

# Comparative Solubility Study of Four Phosphatic Fertilizers in Different Solvents and the Effect of Soil

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**Abstract** Phosphate rocks (PRs) are suitable for direct application as a possible alternative to more expensive soluble phosphate fertilizers in agricultural fields. But the ability of the PRs to release phosphates in the plant available forms depends on the particle size and chemical and mineralogical characteristics of the PRs 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 phosphate rock (PAPR – 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, 0.002N Hydrochloric acid, N-Ammonium citrate, Bray-2P extractant, Olsens'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 PRs 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 2P and Olsen's extractants.

**Keywords** Phosphate Rocks, Acidulated Rock Phosphates, Solubility in Different Extractants

## 1. Introduction

Phosphate rocks (PRs) are suitable for direct application to agricultural fields under certain conditions[1] due to their fairly open, loosely consolidated aggregates of micro-crystals with relatively large surface areas. Direct application of phosphate rock to soil as a possible alternative to the more expensive soluble phosphate fertilizers in tropical cropping system has received considerable attention in recent years[2]. The principal mineral in most PR sources is apatite, but it varies widely in physical, chemical, and crystallographic properties[3]. The solubility of PR reflects the chemical and mineralogical characteristics of the specific P minerals. Naturally occurring PRs differs widely in their mineralogy and their chemical reactivity or solubility is a measure of the PR's ability to release phosphorus (P) for plant uptake. Gholizadeh et al[4] reported that to avoid time, trouble and cost of doing field trials for determining the reactivity of PRs, solubility of these in citric acid could be a criterion for predicting their reactivity.

The effectiveness of phosphate rock relative to soluble P

fertilizer will vary from source to source depending upon the mineralogy and chemistry of each rock as well as the influence of soil, crop, environment and management factors. According to Rajan et al[5] reactivity is 'the combination of PR properties that determines the rate of dissolution of the PR in a given soil under given field condition. The reactivity of PRs, the main constituent of which is mineral apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{X}$ ) where X is predominantly fluorine, is determined by the rate of dissolution in acid and the amount of P recovery. The main factors affecting the reaction rate of acid attack of phosphate are acid concentration, time of the reaction, solid/liquid ratio, particular size and temperature[6]. The reactivity also depends on the composition of the apatite mineral, presence of impurities and particle size.

Increasing degree of substitution of carbonate for phosphate, and of magnesium and sodium for calcium in the apatite structure and decreasing particle size enhance the reactivity of PRs[7]. It is also known that decreasing soil pH increases PR effectiveness[8],[9],[3] and rock phosphate dissolution was also shown to be linearly correlated with the reserve acidity of the soil. Asomaning et al[10] reported that the two major factors generally recognized as influencing P availability from phosphate rocks are: (i) inherent differences among PR sources, and (ii) soil properties. The release of P from PR generally increases with a greater P-fixing capacity of the soil[3]. Thus soil has an active role in

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dissolution of PRs and releasing P into the soil solution for plant uptake.

With this background an experiment was set in the laboratory of Agricultural and Ecological Research Unit of Indian Statistical Institute, Kolkata, to study the solubility of four phosphatic fertilizers – Triple super phosphate (21.75% P), Morocco rock phosphate (14.87% P), Mussoorie rock phosphate (8.12% P) and Partially acidulated rock phosphate (12.97% P) in six different solvents namely 2% citric acid, 0.002N hydrochloric acid, N-Ammonium citrate, Bray-2P extractant, Olsen's extractant and Morgan's reagent.

## 2. Materials and Methods

The experiment was carried out with each fertilizer for 7 periods of incubation (1, 2, 3, 7, 15 and 30 days), with and without soil, under factorial randomised block design in three replications. The soil added was acid lateritic and rich in iron and aluminium. The physico-chemical properties of the soil under experimentation are given in Table 1.

**Table 1.** Physico-Chemical Properties of the Soil Under Experimentation

Parameters	Values
Physical characteristics :	
Particle density (g/cc).	2.49
Bulk density (g/cc).	1.33
Water holding capacity (%).	23.1
Chemical characteristics :	
pH	5.4
Organic Carbon (%).	0.52
Total Nitrogen (%).	0.059
Available Nitrogen (kg/ha).	135.0
Available P (kg/ha)	5.6
Available K (kg/ha).	89.5
Cation Exchange Capacity (me/100g).	10.19

The soil was collected from the Agricultural farm of Indian Statistical Institute, Giridih, Bihar (presently Jharkhand). The method followed in carrying out the experiment was as per [11] and [12].

