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# Effect of coating phosphorus with humic acids and micronutrients on yield of soybean and maize in succession

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## ABSTRACT

The increasing the efficiency of phosphate and micronutrient fertilization in tropical soils should be better studied to close crop yield gaps. The aim of this study was to evaluate the effect of a soluble P source with or without humic acids (HA) and micronutrients (M) on P-availability and maize and soybean yield in Minas Gerais State, Brazil. The crops were grown under a rainfed and no-till cropping system, with maize grown in the 2016/2017 rainy summer season, wheat grown as a cover crop in the 2017 winter season, and soybean grown in the 2017/2018 crop year. The field trial was organized in a 4 × 2 factorial arrangement [4 sources of P in combination with 2 forms of M supply]. The coated monoammonium phosphate (MAP) P source was supplied in three ways: 1) MAP, 2) MAP + HA, and 3) MAP + HA + M (B, Cu, Mn, and Zn), plus a control for P (no P). The micronutrient supply was 1) Mn + Zn + Cu + B (MZCB) and 2) control for MZCB (no M supply). Coating MAP with HA increased soil P availability but did not increase P content within the soybean leaves. The multivariate approach also showed that soybean yield can increase in response to coating MAP with HA. The study showed that MAP + HA increased soil P content. However, this increase was diminished when micronutrients were included in the same granule (MAP + HA + M). However, P sources raised P in soybean leaves equally compared to control for P. Soybean yield was unaffected by the P source, likely due to adequate leaf P concentrations across all treatments. However, soybean yield generally increased with micronutrient supply. For maize, yields were unaffected by supplying micronutrients with the P source. Conversely, maize yields typically decreased with micronutrient supply, except when using the MAP + HA + M combination granule.

## 1. Introduction

Over the past five decades, food production in Brazil has increased by 700 %, largely due to the expansion of planted area and significant improvements in crop yield [1]. These advancements have been driven by the adoption of new technologies, particularly in plant breeding and soil fertility management. However, Brazil remains a major importer of fertilizers, relying on imports for 80 % of its fertilizer needs [2].

Enhancing fertilizer use efficiency in Brazil is a significant challenge, primarily because the great majority of tropical soils are naturally acidic, contain high levels of aluminum, and have low fertility, including low phosphorus (P) and micronutrient content [3,4]. In these highly weathered soils, P use efficiency is low due to P adsorption onto the surfaces of iron and aluminum (hydr)oxide colloids [5–9]. In addition, the presence of $Fe^{2+}$ and $Al^{3+}$ ions in the soil solution under acidic conditions promotes the formation of iron and aluminum phosphates, further reducing P availability to plants [3,10–12].

In recent years, new technologies have been developed to enhance the effectiveness of P fertilizers, such as using humic acids (HA) to coat soluble P sources. The goal of coating P with HA is to reduce the adsorption of orthophosphate by soil iron and aluminum (hydr)oxides [4,9,13–16] because most of the P applied to acidic tropical soils with high iron and aluminum oxide content ends up being adsorbed to soil colloids and is not available to crops. Recent studies have shown increased P uptake by plants grown with HA–enhanced phosphate fertilizer [17,18]. However, few studies have been conducted to confirm the effectiveness of this practice in field conditions with tropical soils in particular.

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It has been suggested that HA can form complexes with P and metal cations, which can promote gradual solubilization of P and improve the efficiency of phosphate fertilization [10,16,19,20]. In addition, HA may also form complexes with micronutrients, such as zinc (Zn), which can decrease both the adsorption and precipitation of Zn and improve Zn availability to plants [21]. It has also been suggested that HA can improve crop growth and nutrient uptake [22–25] because it can stimulate plants through direct contact with the cell, thus increasing the activity of $H^+$-ATPase of the plasmatic membrane and stimulating high-affinity transporters in roots, a process that can improve plant P uptake [26,27].

Currently, many NPK solid fertilizer formulations include micronutrients in their composition to facilitate uptake of these nutrients, which are required in small amounts. However, some research indicates that the effectiveness of soil-applied micronutrients, particularly Cu and Mn, may be compromised due to their interaction with soil organic matter (OM) [28,29]. As a result, micronutrients are also supplied via foliar application, which has been shown to be as efficient as soil application [30]. Despite ongoing controversy about the need for foliar applications without symptoms of deficiency in leaves [31] and many questions regarding the efficiency of micronutrient application methods (through leaves or the soil), most grain producers in tropical environments apply micronutrients two or more times per crop cycle without assessing actual needs.

The significant innovation of this study was field comparison of the efficiency of conventional soluble P, P coated with HA, and application of the P source coated with HA + micronutrients in the same granule. Therefore, the objective of the study was to evaluate the efficiency of one of the main conventional sources of P (monoammonium phosphate - MAP) and MAP coated with HA in supplying P, and the effects of these treatments on soybean and maize yield, as well as to compare the efficiency of micronutrients supplied via soil (along with P + HA) to foliar application. The hypothesis of this study is that the availability of P and micronutrients to plants increases with their application in NPK + HA formulations and that micronutrients applied via foliar increase the yield of soybean and maize in tropical environments.

