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Studies on the Possible Use of Rock Phosphate in Alkali Soils of Egypt

A.M. Elgala and M.M. Elbordiny
Soils Department, Faculty of Agriculture, Ain Shams University, Cairo, Egypt.

FINELY ground rock phosphate (RP) is successfully used on acidic soils where soil acidity slowly releases plant available P. So, the aim of this work is to assess and evaluate the effect of acidulation of rock phosphate and rock phosphate added to a composting material on the availability of P in an alluvial alkali soil. Pots experiment was conducted to study the availability of acidulated rock phosphate with acetic acid (RPAA), citric acid (RPCA) and sulphuric acid (RPSA) and (RP) added with composted orange peel (RPOM) compared to triple superphosphate (TSP) for corn plants.

Results show that the $NaHCO_3$-extractable P increased in alkaline alluvial soil treated with acidulated and (RP) added to composting of orange residues particularly (RPOM) and (RPCA). The use of (RPCA) or (RPOM) increased the availability of P and consequently increased P uptake by corn plants than the other treatments. The percentage increase of P in corn plants for TSP, RPAA, RPCA, RPSA and RPOM reached about 43.1 34.5,39.7,32.8 and 63.8% above the natural rock phosphate (RP), respectively. The percentage increase in dry weight for TSP, RPAA, RPCA, RPSA and RPOM reached about 60.8, 35.2, 70.0, 57.6 and 94.4% above the (RP), respectively.

It was concluded that acidulation of rock phosphate or adding the material with organic matter plays a role in the availability of P in alkaline soil beside the role of plant roots in solublying insoluble forms.

Keywords: Acidulation, Rock phosphate, Corn plant, Alkaline soil .

Phosphorus is one of the essential nutrients for plant and animal life. Phosphorus availability to plants in alkali and calcareous soils is usually restricted. Maximum availability to plants of both native and applied P is in the pH range of 6.0 to 7.5.

At higher pH values, phosphate anions react with Ca and Mg to form phosphate compounds of limited solubility (Mortvedt *et al.*, 1999).

In Egypt, there are large commercially mine deposits of rock phosphate. They have been mined for over a century. Rock phosphate is successfully used in acid soils as source of P for plants. However, it is believed that conditions in Egypt are not well suited to the use of rock phosphate by direct application. Although, rock phosphate is relatively slowly released but its low price, appears to be a very attractive as phosphate fertilizer. Rock phosphate fertilizer may dissolve so slowly that dissolution would be more limiting than the rate of fixation, giving them a very low residual value in addition to low immediate effectiveness (Fuehring, 1973). Maene (2001) reported that, in Burkina Faso, at Manga village, Burkina rock phosphate is mixed with compost. The compost is applied at a rate of 45 wheelbarrows per ha, 8 bags of rock phosphate per compost pit. There is evidence in other countries and regions of the benefits to the plant availability of P of applying organic matter together with the rock phosphate. Soil humus improves the soil structure, which has a beneficial effect on P uptake. Johnston (2000) reported that soil organic matter can chelate Ca ions derived from PR dissolution and thus increase P release from rock phosphate. It is likely that composting rock phosphate with organic matter follows the same mechanism.

The ineffectiveness of rock phosphates as compared to superphosphates is the result of low water solubility of the rocks. Partial acidulation of rock phosphate is one way to increase water solubility. Evidence has accumulated over the years on the agronomic effectiveness of partially-acidulated rock phosphate vis-à-vis superphosphates (McLean & Wheeler,1964). McLean & Logan (1970) indicated that finely ground and partially acidulated rock phosphate (10-20% acidulation by H_3PO_4) was as good or better than concentrated superphosphate for the German millet, alfalfa, or corn grown in Ohio soils with high P sorption capacity. Lutz (1971) mentioned that rock phosphate acidulation by 20% H_3PO_4 was inferior to concentrated superphosphate for corn in a field experiment. However, in another field experiment using alfalfa and orchard grass as test crops, Lutz (1973) found that 20% partially acidulated rock phosphate was as effective as concentrated superphosphate. Citrate ion is particularly effective in displacing P from goethite and in maintaining a higher level of phosphate in solution (parfitt, 1979). Citrate and bicarbonate at pH >8 compete with P for active Al sites on the clay minerals (Kafkafi *et al.*, 1988).

