APPLICATION OF MICRONUTRIENTS AS P-FERTILIZER COATINGS FOR PRECISION DISTRIBUTION IMPROVES NUTRIENTS USE EFFICIENCY IN SOYBEAN CROP ENVIRONMENT

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Abstract

Problems related to the uniform distribution of micronutrients and their low use efficiency are common. One possible solution is to add micronutrients as fertilizer coating. However, it is necessary to comprehend the use of micronutrients applied via coating and their nutrition in the phenological stages of soybean. Therefore, the objectives of this study were to quantify the diffusion and the availability of P, B, Cu, Mn, and Zn in soil after the incubation of fertilizers coated with micronutrients, as well as to evaluate the nutrition, yield, and recovery of nutrients at different soybean phenological stages under controlled and field conditions. The treatments were MAP and NPS coated with Maxxi-Phós® polymer and one of the micronutrient sources: Wolftrax®, Microsol®, or MIB Precise®. The P-diffusion ranged from 5.58 to 18.88 mm. The nutrient recovery varied according to the phenological stage of the plants with emphasis on the V4 stage, which resulted in the following recoveries: B (13.89 to 0.65%), Cu (62.84 to 6.73%), Mn (3.36 to 0.73%), Zn (2.34 to 0.01%). Nutrient exports by soybean were: 55.7 kg ha-1, 209.6, 109, 216.7, and 64.3 g ha-1 of P2O5, B, Mn, Zn, and Cu, respectively. Under field conditions, there was a significant absorption of B, Mn, and Zn at stages R1 to R5.1, while for Cu it was between V4 and R1. The NPS + MIB Precise® fertilizer showed lower accumulations and yield, indicating lower solubility of micronutrients supplied via oxysulfate. The technologies were able to replace the exported nutrients by the soybean.

1. INTRODUCTION

Micronutrient deficiency in the soil is observed globally and plant symptoms vary according to the element (; As a result, the absorption of micronutrients by the crops becomes limited in cultivated areas given the high rates of nutrient removal, which combined with inadequate fertilization, jeopardizes crop production. Annual micronutrient removal can vary between 0.01 and 4.9 kg ha^{-1} depending on the crop and the element . Nevertheless, most crops demand 0.1 to 100 mg kg^{-1} of a determined micronutrient . Despite the low requirements, amounts of micronutrients extractable by DTPA in the soil vary between < 1 to > 90 mg kg^{-1} and, therefore, most soils are not able to provide adequate amounts to the crops . Therefore, it is necessary to adequately replenish the micronutrients to ensure the crops' demands.

Micronutrient provision is not directly related to increased yield but reflects in plant responses to biotic and abiotic stresses . Several studies report crop responses to diseases depending on the application or presence of zinc (Zn), manganese (Mn), copper (Cu), nickel (Ni), and boron (B. Other studies report the mitigation of effects caused by unfavorable environmental conditions and indicate that micronutrient deficiency can directly and/or indirectly influence the susceptibility of plants to environmental stresses . Therefore, plant nutritional balance reflects on its ability to withstand biotic and/or abiotic stresses.

Micronutrient fertilization must be done consciously considering the 4R management practices: right nutrient source at the right rate, right time, and right place. Considering sustainability goals, high yields must be associated with the optimization of the production in the area and the right resource management. Micronutrients can be applied via soil, foliar fertilization, and seed and plantling treatments . Soil applications aim at increasing the element concentration in the soil solution for root uptake with high use efficiency . For nutrients such as B, Cu, and Zn it is preferable that the supply is made via soil . However, it can be difficult to perform a uniform distribution of micronutrients in the area due to the low amounts required. Another concern is the low use efficiency of fertilizers, commonly less than 5 %

Considering all this, it becomes crucial to develop ways to improve the application and efficiency of micronutrient fertilizers. A viable solution is the application along with the macronutrients, such as nitrogen (N), phosphorus (P), and potassium (K), by mixing the elements with the granules or coating the NPK . Granule coating is generally done by spraying the elements as finely grounded powder into the granules coated with a binding agent to promote adherence. Advantages include consistent adherence to the granules, reduction in application costs, and facilitated transportation, application, and handling . Therefore, the use of micronutrient-coated NPK can increase yield and improve the nutritional quality of beans.

The application of micronutrients via soil can provide the elements faster to the plants and tends to be more effective for a longer period than foliar fertilization. However, it is necessary that the sources solubilize in time and that they be applied in a favorable position since micronutrients are not mobile in the soil . Soybean plants usually respond positively to the application of B, Cu, Mn, and Zn. However, studies about the effects of micronutrients on soybean are scarce and, therefore, studying nutrient accumulation according to the phenological stages becomes essential for recommending fertilizers that meet the needs of the crop. In addition, it is important to know the minimum amounts that must be returned to the soil to maintain soil fertility.

Considering that fertilizers coated with micronutrients can improve supply and distribution and even replenish micronutrients stocks in soils, the objective of this study was to characterize the NPS and monoammonium phosphate (MAP) fertilizers coated with the Maxxi-Phós® polymer and the micronutrients sources Wolftrax®, Precise®, and Microsol®. In addition, we quantified the diffusion of P, the availability of B, Cu, Mn, and Zn, and the nutrition and yield of soybean in both controlled and field conditions. We hypothesized that these technologies could influence the P dynamics as well as efficiently provide micronutrients to soybean plants. To test this hypothesis, MAP and NPS fertilizers coated with the polymer and the micronutrient sources were characterized for the availability, diffusion, and mobility of P, B, Cu, Mn, and Zn in laboratory conditions, while soybean nutrition and yield were evaluated in controlled and field trials.

2. MATERIAL AND METHODS

2.1 Controled conditions assays – laboratory

The experiment was carried out in the Laboratory of Fertilizer Technologies, in the Soil Science Department of the Universidade Federal de Lavras (UFLA), Minas Gerais state, Brazil. The treatments consisted of the 11 phosphate fertilizers descripted in Table 1. MAP was used as control.

Table 1. Description of the treatments and the fertilizers

Fertilizer	Description	Nutrient concentration
MAP	*Conventional MAP*	52% P_2O_5; 11% N
MAPSP	*MAP + Sulfurgran® + Maxxi-Phós®*	40% P_2O_5; 10% N; 9% S
MAPSPW	*MAP + Sulfurgran® + Maxxi-Phós® + Wolftrax®*	40% P_2O_5; 10% N; 9% S; 0.15% B and Cu; 0.45
MAPSPP	*MAP + Sulfurgran® + Maxxi-Phós® + MIB Precise®*	40% P_2O_5; 10% N; 9% S; 0.15% B and Cu; 0.45
MAPSPM	*MAP + Sulfurgran® + Maxxi-Phós® + Microsol®*	40% P_2O_5; 10% N; 9% S; 0.15% B and Cu; 0.45
NP	*NPS + Maxxi-Phós®*	40% P_2O_5; 10% N; 9% S
NPW	*NPS + Maxxi-Phós® + Wolftrax®*	40% P_2O_5; 10% N; 9% S; 0.05% B and Cu; 0.15

Fertilizer	Description	Nutrient concentration
NPP	*NPS + Maxxi-Phós® + MIB Precise®*	40% P_2O_5; 10% N; 9% S; 0.15% B and Cu; 0.45
NPM	*NPS + Maxxi-Phós® + Microsol®*	40% P_2O_5; 10% N; 9% S; 0.15% B and Cu; 0.45
NPW2	*NPS + Maxxi-Phós® + Wolftrax®*	40% P_2O_5; 10% N; 9% S; 0.10% B and Cu; 0.30
NPW3	*NPS + Maxxi-Phós® + Wolftrax®*	40% P_2O_5; 10% N; 9% S; 0.15% B and Cu; 0.45

Detailed information about the components of each fertilizer is described below.

