



EFFECT OF ACIDULATED ROCK PHOSPHATE ON MICRONUTRIENTS UPTAKE BY MAIZE

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ABSTRACT

Pot experiment was conducted to investigate the effect of acidulated rock phosphate on micronutrients uptake in calcareous soil, to evaluate RP as cheaper and possible substitute of chemical fertilizer. Fresh silt loam texture soil was taken in plastic pots and mixed with required amount of finely ground RP calculated on % P basis. Results showed that RP untreated or pretreated with equal amounts of H₂SO₄ significantly increased the concentration of P in soil and also P accumulation in plant. Acidulated RP also increases the micronutrients concentration and yield attributes. Pre-treatment of +RP with acid resulted in higher Zn accumulation as compared to untreated RP. The highest total accumulation of 2.04 mg Zn pot⁻¹ was recorded in treatment RP200% + acid and RP100% + acid with statistically similar values of 1.57 and 1.11 mg Zn pot⁻¹. Fe content for RP100% + acid RP100%, RP200% were significantly higher than control, while highest total Fe accumulation was recorded in treatment of RP200% + acid as 38.86 mg pot⁻¹. Significantly higher Cu accumulations of 0.63 and 0.51 mg Cu pot⁻¹ were observed in RP200% + acid and RP100% + acid treatments. RP increased Mn total accumulation by maize plants, the highest accumulation of 3.50 mg Mn pot⁻¹ was recorded in RP200% + acid followed with 2.99 and 2.56 mg Mn pot⁻¹. The highest accumulation of Ca in shoot was observed 0.48 g Ca pot⁻¹ and 0.37 g Ca pot⁻¹ in treatment of RP200% + acid and RP100% + acid. Acidulated RP increased the micronutrients concentration, total accumulation and crop growth, which shows that RP have the ability to substitute Phosphatic fertilizer.

Keywords: acidulated rock phosphate, micronutrients concentration, total uptake, maize yield, calcareous soil.

1. INTRODUCTION

Rock phosphate (RP) is obtained from the mining and subsequent metallurgical processing of P-bearing ores. Sedimentary RP are mainly composed of apatite. This apatite group exhibits extensive isomorphic substitution in the crystal lattice. Thus, they have a wide variation in chemical composition and accordingly show a wide range of properties. In sedimentary deposits, the main phosphate minerals are francolites (microcrystalline carbonate fluorapatites), which occur in association with a variety of accessory minerals and impurities (McClellan and Van Kauwenbergh, 1990). Although considerable amounts of accessory minerals and impurities are removed during beneficiation, the beneficiated ore still contains some of the original impurities. Such impurities include silica, clay minerals, calcite, dolomite, and hydrated oxides of iron (Fe) and aluminum (Al) in various combinations and concentrations, some of which may have a marked influence on the performance of a RP used for direct application (UNIDO and IFDC, 1998). Thus, currently RP is the trade name of about 300 phosphates of different qualities in the world. Rock phosphate can be used either as raw materials in industry to manufacture water-soluble P (WSP) fertilizers or as P sources for direct application in agriculture. Various researchers have worked on direct applications of RP to soil and reported even superior results than commercial fertilizer in some instances (Menkeni *et al.*, 1991; Yost *et al.*, 1982; White *et al.*, 1999). On the other hand some researchers like Bolland *et*

al. (1988) have argued that since RP had inconsistent relative effectiveness of only 5-30% as water-soluble phosphate (WSP) fertilizer in soils of Australia could not be regarded as economically viable substitute for WSP commercial fertilizers. Such erratic and controversial observations might be associated with the fact that suitability and effectiveness of RP varies with RP sources, soil type, crop species and climatic conditions of the areas (Laea, 2002). RP, which is considered slow releasing P source (Jones, 1990; Akande *et al.*, 1998), was also applied in combination with various bio-organic sources such P solubilizing fungi and bacteria (Khalil *et al.*, 2002; Cabello *et al.*, 2005) organic manures (Akande *et al.*, 2005) and inorganic substances like (Harry *et al.*, 2002), pyrite (Singh *et al.*, 1993) or different kinds of acids (Basakar and Deg, 1997) to increase release of P and subsequent influence on crop yield.

