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# Magnesium thermophosphates from the Maicuru complex as sources of P and Mg in maize production

**Abstract** – The objective of this work was to investigate changes in soil chemical characteristics, phosphorous concentrations in maize leaves, and the agronomic efficiency (AE) of magnesium thermophosphates produced from rocks of the Maicuru complex in the Brazilian Amazon Basin, in comparison with triple superphosphate (TSP). The thermophosphates consisted of a mixture of raw material from apatite, dunitite, and quartz sandstone from Maicuru, aiming to adjust the contents of P, Mg, and Si. The mixture was melted, ground, and subjected to the analysis of solubility, chemical characteristics, and granulometry. The experiment consisted of two rates of dolomitic lime (0 and 2.4 Mg ha<sup>-1</sup>), three rates of P (20, 60, and 100 mg kg<sup>-1</sup> soil), and four sources of P (TSP and three Mg thermophosphates), as well as of two control treatments, with and without lime. Three replicates were carried out per treatment in pots containing plants of the BR 5107 maize hybrid. Phosphorous concentration was determined in maize leaves at 45 days after sowing. The Mg thermophosphates showed a high AE and a higher neutralizing effect with the application of lime, which improved soil chemical characteristics and AE. The thermophosphates obtained from rocks of the Maicuru complex can be an alternative P fertilizer in maize production.

**Index terms:** *Zea mays*, Brazilian Amazon, Oxisols, phosphate fertilizers.

## Termofosfatos magnesianos do complexo de Maicuru como fonte de P e Mg na produção de milho

**Resumo** – O objetivo deste trabalho foi investigar mudanças em atributos químicos do solo, concentrações de fósforo em folhas de milho e eficiência agrônoma (EA) de termofosfatos magnesianos produzidos com rochas do complexo de Maicuru, na bacia da Amazônia brasileira, em comparação ao superfosfato triplo (SFT). Os termofosfatos consistiram de mistura de matéria-prima de apatita, dunita e arenito quartzoso de Maicuru, para ajuste dos conteúdos de P, Mg e Si. A mistura foi fundida, moída e submetida à análise de solubilidade, características químicas e granulometria. O experimento consistiu em dois níveis de calcário dolomítico (0 e 2,4 Mg ha<sup>-1</sup>), três níveis de P (20, 60 e 100 mg kg<sup>-1</sup> de solo) e quatro fontes de P (TSP e três termofosfatos magnesianos), além de dois controles, com e sem calcário. Foram realizadas três repetições para cada tratamento, em vasos com plantas de milho do híbrido BR 5107. A concentração de P foi determinada nas folhas de milho aos 45 dias após a semeadura. Os termofosfatos magnesianos apresentaram alta EA e maior poder neutralizante com a aplicação de calcário, o que melhorou as características químicas do solo e a EA. Os termofosfatos obtidos de rochas do complexo Maicuru podem ser alternativa de fertilizante fosfatado na produção de milho.

**Termos para indexação:** *Zea mays*, Amazônia brasileira, Latossolos, fertilizante fosfatado.

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## Introduction

Von Uexküll & Mutert (1995) carried out a global survey that estimated that over 40% of soils in the Americas are acidic. This percentage doubles if considering only tropical South America, where 85% of the soils are acidic, representing more than 800 million hectares (Fageria & Nascente, 2014). Specifically in the Amazon Basin, 60% of the soils have a low fertility and high acidity (Quesada et al., 2010) and most of them are classified as Oxisols and Spodosols, with low phosphorus contents, which hinders agricultural production. Under these conditions, the continuous input of P fertilizers is necessary for the establishment and maintenance of intensive crops.

According to estimates, the demand for P fertilizers worldwide should increase from 51 to 86% by 2050 (Mogollón et al., 2018). In South America and the Caribbean, this demand has already grown and was predicted to exceed 8 million tons in 2022 (FAO, 2019). In this scenario, Li et al. (2018) concluded that phosphate rock reserves will be depleted in 65 to 135 years. Although the predictability of this depletion is low, within a 70 year gap, it highlights the need of seeking alternatives to meet the increasing P demand for fertilizer production.

In agriculture, the most widely used P sources are water-soluble phosphates, which make P readily available and are highly efficient in agronomic terms, including simple superphosphate (SSP), triple superphosphate (TSP), and monoammonium phosphate (Oliveira Junior et al., 2011). According to these same authors, other fertilizers less commonly used are thermophosphates and natural phosphates; the latter, however, are less efficient, mainly in annual crops on non-acidic soils due to the high demand for P over a short period.

Regarding phosphate rocks, an alternative is the production of molten magnesium thermophosphate from the fusion of a mixture of P, silica, and Mg (Guardani, 1987), cooled down to avoid the recrystallization of the phosphate mineral (Guardani, 1987; Tônsuaadu et al., 1993). The obtained fertilizer is more soluble and contains significant amounts of Mg, meaning that it can be used as an alternative to dolomitic lime, showing its importance since many cultivated areas on tropical soils have low contents of that mineral (Guo et al., 2016). Other positive aspects of the use of thermophosphates, which may be related

to their acid-neutralizing power, are an increase in biomass production and crop yield (Fageria & Santos, 2008; Medeiros et al., 2019).