## 2. Materials and methods

### 2.1. Description of the experimental area

The study was carried out at the Muquém Farm, in the municipality/county of Ijaci, Minas Gerais, Brazil (Fig. 1). The altitude of the experiment site is 918 m above sea level. The local climate is classified as subtropical, with a rainy summer and dry winter (Cwa), based on Köppen's classification [32], with mean annual rainfall of 1529.7 mm and main annual temperature of 19.5 °C. The average temperatures and rainfall observed throughout the experimental period are shown in Fig. 2.

The soil at the experiment site was classified as a *Latossolo Vermelho Amarelo* in the Brazilian Soil Classification System [33] and as a Typic Hapludox (Oxisol) in U.S. Soil Taxonomy [34]. Soil characterization before implementation of the experiment is described in Silva [35]. Soil samples were taken, air-dried at room temperature, broken up, and sieved (<2 mm). The soil characteristics are shown in Table 1.

The experimental area has been part of a plant breeding research field for over twenty years, and a continuous no-till system has been used for 20 years. In the first ten years of cultivation, the cropping system consisted of maize (*Zea mays* L) in the summer season (October to February) and common bean (*Phaseolus vulgaris* L) in the winter season (February to May).In the last ten years before this assessment, the cropping system consisted of soybean (*Glycine* max L) in rotation with maize in the summer season and common bean in the winter season.

### 2.2. Experimental design

The field trial was carried out in a completely randomized block design, in a 4 × 2 factorial arrangement (three sources of P + control without P in combination with two forms of micronutrient (M) supply: with and without), for a total of eight treatments, with four replications (32 plots). Each plot was 28.8 $m^2$ (6 × 4.8 m). P application was in three forms for the coated granulated fertilizer monoammonium phosphate (MAP) and control for P – no P application. The sources of P were 1) MAP alone; 2) MAP + humic acid (HA); 3) MAP + HA + M (micronutrients B, Cu, Mn, and Zn), and 4). Coating the MAP granules with HA has a patent number: 10–519072/B2 Produquímica Indústria e Comércio S.A.