Rock phosphate has some other minerals which supply micronutrient for plant growth but not very sufficient information about direct application of RP to the plant. Rock phosphate has the capacity to increase the micronutrient concentration in soil as well as in crop growth and yield.

Sinclair *et al.* (1990) found that Sechura RP (Peru), which contains 43 mg of molybdenum (Mo) per kilogram, increased dry-matter yields of pasture herbage more than TSP did at sites where the RP increased Mo levels in clover.



Maize is economically important cereal grain crop after wheat and rice. It is used as staple food for human, livestock and as raw material for industries. Maize can be grown on variety of soil having texture from sandy to clay, but the best yield can be obtained on the medium texture having good drainage system. Maize is rapidly growing crop with short duration and considered one of the most exhaustive crops. On average basis it takes up about 40 kg P ha⁻¹ Mg⁻¹ of fresh biomass (Sharif *et al.*, 1985). In a different of soil and climatic conditions it quickly responses to fertilizer application. Many researchers reported increase of maize yield with P fertilizer application (Akande *et al.*, 1998). Given the unaffordable cost of P fertilizer, it is imperative to evaluate the direct application of RP for maize productions. Pretreatment of RP with acids like concentrated H₂SO₄ seems easier, more effective in our calcareous soil conditions and can be adapted on mass scale if reliability and economics of the technology is properly investigated under various crops and climatic conditions. An attempt, in the present study was made to compare various sources of RP to increase the efficiency of RP through pretreatment with commercial sulfuric acid and evaluate comparative influences on maize plant growth in a pot experiment. It was also investigated that RP treated with sulfuric acid effect the micronutrient concentration and total uptake in maize.

2. MATERIALS AND METHODS

To study the effect of different sources of RP at various levels untreated or pretreated with equal amount of concentrated H₂SO₄ on micronutrient uptake on maize crop in calcareous soil. The experiment was conducted in

the Department of Soil and Environmental Sciences, KPK Agricultural University, Peshawar during 2008. Soil used in the experiment was collected from upper surface (0-15 cm) of the field. The soil was low in organic matter, mineral N, marginal in AB-DTPA extractable P 5.92 mg kg⁻¹, contained K 233 mg kg⁻¹, non-saline, calcareous soil (lime = 16.5%) with initial pH (1:5) of 8.5 and texture silt loam.

The treatments included RP at 100% and 200% based on P recommended levels either untreated or pretreated with equal amounts of H₂SO₄. Plastic pots containing 7 kg fresh soil were treated with treatments in triplicates (Table-1). The experiment was laid out according to RCB- design. Required amounts of finely ground untreated RP was thoroughly mixed with soil before filling up pots while in case of H₂SO₄ (Table-1) treatments the required amount of acid and RP was first dissolved in 20 mL distilled water then diluted to 500 mL water before mixing with soil. The control and those pots receiving untreated RP were supplied with equal amount of water to bring all pots to same moisture level. Twelve seed of 'Jalal' maize (*Zea mays* L.) were sown in each pot on August 20, 2008 after attaining field capacity level. Plants were harvested on September 22, 2008 and fresh biomass and air-dried biomass including upper aerial shoot and roots were weighed separately. Both shoot and roots samples were analyzed for P and micronutrient concentrations and total accumulation was calculated by multiplying dry weight into concentrations of respective nutrient. Similarly, soil samples were also analyzed for AB-DTPA extractable P to investigate comparative residual effect of RP untreated or pretreated with H₂SO₄.

Table-1. Treatment combinations for the effect RP untreated or pretreated with H₂SO₄ on maize plants and micronutrients uptake.

Treatments	H ₂ SO ₄ mg kg ⁻¹ soil	Mg P kg ⁻¹ soil	% P in source	RP mg kg ⁻¹
Control	0			
RP100%	0	20	6.8	300
RP200%	0	40	6.8	600
RP (100%)+Acid	300	20	6.8	200
RP (200%)+Acid	600	40	6.8	300

Laboratory analysis

Total P in various RP sources

Total P in RP was determined by the procedure of Sridhar and Jackson (1974). A 0.2g ground sample was shaken for two hours with 2 mL of aquaregia (1 mL HNO₃+3 mL HCl) and 10 mL of conc. HF (hydrofluoric acid) in 250 mL of plastic bottle on horizontal to and fro shaker. The suspension was kept over night and dissolved in 100 mL of saturated H₃BO₃ solution next day. The sample was then diluted by adding 100 mL distilled water.