In the Amazon Basin, the largest phosphate deposit is found in the Maicuru alkaline-ultramafic-carbonatite complex, located in the municipality of Monte Alegre, in the northwest region of the state of Pará. There, Costa et al. (1991) recorded ~200 million tons of phosphate ore and a large volume of dunite, sandstone, and other important rock minerals.

The objective of this work was to investigate changes in soil chemical characteristics, P concentrations in maize leaves, and the agronomic efficiency of Mg thermophosphates produced from rocks of the Maicuru complex in the Brazilian Amazon Basin, in comparison with TSP.

## Materials and Methods

The Mg thermophosphates used in this study were produced from apatite ore and rocks from the Maicuru alkaline-ultramafic-carbonatite complex, located 200 km from the center of the municipality of Monte Alegre, in the state of Pará, Brazil (00°30'S, 54°15'W). The Mg thermophosphates were synthesized at Instituto de Pesquisas Tecnológicas, in the municipality of São Paulo, in the state of São Paulo, Brazil.

Raw materials of apatite, dunite, and quartz sandstone were used as P, Mg, and silica sources, respectively, being mixed to adjust the contents of these elements (Table 1). The products were, then, melted in the Q318A24 electric muffle furnace (Quimis, Diadema, SP, Brazil), heated for 18 min between 1.400 and 1.450°C, and cooled immediately in water. Temperatures were measured every minute with the 8631-C optical pyrometer (Leeds & Northrup, Philadelphia, PA, USA), and AN-F1 carbon crucibles (Salamander, Morganite Brasil –Morgan Advanced Materials Company, São Bernardo do Campo, SP, Brazil) were used to hold the samples during fusion.

After the fusion process, the products were ground until 75% passed through a 100 mesh with a 0.149 mm sieve opening, in order to have the same granulometry as that of commercial thermophosphates. Then, the solubility of the obtained Mg thermophosphates was determined in 2% citric acid (1:100 ratio), and, 2 hours later, pH values were measured in water (1:4 ratio). The final products were glassy and soluble in soil solution,

containing 20% P<sub>2</sub>O<sub>5</sub> combined the following MgO/SiO<sub>2</sub> molar ratios: 0.75, 1.05, and 1.35, corresponding to Mg thermophosphates T-1, T-2, and T-3, respectively. The chemical and granulometric characteristics of the Mg thermophosphates and the phosphate fertilizer used in the present study are shown in Table 2.

The produced Mg thermophosphates were tested in a greenhouse using soil collected from a native vegetation area in the municipality of Santa Isabel, in the state of Pará. The soil was classified as a Latossolo Bruno (Santos et al., 2018), i.e, a Xanthic Hapludox (Soil Survey Staff, 2014), with a sandy loam texture, containing 750 g kg<sup>-1</sup> sand, 103 g kg<sup>-1</sup> silt, and 146 g kg<sup>-1</sup> clay according to Gee & Bauder (1986). The analysis of the chemical characteristics of the soil showed: pH<sub>H2O</sub> 4.7, 5.0 mg dm<sup>-3</sup> P (Bray & Kurtz, 1945), 0.60 cmol<sub>c</sub> dm<sup>-3</sup> Ca, 0.43 cmol<sub>c</sub> dm<sup>-3</sup> Mg, 0.04 cmol<sub>c</sub> dm<sup>-3</sup> K, 0.8 cmol<sub>c</sub> dm<sup>-3</sup> Al, and Al saturation of 42.8%.

The experimental design was a randomized complete block in a 2x3x4 factorial arrangement, corresponding to: two rates of dolomitic lime,

containing 32% CaO and 19% MgO (0 and 2.4 Mg ha<sup>-1</sup>), three rates of P (20, 60, and 100 mg kg<sup>-1</sup> soil), and four sources of P (TSP and T-1, T-2, and T-3). In this case, the experimental units totaled 72. The evaluated treatments were: the three Mg thermophosphates; and two controls, with and without liming. The amount of lime was calculated to elevate the sum of Ca+Mg to 2.0 cmol<sub>c</sub> kg<sup>-1</sup>. Both control treatments were used to calculate the agronomic efficiency index (AEI) of the thermophosphates. All treatments had three replicates, totalizing 78 experimental units.

To determine the amount of P in the leaves of maize plants, eight seeds of the BR 5107 hybrid were sown in plastic pots containing 3.35 kg soil with lime, at 70% moisture relative to field capacity, being incubated for 30 days. During this period, moisture was checked and measured daily. For all treatments, a complementary fertilization was carried out using a nutrient solution composed of 90 mg kg<sup>-1</sup> N as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 80 mg kg<sup>-1</sup> K as KCl, 1.2 mg kg<sup>-1</sup> Zn as ZnSO<sub>4</sub>, 0.3 mg kg<sup>-1</sup> B as H<sub>3</sub>BO<sub>3</sub>, 0.45 mg kg<sup>-1</sup> Cu as CuSO<sub>4</sub>.5H<sub>2</sub>O, 3.0 mg kg<sup>-1</sup> Mn as MnSO<sub>4</sub>.H<sub>2</sub>O, and 0.104 mg kg<sup>-1</sup> Mo as Na<sub>2</sub>MoO<sub>4</sub>.2H<sub>2</sub>O; half of the solution was applied at sowing and the other at 15 days after plant emergence. Thinning was performed five days after emergence, maintaining three plants per pot until the end of the experiment. The plants were harvested 45 days after emergence and dried in the SSDC-630L oven