The dose of P applied as MAP was 35 kg/ha for soybean and 52 kg/ha

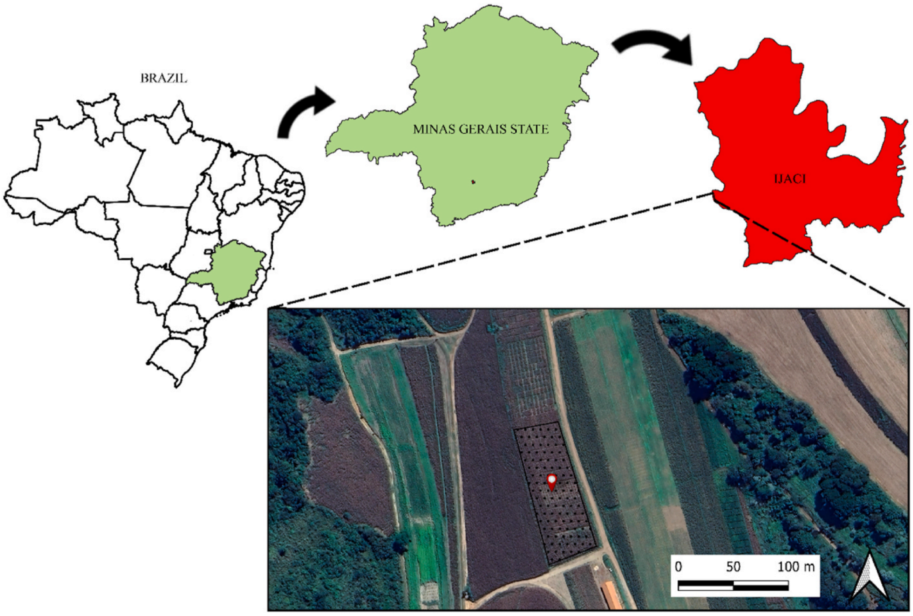

**Fig. 1.** Details of the location where experiment was located.

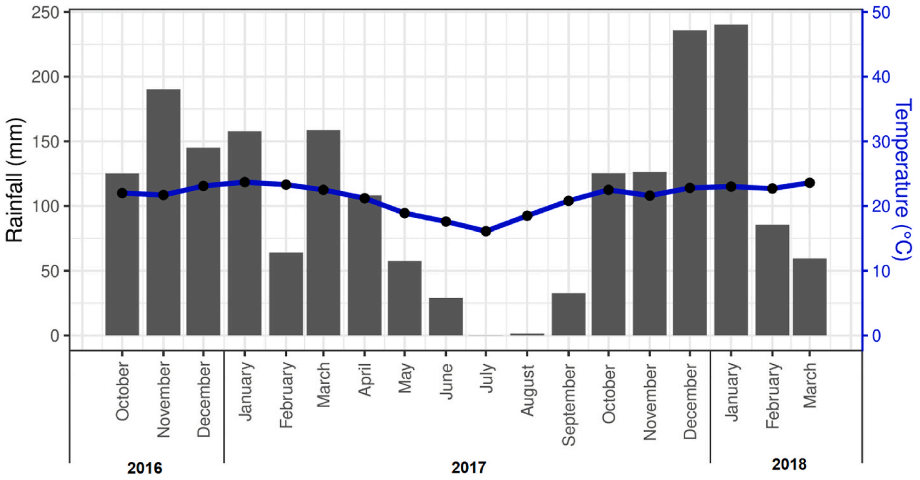

**Fig. 2.** Average temperatures and rainfall during the period of the two stages of the experiments in the 2016/2017 and 2017/2018 cropping years.

**Table 1**
Chemical and physical properties of the Typic Hapludox (0–0.2 m).

| pH[a] | SOM[b] | K[c] | P[c] | Ca[d] | Mg[d] | Al[d] | H + Al[e] | CEC[f] | Zn[c] | Fe[c] | Mn[c] | Cu[c] | B[g] | S[h] | Sand[i] | Silt[i] | Clay[i] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | — mg $dm^{-3}$ – | | cmol$_c$ $dm^{-3}$ | | | | | mg $dm^{-3}$ | | | | | | g $kg^{-1}$ | | |
| 5.7 | 3.0 | 112.4 | 6.0 | 3.3 | 0.8 | 0 | 2.7 | 7.1 | 4.9 | 55.2 | 9.7 | 0.5 | 0.3 | 9.9 | 28.7 | 3.1 | 68.2 |

[a] pH - pH in water (1:2.5 soil/solution).
[b] SOM - soil organic matter ($Na_2Cr_2O_7$ 4 mol $L^{-1}$ + $H_2SO_4$ 5 mol $L^{-1}$) by Silva (2009).
[c] P, K, Fe, Zn, Mn and Cu - extracted by the Mehlich-1 (Mehlich, 1953).
[d] Ca, Mg e Al (KCl 1.0 mol $L^{-1}$).
[e] (H + Al) - potential acidity (SMP).
[f] CEC - cation exchange capacity at pH 7.0.
[g] B - extracted with hot water method.
[h] S - extracted as sulfate and the result was converted to S.
[i] Sand, silt and clay (Bouyoucos, modified by Carvalho (1985).

for maize. In the MAP + HA + M treatment, we applied 0.45 kg/ha B, 0.45 kg/ha Cu, 1.35 kg/ha Mn, and 1.35 kg/ha Zn for the maize crop. In this same treatment (MAP + HA + M) for soybean, we applied 0.30 kg/ha B, 0.30 kg/ha Cu, 0.90 kg/ha Mn, and 0.90 kg/ha Zn. The 2 forms of micronutrient supply were 1) Mn + Zn + Cu + B (MZCB) and 2) control for MZCB – no application of micronutrients. The sources of micronutrients were ulexite for B and EDTA (liquid fertilizer) for Cu, Mn, and Zn. The micronutrient application rates calculated for each nutrient in each crop (in g/ha) were as follows: Cu (19 for maize and 10 for soybean), Mn (47 for maize and 30 for soybean), and Zn (165 for maize and 40 for soybean), exported considering 10,000 kg/ha of maize and 4000 kg/ha of soybean grain, according to Raij [36] and Resende et al. [37]. The MZCB treatment also included 2 kg/ha of B in the soil for both crops, using ulexite as a source. Details of the treatments are shown in Table 2.

All plots were fertilized with 190 and 20 kg/ha of nitrogen (N), 125 and 125 kg/ha of potassium (K), and 54 and 38 kg/ha of sulfur (S) for maize and soybean, respectively. These doses were calculated based on local recommendations for each specific crop [37,38].

The crops grown were maize in the 2016/17 summer season, followed by wheat in the 2017 winter season, and soybean in the 2017/18 summer season, using the cultivars KWS 9004, BRS 264, and M6410 IPRO, respectively. The maize (Oct. 2016 to Feb. 2017) and soybean (Nov. 2017 to Mar. 2018) crops were grown under a rainfed no-till system. Both were sown manually with a spacing of 0.6 m between rows. The wheat, used as a cover crop, was broadcast sown in April 2017. For wheat, 100 kg/ha N and 83 kg/ha K were applied in the soil.

### *2.3. Sowing and conducting the experiment*

For sowing both soybean and maize, first, furrows were opened and then seeds were added to the furrows following each treatment, as previously described (Table 2). After harvesting, the crop residue remained on the soil surface. The soybean sowing furrows were created at the same initial positions as the furrows used for planting maize. P fertilizers were placed in the sowing furrows at a depth of 10 cm. Subsequently, a 7-cm layer of soil was placed within the furrow before sowing to prevent direct contact between the fertilizer and the seeds.