### 2.1. Treatment Details

**Table 2.** Extractants used and days of incubation for the experiment, with and without soil

Extractant used	Periods of incubation	Remarks
2% Citric acid	1 day, 2 days, 3 days, 7 days, 10 days, 15 days and 30 days	With and without soil (10g of soil taken in each case with soil as per treatment )
0.002N Hydrochloric acid		
N- Ammonium citrate		
Bray – 2P extractant		
Olsen's extractant		
Morgan's reagent		

### 2.2. Extraction

Ten gram (10 g) of air dried, 2 mm sieved soil, was taken in 100 ml conical flask and to it 20 mg of desired phosphatic fertilizer was added. Then 50 ml of the desired solvent was added and the flasks were shaken on a mechanical shaker for 15 minutes and kept in a biochemical/biological oxygen demand (BOD) incubator at 30°C for different periods of time. BOD are suitable for closed control incubation and are also called low temperature incubator. After the specified periods as per treatment, each flask was taken out of the BOD and the materials were filtered. An aliquot of 5 ml was taken per treatment and its phosphate (available P) content was determined following the standard procedure using the ammonium meta vanadate [11] solution.

In another set of experiment, the same procedure was followed for extraction of phosphate from the phosphatic fertilizers as mentioned above but without adding soil to determine the role of soil, if any, in the method of extraction of phosphorus.

## 3. Results and Discussions

The data on P- solubility revealed that among P sources, the water soluble and partially soluble sources released almost double the amount of P, with soil than that without soil, for all the extractants (Figures 1,2). This can be explained due to the fact that in the treatments with soil, the readily available P, reacts with the Fe and Al ions in the acid soil thereby forming iron and aluminium phosphate complex as intermediate products which are also extracted by the extractants along with the fertilizers. An increase in the P solubility of the rock phosphate source was also noted as affected by the soil. Rajan et al [5] expressed dissolution of rock phosphate in acid soils as,  $-Ca_{10}(PO_4)_6F_2 + 12H_2O \rightarrow 10Ca^{+2} + 6H_2PO_4^- + 2F^- + 12OH^-$

Although the above reaction was for fluorapatite, it applies to other members of the apatite minerals including reactive rock phosphates (francolites). The increase in dissolution of the rock phosphates when treated with soils may also be attributed to the neutralization of the OH<sup>-</sup> ions, released on hydrolysis of the phosphate ions, due to soil acidity. The solubility of P may influence PR dissolution products since the P released from PRs is effectively removed from solution by iron and aluminium oxides, thus, creating a gradient for further dissolution of the PR [13]. Chhonkar [14] also reported that P availability to plants was significantly increased by the action of soil. It was interesting to note that at 15 and 30 days of incubation, P released from TSP, without soil was more (1.94%, 1.43%) than that with soil (1.68%, 0.84%) (Table 3, Figure 1- a,b). This can be ascribed to adsorption of soluble P from soil solution by the reprecipitated poorly crystalline ferrous hydroxides or carbonates from Fe<sup>+2</sup> ions formed by soil reduction ([15], [16], [17]).

The water soluble source (TSP) was found to release the maximum P (3.05%-3.27% with soil, 2.11%-2.22% without soil) by the 7<sup>th</sup> day of incubation where as the rock phosphate

sources released maximum amount of P after the 7<sup>th</sup> day (Fig 1,2). 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 (7<sup>th</sup> day onward) (1.27%-1.92% with soil, 0.55%-0.66% without soil) (Table 4, Figure 1 – c,d). This is obviously due to the presence of partly water soluble P which was released earlier. The trend of P-release by the fertilizers was more pronounced for the treatments with soil. The results on P release thus showed that maximum release of P from the unacidulated and partially acidulated rock phosphates needs some more periods of incubation for thorough acidulation of the fertilizer with the extractant to come into equilibrium with P in solution. Singh et al[18] and Barnes and Kamprath[19] also reported an increase in P-availability with the length of incubation period and opined that it may take 4 to 8 weeks for phosphate rocks to reach their maximum solubility. Rajan et al[20] and Sinclair et al[21] explained that this is due to the insoluble characteristic of the phosphate rock where a time lag is experienced for unacidulated rock phosphates to reach the maximum effectiveness.