Phosphorus was determined by spectrophotometer Perkin Elmer (Rlamda 35).

Water soluble P in RP sources

For water soluble P in RP, five gram of RP was added with 50 mL distilled water in conical flasks and shaken for 15 min on reciprocating shaker. The suspension was filtered through whatmann no. 42 and P was determined by Spectrophotometer, Pekin Elmer (RLambda 35). AB-DTPA extractable P was extracted (Soltanpour (1985) and determined through NH₄-molybdate complex



method (Page *et al.*, 1996). Soil pH was determined by the method as determined by Rhoads, (1996).

Soil texture was determined by the procedure as described by Koehler *et al.* (1984). Soil organic matter was determined by using $K_2Cr_2O_7$ as an oxidizing agent as described by Nelson and Sommer (1996). Total N in soil and plant samples was determined by Kjeldahl method of Bremner (1996). Soil K was determined by AB-DTPA extracting solution as described by Soltanpour and Schawab (1977). K was determined by flame photometer (Jenway PFP 7). Roots and shoots samples were kept at 60-70 °C for 48 hours in oven. The samples were then grinded and analyzed for P and micronutrients. Phosphorus and micronutrients were determined after acid digestion (Benton *et al.*, 1991). One gram of ground sample was added with 10 mL concentrated nitric acid and kept over night. The sample was then added with 4 mL concentrated perchloric acid and heated until it became transparent. The digest was transferred to 100 mL flask and volume was adjusted by adding distilled water. Formation P-color complexes in ascorbic acid determined P by spectrophotometer (Perkin Elmer Lambda, 35). While micronutrient was determined by using atomic absorption photometer (Perkin Elmer 2380). Plant height was recorded from the base of the plant to the tip at the time of harvesting. Plant heights of each pot were then averaged separately. The upper aerial portion of the maize plant was weighed both at fresh and air-dried conditions for each pot separately. Roots from each pot were collected after harvest. Washed with tap water and weighed at both

fresh and air-dried conditions. The data obtained was analyzed statistically by computer using MSTATC package (Russell, 1989). ANOVA were computed and means were compared through Least Significant Test (Steel and Torrie, 1980)

RESULTS AND DISCUSSIONS

AB-DTPA extractable P concentrations and accumulation by plant as by RP

Concentration of P in soil is influenced by RP200% + acid of 6.00 mg P kg⁻¹ compare with control of 5.50 mg P kg⁻¹ and also concentration of P in shoot, Root effected by RP RP200% + acid of 1277 mg P kg⁻¹ in shoot while in root is 758 mg P kg⁻¹. Addition of RP100% + acid gave total P accumulation of 54.7 mg pot⁻¹ higher accumulations and AB-DTPA extractable P in post harvest soil revealed increasing availability of P from RP when pre-treated with acid compared to untreated RP (Table-2).

It is concluded that decrease in P concentration over incubation time shows that P is immobilized or precipitated as Ca or Mg complexes, adsorbed or fixed on clay particles with time. The RP could be associated with higher release of P that enhanced P availability and crop growth. Rock phosphate treated with H₂SO₄ has the potential to increase crop yield and plant nutrient accumulation in calcareous soil. Field research is recommended to standardize various methods for RP+ acid applications, which are practicable for achieving maximum yield.

Table-2. Post harvest soil AB-DTPA extractable P concentrations and its accumulation by plant as influenced by RP untreated or treated with H₂SO₄.

Treatments	P	H ₂ SO ₄	Concentrations of P			Accumulation of P		
			Soil	Shoot	Root	Shoot	Root	Total uptake
	(mg kg ⁻¹)		-----mg P kg ⁻¹ -----			-----mg P pot ⁻¹ -----		
Control	0	0	5.50 ab*	1130ns	834ns	26.8d**	2.5 d*	29.3 d*
RP100%	20	0	6.88 a	1118	800	36.5 cd	2.8 cd	39.3 cd
RP200%	40	0	6.22 ab	1212	800	42.3 bcd	3.3 bcd	45.6 bcd
RP100%+acid	20	300	5.57 abc	1056	718	50.7 bc	4.0 abc	54.7 bc
RP200%+acid	40	600	6.00 abc	1277	758	72.3 a	4.9 a	77.2 a
LSD (0.05)			1.53	-	-	20.3	1.3	20.7