The crop seeds were sown in the soil (in the furrow) at a 3-cm depth for maize and soybean. Soybean seeds received in-furrow inoculation using a liquid inoculant (Rhizomax®) with *Bradyrhizobium japonicum* SEMIA 5079 and *B. diazoefficiens* SEMIA 5080 strains at a bacterial concentration of 2.0 × $10^9$ CFU/ml.

Foliar fertilizers were sprayed on maize when maize plants were at the V4 and V5 stages (fourth and fifth leaves fully expanded). On soybean, foliar fertilizers were sprayed four times, every seven days, starting when soybean plants were at the V4 stage (fourth visible node) to avoid phytotoxicity. Soybean received cobalt (Co) and molybdenum (Mo), which were applied through 96 ml/ha of the nutritional compound Quimifol CoMo Plus®, composed of 11.6 g/l of Co and 69.6 g/l of Mo as chelated cobalt sulfate and sodium molybdate.

Maize received N in the form of urea divided into two applications: 114 kg/ha of the recommended amount 15 days after sowing, and the remaining amount (76 kg/ha) 28 days after sowing. In both applications, urea was applied next to the plant row, without incorporation into the soil.

During the two cropping years, assessments were made regarding the presence of weeds, pests, and diseases in the crops and, when necessary, management measures were implemented, involving the application of appropriate herbicides, fungicides, and insecticides at the rates recommended for each crop. The plant population was 75,000 plants/ha for

**Table 2**

Description of the treatments used in the experiments.

| P source | Micronutrients | P | B | Cu | Mn | Zn |
|---|---|---|---|---|---|---|
| | | kg/ha | | | | |
| | | Maize | | | | |
| Control for P | Control for MZCB | 0 | 0 | 0 | 0 | 0 |
| | MZCB | 0 | 2 | 0.019 | 0.047 | 0.165 |
| MAP | Control for MZCB | 52 | 0 | 0 | 0 | 0 |
| | MZCB | 52 | 2 | 0.019 | 0.047 | 0.165 |
| MAP + HA | Control for MZCB | 52 | 0 | 0 | 0 | 0 |
| | MZCB | 52 | 2 | 0.019 | 0.047 | 0.165 |
| MAP + HA + M | Control for MZCB | 52 | 0.45 | 0.45 | 1.35 | 1.35 |
| | MZCB | 52 | 0.45 + 2 | 0.45 + 0.19 | 1.35 + 0.47 | 1.35 + 0.165 |
| | | Soybean | | | | |
| Control for P | Control for MZCB | 0 | 0 | 0 | 0 | 0 |
| | MZCB | 0 | 2 | 0.01 | 0.03 | 0.04 |
| MAP[a] | Control for MZCB | 35 | 0 | 0 | 0 | 0 |
| | MZCB | 35 | 2 | 0.01 | 0.03 | 0.04 |
| MAP + HA[b] | Control for MZCB | 35 | 0 | 0 | 0 | 0 |
| | MZCB | 35 | 2 | 0.01 | 0.03 | 0.04 |
| MAP + HA + M[c] | Control for MZCB | 35 | 0.3 | 0.3 | 0.9 | 0.9 |
| | MZCB[d] | 35 | 0.3 + 2 | 0.3 + 0.01 | 0.9 + 0.03 | 0.9 + 0.04 |

[a] MAP - monoammonium phosphate.

[b] MAP + HA - humic acid coated monoammonium phosphate.

[c] MAP + HA + M – monoammonium phosphate coated with humic, B, Mn, Zn and Cu.

[d] MZCB - Mn, Zn, Cu and B supply (B applied via soil B and Mn, Zn and Cu applied via foliar).

maize and 180,000 for soybean.

### 2.4. Evaluated variables

Soil samples were collected in the 0–20 cm layer after the soybean season. Two soil samples were taken from the plant rows, while four additional samples were collected from between the rows. These six samples were subsequently combined to create a composite sample for each individual plot. The samples were dried naturally at ambient temperature and then broken up, homogenized, and sieved through a 2 mm mesh to obtain fine earth for analysis in an air-dried state.

Soil phosphorus was extracted using the Resin method (ion exchange resin) [39]. The extractant resin used simulates the response of the plant root system in taking up nutrients from the soil [39]. The micronutrients Zn, Cu, and Mn in the soil were extracted using Mehlich-1 as the extractant [40]. B in the soil was extracted by the hot water method [41]. After each method, the nutrient concentrations were determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) (PerkinElmer®, Optima 8300 model, Waltham, USA).