**Table 1.** Chemical composition of the raw materials used for the production of the magnesium thermophosphates after apatite and dunite demagnetization.

| Component (%)                  | Apatite | Dunite | Sandstone <sup>(1)</sup> |
|--------------------------------|---------|--------|--------------------------|
| P <sub>2</sub> O <sub>5</sub>  | 36.60   | 1.30   | -                        |
| CaO                            | 52.88   | 4.30   | -                        |
| MgO                            | 0.10    | 33.70  | -                        |
| Al <sub>2</sub> O <sub>3</sub> | 0.16    | 1.20   | -                        |
| Fe <sub>2</sub> O <sub>3</sub> | 4.90    | 10.0   | -                        |
| SiO <sub>2</sub>               | 0.42    | 30.10  | 96.01                    |
| F                              | 3.40    | 0.23   | -                        |
| K <sub>2</sub> O               | 0.07    | 0.62   | -                        |
| FeO                            | 0.28    | 6.80   | -                        |
| Na <sub>2</sub> O              | 0.07    | 0.08   | -                        |
| TiO <sub>2</sub>               | 0.12    | 3.50   | -                        |
| MnO                            | 0.27    | 0.34   | -                        |
| BaO                            | 0.04    | 0.04   | -                        |
| Cr <sub>2</sub> O <sub>3</sub> | 0.01    | 0.06   | -                        |
| CO <sub>2</sub>                | 1.00    | 2.40   | -                        |
| S                              | 0.01    | 0.07   | -                        |
| H <sub>2</sub> O <sup>+</sup>  | 0.89    | 5.33   | -                        |
| H <sub>2</sub> O <sup>-</sup>  | 0.15    | 0.80   | -                        |
| NiO                            | 0.01    | 0.05   | -                        |
| Cl (ppm)                       | 20.00   | 180.00 | -                        |
| Total sum                      | 101.03  | 100.09 | 96.01                    |
| Loss of ignition               | 2.04    | 8.53   | -                        |
| O ≡ F                          | 1.43    | 0.06   | -                        |
| Final sum                      | 99.60   | 100.03 | 96.01                    |

-, not analyzed.

**Table 2.** Chemical characteristics of the evaluated phosphorous fertilizers.

| Chemical  | Fertilizer <sup>(1)</sup> |       |       |       |      |
|---|---------------------------|-------|-------|-------|------|
|   | TSP                       | T-1   | T-2   | T-3   |      |
| P <sub>2</sub> O <sub>5</sub> (%)                 | Total                     | 46.40 | 20.0  | 20.0  | 20.0 |
|   | CA <sup>(2)</sup>         | -     | 19.2  | 20.0  | 20.0 |
|   | WS <sup>(3)</sup>         | 44.70 | -     | -     | -    |
| Soluble/total P <sub>2</sub> O <sub>5</sub> ratio | 0.95                      | 96.0  | 100.0 | 100.0 |      |
| CaO (%)   | 15-20 <sup>(4)</sup>      | 30.4  | 30.7  | 30.9  |      |
| MgO (%)   | -                         | 12.0  | 14.1  | 15.7  |      |
| SiO <sub>2</sub> (%)                              | -                         | 24.0  | 20.2  | 17.5  |      |
| pH  | -                         | 9.6   | 9.6   | 9.6   |      |
| Total oxides (%)                                  | -                         | 42.4  | 44.8  | 46.6  |      |
| ENV (%) <sup>(5)</sup>                            | -                         | 84.1  | 89.9  | 94.3  |      |

<sup>(1)</sup>TSP, triple superphosphate; and T-1, T-2, and T-3, Mg thermophosphates containing 20% P<sub>2</sub>O<sub>5</sub> combined with the MgO/SiO<sub>2</sub> molar ratios of 0.75, 1.05, and 1.35, respectively. <sup>(2)</sup>Content of P soluble in 2% citric acid at a ratio of 1:100. <sup>(3)</sup>Content of P soluble in water and neutral ammonium citrate. <sup>(4)</sup>Data obtained from Associação Nacional para Difusão de Adubos (ANDA, 2010). <sup>(5)</sup>Effective neutralizing value.

(Solidsteel, Piracicaba, SP, Brazil), at 70°C, until reaching a constant mass. The dry mass of the aerial part of the plant was weighed on the AD3300 precision balance (Marte Científica, São Paulo, SP, Brazil) and, then, ground using the MA1680 knife mill (Marconi Equipamentos para Laboratórios Ltda, Piracicaba, SP, Brazil). Afterwards, the material was passed through a 50 mesh sieve and homogenized for 5 min. A sample of 1.0 g was taken to be digested, and a solution of HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> + HCl, at the ratio of 9:4:1, was added to it. The mixture was heated at 190°C, for 60 min, until the extracts were colorless and there were no more red NO<sub>2</sub> fumes. Total P concentrations in the extracts were determined by the spectrophotometry vanadium phosphomolybdate method, at 420 nm, using the 600 Plus spectrophotometer (Femto, São Paulo, SP, Brazil) as described in Gee & Deitz (1953).