Further, among the different solvents, maximum release of phosphorus was observed by 2% citric acid followed by Bray 2 and Olsen's extractants from TSP, PARP, MORP and MRP, with and without soil. Similar observations were also reported earlier by[12]. Higher solubility of the PRs in 2% citric acid possibly results from higher reactivity rather than from any difference in surface area presented for dissolution[22]. Among the two rock phosphate sources, MORP was found to release greater amount of P than MRP. This can be attributed to larger  $\text{CO}_3^{2-}$  substitution for  $\text{PO}_4^{3-}$  in MORP (5.60%  $\text{CO}_2$ ) crystal lattice which renders MORP to be unstable and more reactive than MRP, which is also a francolite (carbonate apatite) but with a smaller degree of

carbonate substitution[23]. Rajan et al[5] opined that apatites are not soluble in bicarbonate solutions and therefore Olsen's extractant cannot be expected to predict potential P-release from rock phosphates. But the perusal of the solubility data (Figure 1,2) revealed that Olsen's extractant showed more P than some acidic extractants, both in treatments with and without soil. A probable explanation for this may be the presence of Al-P and Fe-P in the rock phosphate crystals and in the intermediate products of the soil-PR interaction, from where, alkaline Olsen's extractant may dissolve potentially unavailable P and thus overestimate P[5].

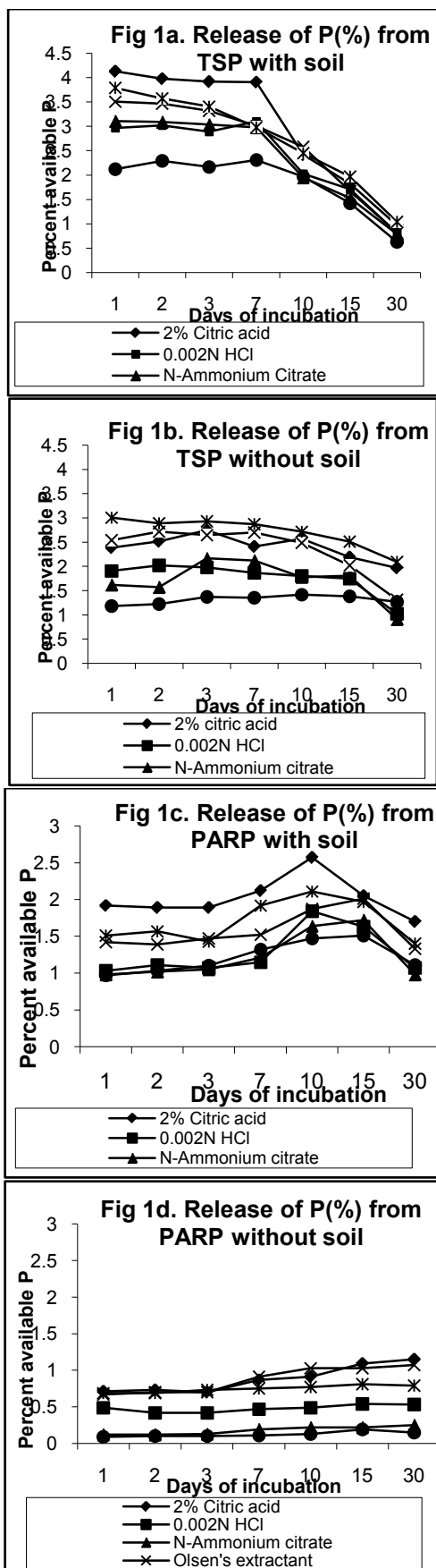
The study on the solubility pattern of the water soluble triple super phosphate, two rock phosphates – Morocco and Mussoorie and one partially acidulated rock phosphate thus suggested the order of solubility of P or its reactivity as  $\text{TSP} > \text{PARP} > \text{MORP} > \text{MRP}$ . Hammond et al[23] reported, however, that the effectiveness of a P source measured under actual field condition will vary with changes in a number of climatic and agro-edaphic conditions. Thus, their mean value of soluble P from the treated fertilizers with soil (TSP, PARP, MORP and MRP) varied from 3.27 to 0.84%, 1.92 to 1.27%, 0.81 to 0.31% and 0.47 to 0.6% respectively.