Leaf samples were obtained for nutritional assessment of soybean during its flowering phase. Thirty-five (35) leaves were collected from each plot. The third fully developed trefoil, excluding the petiole, was collected from the tip of the branch. Leaves were dried in a forced-air oven at 65 °C until constant weight. Phosphorus and micronutrient levels were determined according to Malavolta et al. [42]. Crop yield was determined by harvesting the ears or pods within the area of each plot used for data analysis (21.6 $m^2$) for maize and soybean.

### 2.5. Statistical analysis

All statistical analyses were performed in the R environment, version 4.1.2 [43]. An analysis of variance (ANOVA) was carried out and tested for significance ($P < 0.05$). Statistically significant distinctions among the treatments were evaluated through the Scott-Knott means comparison test ($P < 0.05$) with the *easyanova* v7.0.4 package [44]. Principal component analysis was performed to show the importance of the forms of P application on nutritional status and yield for soybean using the *factoMineR* v2.4 [45], *factoextra* v.1.0.7 [46], and *vegan* v2.5.6 [47] packages.

## 3. Results

### 3.1. Phosphorus content in the soil and in soybean leaves

The different forms of P application (MAP, MAP + HA, MAP + HA + M) and micronutrient supply (MZCB) combinations significantly affected the concentrations of soil P extracted after soybean harvest. However, the response depended on the interaction between the form of P application and the micronutrient supply (Fig. 3a). Plots that received MAP coated with HA exhibited an increase in soil P content compared to the uncoated MAP. When micronutrients (MZCB) were supplied, the plots that received MAP + AH had higher P content than those without micronutrients supplied (control for MZCB). The MAP coated with HA and micronutrients (MAP + HA + M) provided less addition of P to the soil, while the association of MZCB with the MAP + HA + M treatment increased P in the soil.

There was no significant interaction between MZCB and the forms of P application regarding P concentration in soybean leaves (Table 3). P sources significantly increased the concentration of P in soybean leaves compared to the control treatment, without P. While soybean leaves grown without P presented 3.6 g/kg, plants fertilized with MAP, MAP + HA and MAP + HA + M presented 4.1, 4.3, 4.1 g/kg, respectively (Fig. 3b).

### 3.2. Micronutrient content in soybean leaves

A significant interaction was observed between forms of P application and micronutrient supply concerning Zn and B concentrations in soybean leaves (Table 3). Considering P application without addition of micronutrients (MZCB), the Zn concentration was higher in the control for P. When the plants were fertilized with MAP and MAP + HA + M and with foliar micronutrient application + boron via soil (MZCB), they showed the highest concentrations of Zn in soybean leaves (Table 3). For B, leaf concentration was lower when MAP and MAP + HA were used without micronutrient supplementation (control for MZCB). However, the combination of MAP and MAP + HA with MZCB increased B concentrations in soybean leaves by 11 and 12 mg/kg, respectively (Table 3).

The Cu and Mn concentrations in soybean leaves varied only with the forms of P application or micronutrient applications (MZCB), in the case of Mn. The plants that received MAP + HA + M had lower Cu concentrations compared to other forms of P application. In the case of Mn, higher leaf concentrations of the nutrient were found in treatments in which the plants were fertilized with MAP or MAP + HA + M (Table 3). Regardless of the forms of P application, plants that received foliar Mn (MZCB) showed higher foliar Mn concentrations compared to the control without foliar micronutrient application.

### 3.3. Crop yield

The interaction between forms of P application and micronutrient supply was not significant for soybean yield (Fig. 4a). However, plants supplied with micronutrients (MZCB) showed higher yield (3386 kg/ha), i.e., around 11 % higher than those without MZCB application. In

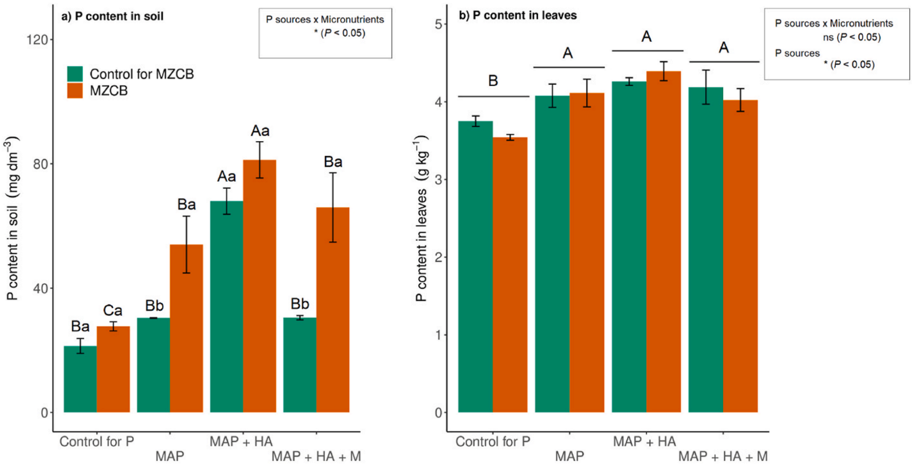

**Fig. 3.** P content in soil (a) and soybean leaf (b) as a function of P sources: MAP (monoammonium phosphate), MAP + HA (MAP coated with humic acid), MAP + HA + M (B, Mn, Zn, and Cu) and forms of micronutrient supply (B, Mn, Zn, and Cu - MZCB). The averages followed by the same capital letter for source of P and the same lowercase letter for micronutrients do not differ statistically by the Scott-Knott test (**P* < 0.05). Vertical lines represent mean standard deviation.

