
T5: Soil + NRP (5%)	2.3	3.2	4.3	5.4	6.4	7.4	8.2	9.1	9.8	10.6	11.2	11.6	11.9
T6: Soil + NRP (2%) +PC	5.8	10.4	15.4	19.6	23.1	26.4	29.1	31.9	33.7	35.0	35.6	36.0	36.4
T7: Soil + NRP (5%) +PC	6.1	10.5	15.5	19.8	23.3	26.6	29.4	32.2	34.0	35.3	36.0	36.7	36.9

Table 4.1.2.2: Release of P (mg/kg) in alluvial soil

Treatment	No. of Days												
	0	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**	**100**	**110**	**120**
T1: Soil (Control)	3.0	3.8	6.2	7.9	9.5	10.5	12.4	13.2	14.3	15.3	16.2	17.3	17.5
T2: Soil + TRP (2%)	4.9	6.8	10.0	13.4	16.6	19.7	22.6	25.3	27.5	29.0	30.6	31.9	32.7
T3: Soil + TRP (5%)	6.1	8.4	13.5	18.7	23.1	27.5	31.0	35.0	38.0	40.3	42.2	44.0	45.1
T4: Soil + NRP (2%)	3.2	4.7	6.2	7.6	9.4	10.5	11.5	13.1	14.2	15.0	16.0	16.7	17.1
T5: Soil + NRP (5%)	3.9	5.7	7.5	10.1	12.1	13.4	13.8	15.7	17.0	18.0	19.2	20.1	20.5
T6: Soil + NRP (2%) + PC	6.4	11.5	16.9	21.6	25.4	29.0	32.0	35.1	37.0	38.5	39.1	39.6	40.1
T7: Soil + NRP (5%) + PC	7.3	12.9	19.3	24.6	28.5	32.1	36.5	40.0	42.2	43.9	44.6	44.9	45.3

Table 4.1.3.1: Coefficient of determination and Elovich b value (mg kg^{-1} ln (day^{-1}) of P release curves as estimated by Elovich equation

Treatment	Black Soil		Alluvial Soil	
	R^2	b	R^2	b
(T1) Control	0.952	8.02	0.967	13.40
(T2) Soil + TRP (2%)	0.959	26.38	0.959	26.38
(T3) Soil + TRP (5%)	0.960	36.50	0.979	36.33
(T4) Soil + NRP (2%)	0.948	8.27	0.948	12.40
(T5) Soil + NRP (5%)	0.953	8.78	0.963	14.59
(T6) Soil + NRP (2%) +PC (@20 kg P/ha)	0.983	26.62	0.983	29.27
(T7) Soil + NRP (5%) +PC (@20 kg P/ha)	0.984	27.00	0.980	33.37

Table 4.1.3.2: Coefficient of determination, rate of release (b, day^{-1}), and maximum release (P_t) of P release as estimated by First order equation

Treatment	Black Soil			Alluvial Soil		
	R^2	b	Pt	R^2	b	Pt
(T1) Control	0.999	0.008	17.47	0.997	0.009	26.01
(T2) Soil + TRP (2%)	0.998	0.010	46.67	0.996	0.009	49.86
(T3) Soil + TRP (5%)	0.998	0.010	64.00	0.996	0.010	65.96
(T4) Soil + NRP (2%)	0.998	0.008	18.02	0.998	0.008	27.00
(T5) Soil + NRP (5%)	0.998	0.008	18.65	0.996	0.010	28.25
(T6) Soil + NRP (2%) +PC (@20 kg P/ha)	0.997	0.018	41.56	0.997	0.018	45.71
(T7) Soil + NRP (5%) +PC (@20 kg P/ha)	0.997	0.018	42.43	0.995	0.018	52.17

Table 4.1.3.3: Standard error of estimates in Elovich and First order kinetic equations.

Treatments	Elovich		First order	
	Black soil	**Alluvial soil**	**Black soil**	**Alluvial soil**
T1: Soil (Control)	0.17	0.85	0.06	0.28
T2: Soil + TRP (2%)	0.36	1.87	0.21	0.66
T3: Soil + TRP (5%)	0.46	2.40	0.30	0.93
T4: Soil + NRP (2%)	0.18	1.01	0.06	0.20
T5: Soil + NRP (5%)	0.16	0.99	0.08	0.36
T6: Soil + NRP (2%) + PC	0.24	1.31	0.27	0.65
T7: Soil + NRP (5%) + PC	0.24	1.64	0.29	0.93

Note: - TRP – Treated Rock Phosphate, NRP – Normal Rock Phosphate, PC - Phosphocompost

Yield and P uptake in pot culture experiment

4.2.2.1 Yield of mung bean in pot culture experiment under different treatments

The grain and stover yield of mung bean is shown in table 4.2.2.1 for black soil. Significant differences in the yield of mung bean pod were observed between no-P (control) versus rest of the treatments. Stover yield also increased significantly with addition of acid clay incubated rock phosphate (T2 and T3) when compared to normal rock phosphate (T4 and T5). Also, significantly higher grain yield was observed in phosphocompost treated pots (T6 and T7) in both the soils though T6 and T7 were on par. The data on uptake of P by mung bean is presented in table 4.2.2.2. The uptake of has followed the similar trend as that of yield. Significantly higher uptake is observed in all the treatments over control except treatment T4 and T5 which were on par with control.

