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Agronomic efficiency of partially acidulated and granulated Arraias phosphate rock

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ABSTRACT: Natural phosphate rocks (PR) are characterized by low phosphorus (P) solubility in water. Acidulation is the normal method to raise P solubility of these materials, however, it increases the cost and causes operational issues. The aim of this study was to evaluate the agronomic efficiency of partially acidulated and micro-granulated Arraias phosphate rock, which has a lower P content (6.88 %) than normal apatite concentrates. Two experiments were carried out in a greenhouse at the University of Rio Verde, Goiás State, in which corn was grown in pots with two kg of red clayey Oxisol (Latossolo). Treatments for the first experiment were the natural Arraias phosphate rock; triple superphosphate (TSP); and three partially acidulated phosphate rock (PAPR) with 5, 10 and 15 % of H_2SO_4 relative to PR mass. Phosphorus diffusion from each fertilizer source was evaluated using Petri dishes filled with soil, with diffusion assessed at 1, 7, 14, 30, and 60 days after preparation. For the second experiment, treatments were 15 % PAPR granulated to average sizes of 0.25, 0.75, 1.50, and 2.4 mm. The agronomic efficiency of all variations of the PR was lower than the TSP. The 15 % PAPR treatment resulted in the highest corn dry mass yield among partially acidulated PR. The phosphorus diffusion radius was greatest with TSP, while diffusion from unacidulated Arraias rock phosphate was undetectable. Diffusion from acidified phosphate rocks increased with higher acidification rates. Granule size affected P absorption and, consequently, the agronomic efficiency of PAPR, but did not significantly influence its overall efficiency. Under the conditions of this study, partially acidulated and granulated phosphate rock was not an effective alternative to TSP.

Keywords: phosphate, partial acidulation, granulation, agronomic efficiency, greenhouse experiment.

INTRODUCTION

Brazilian Cerrado soils are naturally low in available phosphorus (P), limiting plant growth and crop yields (Santos et al., 2011; Rodrigues et al., 2016). High rates of P fertilizers are needed for adequate crop growth in these soils, due to the high P adsorption capacity of iron oxides (Fink et al., 2016). After several years of P fertilization, the fertilizer demand for P decreases as soil test P levels increase (Withers et al., 2018). However, even after adequate soil test P levels have been achieved, additions of P fertilizer are needed to maintain adequate P levels.

Alternative P sources, such as phosphate rock (PR), may be used to provide P for soil and plants. However, due to low P solubility, PR normally has lower agronomic efficiency than soluble fertilizers (Resende et al., 2006; Fayiga and Nwoke, 2016). In Brazil, the majority of phosphate rocks come from igneous rock formations, and only 20 % of Brazilian reserves are sedimentary rocks (Abram, 2016; Jasinski, 2016). The formation of Arraias phosphate is associated with marine sediments belonging to the geological unit of the Bambuí Group, specifically the Sete Lagoas Formation, which dates back approximately 600 million years to the Neoproterozoic era (Abram, 2016; Ribeiro, 2016). The average total P content of this carbonate/silicate phosphate rock is 5.07 % P (Abram, 2016).

As with other phosphate rocks, only a small fraction of the P is soluble. Approximately 25 % of the total P in Arraias phosphate rock is soluble in 2 % citric acid, which is relatively high compared to other Brazilian phosphate rock (Goedert et al., 1990; Abram et al., 2011; Porto et al., 2018). However, when soil P levels are very low, and crop demand is high, phosphate rock is not a satisfactory P source.

Partial acidulation has increased both water-soluble P and P release from phosphate rock (Mokwunye and Chien, 1980; Ghani and Rajan, 1997). This technique can transform a low-reactivity phosphate rock into a more efficient source of phosphorus at a lower cost than that required to produce fully acidulated fertilizers (Hammond et al., 1980; Rajan and Marwaha, 1993).

The objectives of this study were to evaluate the effect of acidulation and granulation of Arraias phosphate rock on: (1) growth and P uptake by corn; and (2) P solubility and diffusion in soil.

MATERIALS AND METHODS

The experiments were carried out at the Fertilizer Laboratory of the University of Rio Verde (UniRV) located in Rio Verde, Goiás State. Two pot experiments were carried out simultaneously in a greenhouse to evaluate the agronomic efficiency.