After the maize plants were harvested, the soil from the pots was crushed using the MA880 ball mill (Marconi Equipamentos para Laboratórios Ltda, Piracicaba, SP, Brazil) and, then, manually homogenized. Samples of 0.5 kg, which were air dried and passed through a 2.0 mm sieve, were subjected to chemical analyses to determine: pH in H<sub>2</sub>O, using the soil/solution ratio of 1.0:2.5; available P, extracted with 0.03 mol L<sup>-1</sup> NH<sub>4</sub>F and 0.025 mol L<sup>-1</sup> HCl (Bray & Kurtz, 1945); exchangeable K, obtained by Mehlich-1; and exchangeable concentrations of Ca, Mg, and Al, extracted with 1.0 mol L<sup>-1</sup> KCl (Suarez, 1996). Aluminum contents were determined by titration using 0.025 mol L<sup>-1</sup> NaOH, and Al saturation was estimated with the following equation:

$$\%Al = \frac{100 \times Al^{3+}}{(Ca^{2+} + Mg^{2+} + K^{+} + Al^{3+})}$$

After harvest, the AEI of the Mg thermophosphates for dry matter mass (DMM) production was calculated according to Novais & Smyth (1999), using the following equation and TSP as a reference:

$$AEI = \frac{\text{Thermophosphate DMM} - \text{Control DMM}}{\text{Triple super phosphate DMM} - \text{Control DMM}} \times 100$$

The results were tested for parametric statistical assumptions. The tests of Shapiro-Wilk, Hartley, Durbin-Watson, and Farrar-Glauber were used to check for normality, homoscedasticity, independence of errors, and multicollinearity, respectively. Once

the assumptions were checked, data were subjected to a three-way analysis of variance, at 5% probability. Tukey's test and Student's t-test, also at 5% probability, were used to evaluate fixed effects of P sources and P rates and to compare means of the liming effect, respectively. All statistical assumptions were met.

## Results and Discussion

Regarding the used P source, soil pH values did not differ significantly with TSP ( $p > 0.05$ ), but increased with Mg thermophosphates (Table 3). Regardless of liming, pH values went from 4.82 to 5.24 with increasing P rates in all treatments and also rose at the highest P rate of 100 mg kg<sup>-1</sup> in all treatments with Mg thermophosphates.

The increase in pH when using Mg thermophosphates usually leads to the precipitation of exchangeable forms of Fe<sup>2+</sup> and Al<sup>3+</sup> (Haynes et al., 2013; Keeping, 2017), reducing the fixation of P in the soil and, consequently, increasing the availability of this nutrient to the plants (Haynes, 1984). Guelfi et al. (2022) attributed the alkalizing effect of Mg thermophosphates to the neutralizing capacity of the silicate anion in the form of Ca and Mg silicates, contributing to the maintenance of the adsorbed P in its labile form since an increased pH decreases Al solubility (Table 3).

As a function of lime application, soil Ca and Mg exchangeable contents increased from 0.62 to 1.05 cmol<sub>c</sub> dm<sup>-3</sup> and from 0.12 to 0.27 cmol<sub>c</sub> dm<sup>-3</sup>, respectively. The exchangeable Ca of the soil was higher at any P rate when Mg thermophosphates were used as an alternative to TSP ( $p < 0.05$ ), with the highest value found at 100 mg kg<sup>-1</sup> P (Table 3). The high Ca contents in the soil after the application of Mg thermophosphates may be explained by the high Ca concentrations of these fertilizers when compared with TSP (Table 2), reinforcing the assumption that Mg thermophosphates have a secondary effect, acting as a Ca source.

A similar behavior was observed for exchangeable Mg at the P rates of 60 and 100 mg kg<sup>-1</sup>, regardless of liming. Moreover, liming had a positive effect on exchangeable Mg, which shows the importance of dolomitic lime in the supply of this nutrient, as well as of Ca.

Pereira et al. (2014) also found that the Mg thermophosphate was more efficient than TSP in

providing nutrients, especially Mg. Fageria & Santos (2008) concluded that thermophosphates increased Ca and Mg contents in a Typic Haplaquept cultivated with rice (*Oryza sativa* L.) for two years, besides improving soil chemical characteristics, grain yield, and shoot dry matter.

Regarding Al saturation, one of main acidity components of the soil, there was a reduction from 48% without liming to 27% with liming. In the case of liming, the action of exchangeable Al over P fixation in the soil is neutralized, increasing the availability of this nutrient (Opala, 2017). In the treatments with Mg thermophosphates, the increase in P rates was efficient in reducing Al saturation in the soil (Table 3), which is in agreement with the results of Keeping (2017) and shows the importance of the presence of CaO and MgO concentrations in the produced P sources (Table 2). Specifically in treatment T-3, at the P rate of 100 mg kg<sup>-1</sup>, Al saturation decreased to ~10%, a level usually considered nontoxic to plants (Machado, 1990). Since thermophosphates are alkaline, presenting a pH between 8.0 and 9.0 (Haynes et al., 2013; Castro et al., 2016), it was expected that, in the present study, the Mg thermophosphates, with a pH of 9.2, would partially

neutralize the acidity of the acidic soils common in the Amazon.