*MAP***:** Monoammonium phosphate is a commercial granular fertilizer widely used in the industry obtained after treating ammonia with phosphoric acid. Usually contains 50 to 54 % of P_2O_5 and 10 to 12 % of nitrogen (N).

*NPS***:** It is a granular fertilizer containing N, P, and S in the same granule, with 42 % of P_2O_5, 10 % of N and 10 % of sulfur (S). The NPS fertilizer was initially introduced by the Ministry of Agriculture of Ethiopia to replace the diammonium phosphate (DAP), since the use of DAP and urea in the country did not satisfy the needs of the crops .

Maxxi-Phós® **polymer:** This technology consists of anionic polymers and humic substances which, according to the manufacturer, can reduce P fixation into the soil, promoting greater release and availability of P to the crops .

Microsol®**:** This technology supplies B, Zn, Cu, and Mn in completely soluble forms. Granules provide a gradual release of nutrients into the soil, thus not being fully available when applied. B is provided as boric acid and the other micronutrients are provided as sulfates (Cu, Mn, and Zn).

Sulfurgran ®**:** This technology is composed of approximately 90 % of elemental sulfur (S^0) as pellets to ensure a gradual release. In this work, it was used only in treatments containing MAP as a physical mixture of granules (ICL America do Sul).

MIB Precise ®**:** Technology composed of powder oxysulfates. It is coated onto MAP using an adhesive polymer

Wolftrax ®**:** According to the manufacturer, *Wolftrax* ® is a finely grounded source of micronutrients with a large surface area, being used to coat fertilizers in a dry application. Nutrients are provided as part soluble and part insoluble to ensure an immediate release and a release throughout the crop cycle. The source of the elements are as follows: B as boric acid, disodium octaborate tetrahydrate, and potassium tetraborate tetrahydrate; Cu as Cu oxide and Cu sulfate pentahydrate; Mn as Mn sulfate and Mn oxide; and Zn as Zn oxide and Zn sulfate monohydrate (.

2.1.1 P diffusion

P diffusion was evaluated by capturing the diffusible P in filter paper soaked with iron oxide . The experiment was set up in a completely randomized design, with 4 replicates, 10 treatments and 1 control. Petri dishes were filled with soil samples collected in the municipality of Lavras, Minas Gerais state, Brazil. The soil was incubated in BOD chambers at 25 °C at 70 % of field capacity. The plates were opened at 1, 3, 6, 12, and 24 hours, and 3, 7, 14, and 28 days after the fertilizer application to evaluate the P diffusion. The filter papers were then scanned, and the mirror image of the diffusion zone was determined using the imaging software GNU (Image Manipulation Program – GIMP) to quantify the extent and intensity of the diffusion zone.

2.1.2 Micronutrients movement

To assess the micronutrient movement, 500 mg of each fertilizer was placed in the center of Petri dishes filled with the same soil also at 70 % of field capacity. The dishes were incubated in BOD chambers at 25 °C. The soil was collected at 7, 14, and 28 days after adding the fertilizer with cork borers in three concentric zones and airflow-dried at 60 °C. Nutrients were extracted by Mehlich-1 and nutrient availability was determined by inductively coupled plasma atomic emission spectrometry (ICP – METES model FME16). Only the fertilizers that contained micronutrients in the composition were used in this test (MAPSPW, MAPSPP, MAPSPM, NPW, NPP, NPM, NPW2, and NPW3, as described in Table 1).

2.1.3 Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

Scanning electron microscopy (SEM) was used to observe the fertilizer granules. The granules were cut with a scalpel, placed on aluminum stubs, and covered with a carbon evaporator (model Union CED 020). The EDS coupled to the SEM microscope allowed us to obtain the qualitative elemental composition of the phosphate fertilizers under study.

2.2 Greenhouse experiment

2.2.1 Soybean sowing and fertilization

The experiment was conducted in a greenhouse located at the Soil Science Department of the Universidade Federal de Lavras (UFLA). The soil collected in Lavras, Minas Gerais state, Brazil, was classified as Latossolo Vermelho distroférrico (with a clayey texture. The chemical and granulometric characterization are displayed in Table S1.

A completely randomized experiment in a 9 × 2 factorial scheme with 9 treatments (including a control without P application) and three replicates was designed. For this test, only treatments NPW2 and NPW3 were not included. The soil was previously limed with calcium and magnesium carbonate at a 3:1 rate (Total neutralizing power of 200.68 %) to ensure the desired base saturation. Incubation was carried out for 60 days at 80 % field capacity. After incubation, the soil was fertilized with 300 mg kg^{-1} of P and N, 0.1 mg kg^{-1} of Mo, and 5 mg kg^{-1} of Fe, using potassium chloride, ammonium molybdate, iron nitrate, and ammonium nitrate (dissolved in water). The elements P, B, Cu, Zn, and Mn were provided via the fertilizers tested. For the MAPSP and NP treatments, the same amounts of micronutrients contained in the other treatments were applied using soluble sources. The control treatment did not receive fertilization. Pots were sowed with six soybean (*Glycine max*) seeds, cultivar 95R90IPRO, from Pioneer®. Sixteen days after emergence, plants were thinned to two plants per pot and kept until stages V6-R1 (flowering) when they were harvested for the analyses.

2.2.2 Agronomical variables assessed: *plant dry mass, nutrient accumulation, and nutrient recovery*

Plants were divided into shoots (leaves and stems) and roots and air-dried at 60 °C. A nitric-perchloric digestion (Tedesco et al., 1995) was done and micronutrient concentrations were determined by ICP-OES (ICP-METES model FME16). Nutrient accumulation was determined by multiplying the plant's dry mass by the element concentration. Nutrient recovery was determined according to the formula (1):

$$Recovery = [(mg\ of\ the\ accumulated\ nutrient\ in\ the\ plant - mg\ of\ the\ nutrient\ acumulated\ in\ the\ control) \div dose\ of\ the\ nutrient\ applied\ for\ each\ pot] \times 100$$

2.3 Field experiment

2.3.1 Experimental area characterization

The experiment was conducted at the Palheta farm, located in the municipality of Ingaí, Minas Gerais state, Brazil, in the 2019/2020 crop season. Table S2 presents the results of granulometric and chemical analysis of the soil in the area.

2.3.2 Experimental design

A randomized block design with 7 treatments (NP, NPW, NPW2, NPW3, NPP, NPM, and a control without fertilization) and 4 blocks was used. The experimental plots consisted of 6 sowing lines of 24 m spaced at 0.6 m with the 4 central lines considered as useful area. Lines 2 and 5 were used to harvest plants at stages V4, R1, R5.1, and R6, and lines 3 and 4 were used to assess yield.

2.3.3 Soybean sowing and fertilization

Seeds of soybean cultivar 95R90IPRO (Pioneer®) were sown to reach 316.600 plants ha^{-1}. Fertilization was done with 185 kg ha^{-1} of potassium chloride and 250 kg ha^{-1} of each treatment. Both sowing and fertilization were done mechanically.

2.3.4 Agronomical variables assessed

2.3.4.1 Plant dry mass, nutrient content, and nutrient accumulation at different phenological stages

Plants were assessed at phenological stages V4, R1, R5.1, and R6 . Determinations of plant dry mass and nutrient content (in stem, leaves, roots, and pods/beans) were done to track the absorption march of B, Zn, Cu, and Mn during the crop cycle. Plant dry mass and nutrient accumulation were obtained as described previously.

2.3.4.2 Soybean yield

Soybean harvest was done 128 days after sowing (R8). Yield determination was done by harvesting the beans of plants in 2 m of the two central lines (totaling 4 m). After harvesting, bean moisture was determined with a portable moisture meter (Gehaka Agri G600i). Bean moisture was adjusted to 13 % and the amount was converted to kg ha^{-1}.

2.4 Statistical analyses

Statistical analyses were performed using the R statistical software . The data were submitted to analysis of variance (ANOVA), and the comparisons were performed through the Scott-Knot test (p [?] 0.05), using the *emmeans* package.

