MATEUS OLÍMPYO TAVARES DE ÁVILA

PHOSPHORUS SOURCES AND MICRONUTRIENT SUPPLY METHODS IN ANNUAL CROPPING SYSTEM

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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Agronomia/Fitotecnia, área de concentração em Produção Vegetal, para a obtenção do título de Doutor.

Prof. Dr. Silvino Guimarães Moreira
Orientador

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FONTES DE FÓSFORO E MÉTODOS DE APLICAÇÃO DE MICRONUTRIENTES NO SISTEMA DE PRODUÇÃO DE CULTURAS ANUAIS

Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Agronomia/Fitotecnia, área de concentração em Produção Vegetal, para a obtenção do título de Doutor.

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LAVRAS – MG
2020

À Deus.

Aos meus pais Adenilson e Elisete,

Ao meu irmão Vinícius,

A toda minha família e amigos,

Ao povo brasileiro

DEDICO

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RESUMO

Devido às características dos solos tropicais e dos sistemas de produção utilizados, é desafiador reduzir as perdas de fósforo, determinar o melhor manejo da adubação com micronutrientes e escolher corretamente o extrator para extração dos nutrientes. O presente trabalho foi dividido em dois artigos. No primeiro artigo avaliou-se o efeito do revestimento do MAP com ácidos húmicos e micronutrientes em fornecer fósforo às plantas, bem como a eficiência dos extratores Mehlich-1, Mehlich-3 e resina de troca iônica em avaliar a disponibilidade de fósforo. No segundo artigo, o objetivo foi determinar o melhor método de fornecimento de micronutrientes. Os experimentos foram realizados na Fazenda Muquém da Universidade Federal de Lavras, Lavras, MG, durante duas safras. Foi utilizado o delineamento em blocos casualizados, em esquema fatorial 4 x 6, sendo quatro fontes de fósforo (MAP; MAP revestido com ácidos húmicos (AH); MAP revestido com AH, zinco (Zn), manganês (Mn), cobre (Cu) e boro (B), além de um controle, sem aplicação de fósforo e micronutrientes). Esses tratamentos foram combinados com aplicação de micronutrientes, sendo 1- Zn; 2- Mn; 3- Cu; 4- B + Zn + Mn + Cu via foliar, 5- B via solo e 6- controle), com quatro repetições. As parcelas consistiram em oito linhas no tamanho 6,0 m x 4,8 m, totalizando 28,8 m^2. As culturas utilizadas foram milho primavera/verão (Safra 2016/17), seguido de trigo no outono/inverno (2017) e soja primavera/verão (2017/18), sem irrigação, utilizando-se as cultivares KWS 9004, BRS 264 e M6410 IPRO, respectivamente. Após o cultivo de verão da safra 2017/18, em cada parcela, foram retiradas duas amostras de solo na linha de semeadura e quatro nas entrelinhas, de forma aleatória, para compor a amostra composta. A extração dos teores dos nutrientes no solo foi realizada pelos métodos Mehlich-1, Mehlich-3 e resina de troca catiônica e aniônica. Amostras de folhas foram coletadas para o diagnóstico do estado nutricional na cultura do milho e da soja. Os dados foram submetidos à análise de variância e os resultados significativos ao teste de Scott-Knott a 5% de probabilidade. O revestimento do MAP por ácidos húmicos proporcionou aumento no teor de fósforo disponível no solo, independentemente do extrator utilizado, no teor foliar de fósforo e na produtividade de grãos de milho e soja. O extrator Mehlich-3 foi adequado para a extração de fósforo em solos de Cerrado. Apenas os teores disponíveis de Cu no solo foram superiores quando do uso do MAP revestido com micronutrientes. Não houve alteração nos teores disponíveis no solo de nenhum micronutriente quando determinados pelo Mehlich-3. Os teores de B, Cu, Mn e Zn utilizados no revestimento do MAP não proporcionam aumento dos teores foliares destes micronutrientes nas folhas diagnóstica. A aplicação de B via solo e de Cu, Mn e Zn via foliar proporcionou aumento dos teores foliares destes nutrientes, independentemente do uso de fertilizante fosfatado revestido com estes micronutrientes.

Palavras-chave: Nutrientes, extratores, sistema de produção, *Zea mays*, *Triticum* spp, *Glycine max*.

ABSTRACT

Due to the characteristics of the tropical soils and cropping systems used, it is challenging to reduce phosphorus losses, to determine the best method of micronutrient supply, and to choose the nutrient extractor correctly to determining micronutrients. The present work was divided into two articles. In the first article, the aim were evaluate the effect of MAP coated by humic acids and micronutrients on providing phosphorus to plants, as well as the efficiency of efficiency of Mehlich-1, Mehlich-3 and ion exchange resin in phosphorus availability evaluating. In the second article, the aimed to determine the best micronutrient supply method. The experiments were carried out at Muquém farm at Federal University of Lavras, Lavras, MG. A randomized block design in a 4 x 6 factorial scheme was used, with four sources of phosphorus (MAP; MAP coated by humic acids (AH); MAP coated by HA, zinc (Zn), manganese (Mn), copper (Cu) and boron (B), as well as a control, without phosphorus and micronutrients supply). These treatments were combined with micronutrients supply, being 1- Zn; 2- Mn; 3- Cu; 4- B + Zn + Mn + Cu, both by spraying; 5- B by soil and 6 - control), with 4 repeats. The plots consisted of eight lines in size 6.0 mx 4.8 m, totaling 28.8 m^2. The crops used were corn spring/summer (crop year 2016/17), followed by wheat in fall/winter (2016) and soybean spring/summer (2017/18), without irrigation, using cultivars KWS 9004, BRS 264 and M6410 IPRO, respectively. After soybean harvest, in each plot two soil samples were taken from the sowing line and four between the rows, randomly, to the composite sample. The extraction of nutrient contents in the soil was performed by Mehlich-1, Mehlich-3 and ion exchange resin. Leaf samples were collected for the diagnosis of nutritional status in corn and soybean crop. Data were subjected to analysis of variance and significant results to the Scott-Knott test at 5% probability. The coating of MAP by humic acids increases the available phosphorus content in the soil, regardless of the extractor used, the phosphorus leaf content and the yield of corn and soybeans. Mehlich-3 extractor is appropriate for phosphorus extraction in Cerrado soil. Only available soil Cu levels were higher when using MAP coated by micronutrients. There was no change in the available soil contents of any micronutrient when determined by Mehlich-3. The B, Cu, Mn and Zn contents used in the MAP coating do not increase the leaf contents of these micronutrients in diagnostic leaves. The B supply by soil and Cu, Mn and Zn by spraying, provides increase of leaf contents of these nutrients, regardless of the use of phosphate fertilizer coated with these micronutrients.

Keywords: Nutrients, extractors, cropping system, *Zea mays*, *Triticum* spp, *Glycine max*.

SUMÁRIO

FIRST PART

1 INTRODUCTION

Phosphorus (P) is one of the most limiting nutrients for crops, especially in tropical soils, and the main reasons found in the literature are the low available P content and the predominance of acidity, which makes it essential to reach the plant demand through of the fertilizers supply (LI et al., 2019). According to Silva et al. (2012), the low amount using of phosphate fertilizers due to the physical-chemical characteristics of tropical soils also contributes to the decrease of crop yield.

In tropical soils part of P added to the soil is adsorbed to the soil colloids, becoming unavailable to plants leading to the need for high doses of this nutrient to meet crop demand. Being from non-renewable sources, its scarcity is worrying, a circumstance that endangers the food security of future generations, and a fact that has aroused the interest of the industry.

The most used phosphate fertilizer in Brazil is monoammonium phosphate (MAP), which presents high solubility in water. It is estimated that approximately 75% of the P applied is sorbed in the soil particles (RAIJ, 2004), resulting in an agronomic efficiency of less than 25% (ARAÚJO et al., 2003; RAMOS et al., 2009). Because of this, is required frequent supply of high doses of phosphate fertilizers, to provide and maintain high crop yield.

New phosphate fertilizer technologies have been developed with the aim of increasing the efficiency of P supply to plants. An example is the coating of MAPs by humic acids in order to reduce the interaction of P with iron (Fe) and aluminum (Al) oxides, because the functional groups of humic acids compete for the adsorption sites present in soils, promoting increases in fertilizer efficiency (ERRO et al., 2010).

What is sought with the new technology of fertilizer coating is that if a protective layer is formed against the agents that cause the loss of nutrients and that this protection does not interfere in the availability of the nutrient to the plant. Another aspect sought is a different behavior from the conventional soluble sources, that is, that the coating causes a gradual availability and not a total release (SILVA et al., 2012).

Some searches have been carried out to observe the efficiency of humic acids to increase P availability in soil and in crop yield. However, little is known about its behavior in Cerrado soils and the residual effect of these fertilizers on cropping systems.

Plant nutrition experts and agronomists have been showing interest in micronutrients because of their importance to crop yield. Inadequate micronutrient content in crops, which is limiting growth, and which may go unnoticed, not only has a direct effect on crop development, but also reduces the efficiency of macronutrient supply because the lack of any one nutrient limits plant development. One of the main challenges related to micronutrients is the best way to apply them.

The two main methods to apply micronutrients are by soil or leaf, have advantages and disadvantages. Thus, it is common to observe both methods in the farms. Some have reported that even using N-P-K fertilizers combined with micronutrients, the levels are not sufficient to meet plant demand, so they make micronutrient supply on leaves to avoid nutritional deficiency in plants. There is still a lack of on-farm research to make sure how the best micronutrients supply method for plants on cropping systems is.

The evaluation of soil fertility is fundamental for the proper use of correctives and fertilizers in order to obtain high yield and to provide sustainable natural resources in use. Some methods are available to be used to evaluate nutrients availability to plants in soil. However, to choose the best method it is important to observe the accuracy and precision, robustness, easy execution, good sensitivity of the methods, low cost and ability to extract multiple elements simultaneously (LEAL et al., 2007; HOLLER, SKOOG, CROUCH, 2009).

One of the most used extractors in Brazil is Mehlich-1. However, this puller has wear that can mask the true available P levels in the clay soils. It is also related to literature that this extractor may underestimate the available levels of micronutrients in the soil. In this context, the use of Mehlich-3 extraction solution in tropical soils may be an alternative to consider. Nevertheless, there is doubt about the best extractor for Cerrado tropical soil conditions.

Therefore, the aims of this study were to evaluate the effect of MAP coated by humic acids in soil P, B, Cu, Mn e Zn availability and in corn, wheat and soybean yield, the best micronutrients supply method and to evaluate extraction methods in a very clay Red-Yellow Latosol of Cerrado.

2 THEORETICAL BACKGROUND

2.1 Phosphorus in tropical regions

The average concentration of phosphorus (P) in the earth's crust is approximately 0.12% (FASSBENDER, 1978) and may vary from 0.005% to 0.15% in its total amount in the topsoil (TISDALE et al., 1993, HAVILIN et al., 2005).

Despite its relative abundance in the earth's crust, P is considered as one of the most limiting nutrients for plant development. In most cases, even if the total soil P content is higher than that required for plants, the largest fraction is present in compounds with high binding energy, which makes colloid desorption and plant availability difficult (SCHALLER et al., 2019).

As a result of the intense weathering in tropical regions, the soils formed are no longer a source of P and have become drains, becoming more electropositive and with a great ability to adsorb and retain anions, such as phosphates (NOVAIS; SMYTH, 1999). In this scenario, the Oxisols are usually clay and with the clay fraction with oxide accumulation. Therefore, with low P contents available in the soil solution. P sorption and/or fixation, which includes both mineral surface adsorption and precipitation as low-soluble phosphates, is common in acidic soils rich in Fe (hematite and goethite) and Al (gibbsite) oxides (SCHALLER et al., 2019).

P precipitation is a consequence of the reaction that happen as a result of the combination of phosphate ion with Fe^{2+}, Al^{3+} and Mn^{2+} ions in acidic conditions and Ca^{2+} in alkaline conditions, making it unavailable to plants (NOVAIS et al., 2007). To reduce precipitation, soil acidity correction is required, increasing the pH, as pH tends to values close to 6.0, practically all Al^{3+} is neutralized (RAIJ, 2011) and part of the micronutrients Fe^{2+} and Mn^{2+} is also oxidized. When the soil has pH values close to 7.0, phosphate ion precipitation occurs with Ca^{2+}. However, this type of loss is not common under Brazilian conditions. However, in recent years there has been increasing concern about this loss form, due to the P supply to pull on the soils surface that have received limestone supply also on the surface (SOUSA et al., 2016).

The practical implication of the high P adsorption capacity in tropical soils is that, although the requirement of P for plants is not very high, it is necessary to apply large amounts of this nutrient via fertilizers to promote some soil saturation and lead to a surplus that meets the nutritional requirements of crops (RESENDE et al., 2016).

Due to the high P adsorption capacity in tropical soils, in general, Brazilian crop fields have received more phosphate fertilizers than necessary to meet crop demands since 1970 and thus have accumulated P reserves in the soil. It is estimated that a cumulative total of more than 45.7 Tg of inorganic phosphate fertilizers has been applied in Brazil since 1960, and 22.8 Tg of this input remain in the soil (WITHERS et al., 2018).

A part of this reserve of P is in labile or moderately labile forms. Evidence from the field suggests that P recovery can reach 80% of the total, depending on the cropping system and the amount of P available in this reserve. Thus, this P could be used to cushion the economic impact of future fertilizer price volatility, allowing for the supply of smaller quantities of P than required by crops. It may be possible to eliminate or reduce other P supply if sufficient P reserves are available to maintain P soil supply and avoid any decline in crop yield (WITHERS et al., 2018).

In soil solution, P is found mainly as primary $H_2PO_4^-$ and secondary HPO_4^{2-} orthophosphate ions, and the pH of the medium is the determining factor for the predominance of one of these forms (TISDALE et al., 1993; BARBER, 1995; RAIJ, 2011). In general, in relatively acidic soils (pH ranging from 4.0 to 6.0) as most found in Brazil, there is a predominance of the ionic form $H_2PO_4^-$ (RAIJ, 2011).

Still in the soil solution, P has very low mobility, being able to move for only a few centimeters in the solution. Diffusion is the main mechanism of P transport from soil to plant roots (BRAIDA et al., 1996; NOVAIS; MELLO, 2007). According to Malavolta (2006), diffusion is the movement of an element at close range within a stationary aqueous phase (soil solution), in favor of the concentration gradient, that is, from a higher concentration region to another lower concentration, which in this case is the root surface, where absorption by the plant causes the lower concentration.

The orthophosphate present in the soil solution is quickly absorbed by the plants roots by means of a simporter-type carrier, when two substances are transported and cross the membrane in the same direction. After reaching the xylem vessels, P is stored in the shoots and other organs for later redistribution (TAIZ; ZEIGER, 2013; IRFAN et al., 2019).

P is considered a very mobile nutrient for redistribution in plant tissues, and this nutrient is quickly mobilized from old to younger or forming tissues. In the plant, the ion is incorporated into a variety of organic compounds. During this process, one of the major phosphate entry points in the assimilation pathways occurs during the formation of the cell energy adenosine triphosphate (ATP) (TAIZ; ZEIGER, 2013; IRFAN et al., 2019).

