Original article

# Chemical evaluation of partially acidulated phosphate rocks and their impact on dry matter yield and phosphorus uptake of maize

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ABSTRACT

Previous studies investigated the direct application of phosphate rock and its partially acidulated to enhance its solubility compared to soluble fertilizers. However, the interaction between the effect of particles diameter and partial acidulation of phosphate rock on phosphorus (P) availability and its effect on dry matter yield and P uptake is still elusive. This study was conducted to assess the effect of partially acidulated Egyptian phosphate rocks with different particle size diameters on P availability and its effect on dry matter yield and P uptake of maize (*Zea mays* L.). A pot experiment was conducted on maize plants grown on light clay soil for 42 days. Acidulation was done by mixing phosphate rock with single superphosphate or triple superphosphate at a total rate of 200 mg P kg$^{-1}$ with five acidulation mix ratios (100:0, 75:25, 50:50, 25:75, and 0:100). Different particle size diameters of phosphate rocks (500, 212, 75, and <45 μm included nano-particles ranged from 69.3 to 25.7 nm) were used. We found that dry matter yield and P uptake increased significantly due to the use of partially acidulated phosphate rocks especially when triple superphosphate was used for acidulation and the mixing ratio of 50:50 was the best. We also found that maize yield and P uptake increased significantly with decreasing particle size. It is recommended to use finely grounded partially acidulated phosphate rocks with particles diameter less than 45 μm at acidulation ratio 50% and no need to increase acidulation ratio above that as a slow-release phosphate fertilizer.

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## 1. Introduction

Phosphorus (P) is amaster key of plant nutrition where it is the second nutrient added as fertilizer. Phosphate rock (PR) is the basic raw material for manufacturing soluble phosphate fertilizers. It can be chemically reactive and may substitute ordinary soluble phosphate fertilizers if given in finely ground forms (El-Sayedet al.,

2009; Saied, 2016). The decrease in the particle size of PR is associated with an increase in its solubility (Oteroet al., 2013; Saied, 2016). Chienet al. (1996) used a mixture of PR and the water-soluble P fertilizer of triple super-phosphate (TSP) at 50:50 (w:w) on maize and obtained a 123% increase in yield and 83% increase in relative agronomic efficiency(RAE). Other researchers (Hammond et al., 1986; Bolan et al., 1993; Rajan and Marwaha1993; Chien and Menon,1995; Chien, 2003) found that partial acidulation of PR is the highest economic way for improving RAE. They also revealed that acidulation at 40–50% using $H_2SO_4$ or 20–30% using $H_3PO_4$ was as effective as superphosphate. Mc Lay et al. (2000) and Chien (2003) reported that partially acidulated phosphate rock (PAPR) added to a soil having a pH of 6.5 –8.0 was as effective as superphosphate. They also found that when using $H_3PO_4$ up to 50%, the produced fertilizer containing 66% of its total P as water-soluble. The dissolution of the un-acidulated PR was proven by greenhouse and field experiments conducted

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by Rajan and Watkinson (1992), Rajan and Ghani(1997), and Mc Lay et al. (2000). Mc Lay et al. (2000) assessed the viability of PR and partially acidulated PR in comparison with soluble superphosphate (SSP) to maize, and found that acidulation PR gave more yield increase than un-acidulated PR. They calculated the RAE as mentioned by Chienet al. (1990), and found a linear relationship between yield or P uptake and SSP. They concluded that there was no benefit for exceeding acidulation above such a level of 66% acidulation. (Nurjaya,2013) noted that the effectiveness of acidulated PR or PAPR depends on soil properties and plants and that PAPR for acid soils can be as effective as SSP. Yamprachaet al. (2006) predicted the dissolution of four phosphate rocks in flooded acid sulphate soil in Thailand, differing in their solubility dissolution as affected by PR and soil properties. They incubated six flooded acid sulphate soils with PRs. They calculated that 2% citric acid rock and the particle size (<100 mesh) were important in predicting P dissolution of PR. Moreover, Rajan*et al.* (1992) reported that the increase in chemically extractable P with grinding of PR is related positively to the reactively of PRs. They found that the greater the reactivity of PR, the greater the increase in extractable P on grinding. When the rocks were finely ground (at least 80% passing 200 mesh i.e.74 μm), the problems of stickiness and high levels of un-reacted acids were largely eliminated. The solubility of PR increases with decreasing particle size (Oteroet al., 2013; Saied, 2016).

Previous studies investigated the direct application of PR and its partially acidulated to improve its solubility compared to soluble fertilizers. However, as far as we know, there is no study focusing on the interaction between the effect of decreasing particles diameter and partial acidulation of PR on P availability and its effect on dry matter content and P uptake of maize (*Zea mays* L.)plants. Our study aimed to make a chemical evaluation of partially acidulated phosphate rocks with different particle size diameters and their impact on P uptake and dry matter yield of maize to test the possibility of using PRs as slow-release fertilizers. We hypothesize that using of partially acidulated PR at a mixing ratio of 50:50 as a slow-release phosphate fertilizer with reducing particle size diameter of PR would be the best to increase soil P availblity and its effect on P uptake and dry matter yield of maize plants. Thus, it can decreas the drastic effect caused by manufacturing P fertilizers on environment.

## 2. Materials and methods

Two PRs were obtained from Abou-Tartour(AT) and El-SibaiaGharb (ES). Two water-soluble phosphate fertilizers were used for acidulation: single superphosphate (SSP) and triple superphosphate(TSP) (Table.1). The soil used was obtained from the Experimental Farm of the Faculty of Agriculture Zagazig University, Zagazig, Egypt. The soil is classified as a light clay texture with pH of 8.10 in soil–water suspension (1:2.5), electric conductivity of 0.47dS m$^{-1}$in soil–water suspension (1:5), organic matter of 6.80 g kg$^{-1}$, CaCO$_3$ of 20 g kg$^{-1}$, total P of 0.23 g P kg$^{-1}$ (Jackson, 1958), and available P of 21.0 mg kg$^{-1}$(Olsen et al., 1956).