In the treatment with TSP without liming, increasing P rates did not significantly affect Al saturation ( $p>0.05$ ), whose value remained at ~68% (Table 3). However, with liming, the P rates of 60 and 100 mg kg<sup>-1</sup> reduced Al saturation up to ~41%. In spite of this reduction, Al saturation was still high and harmful for maize development, also reducing P availability (Penn & Camberato, 2019).

As to phosphorous concentration in maize leaves, available P in the soil, and DMM, the average values obtained were: 1.55 g kg<sup>-1</sup>, 18.2 mg dm<sup>-3</sup>, and 36.6 g per pot, respectively.

Available P contents in the soil were affected by P rates and sources ( $p<0.05$ ) (Figure 1 A and B). The highest contents of available P were obtained with the T-1 and T-3 Mg thermophosphates, compared with TSP (Figure 1 A). T-2, however, did not differ from the other sources ( $p<0.05$ ), except from the control treatment, which showed the lowest mean of 3.4 mg kg<sup>-1</sup>. Of the P rates, that of 100 mg kg<sup>-1</sup> was the most efficient, increasing available P in the soil to 29.1 mg kg<sup>-1</sup>.

Regarding P concentration in maize leaves, all P sources resulted in higher values than that of

**Table 3.** Exchangeable calcium and magnesium contents as a function of the interaction among phosphorous rates and sources, as well as liming<sup>(1)</sup>.

| P rate<br>(mg kg <sup>-1</sup> ) | Fertilizer <sup>(2)</sup> | Soil pH             |                | Ca (cmol <sub>c</sub> dm <sup>-3</sup> ) |                | Mg (cmol <sub>c</sub> dm <sup>-3</sup> ) |                | Al saturation (m, %) |                |
|----------------------------------|---------------------------|---------------------|----------------|--|----------------|--|----------------|----------------------|----------------|
|                                  |                           | Without<br>liming   | With<br>liming | Without<br>liming                        | With<br>liming | Without<br>liming                        | With<br>liming | Without<br>liming    | With<br>liming |
| 20                               | Control                   | 4.50 <sup>ns</sup>  | 5.10a          | 0.39 <sup>ns</sup>                       | 0.84bc         | 0.11 <sup>ns</sup>                       | 0.38a          | 54.0b                | 24.3b          |
|                                  | T-3                       | 4.60A <sup>ns</sup> | 5.07Aa         | 0.43A <sup>ns</sup>                      | 0.95Aab        | 0.12B <sup>ns</sup>                      | 0.27Bb         | 58.0Ab               | 32.3Aab        |
|                                  | T-2                       | 4.53A <sup>ns</sup> | 4.93Aab        | 0.41A <sup>ns</sup>                      | 0.98Aa         | 0.10B <sup>ns</sup>                      | 0.29Ab         | 59.6Aab              | 29.0Aab        |
|                                  | T-1                       | 4.50A <sup>ns</sup> | 4.83Ab         | 0.43A <sup>ns</sup>                      | 0.91Aab        | 0.12B <sup>ns</sup>                      | 0.30Aab        | 55.5Ab               | 31.3Aab        |
|                                  | TSP                       | 4.63A <sup>ns</sup> | 5.07Aa         | 0.35A <sup>ns</sup>                      | 0.76Ac         | 0.09A <sup>ns</sup>                      | 0.23Ab         | 66.0Aa               | 37.0Ba         |
| 60                               | Control                   | 4.53c               | 5.10b          | 0.39b                                    | 0.84b          | 0.11b                                    | 0.38a          | 54.0b                | 25.0b          |
|                                  | T-3                       | 5.17Ba              | 5.47Ba         | 0.74Ba                                   | 1.19Ba         | 0.16Ba                                   | 0.36Aa         | 36.2Bc               | 20.8Bb         |
|                                  | T-2                       | 4.97Bab             | 5.40Ba         | 0.78Ba                                   | 1.18Ba         | 0.14Bab                                  | 0.28Aab        | 38.9Bc               | 19.8Bb         |
|                                  | T-1                       | 4.73Bbc             | 5.17Bb         | 0.69Ba                                   | 1.13Ba         | 0.10Bb                                   | 0.26Ab         | 43.7Bc               | 22.0Bb         |
|                                  | TSP                       | 4.60Abc             | 5.07Ab         | 0.34Ab                                   | 0.68Ab         | 0.04Bc                                   | 0.11Bc         | 71.1Aa               | 45.0Aa         |
| 100                              | Control                   | 4.50b               | 5.10c          | 0.39b                                    | 0.84b          | 0.11c                                    | 0.38a          | 54.0b                | 24.4b          |
|                                  | T-3                       | 5.33Ba              | 5.70Ca         | 1.00Ca                                   | 1.41Ca         | 0.22Aa                                   | 0.36Aa         | 22.8Cc               | 10.0Cd         |
|                                  | T-2                       | 5.27Ca              | 5.63Cab        | 1.09Ca                                   | 1.40Ca         | 0.21Aab                                  | 0.32Aab        | 23.3Cc               | 17.3Bc         |
|                                  | T-1                       | 5.20Ca              | 5.50Cb         | 0.96Ca                                   | 1.51Ca         | 0.17Ab                                   | 0.30Ab         | 27.2Cc               | 18.2Bc         |
|                                  | TSP                       | 4.63Ab              | 5.17Ac         | 0.37Ab                                   | 0.73Ab         | 0.04Bd                                   | 0.09Bc         | 67.4Aa               | 42.0ABa        |

