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TECNOLOGIAS PARA O USO EFICIENTE DE FERTILIZANTES FOSFATADOS NA SOJA:
CARACTERIZAÇÃO, APLICAÇÕES E PERSPECTIVAS INTEGRADAS

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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Ciência do Solo, área de concentração em Fertilidade do Solo e Nutrição de Plantas, para a obtenção do título de Doutor.

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TECNOLOGIAS PARA O USO EFICIENTE DE FERTILIZANTES FOSFATADOS NA SOJA: CARACTERIZAÇÃO, APLICAÇÕES E PERSPECTIVAS INTEGRADAS

TECHNOLOGIES FOR THE EFFICIENT USE OF PHOSPHATE FERTILIZERS IN SOYBEANS: CHARACTERIZATION, APPLICATIONS, AND INTEGRATED PERSPECTIVES

Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Ciência do Solo, área de concentração em Fertilidade do Solo e Nutrição de Plantas, para a obtenção do título de Doutor.

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Aos meus pais, Marina e Paulo.

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"O verdadeiro heroísmo consiste em persistir por mais um momento quando tudo parece perdido."

- W. F. Grenfel

RESUMO GERAL

Em solos tropicais, a eficiência de uso do fósforo (P) na agricultura é frequentemente prejudicada pela baixa disponibilidade do nutriente, pela presença de óxidos de ferro (Fe) e alumínio (Al) e pela acidez. Diante disso, os fertilizantes de liberação controlada (CRF) são opções viáveis para aprimorar a eficiência de uso dos nutrientes porque os liberam gradualmente, reduzindo perdas e melhorando sua disponibilidade para as plantas ao longo do tempo. Por outro lado, além da problemática com o P, esses solos muitas vezes apresentam deficiências de micronutrientes, como zinco (Zn), cobre (Cu), manganês (Mn) e boro (B), que aliados a baixa quantidade exigida pelas culturas, gera um problema de uniformidade em sua distribuição, representando assim outro desafio. Nesse sentido, o objetivo do primeiro capítulo deste trabalho foi investigar a adição de micronutrientes como revestimento em fertilizantes fosfatados, criando fertilizantes multinutrientes, os quais foram testados posteriormente na cultura da soja. Utilizando o MAP e um fertilizante NPS revestido com Maxxi-Phós®, juntamente com tecnologias como Wolftrax®, Microsol® ou MIB Precise®, os resultados indicam que a difusão de P variou de 5,58 a 18,88 mm em 336 horas. A eficiência no uso de micronutrientes variou de acordo com os estágios fenológicos da soja, com destaque para o estágio V4. As exportações de nutrientes foram: 55,7 kg de P_2O_5 ha^{-1}, 209,6 g ha^{-1} de B, 109 g ha^{-1} de Mn, 216,7 g ha^{-1} de Zn e 64,3 g ha^{-1} de Cu. No ensaio de campo, ocorreu absorção significativa ($p \leq 0,05$) de B, Mn e Zn nos estágios R1 a R5.1, enquanto para Cu, ocorreu entre V4 e R1. Os fertilizantes fosfatados revestidos com micronutrientes demonstraram a capacidade de repor os nutrientes exportados, configurando-se como uma alternativa eficaz para a fertilização multinutriente da soja. Em relação ao segundo capítulo, quatro CRFs comerciais (Agrocote® E-Max 10-48-00 e Agrocote® E-Max 09-47-00, Multicote™ Agri 4 e Multicote™ Agri 8) foram avaliados quanto às suas propriedades físicas e químicas, incluindo difusão de P, liberação de nutrientes em água, estabilidade térmica, índice de salinidade, pH, higroscopicidade e dureza. Os resultados indicam que o MAP liberou a maior quantidade de P_2O_5 no primeiro dia, enquanto o Agrocote® 10-48-00 teve maior difusão ao longo do tempo. O uso de polímeros no revestimento do fertilizante reduziu e retardou o pico do índice de salinidade, diminuiu a acidez e promoveu uma difusão contínua do fertilizante fosfatado. A liberação de nitrogênio (N) diferiu em relação à liberação de P_2O_5 nos fertilizantes, com variações em dias. O estudo destaca a importância da liberação de nutrientes em todos os índices químicos dos CRFs, destacando a possibilidade de otimização ao escolher os materiais adequados de fertilizantes e revestimento. Essas descobertas fornecem informações valiosas para o uso mais eficiente e sustentável de fertilizantes em solos tropicais, contribuindo para melhorar os rendimentos das culturas e reduzir o impacto ambiental.

PALAVRAS-CHAVES: fertilizantes fosfatados; fosfóro; liberação controlada.

ABSTRACT

In tropical soils, phosphorus (P) efficiency in agriculture is often compromised by low nutrient availability, the presence of iron (Fe) and aluminum (Al) oxides, and soil acidity. Consequently, controlled-release fertilizers (CRFs) are viable options to enhance nutrient use efficiency by gradually releasing nutrients, thus reducing losses and improving their availability to plants over time. Furthermore, apart from phosphorus-related issues, these soils frequently exhibit deficiencies in micronutrients such as zinc (Zn), copper (Cu), manganese (Mn), and boron (B). Coupled with the low quantities required by crops, this creates a challenge of uniform distribution. Thus, the primary objective of the first chapter of this study was to investigate the addition of micronutrients as coatings on phosphate fertilizers, thereby creating multinutrient fertilizers. These were subsequently tested in soybean cultivation. Utilizing MAP and an NPS fertilizer coated with Maxxi-Phos®, alongside technologies like Wolftrax®, Microsol®, or MIB Precise®, results showed phosphorus diffusion ranging from 5.58 to 18.88 mm over 336 hours. Micronutrient use efficiency varied with soybean phenological stages, particularly highlighting stage V4. Nutrient exports were as follows: 55.7 kg of P_2O_5 ha^{-1}, 209.6 g ha^{-1} of B, 109 g ha^{-1}of Mn, 216.7 g ha^{-1}of Zn, and 64.3 g ha^{-1}of Cu. In the field trial, significant absorption ($p \leq 0.05$) of B, Mn, and Zn occurred during stages R1 to R5.1, while for Cu, it occurred between V4 and R1. Micronutrient-coated phosphate fertilizers demonstrated the capacity to replenish exported nutrients, serving as an effective alternative for multinutrient fertilization of soybeans. As for the second chapter, four commercial CRFs (Agrocote® E-Max 10-48-00 and Agrocote® E-Max 09-47-00, Multicote™ Agri 4, and Multicote™ Agri 8) were evaluated for their physical and chemical properties, including P diffusion, nutrient release in water, thermal stability, salinity index, pH, hygroscopicity, and hardness. Results revealed that MAP released the highest amount of P_2O_5 on the first day, while Agrocote® 10-48-00 exhibited greater diffusion over time. Polymer use in fertilizer coating reduced and delayed the peak salinity index, decreased acidity, and promoted continuous diffusion of phosphate fertilizer. Nitrogen (N) release differed from P_2O_5 release in fertilizers, with variations over days. The study underscores the significance of nutrient release across all CRF chemical indices, highlighting optimization possibilities by selecting suitable fertilizer and coating materials. These findings provide valuable insights for the more efficient and sustainable use of fertilizers in tropical soils, contributing to enhanced crop yields and reduced environmental impact.

KEYWORDS: phosphate fertilizers; phosphorus; controlled release.

INDICADORES DE IMPACTO

Este estudo explora os impactos da adição de diferentes fontes de micronutrientes em fertilizantes fosfatados na cultura da soja em solos tropicais, destacando suas características físico-químicas e comportamento agronômico. No segundo capítulo, o foco é nos fertilizantes fosfatados de liberação controlada (CRFs), avaliando suas propriedades físico-químicas e eficácia em atender aos padrões exigidos para um fertilizante de qualidade. Os resultados revelam impactos significativos nos âmbitos social, tecnológico e cultural. A aplicação de fertilizantes fosfatados com a adição de micronutrientes mostrou-se uma prática agrícola viável, podendo não somente resultar em maiores produtividade, como também em evitar a escassez e exaustão dos solos, sendo capaz de restituir a quantidade de micronutriente exportada pela soja. Do ponto de vista social, o trabalho promove o desenvolvimento de conhecimento em relação a informação para agricultures e uma agricultura mais eficiente e sustentável. Tecnologicamente, a adoção de CRFs é capaz de diminuir o pico de salinidade e pH, enquanto tecnologias de micronutrientes como Maxxi-Phós®, Wolftrax®, Microsol® e MIB Precise® demonstraram maior eficiência na liberação e absorção de nutrientes, reduzindo perdas e mantendo a disponibilidade contínua de P e micronutrientes ao longo do tempo. Culturalmente, o estudo promoveu a conscientização e a adoção de práticas agrícolas sustentáveis, incentivando o uso de tecnologias que minimizam o impacto ambiental e promovem a sustentabilidade dos recursos naturais. Os impactos do trabalho estão alinhados com os Objetivos de Desenvolvimento Sustentável (ODS) da ONU, especialmente o ODS 2 (Fome Zero e Agricultura Sustentável), ODS 12 (Consumo e Produção Responsáveis) e ODS 15 (Vida Terrestre), promovendo práticas que aumentam a produtividade e a sustentabilidade ambiental. Este estudo fornece informações para o uso mais eficiente e sustentável de fertilizantes em solos tropicais, contribuindo para melhorar os rendimentos das culturas e reduzir o impacto ambiental, beneficiando diretamente agricultores e comunidades rurais.

IMPACT INDICATORS

This study explores the impacts of adding different sources of micronutrients to phosphate fertilizers in soybean cultivation in tropical soils, highlighting their physicochemical characteristics and agronomic behavior. In the second chapter, the focus is on controlled-release phosphate fertilizers (CRFs), evaluating their physicochemical properties and efficacy in meeting the required standards for a quality fertilizer. The results reveal significant impacts in the social, technological, and cultural domains. The application of phosphate fertilizers with added micronutrients has proven to be a viable agricultural practice, potentially resulting in increased productivity and preventing soil depletion and exhaustion by replenishing the amount of micronutrients exported by soybeans. From a social perspective, the work promotes knowledge development and information dissemination to farmers, leading to more efficient and sustainable agriculture. Technologically, the adoption of CRFs can reduce the peak of salinity and pH, while micronutrient technologies such as Maxxi-Phós®, Wolftrax®, Microsol®, and MIB Precise® have shown greater efficiency in nutrient release and absorption, reducing losses and maintaining the continuous availability of P and micronutrients over time. Culturally, the study has promoted awareness and the adoption of sustainable agricultural practices, encouraging the use of technologies that minimize environmental impact and promote the sustainability of natural resources. The impacts of the work are aligned with the United Nations Sustainable Development Goals (SDGs), especially SDG 2 (Zero Hunger and Sustainable Agriculture), SDG 12 (Responsible Consumption and Production), and SDG 15 (Life on Land), promoting practices that enhance productivity and environmental sustainability.This study provides valuable information for the more efficient and sustainable use of fertilizers in tropical soils, contributing to improved crop yields and reduced environmental impact, directly benefiting farmers and rural communities.

SUMÁRIO

Primeira Parte

1.Introdução Geral

A crescente demanda por alimentos em um cenário de aumento populacional coloca a agricultura diante de desafios complexos e interligados. Em particular, a gestão eficiente dos fertilizantes fosfatados, fundamentais para a produção de culturas, torna-se essencial à medida que enfrentamos a necessidade de maximizar a produtividade agrícola, minimizar os impactos ambientais e garantir a segurança alimentar global. Na busca por soluções sustentáveis que promovam o desenvolvimento agrícola e alimentar, a eficiência no uso de fertilizantes fosfatados emerge como um tema central.

Os fertilizantes fosfatados são fontes indispensáveis de fósforo (P), nutriente necessário para o desenvolvimento vegetal. Em regiões tropicais, como no Brasil, o manejo eficiente dos fertilizantes fosfatados assume uma importância singular, uma vez que as características específicas desses ambientes introduzem desafios distintos em comparação com climas temperados. Fertilizantes solúveis, como o monoamônio fosfato (MAP), são amplamente empregados na agricultura, proporcionando uma rápida disponibilidade de P após a aplicação. Contudo, devido ao alto intemperismo dos solos tropicais, combinado a sua alta solubilidade, é comum ocorrer a fixação ou adsorção do P pelos constituintes do solo, como os óxidos de ferro (Fe) e alumínio (Al), resultando em baixa disponibilidade e aumentando a dificuldade de absorção do P pelas raízes das plantas. Portanto, a busca por uma abordagem mais eficiente no uso de P se torna crucial, ainda mais considerando a natureza finita e não renovável das fontes tradicionais de P, como rochas fosfáticas e depósitos ígneos. Ainda, deve-se levar em consideração que é necessária uma gestão adequada dos fertilizantes para reduzir perdas significativas, predominantemente relacionadas aos processos de fixação.

Nesse contexto, a caracterização físico-química desses insumos, aliada a fertilizantes com tecnologias agregadas, como a liberação controlada e o revestimento dos fertilizantes por micronutrientes, desempenha um papel crucial na otimização de sua aplicação, visando não apenas aumentar a produtividade agrícola, mas também mitigar os impactos ambientais associados. Ao compreender minuciosamente as propriedades dos fertilizantes, como a solubilidade, granulometria, liberação, higroscopicidade, estabilidade térmica, composição química, entre outros, podemos adaptar estratégias de manejo que levem em consideração as especificidades dos solos tropicais e das diferentes culturas. A análise detalhada dessas características proporciona *insights* valiosos sobre como os fertilizantes fosfatados interagem com os componentes do solo. Essas tecnologias buscam maximizar a absorção pelas plantas, reduzir desperdícios e minimizar os impactos ambientais adversos. A integração dessas abordagens promissoras abre caminho para práticas agrícolas mais sustentáveis e resilientes.

Os fertilizantes fosfatados com tecnologias agregadas representam um avanço significativo na otimização da eficiência agrícola. Ao incorporar inovações como os fertilizantes de liberação controlada (CRF) ou até mesmo revestidos por micronutrientes, pode-se promover uma gestão mais precisa dos nutrientes no solo. Os CRF atuam como barreiras físicas, controlando a liberação gradual de P ao longo do tempo. Isso não apenas reduz as perdas, mas também prolonga a disponibilidade do nutriente para as plantas, maximizando sua absorção. Além disso, a adição estratégica de micronutrientes, como zinco (Zn), cobre (Cu), manganês (Mn) e boro (B) não apenas suplementa as necessidades das plantas, mas também contribui para a fertilidade do solo, evitando que ocorra a total exportação de nutrientes, sem reposição. Essa abordagem integrada não só aumenta a eficiência no uso de fertilizantes, mas também responde à demanda crescente por práticas agrícolas sustentáveis e inovadoras.

Diante disso, o primeiro capítulo deste trabalho teve como objetivo estudar fertilizantes fosfatados revestidos com micronutrientes na cultura da soja, explorando aspectos como a absorção e exportação de micronutrientes em diferentes estádios do desenvolvimento da cultura. Adicionalmente, foram conduzidas análises laboratoriais para avaliar processos fundamentais, como a difusão e movimentação de nutrientes no solo. No segundo capítulo, a pesquisa voltou-se para a caracterização físico-química de fertilizantes fosfatados de liberação controlada (CRF), com foco na compreensão detalhada de propriedades que influenciam diretamente a eficiência desses insumos. Por meio desses estudos, busca-se contribuir para o avanço do conhecimento científico e oferecer percepções relevantes para o aprimoramento das práticas agrícolas, especialmente no contexto da cultura da soja e na gestão eficiente de fertilizantes fosfatados.

SEGUNDA PARTE- ARTIGOS

Artigo 1- MICRONUTRIENTS IN COATED PHOSPHATE FERTILIZER IMPROVE PRECISION DISTRIBUTION AND NUTRIENT USE EFFICIENCY OF SOYBEAN

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MICRONUTRIENTS IN P-FERTILIZER COATINGS IMPROVES PRECISION DISTRIBUTION AND NUTRIENTS USE EFFICIENCY BY SOYBEAN

Core Ideas

- By the combination of coated MAP and NPS with micronutrients are produced a multinutrient fertilizer

-Micronutrients in coated P-fertilizers technologies replace exported nutrients in soybean grains

- Detailed scientific research showing the micronutrient use efficiency by soybean

- Scientific data about partitioning of B, Zn, Cu, Mn in soybean at different phenological stages

Abbreviations

MAP, Conventional MAP ; MAPSP, MAP + Sulfurgran® + Maxxi-Phós® ; MAPSPM, MAP + Sulfurgran® + Maxxi-Phós® + Microsol® ; MAPSPP, MAP + Sulfurgran® + Maxxi-Phós® + MIB Precise® ; MAPSPW, MAP + Sulfurgran® + Maxxi-Phós® + Wolftrax® ; NP, NPS + Maxxi-Phós® ; NPM, NPS + Maxxi-Phós® + Microsol® ; NPP, NPS + Maxxi-Phós® + MIB Precise® ; NPW, NPS + Maxxi-Phós® + Wolftrax® ; NPW2, NPS + Maxxi-Phós® + Wolftrax® ; NPW3 NPS + Maxxi-Phós® + Wolftrax®

ABSTRACT

Challenges towards micronutrients uniform distribution and phosphorus use efficiency in agricultural soils are usual. To address this, micronutrients can be added as P-fertilizer coatings, creating a multinutrient fertilizer for crops. The objectives of this study were to quantify the diffusion and availability of phosphorus (P), boron (B), copper (Cu), manganese (Mn), and zinc (Zn) from coated P-fertilizers. Another objective was to evaluate soybean nutrients uptake, partitioning and yield. Treatments were monoammonium phosphate (MAP) and NPS fertilizer coated with Maxxi-Phós® and a one of these technologies: Wolftrax®, Microsol® or MIB Precise®. Applied concentrations of B and Cu varied between 0.15% and 0.05%. For Mn and Zn, they ranged from 0.45% to 0.15%. Inside greenhouse and in a field trial nutrient accumulation and recovery were assessed. P diffusion ranged from 5.58 to 18.88mm in 336 hours. Micronutrients use efficiency varied according to the soybean phenological stages, with emphasis on V4 stage, which resulted in these values: B (0.65% to 13.89%), Cu (6.73% to 62.84%), Mn (0.73% to 3.36%), Zn (0.01% to 2.34%). Nutrient exports were: 55.7 kg of P_2O_5 ha^{-1}, 209.6 g of B ha^{-1}, 109 g of Mn ha^{-1}, 216.7 g of Zn ha^{-1}, and 64.3 g of Cu ha^{-1}. In field trial, there was significant absorption ($p \leq 0.05$) of B, Mn, and Zn at stages R1 to R5.1, while for Cu, it was between V4 and R1. Micronutrients coated P-fertilizers were able to replace the exported nutrients in a way to multinutrient fertilizer for soybean.

1. INTRODUCTION

Micronutrient deficiency in the soil is observed globally and plant symptoms vary according to the element (Voortman & Bindraban, 2015; Monreal et al., 2016). As a result, the absorption of micronutrients by crops in agricultural areas is limited due to their unavailability resulting from the combination of high rates of nutrient removal and inadequate fertilization, which jeopardizes crop production. Soybean plants usually respond positively to the application of B, Cu, Mn, and Zn. It is estimated that the extraction of nutrients P, B, Mn, Cu, and Zn by soybean is 7.3 kg, 77 g, 130 g, 26 g, and 61 g per ton of grains, respectively (Zancanaro et al., 2020).

In a study conducted by Bender et al. (2015), they presented research discussing the vital role of nutrient uptake and accumulation for the growth and development of soybeans. The authors found total uptake values of 20 kg ha-1 of P, 318 g ha-1 of Zn, 326 g ha-1 of Mn, 315 g ha-1 of B, and 61 g ha-1 of Cu. The authors explained the process of nutrient absorption by the plant and monitored the changes in nutrient accumulation throughout the growing season. They also discussed the influence of environmental factors, such as temperature and rainfall, on nutrient uptake and accumulation. However, further research is still needed to understand how the application of micronutrients via coating of P-fertilizers impacts during the stages of development and the nutrition of soybean crops. Therefore, studying nutrient accumulation according to the phenological stages becomes essential to recommend fertilizers that meet the crop's needs. Additionally, it is vital to determine the minimum amounts that must be returned to the soil to maintain soil fertility.

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 (Dimkpa & Bindraban, 2016; Samourgiannidis & Matsi, 2013; Sobral et al., 2013). Additionally, critical levels of micronutrients in the soil, extractable by Mehlich-1, are estimated to be: 2.5 to 1.3 mg dm^3 for Zn, 0.8 mg dm^3 for Cu, 5 to 10 mg dm^3 for Mn, and 0.5 for B ((Zancanaro et al., 2020). Therefore, it is necessary to replenish micronutrients adequately to meet the demands of the crops.

Micronutrient provision is not directly related to increased yield but reflects in physiological plant responses to biotic and abiotic stresses (Ahmad & Prasad, 2012; Dimkpa & Bindraban, 2016). 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, seed and plantling treatments (Lopes, 1999). For nutrients such as B, Cu, and Zn it is preferable that the supply is made via soil (Silva et al., 2022). However, it can be difficult to perform a uniform distribution of micronutrients in the area due to the low amounts required; according to Alvarez (et al., 1999), soybeans require the application of 4 to 6 kg ha^{-1}of Zn, 0.5 to 1 kg ha^{-1}of B, 0.5 to 2 kg ha^{-1} of Cu, and 2.5 to 6 kg ha^{-1} of Mn. Another concern is the low use efficiency of micronutrients fertilizers, commonly less than 5 % (Monreal et al., 2016; Ryan et al., 2013; Singh, 2008). There are reports of low plant recovery after zinc application, with studies reporting variation ranging from 0.33% (applied as ZnO) to 13% (applied as zinc sulfate in upland rice genotypes) (Kumar Fageria & Chanabasappa Baligar, 2005; Matiello et al., 2021)

Considering all this, it becomes crucial to develop innovative approaches to improve efficiency of micronutrient in 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 (Abreu et al., 2007; Lopes, 1999). Granule coating is generally done by spraying the micronutrients 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 (Lopes, 1999). Therefore, the use of micronutrient coated NPK can promote better soybean nutritional equilibrium and increase yield.

The application of micronutrients in soil is an effective way to provide adequate crop nutrition (Thapa et al., 2021). This technique does not require additional equipment or labor for spraying, making it practical and economical. Soil application remains a valid and advantageous alternative to ensure that plants have access to the necessary micronutrients for their proper development. It is important to emphasize that the choice of micronutrient application technique will depend on the specific soil conditions and nutritional demands of soybean. It's important to note that soil conditions such as high pH, high CEC, and/or reduced organic matter content can affect the availability of some micronutrients (McCauley et al., 2009), which may make foliar fertilization more appropriate in some situations.

Sources of micronutrients that solubilize in time should be applied in a favorable position since micronutrients are not mobile in the soil (Abreu et al., 2007). The use of technologies on phosphate fertilizers is an important to improve phosphorus use efficiency by crops . These technologies can serve to protect phosphorus present in the fertilizers, thereby increasing their efficiency and prolonging the release of nutrients to the soil and plants. Some examples of technologies used in phosphate fertilizers include polymers, sulfur, organic and inorganic materials, among others. Cation-sequestering agents such as organic acids can act as adsorption blockers and are classified as fixation inhibitors, which basically refers to compounds added to phosphate fertilizers that reduce the precipitation and adsorption reactions of phosphorus in the soil (Guelfi et al., 2022). In combination with this type of technology, micronutrients can be included in the coatings, facilitating their spreading in soil.

According the insights listed upward in this scientific paper we propose to characterize NPS and monoammonium phosphate (MAP) fertilizers coated with the Maxxi-Phós® (negative charge polymer) and micronutrient coating technologies such as: Wolftrax®; Precise® and; Microsol®. The study was realized to add some improvements in scientific knowledge in a way to answer how these fertilizers and micronutrient coating technologies could enhance the supply, distribution and replenish the micronutrient availability in soils cultivated with soybean. In addition, we quantified the P-diffusion, the availability in soil of B, Cu, Mn, and Zn, and the nutrition and yield of soybean in both greenhouse and field conditions. We hypothesized that the innovative fertilizer coating technologies could efficiently provide micronutrients and improve phosphorus uptake by soybean. Technologies of incorporating micronutrients into the coating of the phosphate fertilizer has the potential to offer innovative approaches to manufacturing a multinutrient fertilizer to supply nutrients for soybean.