**Table 1**
Total P (gkg$^{-1}$) of different phosphate fertilizer sources.

| Diameter (μm) | AT | ES | SSP | TSP |
|---|---|---|---|---|
| 500 | 129.4 | 78.5 | 64.4 | 200.8 |
| 212 | 133.7 | 91.7 | 68.6 | 200.8 |
| 75 | 135.7 | 93.7 | 68.6 | 200.8 |
| <45[§] | 137.8 | 95.9 | 68.6 | 200.8 |

AT, Abou-Tartour; ES, El-SibaiaGharb; SSP, Single Super Phosphate and TSP, Triple Super Phosphate.[§]included nano-particles ranged between 69.3 and 25.7 nm.

### 2.1. Materials preparation

Phosphate rocks and phosphate fertilizers were crushed to pass a set of sieves with the diameters of 500, 212, 75, and <45 μm included nano-particles ranged from 69.3 to 25.7 nm. The soil was air dried, crushed, sieved through a 2 mm screen, and stored for analysis and experimental work.

### 2.2. The experiment layout

A pot experiment was carried out using different diameters (500, 212, 75, and <45 μm included nano-particles ranged from 69.3 to 25.7 nm) of two types of PRs named Abou-Tartour PR (ATPR) and El-Sibaia Gharb PR (ESPR) with the rate of 200 mg P kg$^{-1}$soil. We then mixed ATPR or ESPR with both SSP and TSP in five different ratios of 100:0, 75:25, 50:50, 25:75, and 0:100. The experiment design was a randomized complete block design with three replicates. The pots were PVC of 500-g soil capacity (10 cm diameter and 12 cm depth). The fertilizers were mixed thoroughly with the soil before seeding. Ten seeds of maize were sown at a depth of 3.0 cm below the soil surface of each pot. Pots were watered and kept around field capacity. After germination, plants were thinned to seven plants per pot, and then supplied with nitrogen and potassium fertilizers (100 mg N kg$^{-1}$ as NH$_4$NO$_3$ and 100 mg K kg$^{-1}$as K$_2$SO$_4$). Pots were rearranged randomly for minimizing the effect of pot's location. Plants were allowed 6 weeks for growth then cut at the soil surface, dried at 70 °C weighed, ground, and stored for analysis.

### 2.3. Methods of analysis

Water-soluble P was determined in 1:5 (w:v) water extract. Available P was determined according to Olsen (Olsen et al., 1956). Total P was estimated by a digest of conc. H$_2$SO$_4$ + HClO$_4$ (Chapman and Pratt,1961; O'Connor and Syers, 1975). Measurement of P in extracts was done calorimetrically by the ascorbicacid method (Murphy and Riley, 1962). Relative agronomic efficiency (RAE) for dry matter was calculated as follow (Chienet al., 1990):

$$RAE = \frac{Dry\ matter\ yield\ of\ PAPR - Dry\ matter\ yield\ of\ Control}{Dry\ matter\ yield\ of\ SP - Dry\ matter\ yield\ of\ Control} \times 100$$

According to the classification supposed by Hammond and Leon (1983), the RAE classes are as follow: >90 (High, H), 90–70(Medium, M), 70–30(Low, L), and < 30 (Very Low, VL). Phosphorus recovery efficiency(PRE) was computed according to (Basak,2019):

$$PRE = \frac{P\ Uptake\ of\ PAPR - P\ Uptake\ of\ Control}{P\ Uptake\ of\ SP - P\ Uptake\ of\ Control} \times 100$$

Phosphorus dissolution and alteration are calculated by using the following equation:

$$[(available\ P\ of\ soil + added) - (available\ P\ after\ harvesting + P\ uptake)]$$

### 2.4. Statistical analysis

Data were statistically analyzed via a randomized complete block design ANOVA design. Combined data analysis with the least significant difference (LSD) was carried out at a probability level of 95% ($p \leq 0.05$) for each treatment by Duncan's multiple range test.
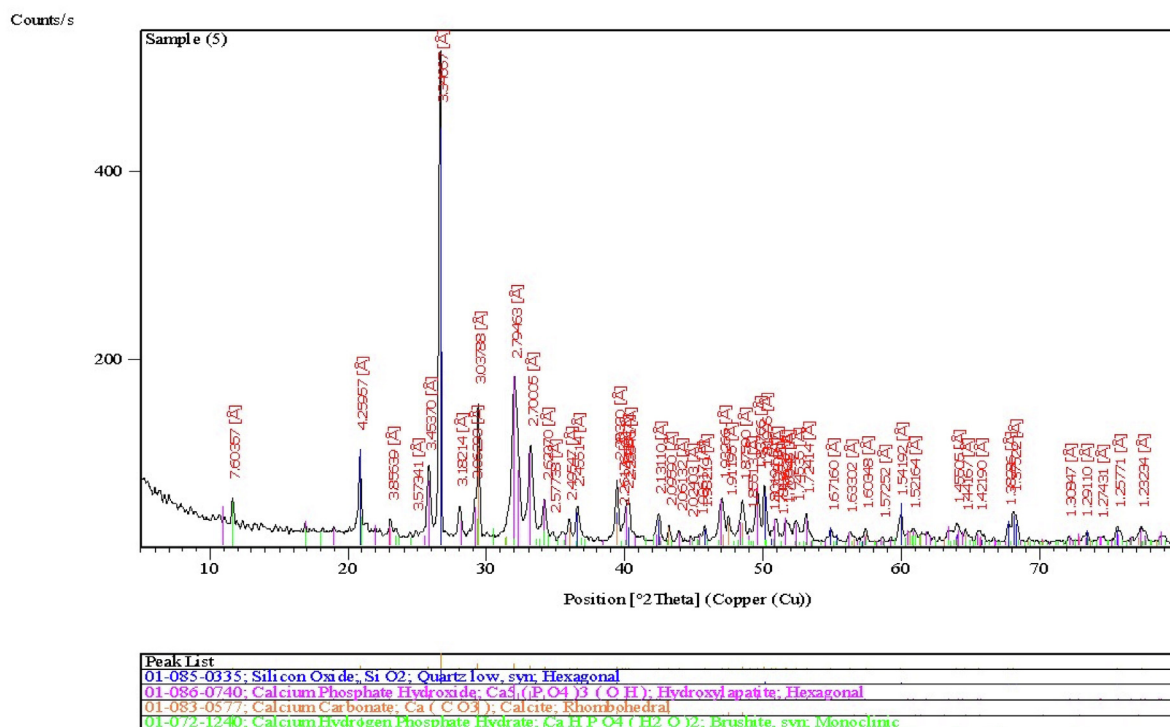
## 3. Results