Table 4.2.2.1 Yield (g/pot) by mung bean under different treatments

S. No.	**Treatment**	**Grain yield (g/pot)**		**Stover Yield (g/pot)**	
		Black	**alluvial**	**black**	**Alluvial**
T1	Soil (Control)	3.10	2.73	3.70	3.80
T2	Soil + TRP (2%)	3.76	3.48	4.30	4.72
T3	Soil + TRP (5%)	3.47	4.36	4.71	5.45
T4	Soil + NRP (2%)	3.12	2.73	3.97	3.84
T5	Soil + NRP (5%)	3.39	2.82	4.40	4.16
T6	Soil + NRP (2%) + Phosphocompost	3.69	4.03	5.10	5.35
T7	Soil + NRP (5%) + Phosphocompost	3.80	4.32	5.08	5.46
CD=0.5%		0.54	0.41	0.61	0.44

Table 4.2.2.2 Uptake of P (mg/pot) by mung bean under different treatments

Treatment	Black Soil		Alluvial Soil	
	Grain (mg/pot)	Stover (mg/pot)	Grain (mg/pot)	Stover (mg/pot)
(T1) Control	7.17	4.30	10.24	7.13
(T2) Soil + TRP (2%)	12.85	9.73	12.50	8.60
(T3) Soil + TRP (5%)	15.03	11.53	12.96	10.00
(T4) Soil + NRP (2%)	7.10	4.80	10.89	7.53
(T5) Soil + NRP (5%)	7.60	5.60	11.30	8.03
(T6) Soil + NRP (2%) +PC (@20 kg P/ha)	12.85	9.37	14.07	10.33
(T7) Soil + NRP (5%) +PC (@20 kg P/ha)	14.30	12.10	15.03	11.43
CD (P=0.05)	0.69	0.49	0.66	0.49

Post harvest P soil test values

The available soil P status in different treatments after the harvest of mung bean crop is given in figure 4.3.1 for black soils. The highest values were obtained in treatment T7 where higher dose of phosphocompost was applied closely followed by closely treatment T3 where treated rock phosphate was applied @ 5% by weight. The trend in available P status was T7>T3>T6>T2>T5>T4>T1. In contrast to black soils, the changes in available P status among the treatments in alluvial soils are relatively less. Also, the absolute values of available P status are relatively larger than in black soils. In alluvial soils, the treatments T7, T6, T3 and T2 have shown higher values of available P than the treatments T1 (control), T4 and T5 where untreated normal rock phosphate was incubated with soil.