2. MATERIAL AND METHODS

2.1 Controlled conditions assays – laboratory

The experiment was carried out in the Laboratory of Fertilizer Technologies – INOVAFERT, in the Soil Science Department of the Federal University of Lavras (UFLA), Lavras, Minas Gerais state, Brazil. The treatments consisted of the 11 phosphate fertilizers descripted in Table 1. MAP was used as positive 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% Mn and Zn
MAPSPP	*MAP + Sulfurgran® + Maxxi-Phós® + MIB Precise®*	40% P_2O_5; 10% N; 9% S; 0.15% B and Cu; 0.45% Mn and Zn
MAPSPM	*MAP + Sulfurgran® + Maxxi-Phós® + Microsol®*	40% P_2O_5; 10% N; 9% S; 0.15% B and Cu; 0.45% Mn and Zn
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% Mn and Zn
NPP	*NPS + Maxxi-Phós® + MIB Precise®*	40% P_2O_5; 10% N; 9% S; 0.15% B and Cu; 0.45% Mn and Zn
NPM	*NPS + Maxxi-Phós® + Microsol®*	40% P_2O_5; 10% N; 9% S; 0.15% B and Cu; 0.45% Mn and Zn
NPW2	*NPS + Maxxi-Phós® + Wolftrax®*	40% P_2O_5; 10% N; 9% S; 0.10% B and Cu; 0.30% Mn and Zn
NPW3	*NPS + Maxxi-Phós® + Wolftrax®*	40% P_2O_5; 10% N; 9% S; 0.15% B and Cu; 0.45% Mn and Zn

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 (Alemayehu & Jemberie, 2018).

***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 (Phusion Super | Fertilizantes de Solo - ICL America do Sul).

***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 (LINHA MIB PRECISE - ICL América Do Sul)

***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 (Koch Agronomic Services).

2.1.1 P diffusion

P diffusion was evaluated by capturing the diffusible P in filter paper soaked with iron oxide (Degryse & McLaughlin, 2014). The experiment was set up in a completely randomized design, with 4 replicates, 10 treatments and 1 control. Petri dishes (90 mm diameter) were filled with samples of approximately 90 g of soil, which were collected in the municipality of Lavras, Minas Gerais state, Brazil. The soil was incubated in Biochemical Oxygen Demand (BOD) chambers at 25 °C at 70 % of field capacity. A single fertilizer granule of each treatment, containing approximately 8.8 mg of P, was applied to the center of each Petri dish, and the moisture was regularly monitored and adjusted using a precision balance to maintain the desired conditions for the experiment. 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 (5, 25, and 45 mm away from the center of the Petri dish) and airflow-dried at 60 °C. Nutrients were extracted by Mehlich-1 (Mehlich, 1953) 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 characterize 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/Oxisol (Santos et al., 2018; Soil Survey Staff, 2014) with a clayey texture. The chemical and granulometric characterization are displayed in Table S1.

A completely randomized experiment was conducted with a 9 × 2 factorial design, including 9 treatments (including a control without P application) - MAPSP, MAPSPM, MAPSPP, MAPSPW, NP, NPM, NPP, NPW - at 2 base saturations (70% and 60%), and with three replicates. 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. Pots with a capacity of 10 L were full filled with soil previously corrected, and 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®. The moisture in the pots was maintained at 70% field capacity through irrigation with deionized water whenever necessary. The weight of the pots was continuously monitored using a balance to ensure proper irrigation. 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 Agronomic variables assessed: ***plant dry mass, nutrient accumulation, and nutrient recovery***

Plants were divided into shoots (leaves and stems) and dried in a forced-air oven 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 using the formula adapted from (1):

$$(1)\ R = \left[\left(\frac{M-MC)}{D}\right)\right] x100$$

Where: R (%): Amount of nutrient accumulated per unit of nutrient applied; M, nutrient accumulation (mg) in the fertilized plant; MC, nutrient accumulation (in mg) in the non-fertilized plant (control); D, nutrient dose applied.

2.3 Field trial

2.3.1 Experimental site 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 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 (treatments used are listed in section 2.2.1). Both sowing and fertilization were done mechanically.

2.3.3 Experimental design

The experiments conducted under controlled conditions also served to screen treatments for the field experiment. As a result, only a subset of the treatments used in the laboratory and greenhouse experiments were chosen for the field experiment. Therefore, 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, of which the 4 central lines were considered as the useful area for sampling. Plants sampled from lines 2 and 5 were used to harvest plants at phenological stages, and lines 3 and 4 were used to assess grain yield.

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 (Pederson, 2009). 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 described in section 2.2.2

2.3.4.2 Soybean yield

Soybean harvest was done 128 days after sowing (R8). Soybean were harvested from 2 m of the two central lines (totaling 4 m) to determine yield. Then, the soybean seeds were weighed, and their moisture content was determined was determined with a portable moisture meter (Gehaka Agri G600i). Moisture was adjusted to 13%, and the weight of the beans was converted to kg ha^{-1}.

2.4 Statistical analyses

Statistical analyses were performed using the R statistical software (R Core Team, 2022). The GVLMA package (Global Validation of Linear Model Assumption) was used to validate the data, and the assumptions of normality, homogeneity of variance, homoscedasticity, and the presence of outliers were manually checked for the models using the plots generated by the plot function. Analysis of variance (ANOVA) was applied to the variables of P diffusion, P movement, micronutrients, nutrient accumulation in greenhouse and field conditions, grain productivity, and nutrient recovery in greenhouse and field conditions. The means comparisons of the variables were performed through the Scott-Knott test ($p \leq 0.05$), 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 ($p \leq 0.05$) interaction between the treatments and the incubation period. After the 1st hour, MAPSP (14.18 mm) and MAPSPM (15.81 mm) fertilizers exhibited greater diffusion compared to others, and after 3 hours, only MAPSPM (17.18 mm) exhibited greater diffusion. P-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 P-diffusion 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)

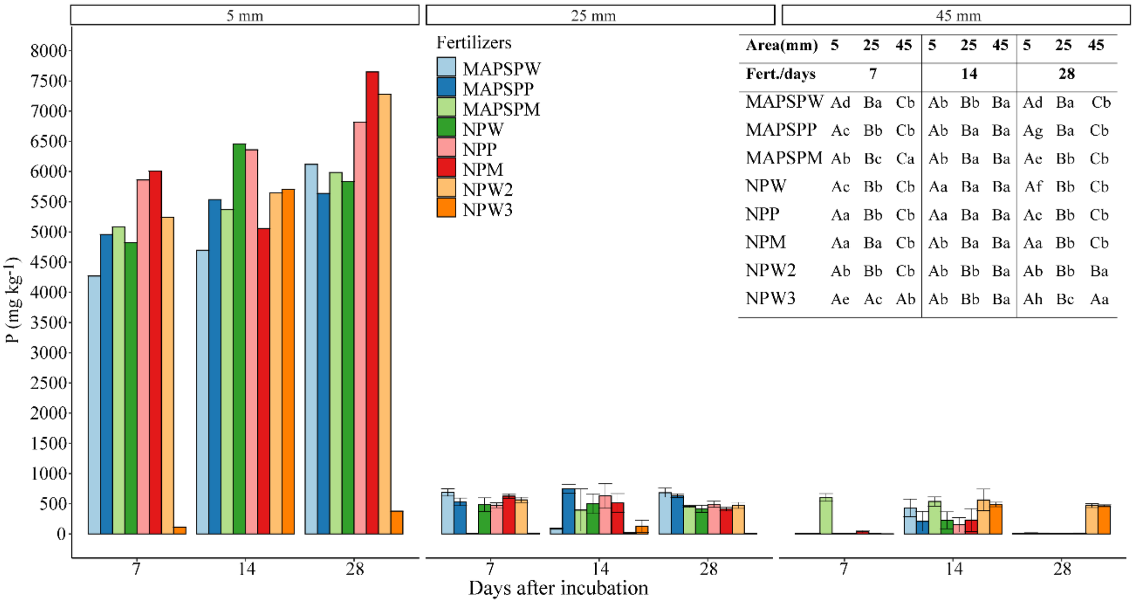
	Incubation Period (hours)							
	1h	3h	6h	12h	24h	72h	168h	336h
Fertilizers	***Diffusion radius (mm)***							
MAP	7.63 Ac	8.56 Ac	11.13 Ab	10.15 Aa	8.94 Ab	7.38 Aa	8.97Aa	4.25 Ba
MAPSP	14.18 Aa	12.44 Ab	11.76 Ab	11.77 Aa	13.37 Aa	12.04 Aa	8.00 Ba	5.06 Ba
MAPSPW	11.14 Bb	13.00 Ab	15.42 Aa	10.35 Ba	13.48 Aa	10.90 Ba	8.93 Ba	6.19 Ca
MAPSPP	10.45 Ab	10.70 Ac	10.71 Ab	13.52 Aa	11.18 Ab	10.04 Aa	11.16 Aa	7.00 Aa
MAPSPM	15.81 Ca	17.18 Aa	18.88 Aa	13.09 Ca	14.90 Ca	12.05 Ba	9.49 Ba	6.13 Da
NP	12.72 Ab	10.52 Ac	12.61 Ab	10.61 Aa	10.08 Ab	9.88 Aa	7.87 Aa	8.31 Aa
NPW	12.12 Ab	10.26 Ac	12.31 Ab	11.47 Aa	8.61 Bb	8.27 Ba	5.99 Ba	6.59 Ba
NPP	6.99 Ac	8.93 Ac	11.49 Ab	9.85 Aa	9.91 Ab	9.35 Aa	9.71 Aa	7.80 Aa
NPM	7.44 Bc	7.17 Bc	10.19 Ab	10.91 Aa	9.12 Bb	11.94 Aa	6.83 Ba	7.23 Ba
NPW2	5.58 Bc	10.50 Ac	9.61 Ab	9.48 Aa	10.37 Ab	11.73 Aa	9.00 Aa	6.46 Ba
NPW3	6.65 Bc	13.58 Ab	13.02 Ab	11.26 Aa	10.48 Ab	12.88 Aa	8.97 Ba	8.34 Ba

Means followed by the same letter (lowercase for the columns and uppercase for the lines) do not differ according to the Scott-Knott test ($p \leq 0.05$). MAP, Conventional MAP ; MAPSP, MAP + Sulfurgran® + Maxxi-Phós® ; MAPSPM, MAP + Sulfurgran® + Maxxi-Phós® + Microsol® ; MAPSPP, MAP + Sulfurgran® + Maxxi-Phós® + MIB Precise® ; MAPSPW, MAP + Sulfurgran® + Maxxi-Phós® + Wolftrax® ; NP, NPS + Maxxi-Phós® ; NPM, NPS + Maxxi-Phós® + Microsol® ; NPP, NPS + Maxxi-Phós® + MIB Precise® ; NPW, NPS + Maxxi-Phós® + Wolftrax® ; NPW2, NPS + Maxxi-Phós® + Wolftrax® ; NPW3, NPS + Maxxi-Phós® + Wolftrax®

3.1.2 P and micronutrients movement in soil

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 ($p \leq 0.05$) 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 excelled and after 28 days, the NPM fertilizer showed the highest P release. NPW3 fertilizer, however, did not release P up to the 7th day, but it displayed considerable P availability at 14 days and returned to almost no available P after 28 days of incubation.

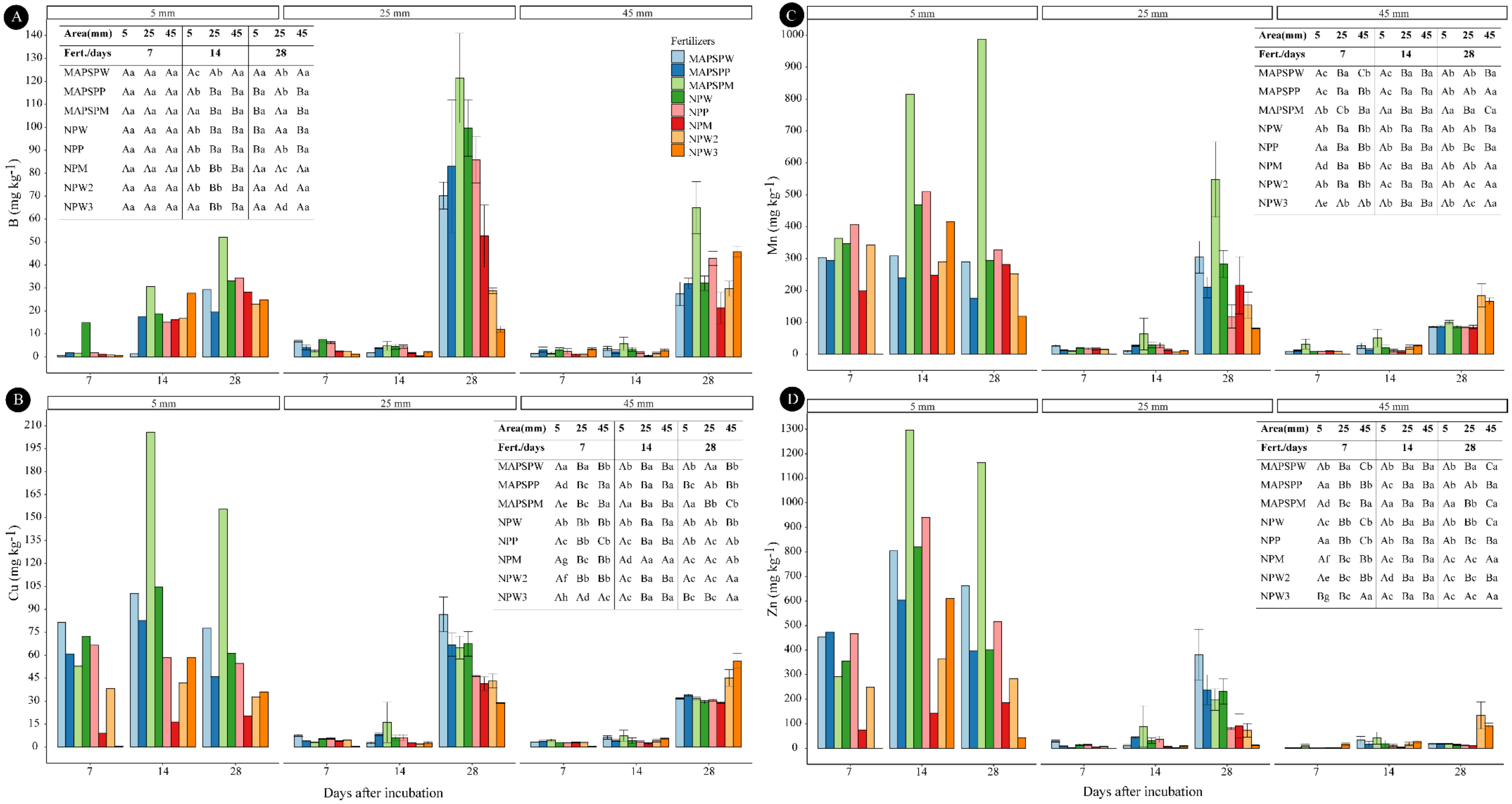


Area(mm)	**5**	**25**	**45**	**5**	**25**	**45**	**5**	**25**	**45**
Fert./days		**7**			**14**			**28**	
MAPSPW	Ad	Ba	Cb	Ab	Bb	Ba	Ad	Ba	Cb
MAPSPP	Ac	Bb	Cb	Ab	Ba	Ba	Ag	Ba	Cb
MAPSPM	Ab	Bc	Ca	Ab	Ba	Ba	Ae	Bb	Cb
NPW	Ac	Bb	Cb	Aa	Ba	Ba	Af	Bb	Cb
NPP	Aa	Bb	Cb	Aa	Ba	Ba	Ac	Bb	Cb
NPM	Aa	Ba	Cb	Ab	Ba	Ba	Aa	Bb	Cb
NPW2	Ab	Bb	Cb	Ab	Bb	Ba	Ab	Bb	Ba
NPW3	Ae	Ac	Ab	Ab	Bb	Ba	Ah	Bc	Aa

Figure 1. P availability in three concentric zones (5, 25 and 45 mm) 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 ($p \leq 0.05$). 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 (Figure 2). The interaction between treatments and distance was significant ($p \leq 0.05$). Regarding Cu availability, in 7 days, the MAPSPW fertilizer showed a higher availability, followed by NPW in the 5 mm and 25 mm regions (81.6 and 72.4 mg kg^{-1}), while MASPP and MAPSPM exhibited higher availability in the 45 mm region (4.5 and 4 mg kg^{-1}). After 14 days, the availability remained more pronounced in the 5 mm region, especially for the MAPSP fertilizer (205.8 kg^{-1}). After 28 days of incubation, the availability of Cu was evenly distributed over the dish area, with MAPSM showing higher availability in the 5 mm region (155.4 mg kg^{-1}), MAPSPW in the 25 mm region (86.6 mg kg^{-1}), and NPW2 and NPW3 in the 45 mm region (56.2 and 45.2, respectively).

Boron 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 (99.6 and 121.4 mg kg^{-1}).



Area(mm)	5	25	45	5	25	45	5	25	45
Fert./days		**7**			**14**			**28**	
MAPSPW	Aa	Aa	Aa	Ac	Ab	Aa	Aa	Ab	Aa
MAPSPP	Aa	Aa	Aa	Ab	Ba	Ba	Ba	Ab	Ba
MAPSPM	Aa	Aa	Aa	Aa	Ba	Ba	Ba	Aa	Ba
NPW	Aa	Aa	Aa	Ab	Ba	Ba	Ba	Aa	Ba
NPP	Aa	Aa	Aa	Ab	Ba	Ba	Ba	Ab	Ba
NPM	Aa	Aa	Aa	Ab	Bb	Ba	Aa	Ac	Aa
NPW2	Aa	Aa	Aa	Ab	Bb	Ba	Aa	Ad	Aa
NPW3	Aa	Aa	Aa	Aa	Bb	Ba	Aa	Ad	Aa

Area(mm)	5	25	45	5	25	45	5	25	45
Fert./days		**7**			**14**			**28**	
MAPSPW	Ac	Ba	Cb	Ac	Ba	Ba	Ab	Ab	Ba
MAPSPP	Ac	Ba	Bb	Ac	Ba	Ba	Ab	Ab	Aa
MAPSPM	Ab	Cb	Ba	Aa	Ba	Ba	Aa	Ba	Ca
NPW	Ab	Ba	Bb	Ab	Ba	Ba	Ab	Ab	Ba
NPP	Aa	Ba	Bb	Ab	Ba	Ba	Ab	Bc	Ba
NPM	Ad	Ba	Bb	Ac	Ba	Ba	Ab	Ab	Aa
NPW2	Ab	Ba	Bb	Ac	Ba	Ba	Ab	Ac	Aa
NPW3	Ae	Ab	Ab	Ab	Ba	Ba	Ab	Ac	Aa

Area(mm)	5	25	45	5	25	45	5	25	45
Fert./days		**7**			**14**			**28**	
MAPSPW	Aa	Ba	Bb	Ab	Ba	Ba	Ab	Aa	Bb
MAPSPP	Ad	Bc	Ba	Ab	Ba	Ba	Bc	Ab	Bb
MAPSPM	Ae	Bc	Ba	Aa	Ba	Ba	Aa	Bb	Cb
NPW	Ab	Bb	Bb	Ab	Ba	Ba	Ab	Ab	Bb
NPP	Ac	Bb	Cb	Ac	Ba	Ba	Ab	Ac	Ab
NPM	Ag	Bc	Bb	Ad	Aa	Aa	Ac	Ac	Ab
NPW2	Af	Bb	Bb	Ac	Ba	Ba	Ac	Ac	Aa
NPW3	Ah	Ad	Ac	Ac	Ba	Ba	Bc	Bc	Aa

Area(mm)	5	25	45	5	25	45	5	25	45
Fert./days		**7**			**14**			**28**	
MAPSPW	Ab	Ba	Cb	Ab	Ba	Ba	Ab	Ba	Ca
MAPSPP	Aa	Bb	Bb	Ac	Ba	Ba	Ab	Ab	Ba
MAPSPM	Ad	Bc	Ba	Aa	Ba	Ba	Aa	Bb	Ca
NPW	Ac	Bb	Cb	Ab	Ba	Ba	Ab	Bb	Ca
NPP	Aa	Bb	Cb	Ab	Ba	Ba	Ab	Bc	Ba
NPM	Af	Bc	Bb	Ae	Ba	Ba	Ac	Ac	Aa
NPW2	Ae	Bc	Bb	Ad	Ba	Ba	Ac	Bc	Ba
NPW3	Bg	Bc	Aa	Ac	Ba	Ba	Ac	Ac	Aa

Figure 2. B, Cu, Mn and Zn availability in three concentric zones (5, 25 and 45 mm) 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 ($p \leq 0.05$). Vertical bars indicate the standard error ($n = 4$).

Manganese had expresive availability only in the 5 mm region and after 7 and 14 days of fertilization with NPP and MAPSPM (407.4 and 814.7 mg kg^{-1}), respectively. However, after 28 days of incubation, a greater availability was observed between the 5 and 25 mm regions especially with MAPSPM (987.8 and 548. mg kg^{-1}, respectivaly) fertilizer.

For Zn, the availability was more relevant in the 5 mm region for the fertilizers MASPP (474 mg kg^{-1}) and NPP (466 mg kg^{-1}) (7 days) and MAPSPM (1295.6 mg kg^{-1}) (14 days). After 28 days, only MAPSPM was expressive in the 5 mm region (1164.5 mg kg^{-1}) 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 ($p \leq 0.05$) on the accumulation of micronutrients in the shoot (Figure 3). However, there was a significant main effect of fertilizers and base saturation (only for Mn) on the accumulation of micronutrients, regardless of their interaction. Boron accumulation was similar among the fertilizers, except for MAPSP and NP, both exhibiting lower accumulation (1.27 and 1.52 mg kg^{-1}). For Mn, the fertilizers MAPSP, MAPSPW, and NP showed the lowest accumulation (8.1, 8.2 and 8.4 mg kg^{-1}). Furthermore, plants under the condition of 60% base saturation exhibited higher Mn accumulation (9.9 mg kg^{-1}) compared to a base saturation of 70% (8 mg kg^{-1})$^{.}$ Regarding Zn, the MAPSPW, NPW, and NPP fertilizers presented higher accumulations (3.18 and 3.17 mg kg^{-1}), while MAPSP and NP showed lower accumulations (1.3 and 1.4 mg kg^{-1}). We did not observe a significant disparity in Cu accumulation. The accumulation of micronutrients in the shoots (Figure 3) and leaves (Figure S2) followed similar patterns.

Nutrient accumulation in the stem showed that B accumulation was favored by fertilizers NPW, NPP, and NPM (1.26, 1.25 0.9 mg kg^{-1})$^{.}$ And lowered on the MAPSP, MAPSPW, and NP treatments (0.6, 0.5 and 0.3 mg kg^{-1}). (Figure S3). Mn accumulation was favored by the application of MAPSPM and NPM (2.5 and 2.4 mg kg^{-1}). For Zn, MAPSP and NP showed lower accumulations (0.4 mg kg^{-1} for both). There was no significant difference in Cu accumulation. We observed a greater B accumulation when base saturation was at 70 %.