**Table 3**

Average content (± mean standard deviation) of Mn, Zn, Cu and B in leaves for soybean after cultivation in Typic Hapludox with MAP (monoammonium phosphate), MAP + HA (MAP coated by humic acid MAP), MAP + HA + M (B, Mn, Zn and Cu) and forms of micronutrient supply (B, Mn, Zn, and Cu - MZCB). The averages followed by the same capital letter for source of P and the same lowercase letter for micronutrients do not differ statistically by the Scott-Knott test.

| P source | Micronutrients | Mn | Zn | Cu | B |
|---|---|---|---|---|---|
| | | mg kg$^{-1}$ | | | |
| Control for P | Control for MZCB | 24.3 ± 3.4 Bb | 52.8 ± 1.9 Aa | 9.5 ± 0.4 A | 82.0 ± 3.0 Aa |
| | MZCB | 27.7 ± 1.5 Ba | 43.3 ± 3.8 Bb | 8.5 ± 0.5 A | 82.0 ± 5.5 Aa |
| MAP | Control for MZCB | 29.6 ± 5.8 Ab | 38.3 ± 1.8 Bb | 8.2 ± 0.3 A | 68.7 ± 3.1 Bb |
| | MZCB | 36.9 ± 2.9 Aa | 52.0 ± 2.8 Aa | 9.3 ± 1.9 A | 79.7 ± 2.0 Aa |
| MAP + HA | Control for MZCB | 25.7 ± 3.0 Bb | 43.9 ± 2.7 Ba | 10.2 ± 1.4 A | 70.2 ± 5.0 Bb |
| | MZCB | 30.2 ± 2.3 Ba | 43.5 ± 2.8 Ba | 9.5 ± 0.9 A | 82.1 ± 0.5 Aa |
| MAP + HA + M | Control for MZCB | 32.0 ± 3.8 Ab | 43.4 ± 6.8 Bb | 6.1 ± 1.9 B | 80.8 ± 2.3 Aa |
| | MZCB | 31.8 ± 5.2 Aa | 50.0 ± 1.8 Aa | 7.3 ± 1.0 B | 82.1 ± 5.0 Aa |
| P source | | [a] | [a] | [a] | [a] |
| Micronutrients | | [a] | [a] | ns | [a] |
| P source × Micronutrients | | ns | [a] | ns | [a] |

[a] $P < 0.05$.

the case of maize yield, there was an interactive effect between forms of P application and micronutrient supply (Fig. 4b). Plants fertilized with MAP + HA and without MZCB application showed higher maize yield, but there was no significant difference in relation to any other P treatments, as well as the control for P. In plants fertilized with the different forms of P application associated with MZCB, the highest maize yield occurred with the application of MAP + HA + M, i.e., an increase of 1949 kg/ha in grain yield (16 %) compared to the MAP treatment. These results indicate that coating MAP + HA + M could serve as a viable alternative in supplying these nutrients to maize.

### 3.4. *Principal component analysis*

Principal component analysis (PCA) revealed that two principal components collectively explain 40.5 % of the total data variance (Fig. 5). The variables with the lowest importance in PCA are those that contribute the least to the variance in the data. These variables tend to have small loadings on the principal components and may not be critical in explaining the results (e.g., Cu content in soil: Cu soil). The opposite is true for variables with high loadings. Proximity between variables demonstrates a covariance between these variables in the data set under study. Soybean yield had a greater association with P and B content in the soil and P content in leaves, and these variables were favored by MAP + HA + M + MZCB; and MAP + HA + MCZB and MAP + MZCB clustered and were negatively related to Cu availability in the soil and the treatments Control for P + Control for MZCB and Control for P + MZCB.

## 4. Discussion

### 4.1. *Phosphorus content in the soil*

When MAP + HA was applied, there was an increase in the P content of the soil compared to the application of MAP without coating (Fig. 2), as had also been observed in other studies [15,16,20,48]. Thus, the results suggest that the HA present in the coated MAP decreased P adsorption on soil colloids and increased the P content in the soil solution. One of the main mechanisms described in the literature to explain the reduction in P adsorption is that carboxylic (R–COOH) groups present in humic substances [27,49–52] compete for the same P adsorption sites ($H_2PO_4^-$ and $HPO_4^{2-}$) on the surfaces of Fe and Al oxides. This reduces the maximum adsorption capacity of the soil, the colloidal surface binding energy, and maximum P buffering [13]. It has also been reported that HA decreases phosphate binding to soil colloids by creating a repulsive negative electrostatic field, attributed to its high charge density within the pH range commonly found in cultivated soils [53]. Furthermore, due to its high molecular weight, HA can establish a physical shield on mineral surfaces [54–56], decreasing the specific surface area of the oxides present in the soil and, consequently, P adsorption capacity of soil [54,55].