3. RESULTS

3.1 Laboratory assays

3.1.1 P diffusion

The diffusion radius (mm) of each fertilizer is displayed in Table 2. There was a significant interaction with the P diffusion (p [?] 0.05). After the first hour, MAPSP (14.18 mm) and MAPSPM (15.81 mm) fertilizers stood out and after 3 hours, only MAPSPM (17.18 mm) stood out. The diffusion was more expressive 6 hours after the incubation, evidencing MAPSW (15.42 mm) and MAPSPM (18.88 mm) fertilizers, with the latter having the highest mean observed. After 12 hours, the diffusion between the fertilizers had no differences. During the experiment, a reduction followed by stability in P diffusion was observed by the intensity of the color on the filter papers (Figure 1) and by the diffusion radius obtained (Table 2). Despite being conducted for 28 days, it was not possible to capture the diffusion of P up to the 28th day (Figure S18) and, therefore, we only considered the results up to the 14th day after the incubation of the fertilizers.

Table 2. Diffusion radius (mm) of the phosphate fertilizers along the incubation period (hours)

Treatment/ hours	1	3	6	12	24
	Diffusion radius (mm)	*Diffusion radius (mm)*	*Diffusion radius (mm)*	*Diffusion radius (mm)*	*Di*
MAP	7.63 Ac	8.56 Ac	11.13 Ab	10.15 Aa	8.9
MAPSP	14.18 Aa	12.44 Ab	11.76 Ab	11.77 Aa	13
MAPSPW	11.14 Bb	13.00 Ab	15.42 Aa	10.35 Ba	13
MAPSPP	10.45 Ab	10.70 Ac	10.71 Ab	13.52 Aa	11
MAPSPM	15.81 Ca	17.18 Aa	18.88 Aa	13.09 Ca	14
NP	12.72 Ab	10.52 Ac	12.61 Ab	10.61 Aa	10
NPW	12.12 Ab	10.26 Ac	12.31 Ab	11.47 Aa	8.6
NPP	6.99 Ac	8.93 Ac	11.49 Ab	9.85 Aa	9.9
NPM	7.44 Bc	7.17 Bc	10.19 Ab	10.91 Aa	9.1

Treatment/ hours	1	3	6	12	24
NPW2	5.58 Bc	10.50 Ac	9.61 Ab	9.48 Aa	10
NPW3	6.65 Bc	13.58 Ab	13.02 Ab	11.26 Aa	10

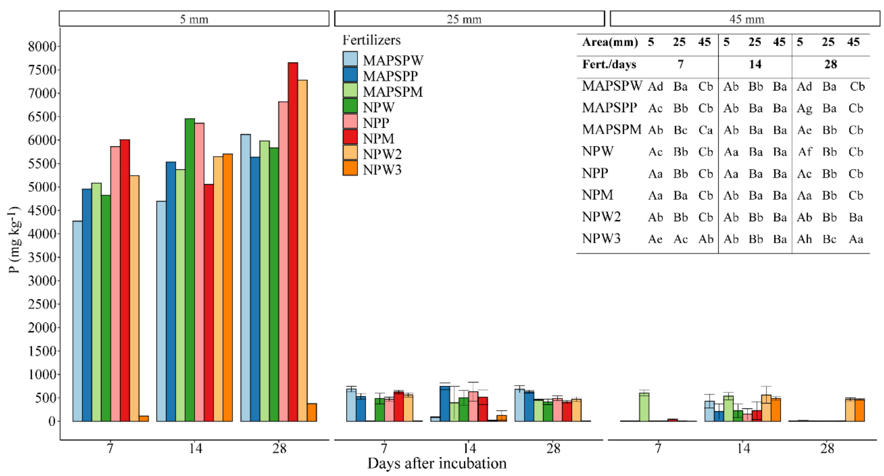
Means followed by the same letter (lowercase for the columns and uppercase for the lines) do not differ according to the Scott-Knott test (p [?] 0.05).

3.1.2 P and micronutrients movement

Concentric zones in the soil placed in the Petri dishes were collected at 7, 14, and 28 days to evaluate the movement of P, B, Cu, Mn, and Zn. Significant interactions (*p [?]* 0.05) were observed for the interaction between the fertilizers and the zones. Despite the incubation time and the fertilizer used, the presence of P was pronounced where the granules were deposited (5 mm) with a significant decrease in the following areas (25 and 45 mm). Overall, the availability of P followed the sequence 5 mm > 25 mm > 45 mm.

Since the main availability of P was observed exclusively in the 5 mm area, the patterns for this region were observed (Figure 1). After 7 days of incubation, NPP and NPM fertilizers showed the highest availability of P. After 14 days, the NPW and NPP fertilizers stood out and after 28 days, the NPM fertilizer had the highest P release. NPW3 fertilizer, however, did not release P up to the 7thday, but it had considerable P availability at 14 days and returned to almost no available P after 28 days of incubation.

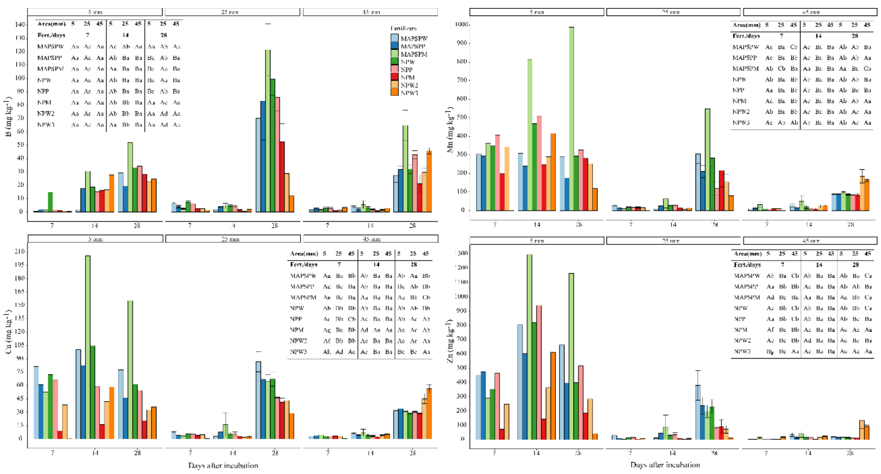
Figure 1 . P availability in three concentric zones after the incubation of the treatments for 7, 14, and 28 days. Lowercase letters indicate comparisons in the column and uppercase letters indicate comparisons in the line according to the Scott-Knott test (p [?] 0.05). Vertical bars indicate the standard error (n = *4*).



The availability of B, Cu, Mn, and Zn varied depending on the incubation time, region, and micronutrient evaluated. Regarding Cu availability, the MAPSPW fertilizer stood out, followed by NPW in the 5 mm and 25 mm regions, while MASPP and MAPSPM stood out in the 45 mm region. After 14 days, the availability remained more expressive in the region of 5 mm, especially for the MAPSP fertilizer. After 28 days of incubation, the availability of Cu was uniformly distributed over the area of the dishes, highlighting MAPSM in the 5 mm region, MAPSPW in the 25 mm region, and NPW2 and NPW3 in the 45 mm region.

B availability was not expressive up to the 7th day of incubation but it was more significant after 14 days in the 5 mm region, with emphasis on the NPW3 and MAPSPM fertilizers. After 28 days of incubation, we observed an increase in the availability of B with consequent distribution across the evaluated regions being more expressive in the region of 25 mm. MAPSPM and NPW showed the highest B availabilities in this period.

Figure 2 . B, Cu, Mn and Zn availability in three concentric zones after the incubation of the treatments for 7, 14, and 28 days. Lowercase letters indicate comparisons in the column and uppercase letters indicate comparisons in the line according to the Scott-Knott test (p [?] 0.05). Vertical bars indicate the standard error ($n = 4$).