In supply by spraying on leaves it is known that approximately 60% of P can be conducted by phloem from supply on leaf or from aged leaves to the growth points. Thus, the characteristic symptoms of P deficiency are observed first in the basal parts of the plants where mature tissues predominate, developed prior to the deficiency. Firstly, the older leaves acquire a purple color, due to the accumulation of anthocyanin pigment. Over time, if the nutrient is not available, the entire plant may show symptoms, due to the exhaustion of reserves (MALAVOLTA; VITTI; OLIVEIRA, 1997).

P is found in concentrations ranging from 0.1 to 1% in plant tissue dry matter (MARSCHNER, 2012), and these amounts are relatively much lower than those of nitrogen (N) and potassium (K) (RAIJ, 1991). However, despite its lower N and K requirements, P is one of the most limiting nutrients in crop yield. This is because it is present in plants in structural components of cells, such as nucleic acids and phospholipids in cell membranes and also as a constituent of high energy compounds. In addition, this element plays a key role in post-transductional regulation of enzymes and control of signaling during transduction, participates in protein phosphorylation and dephosphorylation, making P one of the most limiting nutrients to plants development (WHITE; HAMMOND, 2008).

Several mineral fertilizers are used to supply P to plants, from natural phosphates of igneous or sedimentary origin, to traditional thermophosphates and acidulated phosphates, also called soluble ones. Among the acidulated, triple superphosphate (STP), simple superphosphate (SSP), ammonium monophosphate (MAP) and ammonium diphosphate (DAP) stand out (NOVAIS et al., 2007). Among the sources of igneous rocks with low solubility are the natural phosphates of Araxá, Catalão and Abaeté. Among the reactive natural phosphates can be cited natural Gafsa phosphates from Morocco, among others (NOVAIS; SMYTH, 1999).

In Brazilian agriculture, water-soluble P sources with high soil solubility correspond to 95% of the phosphorus used in the country (SOUSA et al., 2010). The use of soluble sources in tropical soils can lead to considerable losses of P. It is estimated that approximately 75% of the applied P is adsorbed on soil particles (RAIJ, 2004), resulting in an agronomic efficiency of less than 25% (ARAÚJO et al., 2003; RAMOS et al., 2009). As a result, frequent phosphate fertilizer supplies are required to provide and support high crop yields. Part of the P supplied to these soils by fertilization is strongly bound to clay components, particularly Fe and Al oxides, by specific adsorption or inner sphere complex, making them unavailable to plants (ROY et al., 2016).

The loss of P from fertilizers is one aspect that contributed to the worldwide demand for phosphate gradually increasing in recent decades, reaching alarming levels nowadays, considering the available rock reserves (GUMIERE et al., 2019). Cordell and White (2015) consider that current reserves can be exhausted even in this century.

In the last years the industry has been presenting to the market phosphate fertilizers with increased efficiency, with the promise of minimizing P losses by adsorption in soils. These include conventional fertilizers with granules coated by humic acids. According to the manufacturers, these fertilizers have properties that favor the maintenance of P in soil solution. In addition to this coating, the addition of micronutrients in fertilizers has also been presented as a way to improve micronutrient distribution in crop field and confer greater grain yield.

According to URRUTIA et al. (2014), humic acids can reduce the P adsorption, so phosphate fertilizers coated by these acids have the advantages of reducing the adsorption sites of P. Thus, the nutrient would be less subject to soil insolubilizes reactions, which would increase its efficiency (YANG et al., 2019). However, this is a recent technology and therefore research is needed to evaluate the behavior of these fertilizers for different crop systems.

It is noteworthy that the soil organic matter (OM) itself can contribute to the improvement in the efficiency of use of the applied P when decomposed OM can be divided into two groups, consisting basically of non-humic substances and humic substances. The first is formed by simple compounds, well-defined structure and in the early stage of decomposition. The second is represented by humus, which is a material in a more advanced stage of decomposition, composed of dark colored compounds with high molecular weight, stable and difficult to degrade (STEVENSON, 1994; MENDONÇA; MATOS, 2005; OLIVEIRA, 2010).

Humus is formed by three humic fractions: humic acids, fulvic and humines (STEVENSON, 1994). These compounds have similar characteristics, but differ in molecular weight, solubility, reactivity and functional groups (BENITES; MADARI; MACHADO, 2003). These substances interact in the soil interfering in the chemical, physical and biological properties (CANELLAS et al., 1999; EYHERAGUIBEL; SILVESTRE; MORARD, 2008).

The humic acids, fraction aim of the present study, constitute the largest fraction of humic substances. These are dark precipitates, soluble in mineral acids and organic solvents. It has high molecular weight and cation exchange capacity (CEC) between 350 and 500 meq 100 g^{-1} (TAN, 1993).

There has been much discussion in recent years about the role of humic acids in reducing P adsorption. Studies have shown that the presence of these compounds can decrease P adsorption. According to Cessa et al. (2010) and Jindo et al. (2016), the increase of the humic acids contents in the soil, which, due to the competition for the same adsorption sites with P, play a fundamental role in the availability of this element in the soil. This effect is attributed to the fact that humic substances have carboxylic (R-COOH) and hydroxyl (R-OH) groups, dissociated under soil pH conditions. The carboxylic groups present in humic substances have a pKa value between 3 and 4. Thus, they are always dissociated under soil pH conditions. Thus, they are responsible for the generation of negative charges and also interact with the surface of Fe and Al oxides, competing for the same adsorption sites with P (GUPPY et al., 2005).

The reduction of P adsorption by humic acids is not exclusively due to the presence of these groups that block the adsorption sites. Consideration should also be given to the interaction of humic acids with free Fe, Al and Ca in the soil solution, forming chelates. This reduces phosphate precipitation in insoluble forms by increasing plant availability (BRADY; WEIL, 2013; PICOLI, 2017).

Another form of action of humic acids that provides increased availability of P in solution, but is still little discussed in the literature, is through its reaction with organic substances present in the soil indirectly. A metal bridge is formed, usually in the presence of Fe and Al ions and binds P to the organic radical of humic substances, generating the so-called P-metal-humic substance complex. This complex can be dissolved by low molecular weight organic acids (oxalate and citrate) and can represent 50% of the dissolved P in the soil solution, thus having great relevance in the availability of P to plants, unlike when it occurs the adsorption of P on the surfaces of Fe and Al oxides (PAVINATO; ROSOLEM, 2008; GERKE, 2010).

The efficiency in decrease P adsorption by humic acids is closely linked to the content of these acids in the soil. Nevertheless, research shows that even at low concentrations, a reduction in P adsorption is observed (STEVENSON, 1994; PAVINATO; ROSOLEM, 2008). Andrade et al. (2003), evaluating the effect of humic acids in latosols on phosphate adsorption, observed that humic acids were able to promote the reduction of P adsorption.

In addition to the influence of humic acids on soil P levels, their effect on plant nutrition has been extensively evaluated in different crops. Jannin et al. (2012) suggest that humic acids promote the growth of rapeseed (*Brassica napus*) plants and nutrient uptake, and these acids can be used as a complementary tool to improve the efficiency of nitrogen use in rapeseed. Ameri and Tehranifar (2012), investigating the effects of humic acids on nitrogen (N), P and potassium (K) absorption in strawberry (*Fragaria ananassa*), found that humic acids positively influenced the absorption of these nutrients. Khan et al. (2018) found 22% increase in wheat (*Triticum spp.*) yield with humic acids supply.

2.2 Micronutrients in soil and plant

Despite the high concentration of most micronutrients in soils, only a small fraction is available to plants. Micronutrient deficiencies are more common in humid tropical regions due to intense leaching associated with high precipitation (GUPTA et al., 2018).

Nutrient availability to plants is affected by various soil attributes such as organic matter (OM) of soil, redox potential, temperature, humidity and microbial activity, in addition to Cation Exchange Capacity (CEC), soil mineralogy, among other factors (MOREIRA et al., 2017; GONÇALVES et al., 2018; GRUJCIC et al., 2019). Soil pH is one of the most important factor affecting the availability of micronutrients to plants. With increasing pH, the availability of these nutrients is reduced, except for molybdenum (Mo) and chlorine (Cl), whose availability increases as soil pH increases (GUPTA et al., 2018).

Boron (B) can be found in soil in primary minerals such as tourmaline and B-rich micas; secondary minerals, especially within the framework of clays; adsorbed to clays, on hydroxide surface and on OM. It can be found in the solution as boric acid (H_3BO_3) and as borate ($H_4BO_4^-$), depending on the pH of the medium, as well as bound to OM and microbial biomass (SHORROCKS, 1997).

Evans (1987) attributed the increase in B adsorption to the increased proportion of borate anions, which accompanies the increase in pH and can form both internal and external sphere complexes with mineral surfaces and complexes with OM. The two species of B ($H_2BO_3^-$ and $H_4BO_4^-$) have different affinities for colloids and appear in varying proportions in the equilibrium solution in response to variations in pH.

B is absorbed by plants as boric acid (H_3BO_3), as there is also evidence of its absorption in the form of borate anion ($H_4BO_4^-$), when the pH is elevated, either by soil or leaf (DECHEN; NACHTIGALL, 2007).

The predominant B species in the soil solution between pH 5 to 9 is the non-ionized molecule H_3BO_3. Its non-ionic nature makes this nutrient highly mobile in the soil, favoring its loss by leaching. Only at pH values greater than 7 units does the hydrolyzation of B passing from $H_2BO_3^-$ to $H_4BO_4^-$ occur, providing a drop in nutrient activity in the soil solution due to the adsorption of this form of B to the clay minerals and Al hydroxide surfaces (TISDALE et al., 1985; MORAGHAN; MASCAGNI, 1991).

As for redistribution mobility, B is considered an immobile nutrient in the plant. It is mainly translocated by xylem, with their limited mobility in the phloem (RAVEN, 1980).

Several functions are performed by B, such as sugar transportation; lignification of the cell wall; cell wall structuring, carbohydrate metabolism, and RNA. In addition, it is linked to breathing, phenol metabolism, membrane function and N_2 fixation. B also plays an important role in flowering, pollen tube growth, fruiting processes and hormone activity (EPSTEIM and BLOOM, 2006; DECHEN; NACHTIGALL, 2007).

Its deficiency affects the ATPase activity linked to the plasma membrane and the ions are reduced rates of absorption. The membranes become permeable, but can be quickly restored by supplying this nutrient. This effect of B deficiency on decreased plasma membrane function may be linked to changes in metabolism of cell wall phenols associated with the deficiency (ZANÃO JÚNIOR et al., 2014).

B deficient plants also exhibit excessive accumulation of auxins and phenols as a result of necrosis often observed in deficient plant tissues. Twisted leaves also tend to be brittle, chlorotic and later necrotic, or with translucent lesions between the ribs. It is also common to arise the overgrowths due to the death of the apical meristems (VITTI et al., 2011).

Other problems caused by B deficiency and directly affecting crop yield are the presence of light grains, as well as lower flowering and seed formation. Common symptoms are dry buds with terminal bud death, providing growth hormone indolacetic acid (IAA) concentration in leaves and branches, small root development (FAVARIN; MARINI, 2000).

Plants with toxic contents of B have yellowish leaves, and this color extends to the margins. Its toxicity is considered as severe as its deficiency (DECHEN; NACHTIGALL, 2007).

Copper (Cu) has low soil solubility, and this characteristic influences its availability to plants, as the nutrient can be strongly hold by soil particles, becoming unavailable and insufficient to supply them (RESENDE et al., 2009). The most common form found in soil is divalent (Cu^{2+}), mainly as a constituent of the crystalline structures of primary and secondary minerals (DECHEN; NACHTIGALL, 2007).

Cu availability is mainly affected by soil pH (FERREIRA et al., 2001), and its solubility is reduced in high pH soils above 7.0 (TROEH; THOMPSON, 2005). In acidic conditions, there is an increase in the amount of Cu^{2+} in the soil solution (BARKER; PILBEAM, 2015).

OM is the main factor that determines the availability and mobility of this nutrient in the soil. This is due to the formation of stable Cu^{2+} complexes with OM components. This can cause deficiency problems in organic soils or leaching losses in sandy soils, usually poorer in OM. Regardless of soil type, the presence of other metal ions such as Fe^{2+}, Mn^{2+} and Al^{3+} may reduce Cu availability (MOREIRA et al., 2017).

Cu is absorbed as Cu^{2+} and as soluble chelates. In the absorption process competition with Zn may occur for the same sites in the loader. Absorption occurs by active process and is considered an element with restricted mobility (MALAVOLTA et al., 1997).

Cu is important in photosynthesis, tending to accumulate in chloroplast as it is a constituent of plastocyanin, where it acts in the transport of electrons. In respiration, it acts on terminal oxidation by the enzyme cytochrome oxidase. It also increases the resistance of plants to disease by the fact that in the presence of Cu the activity of peroxidases and catalases are decreased, causing accumulation of phenols and hydrogen peroxides in tissues, both acting on fungi and bacteria. Cu also participates in protein synthesis and is constituent of several enzymes such as ascorbic acid oxidase, tyrosinase, monoamine oxidase, cytochrome oxidase, and plastocyanine (TAIZ; ZEIGER, 2013).

According to Favarin and Marini (2000), another important contribution of Cu occurs inside the nodules present in the roots of leguminous plants. This is because it participates in the synthesis of leghemoglobin and electron transport during biological nitrogen fixation.

Cu deficiency can happen in soils with high levels of OM, where this element is complexed in insoluble organic forms not available to plants (FERREIRA et al., 2001). Deficiency may also occur in places with soils originating from silica and carbonate (MELLO et al., 1985).

Interneval chlorosis in young leaves is the main symptom of deficiency. This feature is due to poor nutrient mobility in the plant, starting in the younger leaves and progressing to the older ones (MALAVOLTA et al., 1997: TROEH; THOMPSON, 2005). The leaves curl, wither and become brittle; there is an abortion of large numbers of flowers producing little garnet ears in the cereals; there is a compromise in the transport of water and solutes in xylem due to the reduction in lignification (DECHEN; NACHTIGALL, 2007).

Cu can cause toxicity to plants, limiting plant growth and causing imbalances in nutrient absorption and translocation (FREITAS et al., 2013). In toxic amounts in plant tissues, Cu catalyzes the production of reactive oxygen species such as hydrogen peroxide (H_2O_2), which is detrimental to cellular components such as DNA, proteins and lipids, reducing development and causing damage to crop tissues (THOUNAOJAM et al., 2014).

After Fe, manganese (Mn) is the most abundant element on earth, being found mainly in ferromagnesian rocks (RESENDE, 2009) and as a component of oxides, carbonates, silicates and sulfides (DECHEN; NACHIGALL, 2007). This element can exist in soil in some oxidation states (II, III and IV). The most common forms are like Mn^{2+}, coming from the weathering of rocks. Research indicates that most of the Mn in soil solution and rocks is present in this way, being absorbed by plants (TROEH; THOMPSON, 2005). Other identified forms are oxides and hydroxides (MnO_2, MnOOH) or Mn associated with Fe hydroxides, which are poorly soluble, especially in calcareous and alkaline soils in addition to the form present in organic compounds (DECHEN; NACHTIGALL, 2007).