Partially acidulated and granulated fertilizers

A commercial sample of Arraias phosphate rock, supplied by DuSolo Fertilizers, was used in this study. Phosphate rock was in a powdered form. Particle size distribution was as follows: 1.14 % passed through the 4.75 mm sieve, 3.28 % through the 2.8 mm sieve, 2.64 % through the 2 mm sieve, 5.42 % through the 1 mm sieve, 1.00 % through the 0.85 mm sieve, 17.68 % through the 0.3 mm sieve, 8.84 % through the 0.25 mm sieve, and 56.00 % was retained in the bottom fraction. In a preliminary study, 1 kg of ground phosphate rock in a borosilicate glass beaker was treated with 0, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, and 600 g of concentrated sulfuric acid for five days in a fume hood. The acidulated materials were then analyzed for pH and electrical conductivity (EC). Water-soluble phosphorus, 2 % citric acid extractable P (1:100 phosphate/extractant ratio), 10 % nitric acid extractable P (total P), and neutral ammonium citrate extractable P (NAC) were extracted and quantified according to the Manual of Official Analytical Methods for Mineral, Organic, Organomineral Fertilizers and

Correctives (Brasil, 2016) (Table 1). Phosphate rock treated with three rates of sulfuric acid (5, 10, and 15 % H_2SO_4) and the same amount of water were reacted in a beaker for 48 h, and then granulated in the laboratory using a disc granulator. Only distilled water was used for granulation. Samples were oven-dried and sieved to separate the granules in the following sizes: 0.0 to 0.5; 0.5 to 1.0; 1.0 to 2.0; and 2.0 to 2.8 mm. Only a fraction of 2.0 to 2.8 mm was used in the first experiment. In contrast, the second experiment evaluated the agronomic efficiency of PAPR 15 % granules across all size fractions previously described, focusing on the influence of granule size.

Soil

Soil was collected in 0.00-0.20 m layer at the UniRV experimental field in Rio Verde city, Goiás. It was air dried, sieved in a size smaller than 4 mm and stored until use. A clayey dystrophic Red Oxisol very typical from the Brazilian Cerrado, with low P concentration and high P adsorptive capacity, classified, according to the Brazilian Soil Classification System (SiBCS), as a Latossolo Vermelho distrófico típico (Red Oxisol, dystrophic, typical), was used for both pot experiments. The chemical and physical characterization of the soil was performed according to methods described in Teixeira et al. (2017), as shown in table 2.

Table 1. Phosphorus content, pH, electrical conductivity and sulphur (sulfate) in fertilizer samples

Fertilizers sample	Source	Water	Citric Acid	NAC	Total	pH	EC	$S\text{-}SO_{4\text{-}S}$
		% P					$mS\ cm^{-1}$	%
	Arraias	0.18	1.66	0.67	6.88	6.49	0.05	
	TSP	16.31	17.41	20.51	20	2.82	18.36	1.36
Partially Acidulated								
	P/H_2SO_4	% P					$mS\ cm^{-1}$	%
PAPR 5	1.38	0.44	2.28	1.29	6.46	3.89	2.80	2.01
PAPR 10	0.69	0.90	2.28	2.15	6.00	3.51	4.10	2.94
PAPR 15	0.46	1.18	2.54	2.89	7.37	3.20	5.09	3.97
PAPR 20	0.34	1.16	1.77	3.79	5.32	3.03	5.04	5.26
PAPR 25	0.28	1.00	1.87	4.24	5.31	2.93	4.46	6.25
PAPR 30	0.23	0.65	1.26	4.48	5.04	2.74	4.72	7.43
PAPR 35	0.20	0.67	0.97	4.40	4.95	2.34	6.10	8.10
PAPR 40	0.17	1.45	1.66	4.42	4.70	1.96	9.54	8.96
PAPR 45	0.15	2.10	2.38	4.23	4.56	1.73	14.05	9.54
PAPR 50	0.14	2.38	2.61	3.82	4.14	1.63	16.63	10.10
PAPR 55	0.13	3.02	3.47	3.87	4.15	1.54	16.81	10.58
PAPR 60	0.11	3.17	3.63	3.75	3.86	1.60	16.69	11.15

Phosphate rock: Arraias; TSP: Triple superphosphate; Partial Acidulated phosphate rock: PAPR from 5 to 60 % of H_2SO_4 (m/m). Citric acid solution (2 %); NAC: Neutral Ammonium Citrate; Total: Nitric acid solution (10 %); and EC: Electrical conductivity. Stoichiometry basis: P/H_2SO_4.

Table 2. Soil chemical and textural characterization

Clay	S	P*	K*	Cu	Zn	B	Mn
$g\ kg^{-1}$	$mg\ kg^{-1}$						
540	9.9	0.3	87	1.6	0,1	0.5	22.1
pH($CaCl_2$)	**Ca^{2+}**	**Mg^{2+}**	**Al^{3+}**	**H+Al**	**CEC**	**OM**	
	$cmol_c\ kg^{-1}$					%	
5.17	1.1	0.6	0.1	2.6	4.6	1.53	

* Extracted by Mehlich-1.

A preliminary experiment was conducted to assess soil response to phosphorus (P) application and determine the optimal application rate for the treatments. Using a P response curve, it was identified that 50 mg of P per kg of soil was an effective rate, which resulted in 80 % of the maximum dry matter from the growth response curve of corn. Corn was used as the crop in both experiments.