The aim of this work is to compare the availability of rock phosphate partially acidulated or added during composting process to that of triple superphosphate for corn plants grown in alkaline soil in green house experiment.

Material and Methods

Soil sample represents alluvial clay loam soil, *Typic torrets*, taken from Agricultural Experimental Station farm, Faculty of Agriculture, Ain Shams University, was used in this study. The soil samples characterized by having a pH value of 7.35, total soluble salts of 1.13 dS/m, clay content of 36 %, organic matter of 1.12 %, $CaCO_3$ content of 1.61% and 7.59 mg/kg available P (Olsen *et al.*, 1954).

The soil sample was collected from the top 30 cm of the soil profiles, air dried and crushed to pass through a 2mm sieve.

Rock phosphate of the Red-Sea mined by AL-Ahram Mineral Company was acidulated with 20% of the follows acids:

i. Acetic acid

ii. Citric acid

iii. Sulphuric acid

iv. Natural organic acids: A sample of rock phosphate was composted with orange material as a source for natural organic acid. 10 kg of orange peal were cut to small pieces and 180 g rock phosphate were added between in 5 equal layers to enhance the aeration and decomposition process. To activate the decomposition process, an activator mixture of 275g ammonium sulphate and about 1kg of farmyard manure were added to the composting materials according to the method described by Abou El- Fadle (1960).

The four rock phosphate treated products were first air dried, well crushed, finely ground to pass through a 2mm sieve. Analysis of the products are shown in Table 1.

A pot experiment was conducted under greenhouse conditions, to study the availability of P from rock phosphate in soil with and without plants. Thirty-six plastic pots (25cm height and 28 cm diameter) were packed with 40 kg air-dried soil sample for each. Each pot received 2g pot^{-1} K_2O as potassium sulphate (48 % K_2O) (equivalent to 50 kg fed^{-1}) and thoroughly mixed with the soil before cultivation. The following P treatments were applied on the bases of the reactivity of natural rock phosphate (30.65%) to pots with or without plants.

i. 8 Triple superphosphate (TSP).

ii. Natural rock phosphate (RP).

iii. Rock phosphate acidulated with acetic acid (RPAA).

iv. Rock phosphate acidulated with citric acid (RPCA).

v. Rock phosphate acidulated with sulphuric acid (RPSA).

vi. Rock phosphate composted with orange peal (RPOM).

TABLE 1. Composition of the rock phosphate and partially acidulated and composted samples.

Treatment	Total P	Water soluble	Citric acid -soluble	Reactivity
	%			
Rock phosphate (RP)	12.92	0.03	3.96	30.65
Rock phosphate acidulated with acetic acid (RPAA)	12.92	0.12	6.85	53.02
Rock phosphate acidulated with citric acid (RPCA)	12.92	0.19	8.79	68.03
Rock phosphate acidulated with sulphuric acid (RPSA)	12.92	0.46	10.76	83.28
Rock phosphate composted with orange peal (RPOM)	13.14	0.28	9.94	75.65

For the green house experiment pots were seeded with 7 corn grains (Triple hybrid 310) then thinned to three plants to study the effect of root exudate on solubility of phosphorus. There were three replicates for each treatment; the different treatments were irrigated twice a week with tap water. Soil moisture was maintained between 60-80 % of field capacity. Ammonium nitrate (33% N) at the rate of 4.8 g N pot^{-1} (120 kg N fed^{-1}.) was applied in two equal splits (after 20 and 35 days from sowing). Representative soil samples were taken from the treated pots at zero time and after 7, 15, 30 and 45 days from planting (before planting, at germination, at beginning vegetative stage, at medium vegetative stage and at flowering stage). The collected samples were air dried, crushed, sieved through a 2-mm sieve and stored for available P determination, (Watanabe & Olsen 1965). The corn plants were harvested (45 days after planting), oven-dried at 70C°, the dry matter yield were recorded and the concentration of P was determined by method described by Watanabe & Olsen (1965).