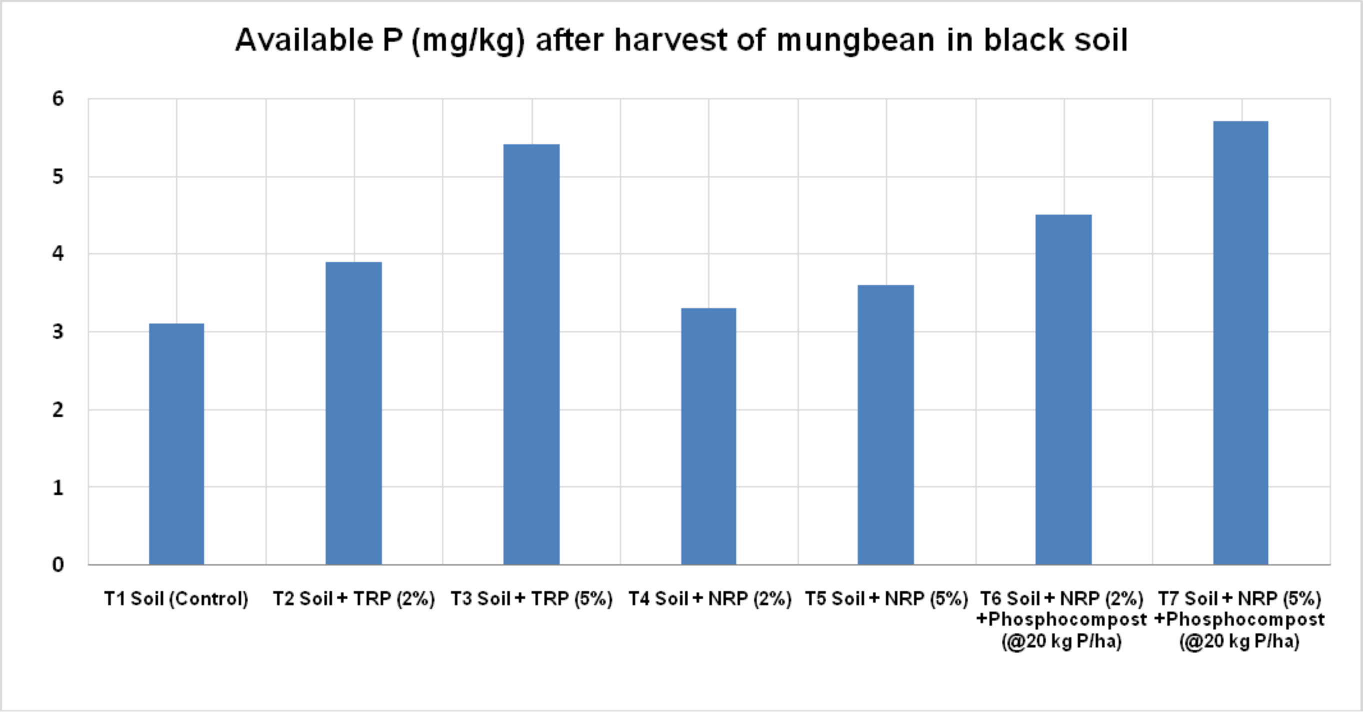


Figure 4.3.1: Available P (mg/kg) after harvest of Mung bean in black soil

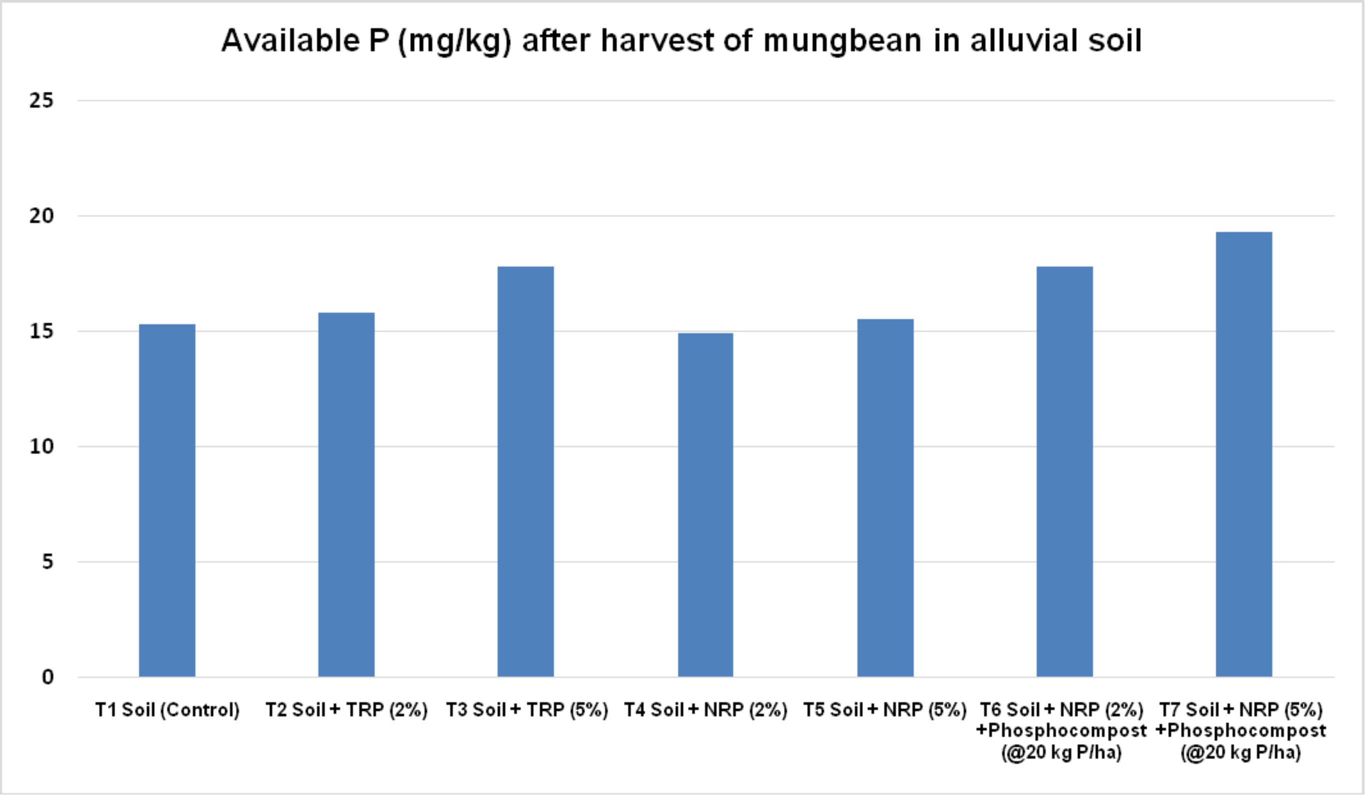


Figure 4.3.2: Available P (mg/kg) after harvest of Mung bean in alluvial soil

CHAPTER-V
DISCUSSION

The results of the present investigation “**Impact of Treated Rock Phosphate (TRP) on Phosphorus Availability and Growth of Mung Bean (*Vigna radiata*)**’’ related to the study of P release from treated rock phosphate, availability & uptake of P by mung bean from treated rock phosphate and the yield of mung bean and residual fertility status of experimental soil are displayed and explained in the preceding chapter.

The results are discussed in this chapter in the light of scientific reasoning to understand the cause and effect relationship.

: Results of incubation experiments

The results of the incubation experiment carried out with two soils are presented. The incubation experiment was carried out at room temperature and continued upto 120 days with samples drawn for analysis after every ten days.

Properties of soils used for incubation experiment

Two soils, one black soil collected from ICAR-IISS farm and another alluvial soil collected from Indo Gangetic plains of Ludhiana, Punjab were used for the study.

