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Investigating the release of phosphorus from rock phosphate pretreated with humic acid, farm yard manure and effective microbes

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Abstract

Rock phosphate is a cheap source of soil P but it is not solubilized in alkaline soils when applied directly. An incubation experiment was conducted in laboratory to assess the release of P from rock phosphate (RP) applied alone or in combination with humic acid (HA), farm yard manure (FYM) and effective microbes (EM) during 2016. Treatments included (T₁) control, (T₂); RP applied at 90 mg P₂O₅ ha⁻¹ (T₃); HA at 3 mg kg⁻¹, (T₄); FYM at 5 g kg⁻¹, (T₅); EM at 1 mL kg⁻¹, (T₆); RP+HA, (T₇); RP+FYM, (T₈); RP+EM, (T₉); RP+HA+FYM, (T₁₀); RP+HA+EM, (T₁₁); RP+FYM+EM, (T₁₂); RP+FYM+HA+EM and (T₁₃) SSP fertilizer at 90 mg P₂O₅ ha⁻¹. The treatments were added in one kg soil in pots following CRD with three replications. The pots were placed in incubators at 25% moisture and 30°C temperature respectively. AB-DTPA extractable P (P_{AB}) and water soluble P (P_{WS}) were determined in the soil at 0, 15, 30, 45, 60, 75 and 90 days of incubation whereas pH, EC, lime and organic matter were determined only at the end of study. It was noted that sole application of HA, FYM and EM yielded higher P_{AB}, 4.22, 4.76, 4.03 mg kg⁻¹ respectively while P_{WS} from these treatments was 0.95, 0.88, 0.95 mg kg⁻¹ respectively. RP+HA+FYM+EM gave the highest value of AB-DTPA extractable P (4.96 mg kg⁻¹) and water soluble (1.69 mg L⁻¹) at the end of incubation time. This treatment also suggested the optimum combination for higher release of P from rock phosphate and keeping it in available form in soil.

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Introduction

Phosphorus (P) is broadly distributed in nature and constitutes 0.12 % of the earth crust on average (Marschner, 1993). Life is difficult to persist without P and primarily no soil can achieve higher yields if it is deficient in P (Sarir *et al.*, 2006). It is a second most essential macronutrient of plant and animal life, playing dynamic role in many metabolic processes such as energy transport as ATP in metabolic pathway of biosynthesis and root development for the efficient use of nutrients (Sharif *et al.*, 2015). According to Rashid (2005) and Anon (2010) most of the Pakistani soils are deficient in P which in turn results in the massive import of thousands of tons of P to overcome P deficiency in soil. In order to increase the efficiency of P fertilizers, it is necessary to explore the different sources of P and the efficient use of soil's fertility related technologies (Rosa *et al.*, 2018). In developing countries the use of natural source of nutrients and chemical fertilizers, such as animal, green manures, biological nitrogen fixation and rock phosphate in combination with the recycling of crop residue can play an important role (FAO, 1995). However, locally available materials used as nutrient sources should be tested for nutrient delivery before further adaptation of these techniques (Chalk *et al.*, 2002). This is mostly the case of the native rock phosphate resources in agricultural system in poor agricultural systems where the cost of chemical fertilizers is increasing.

Rock phosphate containing appreciable quantity of phosphate minerals is mainly used for phosphatic fertilizers for the agriculture sector. Phosphorite deposits of Hazara are the sources of raw material for phosphate fertilizer production in Pakistan which are situated in the north-western part of the country. Rock Phosphate is beneficiated, mined, smelted to produce elemental P and solubilized to produce wet-process phosphoric acid. Phosphoric acid reacted with RP to produce the fertilizer such as SPP, TSP or with anhydrous ammonia to produce the ammonium phosphate fertilizers. The elemental P is the base for furnace-grade phosphoric acid, phosphorus pentoxide, phosphorus pentasulfide, and phosphorus