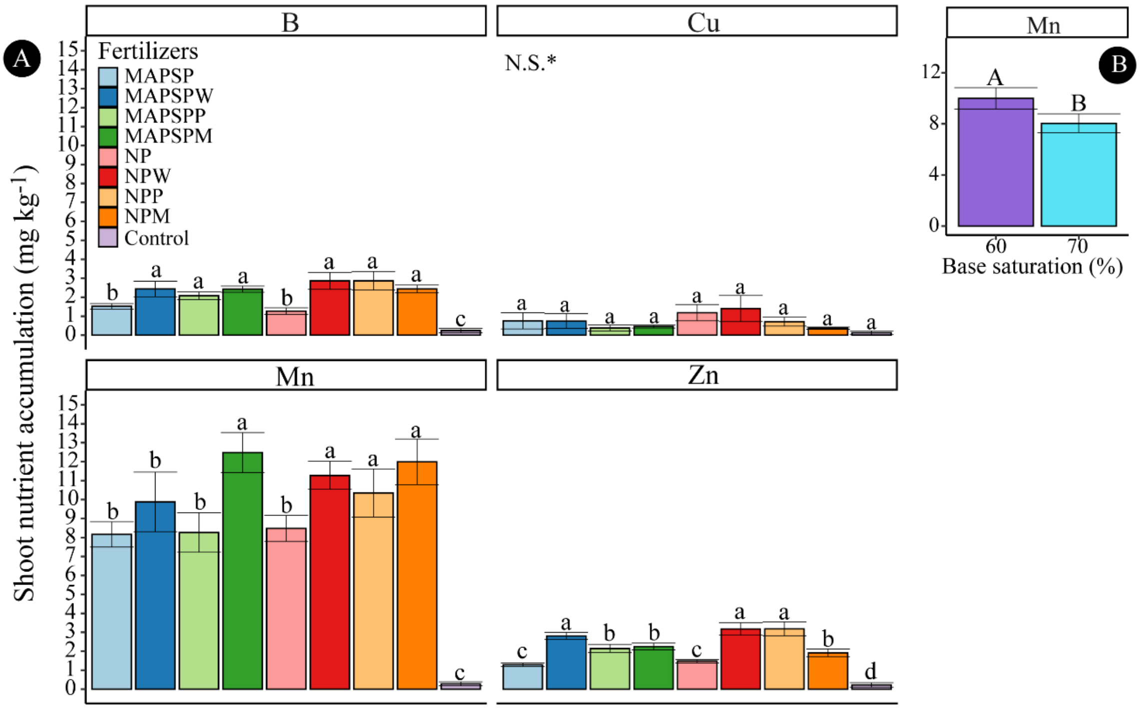


Figure 3. Accumulation of B, Cu, Mn, and Zn in the shoots of soybean plants. A – nutrient accumulation for each fertilizer. B – Mn accumulation for different base saturation levels. Means followed by the same letter do not differ according to the Scott-Knott test ($p \leq 0.05$). Vertical bars indicate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

The accumulation of B, Zn, and Mn in the roots was significantly influenced by the treatments ($p \leq 0.05$) (Figure 4). The treatments led to accumulations statistically equal (Means – B: 0.85; Mn: 12.86; Zn: 3.49 mg kg^{-1}), differing only from the control (B: 0.06; Mn: 0.75; Zn: 0.17 mg kg^{-1}). 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 (1.2 mg kg^{-1}) = MAPSPW (1.59 mg kg^{-1}) = MAPSPP (2.0 mg kg^{-1}) = MAPSPM (2.4

mg kg^{-1}) = NP (1.7 mg kg^{-1}) = NPW (1.6 mg kg^{-1}) = NPP (1.2 mg kg^{-1}) > NPM (0.8 mg kg^{-1}) > Control (0.03 mg kg^{-1}). 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. In general, soybean exhibited a root accumulation relative to the total accumulation of 45.4% for B, 49.2% for Cu, 52.9%, and 61.5% for Mn (Table S3).

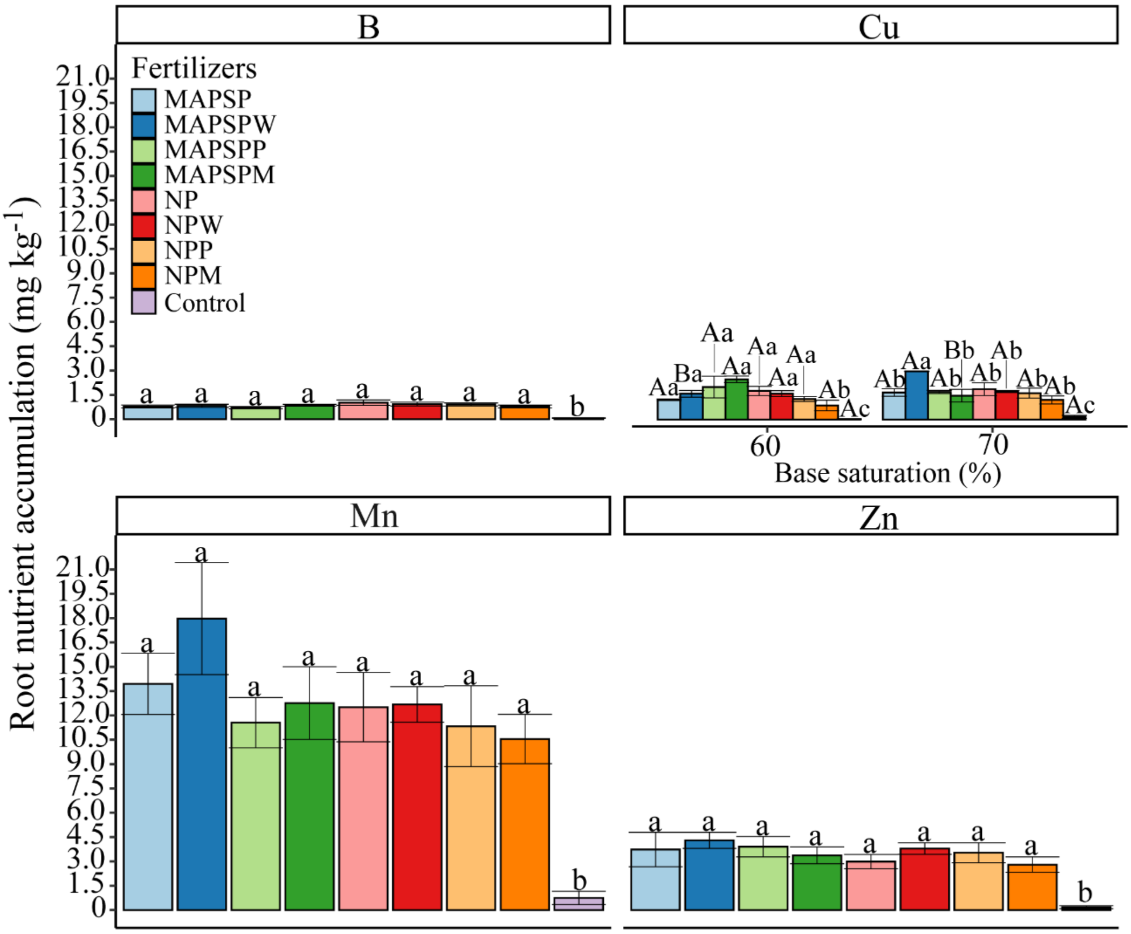


Figure 4. Accumulation of B, Cu, Mn, and Zn in the roots of soybean plants. Uppercase letters for treatment within saturation and lowercase letters for saturation within treatment compare means according to the Scott-Knott test ($p \leq 0.05$). Vertical bars indicate the standard error (*n = 4*).

3.2.2 Micronutrient recovery

Micronutrient recovery (Figure 5) observed under greenhouse conditions varied according to the fertilizers technologies for B and Cu and soil base saturation to Mn e Zn. For B, the highest recoveries were observed on treatments NPM (25.9%), MAPSPW (26.2%), MAPSPM (26.4%), NPP (17.6%), and NPW (31.0%). The application of the different fertilizer's technologies 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.

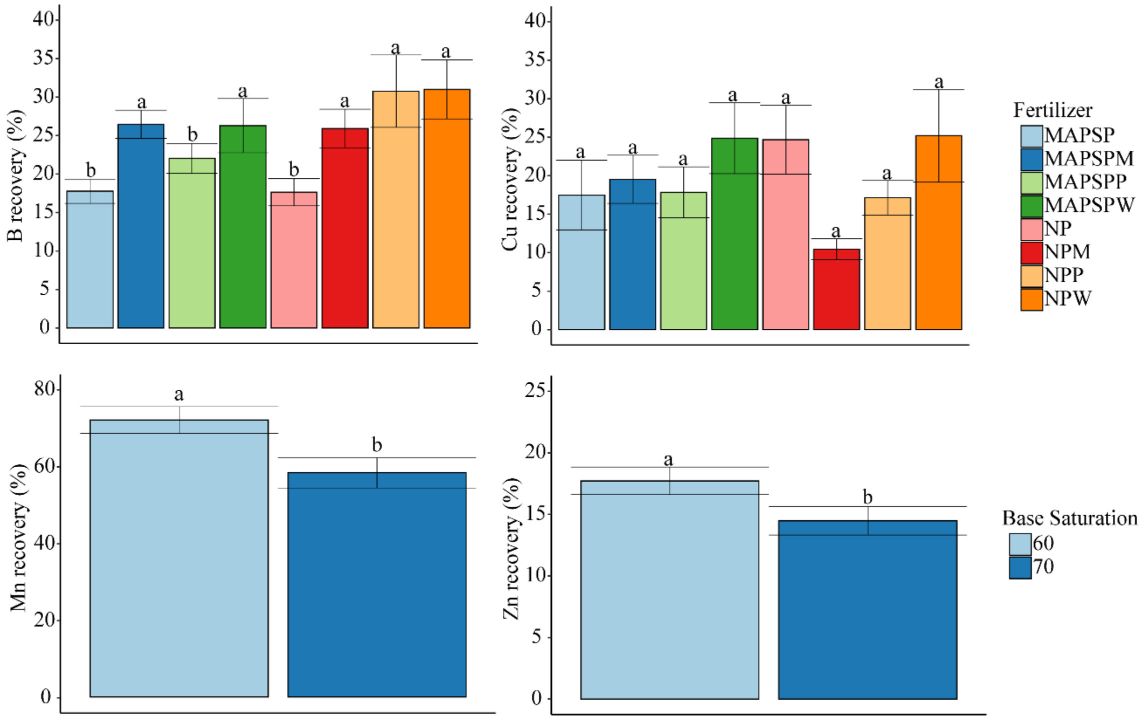


Figure 5. Recovery of B, Cu, Mn, and Zn in soybean plants after the application of fertilizers coated with different sources of micronutrients and different base saturation levels in greenhouse test. Means followed by the same letter do not differ according to the Scott-Knott test ($p \leq 0.05$). Vertical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

3.3 Field experiment

3.3.1 Nutrient accumulation

Significant differences ($p \leq 0.05$) were found in the nutrient accumulation at different phenological stages of soybean (Figure 6). The highest total accumulation observed for B was at stage R5.1 (422.4 g ha^{-1}). Boron 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.

Significant statistical differences were found for nutrient accumulation in different plant parts based on the treatments used (Figure 7). Boron accumulation showed significative differences ($p \leq 0.05$) both in the stem (119.9 g ha^{-1}) and in the total accumulation (282.3 g ha^{-1}), with higher values for the NPW fertilizer. As for Cu, significative differences ($p \leq 0.05$) were found in both stem and total accumulation for both NPW and NPM fertilizers. Copper accumulations in the stem was 89.13 g ha^{-1} (NPW) and 79.67 g ha^{-1} (NPM), while the total accumulation was 183.7 g ha^{-1} (NPW) and 174.3 g ha^{-1} (NPM).

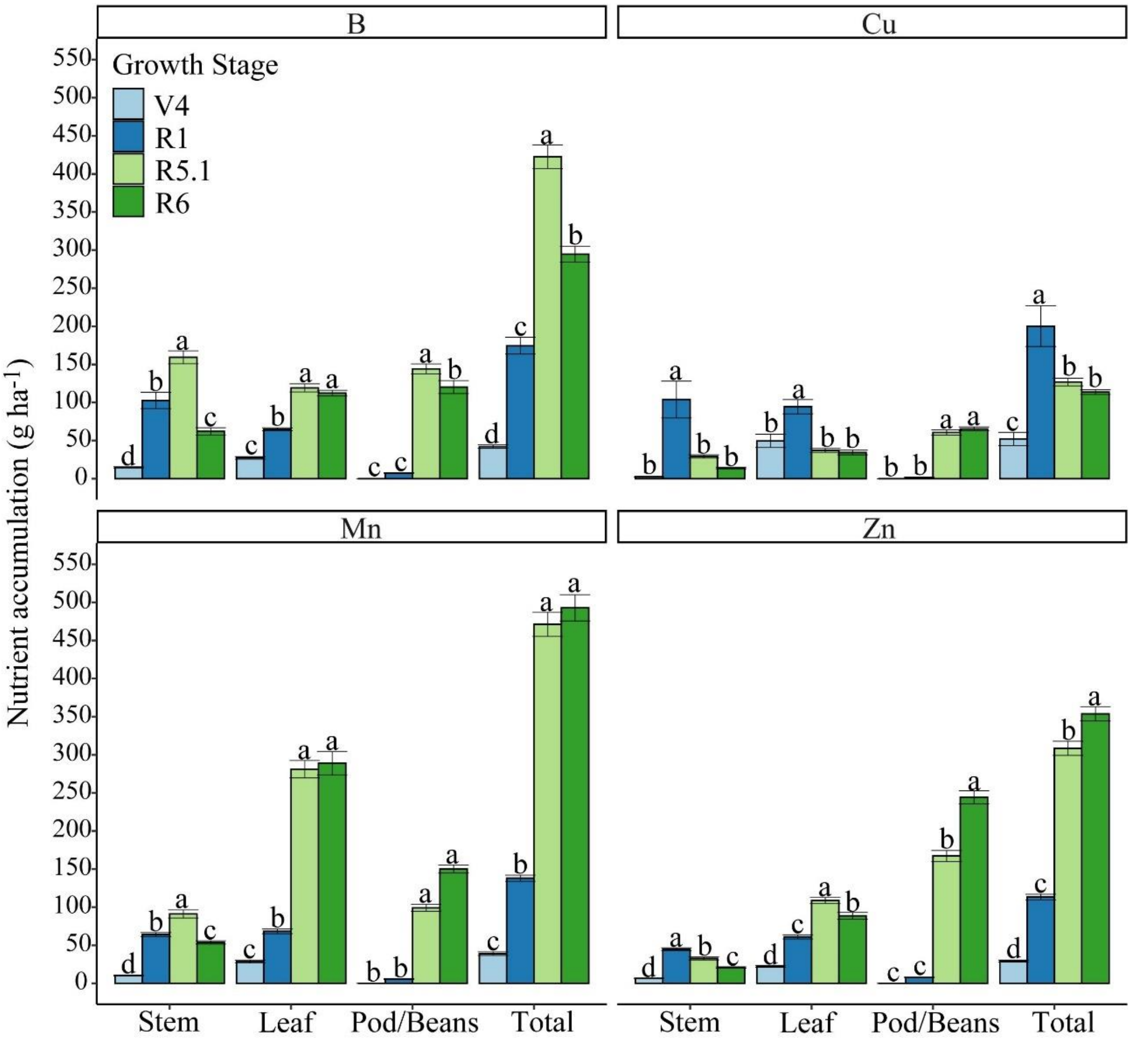


Figure 6. Accumulation of B, Cu, Mn, and Zn in soybean plants (stem, leaves, pods/beans, and whole plant) at different phenological stages of the plants. Means followed by the same letter do not differ according to the Scott-Knott test ($p \leq 0.05$). Vertical bars indicate the standard error (*n* =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

The accumulation of Mn showed statistical differences ($p \leq 0.05$) 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.

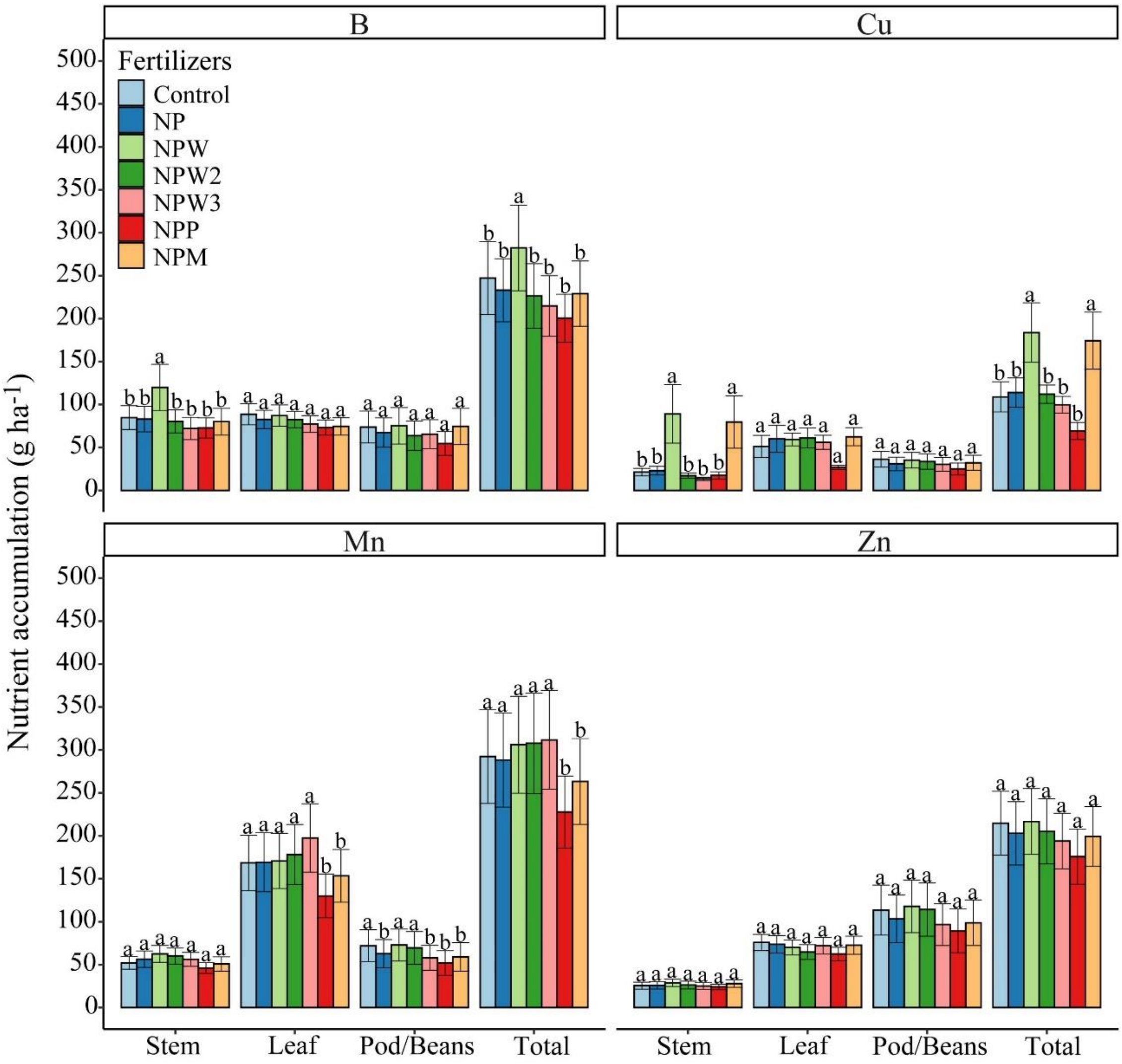


Figure 7. Accumulation of B, Cu, Mn, and Zn in soybean plants (stem, leaves, pods/beans, and whole plant) with the application of different P-fertilizers technologies. Means followed by the same letter do not differ according to the Scott-Knott test ($p \leq 0.05$). Vertical bars indicate the standard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

There were statistical differences for grain yield ($p \leq 0.05$). The maximum grain 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 (359.3 kg ha^{-1}) represents a 7.12% increase in yield.

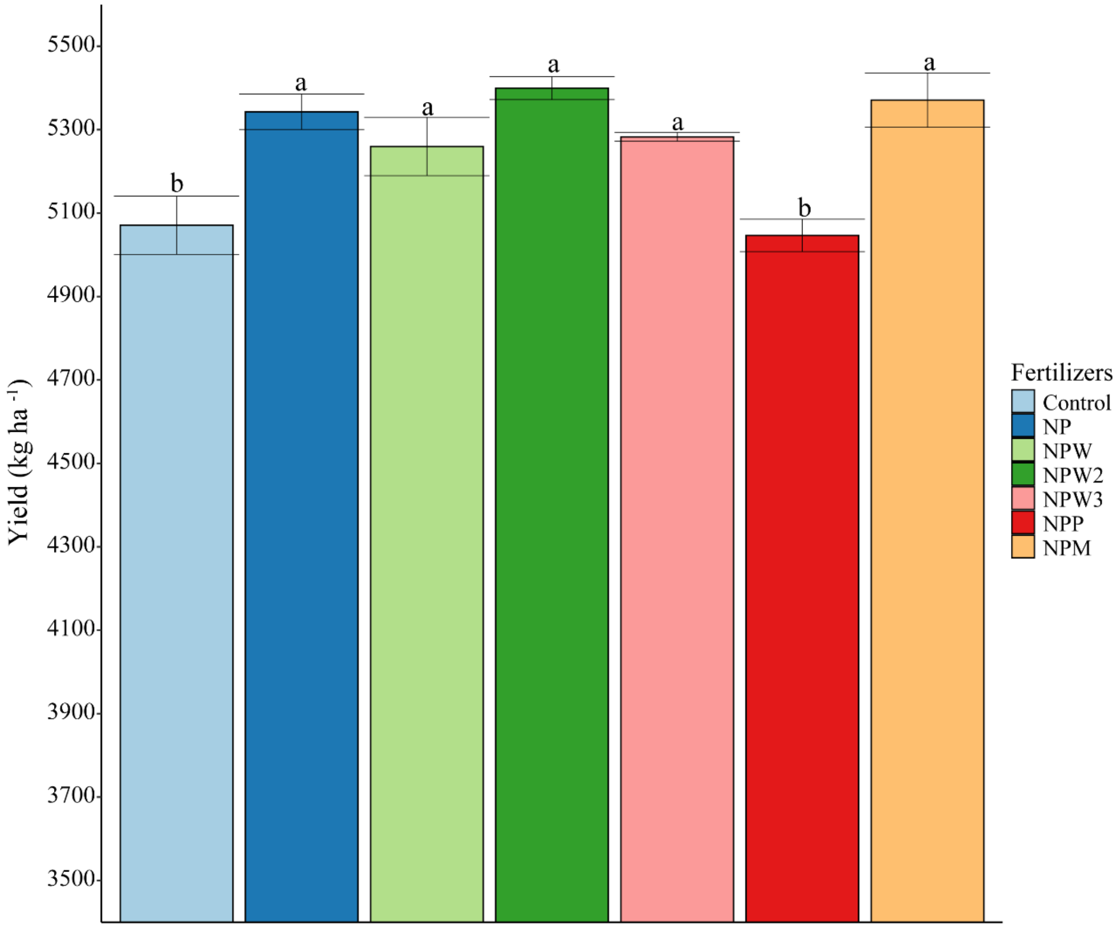


Figure 8. Grain yield (kg ha^{-1}) of soybean plants cultivated with different P-fertilizers technologies. Means followed by the same letter do not differ according to the Scott-Knott test ($p \leq 0.05$). Vertical bars indicate the standard error (n = 4).

3.3.2 Nutrients recovery in field conditions

Overall, we observed greater nutrients recoveries at stages V4 and R1 (Table 3) following the sequence Cu (62.8 and 197.8%) and B (13.89 and 74.93%)> Mn (3.36 and 74.93 %) > Zn (2.3 and -1.64 %). In general, the NPP fertilizer had the lowest nutrient recovery (with a lower accumulation of -33%), while NPW and NPW2 had the highest recovery values (62.8 and 38 % at V4 stage). 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 under field conditions.

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

The negative values indicate that the control treatment showed higher recovery (in %) than the observed treatments.

4. DISCUSSION

4.1 Laboratory assays

4.1.1 P diffusion

A proper characterization of fertilizer coatings technologies is important to improve industrial production and innovation to overcome important changes such as adequate micronutrient fertilization and phosphorus use efficiency. The P-diffusion is a fundamental characteristic of phosphate fertilizers that can be altered by coating additives. Therefore, we assessed the P-diffusion of the coated fertilizers used in this scientific paper. After 12 hours of incubation, all fertilizers technologies reached similar diffusion rates to conventional MAP, followed by stability in P-diffusion. The reduction in diffusion values and the lower intensity of coloration in the filter paper after 14 days of incubation (Figure S1) indicates the adsorption of P by soil. Similar results were observed by Nunes et al. (2022), using MAP coated with organic substances, Zn, and B or Mg.

As it is considered a soluble source, the similarity between the P-diffusion values of MAP and the other treatments in a short period (12 hours) indicates that the use of micronutrients as coatings for P-fertilizers does not negatively affect the P-diffusion in soil, allowing for normal P-diffusion. Therefore, its use in agriculture can be effective in providing micronutrients without limiting the application and supply of P to the soybean.

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 (Degryse et al., 2013; Lombi et al., 2006; Montalvo et al., 2014; Nunes et al., 2022; Volf & Rosolem, 2021). 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 (Novais et al., 2007; Sample et al., 1980; Tiecher et al., 2012).