Physical and chemical properties of soil characteristics were determined using standard methods outlined by Baruah & Barthakur (1997).

Results and Discussion

It is interesting note that acidulation of rock phosphate resulted in increasing the reactivity with high value with the rock phosphate treated with sulphuric acid (Table 1). Reactivity of the composted rock phosphates is relatively higher than when the material was acidulated a single organic acid as acetic or citric acid. Table 2 shows $NaHCO_3$ –soluble P concentration after addition of acidulated rock phosphate to soil. Data indicate that the acidulation of rock phosphate significantly increased the levels of available P in the soil as compared to the control. The available P concentration showed the following order: PROM> PRCA > PRAA > PRSA>. The highest level of extractable P was recorded in the soil treated with rock phosphate added during composting (RPOM). Application of (RPOM) to soil increased available P concentration by 59 and 115 % more than the triple superphosphate (TSP) and untreated rock phosphate (RP) treatments, respectively. Also, available P concentration in the soil increased with time recording the highest values after 45 days from incubation. In biologically active soil there is continues immobilization of inorganic P into organic phase and mineralization of organic-P to inorganic forms, (Gerke,1992).

TABLE 2. Effect of acidulated rock phosphate on $NaHCO_3$-soluble P in soil as a function of time.

Time of sample,	$NaHCO_3$-Extract P, ppm					
days	TSP*	RP	RPAA	RPCA	RPSA	RPOM
0	8.07	6.71	7.82	7.54	8.53	9.17
7	9.97	7.70	9.65	9.98	10.52	12.77
15	10.02	8.33	12.66	12.72	12.50	19.96
30	13.98	9.96	15.33	19.98	13.21	22.12
45	16.33	10.32	15.66	23.99	14.13	25.89
$LSD_{0.05}$	0.18	0.59	0.82	1.23	0.49	1.72

Triple superphosphate (TSP) - Rock phosphate (RP)-Rock phosphate acidulated with acetic acid (RPAA)- Rock phosphate acidulated with citric acid (RPCA)-Rock phosphate acidulated with sulphuric acid (RPSA)- Rock phosphate composted with natural organic acids (RPOM).

The availability of P with addition of acetic acid to rock phosphate (RPAA) was less than citric acid. This may be due to differences in stability and to the amount of CO^{2-}_3 release during $CaCO_3$ dissolution to Ca and CO^{2-}_3. Also, citric acid supplies more H+ than acetic acid as well as citrate anion, which serves as a ligand. In the presence of citrate protonation of the RP, surface can weaken critical bonds; thus detachment of lattice species into the solution occurs while, acetate anion is not stable and it soon volatile. The citrate ligand may form an inner-sphere complex with surface Ca, thereby facilitating its detachment and enhancing dissolution; in addition to complex formation in solution that enhances solubility. Moreover, surface phosphate may be exchanged by citrate, ligand exchange. As mentioned above RPOM treatment gave the highest extractable-P from soil. Rynk, *et al.* (1992) noticed that mixed organic materials with rock phosphate will usually create a balanced pH in the optimum range of 6.5-8.0 in a properly made compost. Composting low-grade rock phosphate can enhance P availability to be comparable to applications of single superphosphate (Singh & Amberger, 1995). Amberger (1991) found that composting rook phosphate materials with straw or other organic waste materials resulted in phosphate mobilization. He further indicated that the drawing force for rock phosphate solubilization is the pH decrease and the chelating effect of simple organic acid as citric and malic and complex acids as humic and fulvic acids on Ca^{2+} ions from insoluble phosphate forms.