trichloride. Approximately 90% of RP production is used for fertilizer, animal feed supplements and balance for industrial chemicals (NFDC, 1989). Jalil *et al.* (2017) reported that all organic materials (Farm Yard Manures and Humic Acid etc.) with rock phosphate (RP) enhance the solubility of phosphorus from RP. In another report by Jalil *et al.* (2014) they reported composting manure enriched with RPs enhances the dissolution of rocks. Humic substances are important part of natural ecosystem (Abdelhamid *et al.*, 2011). They are reported to increase the crop yield by enhancing the nutrient uptake by plants (Asik *et al.*, 2009). Humic acid is also reported to increase the solubilization of RP by means of complexation of cations (Ca and Fe) which are already present in these rocks Rosa *et al.* (2018). Effective microorganisms (EM) are another important fraction used in filed in combination with organic and inorganic materials which improve the soil properties (Hussain *et al.*, 1999). Javaid and Bajwas (2010) reported that EM assist in producing bioactive substances (hormones and enzymes) that accelerate the decomposition of organic materials. A very less work has been done on investigating the effectiveness of Rock phosphate in Pakistan. The present study focuses in detail on enhancing the solubilization of RP through its combined application with humic acid, farm yard manure and effective microbes.

Materials and methods

A laboratory study was carried out in 2016 in the Department of Soil Science to investigate the release of P from RP applied in various combinations with farmyard manure, humic acid and effective microbes. Aim was to study in detail the release pattern of P from RP in soil at different incubation intervals when applied alone or in combination with humic acid (HA), farmyard manure (FYM) and effective microbes (EM). The soil was collected from the research area of the university. The soil was thoroughly mixed to get homogenous mixture. Following treatments were applied:

T1 = Control

T2 = RP applied at 90 mg P₂O₅ kg⁻¹ (180 kg P₂O₅ ha⁻¹)

¹, RP contains about 31% P₂O₅

T3 = 3mg HAKg⁻¹ (6 kg HA ha⁻¹)

T4 = 5gm FYM kg⁻¹ (10 ton ha⁻¹)

T5 = EM 1ml kg⁻¹ (2000 l ha⁻¹).

T6 = RP +HA.

T7 = RP+FYM.

T8 = RP+EM.

T9 = RP+HA+FYM.

T10 = RP+HA+EM.

T11 = RP+FYM+EM

T12 = RP+FYM+HA+EM

T13 = single super phosphate at 90 mg P₂O₅ kg⁻¹ (180 P₂O₅kg ha⁻¹).

These treatments were applied to soil on dry weight basis. The prerequisite amount of RP and FYM was applied to soil in solid powder form followed by thorough mixing while HA and EM having minute quantities were applied in solution form and were mixed thoroughly with soil. The EM was first activated and then applied. For activation of EM, 1 L of EM was taken and mixed with 1 L of concentrated sugar solution, diluted with 20 liters of water and kept for three days. After three days the pH of the solution was 3.6 which indicated that EM was fully activated and ready for use.

Plastic pots with porous lids that could accommodate about one kg of soil were selected for the study. The pots were filled with treated soil, arranged in CR design in three replicates and were incubated inside the laboratory at 25% moisture and 30°C to avoid excessive wetting or drying. The amount of water needed was determined by the weight loss on daily basis. AB-DTPA and water soluble P were determined fortnightly i.e. 0, 15, 30, 45, 60, 75 and 90 day of incubation to see the changes and accumulation of available P as influenced by the treatments. Besides the periodical determination of Water soluble P and AB-DTPA extractable P, soil pH, EC, OM, lime, CO₃ and HCO₃ were also determined in the incubated soil.

Analytical methods

Soil pH was noted by 105-ion analyzer pH meter (McClellan, 1982). Soil electrical conductivity was

measured with conductivity meter by the method described by (Black, 1968). AB-DTPA extractable phosphorus was determined by the method of Soltanpour and Schwab (1977). Soil organic matter in soil samples was determined by Walkley-Black procedure as described by Nelson and Sommers (1996). Carbonates and Bicarbonates were determined in soil saturation extract by titration with 0.01 N H₂SO₄ to pH at 8.3 and 4.5, respectively (Richards, 1954). Lime content was calculated in soil according to the procedure given by Page *et al.*, (1982).