The presence of Mn^{2+} in soil solution is dependent on pH as well as soil redox potential. Factors that can induce deficiencies of this nutrient in plants include soil aeration, presence of other ions such as calcium (Ca), magnesium (Mg) and Fe in addition to the OM content. In addition, this micronutrient may complex with OM, forming in some cases stable complexes, and there may be unavailability of the element (MOREIRA et al., 2016). Under field conditions, deficiency usually occurs in plants grown in highly leached or high pH and high OM values (FAGERIA, 2001).

Mn plays an important role in plant metabolism, particularly in activation processes of different enzymes, chlorophyll synthesis and photosynthesis. This micronutrient is absorbed by plants predominantly as Mn^{2+}. However, there may also be absorption in the forms of Mn^{3+} and Mn^{4+}, however, only the smallest form is translocated to the area part. Mn^{2+} has chemical properties similar to those of alkaline earth metals such as Ca^{2+} and Mg^{2+}, and heavy metals such as Fe and Zn, which may inhibit their absorption and transport in plants (MALAVOLTA et al. 1997).

Inside the plant, this cation is relatively immobile, not translocating from one organ to another. As a result, deficiency symptoms appear in new leaves (FAVARIN; MARINI, 2000). Deficient plants show symptoms of interneval chlorosis in younger leaves due to reduced chlorophyll synthesis and poor remobilization of this micronutrient. In turn, its toxicity appears initially, also in young leaves, characterized by leaf curl and necrotic dark brown spots in the leaf limb (EMBRAPA, 2004). Excess Mn^{2+}, in turn, may inhibit the absorption of other cations, such as Ca^{2+}, Mg^{2+}, Fe^{2+} and Zn^{2+} (ST. CLAIR, LYNCH, 2004).

This micronutrient is required for the activity of some dehydrogenases, decarboxylases, kinases, oxidases and peroxidases. It is involved with other enzymes linked to carbohydrate metabolism, phosphorylation reactions, the citric acid cycle and photosynthetic oxygen evolution. It is essential for the photosynthesis process, being also involved in the structure, operation and multiplication of chloroplasts and electron transport (TAIZ; ZEIGER, 2013).

Considering that Mn^{2+} and Zn^{2+} can be found in soil in different ways, the main ones being oxides, silicates and carbonates. Zn is also found as exchangeable cation, dissolved in soil solution and also in the form of chelates with organic radicals (JAMAMI, 2001). The nutrient presents a complex dynamics in the soil, being influenced by the pH, percentage and type of clay, cations, anions, phosphate fertilization and cropping system (ABREU; LOPES; SANTOS, 2007). The available soil Zn content depends on several factors, such as the source material, the amount of OM and Fe and Al oxides. Soil pH is one of the main factors that affect the availability of this nutrient to plants, and the highest availability is observed in the pH range between 5.0 and 6.5 (PEREIRA et al., 2007).

One of the Zn adsorption mechanisms is called specific adsorption or inner sphere complex, formed by a high energy bond, due to the absence of water molecules between the mineral colloid and the ion. Thus, tropical soils with high degree of weathering, such as latosols, have high micronutrient retention capacity (GALRÃO, 2002). Zn adsorption occurs through bonds with hydroxyl groups (OH^-) of silicate clays or in regions of minerals that have crystal lattice ruptures (CUNHA, 1989). According to Harter (1991), as a consequence of adsorption, Zn concentrations in most soils are mainly determined by sorption reactions, since precipitation and dissolution reactions last longer, thus leaving the micronutrient unavailable to plants.

Zn is absorbed by plants as Zn^{2+}, this absorption being performed by active process. It acts in plants as activator of several enzymes, besides being part of several cellular structures. The deficiency of this micronutrient causes severe consequences to plant metabolism, directly affecting the reduction of plant yield. In C4 plants, Zn participates in photosynthesis through the pyruvic carboxylase enzyme, which is fundamental for the production of tryptophan, an amino acid precursor of indoleacetic acid (IAA), an important plant hormone, a growth promoter also participating in nitrogen metabolism (MARSCHNER, 1995). Zn also plays an important role in auxin metabolism, ribosome stabilization, phenol metabolism, protein synthesis and membrane permeability (EPSTEIN and BLOOM, 2006).

Zn-deficient plants have poor growth and therefore have short internodes. In addition, the plants have plants with internerval and/or lanceolate chlorosis in some species. These plants suffer drastic effect on enzymatic activity, chloroplast development, protein synthesis and nucleic acids. Also in seeds, low concentrations of Zn can impair germination, seedling growth, establishment and consequently plant growth and yield (RENGEL; GRAHAM, 1995; MALAVOLTA et al., 1997; TEWARI; KUMAR; SHARMA, 2019).

According to Dechen and Nachtigal (2007), Zn toxicity is not common, especially in high pH soils. However, toxicity can be observed in acidic soils or soils whose source material is high in Zn. Toxicity may also happen due to the supply of high doses of mineral or organic fertilizers containing Zn.

Nascimento and Fontes (2004) evaluating the binding energy of Zn and Cu in six Oxisols of State of Minas Gerais by the Langmuir and Freudlich equations. They concluded that the Langmuir e Freundlich equations have correlation with the micronutrients, being the clay and OM contents the main determinants of Zn and Cu adsorption capacity in the soil, respectively.

2.3 Micronutrients supply methods

There are two ways to provide micronutrients to crops, one is their direct supply to the soil and the other is by spraying them to the leaves (PUGA et al., 2013). The direct supply to the soil can be done by the use of simple fertilizers or with the use of mixed fertilizers that contain micronutrients in their components, applying in total area or concentrating the supply in the sowing furrows.

Fertilizer mixtures according to physical criteria can be classified as: granule mixture, which simply consists of a physical mixture of previously granulated raw materials; granulated mixture means a mixture of powdered products that goes through the granulation process so that the different nutrients are in the same granule, among others (MAPA, 2016).

The micronutrients supply in NPK granulated mixture form, may result in greater uniformity in the distribution due to the fact that the amount of micronutrients to be applied is much smaller compared to those used in NPK fertilizers (SANTOS et al., 2018). This supply mode is advantageous as the limit between sufficiency and toxicity is very narrow and achieving homogeneity in supply is desirable. Another advantage is the reduction in costs with the joint fertilizers supply.

Currently, in field observations, it is common to find farmers using NPK fertilizers coated by some micronutrients such as Zn, Mn, Cu and B. However, they report that the amounts applied in this way are not sufficient to achieve high yields, therefore, they choose to supplement by spraying supply. However, field research is lacking to validate this practice in cropping systems.

2.4 Phosphorus and micronutrient extraction in soil

The aim of assessing soil fertility through chemical soil analysis is to estimate the ability of the soil to provide nutrients to plants and thus to determine the amount of fertilizer required to achieve the best crop yield. Several methods are available to be used to assess nutrient availability to plants. However, when choosing a method it is important to note the accuracy and precision, robustness, ease of execution, good sensitivity of the methods, low cost and ability to extract multiple elements simultaneously (LEAL et al., 2007; HOLLER, SKOOG; CROUCH , 2009).

In addition to all these factors to be observed when choosing the extractor, according to Bissani et al. (2008), it is essential to consider when choosing a soil analysis method that it presents a positive correlation between the value of the extracted nutrient and the amount absorbed by the plant.

The reason for the large number of extractor solutions is due to the case that the availability of the nutrient to plants, in addition to depending on the characteristics and properties of different soils, also depends on the plant, the management of nutrients supply, the association of plants with microorganisms, and of other factors not yet elucidated (NOVAIS; SMYTH, 1999).

For the determination of P, the most used methods by the soil analysis laboratories in Brazil are Mehlich-1 and ion exchange resin (ARRUDA; LANA; PEREIRA, 2015). Mehlich-1 is the most used in routine procedures, because it is fast and low cost (REIS, 2016). In recent years, the use of the Mehlich-3 extractor has been noticed due to its advantages. Bortolon, Gianello and Schilindwein (2009) cite that the main advantages of the Mehlich-3 solution are: ease execution, low cost, speed, greater efficiency in the laboratory for multi-element extraction and for being an extracting solution applicable to a range of soils with variable characteristics. However, there is still little research to validate its use in tropical soils.

The state of Minas Gerais employs the Mehlich-1 extractor, initially used as an official extractor in the State of North Carolina, United States, to evaluate the P, Ca, Mg, K, Na levels considered available to crops (MEHLICH, 1953). This extractor is composed of a mixture of strong acids at low concentrations (HCl 0.05 mol L^{-1} and H_2SO_4 0.0125 mol L^{-1}), with pH around 1.2, and its extraction based on partial acid dissolution of the inorganic colloids by the hydrogen ion (H^+), from which low binding energy compounds such as calcium-bound P (Ca) and, later, aluminum-bound P (Al) and iron (Fe) are extracted (BRAZIL; MURAOKA, 1997). Due to the use of sulfuric acid (H_2SO_4) there may also be an ion exchange effect of phosphate adsorbed by the sulfate ion, although it is less pronounced (RHEINHEIMER, GATIBONI; KAMINSKI, 2008).

Mehlich-1 when used in acidic soils with low CEC, very weathered, poor or without P-Ca, has good predictive capacity ($R^2 \geq 0.7$). However, in clay soils, especially those with high pH and high acidity buffering capacity, the initial pH of 1.2 Mehlich-1 is rapidly raised to near-soil pH values. At the same time, the extractor SO_4^{2-} is also rapidly adsorbed on soil adsorption sites not yet occupied by P (NOVAIS; SMYTH, 1999; SILVA; RAIJ, 1999; BORTOLON; SCHLINDWEINII; GIANELLO, 2009). Under these conditions, the puller loses its extraction power and lower available P values are obtained. In turn, in more sandy soils and acid soils, the Mehlich-1 is powerful.

The ease of extraction, speed, low cost and obtaining clear extracts, which allows the filtering process to be eliminated (SANTOS et al., 2014), are major advantages in using Mehlich-1 (ROSSI;; FAGUNDES, 1998; RAIJ et al., 1984).

Mehlich-3 consists of a mixture of several reagents (NH_4F 0.015 mol L^{-1} + NH_4NO_3 0.25 mol L^{-1} + CH_3COOH 0.2 mol L^{-1} + HNO_3 0.013 mol L^{-1} + EDTA 0.001 mol L^{-1}), which allows simultaneous multi-element extraction. This mixture, besides acid dissolution, has the action of the fluoride ion (F^-), which acts in the formation of strong complexes with Al^{3+} ions, thus releasing the metal-bound P and also extracting the P linked to Ca by precipitation of calcium fluoride. Due to the partial substitution of strong inorganic acids by acetic acid, Mehlich-3 was effective in decreasing the solubilization of calcium phosphates present in low reactivity natural phosphates, and the presence of ethylenediaminetetraacetic acid (EDTA) allowed extraction micronutrients such as Mn, Zn, Cu and B (MEHLICH, 1984). Gatiboni et al. (2005) observed that Mehlich-3, besides removing inorganic forms of P, also removes part of organic P, due to the presence of EDTA, which increases the desorption of organic compounds. Ammonium nitrate present in the solution facilitates potassium extraction (NOVAIS; SMITH, 1999; SAWYER; MALLARINO, 1999; EMBRAPA, 1999).

According to Sims (1989) after testing the Mehlich-3 extractor in 400 soil samples and Bortolon; Gianello (2010) in 130 samples, they observed that the Mehlich-3 method extracts more Cu than Mehlich-1, due to the formation of stable complexes (chelates) between the Cu and the EDTA employed in this solution.

Mylavarapu et al. (2002) compared Mehlich-1 and Mehlich-3 in 519 soil samples and concluded that higher amounts of Cu and Mn were obtained by Mehlich-3. Sarto et al. (2011) concluded that in Paraná soils, the Mehlich-3 extraction solution was more efficient than Mehlich-1 in Cu extraction.

When assessing the prediction capacity of Mehlich-1, Mehlich-3 and ion exchange resin extractors on the availability of P in soil with soluble and natural phosphate supply, Oliveira et al. (2015) concluded that Mehlich-3 and anion exchange resin are efficient methods in determining soil P. Mehlich-1 was inadequate for the determination of P availability upon supply of Arad's natural phosphate.

The first researchers to determine P in soils using the ion exchange resin were AMER et al. (1955). Subsequently, many groups of researchers, such as RAIJ et al. (1986) followed the same line of research. However, it was HISLOP; COOKE (1968) who described the first method routinely employed in a soil analysis laboratory in England.

The method of P extraction using a mixture of cationic and anion exchange resins, called mixed resin or ion exchange resin, saturated with sodium bicarbonate, that buffer the medium and favor the extraction of P (SIBBESEN, 1978; RAIJ et al., 1986). This method has been increasingly used in routine laboratories due to modifications and simplification of the method, with automation in the step of separation of mixed resin with soil.

The extraction process of mixed ion exchange resin, as currently used in Brazil (Raij et al., 2001), has as its principle the continuous removal of P from solution by exchange with resin bicarbonate. This creates a concentration gradient that forces the desorption of P from the colloid surface and the dissolution of P from precipitates until an electrochemical equilibrium between soil or precipitate and resin is achieved (FREITAS, et al., 2013).

The advantages of using ion exchange resins in soil P extraction are: higher amount of extracted element, mainly from clay soils, and non-dissolution of poorly soluble forms (RAIJ et al., 1986). This is because the resins remove P from the solution by a dewatering process without removing non-labile forms incorporated into the soil. Recalling that the mechanism of extraction of resins is a dynamic process by the gradual and continuous removal of ions from the solution, establishing different balances between the solid phase and the solution (SIBBESEN, 1977).

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SECOND PART – PAPERS*

PAPER 1 – Evaluation of MAP coated by humic acid in cropping system in Cerrado

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RESUMO

Devido às características dos solos tropicais em adsorver parte do fósforo adicionado ao solo, é desafiador aumentar a eficiência dos fertilizantes, reduzindo as perdas de fósforo, como também escolher o melhor extrator para extração dos teores disponíveis no solo. Objetivou-se avaliar o efeito do revestimento do MAP com ácidos húmicos e micronutrientes em fornecer fósforo às plantas e a eficiência dos extratores Mehlich-1, Mehlich-3 e resina de troca iônica na avaliação da disponibilidade de fósforo. O experimento foi realizado na Fazenda Muquém da Universidade Federal de Lavras, Lavras, MG. Foi utilizado o delineamento em blocos casualizados, em esquema fatorial 4 x 6, sendo quatro fontes de fósforo (MAP; MAP revestido com ácidos húmicos (AH); MAP revestido com AH, zinco (Zn), manganês (Mn), cobre (Cu) e boro (B), além de um controle, sem aplicação de fósforo e micronutrientes). Esses tratamentos foram combinados com aplicação de micronutrientes, sendo 1- Zn; 2- Mn; 3- Cu; 4- B + Zn + Mn + Cu via foliar, 5- B via solo e 6 - controle), com quatro repetições. As parcelas consistiram em oito linhas no tamanho 6,0 m x 4,8 m, totalizando 28,8 m^2. As culturas utilizadas foram milho primavera/verão (Safra 2016/17), seguido de trigo no outono/inverno (2016) e soja/verão (2017/18), sem irrigação, utilizando-se as cultivares KWS 9004, BRS 264 e M6410 IPRO, respectivamente. Após o cultivo de verão, em cada parcela foram retiradas duas amostras de solo na linha de semeadura e quatro nas entrelinhas, de forma aleatória, para compor a amostra composta. As análises do fósforo das amostras de solo foram realizadas pelas soluções extratoras Mehlich-1, Mehlich-3, além da resina de troca catiônica e iônica. Amostras de folhas foram coletadas para o diagnóstico do estado nutricional na cultura do milho e da soja. Os dados foram submetidos à análise de variância e os resultados significativos ao teste de Scott-Knott a 5% de probabilidade. O revestimento do MAP por ácidos húmicos proporcionou aumento no teor de fósforo disponível no solo, independentemente do extrator utilizado, no teor foliar de fósforo e na produtividade de grãos de milho e soja. O extrator Mehlich-3 foi adequado para a extração de fósforo em solos de Cerrado.