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 (the overall mean was 1.06 mg kg-1 at 7 days and 30.5 mg kg-1 at 28 days). 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® promotes different nutrient availabilities and results are probably related to the solubility of the sources of the elements B, Cu, Mn, and Zn used in coating micronutrients additives. 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 insoluble 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 (for example, at a distance of 50 mm, B: 1.8, 0.7 and 0.6 mg kg^{-1}; Mn : 407.4, 343.1 and 0.7 mg kg^{-1}; P_2O_5: 5860, 5241.4 and 113.2 mg kg^{-1}; Zn: 466.6, 248.4 and 0.15 mg kg^{-1}; Cu: 66.5, 38.3 and 0.6 mg kg^{-1}, respectively for NPW, NPW2 e NPW3) after incubation compared to NPW and NPW2, which may be explained .by the higher concentration

(0.15% B and Cu; 0.45% Mn and Zn to NPW3; 0.10% B and Cu; 0.30% Mn and Zn to NPW3 and 0.05% B and Cu; 0.15% Mn and Zn to NPW3) 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 (Guelfi et al., 2022; Milani et al., 2015). 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 (Guelfi et al., 2022), which may have modified the pH or aided in the solubilization of the micronutrients present in the oxysulfate.

Higher accumulations in the roots before the reproductive period of soybean (Table S3) can be attributed to a greater demand for nutrients during the early stage of growth and development. During this stage, roots play a crucial role in absorbing water and nutrients from the soil. The plant allocates a significant amount of energy and resources to root development, allowing it to explore the soil for essential nutrients.

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 (5.4 mg dm^3). 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 to around 5.5 in water. The availability of manganese is directly affected by the pH change, being potentially unavailable in alkaline soils (around pH 7) and more available in acidic soils, with its availability decreasing approximately 100-fold for each unit increase in pH (Khabaz-Saberi & Rengel, 2010).

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. Probably there was no effect of treatments on the uptake of micronutrients given the low quantities supplied via coating that only helps to replace micronutrients exported in soybean grains. Perhaps it would be necessary to apply higher doses in the coating to achieve more significant results in soybean yields. However, there were differences in micronutrient uptake depending on the crop development stage. Nutrient uptake in soybeans occurs in three distinct phases regardless of the yield level. Firstly, there is a slow rate of nutrient acquisition for around 30 days after emergence; Secondly, there is a maximum rate of nutrient uptake between R2 (full bloom) and R5 (beginning seed); finally, there is a reduced rate of nutrient accumulation during late reproductive growth, such as seed maturation (Bender et al., 2015; Harper, 1971; Usherwood, 1998). The accumulations of each micronutrient varied in the experiment under field conditions according to the absorption march of the plants (Figures S4-S7).

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 Silva et al. (2022). Considering the total accumulation up to the R6 stage, it was observed that the plant parts accumulated, on average:

a) Stem: B – 36.10 %; Cu – 26.9 %; Mn – 20 %; Zn – 13.05 %
b) Leaves: B – 34.8 %; Cu – 46.1 %; Mn – 60 %; Zn – 34.95 %
c) Pods/Beans: B – 29.1 %; Cu – 27 %; Mn – 20 %; Zn – 52 %

The accumulation of these micronutrients in soybean can be attributed to their specific functions within the plant. Zinc plays a crucial role in root development, enzymatic activation, plant stress tolerance, protein synthesis, and grain formation, which explains its higher presence in pods and beans (Kirkby & Römheld, 2007; McBeath & McLaughlin, 2014. Copper is essential for plant metabolism, acting as a component of proteins involved in photosynthesis, respiration, fungal disease control, and plant defense mechanisms (Kirkby & Römheld, 2007; Zhu et al., 2012), which explains its higher presence in leaves. Additionally, the greater accumulation of Cu between growth stages V4 and R1 can be explained by its crucial role in seed formation and pollen viability, as it is necessary for the synthesis of proteins and enzymes involved in these processes (Broadley et al., 2012).

Boron is involved in various physiological processes, including enzymatic activation, cell elongation, protein synthesis, pollen germination, and fruit/grain formation, contributing to overall yield improvement. However, B has limited mobility within the plant (Marschner, 2011). Manganese (Mn) acts as an enzyme activator, promoting the production of lignin, flavonoids, indoleacetic acid, and other compounds. Manganese also plays an active role in photosynthesis and chlorophyll formation, explaining its higher presence in leaves (Burnell, 1988).

We have observed that during the early stages of soybean development, specifically between R1 and R5.1, there is a significant uptake of these micronutrients, followed by a steady absorption rate until R6. This demand is a result of the vital roles these micronutrients play in supporting the plant's physiological functions, making it crucial to ensure an adequate availability of these micronutrients for optimal soybean growth and development, especially during the early stages and the reproductive phase. Insufficient levels of these micronutrients can have a detrimental effect on crop productivity, compromising seed formation and overall yield.

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 coating technologies did not increase the element concentration compared to the control, but smaller accumulations were noted for NPP and NPM treatments. These patterns are in the same way as previously published micronutrient availability results and are related to the solubility of the nutrient sources used in each technology.

The NPP fertilizer led to the lowest averages of accumulation for B, Cu, Mn, and Zn in soybean. 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 grain yield, evaluated after the application of NPS fertilizer and associated technologies, showed a high yield (average of 5253.6 kg ha^{-1}, Figure 8). The productivity observed for the control treatment (5070.0 kg ha^{-1}) indicates that even with nutrient limitations indicated by the soil analysis (Table S2), which showed that the most limiting nutrients in the experimental area were B, Zn, and P, rated as very low or low (with respective critical levels of 0.6, 1.5, and 8.0 mg dm^{3}), while Cu and Mn were rated as having average and good availability, respectively (with critical levels of 1.2 and 8.0 mg dm^{3}) (Alvarez et al., 1999), there was no compromise in grain yield. However, the organic matter content in the area was rated as having average availability (2.72%), which may have influenced the availability of nutrients, mainly B. Therefore, the mineralization of the organic fraction may have released the necessary micronutrients to guarantee high yields even in the non-fertilized treatment. NPM treatment provided a 6% increase in grain 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, grain 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}) (CONAB, 2022). This yield corresponds to 37 bags of soybeans (60 kg) that exceed the Brazilian average (or 81 bushel of soybean).

Grain yield was not negatively affected in treatments NPW and NPW2, even though they both showed lower concentration of micronutrients in relation to other fertilizers. The NPW3 fertilizer showed lower nutrient availability in the Petri dishes during the 28-day evaluation. However, it was able to release the nutrients after this period, which may explain the absence of difference in grain productivity. It is important to highlight that the soybean crop cycle varies between 90 and 150 days, depending on the cultivar (Silva et al., 2022), allowing sufficient time for the release of nutrients from the fertilizer granules.

4.3.3 Micronutrient recovery

During the early stages of soybean development, specifically between stages V4 and R1, it was observed that certain fertilizers showed positive results in micronutrient recovery. These recoveries during the early stages of soybean development suggest that the amount of micronutrients supplied via coating was sufficient to meet the initial demands of the crop. However, during the grain filling and development stage (R5.1 and R6), it became evident that this amount was not able to fulfill all the nutritional needs of soybean, as indicated by the subsequent negative recoveries observed, indicating that the crop started to rely on the micronutrient stock present in the soil to sustain its growth.

It is interesting to note that fertilizers with lower concentrations of micronutrients in their coating layer (Table 1) provided the highest recovery rates for Cu (62.4% for NPW and

38.05% for NPW2). This is since the lower the concentration, the higher the nutrient use efficiency attributed to it. During the initial stages, the fertilizers NPM, NPW3, and NPP showed copper (Cu) recoveries of 19.3%, 11.3%, and 6.73%, respectively. The results indicate that the recovery efficiency of micronutrients in the NPP fertilizer was 2.6 and 1.68 times lower compared to the NPM and NPW3 fertilizers, respectively. This lower recovery can be attributed to the lower solubility of the oxysulfate used as a micronutrient source in this fertilizer.

Furthermore, it is worth noting that the negative values observed in micronutrient recovery indicate the possibility of soil depletion by the crop, as the control treatment (without fertilizer application) showed a significant nutrient accumulation, surpassing even the treatments with fertilizers. Overall, the low recoveries observed align with the low micronutrient utilization efficiency (less than 5%) reported in the literature (Monreal et al., 2016; Ryan et al., 2013; Singh, 2008). For Zn, Singh et al. (2005) estimated a crop absorption of 2% to 5%, with the remaining fixed in the soil. In general, these results highlight the importance of understanding the interactions between micronutrients and soil, as well as the need for appropriate fertilization strategies to optimize the recovery and utilization of these micronutrients. Low utilization efficiency can negatively impact production costs and directly affect the nutrient levels in plants (Monreal et al., 2016), emphasizing the relevance of accurate approaches in fertilizer dosing and application.

Regarding nutrient export, an average of 55.7 kg ha^{-1} of P_2O_5 and 209.6 g of B ha^{-1}, 109 g of Mn ha^{-1}, 216.7 g of Zn ha^{-1}, and 64.3 g of Cu ha^{-1} were exported. These export quantities are similar to those found in the literature. According to EMBRAPA (2013), soybean exports around 10 kg t^{-1} of $^{-1}$ and 20 g t^{-1}, 9.88 g t^{-1}, 29.9 g t^{-1}, and 40.26 g t^{-1} of B, Cu, Mn, and Zn, respectively. In a study conducted by Pauletti (2004), export quantities of 22 g t^{-1}, 13 g t^{-1}, 33.7 g t^{-1}, and 37.7 g t^{-1} of B, Cu, Mn, and Zn, respectively, were found. Bender found values of 40 kg ha^{-1} of P_2O_5, 145 g ha^{-1} of Zn, 97 g ha^{-1} of Mn, 112 g ha^{-1} of B, and 39 g ha^{-1} of Cu.. From now on we also need to understand better how are the relations of soybean genotypes nutrients requirement above productivities levels higher than > 100 bags ha^{-1}. It is important to highlight that in this study, the export of B was almost double the reported values. Additionally, the sequence of micronutrient export was Zn > B > Mn > Cu, contrary to what was reported by Silva et al. (2022), which was Zn > Mn > B > Cu.

It is important to note that the application of 250 kg ha^{-1} of each fertilizer 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. The NPW and NPW2 treatments were exceptions and supplied (in each plot) 0.375 kg ha^{-1} (Mn and Zn) and 0.125 kg ha^{-1} (B and Cu); 0.750 kg ha^{-1} (Mn and Zn) and 0.250 kg ha^{-1} (B and Cu), respectively. Therefore, when comparing nutrient export and the amount supplied via coating, it is evident that the applied concentrations correspond to replacement fertilization (Silva et al., 2022), replenishing the amount of micronutrients exported by the crop. However, it is important to note that various regions in Brazil, especially Cerrado soils, exhibit natural micronutrient deficiencies in soils (Lopes & Guimarães Guilherme, 2016; Sfredo & Oliveira, 2010).It is also important to highlight that the availability of micronutrients in the soil can be influenced by various factors such as pH, adsorption, incorporation into organic matter, and leaching (Dhaliwal et al., 2019; Rengel, 2015; Silva et al., 2022). In this regard, the application of fertilizers with the concentrations mentioned in this study can help maintain adequate levels of micronutrients in the soil, preventing depletion and excessive production costs.

However, if micronutrient levels are below the recommended critical level, it would be advisable to correct them in advance to avoid problems arising from nutritional deficiencies in the crop. If corrective measures are not taken, it may be necessary to increase the amount of micronutrients in the coating of fertilizers to ensure an adequate nutrient supply to the plants, which can result in increased production costs. Therefore, it is essential to carefully assess the specific needs of each crop and soil conditions before determining the amount of micronutrients to be supplied via coating.

Moreover, the application of micronutrients via coating of P-fertilizers has proven to be a viable alternative for supplying the required micronutrients to the crop, especially for replenishing the exported nutrients. Literature has shown that this technique offers advantages over the application of isolated micronutrients via soil, facilitating the distribution of micronutrients through the soil and resulting in a more uniform distribution in the agricultural area (Abreu et al., 2007; Lopes, 1999), as each fertilizer granule receives the coating containing the micronutrients.

Additionally, the use of fertilizers coated with micronutrients allows for controlled release, which can be beneficial in crops that require specific nutrient doses in different developmental stages. This technique can also contribute to cost reduction, as it is possible to reduce transportation and application expenses. Therefore, it is important to consider its use as an interesting alternative for the nutritional management of crops, such as soybean, especially when it comes to micronutrient supplementation. However, it is crucial for producers and researchers to continue investigating the efficiency and economic viability of this technique in different production systems and environmental conditions.

Furthermore, the application of coated fertilizers offers flexibility in nutritional management. Through coating, it is possible to combine different nutrients in a multinutrient fertilizer, allowing for more efficient and precise application. This is particularly useful in specific crop production systems, where the demand for nutrients varies in different growth stages, as can be seen in the absorption curve of soybean (Figures S4 to S7). With the use of coated multinutrient fertilizers, it is possible to adapt the release of nutrients according to the crop's needs, promoting continuous supply throughout the growth cycle. However, it is important to note that the choice of coating type and materials used should consider the specific characteristics of the soil, plants, and environmental conditions. Additionally, the efficiency and performance of coated multinutrient fertilizers may vary depending on the application management and nutrient release time.

5. CONCLUSIONS AND FUTURE PERSPECTIVES

In an innovative way to add micronutrients as P-fertilizer coatings manufacturing a multinutrient fertilizer for soybean is an important technology to replace uniformly micronutrients exported by soybean grains. The amounts of B, Zn, Cu, and Mn applied as a multinutrient fertilizer were sufficient to replace the nutrients exported by the soybean grains. However, in relation of increasing of soybean yields it might be necessary to increase the amount of micronutrients in phosphate fertilizers coatings because there are interesting advantages such as: reduction in the cost of application and improvements due to homogeneity micronutrients spreading in agricultural soils. However, the costs of increasing micronutrients concentrations in coatings additives must be choice according to crop demands and feasibility to fertilizer industry, adequate crop nutrition, productivity and quality.

Nutrient uptake and partitioning were affected by the fertilizer technologies related to the amount and solubility of each micronutrient sources in coating formulations additives used to coating MAP and NPS. Important scientific advancements for nutritional requirements during different phenological soybean growing stages were achieved, however, there is no improvements in soybean yields.

It is important to highlight that the efficiency of coating technologies for solid fertilizers may vary depending on various factors, such as soil type, environmental conditions, crop management, and coating additive formulations. Therefore, it is essential that further studies are conducted to improve our knowledge about coating micronutrients in fertilizer granules.

Continuous scientific research and innovative technologies are necessary to improve the control of quality, formulations, and application processes of coatings for solid fertilizers. This will maximize the efficiency and profitability of this promising technique as an innovative approaches to improve micronutrient use efficiency in a perspective to promotes a sustainable agriculture worldwide.

As a future perspective we suggest that is necessary to put some light on how are the relations of soybean genotypes nutrients requirement above productivities levels higher than > 100 bags ha^{-1}. It’s also necessary scientific knowledge related nutrient uptake and partitioning in determinate and indeterminate of moderns genotypes of soybean in different edaphoclimatic conditions.

SUPPLEMENTAL MATERIAL

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

Figure S1. P diffusion zones on filter paper after incubation of phosphate fertilizers in Petri dishes filled with soil according to the treatments and time. The intense green color in the center of the filter papers represents the diffusion of P.

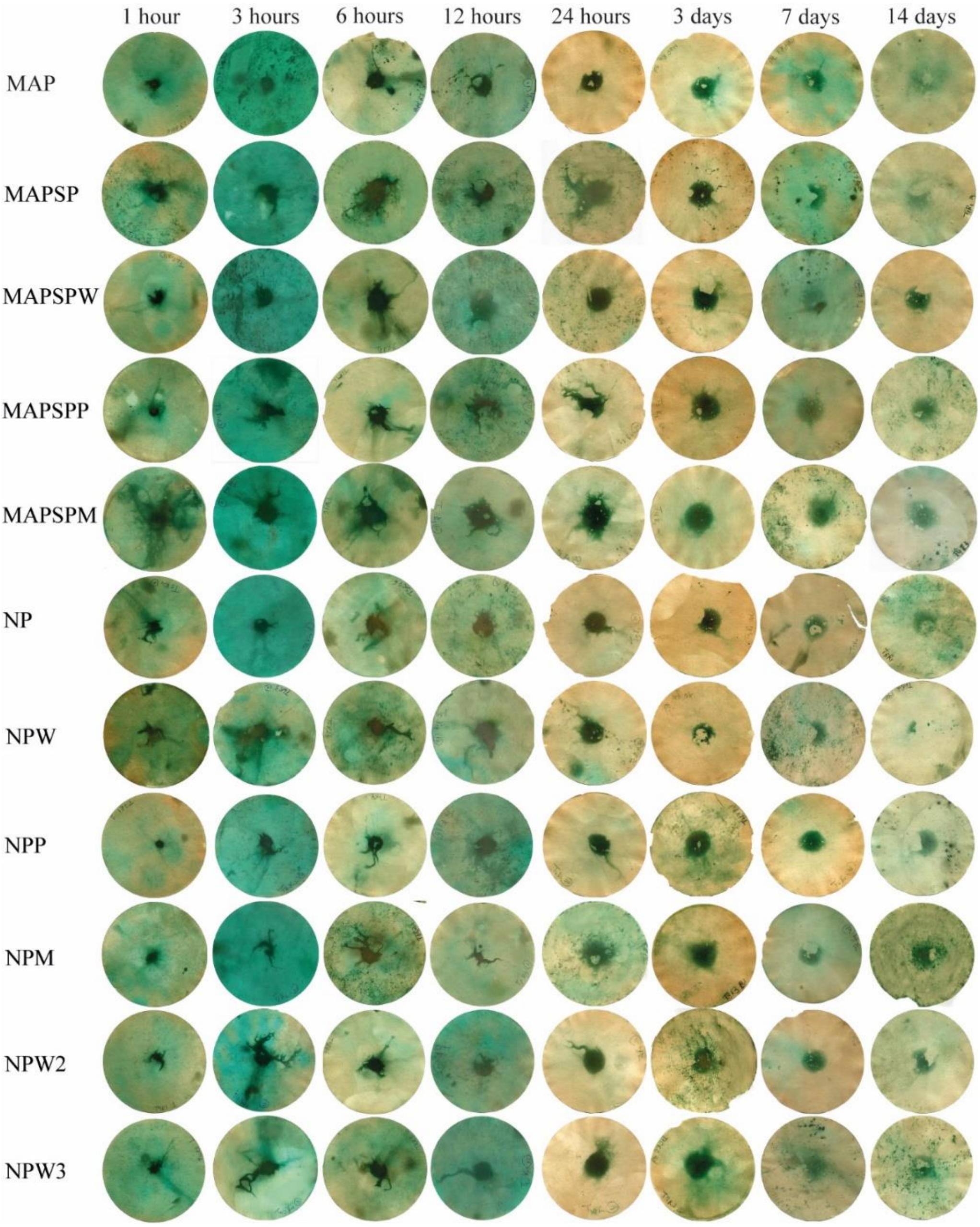


Figure S2. Accumulation of B, Cu, Mn, and Zn in the leaves of soybean plants. A – nutrient accumulation for each fertilizer. B – Mn accumulation for different base saturation levels. Means followed by the same letter do not differ according to the Scott-Knott test ($p \leq 0.05$). Vertical bars indicate the standard error ($n = 4$).

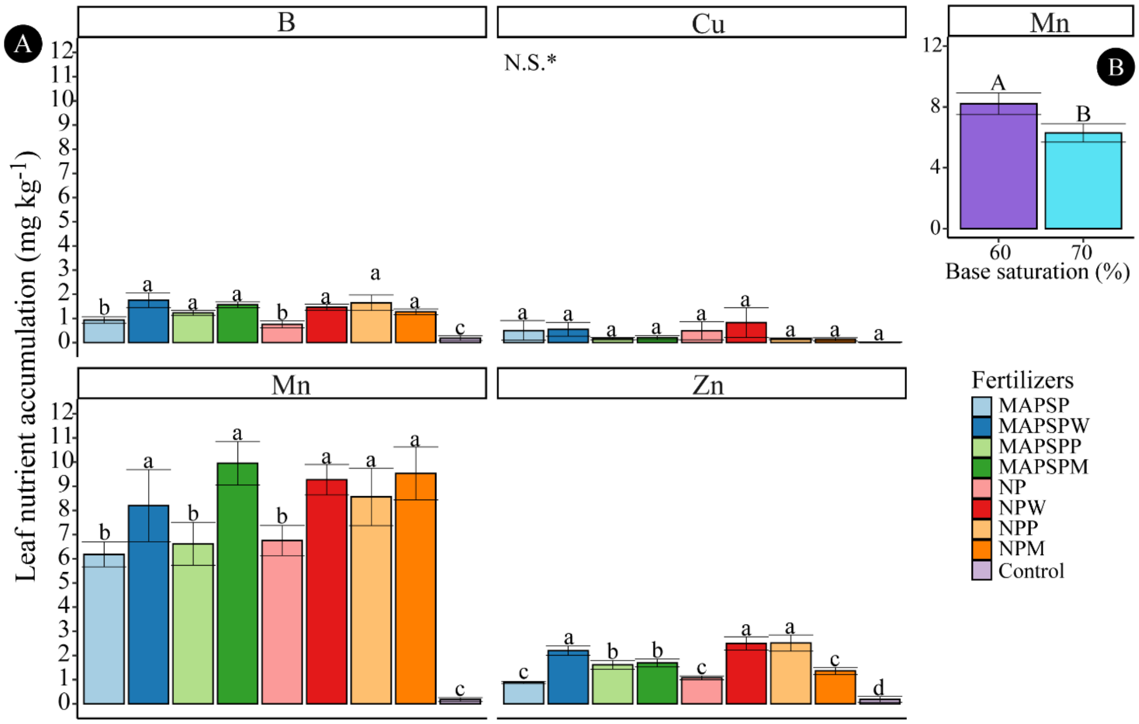


Figure S3. Accumulation of B, Cu, Mn, and Zn in the stem of soybean plants. A – nutrient accumulation for each fertilizer. B – Mn accumulation for different base saturation levels. Means followed by the same letter do not differ according to the Scott-Knott test ($p \leq 0.05$). Vertical bars indicate the standard error (*n* = *4*).

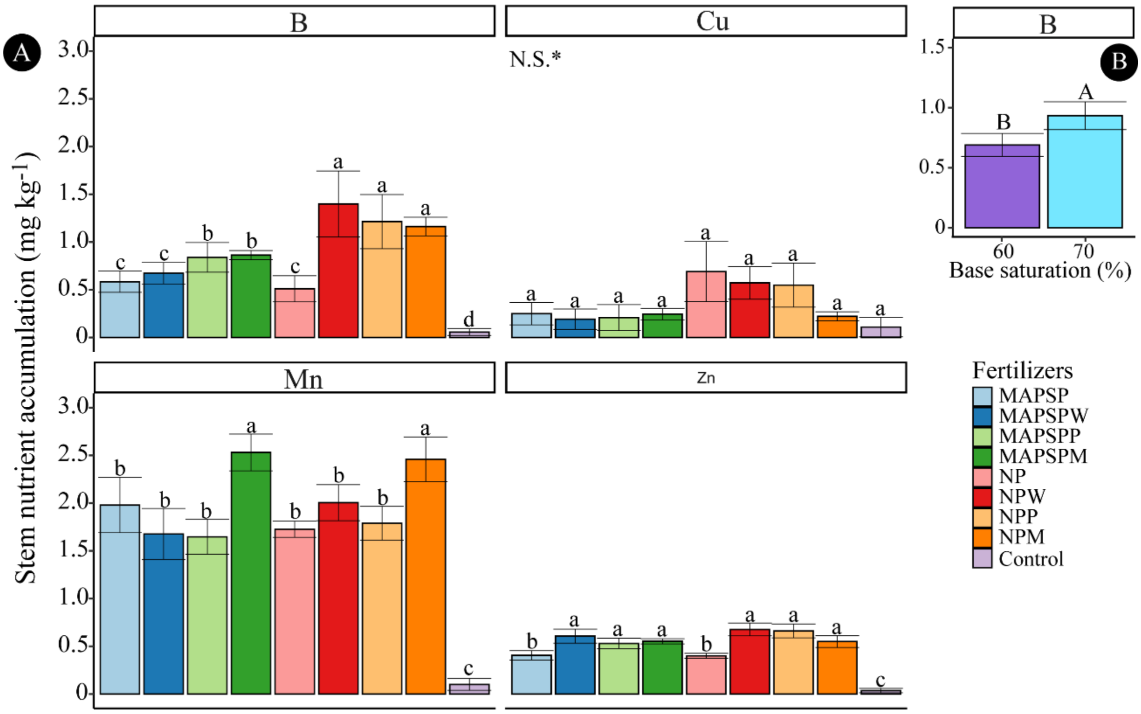


Figure S4. Absorption march of Mn at different phenological stages of the soybean for different parts of the plant. Vertical bars indicate the standard error (*n* = *4*).