Mn had expresive availability only in the 5 mm region and after 7 and 14 days of fertilization with NPP and MAPSPM, respectively. However, after 28 days of incubation, a greater availability was observed between the 5 and 25 mm regions especially with MAPSPM fertilizer.

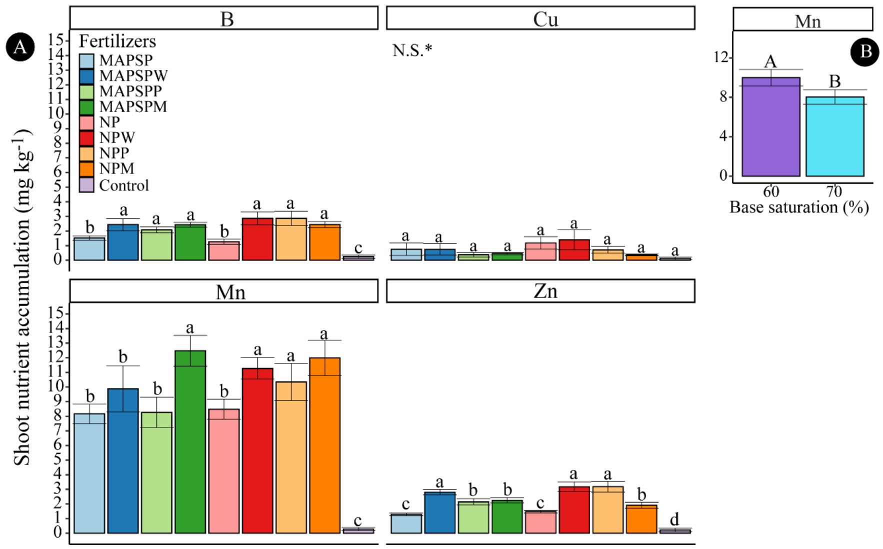
For Zn, the availability was more relevant in the 5 mm region for the fertilizers MASPP and NPP (7 days) and MAPSPM (14 days). After 28 days, only MAPSPM was expressive in the 5 mm region and a small increase in availability was observed in the subsequent 25 mm region.

3.2 Greenhouse experiment

3.2.1 **Nutrient accumulation**

The interaction between base saturation and fertilizers had no significant effect (p *[?]* 0.05) on the accumulation of micronutrients in the shoot (Figure 3). B accumulation was similar among the fertilizers, except for MAPSP and NP, both with lower accumulation. For Mn, fertilizers MAPSP, MAPSPW, and NP had the lowest accumulation. In addition, Mn was more accumulated in the plants under 60 % base saturation. For Zn, the MAPSPW, NPW, and NPP fertilizers stood out, while MAPSP and NP showed smaller accumulations. We did not observe a significant difference in Cu accumulation. The accumulation of micronutrients in the shoots (Figure 3) and leaves (Figure S2) had similar patterns. The control treatment had the lowest element accumulation for all micronutrients.

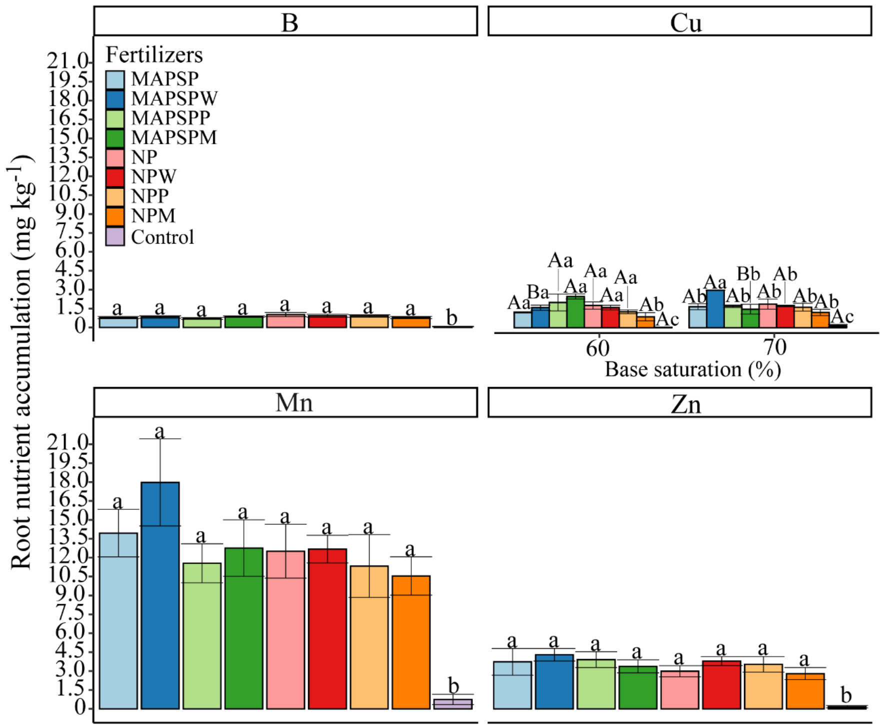
Figure 3 . Accumulation of B, Cu, Mn, and Zn in the shoots of soybean plants. A – nutrient accumulation for each fertilizer. B – Mn accumulation for different base saturation levels. Means followed by the same letter do not differ according to the Scott-Knott test (p [?] 0.05). Vertical bars indicate the standard error ($n = 4$).



Nutrient accumulation in the stem showed that B accumulation was favored by fertilizers NPW, NPP, and NPM and lowered on the MAPSP, MAPSPW, and NP treatments (Figure S3). Mn accumulation was favored by the application of MAPSPM and NPM. For Zn, MAPSP and NP showed lower accumulations. There was no significant difference in Cu accumulation. We observed a greater B accumulation when base saturation was at 70 %.

The accumulation of B, Zn, and Mn in the roots (Figure 4) was significantly influenced by the treatments. The treatments led to accumulations statistically equal to each other, differing only from the control (non-fertilized). There was an effect on the interaction between treatments and base saturation for Cu. Fertilizers showed greater accumulation at the 60 % base saturation following the order MAPSP = MAPSPW = MAPSPP = MAPSPM = NP = NPW = NPP > NPM > Control. When elevating the base saturation to 70 %, only plants fertilized with MAPSPW accumulated more Cu. In addition, MAPSPW treatment presented greater accumulation when at 70 % base saturation, while the MAPSPM was more responsive at 60 %. For the other fertilizers, the accumulation was statistically similar for the two saturations. The control treatment showed the lowest accumulation of the micronutrients.

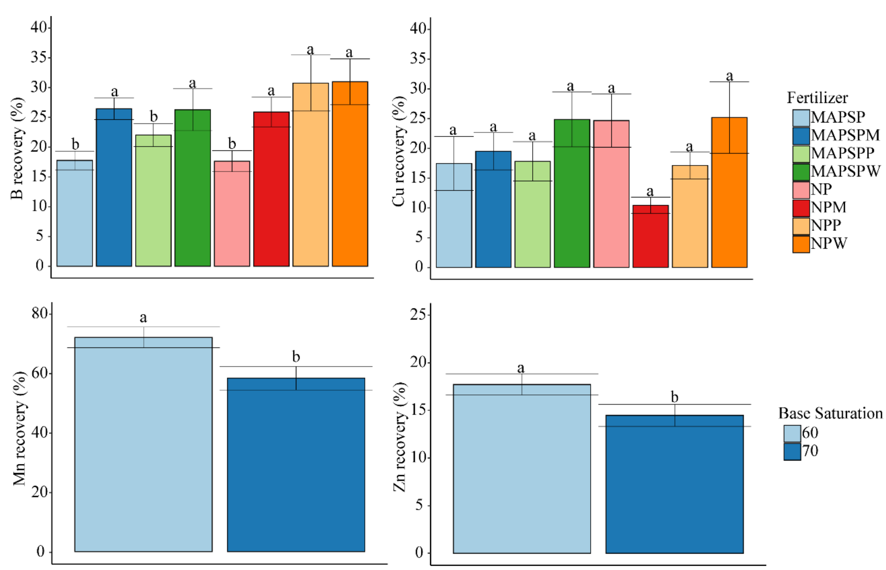
Figure 4. Accumulation of B, Cu, Mn, and Zn in the roots of soybean plants. Uppercase letters for treatment within saturation and lowercase letters for saturation within treatment compare means according to the Scott-Knott test (p [?] 0.05). Vertical bars indicate the standard error ($n = 4$).