Experiment I evaluated the agronomic efficiency of six fertilizer treatments in a completely randomized design with five replications. Treatments were: (1) unfertilized control, (2) unacidulated Arraias phosphate rock, (3) partially acidulated phosphate rock with 5 % sulfuric (PAPR 5 %), (4) PAPR 10 %, (5) PAPR 15 %, and (6) triple superphosphate (TSP). All fertilizers were applied at a rate of 50 mg of total P per kg of soil, resulting in 100 mg of P per pot. Each pot was filled with 2 kg of soil.

Five corn seeds were planted in each pot. After five days, the plants were thinned to two plants per pot. Nutrient solution containing all nutrients, except P, was applied in all pots. For each kilogram of soil, 100 mg N, 80 mg K, 80 mg Ca, 80 mg Mg, 80 mg S, 1 mg B, 4 mg Cu, 8 mg Mn, and 8 mg Zn were applied by the nutrient solution. Soil moisture was controlled every two days by pot weighing, keeping soil moisture between 60 and 70 % of field capacity. Three complementary N applications were performed at rates of 100, 25, and 25 mg per kg of soil at 15, 25, and 35 days after seeding, respectively. Plants were grown in a greenhouse for 45 days.

At harvest, plants were cut to ground level, weighed and P content in shoot tissue were determined after nitric/perchloric digestion, as described by Miyazawa et al. (2009). Phosphorus content in samples was determined by UV/Vis spectrophotometry (Miyazawa et al., 2009). Dry mass yield, P uptake, and relative agronomic efficiency were calculated using the soluble source (TSP) as reference. The RAE was computed using equation 1.

$$RAE(\%) = \frac{\textit{Shoot dry mass PAPR-Shoot dry mass control}}{\textit{Shoot dry mass TSP-Shoot dry mass control}} \times 100 \qquad \text{Eq. 1}$$

Pots were reseeded with corn, and a second crop was grown to evaluate the residual fertilizer effects of the tested products. The methods used and variables measured were the same as those previously described. The objective of the second greenhouse experiment was to evaluate the agronomic efficiency of PAPR with different granule sizes. This experiment was conducted over one growing cycle. There were six treatments in a completely randomized design with four replications per treatment. The treatments were: (1) unfertilized control, (2) PAPR 15 % granules with average size of 0.25 mm (0 to 0.5 mm), (3) PAPR 15 % granules size 0.75 mm (0.5 to 1.0); (4) PAPR 15 % granules size 1.50 mm (1.0 to 2.0); (5) PAPR 15 % granules size 2.4 mm (2.0 to 2.8), and (6) triple superphosphate (TSP), which was applied in its commercial form. All fertilizers were applied at a rate of 100 mg of P (nitric acid) per pot. The greenhouse study and variables measured were the same as those described in experiment 1.

Phosphorus diffusion from fertilizer

Phosphorus diffusion in the soil from each fertilizer source was evaluated in Petri dishes filled with soil, according to the method of Degryse and McLaughlin (2014). This method is based on the radial diffusion of P around fertilizer granules. Determination of the radius of diffusion is carried out by binding the soluble P with paper filter impregnated with iron oxide, which is revealed after a reaction with an ammonium molybdate solution and malachite green (Degryse and McLaughlin, 2014). Afterwards the filters are scanned and analyzed using imaging software to quantify the diffusion zone.

The Petri dishes had a 60 mm diameter and 15 mm height, and each one was filled with 53 g of soil (gravimetric humidity of 0.21 g g^{-1}). Fertilizer granules containing 3 mg of total P (nitric acid extractable) were placed in the center and on the top of the 15-mm soil layer. Treatments were: (1) unfertilized control, (2) unacidulated Arraias phosphate rock, (3) partially acidulated phosphate rock with 5 % sulfuric (PAPR 5 %), (4) PAPR 10 %, (5) PAPR 15 %, and (6) triple superphosphate (TSP). Each treatment was replicated six times, with the same Petri dish used for all observation days.

Diffusion visualization was made on days 1, 7, 14, 30, and 60 after plate preparation. Soil moisture was adjusted only at the start of the experiment, with no additional water added after the plates were prepared. The Petri dishes were covered with their respective lids to prevent drying and remained sealed throughout the 60-day diffusion period. At the end of period (60 days), plates were disassembled, and the contents of water-soluble P (water 1:10 ratio) and total P (aqua regia digestion) were determined on soil in the central ring (0 to 6 mm from the granule) and on soil in the external ring of the plate (6.1 to 20 mm from the granule).

Statistical analysis

Data analysis was conducted using SigmaPlot software (version 13.0). To assess the validity of parametric assumptions, the Shapiro-Wilk test was employed to check for normality of residuals, and Bartlett's test was applied to evaluate homoscedasticity, both at a significance level of 5 %. Logarithmic transformations were applied to datasets that violated these assumptions, and the assumptions were reassessed based on the transformed data. Subsequently, an analysis of variance (ANOVA) was performed to identify significant differences among treatments at a 5 % significance level. When the ANOVA F-test indicated significant results, Tukey's post hoc test was employed to compare treatment means ($p<0.05$).