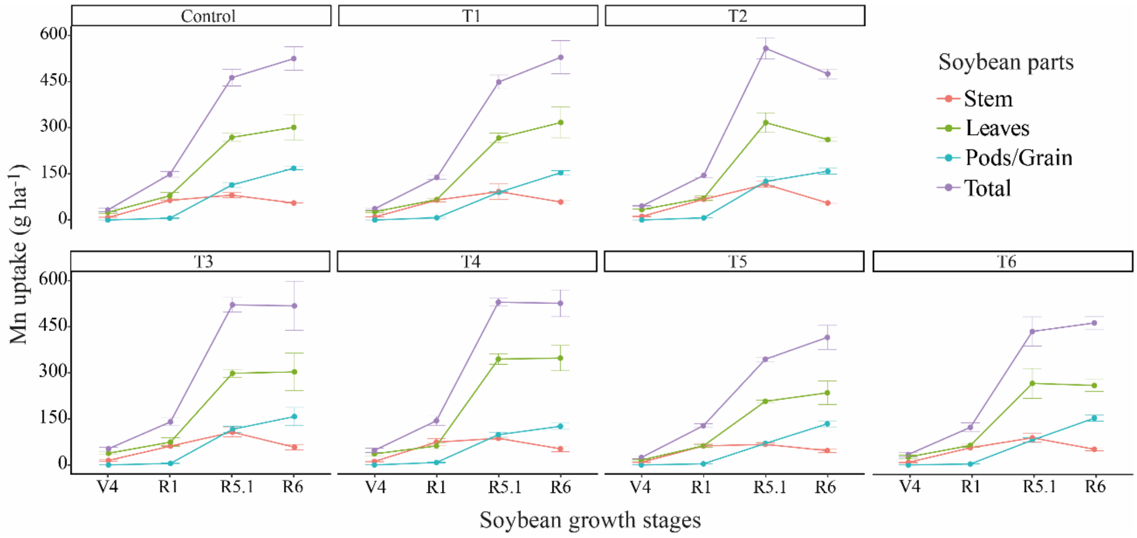


Figure S5. Absorption march of Cu at different phenological stages of the soybean for different parts of the plant. Vertical bars indicate the standard error (*n* = *4*).

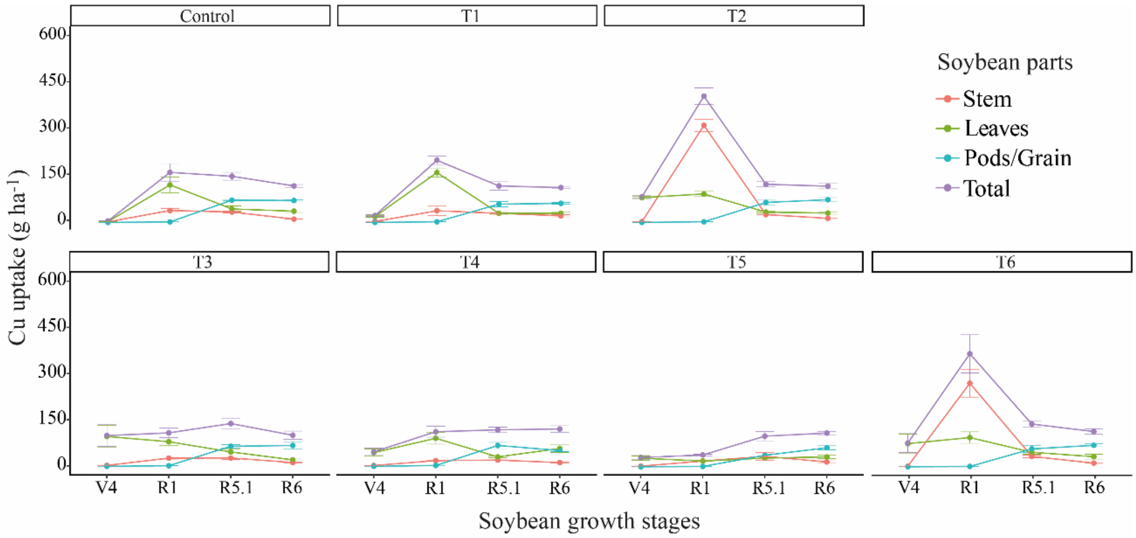


Figure S6. Absorption march of B at different phenological stages of the soybean for different parts of the plant. Vertical bars indicate the standard error (*n* = *4*).

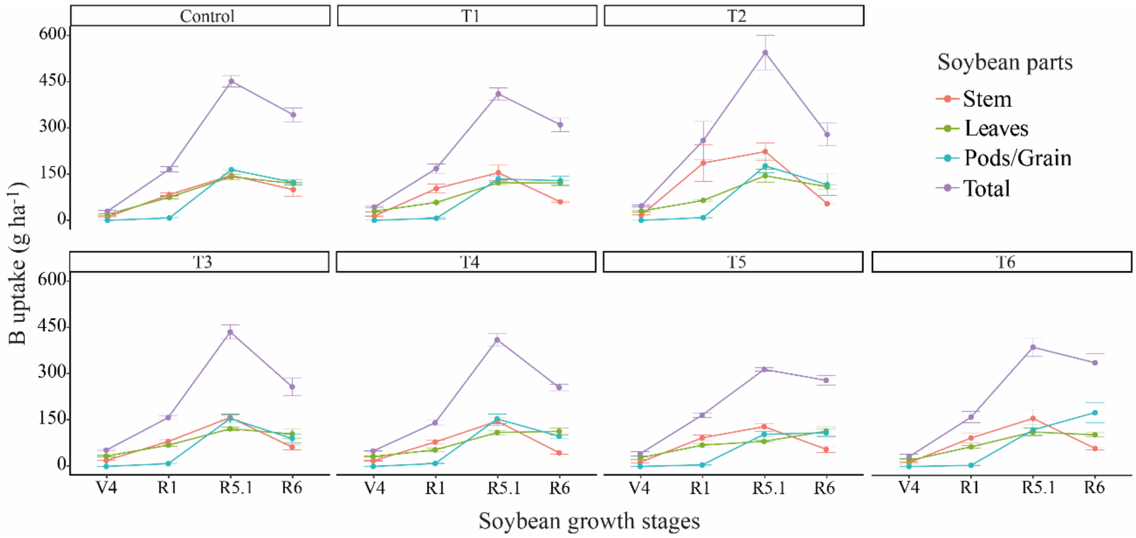


Figure S7. Absorption march of Zn at different phenological stages of the soybean for different parts of the plant. Vertical bars indicate the standard error ($n = 4$).

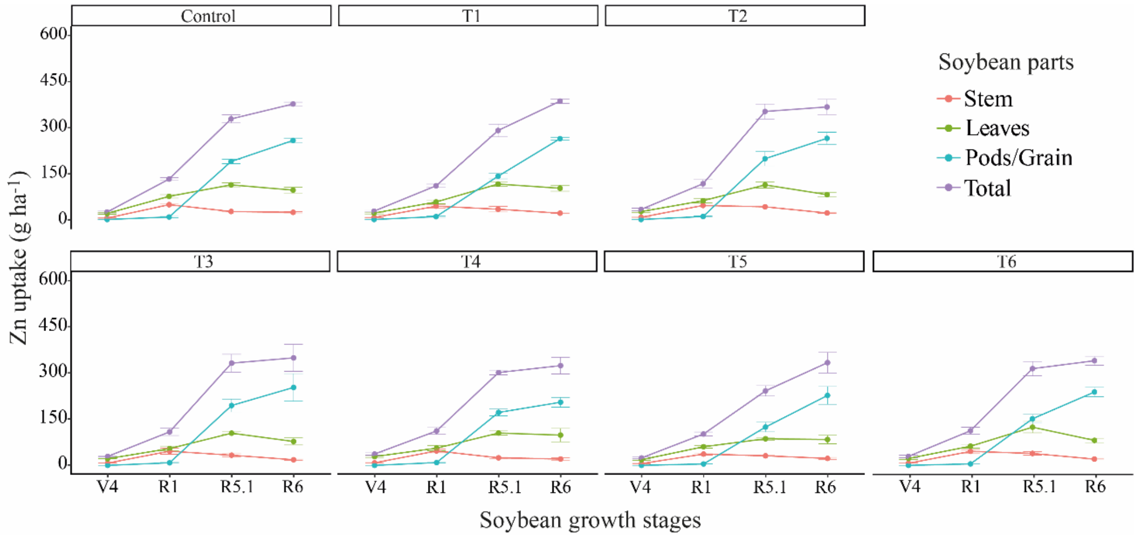


Figure S8. SEM/EDS of the treatment – *MAP + Sulfurgran + Maxxi- phós®*

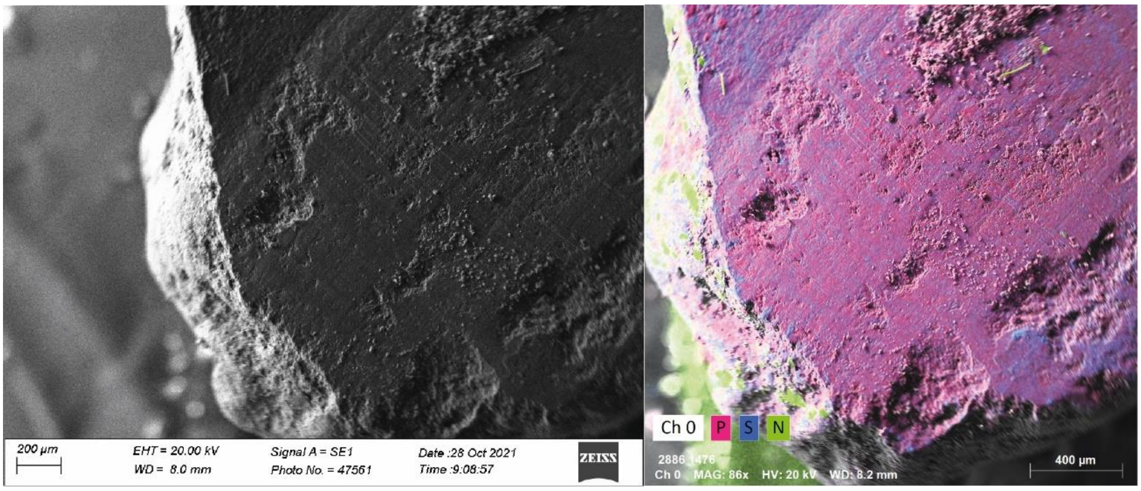


Figure S9. SEM/EDS of the treatment – *MAP* + *Sulfurgran®* + *Maxxi- phós®* + *Wolftrax®*

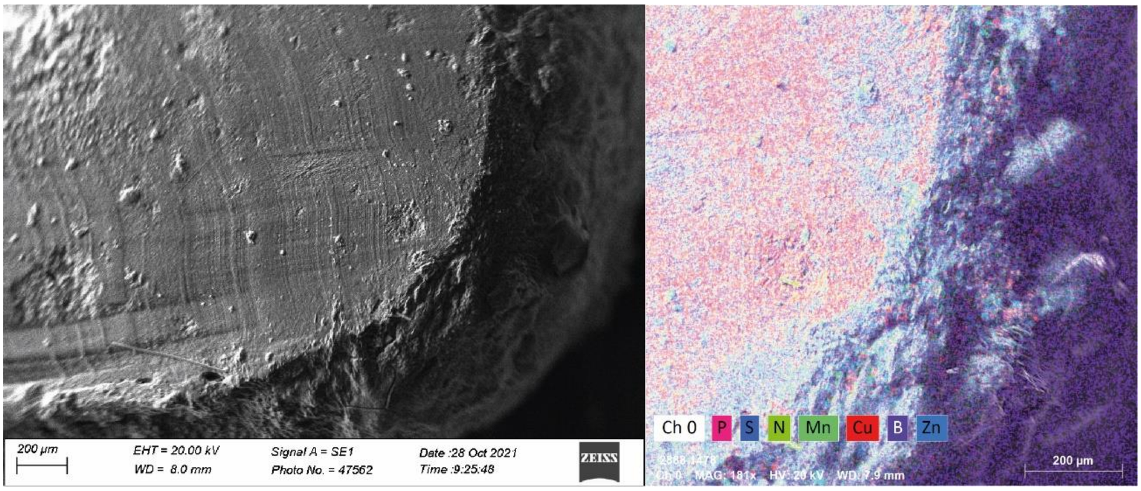


Figure S10. SEM/EDS of the treatment – *MAP* + *Sulfurgran®* + *Maxxi-phós®* + *MIB Precise®*

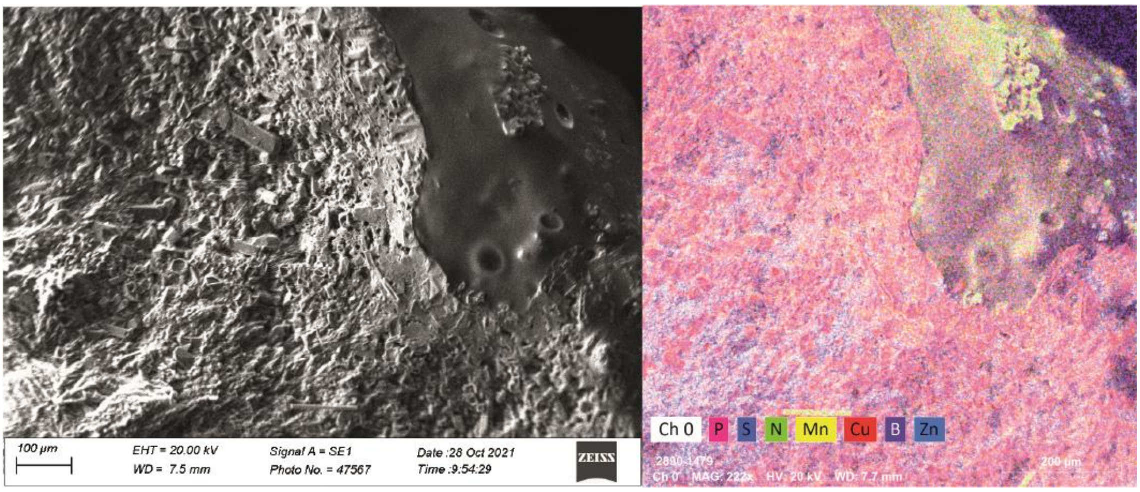


Figure S11. SEM/EDS of the treatment – *MAP* + *Sulfurgran®* + *Maxxi-phós®* + *Microsol®*

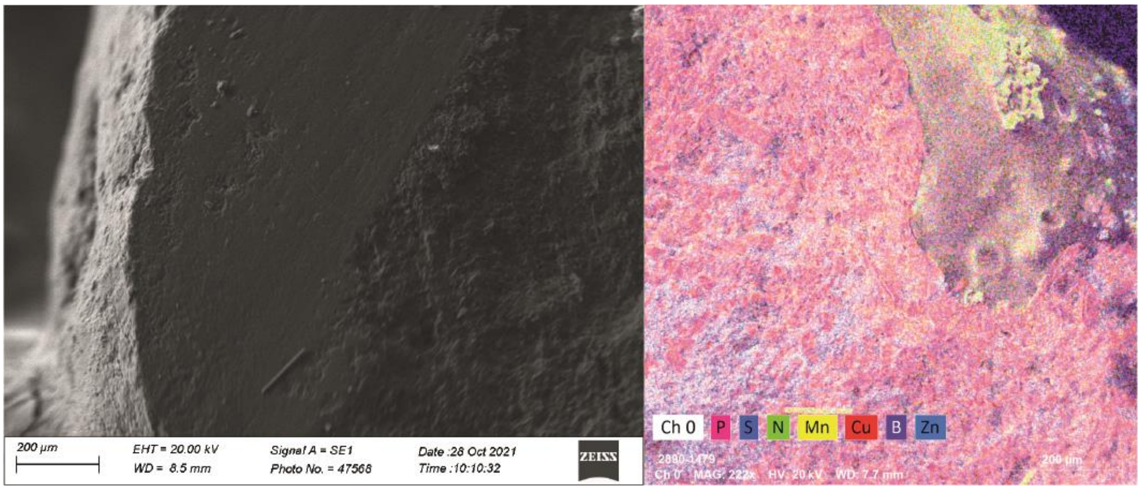


Figure S12. SEM/EDS of the treatment – *NPS* + *Maxxi-phós®*

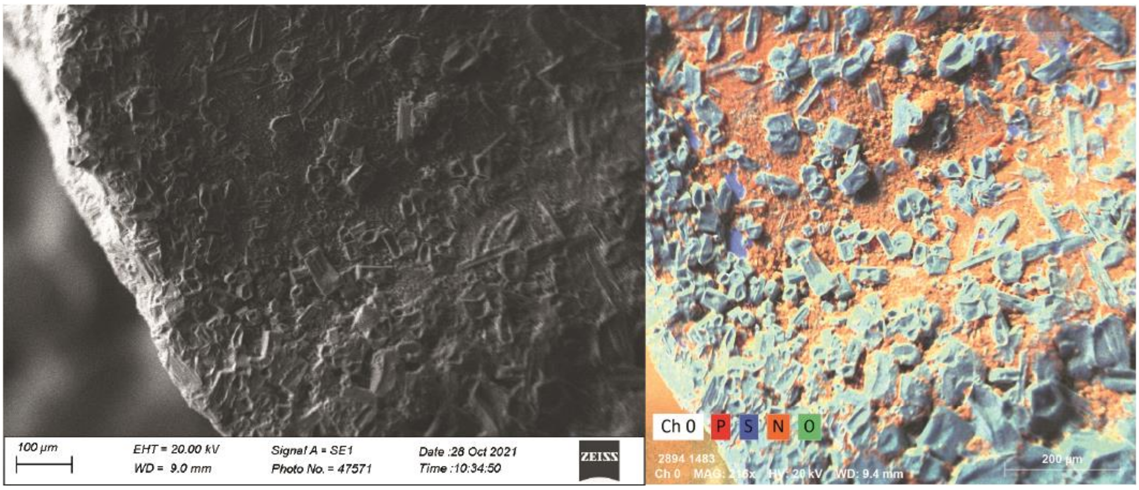


Figure S13. SEM/EDS of the treatment – *NPS* + *Maxxi- phós®* + *Wolftrax®*

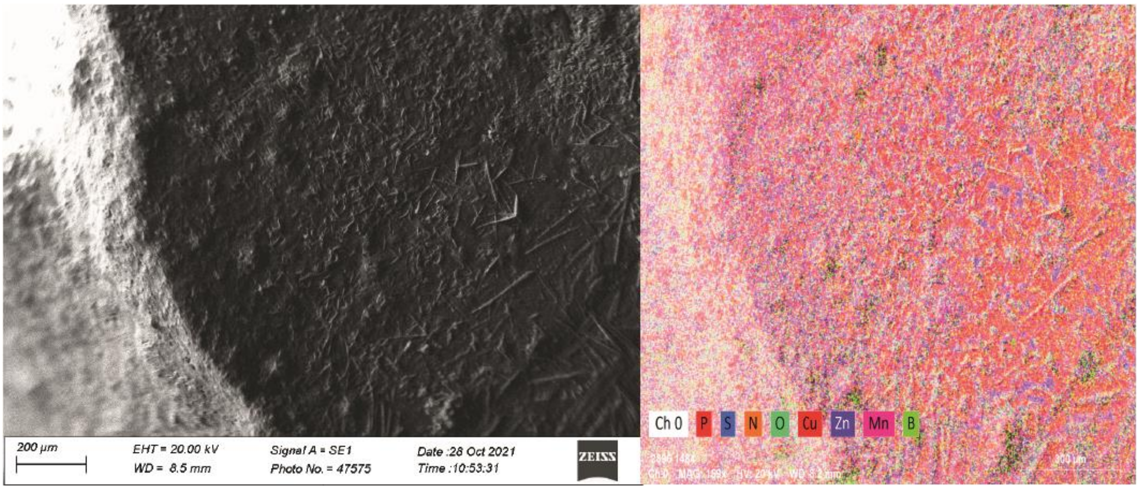


Figure S14. SEM/EDS of the treatment 7 – *NPS + Maxxi- phós® + MIB Precise®*

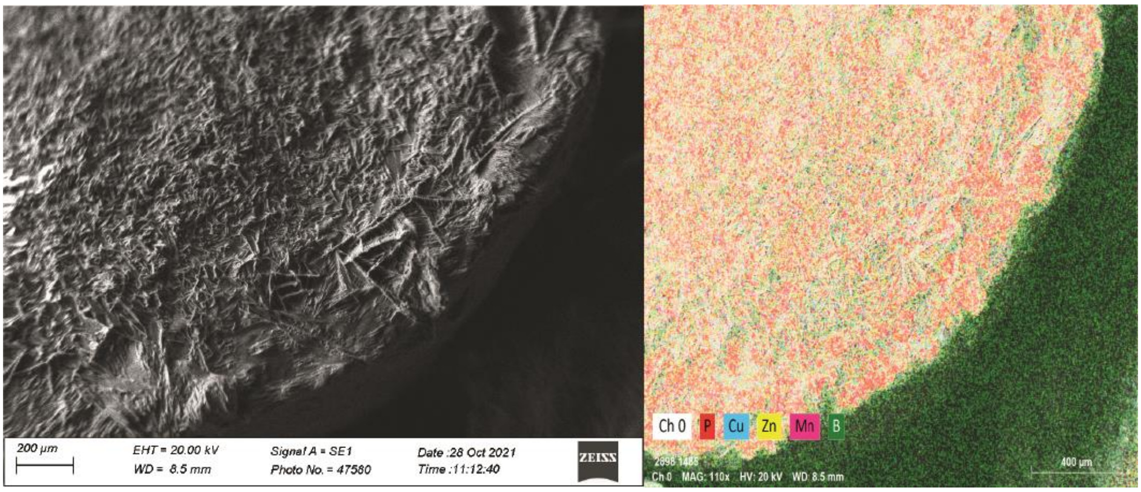


Figure S15. SEM/EDS of the treatment 8 – *NPS + Maxxi-phós® + Microsol®*

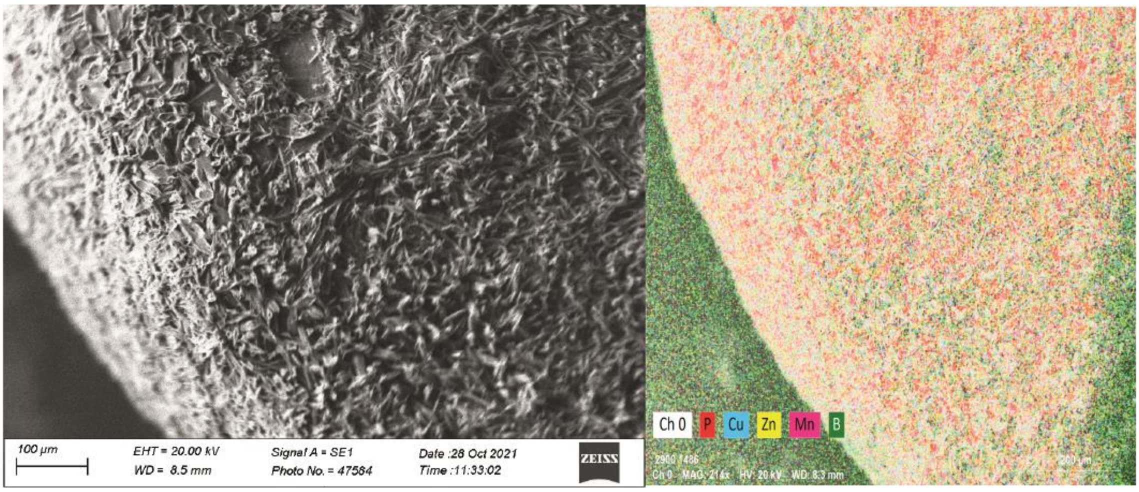


Figure S16. SEM/EDS of the treatment 9 – *NPS + Maxxi- phós® + Wolftrax® dose 2*

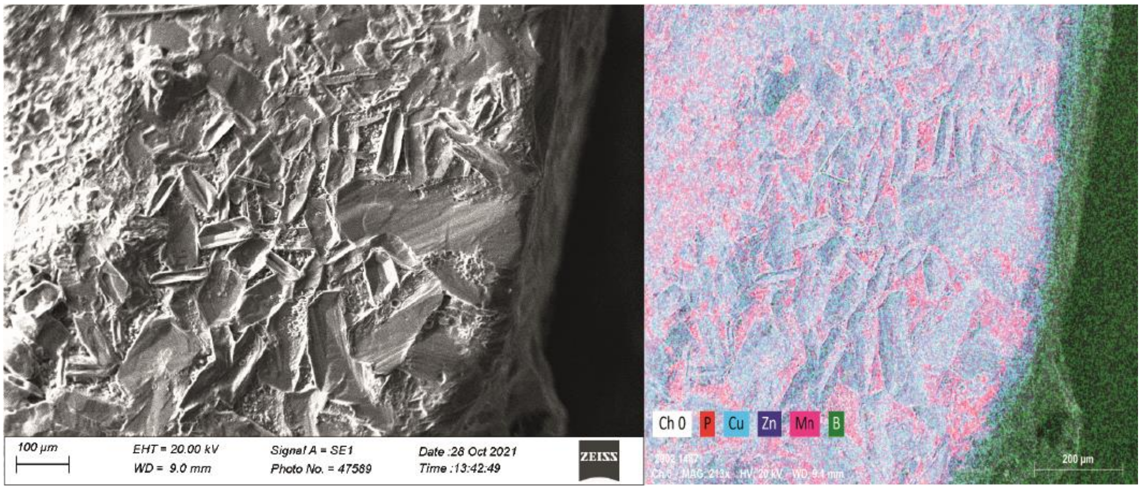


Figure S17. SEM/EDS of the treatment 10 – *NPS* + *Maxxi- phós®* + *Wolftrax® dose 3*