3.2.2 Micronutrient recovery

Nutrient recovery (Figure 5) observed under greenhouse conditions varied according to the element. For B, the highest recoveries were observed on treatments NPM, MAPSPW, MAPSPM, NPP, and NPW. The application of the different fertilizers did not increase Cu recovery and the mean recovery was 19.64 %. Mn and Zn were more recovered in the 60 % base saturation level, reaching 72 % for Mn and 17 % for Zn.

Figure 5. Recovery of B, Cu, Mn, and Zn in soybean plants after the application of fertilizers coated with different sources of micronutrients and different base saturation levels. Means followed by the same letter do not differ according to the Scott-Knott test (p [?] 0.05). Vertical bars indicate the standard error ($n = 4$).



3.3 **Field experiment**

3.3.1 Nutrient accumulation

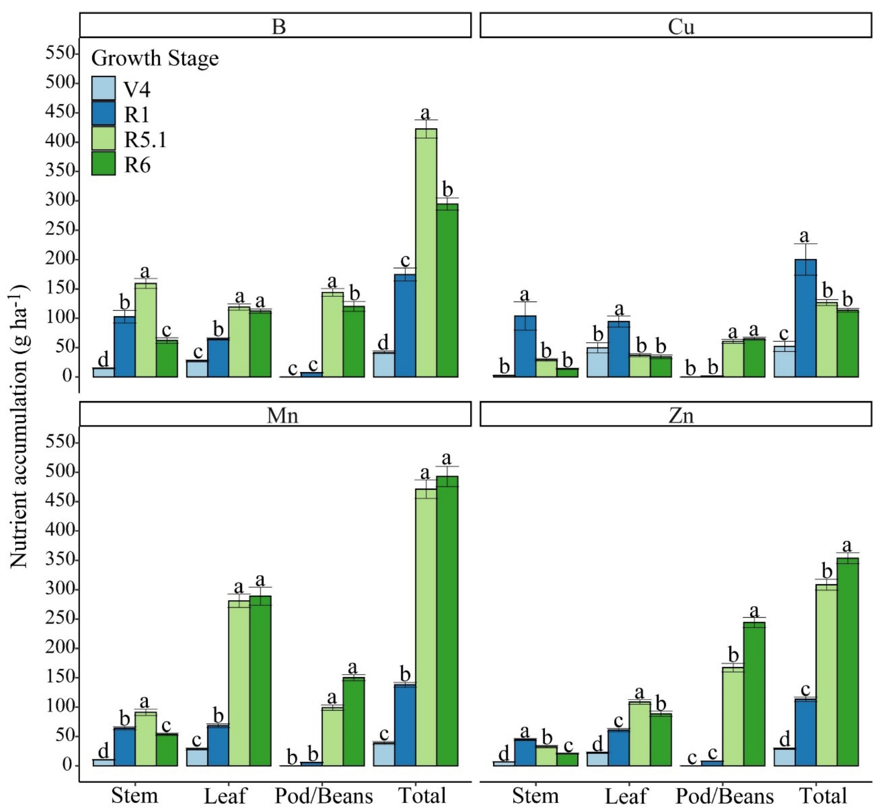
Significant differences were found in the nutrient accumulation at different phenological stages of soybean (Figure 6). The highest B accumulation was found at stage R5.1 (422.4 g ha^{-1}), despite the part of the plant. B accumulations at this stage were 159.2 g ha^{-1} in the stem, 119.1 g ha^{-1} in the leaves, and 144 g ha^{-1} in pods/beans.

The maximum accumulation of Cu in the stem and leaves was observed at stage R1 while in pods/beans were at R5.1 and R6. Mean accumulations observed at this stage were 103.6 (stem), 94.3 (leaves), and 62.9 g ha^{-1} (pods/beans). The total accumulation at stage R1 was 200.1 g ha^{-1} of Cu.

Manganese reached the highest accumulation at stages R5.1 and R6, except in the stem of the plants, which showed higher accumulation at R5.1. Mean accumulations observed were 91 (stem), 285 (leaves), and 124.6 (pods/beans) g ha^{-1}. The total accumulation at stage R6 was 492.92 g ha^{-1} of Mn.

The accumulation of Zn varied according to the part of the soybean plant. Greater accumulations were observed in the stem at the R1 stage (44.6 g ha^{-1}), leaves at stage R5.1 (108.7 g ha^{-1}), and pods/beans at stage R6 (244.2 g ha^{-1}). The highest total accumulation at R6 was 353.7 g ha^{-1} of Zn.

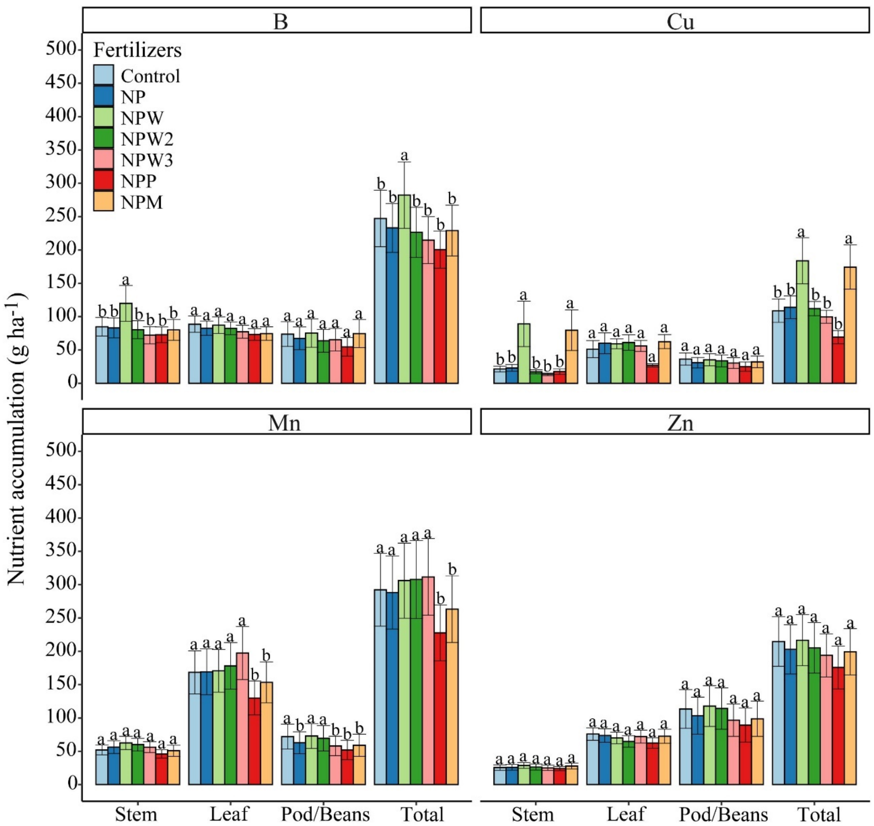
Figure 6. Accumulation of B, Cu, Mn, and Zn in soybean plants (stem, leaves, pods/beans, and whole plant) at different phenological stages of the plants. Means followed by the same letter do not differ according to the Scott-Knott test (p [?] 0.05). Vertical bars indicate the standard error ($n = 4$).