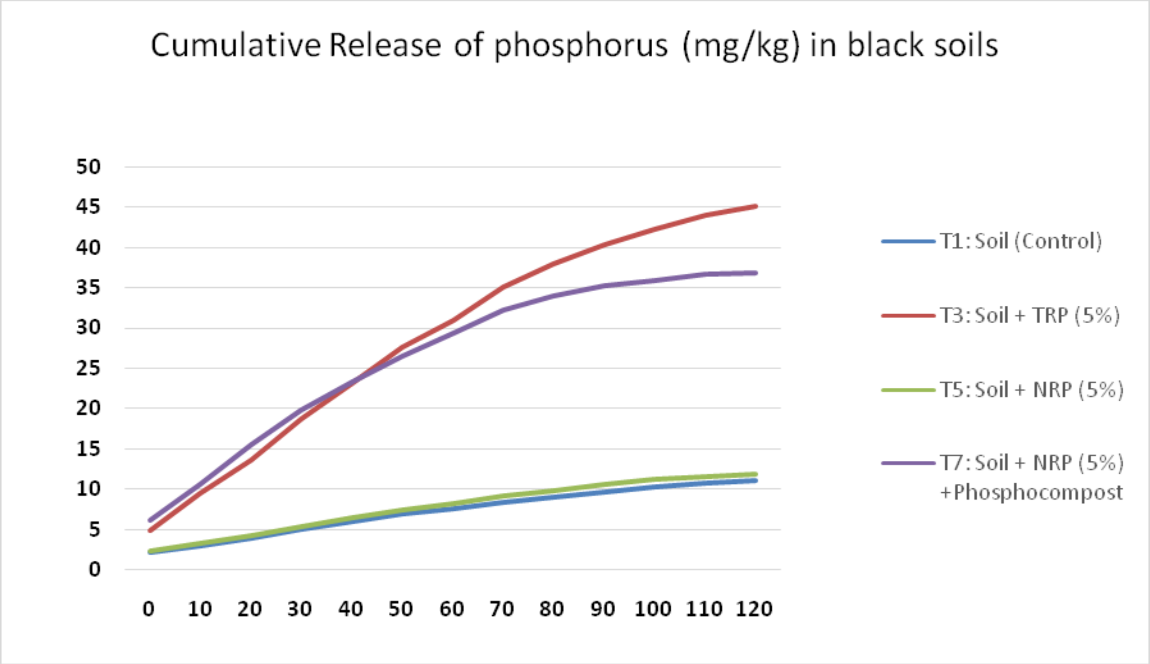
Some properties of the soils used in the incubation experiment are presented in table 5.1.1. Both the soils were alkaline. The black soil was having considerable high clay content and CEC compared to alluvial soil. The available N status was almost similar in two soils. However, available P status was considerable high in alluvial soils. Similarly, available K was high in black soil due to high CEC. In general, black soil was having higher overall fertility as reflected in high organic C content.

Phosphorus release in incubation experiment

The P release was higher in alluvial soil as compared to black soil in all the treatments. This may be due to initial high P status of studied alluvial soils. The release of P from acid treated clay rock phosphate incubated treatments (T2 and T3) was higher than normal soil+rock phosphate treated treatment. It is evident that the dissolution of RP in normal RP and soil mixture (T4 and T5) was limited by high Ca saturation (alkaline soils have high Ca saturation) and insufficient availability of protons, whereas dissolution especially in alluvial soils was limited by the small Ca sink size due to relatively lower CEC. From the thermodynamic standpoint, RP needs sufficient protons to dissolve. Similar effect of pH on the dissolution of RP was also reported by Nying and Robinson (2006). A closure look at figure 5.1 with selected treatments show that in treatments with acid clay RP and soil-RP + phosphoscompost (T3 and T7) there are actually two slopes in contrast to T1 (control) and T5 (soil+normal rock phosphate mixture). The first is a rapid release of P which extend upto a period of 70 days followed by a relatively slower P release. This is expected because acid treated clay could provide H^+ ion to dissolve the RP and adsorb the released Ca but its capacity to continue this reaction would eventually decrease as the H^+ ions are consumed and clay surface becomes saturated with Ca^{2+}. Similarly, the release of P from phosphocompost was rapid in early phase followed by slow release. In contrast a normal slower process of surface or diffusion controlled release of P would occur in the treatments T1 and T5. In general, acid clay increased the initial rate of dissolution of RP due to a rapid acidifying effect.

To utilize this rock phosphate as an effective source of P, management practices that increase Ca sinks and the supply of protons to the soil are necessary. Considerable P release was also obtained in T7 suggesting that phosphoscompost also enhances cation exchange capacity and availability of protons. Khalil (2013) important role of organic matter for releasing phosphorus from rockphosphate. He reported that the combination of soil amendments with

RP as a natural P-source has the possibility of saving significant quantities of industrialized inorganic phosphate fertilizers. These practices should provide adequate sinks for Ca^{2+} and the acidic environment required for the release of P from rock phosphate. In this study the dissolution of RP continued at a higher rate (Treatments T2, T3, T6, T7) upto 70 days and thereafter a slow release was observed. Presumably, at this point, in the absence of any loss mechanisms such as plant uptake or leaching, the P concentration in the soil solution in this study had increased to the point where any further RP dissolution was slowed. In an another incubation study, Mackay and Syers (1986) showed that the dissolution reaction reached equilibrium at about 50 days.