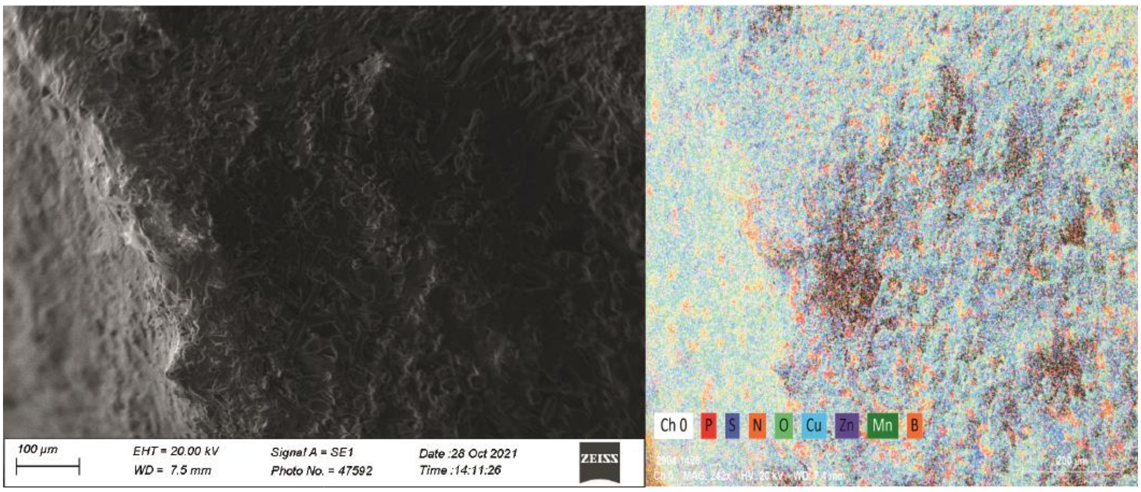


Figure S18. Examples of the filter papers collected after 28 days of incubation of the fertilizers

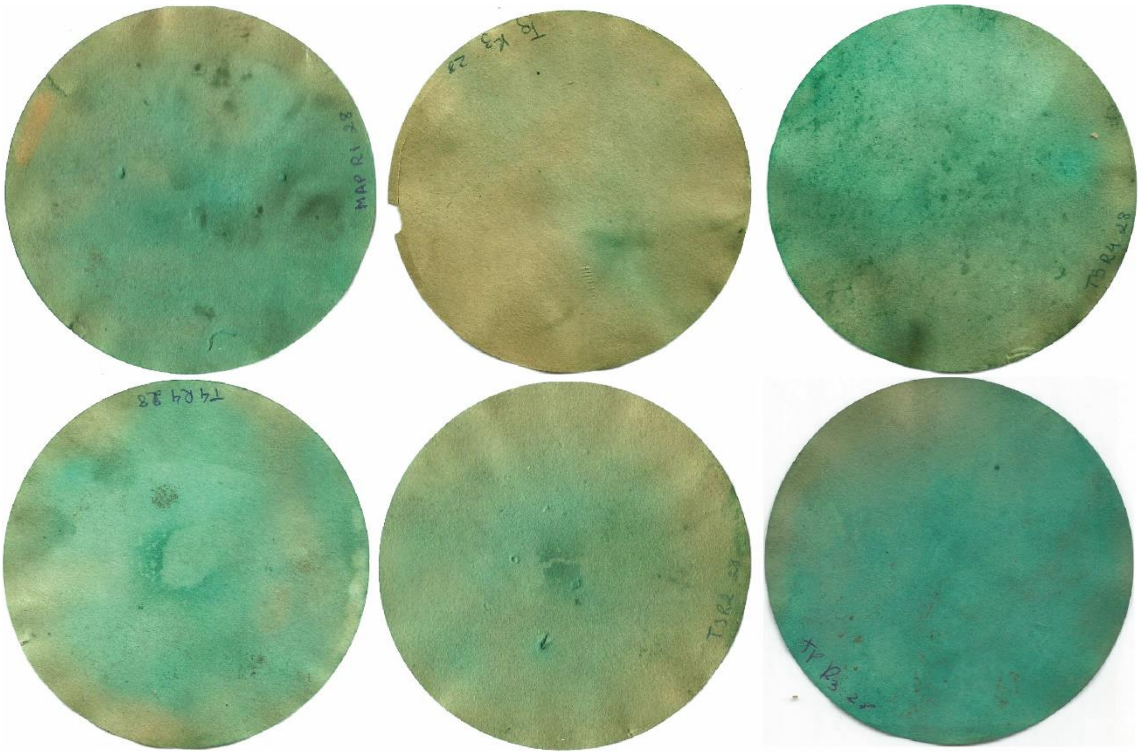


Figure S19. A –Shoot, leaves, stem, and root dry matter of soybean in response to the application of different treatments and the absence of fertilization. B – Shoot dry matter under different base saturation levels. Means followed by the same letter do not differ according to the Scott-Knott test ($p \leq 0.05$). Vertical bars indicate the standard error (*n = 4*).

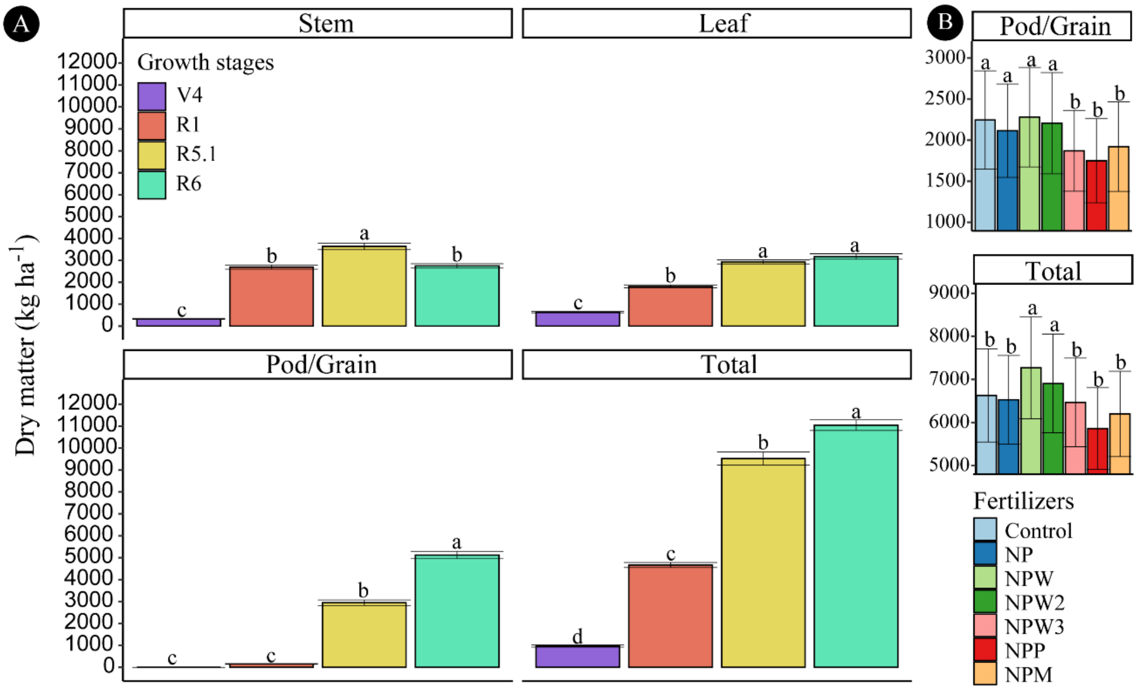


Figure S20. Shoot, leaves, stem, and root dry matter of soybean at different phenological stages of soybean plants. Means followed by the same letter do not differ according to the Scott-Knott test ($p \leq 0.05$). Vertical bars indicate the standard error ($n = 4$).

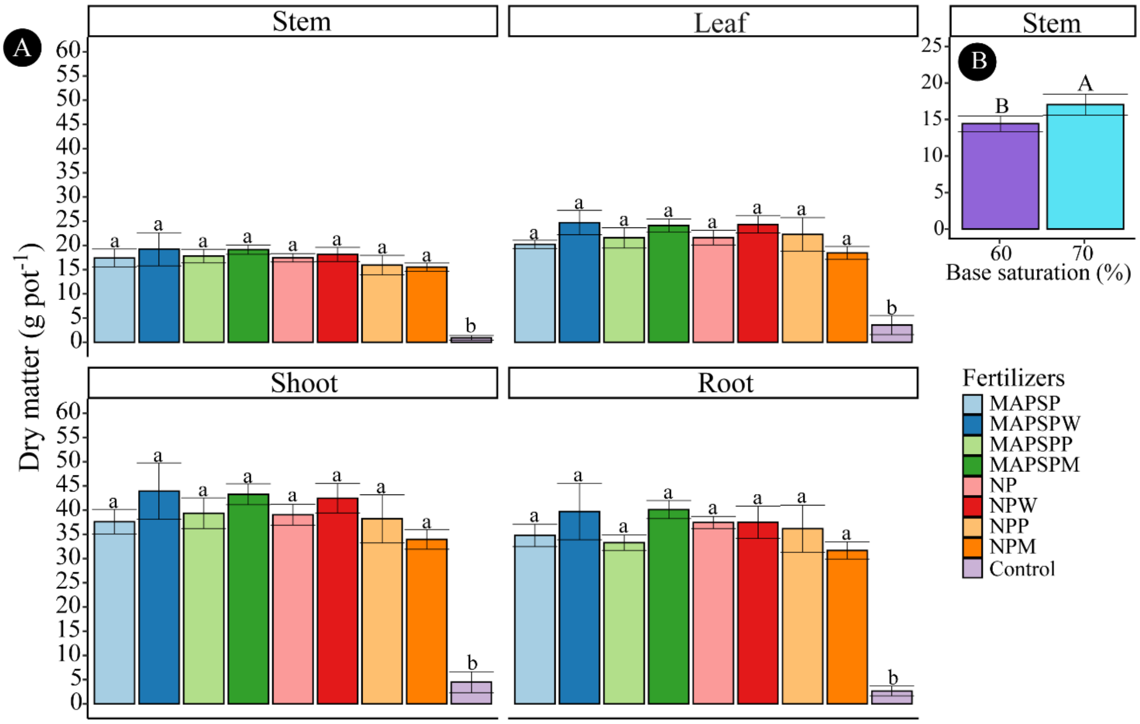


Table S3. Percentage of root accumulation relative to total accumulation in greenhouse-cultivated soybean

Fertilizer	B	Cu	Mn	Zn
	%			
MAPSP	33,98	25,39	56,28	81,38
MAPSPW	60,64	54,27	67,17	74,14
MAPSPP	44,23	65,84	75,47	86,39
MAPSPM	50,55	59,58	52,92	52,26
NP	46,79	72,60	63,07	64,52
NPW	35,33	60,03	66,88	54,42
NPP	52,63	59,38	44,17	74,26
NPM	60,47	22,53	26,07	44,65
CONTROLE	24,56	24,01	24,44	21,53

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Artigo 2 – CONTROLLED-RELEASE PHOSPHATE FERTILIZERS TECHNOLOGIES: CHARACTERIZATION AND PHOSPHORUS DIFFUSION IN SOIL AND RELEASE MECHANISMS

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CONTROLLED-RELEASE PHOSPHATE FERTILIZERS TECHNOLOGIES: CHARACTERIZATION AND PHOSPHORUS DIFFUSION IN SOIL AND RELEASE MECHANISMS

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Abstract

Phosphorus (P) absorption by crops is frequently restricted in tropical soils due to a combination of weathering, acidity, low P availability, and the presence of iron and aluminum oxides and sesquioxides. Given this situation, it is necessary to find ways to improve P efficiency in agriculture, and the use of controlled-release fertilizers can enhance nutrient use efficiency. This is because CRF are designed to prolong and regulate the release of nutrients, providing crops with the necessary amount without excess or deficiency. In this study, four commercial controlled-release phosphate fertilizers (Agrocote® E-Max 10-48-00 and Agrocote® E-Max 9-47-00, Multicote™ Agri 4, and Multicote™ Agri 8) were evaluated for their physical and chemical properties, including phosphorus diffusion, nutrient release in water, thermal stability, salt index, pH, hygroscopicity, and hardness. Results showed that MAP had the highest P_2O_5 release on the first day, while Agrocote® 10-48-00 had the greatest diffusion over time. The use of polymers in fertilizer coating was found to reduce and delay the peak of the salt index, reduce acidity, and promote continuous diffusion of phosphate fertilizer, preventing the P content from being adsorbed too quickly after application. The release of N differed from P2O5 in fertilizers, with differences in days. The study indicates that nutrient release impacts all chemical indices of controlled-release fertilizers and can be optimized by using the appropriate fertilizer and coating materials. Overall, these findings can inform more efficient and sustainable use of fertilizers in tropical soils, helping to improve crop yields while reducing environmental impact.

Keywods: Controlled-Release, Phosphorus Fertilizer, Phosphorus Diffusion, Polymers.

Highlights

- Exploration of coating properties in P-fertilizers
- Studying coated P-fertilizers' nutrient release to evaluate P supply efficacy.
- Characterization guides optimal use of technologies for phosphate fertilize

1.Introduction

Phosphorus (P) uptake by crops is limited in tropical soils, and this limitation is mainly attributed to a combination of weathering, acidity, low P availability, and the presence of many iron and aluminum oxides and sesquioxides in these soils. The strong interaction of these oxides and sesquioxides with P makes for strong adsorption of P, and it remains in forms unavailable for uptake by plants. Therefore, it is necessary to apply phosphate fertilizers for adequate supply of P to crops since the unfertilized soil is generally not able to provide an adequate amount to meet the uptake required for plant development. Fertilizers with high solubility, such as monoammonium phosphate (MAP), are widely used in agriculture, and as they are soluble, their nearly immediate availability after application favors direct contact between P and soil colloids, precipitating it in unavailable forms and reducing uptake by plants.

In this context, the fertilizer industry faces the challenge of promoting a circular and sustainable economy, since phosphorus is extracted from phosphate rock and igneous deposits, considered finite and non-renewable resources. In addition, it is estimated that less than 20% of the phosphorus extracted for fertilizer production arrives at crop plants (Neset and Cordell, 2012a; Sharpley et al., 2018). This makes an increase in the efficiency of phosphorus use an urgent necessity, since phosphorus is a very necessary element and its shortage raises global environmental concerns, such as food security and sustainability (Neset and Cordell, 2012b).

Given this situation, it is necessary to find ways of making P use efficient in agriculture; prominent in this regard are practices such as improvement in application methods, precision agriculture, fertigation, and use of enhanced-efficiency fertilizers (Chen et al., 2018). Multiple technologies have been developed to enhance the efficiency of phosphorus fertilizers, including the application of coated phosphorus fertilizers. These coated fertilizers aim to improve nutrient release and uptake by plants, minimize nutrient losses through leaching and runoff, and reduce environmental impacts. Controlled-release fertilizers (CRF) are part of enhanced-efficiency fertilizers and are defined as conventional fertilizers (like MAP) that receive the application of a compound that serves as a physical barrier, capable of delaying and controlling the release of P, reducing its movement and diffusion in the soil (Weeks and Hettiarachchi, 2019; Lawrencia et al., 2021; Guelfi et al., 2022). Regarding the use of CRF in relation to conventional fertilizers, some advantages can be highlighted. They include greater efficiency in nutrient use, since the CRF are formulated to prolong and retard the release of nutrients, providing crops with the amount necessary without excesses or deficiencies, reducing P loss. Another advantage is reduction in application, since the CRFs are applied with less frequency, which can result in reduction in costs and in negative environmental impact caused by excessive application of fertilizers. Only what is necessary is used, making it economically viable and environmentally friendly (Shaviv, 2001; Trenkel, 2010).

In addition, the material used as a coating plays a fundamental role in the performance of the CRF because it will be a determining factor in controlling release of the nutrient. Release by the coating occurs in three different phases (Shaviv, 2001) – the first is called the delay period, in which nearly no release is observed; the second phase consists of constant release; and in the third, a gradual decline occurs in the release rate. Other factors that affect release are temperature and the thickness of the coating, because they can affect the nutrient diffusion coefficient (Du et al., 2006a). Different compounds can be used for the coating, such as organic polymers (polyurethane, polyethylene, and organic acids) or inorganic polymers (sulfur and bentonite) (Trenkel, 2010; Guelfi et al., 2022). According to Guelfi et al.(Guelfi et al., 2022), an ideal CRF should be coated with biodegradable materials that allow adequate control of release to different environments and for different growing conditions. The release curve should be similar to the uptake curve of the crop on which the fertilizer will be applied, maximizing uptake and reducing losses of the nutrient to the environment.

In spite of the importance of CRFs in increasing the efficiency of phosphorus use, there are few studies regarding the chemical, physical, and physicochemical characterization of controlled-release phosphate fertilizers. However, these characteristics are crucial in ensuring good performance and a greater phosphorus use coefficient by plants. When combined with efficient management practices, such as liming, crop practices, and application of the correct amount of fertilizer at the right time and in the right place, these characteristics are of utmost importance in ensuring favorable responses to the application of fertilizers. The commercial phosphate fertilizers Agrocote® 10-48-00, Agrocote® 09-47-00, Multicote™ 4, and Multicote™ 8 were selected with the aim of physically and chemically characterizing controlled-release phosphate fertilizers. These fertilizers were evaluated regarding phosphorus diffusion, release of nutrients in water, thermal stability, salt index, pH, hygroscopicity, and hardness. We expected to observe favorable characteristics in a phosphate fertilizer, including low salt index and hygroscopicity, appropriate hardness, and to confirm whether the controlled release of nutrients would follow the manufacturer's specifications.

2. Materials and methods

2.1 Description of the phosphate fertilizers used

Commercial fertilizers were used in the present study and they differ from each other in regard to manufacturers, technologies, and longevities. Descriptions of the fertilizers follow.

a) Monoammonium phosphate (MAP): Monoammonium phosphate is a commercial soluble granular fertilizer that is widely used in the industry and is obtained after the treatment of ammonia with phosphoric acid. It generally contains 50% to 54% P_2O_5 and 10% to 12% nitrogen (N). In the present study, the MAP used contained 11% N and 52% P_2O_5.

b) Agrocote® E-Max: in the present study, two Agrocote® fertilizers were used, with different longevities, namely Agrocote® E-Max 10-48-00 (projected longevity from 2 to 3 months) and Agrocote® E-Max 09-47-00 (projected longevity from 3 to 4 months). They are controlled-release soluble phosphate fertilizers produced by the ICL company. According to the company, the technology consists of coating the fertilizer by a polymer, increasing its efficiency in use. Furthermore, release of the nutrient is affected by soil moisture and soil temperature, with a mean of 21ºC, where higher or lower temperatures can make for faster or slower release, respectively.

c) Multicote™ Agri: in the present study, two types of Multicote™ Agri were used, namely, Multicote™ 4 (projected longevity of 4 months) and Multicote™ 8 (projected longevity of 8 months). They are controlled-release phosphate fertilizers produced by the Haifa company. According to the company, the fertilizers are coated using the Multicote™ technology, which impedes the immediate dissolution of the fertilizer when applied on the soil. Furthermore, the thickness of the coating determines the longevity of nutrient release. After application, the soil moisture slowly penetrates the coating, and the release rate depends on and is solely determined by the soil temperature, increasing as the temperature rises. According to the manufacturer, other factors, such as soil type, moisture, pH, and microbial activity, do not affect the release rate.

2.2 Characterization of the fertilizers

The phosphate fertilizers were characterized regarding their physical, chemical, and physicochemical characteristics.

2.2.1 Crushing strength

Fertilizer samples were selected according to the size of the granules for the purpose of measuring the force necessary to break the granules. The samples of granules were separated with the aid of sieves with screen openings that allowed selection of granules with sizes of 2 and 3.35 mm. After separation, six granules were selected at random and crushed using an automatic benchtop penetrometer (model MA 933, Marconi) in order to measure the mechanical resistance of the fertilizer. The granules were placed individually on a flat surface coupled to the penetrometer, and this device measured the applied force (kgf) necessary to break the granule. Means of the replications were calculated to determine the final force necessary for rupturing the granule.

2.2.2 Release of P in water, salt index, and pH

Granules were placed in containers with water for the purpose of observing the release of P and N of the fertilizers in water; the release of these elements was measured over time according to ISO 21263:2017 (International Organization for Standardization, 2017)To do so, small nets were made of nylon cloth; 5 g of each fertilizer was placed in a net; and then the net was closed with a rubber band. The nets containing the fertilizers were placed in containers with 250 ml of deionized water that were then closed and placed in BOD with a constantly controlled temperature of 25 ºC. At the designated periods, the containers were opened and aliquots were collected and then analyzed by the Kjeldahl method for N and in an Inductively Coupled Plasma Optical Emission spectrometer (ICP-OES, METES brand, model FME16) for P. After that, the rest of the solution was substituted by a new 250 ml of water. The samples were collected at 1, 7, 14, 28, 42, 56, 77, 98, 126, and 154 days after incubation of the fertilizers. Together with the collections of solution for reading P in the ICP-OES, the pH and the salt index (SI) of the fertilizers were evaluated. The pH of the solutions was evaluated using a portable pH meter (HANNA, HI 98127). The SI was evaluated following the method described by (MAPA-Ministério da Agricultura, 2014) and concerns the salinity of the material in relation to the ions released in the solution, measuring the electrical conductivity (EC) of the solution and comparing it with sodium nitrate ($NaNO_3$). SI is expressed in percentage (%) and is obtained by equation (1).

$$SI = [(Sample\ EC\ /\ NaNO_3\ EC)\ /100] \quad (1)$$

2.2.3 P diffusion

To understand the response of P diffusion in the soil, the method described by Degryse and McLaughlin (Degryse and McLaughlin, 2014) was adopted, which consists of capturing the diffusible P in filter paper impregnated with iron oxide. Petri dishes were filled using soil samples collected in Lavras, MG, which were moistened at 70% of field capacity (FC). The experiment was incubated in a BOD chamber (model TE-371/240L, Tecnal brand), with temperature control. Moisture content and temperature were maintained at 70% of FC and 25 °C, respectively. A completely randomized experimental design (CRD) was used, containing 4 treatments (composed of the CRFs, described in item 2.1), 1 control (MAP), and 6 replications, for a total of 30 plots. To perform the diffusion reading, the dishes were opened at 1, 7, 14, 28, and 42 days after fertilizer addition. After collection, the filter papers were scanned, and the mirror image of the diffusion zone was determined using imaging software (GNU Image Manipulation Program - GIMP) to quantify the extent and intensity of the diffusion zone.