### 3.1. Identification and classification of phosphate rocks

Total P contents were highest in the TSP (200.8 g kg$^{-1}$) followed by AT (129.4–137.8 g kg$^{-1}$), ES (78.5–95.9 g kg$^{-1}$), and SSP (64.4–68.6gkg$^{-1}$). Total P contents in the two rocks show that

File: Sample (5)                                                                Nanotechnolody & Advanced Material Centeral Characterization Lab.



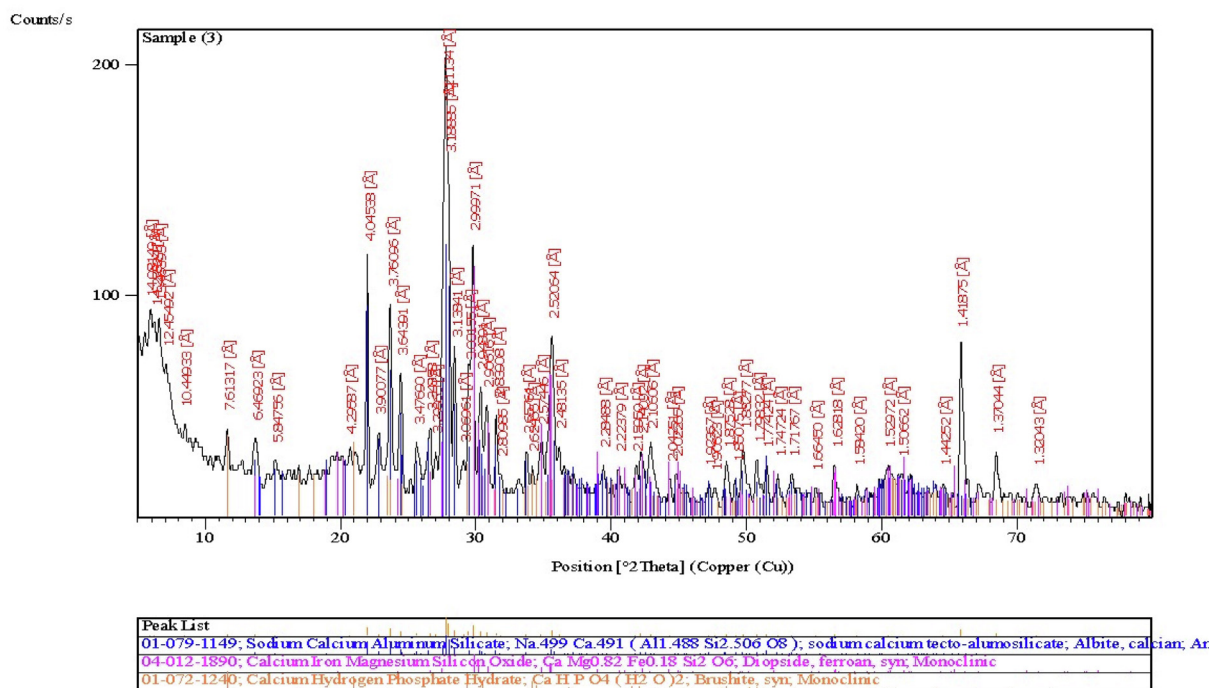Page: 1 of 1

**Fig. 1.** X-ray diffraction of ATPR.

File: Sample (3)                                                                Nanotechnolody & Advanced Material Centeral Characterization Lab.



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**Fig. 2.** X-ray diffraction of ESPR.

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the AT contains higher contents than the ES source (Table 1). Thus, two PRs rank for sustainable agriculture is high and medium, respectively according to Diamond (1979). The X-ray diffraction was carried out by scanning a powdered sample of each PR source (Figs. 1 and 2). The diffraction pattern revealed that P in ATPR exists in the form of calcium phosphate hydroxide "$Ca_5(PO_4)_6OH$; Hydroxylapatite". The other crystalline phase was in the form of silicon oxide "$SiO_2$; Quartz", calcium carbonate "$CaCO_3$; Calcite", and calcium di-hydrogen phosphate hydrate "$CaH_2PO_4(H_2O)_2$; Brushite". Phosphorus in ESPR exists in the form of $CaH_2PO_4.(H_2O)_2$ "Brushite". The other crystalline phase was sodium calcium aluminum silicate "Albite; $Na_{0.499}Ca_{0.491}(Al_{1.488}Si_{2.5}O_8)$"and "Ferroan; calcium iron magnesium silicon oxide ($CaMg_{0.82}Fe_{0.18}Si_2O_6$)".