Regarding the treatments, B accumulation was different only in the stem (119.9 g ha^{-1}) and total accumulation (282.3 g ha^{-1}) for the NPW fertilizer. For Cu, differences were found for stem and total accumulation for the fertilizers NPW and NPM. Cu accumulations in the stem were 89.13 (NPW) and 79.67 (NPM) g ha^{-1} of Cu and total accumulations were 183.7 (NPW) and 174.3 (NPM) g ha^{-1} of Cu.

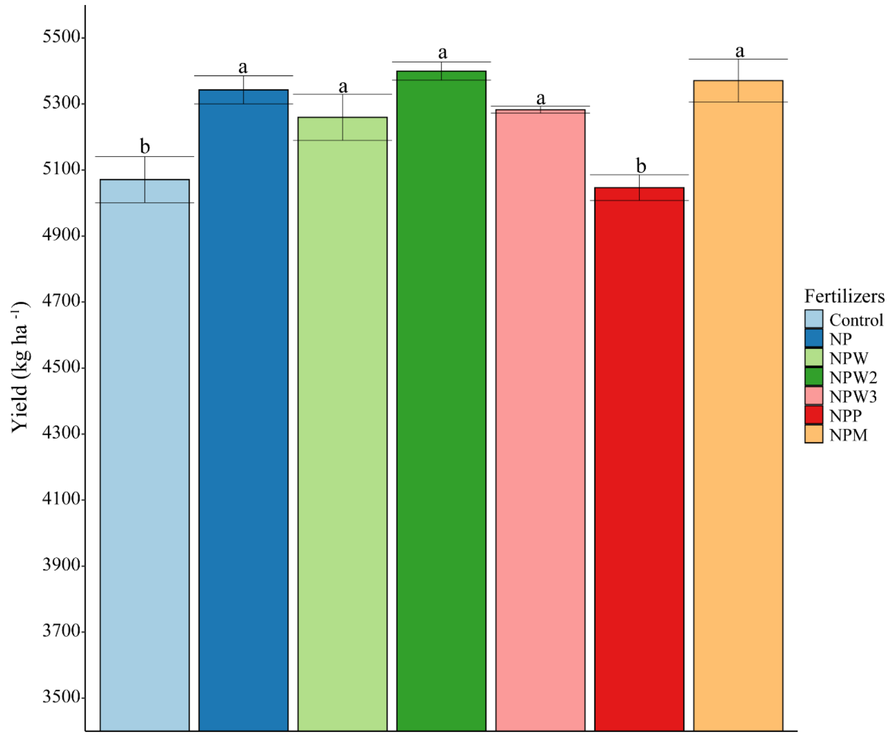
The accumulation of Mn showed statistical differences for the treatments in the leaves, pods/beans, and total accumulation. Accumulation of Mn in the leaves was superior with the treatments control (168.4 g ha^{-1}), NP (169.2 g ha^{-1}), NPW (170.6 g ha^{-1}), NPW2 (178.2 g ha^{-1}), and NPW3 (197.4 g ha^{-1}). The accumulation of Mn in the pods/beans were superior with the treatments NPW (72.8 g ha^{-1}), NPW2 (69.5 g ha^{-1}), and control (71.9 g ha^{-1}). The total accumulation of Mn in the plants was higher with the treatments control (292.3 g ha^{-1}), NP (288.2 g ha^{-1}), NPW (306 g ha^{-1}), NPW2 (307.7 g ha^{-1}), and NPW3 (311.6 g ha^{-1}). There was no difference in the accumulation of Zn among the treatments and the mean accumulation was 201 g ha^{-1} of Zn.

Figure 7. Accumulation of B, Cu, Mn, and Zn in soybean plants (stem, leaves, pods/beans, and whole plant) with the application of different fertilizers. Means followed by the same letter do not differ according to the Scott-Knott test (p [?] 0.05). Vertical bars indicate the standard error ($n = 4$).



The maximum yield (Figure 8) was obtained with the application of the NPW2 fertilizer (5399.7 kg ha^{-1}) while the lowest yield was obtained with NPP (5040.4 kg ha^{-1}). The mean difference between these two treatments (262.65 kg ha^{-1}) represents a 5.19 % increase in yield.

Figure 8. Yield (kg ha^{-1}) of soybean plants cultivated with different phosphate fertilizers. Means followed by the same letter do not differ according to the Scott-Knott test (p [?] 0.05). Vertical bars indicate the standard error (n = 4).



3.3.2 Nurient recovery

Overall, we observed greater nutrient recoveries at stages V4 and R1 (Table 3) following the sequence Cu > B > Mn > Zn. In general, the NPP fertilizer had the lowest nutrient recovery, while NPW and NPW2 had the highest recovery values. The highest recoveries were observed for stage V4 and followed the following decreasing order:

I) Cu: NPW > NPW2 > NPM > NPW3 > NPP

II) B: NPW > NPW2 > NPW3 >NPP > NPM

III) Mn: NPW > NPW2 > NPW3 > NPM > NPP

IV) Zn: NPW > NPW3 > NPW2 > NPM > NPP

Nutrient recovery at stages R1 and R6 was mostly negative. At stage R5.1, however, nutrient recovery followed the decreasing order:

I) Cu: all recoveries for Cu were negative

II) B: NPW > NPW2 > NPW3 > NPM (negative) > NPP (negative)

III) Mn: NPW > NPW2 > NPW3 > NPM (negative) > NPP (negative)

IV) Zn: NPW > NPW2 > NPW3 > NPM > NPP (negative).

Table 3. Recovery of Cu, Mn, Zn, and B from soybean plants after the application of the NPS fertilizer coated with different sources of micronutrients

Treatment	**Stage**	**Cu**	**Mn**	**Zn**	**B**
		%	%	%	%
NPW	V4	62.84	3.36	2.34	13.89

Treatment	Stage	Cu	Mn	Zn	B
NPW2	V4	38.05	2.66	0.67	9.39
NPW3	V4	11.31	1.31	1.14	5.55
NPP	V4	6.73	-0.73	0.01	3.21
NPM	V4	19.3	0.13	0.47	0.65
NPW	R1	197.88	-0.9	-4.06	74.93
NPW2	R1	-21.59	-1.13	-2.99	-2.9
NPW3	R1	-13.41	-0.43	-1.73	-6.39
NPP	R1	-33.12	-1.85	-2.62	0.17
NPM	R1	54.54	-2.33	-1.67	-1.5
NPW	R5.1	-6.94	29.17	16.5	107.2
NPW2	R5.1	-4.45	9.59	5.74	10.37
NPW3	R5.1	-8.40	7.16	1.1	0.16
NPP	R5.1	-13.47	-9.32	-4.19	-25.49
NPM	R5.1	-2.97	-1.29	2.23	-6.21
NPW	R6	-25.7	-4.4	-0.86	-51.03
NPW2	R6	-23.04	-0.65	-2.31	-33.66
NPW3	R6	-7.82	0.08	-4.56	-23.04
NPP	R6	-10.82	-9.76	-3.7	-16.81
NPM	R6	-9.46	-5.59	-3.14	-1.45

4. DISCUSSION

4.1 Laboratory assays

4.1.1 P diffusion

A proper characterization of fertilizer coatings is important to improve industrial production and innovation. The diffusion of P is a fundamental characteristic of phosphate fertilizers that can be altered when the fertilizer is coated. Therefore, we assessed the P diffusion of the coated fertilizers used in this work. Regardless of the technologies used for MAP or NPS fertilizers, there were no significant effects on P diffusion. After 12 hours of incubation, all fertilizers reached similar diffusion rates to conventional MAP, followed by stability in P diffusion. Similar results were observed by Nunes et al. (2022), using MAP coated with organic substances, Zn, and B or Mg.

4.1.2 Nutrients movement

The movements of P and micronutrients were observed after incubation of the fertilizers for 28 days. An expressive P availability was observed in the region where the granules were deposited (5 mm) with a significant reduction in the subsequent areas (25 and 45 mm), regardless of the incubation time. The literature also reports similar patterns found in this work . In addition, the lower movement of P can be explained by a combination of adsorption reactions between P and soil colloids and its low movement, mainly by diffusion .