Palavras-chave: Sistema de produção, extratores, nutrientes, *Zea mays*, *Triticum* spp, *Glycine max*.

ABSTRACT

Due to the characteristics of tropical soils in adsorbing part of the phosphorus added through fertilizers, it is challenging to increase fertilizer efficiency by reducing phosphorus losses, as well as choosing the best extractor to determine available nutrients contents in soil. The aims of this study was to evaluate the effect of MAP coated by humic acids and micronutrients to supply phosphorus to plants and the efficiency of Mehlich-1, Mehlich-3 and ion exchange resin on phosphorus availability evaluating. The experiment was carried out at Muquém farm, Federal University of Lavras, Lavras, MG. A randomized block design in a 4 x 6 factorial scheme was used, with four sources of phosphorus (MAP; MAP coated by humic acids (H); MAP coated by HA, zinc (Zn), manganese (Mn), copper (Cu) and boron (B), as well as a control, without phosphorus and micronutrients supply. These treatments were combined with micronutrients supply, being 1- Zn; 2- Mn; 3- Cu; 4- B + Zn + Mn + Cu by spraying, 5- B by soil and 6 - control), with 4 repeats. The plots consisted of eight lines in size 6.0 m x 4.8 m, totaling 28.8 m^2. The crops used were corn spring/summer (crop year 2016/17), followed by wheat in autumn/winter (2016) and soybean spring/summer (2017/18), without irrigation, using cultivars KWS 9004, BRS 264 and M6410 IPRO, respectively. After summer cultivation, in each plot two soil samples were taken from the sowing furrows and four between the rows, randomly, to the composite sample. The phosphorus extractions on soil samples were performed by Mehlich-1, Mehlich-3, besides the ion exchange resin. Leaf samples were collected for the diagnosis of nutritional status in corn and soybean crop. Data were subjected to analysis of variance and significant results to the Scott-Knott test at 5% probability. The coating of MAP by humic acids increase the available phosphorus content in the soil, regardless of the extractor used, the phosphorus leaf content and the corn and soybean grain yield. Mehlich-3 extractor was suitable for phosphorus extraction in Cerrado soils.

Key-words: Cropping system, extractors, nutrients, *Zea mays*, *Triticum spp*, *Glycine max*.

1 INTRODUCTION

Phosphorus (P) is a fundamental element in food production and one of the most limiting nutrients for agricultural cultivation in Brazil. This nutrient is responsible for several plant functions, being part of the structure of plant cell compounds, promoting premature root growth besides improve plant efficiency in water absorption (TAIZ; ZEIGER, 2013).

In tropical soils, part of P added to the soil is adsorbed to the soil colloids, becoming unavailable to plants leading to the need for high doses of this nutrient to meet crop demand. The P being from non-renewable sources, its scarcity is worrying, a circumstance that endangers the food security of future generations, a fact that has aroused the interest of the industry.

New phosphate fertilizer technologies have been developed to increase the efficiency of this fertilizer. One example is the coating of MAP with humic acids in order to reduce the interaction of P with iron (Fe) and aluminum (Al) oxides, because humic acid competes for adsorption sites present in soils, promoting greater fertilizer efficiency (ERRO et al., 2010).

The evaluation of soil fertility is fundamental to the proper use of correctives and fertilizers in order to obtain high yields and use natural resources in a sustainable manner. Some methods are available to be used to assess nutrient availability to plants. However, when choosing a method it is important to note the accuracy and precision, robustness, ease of execution, good sensitivity of the methods, low cost and ability to extract multiple elements simultaneously (LEAL et al., 2007; HOLLER, SKOOG; CROUCH, 2009).

One of the most used extractors in Brazil is Mehlich-1. However, this extractor has wear that can mask the true available P levels in the soil. In this context, the use of Mehlich-3 extraction solution in tropical soils may be an alternative to consider. The ion exchange resin, although not suffering from this wear, demands more time for its execution, increasing the costs to the laboratories.

The aims of this study were to evaluate the effect of MAP coated by humic acid on P availability on soil and the comparison of Mehlich-1, Mehlich-3 and ion exchange resin on P extraction in a Red-Yellow Latosol in Cerrado.

2 METHODOLOGY

2.1 General information

The study was carried out on-farm at Research Center of the Federal University of Lavras, Lavras, MG, Brazil. The farm is located at 21º40’0” South and 45º00’00” West, at 918 m high. Lavras has a Cwa climate (subtropical, with rainy summer and dry winter), based on Köppen’s classification, with mean annual precipitation and temperature of 1529.7 mm and 19.5°C, respectively.

The soil was classified according to the Brazilian System of Classification of Soils as Yellow Red Latosol (LVA) very clay (EMBRAPA, 2013). The area was used twenty year as plant breeding research field. Before established the experiment, chemical and physics analyses using air-dried surface sample (0-20 cm), were performed according to Silva (2009). The soil characteristics are demonstrated on Table 1. The maximum and minimum temperatures during the experiment period, as well as the average rainfall, are presented in Figure 1.

Table 1 – Chemical and physical properties of the Yellow Red Latossol (Oxisoil) very clay (0-20 cm). UFLA, Lavras-MG, 2020.

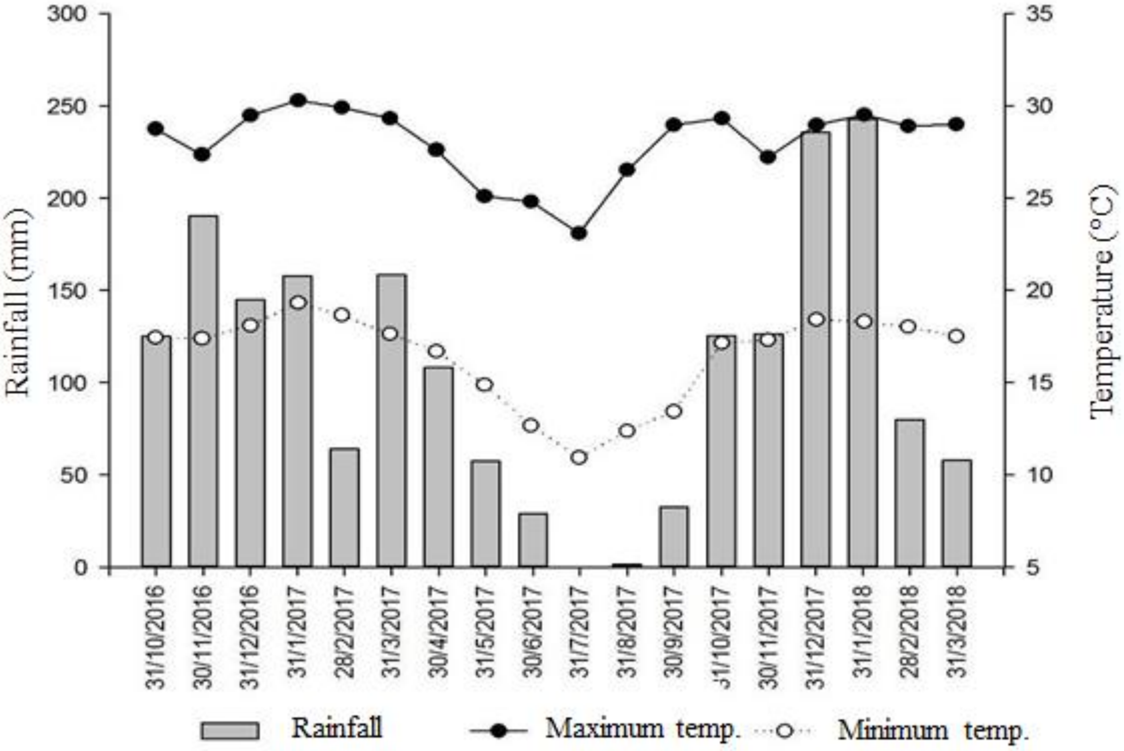
Properties	Unit	LVA
pH water(1)	-	5.7
Potassium (K) (2)	mg dm^{-3}	112.4
Phosphorus (P) (2)	mg dm^{-3}	6.0
Calcium (Ca) (3)	$cmol_c$ dm^{-3}	3.3
Magnesium (Mg) (3)	$cmol_c$ dm^{-3}	0.8
Aluminum (Al) (3)	$cmol_c$ dm^{-3}	0.0
Potencial acidity (H + Al) (4)	$cmol_c$ dm^{-3}	2.7
Bases sum(SB)	$cmol_c$ dm^{-3}	4.4
Cationic Exchange Capacity (T)	$cmol_c$ dm^{-3}	7.1
Bases Saturation (V) (5)	%	61.9
Organic Matter (OM) (1)	dag kg^{-1}	3.0
Remaining Phosphorus (P-Rem) (1)	mg L^{-1}	33.8
Zinc (Zn) (2)	mg dm^{-3}	4.9
Iron (Fe) (2)	mg dm^{-3}	55.2
Manganese (Mn) (2)	mg dm^{-3}	9.7
Copper (Cu) (2)	mg dm^{-3}	0.5

Boron (B) (1)	mg dm^{-3}	0.3
Sulfur (S) (1)	mg dm^{-3}	9.9
Sand(1)	g kg^{-1}	28.7
Silt(1)	g kg^{-1}	3.1
Clay(1)	g kg^{-1}	68.2
Texture	-	Very clay

(1)pH (water); (2)P, K, Fe, Zn, Mn and Cu (Mehlich 1); (3) Ca, Mg e Al (KCl 1mol L^{-1}; (4)potential acidity (SMP); (1)Organic matter ($Na_2Cr_2O_7$ 4 mol L^{-1} + H_2SO_4 5 mol L^{-1}) by Silva (2009) ; (1)Sand, silt and clay (Bouyoucos) modified by Carvalho (1985).

Source: From the Author (2020).

Figure 1 – Maximum and minimum temperatures and rainfall during the period of the two stages of the experiments in the crop years 2016/2017 and 2017/2018. UFLA, Lavras-MG, 2020.



Source: INMET / BDMEP - Teaching and Research Weather Database, Lavras Station.

Source: From the Author (2020).

A cropping system of corn, wheat and soybean, were carried out, respectively, without irrigation in 2016/2017 and 2017/2018 agricultural years, using the cultivars KWS 9004, BRS 264 and M6410 IPRO, respectively. The cultivars used were chosen because they are one of the most planting in Brazil.

2.2 Experimental design and treatments

The plots corresponded to 6.0 m length and 4.8 m width, totalizing 28.8 m^2. To do evaluations, were considered an useful area of 21.6 m^2. The distance between sowing furrows were 0.6, 0.17 and 0.6 m to corn, wheat and soybean, respectively.

The experiment was randomized complete block design, in a 4 x 6 factorial scheme, being four phosphorus (P) levels, 1 - monoammonium phosphate (MAP); 2- MAP coated by humic acids (HA); 3 - MAP coated by humic acids, manganese (Mn), zinc (Zn), copper (Cu) and boron (B) (MAP + HA + M) and 4 - control, without phosphorus, and six levels of micronutrients (M), 1 - Cu; 2 - Zn; 3 - Mn; 4 - B; 5 - Cu, Zn, Mn and B and 6 - control, without micronutrients. The nutrients P and B were applied in soil and the other micronutrients by leaf (Table 2). The experiment had four replicates, totaling 24 treatments and 96 plots.

Table 2 – Fertilizer characteristics. UFLA, Lavras-MG, 2020.

Fertilizers	Characteristics						
	P_2O_5 soluble	N	S	Mn	Zn	Cu	B
	---%						
MAP[1]	50.0	10.0	0.0	0.0	0.0	0.0	0.0
MAP + HA[1]	49.0	10.0	0.0	0.0	0.0	0.0	0.0
MAP + HA + M[1]	40.0	8.0	18.0	0.45	0.45	0.15	0.15
EDTA-Mn[2]	0.0	0.0	0.0	13.0	0.0	0.0	0.0
EDTA-Zn[2]	0.0	0.0	0.0	0.0	15.0	0.0	0.0
EDTA-Cu[2]	0.0	0.0	0.0	0.0	0.0	14.5	0.0
Ulexite[1]	0.0	0.0	0.0	0.0	0.0	0.0	10.0

[1] Granulate fertilizer; [2] Liquid fertilizer; MAP= Monoammonium phosphate; MAP+HA= Monoammonium phosphate coated by humic acid; MAP+HA+M= Monoammonium phosphate coated by humic, zinc, manganese, cupper and boron; P_2O_5= phosphorus pentoxide; N= nitrogen; S= sulfer; Mn= manganese; Zn= zinc; Cu= cooper and B= boron.

Source: From the Author (2020).

The applied amount of each nutrient was calculated according to Resende et al. (2012) to corn and Souza et al. (2004) to soybean and wheat. The nutrient amount supplied by spraying was calculated by export values to corn and soybean crop (Table 3 and 4) (RAIJ, 2011; SILVA, 2016; RESENDE et al., 2012).

All phosphorus was applied during seeding. The others fertilizer were applied manually. The plots that did not receive the treatments MAP + HA + M, received the sulfur in the same amount by manual supply of elemental sulfur so that the effect of sulfur does not interfere in the results. Phosphate fertilization was applied only on corn and soybean crop. The wheat did not receive phosphate fertilizer to observe the residual effect.

Table 3 – Amount of nutrients applied by soil. UFLA, Lavras-MG, 2020.

	Nutrients (kg ha^{-1})							
Crop	N	P_2O_5	K_2O	S	B	Zn	Cu	Mn
Corn	190.0	120.0	150.0	54.0	0.45	1.35	0.45	1.35
Wheat	100.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0
Soybean	20.0	80.0	150.0	38.0	0.3	0.9	0.3	0.9

N= nitrogen; P_2O_5= phosphorus pentoxide; K_2O= potassium oxide; S= sulfer; Mn= manganese; Zn= zinc; Cu= cooper and B= boron.

Source: From the Author (2020).

Table 4 – Amount of nutrients applied by spraying on leaf to achieve grain yield of 10 and 4 tons ha^{-1} to corn and soybean, respectively. UFLA, Lavras-MG, 2020.