### 3.2. Effect of acidulation sources, ratios and particle diameter of PRs on maize dry matter yield

Data in (Table 2) show that dry matter yield of maize plants fertilized with ATPR partially acidulated with SSP or TSP ranged between 0.93–1.60 and 1.15 – 2.50 gpot$^{-1}$, respectively. For ESPR, the corresponding values were 0.75–1.60 and 0.72–2.40 g pot$^{-1}$, respectively. Data in Figs. 4 and 5 show that decreasing the diameter of ATPR and ESPR particles increased the dry matter yield of maize plants. The highest values were obtained by the lowest particle diameter. The relative increase in dry matter due to the effect of particles diameter was calculated as relative to the non-acidulated rock of over the 500 μm particle diameter i.e. the 212, 75 and <45 μm for ATPR 6.48, 8.33, and 21.30% when SSP used for partial acidulation, or TSP (13.21, 20.75, and 32.08%), and for ESPR partially acidulated with SSP were 9.26, 13.9, and 22.2%, and with TSP were 6.00, 7.33 and 28.67%, respectively.

### 3.3. Effect of acidulation sources, ratios and particle diameter of PRs on P uptake

The obtained data in (Table 3) indicate that, P uptake ranged between 2.55 and 5.24 mg P kg$^{-1}$ for SSP and 3.17–8.91 mg P kg$^{-1}$ for TSP with ATPR. When ESPR was used P uptake ranged from
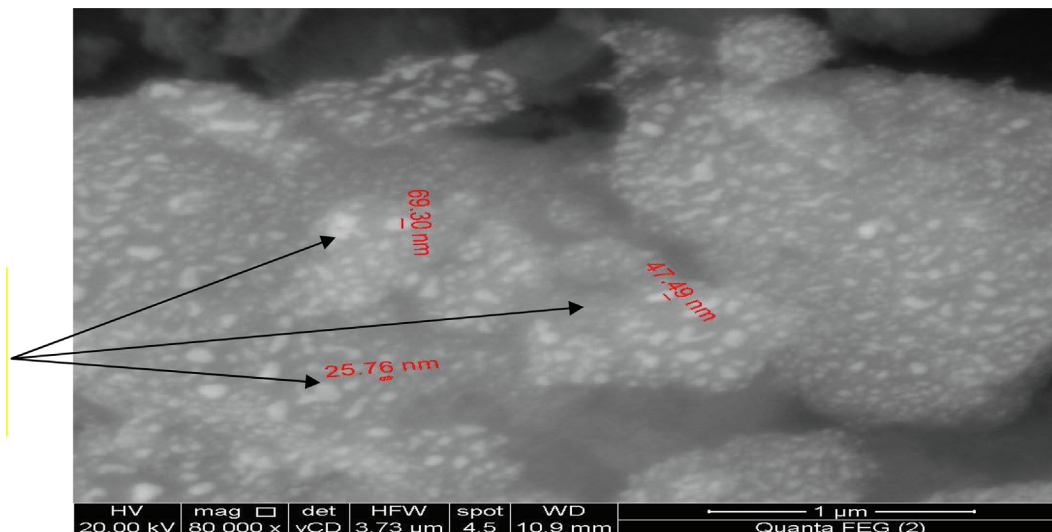


**Fig. 3.** Scanning Electron Microscope of ATPR.

**Table 2**
Dry matter yield (g pot$^{-1}$) of maize plants (42-day growth) as affected by PAPR (ATPR or ESPR by soluble P fertilizers).