The plots that received the application of MAP + HA + M had lower P content than the plots that received only MAP + HA, indicating that micronutrients supplied in the same P granule (MAP + HA + M) can contribute to reducing P content in the soil (Fig. 3a). However, the effect of HA on P availability and the response of plants depends on the interaction with other elements, mainly cationic nutrients in the soil [57,58]. The reduction in soil P content may have occurred due to the interaction of P+ micronutrients, with the formation of P-metal-HA complexes [10,19,59]. However, the reduction was not important in

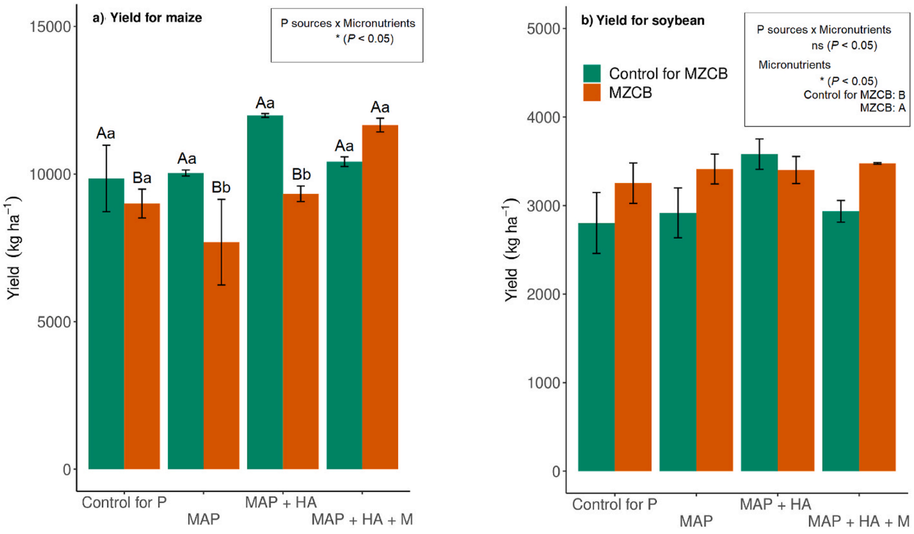

**Fig. 4.** Maize (a) and soybean (b) yields as a function of P sources: MAP (monoammonium phosphate), MAP + HA (MAP coated with humic acid), MAP + HA + M (B, Mn, Zn, and Cu) and forms of micronutrient supply (B, Mn, Zn, and Cu - MZCB). The averages followed by the same capital letter for source of P and the same lowercase letter for micronutrients do not differ statistically by the Scott-Knott test (*$P < 0.05$). Vertical lines represent mean standard deviation.

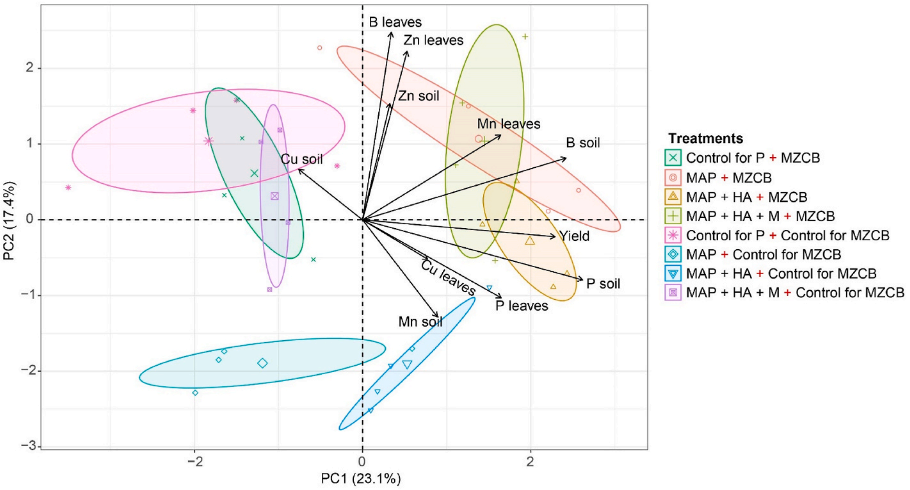

**Fig. 5.** Principal Component Analysis for yield, P, Zn, Cu, B and Mn in soil and leaves of soybean after cultivation in Typic Hapludox fertilized with: MAP (monoammonium phosphate), MAP + HA (MAP coated with humic acid), MAP + HA + M (MAP coated with humic acid, B, Mn, Zn and Cu) and Mn, Zn, Cu and B supply (MZCB).

practical terms, as both plots remained with high P content in accordance with regional standards [38].