2.2.4 Characterization of the polymers by Fourier transform infrared spectroscopy (FTIR) analysis

Characterization of the main chemical groups of the polymers of the CRFs was performed through Fourier transform infrared spectroscopy (FTIR). First, the four samples of the polymers of the fertilizers Agrocote® 10-48-00, Agrocote® 09-47-00, Multicote™ 4M, and Multicote™ 8M were dried in a laboratory oven at 70 °C, ground until having the appearance of powder, and then passed through a 100-mesh sieve. The spectrophotometer Nicolet 4700 FT-

IR from Thermo Nicolet was used in this study. First the samples were incorporated in potassium bromide (KBr) disks and then the disks were analyzed by transmittance with 32 replications, reading from 4,000 to 400 cm^{-1}, and resolution of 4 cm^{-1}.

2.2.5 Thermogravimetric analysis (TGA)

To determine the thermogravimetry (TG) of the CRF polymers, a sample of the polymer was placed on an alumina sample holder, where its mass was constantly monitored by a thermobalance. The samples were heated from room temperature to a temperature of 600ºC, using a heating rate of 20 ºC min^{-1} in a dynamic atmosphere of nitrogen (N_2) with a flow rate of 50 mL/min. Thermogravimetric and derivative thermogravimetric (DTG) curves were obtained on a TGA Q500 thermal analyzer (TA Instruments).

2.2.6 Electron micrograph of the phosphate fertilizers (SEM)

A scanning electron micrograph (SEM) was performed to observe the thickness and uniformity of the coating on the phosphate fertilizers (Figure 8). For this, the fertilizer samples were cut with a scalpel, placed in aluminum stubs, and then coated using a carbon evaporator (Union CED 020 model). An SEM function was used, and two measurements were taken in different areas of the coated MAP granules to measure the MAP coating thickness. The samples were observed using a scanning electron microscope (LEO EVO 40 XVP - Zeiss model) with a secondary electron detector, a voltage of 20 kV, and a working distance ranging from 7.5 to 9.5 mm.

2.2.7 Hygroscopicity

The hygroscopicity of the fertilizers was evaluated according to the methodology described by Rutland et al (Rutland et al., 1986). For that purpose, 4-g samples of each fertilizer were weighed and placed in aluminum containers, covered with a plastic film, and then placed in a laboratory oven with a constant temperature of 30ºC for preheating and removal of any moisture from the sample. After that, the plastic was removed and the samples were placed and kept in a chamber with controlled relative humidity of 85% and temperature of 35 ºC. The samples were weighed, and moisture gain was determined at 1, 7, 14, and 21 days after incubation.

2.3 Statistical analyses

Statistical analyses were performed using the R statistical software (R Core Team, 2022). The GVLMA package (Global Validation of Linear Model Assumption) was used to validate the data, and the assumptions of normality, homogeneity of variance, homoscedasticity, and the presence of outliers were manually checked for the models using the plots generated by the plot function. Analysis of variance (ANOVA) was applied to the variables. The means comparisons of the variables were performed through the Scott-Knott test ($p \leq 0.05$), using the emmeans package.

3. Results

3.1 Crushing strength

A direct relationship is observed between the size of the granules and their resistance to rupture in the crushing (or hardness) test of the phosphate fertilizers (Figure 1). Larger granules proved to be more resistant than smaller ones, requiring the application of greater force (kgf) to rupture them. The force necessary to break the granules ranged from 13.92 kgf for granules of size 3.35 mm to 6.05 kgf for those of 2 mm. Regarding particle size, granules of 3.35 mm showed greater resistance than those of 2 mm, with increases of force necessary for rupture of 3.5 kgf (Agrocote® 10-48-00), 5.5 kgf (Agrocote® 09-47-00), 2.52 kgf (MAP), 3.37 kgf (Multicote™ 4M), and 1.25 kgf (Multicote™ 8M) in comparing the larger granules with the smaller. Except for Multicote™ 8M, which exhibited the least hardness observed among the treatments for the two particle sizes (6.05 for 2 mm and 7.3 for 3.35 mm), the fertilizers had similar hardnesses.

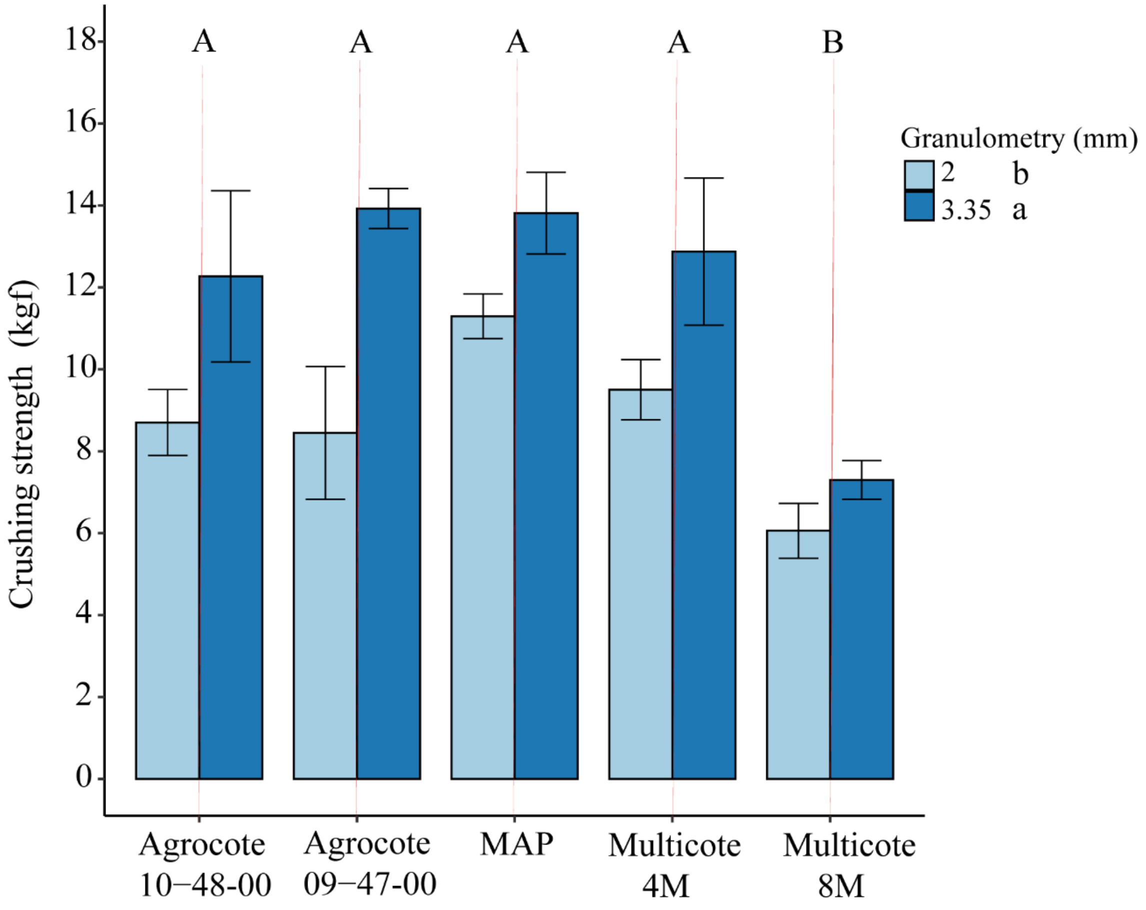

Fig. 1 Crushing strength of phosphate fertilizer granules with different particle sizes (mm) according to the force applied (kgf). The vertical bars represent standard error (*n* = 5)

3.2 Release in water

The results of release in water of the P and N nutrients are shown in Figure 2. As expected, the use of polymers altered release of the nutrients. After one day of incubation, the Agrocote® 10-48-00 exhibited a release rate of 26.3% of P_2O_5, compared to 85.6% from MAP, which obtained an expressive rate. Even though it was the CRF with the highest rate of release on that day, Agrocote® 10-48-00 provided for a reduction of 30.72% in release rate in relation to MAP. After 7 days of incubation, Agrocote® 10-48-00 had released 68.3% of its P_2O_5, whereas the Agrocote® 09-47-00 had released only 22.7%, a difference of 45.6% between the two. The Multicote™ 4M and 8M fertilizers had release rates of 10.7% and 9.3%, respectively. Even though Agrocote® 9-47-00 had an initial release rate greater than the rates of the

Multicote™s 4M and 8M, the Multicote™s matched the rate after 28 and 56 days, respectively, and they exceeded the release rate of Agrocote® 9-47-00 after these days.

In relation to release of P_2O_5 greater than 75% from the fertilizers, MAP reached 85% on the first day after incubation, Agrocote® 10-48-00 in 15 days, Agrocote® 9-47-00 in 82 days, Multicote™ 4M in 57 days, and Multicote™ 8M in 86 days. The release of N differed from release of P_2O_5 in the fertilizers with differences of days, at 37 days for Multicote™ 4M and 56 days for Multicote™ 8M, and Agrocote® 9-47-00 in 63 days.

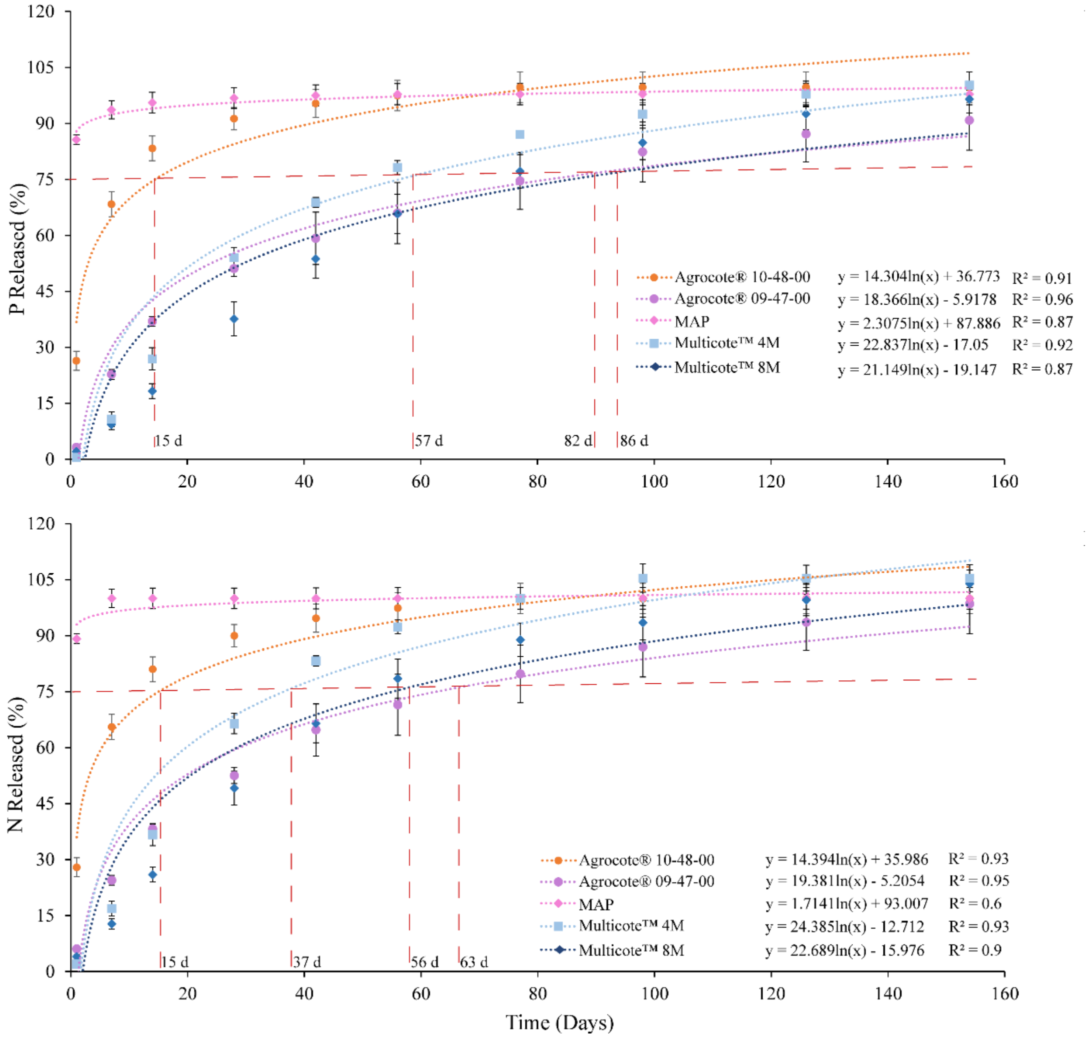

Fig. 2 Release of P_2O_5 and N in water (%) according to the incubation time of the phosphate fertilizer granules with or without controlled-release technologies. Vertical bars indicate standard error (*n* = 4)

3.3 Salt index and pH

Figure 3 shows the results for pH and the salt index according to the incubation time of the phosphate fertilizers. The pH and the salt index varied as the fertilizer was released in the water. The peak of the salt index of the MAP (89.5%) occurred in the first day after incubation, corroborating with the expressive release of 85% of P_2O_5 on the same day (Figure 3). For the same day, the pH of 4.28 (more acidic than the others) is observed. There was an expressive decline in SI up to the 56th day after incubation (arriving at 3%).

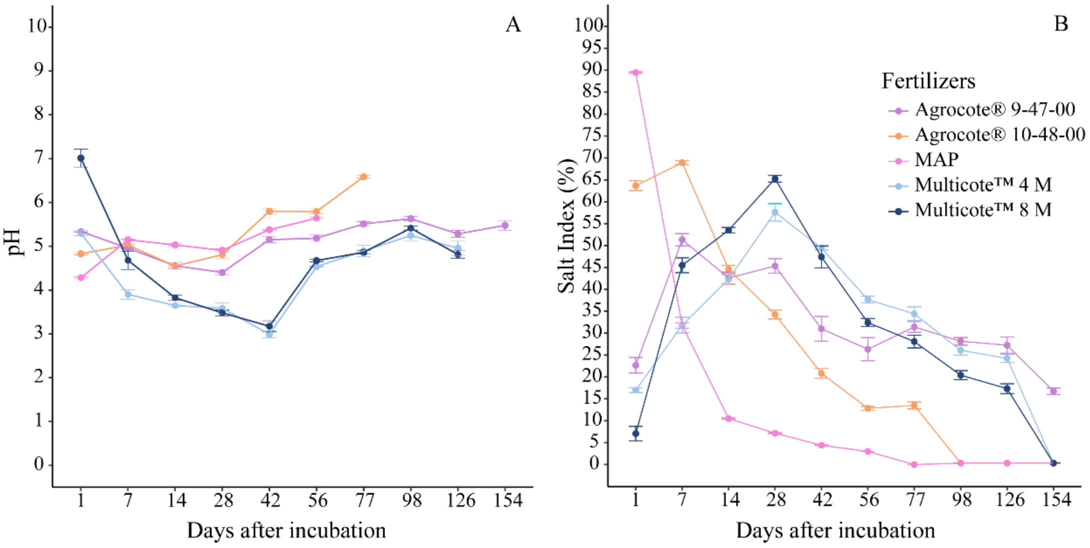

Fig. 3 pH and salt index of the phosphate fertilizers according to incubation time. In the figure: A – pH; B – salt index. The vertical bars indicate standard error (*n* = 4)

Multicote™ 8M initially had neutral pH (7), equivalent to the pH of the deionized water, due to minimal release of fertilizer of only 3% on the first day of incubation. With release intensifying after 28 and 42 days, there was corresponding acidification of the solution (3.48 and 3.17). This response was also observed for Multicote™ 4M, which showed peak salt index (57.8%) and acidification of the medium (pH of 3.58) after 28 days, simultaneously with the more expressive release of P_2O_5 from this fertilizer (54%), which occurred on the same day.

Agrocote® 10-48-00 exhibited its peak SI (around 70%) at 7 days after incubation, equivalent to the more expressive release during the period analyzed – from the first to the seventh day after incubation, there was release of around 42% of P_2O_5. With the intense release from this CRF, there was equivalent acidification of the medium, exhibiting pH of 4.5. In relation to Agrocote® 9-47-00, its peak salt index also occurred after 7 days (51.3%) and acidification of the medium occurred as of the 7th day after incubation (pH 4.95). Constant acidification was observed up to the 28th day, occurring at the same time as increase in release of P_2O_5 occurred.

3.4 P diffusion

The diffusion radius (mm) of the fertilizers is shown in Table 1. After one day of incubation of the granules, there was greater diffusion for MAP (7.55 mm), followed by Agrocote® 10-48-00 (3.12 mm). The other fertilizers showed practically negligible diffusion for that day. After 7 days of incubation, the MAP exhibited a decline of 59.6% in diffusion (4 mm) and was exceeded by Agrocote® 10-48-00, which showed greater diffusion (6 mm) for that day. The CRFs exhibited their peak diffusion after 28 days of incubation of the granules, except for Multicote™ 4M, which occurred at 42 days. Throughout the period analyzed, Agrocote® 10-48-00 exhibited the largest diffusion radii (among the CRFs), while Agrocote® 9-47-00 exhibited the smallest diffusions. As of 28 days of incubation, the fertilizers Agrocote® 10-48-00 and Multicote™ 4M exhibited the largest diffusions observed, arriving at maximum diffusions of 7.87 mm (28 days) and 7.3 mm (42 days), respectively. Multicote™ 8M exhibited constant diffusion over the period analyzed.

Table 1. Diffusion radius (mm) of the phosphate fertilizers according to days after incubation (days).

Days after incubation / Fertilizer	1	7	14	28	42
	Diffusion radius (mm)				
MAP	7.55 a	4.05 b	3.13 b	0.52 c	0 c
Agrocote® 10-48-00	3.12 b	6 a	6.33 a	7.87 a	7.07 a
Agrocote® 09-47-00	0.4 c	1.9 b	2.55 b	2.57 c	1.45 c
Multicote™ 4M	0 c	3.35 b	3.35 b	6.37 a	7.3 a
Multicote™ 8M	0.9 c	3.4 b	3.9 b	4.67 b	3.22 b

Mean values followed by the same letter in the column do not differ from each other at 5% probability by Tukey's test..

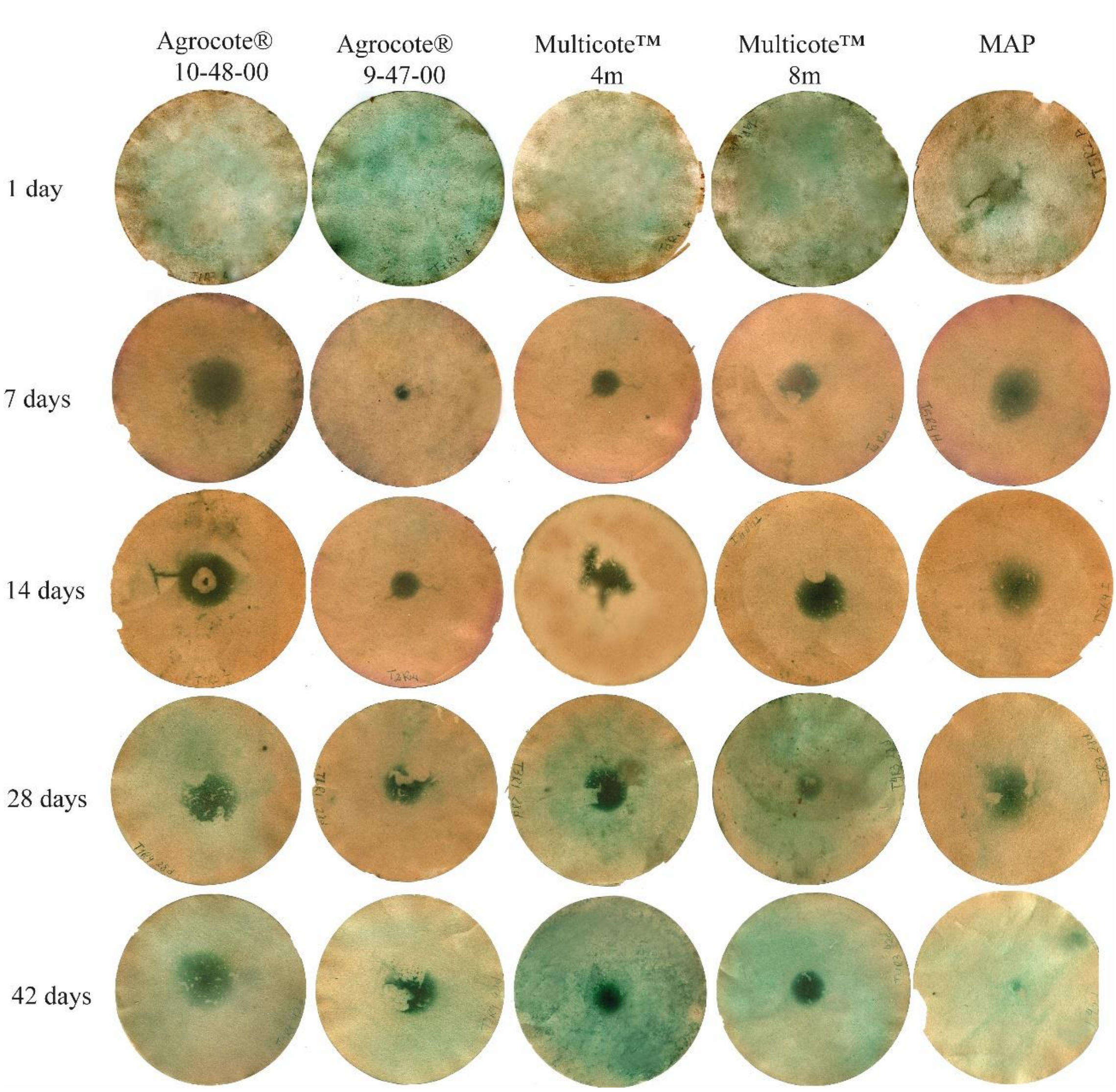

Fig. 4 Zones of P diffusion visualized in filter paper after the incubation of phosphate fertilizers in Petri dishes, as a function of treatments and time. In figure: The more intense green color seen in the center of the filter papers represents the P diffusion.

3.5 Hygroscopicity

Figure 5 shows the hygroscopicity data of the phosphate fertilizers according to incubation time. There was practically no absorption of water from the atmosphere, even under high temperature (35 °C) and high humidity (95% RH) conditions. Although the CRFs had maximum gains at 14 days after incubation of 7.7 (Agrocote® 10-48-00), 5.4 (Agrocote® 09-

47-00), 3.9 (MAP), 7.9 (Multicote™ 4M), and 2.2% (Multicote™ 8M), droplets of water were observed on the surface of the CRFs, as shown in Figure S1.

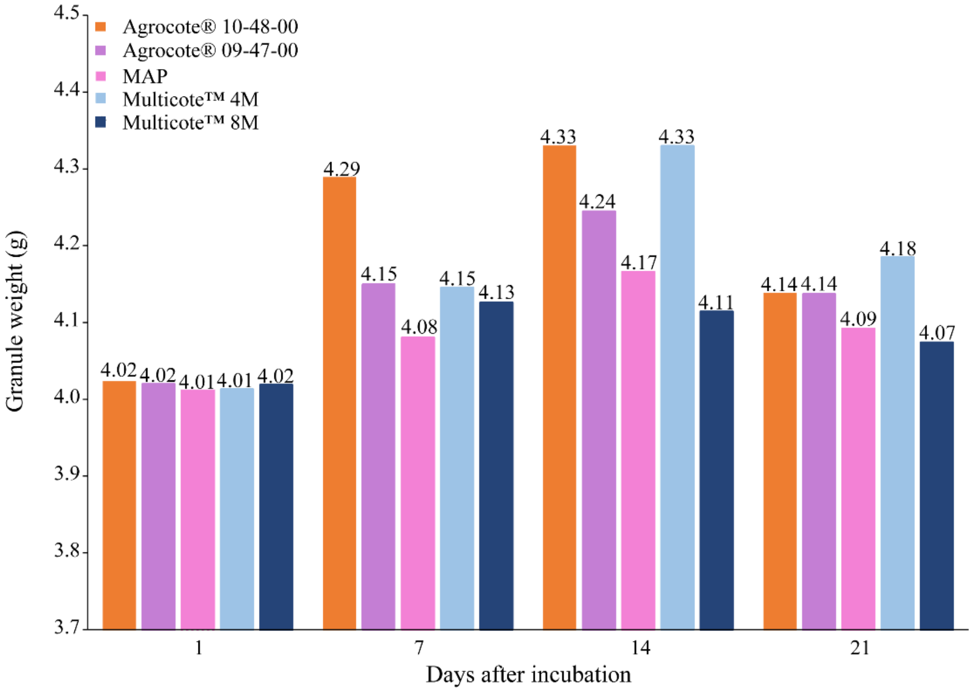

Fig. **5** Weight gain (hygroscopicity) of phosphate CRFs according to days after incubation under controlled temperature and humidity conditions

3.6 Characterization of the polymers by FTIR and TGA

The thermal stabilities of the polymers used for coating were evaluated by thermogravimetric analysis, and the results are shown in Figure 6. The polymers did not show expressive weight loss until reaching approximately 200ºC, at which time initial decomposition of the material occurs. At 302 ºC (Figure 6C and 6D), there was another loss of weight, where the material still had around 80% of its initial weight. The curve shows there were 4 intervals of weight loss that were more expressive; they were at approximately 200 ºC, 303 ºC, 380 ºC, and (for Figure 6D) 455 ºC. Up to the temperature analyzed, the material was not completely degraded, with the residue of all the polymers having weight greater than 30% of the initial value.