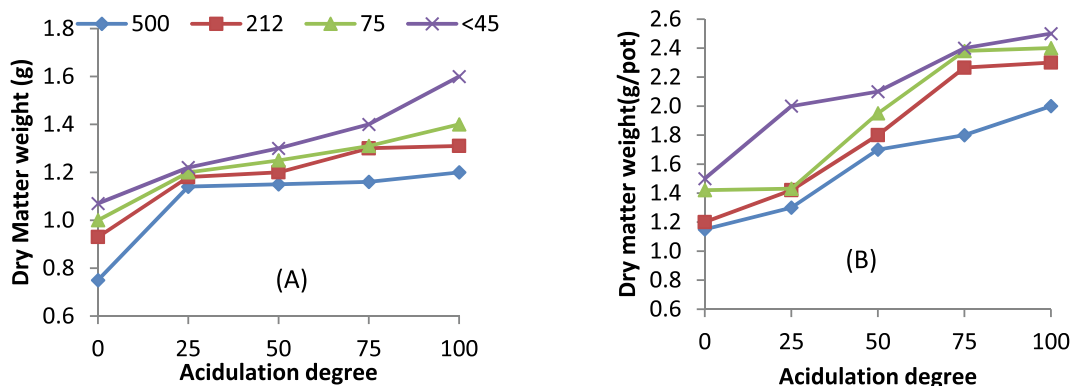| PR:SP Ratio, R | ATPR | | | | | ESRP | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Particle diameter, D (μm) | | | | | | | | | |
| | 500 | 212 | 75 | <45$^§$ | Mean | 500 | 212 | 75 | <45 | Mean |
| Acidulation source, S (SSP) | | | | | | | | | | |
| 100:0 | 0.93 | 1.10 | 1.20 | 1.20 | **1.11b** | 0.75 | 0.93 | 1.00 | 1.07 | **0.94a** |
| 75:25 | 1.10 | 1.12 | 1.21 | 1.29 | **1.18b** | 1.14 | 1.18 | 1.20 | 1.22 | **1.16a** |
| 50:50 | 1.10 | 1.12 | 1.25 | 1.35 | **1.21ab** | 1.15 | 1.20 | 1.25 | 1.30 | **1.23a** |
| 25:75 | 1.11 | 1.13 | 1.28 | 1.45 | **1.22ab** | 1.16 | 1.30 | 1.31 | 1.40 | **1.29a** |
| 0:100 | 1.28 | 1.30 | 1.40 | 1.60 | **1.40 a** | 1.20 | 1.31 | 1.40 | 1.60 | **1.38a** |
| **Mean** | **1.08 a** | **1.15 a** | **1.17 a** | **1.31 a** | **1.22 a** | **1.08a** | **1.18a** | **1.23a** | **1.32a** | **1.2a** |
| **LSD 0.05** | R:** | D:NS | S:** | RxD:** | | R:NS | D: NS | S: NS | RxD: NS | |
| | RxS:** | DxS:** | RxDxS:** | | | RxS:NS | DxS:NS | RxDxS: NS | | |
| (TSP) | | | | | | | | | | |
| 100: 0 | 1.15 | 1.15 | 1.20 | 1.42 | **1.50b** | 0.72 | 1.09 | 1.00 | 1.10 | **0.98a** |
| 75:25 | 1.30 | 1.30 | 1.42 | 1.43 | **2.00b** | 1.50 | 1.42 | 1.47 | 1.85 | **1.56a** |
| 50:50 | 1.70 | 1.70 | 1.80 | 1.95 | **2.10ab** | 1.60 | 1.61 | 1.70 | 1.99 | **1.72a** |
| 25:75 | 1.80 | 1.80 | 2.27 | 2.38 | **2.40ab** | 1.70 | 1.85 | 2.20 | 2.30 | **2.01a** |
| 0:100 | 2.00 | 2.00 | 2.30 | 2.40 | **2.50a** | 2.00 | 2.30 | 2.35 | 2.40 | **2.26a** |
| **Mean** | **1.59a** | **1.80a** | **1.92a** | **2.10a** | **2.1 a** | **1.50a** | **1.59a** | **1.61a** | **1.93a** | **1.70a** |
| **LSD 0.05** | R:** | D:** | S:** | RxD:** | | R:NS | D: NS | S:NS | RxD: NS | |
| | RxS:** | DxS:** | RxDxS:** | RxS:** | | RxS:NS | DxS:NS | RxDxS:NS | | |

See footnote of Table 1.

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**Fig. 4.** Dry matter yield (g pot$^{-1}$) of maize plants as affected by particles diameter and AbouTartourPAPR by SSP (A) and TSP (B).
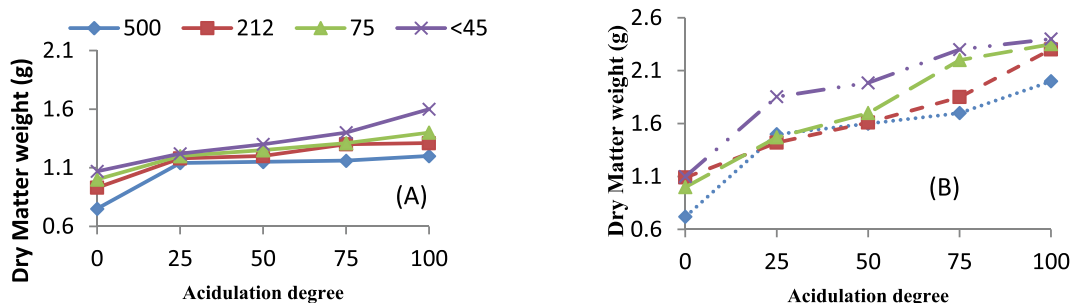


**Fig. 5.** Dry matter yield (g pot$^{-1}$) of maize plants as affected by particles diameter and El-SibaiaPAPR by SSP (A) and TSP (B).

**Table 3**
Phosphorus uptake (mg kg$^{-1}$) of maize plants as affected by different P sources (ATPR and ESPR acidulated with SSP or TSP).

| PR:SP (R) | ATPR | | | | | ESPR | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Particle diameter, D (μm) | | | | | | | | | |
| | 500 | 212 | 75 | <45 | Mean | 500 | 212 | 75 | <45 | Mean |
| **Acidulation source, SSP** | | | | | | | | | | |
| 100: 0 | 2.55 | 3.02 | 3.32 | 3.34 | **3.05e** | 1.93 | 2.49 | 2.79 | 2.87 | **2.50c** |
| 75:25 | 3.02 | 3.12 | 3.45 | 3.91 | **3.37d** | 3.06 | 3.22 | 3.37 | 3.43 | **3.27b** |
| 50:50 | 3.08 | 3.23 | 3.76 | 4.27 | **3.58c** | 3.20 | 3.35 | 3.72 | 3.86 | **3.53ab** |
| 25:75 | 3.11 | 3.34 | 3.97 | 4.67 | **3.76b** | 3.25 | 3.67 | 4.09 | 4.23 | **3.78ab** |
| 0:100 | 3.65 | 3.91 | 4.46 | 5.24 | **4.32a** | 3.78 | 3.78 | 4.30 | 4.91 | **4.19a** |
| **Mean** | **3.08d** | **3.32c** | **3.79b** | **4.28a** | **3.59b** | **3.04b** | **3.30b** | **3.61ab** | **3.86a** | **3.45b** |
| LSD 0.05 | R:*** | D:*** | S:*** | RxD:*** | | R:*** | D: ** | S:*** | RxD: NS | |
| | RxS:*** | DxS:*** | RxDxS:*** | | | RxS:NS | DxS:NS | | RxDxS: NS | |
| **TSP** | | | | | | | | | | |
| 100: 0 | 3.17 | 3.32 | 4.00 | 4.19 | **3.67e** | 2.00 | 2.93 | 2.94 | 2.97 | **2.71c** |
| 75:25 | 3.71 | 4.40 | 4.92 | 7.05 | **5.02d** | 4.24 | 4.04 | 4.27 | 5.50 | **4.5b1** |
| 50:50 | 5.06 | 5.80 | 6.87 | 7.66 | **6.35c** | 4.71 | 4.77 | 5.14 | 6.10 | **5.18ab** |
| 25:75 | 5.50 | 7.57 | 8.59 | 8.71 | **7.59b** | 5.09 | 5.16 | 6.79 | 7.17 | **6.05ab** |
| 0:100 | 6.32 | 7.83 | 8.60 | 8.91 | **7.92a** | 6.08 | 6.19 | 7.26 | 7.58 | **6.78a** |
| **Mean** | **4.75d** | **5.78c** | **6.60b** | **7.31a** | **6.09a** | **4.42b** | **4.62b** | **5.28ab** | **5.86a** | **5.04a** |
| LSD 0.05 | R:*** | D:*** | S:*** | RxD:*** | | R:*** | D: ** | S:*** | RxD: NS | |
| | RxS:*** | DxS:*** | RxDxS:*** | | | RxS:NS | DxS:NS | RxDxS: NS | | |