Statistical analysis

Statistical analysis of data was performed by using Statistix 8.1 and by using (ANOVA) following completely randomized design (CRD). Mean difference was acknowledged at < 0.05 significance level (Steel *et al.*, 1997).

Results and discussion

AB-DTPA extractable P

The AB-DTPA extractable P significantly ($p < 0.05$) varied at all incubation intervals to applied treatments (Table 1). Except at 0 d where some treatments produced at par values to control, the application of RP, FYM, EM and HA alone or in combination significantly enhanced AB-DTPA extractable P over control showing contribution toward P build up in the soil with time. At 0 d, since the RP which is slightly soluble did not increase the AB-DTPA extractable P remarkably unless it was applied with FYM alone or in combination.

The higher P in case of FYM addition could be attributed to the P content that it contains as well rotten FYM was used in the study (Misra, 2004). The AB-DTPA extractable P progressively increased with increase in incubation time and at d 90 the AB-DTPA attained a range of 2.02 to 4.96 against the range of 0.58 to 1.93 mg kg⁻¹ at d 0. This increase in P with passage of time showed the release of P from the source like RP, desorption of adsorbed P on soil colloids, dissolution of precipitated P with changing in soil properties associated with continuous watering

and incubation and mineralization of immobilized or organic P with time. Similarly any visual unexpected decrease could be associated to the same above process but taking place in the opposite direction. As such it is very difficult to precisely explain such type of changes but they do occur simultaneously at given incubation interval. However, one thing is obvious and that is that at all incubation intervals except at d 0 the treatments more or less behaved alike and produced AB-DTPA extractable P with more or less in the same passion. At d 90, all the applied treatment

like other incubation intervals produced significantly higher AB-DTPA extractable P than control showing the release of P from RP or at least the role of EM, FYM and HA in keeping the P in solution or more readily soluble and chelated form.

The sole application of FYM at 5 g kg⁻¹ (equals to 10 t ha⁻¹) superseded RP, EM and HA when applied alone. Combination of RP with sole FYM, EM, or HA did not produced higher AB-DTPA extractable P than their sole application.

Table 1. AB-DTPA extractable P at the given intervals of incubation as influenced by RP, HA, EM, FYM alone or in combination.

Treatments	----- Incubation time (d) -----						
	0	15	30	45	60	75	90
Control	0.58 e	1.45 c	1.31 e	1.69 e	2.00 d	2.00 d	2.02d
RP	0.54 e	1.87 bc	1.97 cde	2.57 cde	2.71 cd	3.38 c	3.43c
HA	0.75 cde	2.88 b	1.89 cde	3.50 abc	3.49 abc	4.16 abc	4.22abc
FYM	1.40 bcd	3.01 ab	1.60 de	3.78 ab	4.04 ab	4.71 ab	4.76ab
EM	0.48 e	2.76 b	1.90 cde	3.30 abcd	3.31 abc	3.98 abc	4.03abc
RP +HA.	0.55 e	2.26 bc	1.92 cde	3.48 abcd	3.50 abc	4.17 abc	4.22abc
RP+FYM	1.47 bc	2.78 b	3.31 ab	2.49 de	2.61 cd	3.28 c	3.33c
RP+EM.	0.55 e	2.77 b	2.04 cde	2.54 cde	2.64 cd	3.31 c	3.36c
RP+HA+FYM.	1.87 b	2.84 b	2.30 cd	2.83 bcd	3.01 bcd	3.68 bc	3.74dc
RP+HA+EM.	0.63 de	2.09 bc	2.55 bc	2.61 cde	2.64 cd	3.31 c	3.36 c
RP+FYM+EM	1.93 b	2.31 bc	2.34 cd	3.18 abcd	3.29 abc	3.96 abc	4.01abc
RP+FYM+HA+EM	0.80 cde	3.06 ab	3.88 a	4.02 a	4.24a	4.91 a	4.96 a
SSP	3.82 a	4.13 a	4.10 a	4.05 a	3.99 ab	4.81 ab	4.64 ab

*Means followed by same letter (s) in the given column do not significantly different at $p < 0.05$.