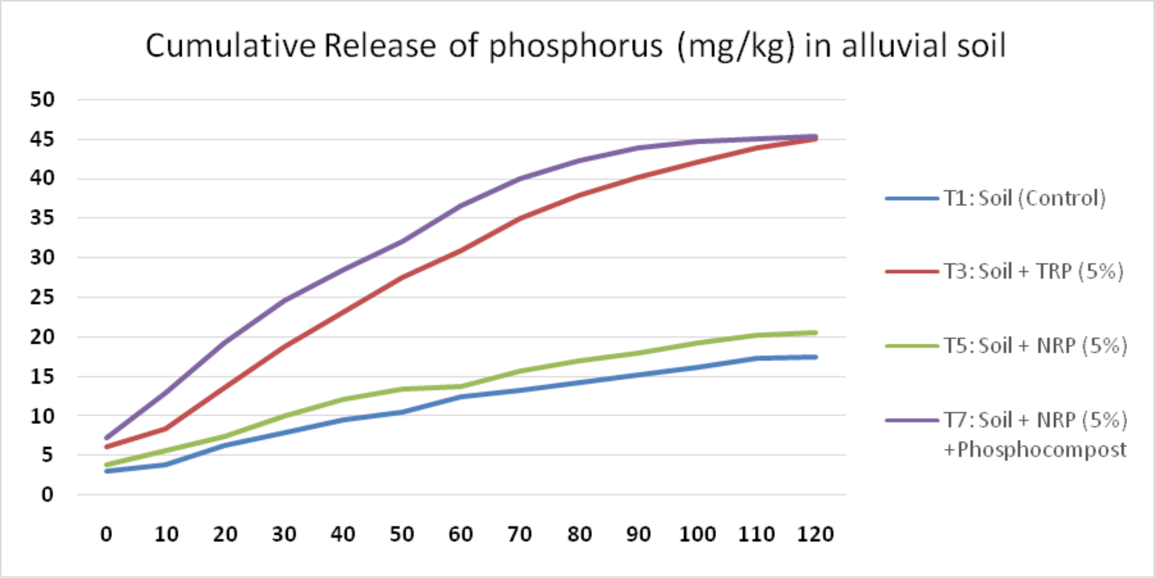


Figure 5.1: Cumulative release of P (mg/kg) under different treatments in incubation experiment

Kinetics of P release in incubation experiment

Two kinetic models were used for explanation of P release from the soils incubated with different treatments. Phosphorus release data were could be explained by both First order and Elovich model. The conformity of P release data to a particular kinetic equation was judged by the highest coefficient of determination (R^2) and the lowest standard error (SE) of the regression relation. The coefficients of determination (R^2) and the standard errors of estimate (S.E.) for kinetic equations tested to describe the P release data are shown in the previous chapter. Based on the relatively higher values of r^2 and the lower values of S.E., the first order model was considered the most appropriate equation describing the release of P with time in both the soils. This shows that the release of P from these soils under experimental condition is a surface reaction – controlled process. A number of workers have demonstrated that the release of P from RP follows first order equation and is a surface controlled reaction (Ravan, and Hossner, 1994; El-Kherbawy *et al.*, 2014). The release of P, however, could also be modelled by (Elovich equation) diffusion controlled release of P (Cooke, 1966). It is possible that both the mechanisms of P release were simultaneously occurring in soil. Shariatmadari *et al.* (2006) in a study of P release in Iranian soils, reported that Elovich equation best described the kinetics of P release data, as evidenced by the relatively higher values of determination coefficient (r^2) and the relatively lower values of the standard error of estimate. Ahroni *et al.* (1991) have also reported that Elovich and First order models could describe the kinetics of P release from RPs. It is generally believed that there is no single equation that describe equally well the desorption kinetics of soils (Ravan, and Hossner, 1994).

Rate of P release in incubation experiment

The rate constants of P release are shown in tables 4.1.3.1 and 4.1.3.2 and presented in figures 5.2 and 5.3 for alluvial and black soils, respectively. Elovich model differentiate better the release rate constants among the different treatments. The highest rate of release was observed in T3 followed by treatments T2, T6 and T7 in black soils from Elovich model. However, in case of alluvial soil the sequence was T3>T7>T6>T2. In both the cases rate constants was lower for T1, T4 and T5. This shows that acid treated clay + RP enhanced the rate of release of P, and this release was also enhanced by phosphocompost addition. Yang *et al.* (2019) also reported enhanced rate of release of P from RPs when treated with organic acids. Sarangi *et al.* (2019) reported that additions of FYM could enhance the rate of release of P from Udaipur rock phosphate. Also, a closure look at the rate constants reveals a similar rate of release in black and alluvial soils in the treatments T2 and T3 showing that showing the strong influence of acid treated clay on P release across the two soils. First order equation (black and alluvial soil) showed highest rate of release in treatment 6 and 7. However, the differences for other treatments were small. This data has to be looked along-with the parameter of maximum potential release (P_t) which is much larger in magnitude in the treatments T2, T3, T6 and T7 when compared with T1, T4 and T5 possibly due to higher intercept values and higher rate of release in the initial period of 70 days (Yang *et al.* 2019).