See footnote of Table 1.

1.93 to 4.91 mg P kg$^{-1}$ for SSP and 2.00–7.58 mg P kg$^{-1}$ for TSP. Comparing the effect of acidulated portions shows that increasing acidulation increased P uptake. Using SSP for partial acidulation caused increases in P uptake by 10.5, 17.4, 23.3, and41.6%, respectively. With the use of TSP, the increases were 36.8, 73.0, 106.8, and 115.8%, respectively. Using ESPR, the percent increases were 30.8, 41.2, 51.2, and 67.6% for SSP; and 67.0, 91.9, 124, and 151.1% for TSP. There was a negative relationship between P uptake and particle size of PRs. The highest values were obtained by the lowest particle diameter. The relative increase for the 212, 75, and <45 μm diameters compared to the 500 μm was 7.79, 23.1, and

39.0% for ATPR acidulated with SSP, and 21.7, 39.0, and 53.9% for ATPR acidulated with TSP. Whilst, it was 8.55, 18.8, and 27.0% for ESPR acidulated with SPP, and 4.52, 19.5, and 32.6% for ATPR acidulated with TSP.

### 3.4. Relative agronomic efficiency (RAE)

RAE increased, in general, with increasing the ratio of acidulation (Table 4). The mean values of RAE when ATPR was mixed with SSP at the ratios of 100:0, 75:25, 50:50, 25:75, and 0:100 were 65.1, 70.7, 76.9, and 80.9%. For TSP the values were 42.9, 55.3,

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**Table 4**
Relative agronomic efficiency of dry matter yield of maize plants as affected by different PR sources acidulated with SSP or TSP.

| PR:SP | Particle diameters (μm) | | | |
|---|---|---|---|---|
| | 500 | 212 | 75 | <45 |
| **SSP** | | | | |
| 100:0 | 50.7 | 72.6 | 75.9 | 61.2 |
| 75:25 | 60.5 | 75.3 | 77.1 | 69.9 |
| 50:50 | 74.6 | 75.3 | 81.9 | 75.7 |
| 25:75 | 76.1 | 76.7 | 85.5 | 85.4 |
| 0:100 | 100 | 100 | 100 | 100 |
| **TSP** | | | | |
| 100:0 | 40.6 | 36.4 | 46.5 | 48.2 |
| 75:25 | 51.1 | 49.1 | 46.9 | 74.1 |
| 50:50 | 79.0 | 71.1 | 75.4 | 79.3 |
| 25:75 | 86.0 | 97.9 | 98.9 | 94.8 |
| 0:100 | 100 | 100 | 100 | 100 |

According to the classification supposed by Hammond and Leon (1983), the RAE classes are as follow:>90 (High, H), 90–70(Medium, M), 70–30(Low, L), and < 30 (Very Low, VL).See footnote of Table 1.

**Table 5**
Phosphorus recovery efficiency of P-uptake of maize plants as affected by different PR sources acidulated with SSP or TSP.

| PR:SP | Particle diameters (μm) | | | |
|---|---|---|---|---|
| | 500 | 212 | 75 | <45 |
| **SSP** | | | | |
| 100:0 | 18.3 | 40.8 | 40.4 | 38.5 |
| 75:25 | 80.5 | 74.4 | 65.7 | 55.3 |
| 50:50 | 88.2 | 80.3 | 78.7 | 68.5 |
| 25:75 | 91.3 | 95.0 | 88.5 | 79.3 |
| 0:100 | 100 | 100 | 100 | 100 |
| **TSP** | | | | |
| 100:0 | 8.89 | 22.91 | 23.6 | 22.9 |
| 75:25 | 59.1 | 53.11 | 47.1 | 65.1 |
| 50:50 | 69.5 | 69.18 | 62.6 | 75.2 |
| 25:75 | 78.0 | 77.73 | 91.7 | 93.0 |
| 0:100 | 100 | 100.0 | 100 | 100 |

According to the classification supposed by Hammond and Leon (1983), the RAE classes are as follow:>90 (High, H), 90–70(Medium, M), 70–30(Low, L), and < 30 (Very Low, VL).See footnote of Table 1.

76.2 and 94.4%, respectively. In addition, the corresponding values were 52.0, 74.7, 82.5, and 90.5% for SSP and 23.4, 60.0, 68.2, and 84.1% for TSP when ESPR was used.