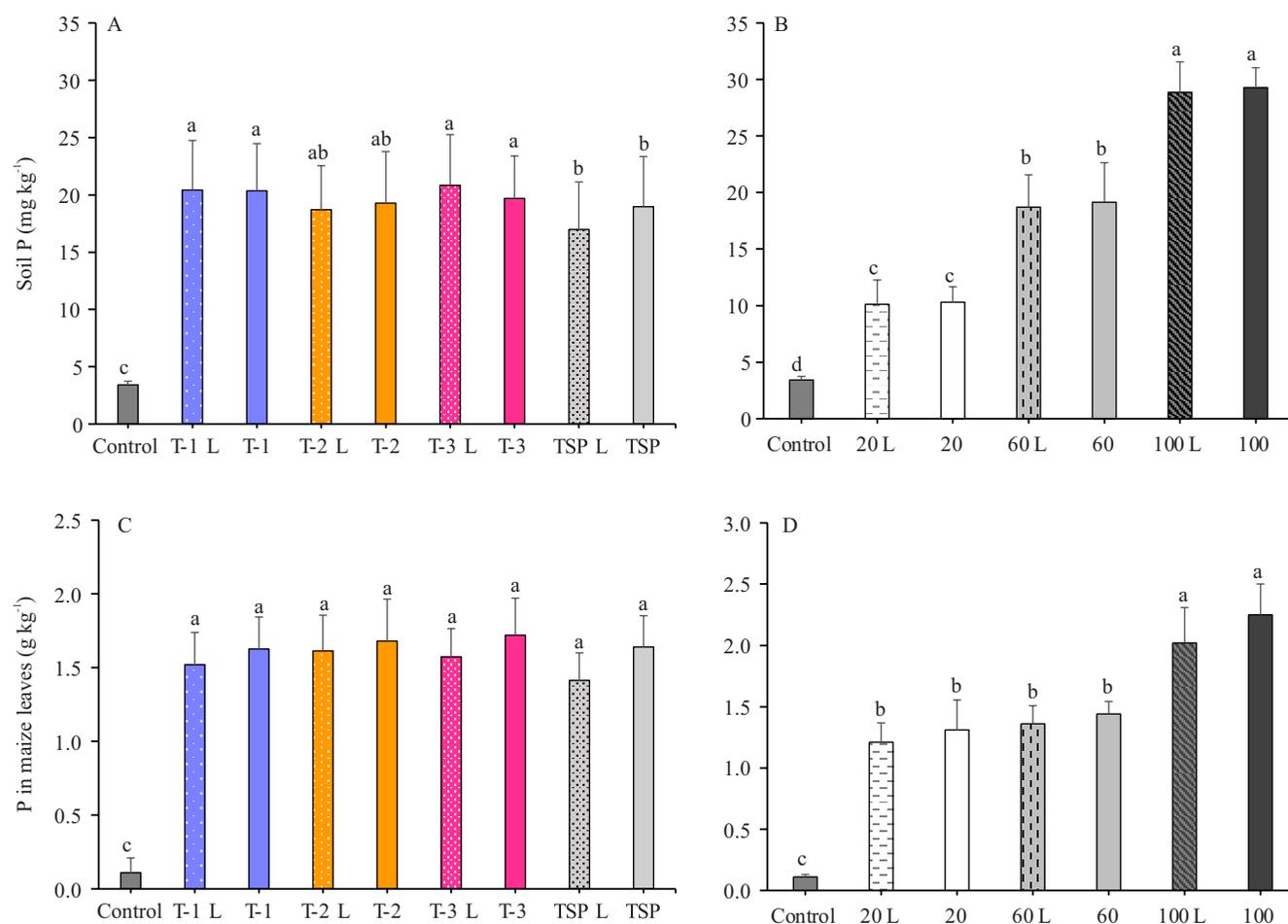
<sup>(1)</sup>Means followed by different letters, uppercase in the columns for the same fertilizer at different P rates and lowercase within each P rate for different fertilizers, differ by Tukey's test at 5% probability. <sup>(2)</sup>Control, with and without liming; T-1, T-2, and T-3, Mg thermophosphates containing 20% P<sub>2</sub>O<sub>5</sub> combined with the MgO/SiO<sub>2</sub> molar ratios of 0.75, 1.05, and 1.35, respectively; and TSP, triple superphosphate. <sup>ns</sup>Nonsignificant.

0.11 g kg<sup>-1</sup> of the control treatment (Figure 1 C). With increasing P rates, leaf P concentration ( $p < 0.05$ ) also significantly increased, showing values of  $1.3 \pm 0.2$ ,  $1.4 \pm 0.1$ , and  $2.1 \pm 0.3$  g kg<sup>-1</sup> at 20, 60, and 100 mg kg<sup>-1</sup> P, respectively (Figure 1 D). This indicates that there were no significant effects of phosphate sources since the obtained values remained below the critical level established for the crop even at the highest P rate (Oliveira Junior et al., 2011). In addition, liming had no effect on P concentrations in maize, with no direct influence on the absorption of this nutrient.