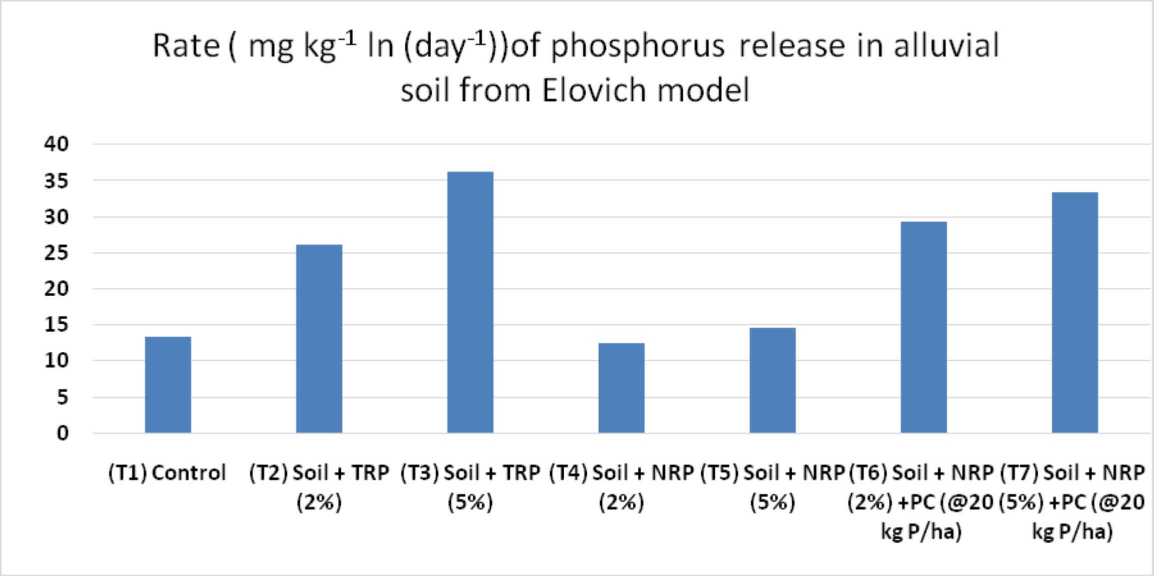


Figure 5.2: Rate of phosphorus release (b) in alluvial soils from Elovich model

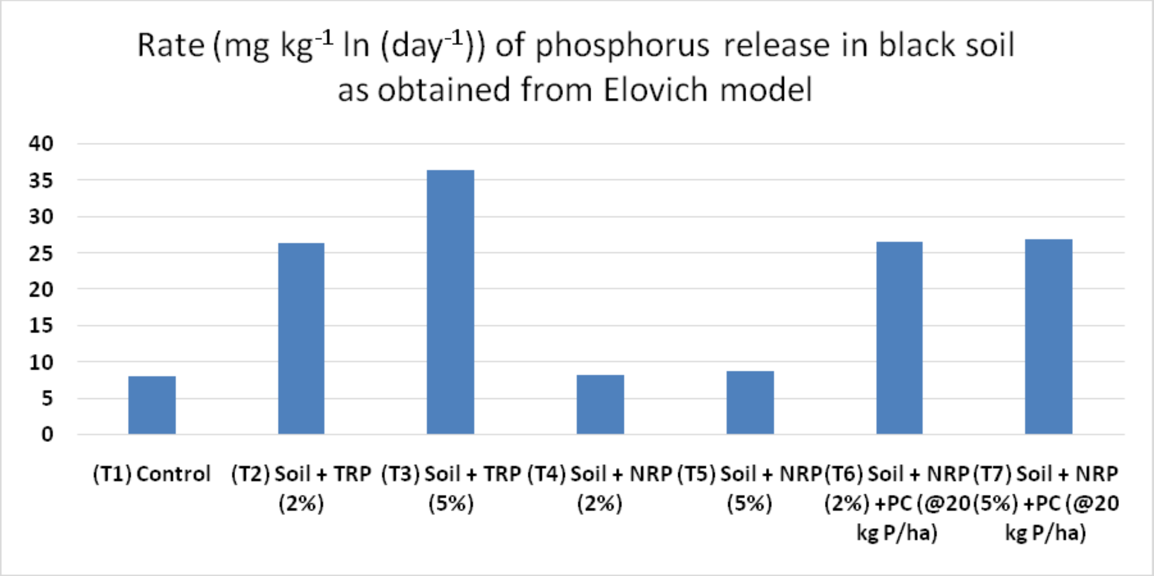


Figure 5.3: Rate of phosphorus release (b) in black soils from Elovich model

Yield and P uptake in pot culture experiment

Yield of mung bean in pot culture experiment under different treatments

The grain and stover yield of mung bean is shown in table 4.2.2.1 for black soil. The two soils used were a black soil from Bhopal, and an alluvial soil from Ludhiana. Black soils were deficient in available P whereas alluvial soils were adequate in available P. Black soils, however, were having better overall fertility as reflected in higher organic carbon content (0.64%). The treatments with acid clay + RP (T2 and T3) produced higher grain and stover yield over control and treatments where untreated RP soil mixture was incubated (T4 and T5). This shows that the clay with high surface area provided the necessary exchange sited for the adsorption of release calcium and continued the reaction in forward direction. Roy *et al.* (2018) reported the use of nano clay polymer in increasing the release of P from Purulia and Udaipur rock phosphates in citric acid medium. Misra *et al.* (2002) reported that when Mussourie, Udaipur, Purulia and Jhabua rock phosphates modified by mixing either with iron pyrite or composting with paddy straw along with or without PSM inoculation (Phospho-compost) increased the uptake of P and yield of rice crop. Sarwar *et al.* (2018) reported that application of organic matter i.e. de waxed filter cake press mud (FCP) proved beneficial for the release of P from local red rock phosphate and enhanced the uptake and yield. Use of poultry manure in enhancing the P uptake and yield has been demonstrated by Zafar *et al.* (2017). The treatments with addition of phosphocompost produced significantly higher yield of T2 but not over T3 in alluvial soils. This shows that importance of higher rate of RP application. Though, the actual yield data for the RP treatments varied in the two soils but the relative ranking of RP treatments remained almost the same.

However, the relationship is not direct because of the many factors and their interactions that affect the agronomic effectiveness of RPs (Mackay *et al.*, 1984, Rajan *et al.*, 1996). Normally, the predicted reactivity of PRs, assessed from solubility tests, should be validated in greenhouse and field experiments. The data on uptake of P by mung bean is presented in table

4.2.2.2. The uptake of has followed the similar trend as that of yield. Phosphorus uptake is a more sensitive parameter than dry matter for discriminating between RP treatments. In general, the results confirmed that the release of P and its availability to mung bean crop was significantly enhanced when rock phosphates were treated with acid treated high CEC clay resulting into their solubilization and eventual release of P. Roy *et al.* 2018 reported direct effect of citric acid nano clay polymer (CA-NCPC) + RP on yield and P uptake by wheat and showed that these parameters were comparable with DAP. Kumar *et al.* (2018) in a field experiment with different crops showed that the uptake of P and yields of crops could be significantly increased when press mud and gypsum was used for acidulation. Significantly higher uptake is observed in all the treatments over control except treatment T4 and T5 which were on par with control. In general, increased RP dissolution is expected to increase available P, and this has resulted in improved P uptake and crop yield.