RESULTS AND DISCUSSION

Phosphorus diffusion from fertilizer

The largest P diffusion radius (6.36 mm) was observed with TSP fertilizer (Figure 1a). There was no evidence of P diffusion from unacidulated Arraias PR, which was likely due to the low water solubility of this material. Although P diffusion had likely occurred with unacidulated phosphate rock in short distances from granules, the method used did not detect it. Phosphorus diffusion rates, as noted by the radius, were much higher with PAPR and increased with increasing rates of H_2SO_4 acid (Figure 1a). Increases in P diffusion rates are due to increases in P solubility that occurred with acidulation of the phosphate rock, making P more labile in soil. Although the average P diffusion radius slightly grew for the first 14 days, it shrunk after that (Figure 1b). This provides evidence of the high P adsorptive capacity of Brazilian Cerrado soils.

Water-soluble P content was higher for TSP in both the central and outer soil rings (Figure 1c). In the central ring, values were well above those found in the external ring, and TSP was similar to acidulated phosphate rock and larger than unacidulated Arraias PR and the control. Water-soluble P in the external ring was higher with TSP and PAPR 5 % than the other treatments. These higher P-water values for TSP are due to the high solubility of fertilizer found in the central ring and to the higher diffusion in soil (Figure 1a) reaching the external ring.

The highest levels of nitric acid extractable P in soil were found in the central ring for all fertilizers. Phosphorus mobility in soil is very low, and even when sources of high solubility are used, higher concentrations occur near the fertilizer granule (Castro et al., 2015). Nitric acid extractable P in the soil in the center ring of all the acidulated phosphate rocks was higher than that for TSP, which indicates TSP had the greatest migration of P added to areas farthest from granule placement. Nitric acid extractable P in the external ring increased as soluble P in the fertilizers increased, with TSP resulting in the highest concentration, indicating the greatest diffusion rate in soil (Figure 1d).

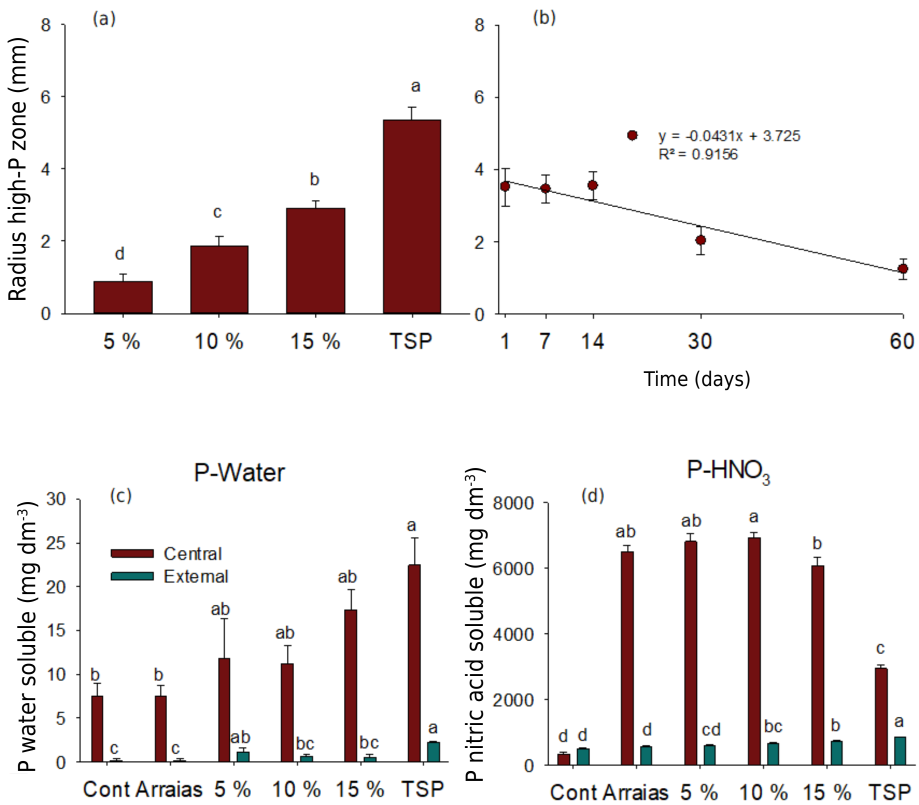

Figure 1. Diffusion radius of high concentration zone of phosphorus for each fertilizer (a) and variation over time (b). Soil phosphorus content in water (c) end Nitric Acid (d) extractants for each fertilizer in samples from the central ring (0 to 6.0 mm) and external ring (6.1 to 20 mm) after 60 days. Data shown in panel (b) reflect the variation over time, while the other panels (a, c, d) represent the data obtained at the 60-day endpoint. Equal letters do not differ by Tukey test ($p \leq 0.05$). ** Significant to $p \leq 0.01$.