Concerning the extractability of P from the soil in the presence of corn plants, data presented in Table 3 show that extractable-P increased in cultivated soil more than non cultivated soil. This may be due to one or all the following as indicated by Marschner (1995). 1- Decrease in pH as a consequence of preferential cation uptake; 2- exudation of organic acids by the roots; 3- release by roots of photosynthates as substrate for rhizosphere microorganisms, which in turn affect pH, redox potential, and chelator concentrations (*e.g.*, siderophores) in the rhizosphere. Results indicate that with composting and citric acid treatments there were more solublization of P from rock phosphate with time as compared to other treatments in the presence of plants. Gahoonie *et al.* (1992) reported that soil pH at the root surface of ryegrass plants decreased by up to 1.6 unit and these changes extended to a distance between and 4 mm from the root surface depending on the soil type. Hoffland *et al.* (1989) indicated that the major part of local rhyzosphere acidification by P-stressed plants has to be attributed to exudation of organic acid malate and to a lower extent citrate. Ratnayake *et al.* (1978) mentioned that exudation of amino acids and reducing sugars was more induced by P- stressed sudan grass plants.

Dry weight of corn plants grown on alluvial soil treated with acidulated rock phosphate is presented in Table 4. The obtained results indicate that the amounts of dry weight of corn plants significantly increased due to the application of acidulated rock phosphate as compared with the control treatment. Application of (RPOM) or (RPCA) treatment recorded the highest values of dry weight of corn plants. This confirms the previous finding of the role of natural citric acid in mobilizing insoluble rock phosphate beside the activity of root exudate. The percentage increased in dry weight for TSP, RPAA, RPCA, RPSA and RPOM reached about 60.8, 35.2, 70.0, 57.6 and 94.4% above the natural rock phosphate (control), respectively. On the other hand, by comparing acidulated rock phosphate treatments with triple superphosphate treatment it is noticed that the dry weight of corn plants decreased by15.9 and 2% for RPAA and RPSA treatments and increased by about 5.7 and 20.9 for RPCA and RPOM treatments, respectively.

TABLE 3. Effect of acidulated rock phosphate and corn plant on amounts of $NaHCO_3^-$ soluble P in soil as a function of time.

Time of sample,	NaHCO₃-Extract, ppm P					
days	TSP*	RP	RPAA	RP CA	RPSA	RPOM
0	8.07	6.71	7.82	7.54	8.53	9.17
7	12.02	8.81	10.88	11.43	10.95	17.35
15	13.10	11.96	13.91	16.67	14.37	22.50
30	17.05	12.41	26.86	28.18	14.59	35.45
45	23.91	13.05	29.09	36.21	22.39	42.85
$LSD_{0.05}$	1.35	1.11	2.31	2.16	0.17	2.19

Triple superphosphate (TSP) - Rock phosphate (RP) - Rock phosphate acidulated with acetic acid (RPAA) - Rock phosphate acidulated with citric acid (RPCA)-Rock phosphate acidulated with sulphuric acid (RPSA)- Rock phosphate composted with natural organic acids (RPOM).

TABLE 4. Effect of acidulated rock phosphate on dry weight and P concentration in corn plants.

Treatment	Dry weight, g/pot	P concentration, %
TSP*	74.05	0.83
RP	46.05	0.58
RPAA	62.25	0.78
RP CA	78.27	0.81
RPSA	72.58	0.77
RPOM	89.50	0.95
$LSD_{0.05}$	1.12	0.10

Triple superphosphate (TSP) - Rock phosphate (RP)-Rock phosphate acidulated with acetic acid (RPAA) - Rock phosphate acidulated with citric acid (RPCA)-Rock phosphate acidulated with sulphuric acid (RPSA)-Rock phosphate composted with natural organic acids (RPOM).