Regarding the micronutrient availability, despite a prominent presence in the 5 mm region, B was widespread along the entire Petri dish after 28 days of incubation probably because of its high mobility in soils. In addition, the greater availability after the incubation was probably due to a combination between a gradual release and the solubility of the element sources used in the coating, meaning that the B was not immediately solubilized.

Fertilizers with the technologies Precise®, Microsol®, and Wolftrax® showed different nutrient availabilities and results are probably related to the solubility of the sources of the elements B, Cu, Mn, and Zn. According to the manufacturer, MIB Precise® technology (present in MAPSPP and NPP fertilizers) provides micronutrients in the form of oxysulfates synthesized via partial acidulation with sulfuric acid. This technology presents a soluble fraction readily available to the plants and another unavailable part that needs to be solubilized. Therefore, at 7 days after incubation, micronutrient availability probably originated from the soluble fraction and the increase in availability with time probably indicates the beginning of the solubilization of the initially unsoluble fraction.

According to the manufacturer of Microsol® (present in MAPSPM and NPM fertilizers), the technology consists of completely soluble sources of micronutrients that are gradually released into the soil. This probably explains a generally higher availability of the micronutrients B, Cu, Mn, and Zn. Notably, the NPW3 fertilizer showed a low nutrient availability at 7 and 28 days after incubation compared to NPW and NPW2, which may be explained by the higher concentration of the Wolftrax technology in this fertilizer.

The differences between the treatments MAP and NPS (MAPSPM and NPM treatments) may be related to the core of the fertilizer granule. For instance, NPS contains S in the granule, while in MAP, the pastille S^0 is separated from the core. Differences in the pH of the core of the granule can affect the solubility of the micronutrients from the coating. However, this effect would only happen in the microregion of the granules and on short-term, thus not impairing the release of nutrients. It was possible to notice the presence of S only in the core of the NPS fertilizer (Figures S12-17).

4.2 Controlled condition assays: accumulation and recovery of micronutrients under greenhouse conditions

4.2.1 Nutrient accumulation

Soybean nutrition was evaluated on different parts of the plant according to the phenological stages. Overall, MAPSP, NP, MAPSPP, and MAPSPM treatments led to lower nutrient accumulations. MAPSPP and NP treatments accumulated less B, Mn, and Zn in the shoots (leaves and stem). These fertilizers do not have a micronutrient coating, and soluble sources of the nutrients were applied at the same concentration. Thus, the application of micronutrients via coating was capable of efficiently providing B, Mn, and Zn to the soybean plants. Regarding MAPSPP fertilizer, the lower accumulation observed can be attributed to the lower solubility of the micronutrient source, an oxysulfate. The difference observed by the lower accumulation of MAPSPP in relation to NPP was, as previously explained, in relation to the S present in the core of the NPS, which may have modified the pH or aided in the solubilization of the micronutrients present in the oxysulfate.

4.2.2 Nutrient recovery

Nutrient recovery is the percentage of determined nutrient that was applied and lately absorbed/accumulated by the soybean plants. In the greenhouse experiment, the most recovered nutrient was Mn, reaching a 72 % recovery under 60 % base saturation. This high recovery is mainly due to the low concentration of the nutrient in the soil used in the experiment. The concentrations of micronutrients in the soil are very pH-dependent. The high Mn and Zn recovered under the 60 % base saturation can be related to the pH which leads to a decrease in the presence of cationic micronutrients such as Mn and Zn in the soil solution and at the cation exchange sites. Conversely, a higher amount of liming would be needed to reach 70 % base saturation, consequently increasing soil pH. According to Lindsay, (1972), Mn availability decreases approximately 100-fold for each unity increase in pH.

The lowest recoveries of B were observed for NP fertilizers (17.63 %), MAPSP (17.76 %), and MAPSPP (22.04 %). The difference between the recoveries of these fertilizers and the others is related to the nutrient accumulation and the supply of B via soil for these sources. Regarding MAPSPP, MIB Precise technology contains oxysulfate as a source of B.

4.3 Field experiment: accumulation and export of nutrients and soybean yield

4.3.1 Accumulation and export of nutrients

To verify whether coated fertilizers were efficient in providing B, Cu, Zn, and Mn to the crop, the accumulation of these micronutrients was assessed in different parts of the plants. Notably, the NP treatment in the field experiment accumulated less micronutrients than in the greenhouse experiment. It is important to emphasize that the soil used in the pots had low amounts of B, Cu, Mn, and Zn. The application of soluble sources of these micronutrients was not sufficient to efficiently supply the nutrients to the plants when compared to the other sources.

Two reasons can explain this result. The first is related to the fact that the soil used in the field experiment may have been able to provide an adequate amount of micronutrients for the soybean since only two micronutrients had low accumulation (B and Zn). The second is related to the different conditions in which the fertilizers were applied. In controlled environments, in addition to smaller environmental variations, the plant does not remain long enough to complete its cycle.

Soybean plants accumulate nutrients in three phases. The first phase has a low nutrient absorption rate up to 30 days after emergency. Second and third phases include, respectively, a reduction in the acquisition rate between phases R2 and R5, followed by a reduction in accumulation during late reproductive growth (seed maturation) .

Plants were cultivated in the pots until R1, comprising only the first phase. It is also possible to notice that the accumulations of each micronutrient varied in the experiment under field conditions according to the absorption march of the plants (Figures S4-S7). For B, Mn, and Zn, absorption occurred more significantly between phases R1 and R5.1 followed by a constant absorption rate until phase R6. For Cu, the absorption was more significant between phases V4 and R1.

We verified that the soybean plants accumulated the micronutrients in the shoots following the sequence of Mn > B > Zn > Cu (Figure 7), as observed by . Considering the total accumulation up to the R6 stage, it was observed that the plant parts accumulated, on average:

1. Stem: B – 36.10 %; Cu – 26.9 %; Mn – 20 %; Zn – 13.05 %
2. Leaves: B – 34.8 %; Cu – 46.1 %; Mn – 60 %; Zn – 34.95 %
3. Pods/Beans: B – 29.1 %; Cu – 27 %; Mn – 20 %; Zn – 52 %

The accumulated amounts can be explained by the functions of each micronutrient in the plant. Zn plays an important role in the root system, enzymatic activation, plant tolerance to stress, synthesis of proteins, and in the formation of grains (thus the greater presence is in the pods/beans) . Cu is important in metabolism, being a component of proteins and participating in processes such as photosynthesis, respiration, control of fungal diseases, and in plant defense metabolism . B has important physiological roles, such as enzymatic activation, cell elongation, protein synthesis, pollen germination, fruit/grain formation, and yield improvement. In addition, B is considered immobile in the plant, being well distributed between plant parts . Mn is an important enzyme activator and plays a role in the production of lignin, flavonoids, indoleacetic acid, among others. Additionally, Mn actively participates in photosynthesis and the formation of chlorophyll , being more present in the leaves.

The amount of Zn applied combined with the low availability of the nutrient in the soil (Table S2) was insufficient to increase its concentration in the different parts of the soybean plant. B accumulation responded to the application of NPW fertilizer. For Cu, the application of NPW and NPM fertilizers resulted in increases in stem accumulation. For Mn, the technologies did not increase the element concentration compared to the control, but smaller accumulations were noted for NPP and NPM treatments. These patterns corroborate previously reported micronutrient availability results and are related to the solubility of the sources used in each technology.

The NPP fertilizer led to the lowest averages of accumulation for B, Cu, Mn, and Zn in the plants. The accumulation is the product of yield and content factors, and the yield in this treatment was also lower. The lower accumulation may also be related to the lower solubility of the oxysulfate sources of the micronutrients in the Precise MIB technology.