Phosphorus diffusion from fertilizer granules in soils may be influenced by several factors. Hedley and McLaughlin (2005) indicated that there are three zones with different characteristics that define P diffusion from fertilizers in soil: (1) the residual granule and the immediate fertilizer interface, (2) a P-saturated zone, and (3) a P-unsaturated zone. The first zone is influenced by the composition of fertilizers and the solubility of the P source; lower solubility of the P source results in a greater amount of the original P (apatite) remaining in the granule zone. The second zone is influenced by the geochemistry. Precipitation reactions can occur under favorable pH conditions and high levels of soluble P and cations such as Ca, Fe, and Al, forming insoluble P precipitates. Finally, the last zone is influenced by soil chemical conditions affecting P adsorption capacity, such as the amount of iron and aluminum oxides and hydroxides. Due to the high content of P as apatite form, and the presence of Ca, partially acidulated phosphates rocks showed lower P solubility near fertilizer granules compared to TSP, but higher than that observed in unacidulated Arraias PR.

Experiment I - First crop

The P source significantly affected the Shoot dry mass yield (Figure 2a). Triple super phosphate applications resulted in the highest dry mass yield (12.18 g pot^{-1}). Dry matter production by the unacidulated Arraias RP and PAPR 5 % was not significantly different from the unfertilized control. However, PAPRs 10 and 15 % had a higher dry mass yield than the control and unacidulated Arraias, but much lower than TSP. These differences in dry mass production are directly related to the solubility of the material, with more soluble P sources resulting in higher dry mass yields (Ghani and Rajan, 1997; Oliveira et al., 2015; Schmitt et al., 2018). This reinforces the importance of the use of soluble P sources for plant nutrition in low P availability soils.

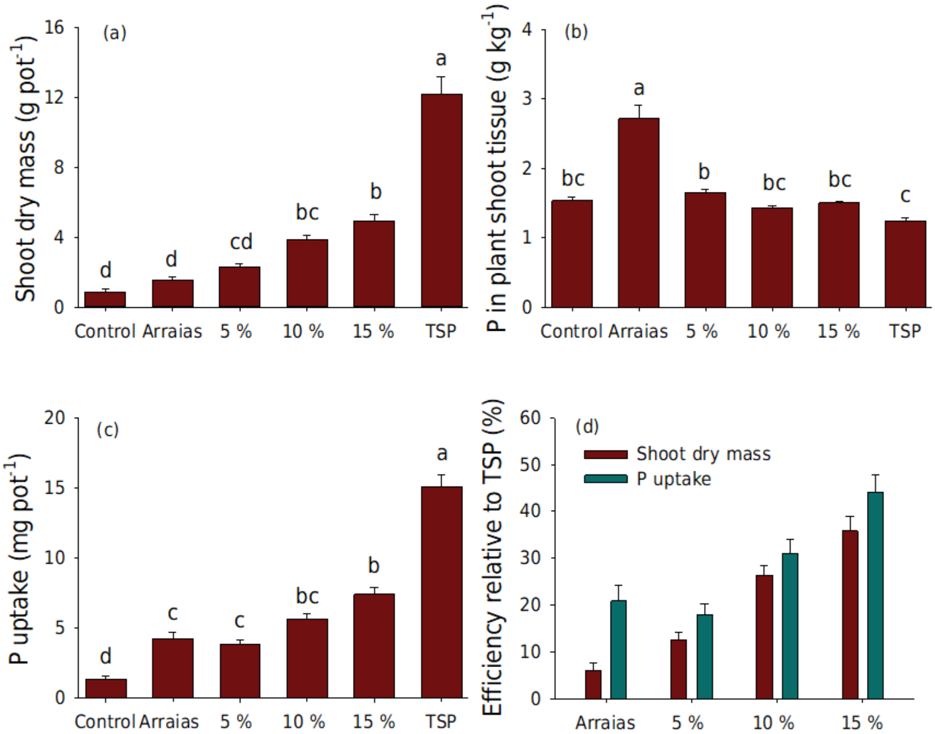

Figure 2. Corn shoot dry mass (a), phosphorus in plant tissue (b), phosphorus uptake (c), and efficiency relative to TSP in yield of shoot dry mass and phosphorus uptake for each fertilizer in the first crop. TSP: Triple superphosphate; Arraias: Phosphate rock; Partial acidulated phosphate rock: 5, 10 and 15 %. Equal letters do not differ by Tukey test ($p \leq 0.05$).