When there was no P supply or when MAP or MAP + HA + M were applied together with the micronutrient supply (MZCB), there was an increase in P content in the soil (Fig. 3) possibly due to the effect of micronutrients on the growth and development of plant roots and shoots. With greater root growth, there is an increase in the release of root exudates and the formation of P complexes in the soil, increasing P availability [57,60,61].

### *4.2. Crop yield and nutrients in soybean*

The increase in P content in the soils that received MAP coated with HA corroborates previous studies [62]. However, the P concentration in soybean leaves did not increase in plants receiving MAP covered with HA compared to MAP alone (Fig. 3) as expected. The use of HA can improve plant P uptake [21] through direct and indirect effects. HA can interact directly with plant cells, acting as a plant biostimulant, improving the $H^+$-ATPase of the plasmatic membrane, stimulating high-affinity transporters in roots, and when used, improving P uptake by plants [26,27,51]. Furthermore, HA affects several physiological aspects in plants, including gene expression [63], organelle presence [22], primary metabolism [64], secondary metabolism [65], growth and development [64], flower, fruit, and seed formation [66], and interactions with biotic factors such as microbes, which may contribute to enhanced yield [67]. Possibly, the P concentration in soybean leaves was not modified by different forms of P application because the P content in the soil was not a limiting factor for soybean and maize growth according to regional standards [38]. Therefore, P concentrations in the leaves were above the critical level for soybean, i.e., above 2.8 g/kg [36,68]. Thus, future studies to evaluate the efficiency of HA-coated fertilizers should consider soils with different P availability.

Although the application of micronutrients + phosphate fertilizer (MAP + HA + M) did not increase micronutrient concentrations in soybean leaves in the present study (Fig. 3b), there is a practical advantage in providing micronutrients within an NPK granulated mixture. This application method results in greater uniformity in micronutrient distribution. As micronutrients are supplied in smaller quantities to crops than macronutrients are, better distribution avoids potential phytotoxicity issues [69]. Additionally, such mixtures in the fertilizer granule reduces costs, since both NPK and micronutrients are applied in a single operation.

In our study, regardless of the treatments, the Zn and Mn concentrations in soybean leaves were within the appropriate range for the crop (Table 3), in accordance with regional standards [36], which may be because the levels of these nutrients were initially high in the soil (Table 1), according to Sousa et al. [38]. However, the Cu and B content were initially low in the soil (Table 1), according to Sousa et al. [38]. The Cu concentrations in soybean leaves were below the appropriate range for the crop, and the B concentrations were well above the range considered ideal for the development of the crop [36], regardless of the treatments.

In a field where P content is already considered sufficient, as in our study, the addition of fertilizers can increase the nutrient content in the soil, as observed (Fig. 3a), but without necessarily increasing nutrient concentrations in leaves (Fig. 3b) or even crop yield, as observed for soybean (Fig. 4) [70,71]. However, it has been common for more nutrient-demanding crops, such as maize, to show responses in grain yields, as observed in this study and by Lacerda et al. [70], even in production fields where P content is considered adequate, according to regional standards [38].

Maize yields were also not modified by the forms of P application when there was no micronutrient supplement (MZCB). However, when micronutrients were applied, maize yields generally decreased, except when MAP + HA + M was applied in the same granule. It is possible that maize yields were reduced by excess micronutrients, especially B, whose toxicity/deficiency range is very narrow [72]. Although no visual symptoms of B toxicity or deficiency were seen, we applied 2,45 kg/ha of B, considering 2 kg/ha for maize and 0.45 kg/ha from MZCB treatment. (MZCB treatment). This amount is twice as high as the 2 kg/ha normally recommended for soil amendment [38].

## 5. Conclusion

Coating monoammonium phosphate (MAP) with humic acid (HA) increased the phosphorus content in the soil, which decreased when micronutrients were supplied in the same granule (MAP + AH + M). However, all the treatments increased P concentration in soybean leaves, without distinction among the forms of P application.

The forms of P application did not affect soybean yield, possibly because leaf concentrations were within the range considered adequate, whether P was supplied or not. However, soybean yield was normally higher when there was a micronutrient supply (MZCB). Maize yields were also not modified by the sources of P when there was no micronutrient supplement. However, when micronutrients (MCZB) were applied, maize yields generally decreased, except when the MAP + HA + M was applied in the same granule.

## CRediT authorship contribution statement

**M.O.T. de Ávila:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **S.G. Moreira:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **F.R.D. Lima:** Writing – review & editing, Writing – original draft. **G.V. Pimentel:** Writing – review & editing, Methodology. **J.R. Macedo:** Writing – review & editing. **M.R. Nunes:** Writing – review & editing. **L.B.W. Gomes:** Writing – review & editing, Methodology. **E.G. Morais:** Writing – review & editing.

## 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.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jafr.2024.101318.

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