	Nutrients (g ha^{-1})		
Crop	Mn	Zn	Cu
Corn	47.0	165.0	19.0
Soybean	30.0	40.0	10.0

Mn= manganese; Zn= zinc; Cu= cooper

Source: From the Author (2020).

2.3 Seeding and experiment conduction

The area was previously cultivated and had already been corrected, therefore, was not necessary to apply limestone and gypsum. The cultivation system used was no tillage, with no soil tillage or plowing. Due to the break that the area was without cropping, the amount of straw on the soil surface was very low. The sowing furrows with tractor implement were opened and the following treatments were applied and the sowing was done manually, except for wheat, where sowing was mechanical.

After each harvest, the crop remains were kept in the area. The soybean seeding furrows were opened following the original location of the corn crop furrows. The same did not happen in wheat sowing due to the furrow spacing was different.

Phosphate fertilizers were applied to the seeding furrows at about 10 cm depth. Afterwards, a soil layer of 7 cm was added before sowing to avoid direct contact between the fertilizers and seeds. The sowing was done at about 3 cm depth of the soil level for corn and soybean and 1.5 cm for wheat. After, another soil layer was added. In soybean crop inoculation was carried out by sowing furrows using liquid inoculant (Rhizomax®) with *B. japonicum* SEMIA 5079 and 5080 strains at a bacterial concentration of 2.0 x 109 cels mL^{-}

^{1}. The recommended dose of this inoculant is the application of 3.0 mL in 2 L of water, however, as soybean had never been grown in the area, it was decided to apply eight doses. After preparing, each treatment was sprayed with syrup volume equivalent to 100 L ha^{-1} into the previously open furrows, which already contained the seeds, using a manual sprayer. Fertilization with N, K, S, and B was performed throughout the plot.

The fertilizers were sprayed in growth stages V4 and V5 (four and five fully expanded leaves) in corn crop. In soybean, the fertilizers were sprayed in four stages, every seven days, started in stage V4 (fourth node visible) to avoid phytotoxicity due to the applied dosage. In soybean crop were sprayed cobalt and molybdenum, using 96 mL ha^{-1} of the nutritional compound Quimifol CoMo Plus®, which constituted 1% of cobalt (Co) and 6% of molybdenum (Mo) in the form of chelated cobalt sulfate and sodium molybdate.

The first nitrogen supply, using urea, in corn happened 15 days after sowing (DAS) with 60% of the dose. The second supply was carried out with 28 DAS with the remaining amount of nitrogen recommended, and the fertilizers were filleted next to the plant line, without incorporation, on both cases.

Specific weed and pest control procedures were adopted when necessary, using appropriate herbicides and insecticides, at the recommended dosages for each crop. The population of plants was 75.000, 300.000 and 180.000 plants ha^{-1} to corn, wheat and soybean, respectively.

2.4 Evaluated variables

Soil samples were collected after soybean harvest. Two simple samples were taken from the seeding rows and four simple samples from the area inter rows in the 0-20 cm layer, to make a composite sample for each plot. The samples were air dried in room temperature, crushed, thoroughly blended and passed through a 2-mm stainless steel sieve.

The P of the soils was extracted by the solution of Mehlich-1 (M1) (HCl 0.05 mol L^{-1} + H_2SO_4 0.0125 mol L^{-1}); pH (2.5) in the soil: solution ratio of 1:10, with agitation for 5 min in horizontal agitator at 180 rpm and after, filtration of the extract after 16 h, according to the method described by Mehlich (1953).

P was also extracted by Mehlich-3 (M3) (CH_3COOH 0.2 mol L^{-1} + NH_4NO_3 0.25 mol L^{-1} + NH_4F 0.015 mol L^{-1} + $HNO_3$0.013 mol L^{-1} + EDTA 0.001 mol L^{-1}, pH (2.5), in the soil: solution ratio of 1:10, with stirring for 5 min on an orbital shaker at 220 revolutions per minute. Extracts filtration proposed by Mehlich (1984) were performed.

After, the P was determined by atomic emission spectrometry using ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) PerkinElmer®, Optima 8300 model.

In order to determine the available phosphorus using the mixed resin, 2.5 cm^3 of dry soil were placed in 80 mL plastic cylindrical flasks, 25 mL of deionized water and a medium-sized glass bead were added. The mixture was stirred in horizontal circular stirring for 15 minutes at 220 rpm to disaggregate the soil. After this period, the glass beads were removed and 2.5 cm^3 of the mixed resin treated with 1 mol L^{-1} $NaHCO_3$ pH 8.5. This solution containing the mixed resin plus water and soil was subjected to a horizontal circular stirring at 220 rpm for 16h after that stirring period. The resin was separated from the soil by the wrapping in sieves with 0.4 mm polyester meshes and washed with deionized water and transferred individually to 100 mL flasks. Then 50 mL of 0.8 mol L^{-1} NH_4Cl solution in 0.2 mol L^{-1} HCl were added and allowed to stand for 30 minutes before the CO_2 removal, to avoid acidification. After this period, the flasks were closed, and the horizontal circular stirring was performed at 220 rpm for one hour. The phosphorus contained in the solution-extract of the mixed resin was determined by atomic emission spectrometry (FREITAS, et al., 2013).

During flowering periods, leaf samples were collected to diagnose the nutritional status of the plants. In the corn crop, the first leaf opposite and below the first ear was collected, being six leaves per plot. In soybean, the first ripened leaf was collected from the tip of the branch, without the petiole, totaling thirty-five per plot. These were placed in paper bags and dried in a forced air oven at a temperature of 65 ° C until constant weight to determine the leaf content of macro and micronutrients, according to the methodologies described by Malavolta et al. (1997). As the four central rows would be used to determine yield, it was decided to collect the leaves in the adjacent rows.

The determination of leaf B content was made by the hot water method, using 1.25 g L^{-1} $BaCl_2$ solution, in the soil solution 1:2 ratio, with microwave heating for 4 minutes at maximum power and 5 minutes 70% of the maximum power of the microwave, as described by Raij et al. (2001).

The yield was obtained by harvesting the ears and pods in the useful area of each plot, of 12 m^2 to corn and soybean, respectively. The wheat grain yield was not determined due to the low yield caused by the water deficit (Figure 1). Was determined the dry mass by collecting all plants in 0.25 m^2 in each plot.

2.5 Statistical Analysis

Data were analyzed by the F test ($P \leq 0.05$). The factors that present a significant difference between the treatments were submitted by Scott-Knott average test ($p \leq 0.05$). The analyses were performed by statistic program Sisvar (FERREIRA, 2014).

Correlation analyzes were performed between P contents in the soil, determined by different extraction methods, Mehlich-1, Mehlich-3 and ion exchange resin (P only). The contents of these nutrients in the soil were also correlated with the leaf contents and the yields obtained.

Confidence intervals between two means of P availability determined by Mehlich-1, Mehlich-3 and mixed resin were performed by Sisvar to compare the extraction power of extractors.

3 RESULTS AND DISCUSSION

3.1 Phosphorus in soil

The P sources significantly influenced the levels of soil P extracted by Mehlich-1, Mehlich-3 and resin in the samples collected after soybean harvest (Table 5).

The plots that received treatment MAP coated by humic acids, in general, showed an increase in P available content comparing to uncoated MAP by humic acids. The P increase ranged from 49% to 50%, 50% to 57% and 50% to 62%, for Mehlich-1, Mehlich-3 and resin, respectively (Table 5).

Table 5 – Available phosphorus in soil after soybean harvest extracted by Mehlich-1, Mehlich-3, and ion exchange resin. UFLA, Lavras-MG, 2020.

Treatments	Phosphorus available (mg dm^{-3})		
	Mehlich-1	Mehlich-3	Resin
MAP	7.2 b	45.3 b	41.6 c
MAP+HA	10.8 a	71.1 a	62.4 b
MAP+HA+M	10.7 a	68.0 a	67.2 a
Control	6.0 c	39.5 b	31.2 d
Average	8.7	55.9	50.6
CV(%)	21.0	21.6	24.2

The averages followed by the same letter in the column do not differ statistically by the Scott-Knott test at 1% probability. MAP= Monoammonium phosphate. MAP+HA= Monoammonium phosphate coated by humic acid. MAP+HA+M= Monoammonium phosphate coated by humic, zinc, manganese, cupper and boron. Control= without nutrients supply.

Source: From the Author (2020).

Changes in interpretation classes were observed when P was extracted by Mehlich-1 and resin. In Mehlich-1 extractions, the levels observed in plots with MAP and control treatments are in the medium availability class, while the treatments where the MAP was coated by humic acids, the P content is classified as high availability (ALVAREZ et al., 1999). In resin extractions, the treatments provided high P content, except the control that had the available P content classified as medium availability (RAIJ, 2011). No changes in interpretation class were observed when Mehlich-3 was used (MUMBACH et al., 2018).

One of the factors that decrease P availability to plants is associated to adsorption and precipitate reactions of the phosphate by the clay minerals. Novais et al. (2007) reported that in tropical soils, retention of P added to the soil occurs by precipitation of ion orthophosphate in solution with ionic forms of Fe^{3+}, Al^{3+} and Ca^{2+}, and more significantly by its adsorption by Fe^{3+} and Al^{3+} hydroxides, decreasing P availability to plants.

The MAP used was in granule form. This characteristic, besides facilitating to provide the fertilizers supply in the crop area, limits the amount of soil that comes into contact with the fertilizer, especially when applied in the seeding furrows, reducing P adsorption in soil. However, its solubilization happen in a short time, which leads to the increase of the P adsorption to the soil colloids, consequently reducing in soil solution content. Santos et al. (2011) found that adsorption of 74% of the added P happened within 5 minutes in soil with a high P sorption capacity (0.3473 mg g^{-1}). Newly, Guedes et al. (2016) studying P adsorption and desorption kinetics using a stirred-flow system, observed that most of the P adsorption process happen in the first minutes of contact with the solution.

The increase of P content available in the soil that received the treatments with the MAP coated by humic acids can be explained by the characteristics of these acids. According to Cessa et al. (2010), humic and fulvic acids, which compete for the same adsorption sites as P, play a fundamental role in the availability of this nutrient in soil. This effect is attributed for the reason that humic acid has functional carboxylic (-COOH) and hidroxyl (-OH) groups, generate negative charges and interact on minerals surface. Guppy et al. (2005), Tejada et al. (2008) and Duarte et al. (2013), found that the use of humic substances in the MAP coating positively influenced the availability of P in the soil solution. Teixeira et al. (2016) evaluating the effect of coating of slow-release phosphate fertilizers coated by organic acids on P availability and corn growth in tropical soil, found that coated fertilizers release less P in percolated water than uncoated fertilizer. Rosa et al. (2018) observed that the use of humic acid applied to the soil, combined with simple superphosphate, increased the extractable P content in the both soils (Red Latosol and Quartzenic Neosol) used in the research.

Another mechanism that promotes the reduction of the P affinity with the soil colloids is the generation of repulsive negative electrostatic field and, due to its high molecular weight, can also promote the physical barrier on mineral surface (WANG et al., 2016; YAN et al., 2016). Furthermore, Wang et al. (2016) found that humic acids reduces 31.03% and 37.45% the specific surface area of synthetic hematite and goethite, respectively, reducing adsorption capacity and P affinity with these minerals.

Yan et al. (2016), in a preliminary investigation of P adsorption onto two types of iron oxide-organic matter complexes, observed that which humic acid reduced the specific surface area of ferrihydrite to one fourth and the specific surface area of goethite to nearly half, which increased the P content in solution. These studies assist in understanding the interaction betweenP and humic acids in tropical soils, since they have a higher rate of iron oxides.

As expected, there was a large difference between the available P levels by the extractors, due to the different characteristics of each extractor. The highest P contents were extracted by Mehlich-3 and resin extractors (Table 6).

Table 6 – Confidence interval between two means of phosphorus availability. UFLA, Lavras-MG, 2020.

Treatments	Available phosphorus (mg dm^{-3})					
	M1 x	M3	M1 x	Resin	M3 x	Resin
MAP	7.2	45.3	7.2	41.6	45.3	41.6
MAP+HA	10.8	71.1	10.8	62.4	71.1	62.4
MAP+HA+M	10.7	68.0	10.7	67.2	68.0	67.2
Control	6.0	39.5	6.0	31.2	39.5	31.2
Average	8.7 B	55.9 A	8.7 B	50.6 A	55.9 A	50.6 B
CV(%)	21.0	21.6	21.0	24.2	21.6	24.2

The averages followed by the same letter do not differ statistically by the confidence interval between two averages. MAP = monoammonium phosphate. MAP + HA = humic acid coated monoammonium phosphate. MAP + HA + M = Monoammonium phosphate coated with humic, zinc, manganese, copper and boron. Control= without nutrients supply.

Source: From the Author (2020).

The extraction principle of Mehlich-1 is based on the fact that sulfate (SO_4^{2-}) prevents the reading of P removed by hydrogen (H^+) ions in solution (pH = 1.2) by blocking P adsorption sites (MEHLICH, 1953; NELSON et al., 1953).

In clay soils with high buffering power, the amount of P extracted is underestimated due to the loss of extraction capacity caused by H^+ and SO_4^{2-} adsorption by non-P-occupied functional groups in inorganic colloids. The settling time of 16 hours, used in the extraction methodology, can also influence the reduction of the extracted contents, due to the promotion of already dissolved P readsorption, resulting in lower extracted P values in clay soils compared to sandy soils (STEINER et al., 2012; FREITAS et al., 2013). This explains the lower values in Mehlich-1 extractions compared to other extractors.

The contents extracted by the resin method were higher than those extracted by Mehlich-1, since the loss of extraction capacity observed in this extractor does not happen with the resin method. This method extracts P from soil solution by ion exchange mechanism. In this case, the P of solution come to the resin by ion exchange, originating from the resin itself, which goes into the solution in order to maintain chemical equilibrium. As the soil solution P decreases, adsorbed forms are replaced by P until the available sources are exhausted, which may pass into the solution during the extraction period favored by water saturation and 16 hours agitation (SCHLINDWEIN; GIANELLO, 2008).

The agitation process facilitates the P extraction from the soil due to the presence of the resin drain. With the resin using, there is no possibility of P being readorbedf to the colloids, because the P removed from the solution does not return to it. Resin-bound P is not in equilibrium with the solution as happen in the Mehlich-1 extraction process. Therefore, in soils with higher P buffering power, such as clay soils, P extraction is higher in the resin method than in the Mehlich-1 method.

Camelo et al. (2015) compared the Mehlich-1 and ion exchange resin methods for P extraction in Ferric and Peripheral Oxisols. Higher levels of P extracted by resin were observed after a single extraction compared to Mehlich-1. It again show the greater efficiency of P removal in weathered soils, such as the Oxisols studied. They also highlight the high sensitivity of the Mehlich-1 extractor in highly buffered soils.

The highest P extraction provided by Mehlich-3 was also found by Bortolon and Gianello (2008), when evaluating Mehlich-1 and Mehlich-3 extraction capacity in 360 soil samples from different soils. The authors observed that on average, the contents of P extracted by Mehlich-3 solution were approximately 50% higher than those extracted by Mehlich-1 solution.