Concentrations of Zn in maize plants

Concentration of Zn did not show significant response to treatments but when data were converted to total accumulations by multiplying concentrations with shoot and root weights, significant increase with P application irrespective of P sources were observed (Table-3). Pre-treatment of RP with acid resulted in higher Zn accumulation as compared to untreated RP. The

highest total accumulation of 2.04 mg Zn pot⁻¹ was recorded in treatment RP200% + acid and RP100% + acid with statistically similar values of 1.57 and 1.11 mg Zn pot⁻¹, respectively. The Zn concentrations ranged from 26.20-29.06 and 49.26-57.93 in shoot and roots respectively fell in adequate range (Tisdale *et al.*, 1993). The higher and significant Zn uptake for the treatments of RP200% + acid could be related to the large increase in biomass.



Table-3. Concentrations of Zn in shoot and roots of maize plants as influenced by RP untreated or treated with H₂SO₄.

Treatments	P	H ₂ SO ₄	Concentrations Zn		Accumulation Zn		
			Shoot	Root	Shoot	Root	Total uptake
	(mg kg ⁻¹)		-----mg Zn kg ⁻¹ -----		-----mg Zn pot ⁻¹ -----		
Control	0	0	27.40 ns	49.40 ns	0.63 c*	0.15c*	0.77 d*
RP100%	20	0	27.93	56.40	0.90 bc	0.19 bc	1.09 d
RP200%	40	0	26.20	49.26	0.91 bc	0.20 bc	1.11 cd
RP100%+acid	20	300	27.06	50.13	1.29 ab	0.28 ab	1.57 bc
RP200%+acid	40	600	29.06	57.93	1.65 a	0.38 a	2.04 a
LSD _(0.05)			-	-	0.11	0.41	0.46

Concentrations of Fe in maize plant

The Fe concentrations in shoot were significantly higher for RP100% as compared to control and other treatments (Table-4). Fe concentrations for RP 100 % + acid RP100 %, RP 200 % were significantly higher than

control but at par with each other with a range from 296 to 426.7 mg kg⁻¹. Total accumulation of Fe in maize plants significantly increased with P application irrespective of source. The highest total accumulation of Fe was recorded in RP 200 % + acid i.e., 38.86 mg pot⁻¹.

Table-4. Concentrations of Fe in shoot and roots of maize plants as influenced by RP untreated or treated with H₂SO₄.

Treatments	P	H ₂ SO ₄	Concentrations Fe		Accumulation Fe		
			Shoot	Root	Shoot	Root	Total uptake
	(mg kg ⁻¹)		-----mg Fe kg ⁻¹ -----		-----mg Fe pot ⁻¹ -----		
Control	0	0	252.3 c**	1804.5	5.81 d*	5.35d *	11.16 e*
RP100%	20	0	296.3 bc	2035.5	9.50 cd	7.17 cd	16.68 cde
RP200%	40	0	298.7 bc	2071.5	10.36 cd	8.57 bcd	18.93 cd
RP100%+acid	20	300	286.9 bc	1765.1	13.63 bc	5.97 bc	23.59 bc
RP200%+acid	40	600	426.7 a	2138.6	24.66 a	14.20 a	38.86 a
LSD _(0.05)			92.75	-----	5.64	4.23	7.61

Concentrations of Cu in maize plants

Copper accumulation also increased with P application irrespective of sources. Significantly higher Cu accumulations of 0.63 and 0.51 mg Cu pot⁻¹ were observed in RP200 % + acid and RP100 % + acid treatments (Table-5), respectively. The Cu accumulation 0.35 and 0.46 mg Cu pot⁻¹ in alone application of RP100% and RP200% were also higher than control which was 0.28 mg Cu pot⁻¹. However, concentrations of Cu in shoot and root

did not show significant variations in respect of different treatments. Concentration of Cu ranged from 9.26 to 11.93 mg kg⁻¹ in shoot and 13.60 to 15.13 mg kg⁻¹ in roots, which fell in adequate region according to the criteria established by Jones and Eck (1973). The non-significant increase due to different treatment might be due to dilution effect. Similarly, the higher significant Cu uptake might be correlated with higher biomass production.