Considering P rate and sources, DMM accumulation increased significantly with increasing P rates and

lime application, showing the highest values when all Mg thermophosphates were used, except at the rate of 20 mg kg<sup>-1</sup> (Figure 2). Therefore, the increasing rates of Mg thermophosphate are an expression of biomass production potential. Without liming, 69% more DMM was produced in the TSP treatment, a value that was only not higher than that of T-2 (Table 4). With liming, all treatments with Mg thermophosphates resulted in a higher DMM.

Since DMM increases as P increases (Figure 2), there is a positive correlation between the content of this element and maize growth, for which P is the second most required nutrient, favoring the development



**Figure 1.** Soil phosphorous contents as a function of P fertilizers (A) and rates (B), as well P concentrations in maize (*Zea mays*) leaves as a function of P fertilizers (C) and rates (D). Means followed by equal letters, do not differ by Tukey's test at 5% probability. The intervals above the bars indicate the standard deviation of the means ( $n = 9$  for P indicated by a and c, and  $n = 12$  by b and d), composed of treatments with (L) and without liming. Control, with and without liming; T-1, T-2, and T-3, Mg thermophosphates containing 20% P<sub>2</sub>O<sub>5</sub> combined with the MgO/SiO<sub>2</sub> molar ratios of 0.75, 1.05, and 1.35, respectively; and TSP, triple superphosphate.

of the aerial part of the plant (Dhillon et al., 2017). Fosu-Mensah & Mensah (2016) also observed DMM increases with increasing P and N rates in Haplic soils of the forest-savannah transition zone of Ghana.

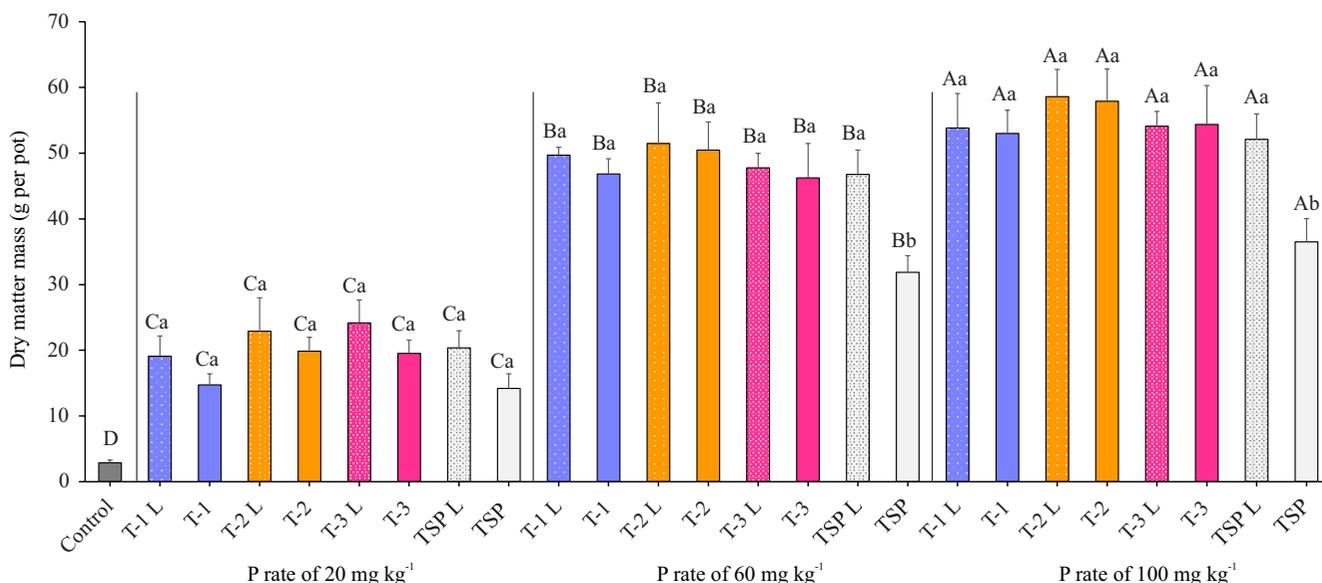
At the highest DMM, the highest P rate was followed by the highest P concentration in maize leaves. However, the obtained value was still lower than that of 2.5 to 3.1 g kg<sup>-1</sup> P concentration in leaves, considered ideal according to Stammer & Mallarino (2018). Despite this, no P deficiency symptoms were observed, which indicates that the plant showed an efficient P use. This situation possibly represents the “dilution effect”, when the speed of dry matter production is greater than the transport of the nutrient, resulting in lower concentrations of the nutrient per unit of plant material (Zhang et al., 2017). This hypothesis is supported by the fact that the residual contents of the nutrient in the soil were above the critical level for the crop (Figure 1).

The AEI values increased from 105.8 to 132.9% considering P rates, reinforcing the importance of liming. As to P sources, with liming, the AEI was higher for all Mg thermophosphates, compared with TSP, with values of 158, 149, and 135% for T-2, T-3,

and T-1, respectively. However, without liming, no significant differences were observed. Comparing the effect of liming on each P source alone, the AEI of the Mg thermophosphates was intensified (Table 4). Resende et al. (2006) also reported a high AEI for Mg thermophosphates, which, in many cases, was higher than that of TSP and several other highly soluble P sources. However, since TSP is usually applied in the sowing line, the probability of any insolubilized residue of P is low compared with the broadcasted fertilizers.