5.2.2. Correlation coefficient (r) of release rate constant with total P uptake

The correlation coefficient (r) between total uptake of mung bean and release rate constants from two kinetic equations is given in table 5.1. The coefficients are high for both the black and alluvial soil. However, it is observed that Elovich b values could explain better the relationship with plant P uptake. This suggests that Elovich b values could be used as index of availability of P to plants from such treated RPs for black and alluvial soils. Shariatmadari *et al.* (2006) also reported that the plant P uptake could be best described by Elovich equation.

Table 5.1 Correlation coefficient (r) of release rate constant with total P uptake

Total uptake of P x Elovich b value in black soil	0.943**
Total uptake of P x Elovich b value in alluvial soil	0.946**
Total uptake of P x First order b value in black soil	0.786*
Total uptake of P x First order b value in alluvial soil	0.773*
** Significant at 1%, * Significant at 5%	

Post harvest P soil test values

The available soil P status in different treatments after the harvest of mung bean crop is given in figure 4.3.1 for black soils and figure 4.3.2 for alluvial soil. The available in black soils increased over control in all the treatments where P was applied. The highest values were obtained in treatment T7 where higher dose of RP along-with phosphocompost was applied closely followed by treatment T3 where treated rock phosphate was applied @ 5% by weight. The trend in available P status was T7>T3>T6>T2>T5>T4>T1. The values in available P in alluvial soils are considerably higher than in black soils presumably because of the higher initial available P status. In alluvial soils also, the treatments T7, T6, T3 and T2 have shown higher values of available P than the treatments T1 (control), T4 and T5 where untreated normal rock phosphate was added.

Zhang *et al.* (2019) reported that the available P after the test crop increased by 56.1% and 89.6%, respectively, with direct use of RP and microcrystallized RP powder compared with the control without any addition of phosphate minerals. Similarly, Dib *et al.* (2006) demonstrated that enough amount of residual P remained in the soil after the application of powdered or dust natural rock phosphate. Also, Sarangi *et al.* (2019) found that Udaipur rock phosphate with amendments increased available P content of soil after the harvest of hybrid napier grass. Basak *et al.* (2017) reported that application of composts in soil remarkably improves water soluble & available P, microbial biomass C and P as well as phosphatase activities which determine the P availability in soil.

CHAPTER - VI

SUMMARY, CONCLUSION AND SUGGETIONS FOR FURTHER WORK

This M.Sc. research work was planned with an objective to evolving some indigenous technique for the direct use of rock phosphates (RP). Rock phosphate deposits are available in the country but their direct use is not in vogue because the release of P is so slow that it cannot be utilized as fertilizer materials. Also, almost 90% of the P fertilizers are imported either as ready fertilizers (DAP and mixed fertilizer grades) or as raw materials (rock phosphates, phosphoric acid, sulfuric acid, sulphure) used in P fertilizer manufacture. This puts India in precarious situation since imported fertilizers are costly and Government has to incur huge expenditure on fertilizer subsidy. Clearly there is a need to evolve some alternative techniques of supplying P to plants. One such possible use is the application of RP. Rock phosphate solubility is affected by many soil factors. One important factor is that the released calcium as a result of RP dissolution is not removed from the system and thus stopping the process of dissolution. Research workers in the past have tried to address this issue by treating RPs with materials like zeolites and nano clay so as to provide the necessary surface area and CEC for the adsorption of released calcium. However, these materials are not ubiquitous and need special techniques of preparation. We tried the use of high surface area and high CEC clay isolated from vertisols of central India. We acidulated this clay and incubated with rock phosphates to study the P release. Thus, this M. Sc research work was planned with the title **“Impact of Treated Rock Phosphate (TRP) on Phosphorus Availability and Growth of Mung Bean (*Vigna radiata)*”** with following specific objectives:

- To study the release of P from rock phosphate under different treatments
- To study the effect of application of rock phosphate on growth of mung bean in a pot experiment

We conducted incubation and pot culture experiments to fulfill the objectives. Both the experiments were conducted in two soils, one black soil collected from Bhopal region and another alluvial soils collected from Ludhiana, Punjab.

There were seven treatments for incubation studies: T1: (Control without addition of RP), T2: soil with treated rock phosphate @ 2% by weight, T3: soil with treated rock phosphate @ 5% by weight, T4 Soil + Normal rock phosphate (NRP) @ 2% by weight, T5 Soil + Normal rock phosphate (NRP) @ 5% by weight and treatments T6 and T7 where phosphocompost @ of 20 kg P /ha was added over T4 and T5.The results revealed that in black soils release of P from acid treated clay rock phosphate incubated treatments T2 and T3 (32.7 and 45.1 mg P/kg) was higher than normal soil+rock phosphate treated treatments (11.4 and 11.9 mg/kg). The similar effect of enhanced release of P was also observed in treatments T6 and T7 (36.4 and 36.9 mg P/kg) where phosphocompost was applied. Similar trend in results was also observed in alluvial soils. The data of P release was also fitted with two kinetic models Elovich and First Order. Both the models could describe the data of P release, however, First order model was better fit. The goodness of fit (R^2) ranged between 0.948 and 0.983 and between 0.948 and 0.984 in case of alluvial and black soil, respectively for Elovich model. And, it ranged between 0.995 and 0.998 and between 0.997 and 0.999 in case of alluvial and black soil, respectively for First order model.