## 5. Conclusions

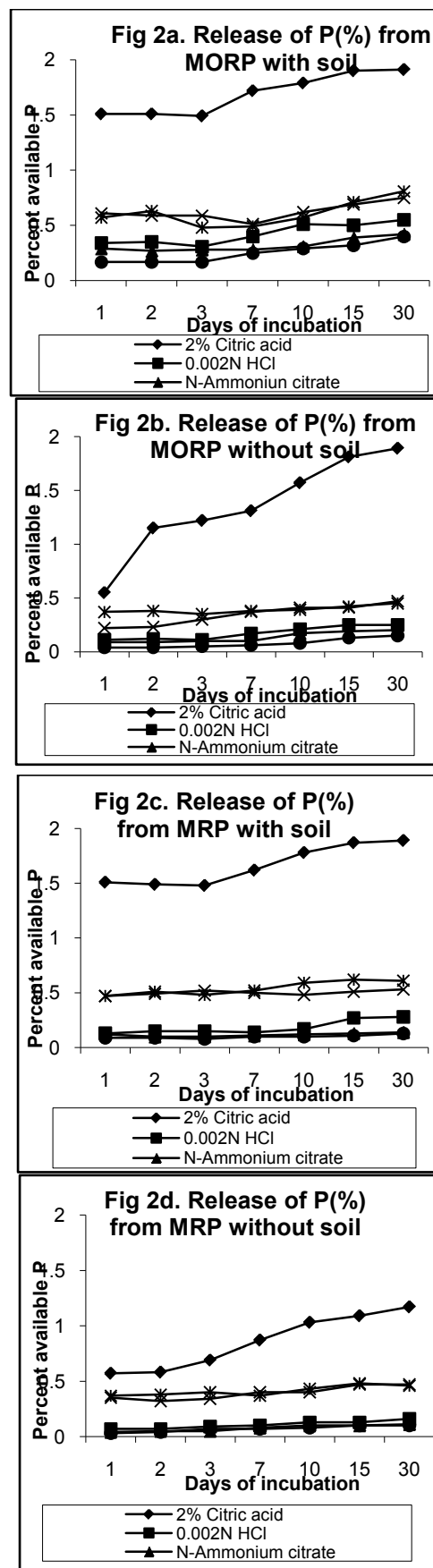
It can thus be concluded that Morocco and Mussoorie phosphate rocks can be efficiently used as fertilizers in acid lateritic soils but have to be applied a bit earlier before crop cultivation as it needs some time for releasing P into the soil solution. But water soluble and partially acidulated phosphate rock can release P immediately for crop uptake. Solubility measurement cannot be used to predict specific yield response but they can serve as a useful means of predicting relative performance of one source to another and this assist in selection of the most appropriate source.

**Table 3.** Statistical analyses of the dissolution of the phosphatic fertilizers by different solvents at different incubation periods, with and without soil

Phosphatic fertilizers ↓		Solvents		Periods of incubation		Solvents X Periods of incubation	
		With soil	Without soil	With soil	Without soil	With soil	Without soil
Tripple Super phosphate	SEm±	0.115	0.102	0.125	0.110	0.305	0.269
	CD <sub>0.05</sub>	0.229	0.202	0.246	0.217	0.604	0.533
Partially Acidulated Phosphate Rock	SEm±	0.083	0.026	0.089	0.028	0.219	0.068
	CD <sub>0.05</sub>	0.164	0.051	0.177	0.055	0.433	0.135
Morocco Rock Phosphate	SEm±	0.029	0.031	0.032	0.033	0.077	0.082
	CD <sub>0.05</sub>	0.057	0.061	0.063	0.066	0.153	0.162
Mussoorie Rock Phosphate	SEm±	0.028	0.015	0.030	0.016	0.074	0.040
	CD <sub>0.05</sub>	0.055	0.029	0.059	0.032	0.145	0.079



**Figure 1.** Release of available P from TSP and PARP by different solvents at different periods of incubation



**Figure 2.** Release of available P from MORP and MRP by different solvents at different periods of incubation

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