These apparent lower AB-DTPA extractable P could not be concluded that combination of FYM, EM or HA did not increase the release of P. But instead the adsorption and desorption and mobilization and immobilization, precipitation and dissolution process which were taking place would have played the dominant role in controlling the AB-DTPA extractable P status of soil. However, RP+HA+FYM+EM that produced the highest values of AB-DTPA extractable P (4.96 mg kg⁻¹) not only at 90 d but the consistently and significantly higher values P with such combination at all incubation interval suggested that this could be the optimum combination. This combination of RP+HA+FYM+EM not only increased the P dissolution from RP but kept the P in more available form during the whole incubation time. Laskar *et al.*, (1990) Majumdar *et al.* (2007) who

reported that P concentrations increased by applying RP mixed with organic fertilizers.

Water soluble P

Water soluble P representing the solution P concentration also showed significant response to applied treatments (Table 2) except at d 0 where control and some applied treatments produced statistically similar values. The application of RP, HA, EM and FYM alone or in combination exhibited higher water soluble P than control at all incubation intervals. Like AB-DTPA extractable P, the water soluble P increased with increase in incubation time. At d 90 the water soluble P ranged from 0.46 to 1.69 against 0.13 to 1.60 mg L⁻¹ at d 0 excluding SSP. However, the applied treatments behaved alike at all incubation intervals and causing similar passion of

variation among the treatments. Alone application of FYM, HA or EM produced significantly higher water soluble P than RP. Combination of RP with FYM, EM or HA produced higher water soluble P than RP but

less than their sole application. The apparent decrease in combination of RP with FYM, HA or EM as compared to their sole application could be associated to unknown factors like immobilization.

Table 2. Water soluble P at the given intervals of incubation as influenced by RP, HA, EM, FYM alone or in combination.

TREATMENTS	----- Incubation interval (d) -----						
	0	15	30	45	60	75	90
RP	0.13 e	0.47bc	0.49 de	0.64 de	0.68de	0.61def	0.67e
CONTROL	0.13 e	0.34 c	0.38 e	0.42 e	0.50e	0.49f	0.46f
HA	0.19 de	0.72 b	0.47 de	0.87bcd	0.87cd	0.85bc	0.95c
FYM	0.27cde	0.75 b	0.40 e	0.94bc	1.01bc	0.94b	0.88cd
EM	0.12 e	0.66 b	0.47 de	0.83bcd	0.83cd	0.86b	0.95c
RP+HA	0.14 e	0.56bc	0.48 de	0.87bcd	0.87cd	0.85bc	0.74de
RP+FYM	0.37bcd	0.70 b	0.83bc	0.62de	0.65de	0.72cd	0.73de
RP+EM	0.14 e	0.69 b	0.51de	0.64de	0.66de	0.67de	0.74de
RP+HA+FYM	0.47bc	0.71 b	0.57de	0.71cd	0.75d	0.58ef	0.66e
RP+HA+EM	0.16 e	0.52bc	0.64cd	0.65de	0.66de	0.87b	0.66e
RP+FYM+EM	0.48 b	0.58bc	0.59de	0.80bcd	0.82cd	1.86a	0.88cd
RP+HA+FYM+EM	1.34 b	1.56 b	1.66a	1.68a	1.88a	1.80a	1.69b
SSP	1.60 a	1.92 a	1.70a	1.87a	1.86a	1.89a	1.90a

*Means followed by same letter (s) in the given column do not significantly different at $p < 0.05$.

The highest water soluble P which is almost 3 times of control with application of RP+HA+FYM+EM at all intervals from 0 to 90 d of incubation suggested that this combination could be the optimum in enhancing the release of P from rock phosphate and the keeping the P in more readily available form. (Basak and Deg, 1997).