### 3.5. Phosphorus recovery efficiency(PRE)

The computed values of PRE using a general mean of P uptake due to acidulation rates (100:0, 75:25, 50:50, 25:75, and 0:100) and PR sources (AT and ES) are presented in (Table 5). PRE values were 53.8, 65.8, 72.9, 78.9 and 100%, respectively for ATPR acidulated with SSP, but were 31.7, 51.2, 72.6, 92.0, and 100%, respectively when ATPR acidulated with TSP. For ESPR acidulated with SSP, PRE values were 34.3, 69.0, 73.0, 88.6, and 100%, repectively, and were 21.1, 56.1, 69.2, 85.1, and 100%, respectively when ATPR acidulated with TSP. The values of PRE as affected by particles diameter irrespective of acidulation ratios are show low increases due to decreasing the particle diameter. The mean values of PRE representing the effect of particle diameter (500, 212, 75, and < 45 μm) were72.4, 80.0, 84.1, and 78.5%, respectively for ATPR acidulated with SSP, but were 71.3, 70.9, 73.6, and 79.3%, repectively when ATPR acidulated with TSP, where as they were 81.3, 79.7, 79.8, and 79.0%, respectively for ESPR acidulated with SSP, and 66.3, 62.7, 65.4, and 74.2%, respectively for ESPR acidulated with TSP.

### 3.6. Phosphorus dissolution and alteration

Acidulation positively affected dissolution during the 42 days of experiment as recorded in (Tables 6 and 7). The highest effect on P dissolution from PAPRs was due to the acidulation ratio of 75:25 PR:SP in the both of acidulation sources and also in the two PR sources. This was more pronounced when TSP was used. The degree of acidulation revealed that the ratio of 50:50 is sufficient for increasing dissolution, and no need for increasing the degree of acidulation. On the other hand, particles diameter also affected the dissolution of P as the highest values were recorded for the lowest particles diameter < 45 μm which containing particles ranged from 69.3 to 25.7 nm Fig. 3.

**Table 6**
Phosphorus dissolution and alteration from PAATPR by SSP or TSP.

| PR:SP | SSP | | | | TSP | | | |
|---|---|---|---|---|---|---|---|---|
| | Particle diameter, D (μm) | | | | | | | |
| | 500 | 212 | 75 | <45§ | 500 | 212 | 75 | <45§ |
| **Available before** | | | | | | | | |
| 100:0 | 42.8 | 42.16 | 41.82 | 41.5 | 42.8 | 42.16 | 41.82 | 41.51 |
| 75:25 | 76.1 | 75.68 | 75.42 | 75.1 | 82.0 | 81.52 | 81.26 | 81.03 |
| 50:50 | 108.6 | 108.2 | 108.1 | 107.8 | 121.5 | 121.2 | 121.05 | 120.78 |
| 25:75 | 143.0 | 142.8 | 142.8 | 142.7 | 160.7 | 160.5 | 160.4 | 160.4 |
| 0:100 | 176.5 | 176.5 | 176.5 | 176.5 | 200.2 | 200.2 | 200.2 | 200.2 |
| **Available After** | | | | | | | | |
| 100: 0 | 87.31 | 87.92 | 89.15 | 90.68 | 88.23 | 90.37 | 92.21 | 93.74 |
| 75:25 | 96.8 | 101.3 | 107.5 | 109.5 | 118.5 | 119.7 | 122.8 | 125.2 |
| 50:50 | 104.4 | 106.8 | 110.2 | 118.8 | 122.1 | 124.3 | 127.4 | 132.9 |
| 25:75 | 110.5 | 115.1 | 120.0 | 120.6 | 127.7 | 130.4 | 133.5 | 136.5 |
| 0:100 | 117.9 | 119.4 | 122.4 | 123.1 | 138.7 | 139.6 | 142.7 | 148.8 |
| **Dissolution and Alteration** | | | | | | | | |
| 100:0 | −47.0 | −48.7 | −50.7 | −53.4 | −50.45 | −54.0 | −57.2 | −59.8 |
| 75:25 | −23.6 | −28.7 | −35.8 | −38.9 | −41.9 | −45.7 | −50.1 | −53.0 |
| 50:50 | 1.1 | −1.7 | −6.0 | −16.2 | −6.86 | −10.9 | −15.2 | −21.5 |
| 25:75 | 29.4 | 24.4 | 19.4 | 18.9 | 29.7 | 26.1 | 22.7 | 23.9 |
| 0:100 | 54.9 | 53.7 | 50.1 | 49.6 | 57.18 | 55.7 | 50.5 | 51.4 |

(−) means dissolution and (+) means alteration

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**Table 7**
Phosphorus dissolution and alteration from PAESPR by SSP or TSP.