The higher P extraction by Mehlich-3 compared to Mehich-1 is justified by its composition. This extractor has ammonium fluoride (NH_4F), which is specific for Al-linked forms of P (P-Al), which is the form that, in soils under tropical conditions, most releases P to plants; followed by the forms of P bound to Fe (P-Fe); and to a lesser extent by calcium-bound P (P-Ca) (NOVAIS; KAMPRATH, 1978; BEEGLE, 2005). It is important to emphasize that in tropical soils predominates P-Fe and P-Al, in relation to P-Ca. In addition, Mehlich-3 calcium fluoride prevents precipitation of fluorine-solubilized P (F^-), avoiding excessive P-Ca dissolution as a function of ethanolic acid buffered pH (CH_3COOH) (pH = 2.5) (BORTOLON et al., 2009); besides decreasing P-Ca solubilization (NOVAIS; SMITH, 1999). Nitric acid (HNO_3) present in the extractor is also responsible for the extraction of P-Fe and P-Al (BORTOLON et al., 2009).

In other studies by Ring et al. (2004) and Wang et al. (2004), the Mehlich-3 method also occupied a prominent position in relation to Mehlich-1, being the most appropriate to estimate P plant availability. Mumbach et al. (2018) found that the Mehlich-3 and resin methods extract on average 11-12% more P than Mehlich-1 by evaluating P by Mehlich-1, Mehlich-3 and anion exchange resin in soils with different clay contents.

However, Mehlich-3 and Resin methods extracted more than Mehlich-1. In this study, Mehlich-3 and resin extractors extracted 542% and 446% more than Mehlich-1 extractor solution, respectively. Similar results have been presented in other studies, with higher values extracted by Mehlich-3 and resin compared to Mehlich-1 (BORTOLON; GIANELLO, 2008; BORTOLON et al., 2009; BORTOLON et al., 2011; STEINER et al., 2012). The different in the mechanisms extraction among the methods may be related to the difference in extraction capacity (MUMBACH et al, 2018).

The correlation coefficient between the amounts extracted by Mehlich-1 and Mehlich-3, Mehlich-1 and resin solutions and between Mehlich-3 and Resin were 0.79, 0.69 and 0.74, respectively, and all significant ($p < 0.01$). (Table 7).

Table 7 – Pearson correlation coefficient between mean values of phosphorus extracted by Mehlich-1 (P-M1), Mehlich-3 (P-M3), resin (P-Resin) in Red-Yellow Latosol very clay. UFLA, Lavras-MG, 2020.

Extractors	P-M3	P- Resin
P- M1	0.79**	0.69**
P- M3		0.74**

**: significant by 1% F test. n = 96.

Source: From the Author (2020).

The results found in the present study endorse the results observed by Steiner et al. (2009). These authors, when evaluating the methods of evaluation of P availability to soybean crop in 12 soil samples of State of Paraná, Brazil, of different classes, texture and source material, found the correlation coefficient between Mehlich-1 and Mehlich-3 extractors of 0.96.

Mumbach et al. (2018) determined the available P content by Mehlich-1, Mehlich-3 and ion exchange resin methods in 301 soil samples to evaluate the influence of clay content on P extraction. The authors observed that the correlation between Mehlich-1 and the other extractors was lower in samples with clay content higher than 60%. According to the authors, the Mehlich-1, Mehlich-3 and resin methods were sensitive to soil clay content, extracting smaller amounts of P in more clay soils, which may have influenced the decreasing of the correlation coefficient between extractors.

In order to correlate the nutrient content extracted by Mehlich-1 and Mehlich-3, Valladares et al. (2001) determined the P content by these methods in 40 soil samples. It was also found in this study that the levels extracted by both extractors correlate with each other (r = 0.88).

3.2 Phosphorus in plant

In addition to soil contents, we analyzed the effects of supply of different sources of P and micronutrients (Cu, Mn, and Zn) by leaf and B via soil on leaf P concentrations in soybean and corn leaves (Table 8). There was interaction between P sources and supply by spraying of Mn, Zn, and Cu, and B supply by soil for leaf P content in corn and soybean (Table 8).

Table 8 – Phosphorus content in corn and soybean leaves by phosphorus and micronutrients sources. UFLA, Lavras-MG, 2020.

Treatment	Corn						
	P (g kg^{-1})						
	Mn	Zn	Cu	B	MZCB	Control	Average
MAP	1.6 aA	1.2 bB	1.3 bB	1.5 aA	1.3 aB	1.3 aB	1.4 b
MAP + HA	1.6 aA	1.6 aA	1.6 aA	1.4 aA	1.5 aA	1.5 aA	1.5 a
MAP + HA + M	1.3 bA	1.5 aA	1.4 bA	1.3 bA	1.4 aA	1.4 aA	1.4 b
Control	1.1 bB	1.5 aA	1.3 bB	1. bB	1.1 bB	1.5 aA	1.3 b
Average	1.4 A	1.4 A	1.4 A	1.3 A	1.3 A	1.4 A	1.4
CV (%)	10.6						

Treatment	Soybean						
	P (g kg^{-1})						
	Mn	Zn	Cu	B	MZCB	Control	Average
MAP	4.3 bA	4.6 aA	4.4 aA	4.1 aA	4.2 aA	4.1 aA	4.3 a
MAP + HA	4.9 aA	4.4 aB	4.4 aB	4.4 aB	4.1 aB	4.3 aB	4.4 a
MAP + HA + M	4.2 bA	4.1 aA	4.2 aA	4.0 aA	4.3 aA	4.2 aA	4.2 b
Control	2.9 cB	3.6 bA	3.9 bA	3.5 bA	3.6 bA	3.8 bA	3.5 c
Average	4.1 A	4.2 A	4.2 A	4.0 A	4.1 A	4.1 A	4.1
CV (%)	6.9						

The averages followed by the same lowercase letter in the column and the same capital letter in the line do not differ statistically by the Scott-Knott test at 1% probability. MAP = monoammonium phosphate. MAP + HA = humic acid coated monoammonium phosphate. MAP + HA + M =

Monoammonium phosphate coated with humic, zinc, manganese, copper and boron. Control= without nutrients supply. Mn=Manganese. Zn= Zinc. Cu= Copper. B= Boron. MZCB= Manganese, zinc, copper and boron.

Source: From the Author (2020).

Although the analysis of variance showed that there was a significant interaction between the factors under study for P content, the mean test identified a difference only for P sources factor (Table 8). It is noted that the difference found by the mean test is petty in practical terms, there was no difference among the leaf contents of P among the sources of P used.

Corn leaves P levels were below the limit of 2.5 g kg^{-1}, considered appropriate for corn in Minas Gerais (MARTINEZ; CARVALHO; SOUZA, 1999), from the range 2.0 to 4.0 g kg^{-1} suggested by Raij (2011), as the sufficiency range from 2.9 to 4.2 g kg^{-1} proposed by Gott et al. (2014), or the minimum limit of 1.8 g kg^{-1}, considered suitable for corn crop in Cerrado soils (Oliveira, 2004). However, Resende (2004) evaluating sources and P supply methods in a typical dystrophic Red Argisol with clay texture, using triple hybrids, also found leaf P contents below the quoted references, and despite this, did not observe P deficiency in plants.

Similar results were observed in the leaf P contents in soybean. Despite the significant difference observed between P sources, in which the plants fertilized by MAP and MAP + HA presented higher contents, in practical terms, the differences are irrelevant. In turn, it was expected that the plants that did not receive P would have the lowest P levels compared to those fertilized with the nutrient (Table 8). Despite the significant difference between treatments, all leaf P contents obtained are within of the appropriate range, ranging from 2.5 to 5.0 g kg^{-1}, according to Raij (2011).

Prado et al. (2016) testing the effect of an organomineral fertilizer containing humic acids on soybean crop, observed an increase in leaf P content in plants that received the fertilizer. According to the authors, the increase in of P leaf content may be related to its higher availability in soil, since functional groups present in humic acids can block P adsorption sites in the mineral fraction and make it available for plant absorption.

It is worth noting that even if the leaf contents are very close, the treatments with MAP coated with humic acids, showed higher levels of P in the soil, after harvest (Table 5).

3.3 Yield

The factor P sources significantly influenced the grain yield of corn and soybean and also the dry matter of wheat (Table 9). Treatment with MAP coated by humic acids increased proportionally corn yield between 4.9 and 9.3% over uncoated MAP by humic acids. Similar results were obtained in the analysis performed after the harvest of soybean crop, whose increase ranged from 0.3 to 11.2% .The dry matter yield of the wheat varied from the decrease of 7.7% and an increase of 6.5% when MAP by humic acids coating was used in relation to uncoated fertilizer (Table 9).

Table 9 – Grain yield of corn and soybean and the dry mass of wheat for phosphorus treatments. UFLA, Lavras-MG, 2020.

	Grain Yield (kg ha^{-1})			Dry Mass (kg ha^{-1})*
Fertilizers	**Corn (C)**	**Soybean (S)**	**C + S**	**Wheat**
MAP	10348 b	3231 b	13579	8697 a
MAP+HA	10864 a	3593 a	14457	8030 b
MAP+HA+M	11311 a	3241 b	14552	9262 a
Control	9995 b	3100 b	13095	7330 b
Average	10630	3291.1	-	8330
CV(%)	10.6	11.4	-	18.7

*Due to low production of wheat grains due to water deficit, the total dry matter analysis was performed.The averages followed by the same letter in the do not differ statistically by the Scott-Knott test at 5% probability. MAP = monoammonium phosphate. MAP + HA = humic acid coated monoammonium phosphate. MAP + HA + M = Monoammonium phosphate coated with humic, zinc, manganese, copper and boron. Control= without nutrients supply.

Source: From the Author (2020).

It can be observed that the corn plants that received MAP coated by humic acids showed higher grain yield compared to the other treatments, except to MAP+HA+M in soybean. It can be inferred that when using MAP coated by humic acids, there was a decrease in P adsorption in soil colloids, increasing the P available content in soil solution. This is evident from Table 1, where soil P levels were higher in the plots that received MAP coated by humic acids compared to the plots that received the conventional MAP.

The yield increase due to the P content available increase can be explained by the importance of this nutrient. P plays several functions in the plants, being essential for metabolism, such as formation and ATP use as an energy source; the cellular processes regulation by metabolite phosphorylation and in nucleic acids structure. It is also a root growth promoter in addition to improving plant efficiency in water absorption, it is a constituent of a number of important respiratory intermediate plant cell compounds, photosynthesis and various functions essential to plant metabolism. Its appropriate supply, since the beginning of plant development, is important for the reproductive parts generation (HERNÁNDEZ; MUNNÉ-BOSCH, 2015; ALMEIDA et al., 2017).

Saldanha et al. (2017), evaluating the effect of phosphate supply on corn crop in a dystrophic Yellow Latosol under field conditions, observed an increase in grain yield due to the P availability increase in soil solution. Barreto and Fernandes (2002) also observed an increase in corn grain yield due to the increase of P uptake in a Yellow Argisol.

When MAP was coated by micronutrients, there was an increase nearly to 972 kg h^{-1} in yield (C+S) and 564 kg h^{-1} of dry mass of wheat, comparing to MAP treatment. This result indicates that micronutrient coating of MAP may be an alternative to supply these nutrients.

Soybean plants that received MAP coated by humic acids achieved higher yields than those of other treatments (Table 9). In addition to the increased availability of P in soil solution, due to the decrease of P adsorption sites, as well as Ca, Fe and Al complexation, reducing phosphate precipitation reactions (PERASSI BORGNINO, 2014; URRUTIA et al., 2014; WANG et al., 2016), humic acids can form variable stability complexes with P, intermediated by metallic cations that can be gradually solubilized, making P available to plants (GERKE, 2010; URRUTIA et al., 2014).

Some research shows that humic acids also act in several stages involved in plant physiology, such as gene expression (ELENA et al., 2009), presence of organelles (JANNIN et al., 2012), primary metabolism (TREVISAN et al., 2011), secondary metabolism (SCHIAVON et al., 2010), growth and development (TREVISAN et al., 2011) and flower, fruit and seed generation (WANGEN et al., 2013; BALDOTTO; BALDOTTO, 2014) which may have contributed to increased yield.

3.4 Correlations

The Mehlich-3 extractor presented slightly higher correlation coefficients between soil extracted P content and P leaf content and yield, all significant ($p < 0.01$). However, these values are below ideal ($r \geq 0.70$) (STAINER et al. (2009) (Table 10).

Table 10 – Pearson correlation coefficient between mean values of phosphorus extracted by Mehlich-1 (P-M1), Mehlich-3 (P-M3), resin (P-Resin), leaf phosphorus content (P-Leaf) and grain yield (Yield) in soybeans. UFLA, Lavras-MG, 2020.

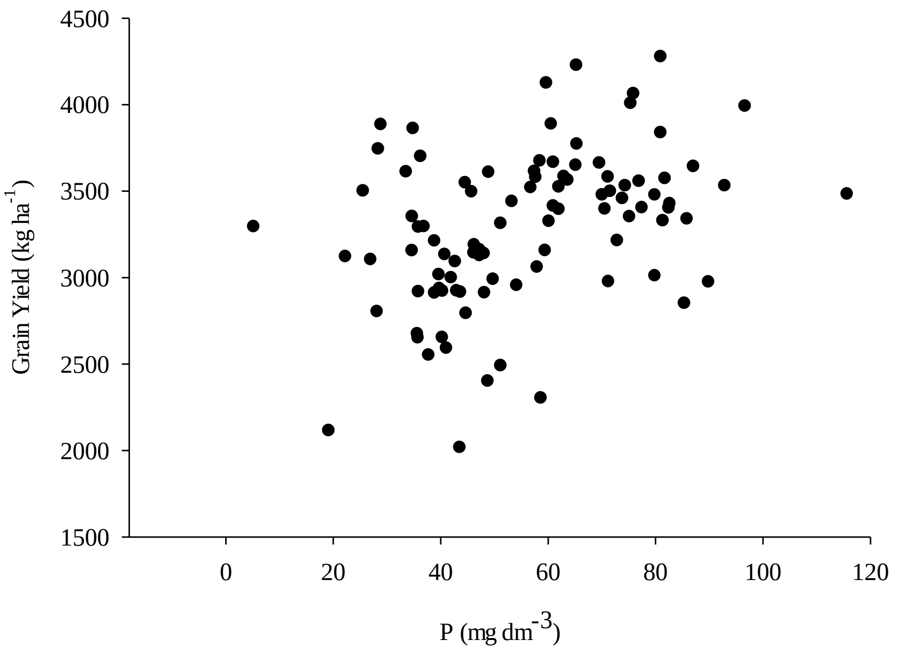
Extractors	**P-Leaf**	**Yield**
P (Mehlich-1)	0.29**	0.25*
P (Mehlich-3)	0.36**	0.39**
P (Resin)	0.33**	0.23**

**, *: significant by 1% and 5% by F test, respectively. n = 96.

Source: From the Author (2020).

One of the explanations for the low correlations found in the present study between soil contents and the other variables is that, the range of phosphorus soil content was not compatible with the range found for yields. It can be observed in Figure 2 that for the plants that produced approximately 3500 kg ha^{-1} of soybeans, some presented available P extracted by Mehlich-3, around 58 mg dm^{-3} while in other plot the content of available P was approximately 118 mg dm^{-3}.