Unacidulated Arraias RP, which is the least soluble P fertilizer tested, resulted in the highest concentrations of P in plant shoots (Figure 2b). Whereas the most soluble P sources (TSP, 15 and 10 %) resulted in similar P concentrations in shoot tissue, compared to the unfertilized control. Low P availability in the unfertilized control resulted in low P levels in shoot tissue and low plant growth. Conversely, treatments with soluble or partially solubilized P sources increased shoot dry mass (Figure 2a), which diluted the shoot P content. Except for Arraias phosphate, the shoot P contents were relatively consistent across treatments, indicating that absorbed P was effectively converted into biomass.

Although the P content in shoot tissue was not proportional to P solubility, P uptake by corn was (Figure 2c). Phosphorus uptake by corn tended to mirror biomass production, with TSP resulting in significantly higher P uptake than the other treatments. This was followed by PAPR 10 and 15 %, which were not significantly different from each other, but showed significant improvement in P uptake in relation to the unacidulated Arraias and PAPR 5 %. These data indicate that the increase in dry mass yield is a direct consequence of higher P uptake, rather than chances in P concentrations. These results clearly demonstrate that higher P solubility in P fertilizer sources results in higher P uptake by plants, as has been shown by others (Ghani and Rajan, 1997; Oliveira et al., 2015; Schmitt et al., 2018).

Yield dry mass efficiency relative to TSP increased as P fertilizer solubility increased (Figure 2d). The PAPR 15 % treatment resulted in the highest biomass efficiency of the phosphate rocks, however, with only 36 %. The lowest relative efficiency was observed with unacidulated Arrais RP (6 %). These results support results found in other studies that also showed low relative plant growth efficiency when phosphate rocks are compared with soluble P sources (Goedert et al., 1990; Ghani and Rajan, 1997; Oliveira et al., 2015). The relative efficiency in P uptake was similar to biomass production, except for the unacidulated Arraias, which resulted in greater P uptake efficiency (Figure 2d). The PAPR 15 % treatment resulted in the highest P use efficiency of the phosphate rocks (44 %).

The relative P uptake efficiencies for the unacidulated Arraias and PAPR 5 % were similar, 21 and 18 %, respectively.

Second crop

Dry matter production increased for corn fertilized with phosphate rocks during the second crop; particularly unacidulated Arraias (Figure 3a). The highest dry mass yields were observed in treatments with higher solubility (TSP and PAPR 15 %) and with Arraias. Although there was a 13 % reduction in dry matter yields with TSP between the first and second crop (12.2 *vs* 10.4 g pot^{-1}), there was 561.78 % increase in dry matter for unacidulated Arraias PR in the second crop (from 1.57 to 10.39 g pot^{-1}). There were similar increases in dry matter production for partially acidulated phosphate rock between crops, with an increase of 286, 161, and 172 % for PAPR 5, 10 and 15 %, respectively. These data indicate a greater residual effect on successive crops with both acidulated and unacidulated phosphate rock, likely due to the slower release of P (Rajan et al., 1994). It is also possible that the unacidulated rock may have had a liming effect on the soil, which could have increased plant growth.

The P content in corn shoot tissue in the second crop was similar for acidulated fertilizers and TSP (Figure 3b). The only significant differences between P content in shoot tissue were observed between corn grown with TSP in relation to the unacidulated Arraias and the control. The P concentrations in plants fertilized with regular Arraias phosphate rock in the second crop were far lower than that observed the first, which was due to the effect of dilution of nutrient concentration in shoot tissue by higher dry mass yield (Figure 3a). The low variation between P contents in shoot tissue observed in the second crop may be a reflection of lower variation observed in dry mass yield, except in the control treatment.