Overall, the P rates used in all treatments applied to the studied maize plants were classified as high according to Smyth & Cravo (1990) and Singh et al. (2011). These findings indicate that Mg thermophosphates and TSP were efficient suppliers of P to the soil, whose original available P value was 5.0 mg kg<sup>-1</sup>, considered low.

TSP, due to its high solubility of ~90% in relation to total P<sub>2</sub>O<sub>5</sub> in 2% citric acid, is highly efficient for annual or short-cycle crops (Tônsuaasu et al., 1993). Phosphates of high solubility, such as TSP and SSP, are almost readily available to plants after contact with soil and water, favoring the absorption and use of P, especially by fast-growing crops. However, this rapid



**Figure 2.** Dry matter mass production of maize (*Zea mays*) plants as a function of P rates and sources. Means followed by different letters, uppercase for the same source of P among rates and lowercase for sources at the same P rate, differ by Tukey's test at 5% probability. The intervals above the bars indicate the standard deviation of the mean (n = 3), composed of treatments with (L) and without liming. Control, with and without liming; T-1, T-2, and T-3, Mg thermophosphates containing 20% P<sub>2</sub>O<sub>5</sub> combined with the MgO/SiO<sub>2</sub> molar ratios of 0.75, 1.05, and 1.35, respectively; and TSP, triple superphosphate.

P release may also favor the process of adsorption and precipitation of soluble forms, reducing fertilization efficiency. Therefore, no effects were expected for TSP at the P rates used in the present study, since this fertilizer does not significantly affect soil pH; however, liming effects were expected, reinforcing the importance of this practice, regardless of the P source.

Contrastingly, Mg thermophosphates, which are less soluble, provide P for slightly longer periods, reducing the loss or fixation of this nutrient, being, therefore, an alternative to soluble phosphates (Fageria & Santos, 2008). In addition, the presence of Mg and Si in the composition of those fertilizers may favor P uptake by plants, as well as the partial neutralization of soil acidity, improving the chemical environment near the root system. Therefore, considering that Mg can limit plant P uptake, sources containing Mg and P are recommended due to a lower P adsorption and higher use efficiency (Lustosa Filho et al., 2020).

In the absence of liming, Mg thermophosphates show a high agronomic efficiency, which indicates their superiority to TSP, especially in soils with high acidity and low levels of exchangeable cations, common in the Amazon region. This occurs since the solubilization speed of Mg thermophosphates, which increases their agronomic efficiency, is favored in more acidic soils, but decreased in soils that receive liming.

Therefore, maize production can be improved by the application of Mg thermophosphates, which is in alignment with the literature. Goedert & Lobato (1980) classified 11 P sources into four categories

of efficiency in a four-year experiment in Brazilian Cerrado soils and included Mg thermophosphate and TSP in the group with the highest agronomic efficiency. In another study carried out in the same type of soil, Rezende et al. (2006) found that maize yield was higher when using Mg thermophosphate instead of TSP and natural phosphates.

## Conclusions

1. The use of magnesium thermophosphates increases significantly the production of maize (*Zea mays*) dry matter mass.
2. The continuous use of Mg thermophosphates increases exchangeable calcium and Mg contents in the soil, elevates pH, and reduces aluminum saturation.
3. In terms of the agronomic efficiency index, Mg thermophosphates show better results than triple superphosphate in the presence of lime.
4. The Mg thermophosphate production methodology is technically efficient to obtain Mg-rich phosphate fertilizers.

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**Table 4.** Total dry matter mass (DMM) of maize (*Zea mays*) plants and agronomic efficiency index (AEI) of magnesium thermophosphates as a function of liming and phosphorous fertilizers<sup>(1)</sup>.

| P fertilizer <sup>(2)</sup> | DMM (g per pot)      |                      | AEI (%)            |                    |
|-----------------------------|----------------------|----------------------|--------------------|--------------------|
|                             | With liming          | Without liming       | With liming        | Without liming     |
| Control                     | 2.1d <sup>ns</sup>   | 3.7c <sup>ns</sup>   | -                  | -                  |
| T-1                         | 38.2b <sup>ns</sup>  | 40.9ab <sup>ns</sup> | 135Ab              | 101Ba              |
| T-2                         | 42.7a <sup>ns</sup>  | 44.3a <sup>ns</sup>  | 158Aa              | 114Ba              |
| T-3                         | 40.0ab <sup>ns</sup> | 42.0ab <sup>ns</sup> | 149Aab             | 110Ba              |
| TSP                         | 27.5Ac               | 39.7Bb               | 100c <sup>ns</sup> | 100a <sup>ns</sup> |

<sup>(1)</sup>Means followed by different letters, uppercase in the rows and lowercase in the columns, differ by Tukey's test at 5% probability. <sup>(2)</sup>Control, with and without liming; T-1, T-2, and T-3, Mg thermophosphates containing 20% P<sub>2</sub>O<sub>5</sub> combined with the MgO/SiO<sub>2</sub> molar ratios of 0.75, 1.05, and 1.35, respectively; and TSP, triple superphosphate. <sup>ns</sup>Nonsignificant.

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