Figure 2 – Soybean grain yield (kg ha^{-1}) as a function of phosphorus content (mg dm^{-3}) in soil, extracted by Mehlich-3. UFLA, Lavras-MG, 2020.



Source: From the Author (2020).

Resende et al. (2016) point out that experimental data and results of farmers observations on acidity correction and fertilization in built fertility areas do not present similar responses described in research conducted in low or medium fertility soils to reach high yields.

By correlating available soil P content and soybean and maize yield in two locations, with Latosol class soils, 20-year cultivation history and high yields, Lacerda (2014) observed that soil P content was not positively correlated with soybean yield in the first crop at one of the study sites. However, the author found that the phosphate fertilizer supply significantly influenced the yield during the three harvests (soybean/corn/soybean) in the second site, presenting correlation coefficient above 0.9.

Also evaluating the agronomic efficiency of phosphates on the yield of several annual crops in a Latossolo in Guarapuava, PR, with high nutrient levels available, Fontoura et al. (2010) found that, except for barley, crop yield was not altered by the addition of any phosphate in the first crop year, probably due to the high P content previously found in the soil. In the other crop year, the yield increase was moderate again, except for barley.

The study on soil fertility management involving experimentation in areas that had been under proper management for several years, where the soil has adequate nutrient levels, shows the decrease in the magnitude of responses to nutrient supply in which moderate doses of fertilizers are sufficient to obtain quite satisfactory yields. There are even cases where even the absence of fertilizers supply has no effect on productivity (RESENDE et al., 2016).

It is clear from the work on soil fertility management involving experimentation in areas that already had adequate nutrient levels that fertilizer supply may, in some cases, increase soil nutrient availability and cause little or no change in soil fertility, nutrient leaf contents as well as grain yield.

For Lacerda (2014) relating soil nutrient content with the amount of nutrient applied, leaf content and crop productivity in built fertility soils is one of the biggest challenges in managing soil fertility today. Even if there is interdependence between these factors, correlations when performed in pairs may be low and not significant. The low correlation between these factors makes it difficult to establish adequate nutrient levels for crops in built fertility soils.

4 CONCLUSIONS

The coating of MAP by humic acids provides increase in soil available phosphorus content, leaf phosphorus content and corn and soybean grain yield.

Mehlich-3 extractor was suitable for phosphorus extraction in Cerrado soils.

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PAPER 2 – Micronutrient supply methods in cropping system of corn, wheat and soybean in Cerrado

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RESUMO

Como os solos sob Cerrado geralmente apresentam baixos teores de micronutrientes, na maioria das vezes há necessidade de aplicação de fertilizantes, para garantir altas produtividades. Produtores rurais têm aplicado fertilizantes fosfatados com micronutrientes no solo. No entanto, em muitos casos, observam que os teores foliares permanecem abaixo do ideal. A avaliação dos nutrientes no solo é necessária para determinar sua disponiblidade às culturas. Diferentes métodos podem ser utilizados como o Mehlich-1 e o Mehlich-3, sende este último citado por autores como mais eficiente para extração em solos tropicais cultivados. Objetivou-se avaliar a melhor forma de fornecimento de micronutrientes às plantas, bem como verificar a eficiência dos extratres Mehlich-1 e Mehlich-3 em um solo de Cerrado. O experimento foi realizado na Fazenda Muquém da Universidade Federal de Lavras, Lavras, MG. Foi utilizado o delineamento em blocos casualizados, em esquema fatorial 4 x 6, sendo quatro fontes de fósforo (MAP; MAP revestido com ácidos húmicos (AH); MAP revestido com AH e zinco (Zn), manganês (Mn), cobre (Cu) e boro (B), além de um controle, sem aplicação de fósforo e micronutrientes. Esses tratamentos foram combinados com aplicação de micronutrientes, sendo 1- Zn; 2- Mn; 3- Cu; 4- B + Zn + Mn + Cu via foliar, 5- B via solo e 6 - controle), com quatro repetições. As parcelas consistiram em oito linhas no tamanho 6,0 m x 4,8 m, totalizando-se 28,8 m^2. As culturas utilizadas foram milho primavera/verão (Safra 2016/17), seguido de trigo no outono/inverno (2016) e soja (2017/18), utilizando-se as cultivares KWS 9004, BRS 264 e M6410 IPRO, respectivamente. Após o cultivo de verão, em cada parcela foram retiradas duas amostras de solo na linha de semeadura e quatro nas entrelinhas, de forma aleatória, para compor a amostra composta. Amostras de folhas foram coletadas para o diagnóstico do estado nutricional na cultura do milho e da soja. A extração dos teores dos micronutrientes (Cu, Mn e Zn) no solo foi realizada pelos métodos Mehlich-1 e Mehlich-3 e boro por água quente. Os dados foram submetidos à análise de variância e os resultados significativos ao teste de Scott-Knott a 5% de probabilidade. Apenas os teores disponíveis de Cu no solo, extraídos por Mehlich-1, foram superiores quando do uso do MAP revestido com ácidos húmicos e micronutrientes. Não houve alteração nos teores disponíveis de micronutrientes no solo quando a extração foi realizada com Mehlich-3. As doses de B, Cu, Mn e Zn empregadas MAP revestido não proporcionam aumento dos teores foliares destes micronutrientes na cultura da soja. A aplicação de B via solo e de Cu, Mn e Zn via foliar, proporciona aumento dos teores foliares destes nutrientes, independentemente do uso de fertilizante fosfatado revestido com estes micronutrientes. O extrator Mehlich-3 é adequado para a extração de fósforo em solos de Cerrado.

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Palavras-chave: Sistema de produção, extratores, nutrientes, *Zea mays*, *Triticum* spp, *Glycine max*.

ABSTRACT

As soils under Cerrado generally have low levels of micronutrients in the soil, most of the time is necessary to apply fertilizers to ensure high yield, farmers have applied phosphate fertilizers coated by micronutrients to the soil. However, in many cases, they observe that leaf levels remain below ideal. The assessment of nutrients in the soil is necessary to determine their availability to crops. Different methods can be used, such as Mehlich-1 and Mehlich-3, the latter cited by authors as more efficient in cultivated tropical soils. The aim of this study were to evaluate the best way to supply micronutrients to plants, as well as to verify the efficiency of Mehlich-1 and Mehlich-3 extracts on Cerrado soil. The experiment was carried out at Muquém farm, Federal University of Lavras, Lavras, MG. A randomized block design was used, in a 4 x 6 factorial scheme, with four sources of phosphorus (MAP; MAP coated with humic acids (AH); MAP coated with AH and zinc (Zn), manganese (Mn), copper (Cu) and boron (B), in addition to a control, without phosphorus and micronutrients supply, these treatments were combined with micronutrients supply, being 1- Zn; 2- Mn; 3- Cu; 4- B + Zn + Mn + Cu by spraying on leaves, 5- B by soil and 6 - control), with 4 repeats. The plots consisted of eight lines in the size 6.0 m x 4.8 m, totaling 28.8 m^2. The crops used were spring/summer corn (2016/17 harvest), followed by wheat in fall/winter (2016) and soybeans (2017/18), using cultivars KWS 9004, BRS 264 and M6410 IPRO, respectively. After soybean harvest, in each plot two soil samples were taken from the sowing line and four between the rows, randomly, to the composite sample. Leaves samples were collected for the diagnosis of nutritional status in corn and soybean crops. The extraction of micronutrient contents (Cu, Mn and Zn) in the soil were carried out by the Mehlich-1 and Mehlich-3 and boron methods by hot water. The data were submitted to analysis of variance and the significant results to the Scott-Knott test at 5% probability. Only the available levels of Cu in the soil were higher when using MAP coated by humic acids and micronutrients. There was no change in the available levels of micronutrients in the soil when the extraction was performed with Mehlich-3. The amount of B, Cu, Mn and Zn used in MAP coating do not increase the leaf contents of these micronutrients in soybean crop. The B supply by soil and Cu, Mn and Zn via spraying on leaves provides an increase in the leaf contents of these nutrients, regardless of the use of phosphate fertilizer coated with these micronutrients. Mehlich-3 extractor is suitable for phosphorus extraction in Cerrado soil.

Key-words: Cropping system, extractors, nutrients, *Zea mays*, *Triticum spp*, *Glycine max*.

1 INTRODUCTION

The supply of crop demand for micronutrients is a major factor for obtaining high productivity in annual crops. These are nutrients required in moderately low concentrations in plant tissues, however, their deficiency reflects not only the productivity of the crops, but also the vigor, tolerance to diseases and pests, and the quality of the harvested product (NASCIMENTO et al., 2010). Discrepant experimental results are found in the literature, demonstrating the great variability in response to the application of micronutrients both in relation to doses and forms of application.

There are numerous foliar fertilizer companies in Brazil, most of them have a specific micronutrient recommendation program. Currently, in most properties with annual crops they apply micronutrients, however, most of the research results that exist, usually older results, show that there is no effect on productivity. It is noted that in many cases, the producer applies micronutrients under commercial pressure.

Many micronutrients are recommended to be supplied to plants via soil. This is due to the fact that some of these micronutrients are not very mobile in the plant, such as B, or other with intermediate mobility (MARSCHNER, 2012). Thus, it remains to be seen whether these micronutrients applied via the leaf would have an effect on productivity. On the other hand, studies show that the fertilizers applied by soil may not be as efficient due mainly to adsorption on the soil's organic matter, mainly Cu and Mn (MOTSCHENBACHER et al., 2014; MOREIRA et al., 2017). The question remains as to the best way to apply micronutrients.

The supply of micronutrients can occur in different methods, and currently there are solid fertilizers such as NPK formulations containing micronutrients in their recipe, making easy supply by soil. Another form used is through supply by spraying. Recently, agronomy professionals report that only the micronutrient levels contained in NPK formulations, even used in successive harvests, are not sufficient, making supply by spraying necessary.

The evaluation of the availability of micronutrients in the soil to the plants is made by the use of extracting solutions, which aim to quantify possible forms of absorption by the plants. Several methods are available to be used to assess nutrient availability to plants. However, when choosing a method it is important to note the accuracy and precision, robustness, ease of execution, good sensitivity of the methods, low cost and ability to extract multiple elements simultaneously (LEAL et al., 2007, HOLLER; SKOOG; CROUCH, 2009).

The most widely used extractor in Brazil is Mehlich-1. However, authors (STEINER et al., 2012; MUMBACH et al., 2018) observed a superior performance of Mehlich-3 extractor in micronutrient as well as phosphorus (P) extraction, making this extractor a possible substitute Mehlich-1. Nevertheless, they are still scarce and there is no doubt about the best extractor for Cerrado tropical soil conditions.

In this context, the aims of this study were to evaluate the best micronutrients supply methods on cropping system of corn, wheat and soybean and to evaluate the extraction efficiency of micronutrients by Mehlich-1 and Mehlich-3 in very clay Red-Yellow Latosol of Cerrado.

2 METHODOLOGY

2.1 General information

The study was carried out on-farm at Research Center of the Federal University of Lavras, Lavras, MG, Brazil. The farm is located at 21º40’0” South and 45º00’00” West, at 918 m high. Lavras has a Cwa climate (subtropical, with rainy summer and dry winter), based on Köppen’s classification, with mean annual precipitation and temperature of 1529.7 mm and 19.5°C, respectively.

The soil was classified according to the Brazilian System of Classification of Soils as Yellow Red Latosol (LVA) very clay (EMBRAPA, 2013). The area was used twenty year as plant breeding research field. Before established the experiment, chemical and physics analyses using air-dried surface sample (0-20 cm), were performed according to Silva (2009). The soil characteristics are demonstrated on Table 1. The maximum and minimum temperatures during the experiment period, as well as the average rainfall, are presented in Figure 1.

Table 1 – Chemical and physical properties of the Yellow Red Latossol (LVA) very clay (Oxisoil) (0-20 cm). UFLA, Lavras-MG, 2020.

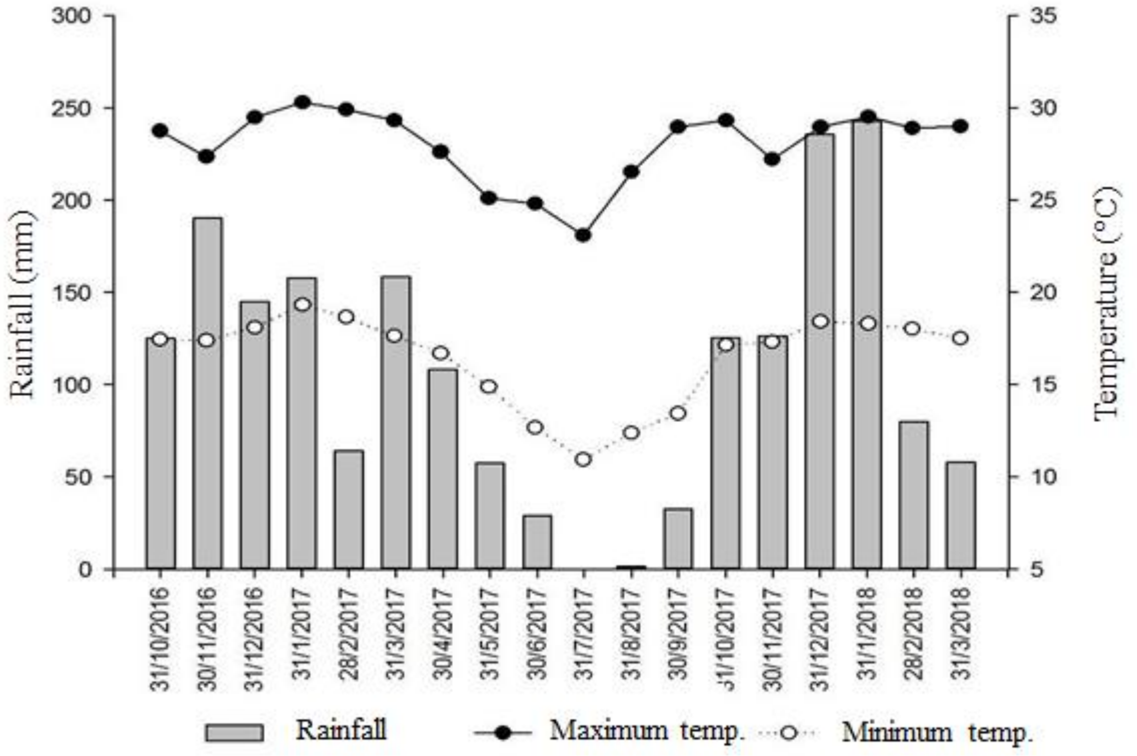
Properties	Unit	LVA
pH water(1)	-	5.7
Potassium (K) (2)	mg dm^{-3}	112.4
Phosphorus (P) (2)	mg dm^{-3}	6.0
Calcium (Ca) (3)	$cmol_c$ dm^{-3}	3.3
Magnesium (Mg) (3)	$cmol_c$ dm^{-3}	0.8
Aluminum (Al) (3)	$cmol_c$ dm^{-3}	0.0

Potencial acidity (H + Al) (4)	$cmol_c\ dm^{-3}$	2.7
Bases sum(SB)	$cmol_c\ dm^{-3}$	4.4
Cationic Exchange Capacity (T)	$cmol_c\ dm^{-3}$	7.1
Bases Saturation (V) (5)	%	61.9
Organic Matter (OM) (1)	$dag\ kg^{-1}$	3.0
Remaining Phosphorus (P-Rem) (1)	$mg\ L^{-1}$	33.8
Zinc (Zn) (2)	$mg\ dm^{-3}$	4.9
Iron (Fe) (2)	$mg\ dm^{-3}$	55.2
Manganese (Mn) (2)	$mg\ dm^{-3}$	9.7
Copper (Cu) (2)	$mg\ dm^{-3}$	0.5
Boron (B) (1)	$mg\ dm^{-3}$	0.3
Sulfur (S) (1)	$mg\ dm^{-3}$	9.9
Sand(1)	$g\ kg^{-1}$	28.7
Silt(1)	$g\ kg^{-1}$	3.1
Clay(1)	$g\ kg^{-1}$	68.2
Texture	-	Very clay

(1)pH (water); (2)P, K, Fe, Zn, Mn and Cu (Mehlich 1); (3) Ca, Mg e Al (KCl 1mol L^{-1}); (4)potential acidity (SMP); (1)Organic matter ($Na_2Cr_2O_7$ 4 mol L^{-1} + H_2SO_4 5 mol L^{-1}) accord to Silva (2009); (1)Sand, silt and clay (Bouyoucos) modified by Carvalho (1985).