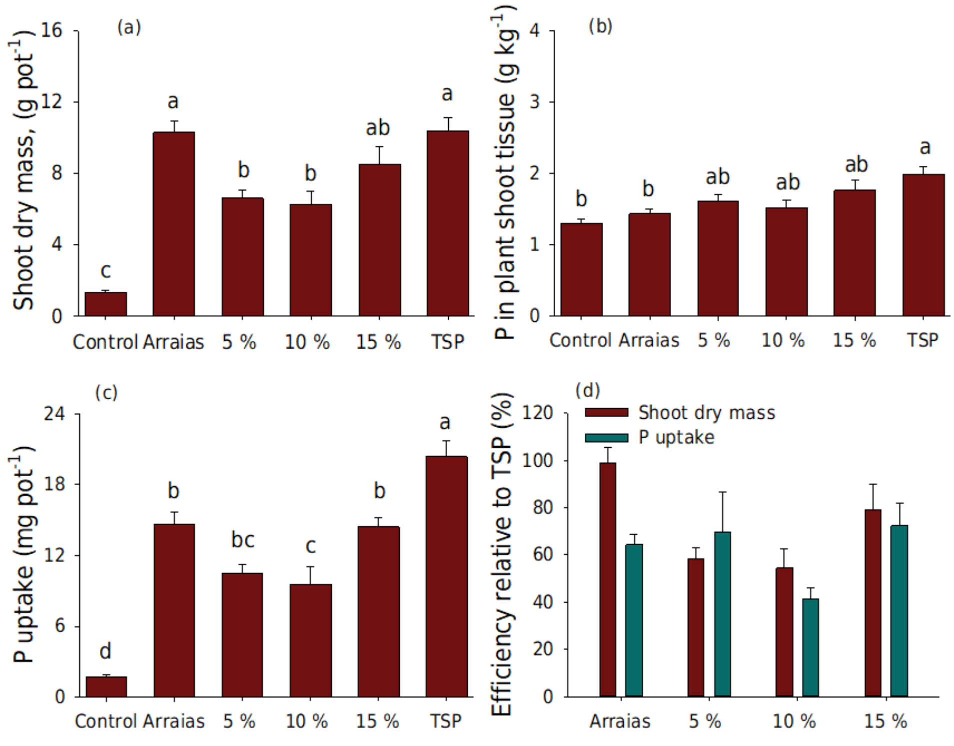

Figure 3. Corn shoot dry mass (a), phosphorus in plant tissue (b), phosphorus uptake (c), and efficiency relative to TSP in yield of shoot dry mass and phosphorus uptake for each fertilizer in the second crop. TSP: Triple superphosphate; Arraias: phosphate rock; Partial acidulated phosphate rock: 5, 10 and 15 %. Equal letters do not differ by Tukey test ($p \leq 0.05$).

Phosphorus uptake by corn was also higher for TSP in the second crop (Figure 3c). Higher P uptake was also observed for unacidulated Arraias and PAPR 5 % in the second crop in relation to the first crop. Relative efficiency in P uptake was similar between sources, with the exception of PAPR 10 %, which was somewhat lower than the other phosphate rocks (Figure 3d). In the second crop, the efficiency in P uptake was superior to the first crop, resulting in higher yields with these treatments due to greater P absorption from soil.

Yield dry mass efficiency relative to TSP increased in all treatmen ts in the second crop (Figure 3d). Yield efficiency with untreated Arraias phosphate rock was 99 % in the second crop. Fertilization with PAPR 5, 10 and 15 % resulted in relative yield efficiencies of 58, 55 and 79 %, respectively, which was superior to the first crop where efficiencies were only 13, 26 and 36 %, respectively. Differences in crop yields from phosphate rocks, either acidulated or untreated, and soluble P fertilizers, such as TSP, often decrease in effectiveness in successive crops. Sometimes less water-soluble P sources may even result in greater yields then soluble ones, because of the greater residual effect demonstrated on the second crop cycle (Rajan et al. 1994; Teles et al., 2020). The agronomic efficiency of Arraias phosphate as a direct source is constrained by its low reactivity. According to Brazilian legislation (MAPA, Normative Instruction No. 46, 2016), a phosphate must have at least 30 % of total P soluble in 2 % citric acid to be classified as reactive, a threshold not met by Arraias phosphate. Compared to sources like TSP or reactive phosphates such as Gafsa and Bayóvar, Arraias phosphate exhibits lower reactivity and initial solubility (Souza et al., 2014). Nonetheless, the observed increase in its efficiency during the second crop underscores its significant residual effect, which can be leveraged in long-term agricultural systems.

The most effective partial acidulation for phosphate rock in the first crop was 10 %, since there was no gain in shoot dry mass yields when compared to 15 % acidulation. Therefore, it is more viable to opt for PAPR 10 % of acidulation due to the lower cost compared to of acidulate rock at 15 %. However, low yield efficiencies relative to TSP indicate that low levels of acidulation are not sufficient to increase crop yield in low phosphorus levels in soils and for crops with high demand for P in a short period. If the first crop being grown does not have large demand for P on a short-term basis, then less soluble P sources, such as the unacidulated Arraias RP may be the most cost-effective choice.

Experiment II

There was no difference in shoot dry mass yield between granule sizes of PAPR 15 % (Figure 4a). All of the granule sizes resulted in higher dry matter production than the control, but lower than TSP. The highest yield among the granule sizes (diameter 0.25 mm) had only 35 % yield efficiency compared to TSP.

The highest P content in corn shoot tissue was observed in the granule size of 0.25 mm (Figure 4b). Phosphorus contents of corn fertilized with PAPR 15 % with diameters of 0.5 and 0.75 mm were higher than the unfertilized control and TSP fertilizer. The only difference in corn P contents was observed between the smallest (0.25 mm) and largest (2.4 mm) granules, with the smallest resulting in the highest concentrations.

Phosphorus uptake in shoot tissue was highest for TSP, followed by 0.25 mm granules of PAPR (Figure 4c). There were no significant differences in P uptake with granules larger than 0.25 mm. Relative efficiency in P uptake was higher for the 0.25 mm granule size (Figure 4d). Among other granule sizes, P uptake was similar.