Phosphorus concentration in corn plants follows the same trend of dry weight as phosphorus content significantly increased with acidulation and composting . The obtained results indicate, also, the superiority of RPOM treatment relative to other treatments. The percentage increased in concentration P, concentration in corn plants for TSP, RPAA, RPCA, RPSA and RPOM reached about 43.1 34.5,39.7,32.8 and 63.8% above the untreated rock phosphate, respectively. The superiority of RPOM treatment finding could be explained as mentioned above, as the direct and indirect role of the organic manure. The direct effect includes the continuous release of organic P into soluble orthophosphates, while the indirect effect is due to the role of organic acids compounds of solubilizing more P from insoluble P bearing compounds, (El-Ghozoli, 1994) beside the role of humus in improving the physical, chemical and biological properties of the soil (Elgala *et al.*, 1975) .

Thus, it could be concluded that the phosphorus concentration in soil and plant was mainly influenced by soil characteristics and presence of plant. The decrease of soil pH and presence of organic acids affect pH, redox potential, and chelation. So, the use of acidulated rock phosphate with citric acid increased the availability of P and consequently increases P uptake by plants and their yields in alkaline soil. However, composted rock phosphate with orange peel was more efficient in increasing P concentration in soil and plant than acidulation. Plant roots had a role in solubling P under alkaline condition. Thus, the use of acidulated rock phosphate or mixing RP with organic residues is recommended for alkaline soil; rock phosphate is a natural, unprocessed product, which makes it acceptable for use in organic farming.

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دراسات عن إمكانية استخدام صخر الفوسفات في الأراضي القلوية بمصر

عبد المنعم محمد الجلا و محمود محمد البرديني
قسم الأراضي – كلية الزراعة – جامعة عين شمس – القاهرة – مصر .

يستخدم ناعم صخر الفوسفات في الأراضي الحمضية بكفاءة عالية لانطلاق الفوسفور الميسر بما يتلاءم مع احتياجات النبات ولهذا فإن هدف هذا البحث هو تقييم تأثير تحميض ناعم صخر الفوسفات ببعض الأحماض العضوية وكذلك إضافته إلى كومة المكمورة أثناء عمل السماد العضوي (الكمبوست) على مدى تيسر الفوسفور لنبات الذرة المنزرع في الأراضي القلوية .ولذلك تم عمل تجربة أصص تحت ظروف الصوبه واستخدام ناعم صخر الفوسفات المحمض بكل من حمض الخليك ، الستريك، الكبريتيك بنسبة ٢٠٪ وكذلك كمر ناعم صخر الفوسفات مع مخلفات الموالح.

أوضحت النتائج مايلي :

أدى استخدام ناعم صخر الفوسفات المحمض بأي من الأحماض إلى زيادة الفوسفور الميسر بالتربة وكانت أوضح الزيادات مع استخدام أي من حمض الستريك أو المكمور مع مخلفات الموالح ونتيجة زيادة الكمية الميسرة من الفوسفور بالتربة زادت الكمية الممتصة بواسطة نبات الذرة خاصة مع استخدام حمض الستريك أو المكمور مع مخلفات الموالح. سجلت نسبة الزيادة في تركيز الفوسفور داخل النبات ٤٣,١، ٣٤,٥،٣٩,٧، ٣٢,٨ ، ٦٣,٨٪ نتيجة استخدام السوبر فوسفات ، ناعم صخر الفوسفات المحمض بالخليك ، ناعم صخر الفوسفات المحمض بالستريك ، ناعم صخر الفوسفات المحمض بالكبريتيك، ناعم صخر الفوسفات المكمور مع مخلفات الموالح على الترتيب مقارنة باستخدام ناعم صخر الفوسفات فقط. بينما سجل وزن النبات الجاف نتيجة المعاملات السابقة ٦٠,٨، ٣٥,٢، ٧٠,٠، ٥٧,٦، ٩٤,٤٪ على الترتيب مقارنة باستخدام ناعم صخر الفوسفات فقط.

من هنا يمكن القول بأن استخدام ناعم صخر الفوسفات المحمض أو المكمور مع المخلفات العضوية في الأراضي القلوية يلعب دور أساسي في تيسر الفوسفات للنباتات المزروعة بجانب تأثير جذور النباتات.