**Table-5.** Concentrations of Cu in shoot and roots of maize plants as influenced by untreated or treated with H₂SO₄.

Treatments	P	H ₂ SO ₄	Concentration		Accumulation		
			Shoot	Root	Shoot	Root	Total uptake
		(mg kg ⁻¹)	----mg Cu kg ⁻¹ ---		-----mg Cu pot ⁻¹ -----		
Control	0	0	10.4ns	13.53ns	0.24 b*	0.04 bc**	0.28 d*
RP100%	20	0	9.26	15.00	0.29 b	0.05 bc	0.35 bcd
RP200%	40	0	11.93	15.13	0.40 ab	0.06 b	0.46 abcd
RP100%+acid	20	300	9.07	13.60	0.43 ab	0.08 a	0.51 abc
RP200%+acid	40	600	9.40	14.20	0.54 a	0.09 a	0.63 a
LSD _(0.05)			-	-	0.21	0.01	0.22

Concentrations of Mn in maize plants

Similar to Fe, Cu and Zn, application of RP increased Mn total accumulation by maize plants irrespective of sources (Table-6). The highest

accumulation of 3.50 mg Mn pot⁻¹ was recorded in RP200% + acid followed with 2.56 mg Mn pot⁻¹. The RP100% and RP200% also treatments resulted in higher accumulation of Mn as compared to control.

Table-6. Concentrations of Mn in shoot and roots of maize plants as influenced by RP untreated or treated with H₂SO₄.

Treatments	P	H ₂ SO ₄	Concentrations Mn		Accumulation Mn		
			Shoot	Root	Shoot	Root	Total uptake
		(mg kg ⁻¹)	-----mg Mn kg ⁻¹ ---		-----mg Mn pot ⁻¹ -----		
Control	0	0	41.93 ns	102.7 a**	0.96 e*	0.36ns	1.32 d*
RP100%	20	0	53.06	112.7 a	1.68 cd	0.39	2.07 c
RP200%	40	0	47.40	106.4 ab	1.64 d	0.44	2.08 c
RP100%+acid	20	300	44.20	83.0 b	2.09 bcd	0.46	2.56 bc
RP200%+acid	40	600	52.26	83.20 b	2.94 a	0.55	3.50 a
LSD _(0.05)			-	26.45	0.51	-	0.56

The variations in total accumulation were largely determined by the size of plant which mainly increased due to better supply of P released through RP.

Concentrations of Ca in maize plants

The Ca accumulation in shoot was significantly higher in pots receiving, RP200%+acid as compared to control and other treatments (Table-7). The accumulation of Ca in shoot significantly increased the higher accumulation in shoot were observed of 0.48 g Ca pot⁻¹ and 0.37 g Ca pot⁻¹ in treatment of RP200% + acid and

RP100% + acid. Total accumulation of Ca in maize plants significantly increased with P application irrespective of source. The highest total accumulation of 0.54 mg pot⁻¹ Ca was recorded in as in followed by 0.41 mg pot⁻¹ in treatments of RP200 % + acid and RP100% + acid, respectively. Pretreatments of RP with H₂SO₄ increased total Ca accumulation, with a large reservoir of exchangeable calcium; precipitation of insoluble Ca-P phases is the predominant process that reduces P availability to plant (Braschi *et al.*, 2004).



Table-7. Concentrations of Ca in shoot and roots of maize plants as influenced by RP untreated or treated with H₂SO₄.

Treatments	P	H ₂ SO ₄	Concentration Ca		Accumulation Ca		
			Shoot	Root	Shoot	Root	Total uptake
		(mg kg ⁻¹)	-----g Ca kg ⁻¹ ----		-----g Ca pot ⁻¹ -----		
Control	0	0	9.15ns	3.09ns	0.21*	0.01ns	0.22*
RP100%	20	0	9.00	3.28	0.29	0.01	0.30
RP200%	40	0	10.72	6.71	0.36	0.03	0.39
RP100%+acid	20	300	7.73	6.87	0.37	0.04	0.41
RP200%+acid	40	600	8.38	8.83	0.48	0.06	0.54
LSD _(0.05)			----	----	0.68	-----	0.78

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