| PR:SP | SSP | | | | TSP | | | |
|---|---|---|---|---|---|---|---|---|
| | Particle diameter, D (μm) | | | | | | | |
| | 500 | 212 | 75 | <45[§] | 500 | 212 | 75 | <45[§] |
| **Available before** | | | | | | | | |
| 100:0 | 53.8 | 52.3 | 51.7 | 51.0 | 53.8 | 52.39 | 51.7 | 51.0 |
| 75:25 | 84.4 | 83.3 | 82.8 | 82.3 | 90.3 | 89.1 | 88.6 | 88.1 |
| 50:50 | 114.1 | 113.5 | 113.0 | 112.6 | 127.1 | 126.5 | 125.9 | 125.6 |
| 25:75 | 145.8 | 145.4 | 145.2 | 145.0 | 163.5 | 163.1 | 162.93 | 162.7 |
| 0:100 | 176.5 | 176.5 | 176.5 | 176.5 | 200.2 | 200.2 | 200.2 | 200.2 |
| **Available After** | | | | | | | | |
| 100: 0 | 85.1 | 86.4 | 87.0 | 87.6 | 88.2 | 90.37 | 92.21 | 93.7 |
| 75:25 | 92.2 | 96.8 | 98.3 | 101.3 | 118.5 | 119.7 | 122.8 | 125.2 |
| 50:50 | 98.3 | 102.9 | 105.3 | 107.5 | 122.1 | 124.3 | 127.4 | 132.9 |
| 25:75 | 104.4 | 108.7 | 110.5 | 119.1 | 127.7 | 130.4 | 133.5 | 136.5 |
| 0:100 | 113.3 | 116.6 | 118.2 | 122.8 | 138.7 | 139.6 | 142.7 | 148.8 |
| **Dissolution and Alteration** | | | | | | | | |
| 100:0 | −33.2 | −36.4 | −37.9 | −39.4 | −36.3 | −40.9 | −43.4 | −45.6 |
| 75:25 | −10.7 | −16.6 | −18.8 | −22.4 | −32.4 | −34.5 | −38.4 | −42.5 |
| 50:50 | 12.6 | 7.3 | 4.0 | 1.3 | 0.3 | −2.5 | −6.5 | −13.3 |
| 25:75 | 38.1 | 33.0 | 30.7 | 21.7 | 30.7 | 27.5 | 22.6 | 19.0 |
| 0:100 | 59.7 | 56.1 | 54.0 | 48.7 | 55.5 | 54.4 | 50.3 | 43.9 |

(−) means dissolution and (+) means alteration.

## 4. Discussion

The results indicated that the dry matter yield was obviously affected by acidulation sorces and their ratios specially when TSP was used. The mean relative increases due to partially acidulated PRs with either SSP or TSP at the ratios of PR:SP (100:0, 75:25, 50:50, 25:75, and 0:100) were as follows on the basis of PR equals 100%. Relative increases for ATPR acidulated with SSP were 6.31, 9.00, 9.91, and 26.1%, but were 16.7, 43.2, 67.4, and 74.2% when ATPR was acidulated with TSP. The relative increases for ESPR acidulated with SSP were 26.6, 30.9, 37.2, and 46.8%, but were 59.2, 75.5, 105 and 131% when ESPR was acidulated with TSP. Acidulation with TSP was more effective than SSP. These data are in agreement with (Chien et al., 1996). The finer the particle size, the greater surface area and degree of contact between the soil PR particles, and thus, the greater PR dissolution rate (Otero et al., 2013; Saied, 2016), so that decreasing the diameter of PR particles increased the dry matter yield of maize plants probably represent in form which P can be controlled, renewed, and decrease the adverse environmental effects for commercial fertilizers. Acidulation increased the P solubility considered to be available P for plants (Chien et al., 2011). The increase in dry matter yield due to acidulation with either SSP or TSP can be explained as a result of the reaction between water-soluble P with apatite P. This result means that PAPR produced materials act as slow-release P fertilizer for sustainable agriculture.

It can be seen that P uptake by maize from ATPR or ESPR in the presence of TSP was higher than that from ATPR or ESPR applied alone. At a given rate of PR applied, the difference between P uptake from PR applied alone and P uptake from PR applied with TSP represents the quantitative estimation of the enhancement effect of water-soluble P (TSP) on the effectiveness of PR (Harun Cicek et al., 2020). The result thus shows a significant beneficial effect of adding water-soluble P fertilizers to increase the effectiveness of PR utilization by crops. So that, the enhancement effect was mostlikely due to an increased early plant root development, as induced by PAPRs with water-soluble P fertilizers, that enabled the plant touse PR more effectively than could a plant treated with PR alone. In general, these results are similar to those of Chien et al. (1996), which showed an enhancement of P uptake from a medium reactive PR by mixing TSP and PR.

Principally, acidulation increased the P solubility of two sources of PR, so that the dry matter increased and the RAE also increased as results indicated that for PAPRs. These results suggested that the PAPRs had a considerable direct impact on dry matter yield and could be used as a slow release-fertilizer. Our results are in agreement with (Fukuda et al., 2021). Furthermore, P is released in the system by the chemical reaction as a result of lowering pH by partial acidulation in the soil so it can be taken by plants or tends to alteration. Therefore, P concentrations in the system are buffered so that the rate of P released is controlled. Near neutral pH values are widely thought to be optimum for the dissolution of phosphate. Dissolution from partially acidulated PR are all consistent with a much lower pH optimum solution. The main reason that has been attributed to this was decreasing soil pH more protons become available for dissolution (Joos and Black, 1951). For example, Kanabo and Gilkes(1987) have shown that when pH had no effect on the P adsorption capacity of soil, the increase in PR dissolution with decreasing soil pH is mainly due to an increase in the supply of protons as measured by titratable acidity. In variable charge soils as pH decreases, the phosphate adsorption capacity increases, and provides a stronger sink for dissolved P. The dissolution of PRs continues only when the dissolution products, $Ca^{2+}$ and $H_2PO_4$, in the solution immediately surrounding the PRs are removed by adsorption/exchange, plant uptake.

## 5. Conclusion

We found that partial acidulation of PR with SSP or TSP at 50:50 or 75:25 changed the rank of PAPR from low to medium, and increase P dissolution in soil. Partial acidulation increased both dray matter yield and P uptake. The data also revealed that partial acidulation was more effective when ATPR and TSP were used, and it can be recommended that 50% mixing ratio was sufficient mainly when TSP used. We also found that maize yield and P uptake increased significantly with decreasingparticle size. Thus, it can be recommended to use finely grounded partially acidulated phosphate rocks with particles diameter less than 45 μm at acidulation ratio 50% and no need to increase acidulation ratio above that as a slow-release phosphate fertilizer. Using PAPRs can substitute chemical fertilizers because they are economically profitable and

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probably less harmful to the environment. Thus, PAPRs can be used instead of commercial fertilizers and it can lower the drastic effect on the environment.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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