Post incubated soil organic matter

The post harvest soil organic matter showed increasing trend over control with application of RP, HA, FYM and EM alone or in combination except RP+EM which had lower values than control. The SOM ranged from 0.53 for RP+EM to 0.94 % in treatments receiving RP+HA+FYM+EM. The SOM were comparatively higher in FYM receiving treatments which is understandable. This higher SOM in RP+HA+FYM+EM could have played the major role in modifying the soil pH and dissolution of P. These results are comparable with Tomayo *et al.*, (1997).

Post incubated soil pH

The post incubated soil pH varied from 7.82 to 8.09 with mean value of 7.95 ± 0.27 showing that all the soils were alkaline in reaction that could be associated to strongly calcareous nature of soil having lime content of 16.9 to 19.9 %. This highly calcareous nature and alkaline pH could be the reason for lower values of AB-DTPA extractable P where none of the treatment including SSP application could fall in adequate range at any incubation interval. In such higher calcareous soil which had the higher buffering capacity the application of FYM could not reduce the soil pH up to appreciable extent (Khattak, 1996). However, application of RP+HA+FYM+EM decreased the post incubated soil pH up to 7.82 which is encouraging. (Table 3).

Post incubated soil EC and lime

The post-harvest soil EC did not show any significant response to applied treatments and varied with a range from 0.20 to 0.24 dS m^{-1} .

Table 3. Post incubated soil pH, SOM, EC, CO₃, HCO₃ and lime content as influenced by RP, HA, FYM, and EM applied alone or in combination.

TREATMENTS	pH	SOM	EC	Lime	CO ₃	HCO ₃
	-	%	dS m ⁻¹	%	meq/L	meq/L
CONTROL	8.02	0.59 j	0.20	16.9g	5.55 a	12.5a
RP	8.02	0.64i	0.20	19.4b	5.56 a	10.41ab
HA	7.99	0.63 i	0.23	17.4 fg	4.86 ab	10.42ab
FYM	8.03	1.07d	0.22	18.1def	5.55 a	9.72b
EM	7.96	0.66 h	0.20	18.3cde	2.78bcd	9.72b
RP+HA	7.96	0.71 g	0.22	18.7bc	2.78bcd	1.46c
RP+FYM	8.09	1.10 c	0.20	19.4ab	2.92bc	1.04c
RP+EM	7.95	0.64 i	0.21	17.9ef	2.99bc	1.04c
RP+HA+FYM	8.02	1.13 b	0.21	19.9 a	0.97cd	1.32c
RP+HA+EM	8.04	0.90 e	0.21	17.7ef	0.97cd	1.81c
RP+FYM+EM	8.07	1.09d	0.20	18.7cd	0.56d	1.60c
RP+HA+FYM+EM	7.82	1.15 a	0.24	19.9 a	0.97cd	2.08c
SSP	7.98	0.77 f	0.20	19.4ab	1.53cd	1.88c
LSD	NS	0.016	NS		2.3553	2.3212

*Means followed by same letter (s) in the given column do not significantly different at $p < 0.05$.

The application of RP, EM, HA and FYM could not be expected to change the EC of soil at large scale as these sourced do not contain soluble salts. The post-harvest soil lime though showed significant variation with a range from 16.9 to 19.9 % CaCO₃ among treatments but such variations could be due to error in analysis. The treatments applied neither consisted CaCO₃ nor such big difference of 3.0% (19.9 – 16.9 = 2.5 %) lime which is equivalent to 30 g CaCO₃ kg⁻¹ could be expected to rise up with such treatments which at the extent were applied as 5 g FYM kg⁻¹ (Table 3).

Conclusion

The progressive increase in both AB-DTPA and water soluble P showed release/desorption of soil P with passage of incubation time. The consistent higher AB-DTPA extractable and water soluble P in treatments receiving FYM, HA and EM over control and alone RP showed their positively role in releasing/desorption of soil P or at least keeping the soil P in more available form. RP applied in combination with all three organic sources (FYM+HA+ EM) enhances release of P and keeps P in more readily available form.

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