4.3.2 Soybean yield

Soybean yield, evaluated after the application of NPS fertilizer and associated technologies, showed a high yield (average of 5253.59 kg ha^{-1}, Figure 8). Soil analysis (Table S2) showed that the most limiting nutrients in the experimental area were B, Zn, and P, rated as very low or low , while Cu and Mn were rated as average availability and good availability, respectively. However, organic matter content in the area was rated as average availability (2.72 dag kg^{-1}), which might have influenced the availability of the nutrients, mainly B.

Therefore, mineralization of the organic fraction may have released the necessary micronutrients to guarantee high yields even in the non-fertilized treatment. The application of 250 kg of each treatment provided 100, 25, and 22.5 kg ha^{-1} of P_2O_5, N, and S, respectively, 1.125 kg ha^{-1} of Mn and Zn, and 0.375 kg $ha^{-1}$of B and Cu. NPW and NPW2 treatments were the exception and received (in each plot) 0.375 (Mn and Zn) and 0.125 kg ha^{-1} (B and Cu); 0.750 (Mn and Zn) and 0.250 kg ha^{-1} (B and Cu), respectively.

NPM treatment provided a 6% increase in yield in relation to the control (5399.7 and 5070.8 kg ha^{-1}, respectively). This increase cannot be necessarily attributed to the application of micronutrients since 100 kg of P_2O_5 were applied in the area. Conversely, yield of the NPP treatment was similar to the control and, as previously reported, the nutrient accumulations for this treatment were also lower. This result may be associated with the lower solubility of the micronutrients contained in the coating of the granules in this treatment. Nevertheless, the average soybean yield in this work (5253.6 kg ha^{-1}) corresponded to 1.73 times the average yield in Brazil (3029 kg ha^{-1}) . This yield corresponds to 37 bags of soybeans (60 kg) that exceed the Brazilian average (or 81 bushel of soybean). Calculating the current price (NYSE Chicago, January/23) of the soybean bushel as $15,3825 (), the average yield in this work would exceed the national average in $1246.

Yield was not negatively affected in treatments NPW and NPW2, even though they both showed lower concentration of micronutrients in relation to other fertilizers. Therefore, yield was probably more influenced by the application of P_2O_5than the amount of micronutrients provided. However, we emphasize that the advantages of providing micronutrients are related not only to yield increase, but also in relation to grain quality, plant vigor, and tolerance against pests and diseases

Regarding the NPW3 fertilizer, we did not find difference in yield even with the fertilizer showing lower availability of nutrients in the Petri dishes. The probable explanation is that the soybean crop cycle varies between 90 and 150 days, depending on the cultivar , and after 28 days, the nutrient from the fertilizer was probably released.

4.3.3 Micronutrient recovery

During the first stages (V4 and R1), some of the fertilizers showed positive nutrient recovery. Cu and B were the most recovered nutrients at these stages, despite the respective availability in the soil of the area being considered as medium and very low . For Cu, NPW and NPW2 fertilizers led to the highest observed recoveries of 62.8 and 38.05 %, respectively. However, both fertilizers had a lower concentration of micronutrients in the coating (Table 1) and probably were quickly solubilized, allowing a high nutrient absorption by the crop in comparison with the highly concentrated fertilizers.

During V4, NPM, NPW3, and NPP fertilizers showed recoveries of 19.3, 11.3, and 6.73%, respectively (Cu). Nutrient recovery from the treatment with NPP was 2.6 and 1.68 times lower than from NPM and NPW3, respectively. The low recovery on this fertilizer corroborates with the results from the previous experiments explained by the lower solubility of the oxysulfate used as a source of micronutrients.

The negative values observed for the recovery of micronutrients indicate possible exhaustion of the soil by the crop, since the control treatment presented high nutrient accumulation, surpassing even the fertilized treatments. In general, the low recoveries corroborate with the low use efficiency of the micronutrients (less than 5 %) reported in the literature . For Zn, estimates a 2 to 5 % absorption by the crop with the remainder being fixed in the soil. In addition, report that low efficiency in the use of micronutrients can result in higher production costs and negatively influence their content in the plants.

Therefore, despite a possible increase in the production cost, a way to improve micronutrients efficiency is to increase the amount of the elements in the fertilizer coating since only a low amount of the micronutrient applied is usually absorbed by the plant. Several factors can determine the micronutrient availability after contact with the soil, such as adsorption, incorporation into organic matter, leaching, pH, among others .

The low nutrient recovery may indicate the need to increase the amount of micronutrients applied to the soil in order to build soil fertility and overcome the consequent export of nutrients when harvesting the beans. The average nutrient exports by the beans were 55.7 kg ha^{-1} of P_2O_5 and 209.6, 109, 216.7, and 64.3 g ha^{-1} of B, Mn, Zn, and Cu, respectively. Similar export amounts are found in the literature. According to , soybean exports correspond to 10 kg $t^{-1}$of P_2O_5 and 20, 9.88, 29.9, and 40.26 g t^{-1} of B, Cu, Mn, and Zn, respectively. found export amounts of 22, 13, 33.7, and 37.7 g t^{-1} of B, Cu, Mn, and Zn, respectively. Noteworthy, the export of B in the present study was almost twice as high as the reported values. In addition, the export of micronutrients followed the sequence Zn > B > Mn > Cu, differing from that reported Zn > Mn > B > Cu.

The amounts of micronutrients provided via fertilizer coating were sufficient to replace the exported amount. However, there is no guarantee of ideal nutrition for the crop, especially in low-fertility areas and for the next crop to be planted. Studies demonstrate that several regions of Brazil have deficiencies of micronutrient, especially in Cerrado soils . Furthermore, it is important to highlight that even with the high yield achieved in the control treatment (without fertilizer application), there was no replacement of the micronutrients exported for this treatment.

Therefore, despite the supply of micronutrients related to the treatments being lower than recommended for the crop, its use as fertilizer coating has several advantages. The application at these concentrations can be considered as replacement fertilization corresponding to the amount of micronutrients exported by the crop. Furthermore, the difficulty in distributing micronutrients via soil is widely reported in the literature and the application via coating results in a more uniform distribution in the agricultural area , since each fertilizer granule will receive the coating containing the micronutrients.

5. CONCLUSIONS

The coating of fertilizers by the technologies did not show improvements in the diffusion of P in the soil. However, Wolftrax® technology altered the mobility and availability of P during 28 days after incubation of the fertilizers in Petri dishes.

Differences were observed between micronutrient availability in soil for MAP or NPS using MIB Precise® technology. It is presumed that the pH of the core of the granule may interfere in the short term with the solubility of micronutrients in the coating.

The accumulation of micronutrients in different parts of the plant was influenced by the fertilizers and their technologies. This difference may be related to the solubility of each source. Plants treated with MIB Precise® technology, which contains oxysulfates of Cu, B, Zn, and Mn, tend to show less accumulation of these nutrients, probably because of the lower solubility of the micronutrient sources.

The fertilizers had the same yield except for the NPP treatment, containing the MIB Precise® technology. Yield increase was approximately 6% superior in relation to the control treatment, where no fertilizers were applied. NPP treatment showed lower yield, lower accumulation of Mn, B, and Zn in the shoots (stem and leaves), and lower recovery of B in the greenhouse experiment.

The amounts of B, Zn, Cu, and Mn applied were sufficient to cover the nutrients exported by the crop harvest. However, it might be interesting to increase the amount of micronutrients since the application of micronutrients in the coating of solid fertilizers has advantages such as the reduction in the cost of application and the homogeneity of distribution of micronutrients in the area. However, the costs of the increase in the amount of micronutrients must be analyzed.

It is important to emphasize for future studies that the increase of repetitions for experiments with tests with micronutrients would be interesting, considering the difficulty of verifying their behavior in the soil due to the low rates applied.

SUPPLEMENTAL MATERIAL

The supplemental material provided is necessary for a complete understanding of this study.

REFERENCES