Pot culture experiments were also conducted with mung bean as test crop. Plastic pots of 10 kg capacity were filled with 7 kg of soil. The treatments for pot culture experiment were T1: (Control without addition of RP), T2: soil with treated rock phosphate @ 2% by weight, T3: soil with treated rock phosphate @ 5% by weight, T4 Soil + Normal rock phosphate (NRP) @ 2% by weight, T5 Soil + Normal rock phosphate (NRP) @ 5% by weight and treatments T6 and T7 where phosphocompost @ of 20 kg P /ha was added over T4 and T5. Significant differences in the yield of mungbean pod were observed between no-P (control) versus rest of the treatments. Stover yield also increased significantly with addition of acid clay incubated rock phosphate (T2 and T3) when compared to normal rock phosphate (T4 and T5). Also, significantly higher grain yield was observed in phosphocompost treated pots (T6 and T7) in both the soils though T6 and T7 were on par. The correlation coefficient (r) of total uptake of P by mung bean crop with the rate constants (b) derived from Elovich model were 0.943 and 0.946, in black and alluvial soil, respectively. The values for First order were 0.786 and 0.773 for black and alluvial soils. This shows that the Elovich rate constant could best describe the availability of P to mung bean crop.

The soils test values after the harvest of mung bean crop were in the sequenceT7>T3>T6>T2>T5>T4>T1 in alluvial T7>T3>T6>T2>T5>T4>T1 in black soils showing that acid clay treated RP and phosphocompost treated RP enhanced the available P status of soil after the harvest of mung bean.

It can be concluded from this study that acid clay and rock phosphate mixture can be a viable technique to enhance the availability of P from rock phosphates. High surface area clay can be easily isolated from black vertisols from central and western India. This clay is rich in smectite minerals provide excellent source of high cation exchange sites for the adsorption of released Ca from RP. Moreover, a treatment of the clay with acid provides exchangeable hydrogen which can attack rock phosphate. This is the basic work and need to be confirmed by others. Also, the calculations with respect to the economics of this technology have to be worked out once an industrial application of the technology is planned.

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Appendix- I

(A) Detail of incubation experiment

(i) Value of P release in black soil of 120 days period of incubation

Days	T1	T2	T3	T4	T5	T6	T7
0	2.1	3.4	4.8	2.1	2.3	5.8	6.1
10	2.9	6.8	9.4	3.2	3.2	10.4	10.5
20	3.9	10.0	13.5	4.2	4.3	15.4	15.5
30	4.9	13.4	18.7	5.1	5.4	19.6	19.8
40	5.9	16.6	23.1	6.3	6.4	23.1	23.3
50	6.8	19.7	27.5	7.0	7.4	26.4	26.6
60	7.5	22.6	31.0	7.6	8.2	29.1	29.4
70	8.3	25.3	35.0	8.7	9.1	31.9	32.2
80	9.0	27.5	38.0	9.5	9.8	33.7	34.0
90	9.6	29.4	40.5	10.0	10.6	35.0	35.3
100	10.2	30.8	41.9	10.6	11.2	35.6	36.0
110	10.7	31.8	44.0	11.1	11.6	36.0	36.7
120	11.0	32.3	45.7	11.4	11.9	36.4	36.9

(ii) Value of P release in alluvial soil of 120 days period of incubation

Days	T1	T2	T3	T4	T5	T6	T7
0	3.0	4.9	6.1	3.2	3.9	6.4	7.3
10	3.8	6.8	8.4	4.7	5.7	11.5	12.9
20	6.2	10.0	13.5	6.2	7.5	16.9	19.3
30	7.9	13.4	18.7	7.6	10.1	21.6	24.6
40	9.5	16.6	23.1	9.4	12.1	25.4	28.5
50	10.5	19.7	27.5	10.5	13.4	29.0	32.1
60	12.4	22.6	31.0	11.5	13.8	32.0	36.5
70	13.2	25.3	35.0	13.1	15.7	35.1	40.0
80	14.3	27.5	38.0	14.2	17.0	37.0	42.2
90	15.3	29.0	40.3	15.0	18.0	38.5	43.9
100	16.2	30.6	42.2	16.0	19.2	39.1	44.6
110	17.3	31.9	44.0	16.7	20.1	39.6	44.9
120	17.5	32.7	45.1	17.1	20.5	40.1	45.3

Appendix- II

1. Value of mean sum of square for yield parameters

Source of Variation	**D.F.**	**Alluvial soil**		**Black soil**	
		Grain Yield (g pot^{-1})	**Stover yield (g pot^{-1})**	**Grain Yield (g pot^{-1})**	**Stover yield (g pot^{-1})**
Treatments	6	1.674	1.706	0.253	0.852
Errors	14	0.054	0.063	0.096	0.120
Total	20	-	-	-	-

2. Value of mean sum of square for P uptake by mung bean

Source of Variation	**D.F.**	**Alluvial soil**		**Black soil**	
		Grain (mg pot^{-1})	**Stover (mg pot^{-1})**	**Grain (mg pot^{-1})**	**Stover (mg pot^{-1})**
Treatments	6	9.093	7.714	37.724	31.782
Errors	14	0.140	0.080	0.153	0.077
Total	20	-	-	-	-

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12th	M.P Board,Bhopal	2012	63.40	
B.Sc. (Ag.)	RVSKVV, Gwalior	2017	71.40	7.14
M.Sc. (Ag.) (Soil Science)	RVSKVV, Gwalior	2019	70.00	7.00

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