Relative efficiency in shoot dry mass yield was very low compared to TSP and similar among granule sizes (Figure 4d). Relative efficiencies were 32, 21, 23 and 29 % for granules with 0.25, 0.75, 1.50 and 2.40 mm, respectively. These values were considerably lower than those observed in the TSP treatment, indicating P deficiencies were occurring. Low P solubility can seriously compromise yields in crops with high nutrient demands, such as corn used in this study.

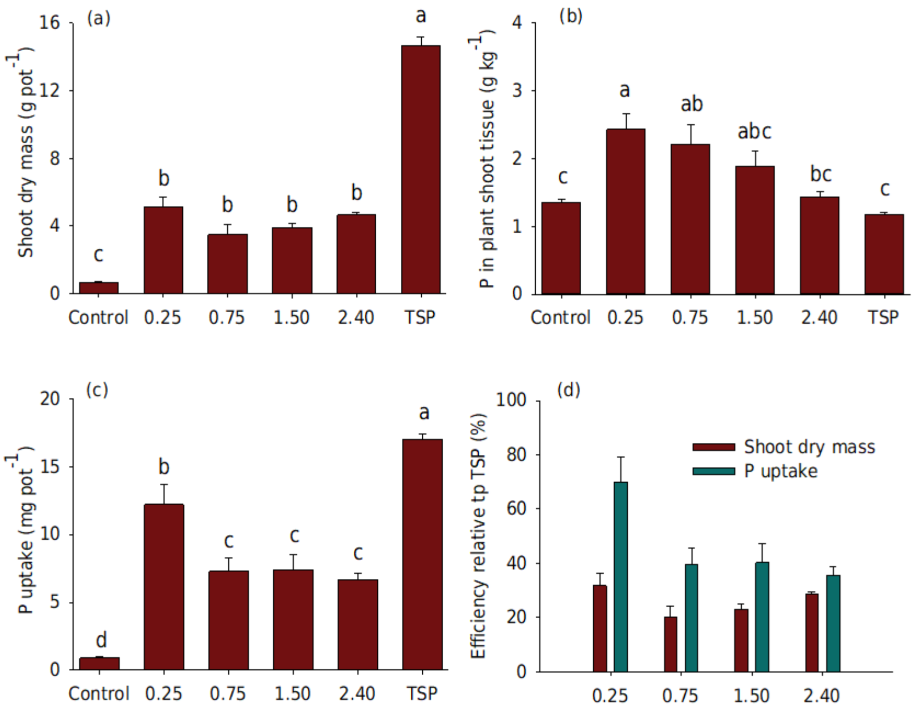

Figure 4. Corn shoot dry mass (a), phosphorus in plant tissue (b), phosphorus uptake (c), and efficiency relative to TSP in yield of shoot dry mass and phosphorus uptake for each fertilizer size. TSP: Triplo superphosphate; Average granule size: 0.25 mm (0.0 to 0.5); 0.75 mm (0.5 to 1.0); 1.50 mm (1.0 to 2.0); and 2.4 mm (2.0 to 2.8). Equal letters do not differ by Tukey test ($p \leq 0.05$).

The relative efficiency of phosphorus uptake for the 0.25 mm granules was notably high during the first crop cycle, highlighting their ability to provide a readily available source of phosphorus (Rajan et al., 1994). However, the subsequent decline in dry mass yield efficiency suggests that phosphorus availability was not sustained over time, likely due to the slower release characteristics of PAPR compared to TSP (Chien, 1993). While this limitation could impact crops with high nutrient demands, the lack of a second crop cycle in this study prevents further exploration of this dynamic.

It is far easier to achieve a high-quality distribution of fertilizers in a field using granulated fertilizers. While particle size is not that important for soluble P fertilizer sources, such as TSP (Muller, 1959), it can be very important for phosphate rock, since the solubilization of phosphorus in soil is inversely to particle size (Kanabo and Gilkes, 1988; McLaughlin et al., 2011). Thus, granulation of phosphate rock, even if partially acidulated, is not recommended due to low solubility, since this material requires a high specific surface area in contact with soil (Chien et al., 2011).

Under the conditions of this study, partially acidulated and micro-granulated phosphate rock was not an effective alternative to TSP. In conditions of low availability of P in soil and with high P-demanding crops, sources with high levels of P solubility are more indicated, particularly when not considering the residual effects.

CONCLUSION

Partial acidulation and granulation of Arraias phosphate rock is not an effective strategy for producing fertilizer for annual crops. The application of partially acidulated Arraias phosphate in the powder form may improve performance, but this study did not evaluate it. Granulation of the partially acidulated phosphate rock, regardless of granule size, did not present satisfactory agronomic efficiency when compared with the TSP.

DATA AVAILABILITY

The data supporting the findings of this study will be provided by the corresponding author upon reasonable request.

AUTHOR CONTRIBUTIONS

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