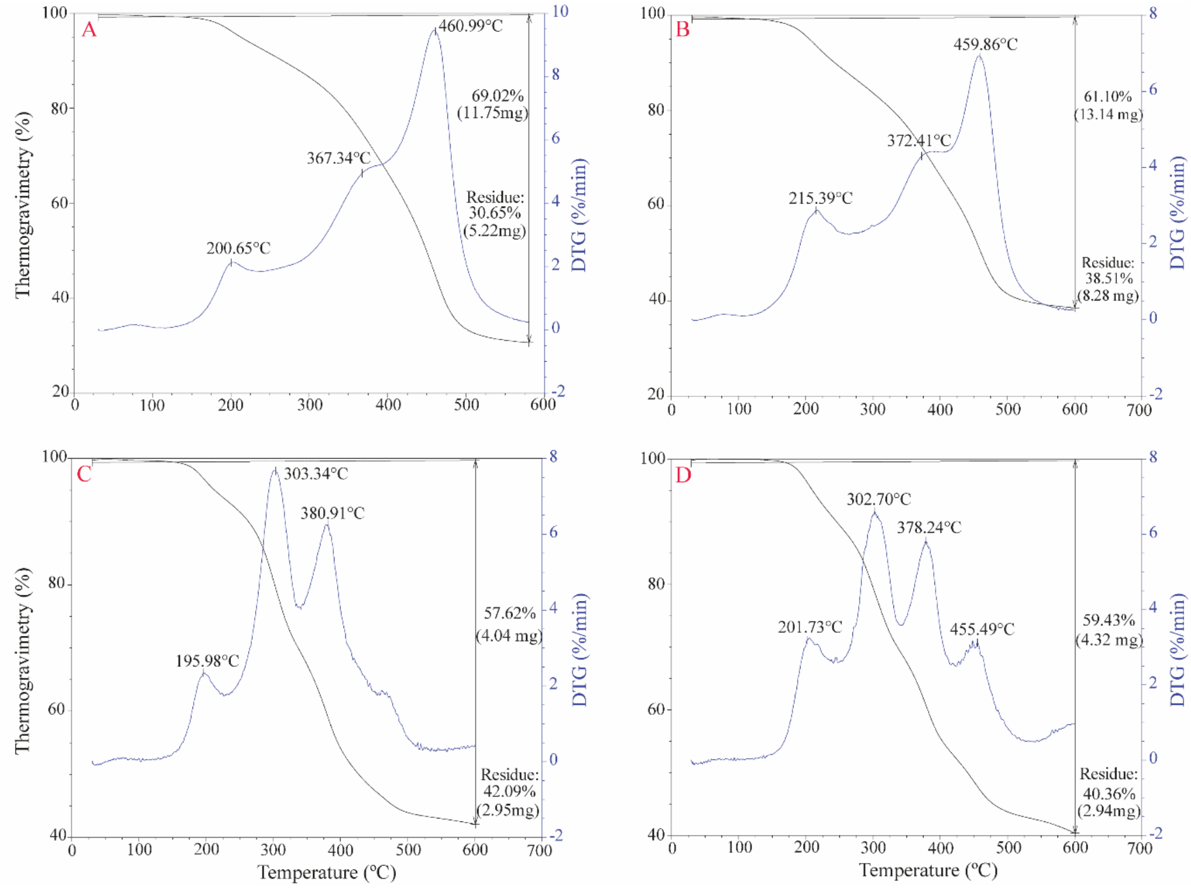

Fig. 6 Curves of thermogravimetric analysis (TGA) / derivative thermogravimetry (DTG) of polymers of CRFs. In the figure: A – Agrocote® 10-48-00; B – Agrocote® 9-47-00; C – Multicote™ 4M; D – Multicote™ 8M

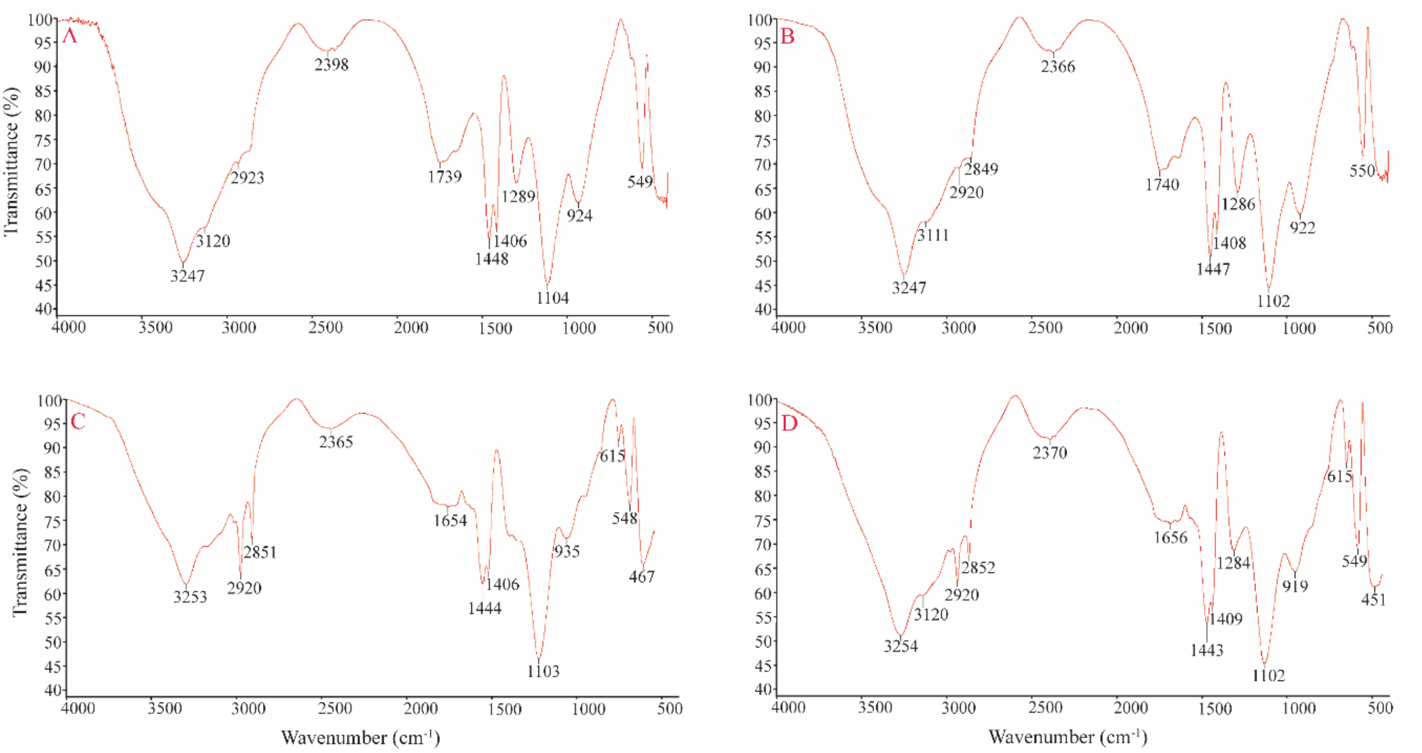

Fig. 7 Spectra of Fourier transform infrared spectroscopy (FTIR) and main spectral bands of polymers of the CRFs. In the figure: A – Agrocote® 10-48-00; B – Agrocote® 9-47-00; C – Multicote™ 4M; D – Multicote™ 8M

The spectra (Figure 7) of the polymers used for coating of the MAP are mainly characterized by bands between 3247 and 3254, indicating an N-H stretching group, followed by a C-O bond in the regions of 1654~1740 in all the samples (Silverstein et al., 2005). An elongated peak near 1320-1210 and 1440 and 1395 cm^{-1} may indicate the presence of a carboxylic acid and may show interaction between the C-O bonds and the C-O-H bending in the plan (Silverstein et al., 2005). The more intense band observed near 1280 indicates a C-O stretching band, and the C-O-H bending band near the region (Silverstein et al., 2005).

3.7 Electron micrograph of the phosphate fertilizers (SEM)

In order to observe the thickness of the coating applied to the phosphate fertilizers, a scanning electron microscopy (SEM) was performed (Fig. 8). It was found that the coatings varied from 152.6 to 98.17 µm for the Agrocote ® 9-47-00 fertilizer; 31.53 to 33.96 µm for the

Agrocote® 10-48-00; 59.22 to 54.86 µm for the Multicote™ 4m, and 69.82 to 67.97 µm for the Multicote™ 8m.

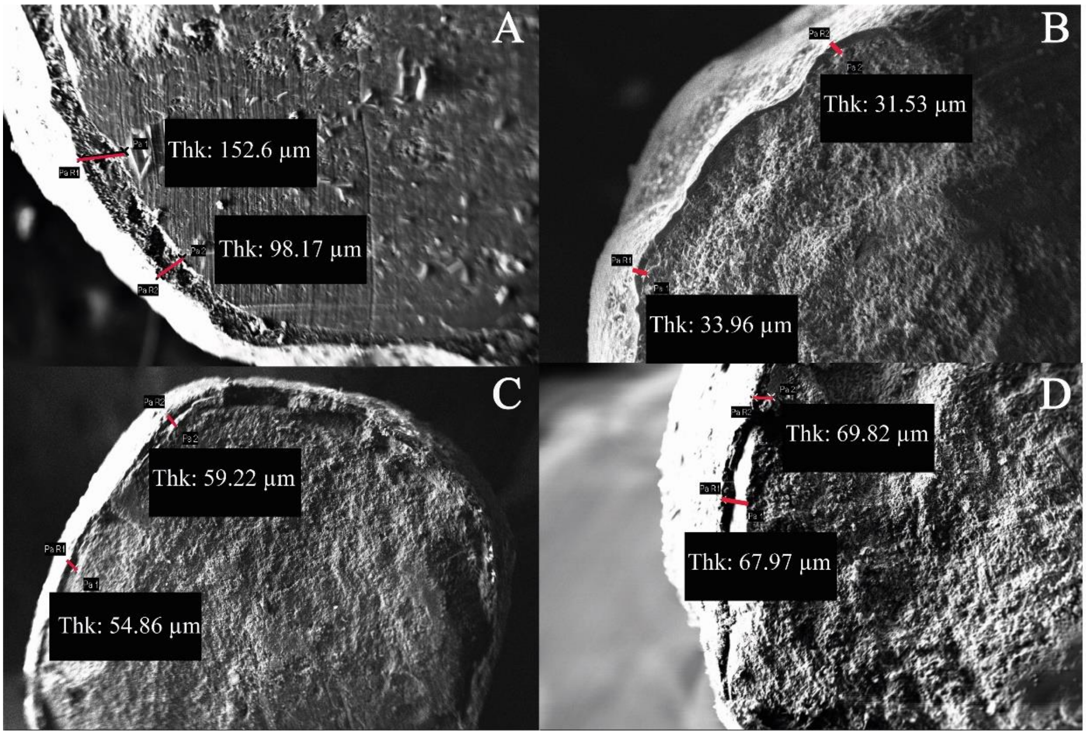

Fig. 8 Scanning electron micrograph (SEM) of the phosphate fertilizers coated. In figure: A – Agrocote® 9-47-00; B – Agrocote® 10-48-00; C – Multicote™ 4m; D – Multicote™ 8m.

4. Discussion

4.1 Crushing Strength

Hardness refers to a physical characteristic of great importance in quality control of fertilizers and determines the resistance of granules to rupture during processes such as handling, transport, storage, and distribution in the field, for example. Maintaining the integrity of the granules assists in uniformity of distribution in an area, because granules with different particle sizes tend to segregate during application and, in the case of fertilizers with added technologies, such as CRFs, rupture of a granule would indicate breakage of the polymer used for coating, which may interfere in the performance of the technology in controlling nutrient release. Therefore, suitable hardnesses can also assist in better agronomic performances of the fertilizers.

Fertilizers require a hardness value adequate for them not to be susceptible to breakage during transport and handling, ensuring the integrity of the granules. According to (F Manual, 1998), standard values of resistance to compression of conventional granules of MAP 11-55-00 range from 2.0 to 3.0 kgf. The hardness values observed indicate increase in resistance as particle size increases. Some studies found in the literature show the same response (Walker et al., 1997; Roshanravan et al., 2015; Taha et al., 2016; Nunes et al., 2022).

Regarding the CRFs, the coating of fertilizers by polymers may be able to change their physicochemical characteristic, which may thus also alter their hardness. The hardnesses of the fertilizers were similar to each other, except for Multicote™ 8M, which had the least hardness. A possible explanation for this response may be related to the results observed in the FTIR (Figure 7), which show the use of the same polymer for coating the fertilizers of different longevities (Multicote™ 4M and Multicote™ 8M). That may indicate that the lower hardness observed was a result of the addition of larger amounts of the polymer for coating the fertilizer. However, in spite of this reduction, the values of hardness observed for this CRF are adequate for commercialization.

4.2 Release in water

As expected, the use of coating on MAP was able to delay the release of P_2O_5, since the fertilizers had a lower rate of release compared to MAP, regardless of the technology used. The unrestrained application of fertilizers is a problem and results in a decline in the efficiency of their use, beyond the environmental and ecological problems (González et al., 2015; Pereira et al., 2015). In this sense, the use of conventional fertilizers needs to be improved, making it extremely necessary to adopt measures to reverse these problems. The expectation is to have the ability to control loss of nutrients, maximizing their availability in the soil, improving the efficiency of their use and reducing environmental impacts.

Therefore, since CRF is designed so that its mechanism delays release of nutrients and coincides with the time of need of the plant, rather than the fertilizer dissolving and making nutrients immediately available, the goal is to allow their release to the crop to occur at a controlled rate, supplying nutrients in sufficient amounts for effective agricultural production, maximizing nutrient use efficiency and reducing negative environmental impact (Vejan et al., 2021). Thus, the fertilizers had various rates of release. The CRF Agrocote® 10-48-00 had a more expressive release than the others, though it was lower than MAP, reaching 75% release in 15 days. This fertilizer could be used in annual crops, such as maize, which due to its rapid development, requires the supply of 55% to 80% P before flowering, with continuous supply throughout its entire cycle for the ideal desired yield to be achieved (Bender et al., 2013). According to the criteria established by Trenkel (2010), the release rates observed were more expressive than those indicated by the manufacturer. To be considered a CRF, fertilizers must fulfill the following criteria: a) their nutrients should not be released by more than 15% in 24 hours; b) they should not release 75% of the nutrients in 28 days; and c) they should ensure that at least 75% of the nutrients will be released within the time established by the manufacturer.

Therefore, under the conditions in which they were evaluated, the fertilizers would have shorter longevities. As an example, Multicote™ 8M, which would have its release of 75% in up to 8 months, exhibited this release 6 months in advance. However, it is important to emphasize that the test of release in water had a constant temperature of 25 ºC, and according to the manufacturers, its longevity is determined in tests with a temperature of 21 ºC. The increase in the release of the nutrient would probably be a consequence of the increase in temperature, since the release rate can even double when there is an increase of 10ºC (Oertli and Lunt, 1962; Kochba et al., 1990; Gandeza et al., 1991; Du et al., 2006b). That is because diffusion of water into the membrane is the factor that governs the release rate in the CRFs, and they are therefore affected by temperature (Kochba et al., 1990).

However, it is important to emphasize that the CRFs sold in tropical countries, such as Brazil, must be able to be used under the characteristic conditions of high temperatures, which favor constant release from the fertilizers. High temperatures, connected with periods of high rainfall, may be able to increase the release from CRFs, since they are factors that directly affect this variable. Although the polymers have high resistance to heat (Figure 6) and are not degraded, the temperature of 25ºC was able to intensely accelerate the release indicated by the manufacturer.

However, another important factor to consider regarding laboratory tests of nutrients in water is related to considering only the physical processes associated with the release, and it is important to emphasize that there may be significant differences between release of the nutrient in water compared to release in the soil. These differences arise from chemical (pH) and physical (diffusion, moisture, temperature) effects or the action of the soil microbiota (Shaviv, 2001), since nutrient release by CRF is directly related to factors such as thickness (Figure 8) and type of material used in the coating and soil conditions, such as temperature, moisture, and rainfall (Azeem et al., 2014; Lawrencia et al., 2021)

Furthermore, the release of N by fertilizers occurs more quickly than the release of P_2O_5, which is probably due to the concentration and solubility of the nutrients in the fertilizer granules. The amount of N found in the fertilizer is much smaller.

4.3 Salt index and pH

In evaluation of the salt index, the probable potential of the fertilizer to cause damage to the plants is noteworthy. The pH, in turn, is related to the potential of the fertilizer of acidifying the soil; phosphate fertilizers containing ammonium are able to raise the pH in the microregion of the granules, followed by acidification of the region due to the ammonium nitrification reaction, which may become a problem for the rhizosphere. Regardless of the treatment, the CRFs were able to reduce the peak of the salt index and the acidification brought about by the MAP already on the first day of incubation. Just as for diffusion, these indices are intensely affected by the release rate from the fertilizers and they are proportional, since the greater the release rate, the higher the salt index and the more acidic the pH of the solution containing the fertilizers.

These considerations show that the use of controlled-release polymers was able to reduce and delay the peak of the salt index compared to conventional MAP. Among the CRFs, the highest peak of the salt index observed was 68.9% for Agrocote® 10-48-00, representing a reduction in salinity of nearly 20% in relation to conventional MAP, which expressed its salinity potential on the first day after incubation. It is known that adequate acidity conditions in the region of dissolution of phosphate fertilizers can attenuate the adsorption and precipitation reactions of P with iron and aluminum, which are pH dependent. Excessive application of nutrients resulting from the use of soluble fertilizers can result in high concentration of salts in the root zone (Shaviv and Mikkelsen, 1993; Trenkel, 1997), increasing the osmotic pressure of the soil solution, which may lead to phytotoxicity and death of seeds and seedlings. Therefore, the use of polymers for coating the phosphate fertilizers (CRFs) plays an important role in reducing their salinity, resulting in chemical conditions more favorable to the growth and development of the root system of the plants, improving the interception of P by roots and P uptake from the soil solution.

4.4 Hygroscopicity

Hygroscopicity refers to the ability of the fertilizer to absorb atmospheric moisture at a certain temperature. Determining factors for hygroscopicity include characteristics such as saline concentration (salt index). The higher the index, the more hygroscopic the material is. This characteristic is considered negative, since there is a physical change in the fertilizer granules, which may cause clumping, where smaller granules join and transform into larger granules, later resulting in undesirable situations such as poor distribution in an area or even an obstacle to distribution. However, in the case of the CRFs evaluated, despite the small changes observed in hygroscopicity, water droplets were found to form on the granules, which affected their final weight. Therefore, the small variation observed is mainly due to the droplets, indicating that the polymers used for the coating are efficient in acting as a barrier to the entry of moisture. According to Timilsena et al. (Timilsena et al., 2015), one of the advantages of coating fertilizers is the low hygroscopicity of the granules, which favors storage and management in the field.

4.5 P diffusion

Improvement in P diffusion is directly related to phosphate fertilizers and their performance. After coating the fertilizer with polymers in order to control nutrient release, there will be changes related to diffusion. Therefore, adequate studies of this variable are essential for innovations in the fertilizer industry. In this respect, the diffusion radii (mm) of the MAP were compared with those of the CRFs. The MAP had the greatest diffusion on the first day after incubation, followed by a significant decline, and this diffusion was then surpassed by the CRFs, which had gradual diffusion throughout the period analyzed. The greater diffusion of MAP can be explained by its high solubility, with release of 85% of P_2O_5 in water (Figure 2) on the first day after incubating the granules. The constant decline in diffusion over time is probably due to adsorption of P to soil colloids and the lower subsequent release, since the fertilizer had already released a large part on the first day.

Regarding the CRFs, Agrocote® 10-48-00 had the greatest diffusion over the time evaluated. Its expressive diffusion of P on the 7th and 14th day after incubation, exceeding that of the MAP, is due to the greater release of P_2O_5 (68.3% and 83.3% observed for these days, respectively) (Figure 2). At 28 and 42 days after incubation of the fertilizers, Agrocote® 10-48-00 (7.87 and 7.07 mm, respectively) and Multicote™ 4M (6.37 e 7.3 mm, respectively) had the greatest diffusions of P observed, also corroborating the releases in water for both on the two days (greater than 90% and 54% for the fertilizers, respectively). Agrocote® 09-47-00 had the least and most constant diffusion observed among the CRFs over the period analyzed, corroborating the constant release observed for this fertilizer.

Even with the expressive release of Agrocote® 10-48-00, comparing it with MAP on the first day after incubation shows that there was a minimum reduction of 41.3% in diffusion due to the use of the polymer. This reduction reinforces the fact that the polymers used as coatings for MAP are able to reduce the rate of P diffusion, which is gradual over time. The diffusion of P is linked to release of the nutrient, increasing at the same time as greater release occurs.

It should be considered that the use of coating for phosphate fertilizers differs from that proposed for nitrogen fertilizers, since the loss of nutrients occurs in a different way: P is lost by fixation and N, for example, is lost by volatilization and leaching. Therefore, evaluating P diffusion is extremely important for characterization of phosphate CRF; constant diffusion over time may indicate the efficiency of the fertilizer in reducing P loss. When using soluble fertilizers such as MAP, P that is immediately available will be susceptible to adsorption by soil colloids, and its availability to / uptake by the plant will be impaired. In this sense, we note the success of the CRFs in maintaining P diffusion constant upon observing that diffusion from

MAP was maintained for only 14 days, while the diffusion from all the CRFs, despite a decline over time, remained constant up to 42 days.

4.6 FTIR,TGA and SEM analysis

Evaluating the TGA of the polymers of the CRFs shows that the polymers used for coating have good thermal stability. The initial decomposition of the material, for all the samples, occurred at a temperature near 200 ºC, indicating that the material is resistant to high temperatures and to variations of temperature that may occur in the soil, during transport, or in storage. These locations will unlikely reach a temperature of 200 ºC. The peaks of temperature are similar to those found by Feng et al. (Feng et al., 2005) and Li et al. (Li et al., 2012) in thermogravimetric analysis of transparent resins of polyurethane and urea CRF coated by polyurethane, respectively. In relation to FTIR, the material used as a coating for all the treatments is similar, and it may be a polyurethane.

5. Conclusion

The salt index, pH, and diffusion are linked to the release of nutrients by the fertilizer. The more intense the release, the more the other indices will be affected. It can be affirmed that the release affects all the chemical indices of the controlled-release fertilizers.

The use of polymers is able to reduce the rate of initial diffusion and release of P by the granules, decrease and delay the peak of the salt index, and decrease the acidity generated by the fertilizer. The reduction of the peak of the salt index and acidity generated by fertilizers is of utmost importance from an agronomic standpoint, as they can result in damage to seedling radicles, negatively affecting the uptake of water and nutrients in early growth stages. As a result, seedlings may exhibit poor growth, reduced resilience to environmental stressors, and diminished final yield. Similarly, the generated acidity can acidify the soil and lower its pH, impacting nutrient availability for plants. This can lead to nutritional deficiencies and compromise proper crop development.

Furthermore, the use of polymer promotes continuous diffusion of phosphate fertilizer, preventing the phosphorus content from being adsorbed within a few days after application, allowing the crop to make better use of the applied phosphorus in the soil.

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Supplementary Material

Fig S1 Water droplets on the surface of CRFs incubated at controlled temperature and relative humidity for evaluation of their hygroscopicity