Source: From the Author (2020).

Figure 1 – Maximum and minimum temperatures and rainfall during the period of the two stages of the experiments in the crop years 2016/2017 and 2017/2018. UFLA, Lavras-MG, 2020.



Source: INMET / BDMEP - Teaching and Research Weather Database, Lavras Station.
Source: From the Author (2020).

A cropping system of corn, wheat and soybean, were carried out, respectively, without irrigation in 2016/2017 and 2017/2018 agricultural years, using the cultivars KWS 9004, BRS 264 and M6410 IPRO, respectively. The cultivars used were chosen because they are one of the most used in Brazil.

2.2 Experimental design and treatments

The plots corresponded to 6.0 m length and 4.8 m width, totalizing 28.8 m^2. To do evaluations, were considered an useful area of 21.6 m^2. The distance between sowing furrows were 0.6, 0.17 and 0.6 m to corn, wheat and soybean, respectively.

The experiment was randomized complete block design, in a 4 x 6 factorial scheme, being four phosphorus (P) levels, monoammonium phosphate (MAP); MAP coated by humic acids (HA); MAP coated by humic acids, manganese (Mn), zinc (Zn), copper (Cu) and boron (B) (MAP + HA + M) and one control, without phosphorus, and five levels of micronutrients (M), Cu; Zn; Mn; B; Cu, Zn, Mn and B and one control, without micronutrients. The nutrients P and B were applied in soil and the other micronutrients by leaf (Table 2). The experiment had four repeats, totaling 24 treatments and 96 plots.

Table 2 – Solid granular fertilizers characteristics. UFLA, Lavras-MG, 2020.

Fertilizers	Characteristics						
	P_2O_5 soluble	N	S	Mn	Zn	Cu	B
	--------------------	--------------------	--------------------	%	--------------------	--------------------	--------------------
MAP[1]	50.0	10.0	0.0	0.0	0.0	0.0	0.0
MAP + HA[1]	49.0	10.0	0.0	0.0	0.0	0.0	0.0
MAP + HA + M[1]	40.0	8.0	18.0	0.45	0.45	0.15	0.15
EDTA-Mn[2]	0.0	0.0	0.0	13.0	0.0	0.0	0.0
EDTA-Zn[2]	0.0	0.0	0.0	0.0	15.0	0.0	0.0
EDTA-Cu[2]	0.0	0.0	0.0	0.0	0.0	14.5	0.0
Ulexite[1]	0.0	0.0	0.0	0.0	0.0	0.0	10.0

[1] Granulate fertilizer; [2] Liquid fertilizer; MAP= Monoammonium phosphate; MAP+HA= Monoammonium phosphate coated by humic acid; MAP+HA+M= Monoammonium phosphate coated by humic, zinc, manganese, cupper and boron; P_2O_5= phosphorus pentoxide; N= nitrogen; S= sulfer; Mn= manganese; Zn= zinc; Cu= cooper and B= boron.

Source: From the Author (2020).

The applied amount of each nutrient was calculated by Resende et al. (2012) to corn and Souza et al. (2004) to soybean and wheat. The nutrient amount supplied by spraying was calculated by export values to corn and soybean crop (Table 3 and 4) (RAIJ, 2011; SILVA, 2016; RESENDE et al., 2012).

All phosphorus was applied during seeding. The others fertilizer were applied manually. The plots that did not receive the treatments MAP + HA + M, received the sulfur in the same amount by manual supply of elemental sulfur so that the effect of sulfur does not interfere in the results. Phosphate fertilization was applied only on corn and soybean crop. The wheat did not receive fertilizer to observe the residual effect.

Table 3 – Amount of nutrients applied by soil. UFLA, Lavras-MG, 2020.

Crop	Nutrients (kg ha^{-1})							
	N	P_2O_5	K_2O	S	B	Zn	Cu	Mn
Corn	190.0	120.0	150.0	54.0	0.45	1.35	0.45	1.35
Soybean	20.0	80.0	150.0	38.0	0.3	0.9	0.3	0.9

Source: From the Author (2020).

Table 4 – Amount of nutrients applied by spraying on leaf to achieve grain yield of 10 and 4 tons ha^{-1} to corn and soybean, respectively. UFLA, Lavras-MG, 2020.

Crop	Nutrients (g ha^{-1})		
	Mn	Zn	Cu
Corn	47.0	165.0	19.0
Soybean	30.0	40.0	10.0

Source: From the Author (2020).

2.3 Seeding and experiment conduction

The area was previously cultivated and had already been corrected, therefore, was not necessary to apply limestone and gypsum. The cultivation system used was no tillage, with no soil tillage or plowing. Due to the break that the area was without cropping, the amount of straw on the soil surface was very low. The sowing furrows with tractor implement were opened and the following treatments were applied and the sowing was done manually, except for wheat, where sowing was mechanical.

After each harvest, the cultural remains were kept in the area. The soybean seeding furrows were opened following the original location of the corn crop furrows. The same did not happen in wheat sowing due to the furrow spacing was difference.

Phosphate fertilizers were applied to the seeding furrows at about 10 cm depth. Afterwards, a soil layer of 7 cm was added before sowing to avoid direct contact between the fertilizers and seeds. The sowing was done at about 3 cm depth of the soil level for corn and soybean and 1.5 cm for wheat. After, another soil layer was added. In soybean crop inoculation was carried out by sowing furrows using liquid inoculant (Rhizomax®) with *B. japonicum* SEMIA 5079 and 5080 strains at a bacterial concentration of 2.0 x 109 cels mL^{-1}. The recommended dose of this inoculant is supply of 3.0 mL in 2 L of water, however, as soybean had never been grown in the area, it was decided to apply eight doses. After preparing, each treatment was sprayed with syrup volume equivalent to 100 L ha^{-1} into the previously open furrows, which already contained the seeds, using a manual sprayer. Fertilization with N, K, S and B was performed throughout the plot.

The fertilizers were sprayed in growth stages V8 and V12 (eight and twelve leaves fully expanded) in corn crop. In soybean, the fertilizers were sprayed in four stages, every seven days, started in stage V4 (fourth node visible) to avoid phytotoxicity due to the applied dosage. In soybean crop were sprayed cobalt and molybdenum, using 96 mL ha^{-1} of the nutritional compound Quimifol CoMo Plus®, which constituted 1% of cobalt (Co) and 6% of molybdenum (Mo) in the form of chelated cobalt sulfate and sodium molybdate.

The first nitrogen supply in corn happened 15 days after sowing (DAS) with 60% of the dose. The second supply was carried out with 28 DAS with the remaining amount of nitrogen recommended, and the fertilizers were filleted next to the plant line, without incorporation, on both cases.

Specific weed and pest control procedures were adopted when necessary, using appropriate herbicides and insecticides, at the recommended dosages for each crop. The population of plants was 75.000, 300.000 and 180.000 plants ha^{-1} to corn, wheat and soybean, respectively.

2.4 Evaluated variables

Soil samples were collected after soybean harvest. Two simple samples were taken from the seeding rows and four simple samples from the area between rows in the 0-20 cm layer, to make a blend sample for each plot. The samples were air dried in room temperature, crushed, thoroughly blended and passed through a 2-mm stainless steel sieve.

The nutrients, except B, were extracted by the solution of Mehlich-1 (M1) (HCl 0.05 mol L^{-1} + H_2SO_4 0.0125 mol L^{-1}); pH (2.5) in the soil: solution ratio of 1:10, with agitation for 5 min in horizontal agitator at 180 rpm and after, filtration of the extract after 16 h, according to the method described by Mehlich (1953).

The nutrients, except B, were also extracted by the solution of Mehlich-3 (M3) (CH_3COOH 0.2 mol L^{-1} + NH_4NO_3 0.25 mol L^{-1} + NH_4F 0.015 mol L^{-1} + $HNO_3$0.013 mol L^{-1} + EDTA 0.001 mol L^{-1}, pH (2.5), in the soil: solution ratio of 1:10, with stirring for 5 min on an orbital shaker at 220 revolutions per minute. Extracts filtration proposed by Mehlich (1984) were performed.

B extraction was made by the hot water method, using 1.25 g L^{-1} $BaCl_2$ solution, in the soil solution 1: 2 ratio, with microwave heating for 4 minutes at maximum power and 5 minutes. 70% of the maximum power of the apparatus, as described by Raij et al. (2001). After, nutrients were determined by atomic emission spectrometry using ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) PerkinElmer®, Optima 8300 model.

During flowering periods, leave samples were collected to nutritional status diagnose of plants. In the corn crop, the first leaf opposite and below the first ear was collected, being six leaves per plot. In soybean, the first ripened leaf was collected from the tip of the branch, without the petiole, totaling thirty-five per plot. These were placed in paper bags and dried in a forced air oven at a temperature of 65 ° C until constant weight to determine the leaf content of macro and micronutrients, according to the methodologies described by Malavolta et al. (1997). As the four central rows would be used to determine the yield, it was decided to collect the leaves in the adjacent rows.

The yield was obtained by harvesting the ears and pods in the useful area of each plot, of 12 m^2 to corn and soybean, respectively. The wheat grain yield was not determined due to the low yield caused by the water deficit. Was determined the dry mass by collecting all plants in 0.25 m^2 in each plot.

2.5 Statistical Analysis

Data were analyzed by the F test ($P \leq 0.05$). The factors that present a significant difference between the treatments were submitted by Scott-Knott average test ($P \leq 0.05$). The analyses were performed by statistic program Sisvar (FERREIRA, 2014).

Correlation analyzes were performed among B, Cu, Mn and Zn contents in the soil, determined by different extraction methods, Mehlich-1and Mehlich-3. The contents of these nutrients in the soil were also correlated with the leaf contents and the yields obtained.

3 RESULTS AND DISCUSSION

3.1 Micronutients in soil

The zinc (Zn), manganese (Mn) and copper (Cu) contents extracted by Mehlich-1 were significantly modified by the sources ($p < 0.01$). No significant differences ($p > 0.05$) were observed between micronutrient contents in soils fertilized with different P sources and extracted by Mehlich-3 (Table 5).

Table 5 – Zinc (Zn), manganese (Mn), copper (Cu) and boron (B) content for phosphorus treatments, after soybean harvest. UFLA, Lavras-MG, 2020.

Treatments	Micronutrients available ($mg\ dm^{-3}$)						
	Zn		Mn		Cu		B
	M-1**	M-3 ^{ns}	M-1**	M-3 ^{ns}	M-1**	M-3 ^{ns}	HW ^{ns}
MAP	2.0 a	4.2 a	6.5 a	3.2 a	0.5 c	1.3 a	0.33 a
MAP+HA	1.9 a	4.3 a	5.8 b	3.3 a	0.8 b	1.3 a	0.36 a
MAP+HA+M	1.9 a	4.1 a	5.8 b	3.1 a	1.6 a	1.3 a	0.40 a
Control	1.7 b	4.2 a	6.7 a	3.3 a	0.3 d	1.2 a	0.40 a
Average	1.9 B	4.2 A	6.2 A	3.2 B	0.8 B	1.3 A	1.9
CV(%)	16.3	28.9	9.4	25.5	77.2	14.0	12.6

MAP = monoammonium phosphate. MAP + HA = hamster acid coated monoammonium phosphate. MAP + HA + M = Monoammonium phosphate coated with humic, zinc, manganese, copper and boron. Control= Without nutrients supply. M-1 = Mehlich-1. M-3=Mehlich-3. HW= Hot water. The averages followed by the same lower case letter in the column do not differ statistically by the Scott-Knott test. Capital letters refer to the confidence interval between two means. ^{ns} Not significative. ** Significative by 1%.

Source: From the Author (2020).

In the case of extraction with Mehlich-1 solution, Zn availability was lower in the soil without P supply, compared to the other treatments but with a low difference. Despite this decrease in content, in all plots the nutrient was at levels above the ideal (1.5 mg dm^{-3}) (ALVAREZ et al., 1999), including the control treatment (Table 5).

The non-change of Zn content by the supply of 2.25 kg ha^{-1} of Zn in the fertilizer containing this micronutrient can also be explained by the dilution of Zn applied to the sowing furrow with the rest of the soil, since only six simple samples were taken, two in the sowing lines. This dilution may also have influenced the results found for Mn extracted by Mehlich-1.

Although the plots that received the MAP coated by humic acids or humic acids and micronutrients (2.25 kg ha^{-1} of Mn) showed decrease of Mn content in rate to the other treatments, the differences with Mehlich-1 were low, not changing the soil content interpretation class, all contents classified as medium availability (ALVAREZ et al., 1999) (Table 5).

Tropical soils have high levels of Fe and Al oxides, and these oxides can significantly affect soil micronutrient reactions, mainly due to their high affinity to metal ions (SCHALLER et al., 2019). Hippler et al. (2014) evaluated the Zn and Mn supply and the adsorption characteristics of two contracting textured Oxisols, one sandy (18% clay) and the other very clay (64% clay). It was observed that the very clay soil had the highest Zn and Mn adsorption capacities, which shows its higher adsorption affinity of these micronutrients with the clay (NASCIMENTO; FONTES, 2004). However, it is noteworthy that soils with higher clay contents do not always have a higher maximum adsorption capacity, since the types of clay minerals also influence this adsorptive capacity, as they control the physical and chemical properties of the soil (SPOSITO, 1989, FONTES; SANTOS, 2010).

In addition to the clay content of soils, organic matter (OM) also contributes to increased micronutrient adsorption in the soil. According to Fontes and Santos (2010), the influence of (OM) on metal adsorption is a result of the presence of active groups in its structures, forming complexes and chelates. According to Piri et al. (2019), the soil OM consists of several compounds, mainly humic and fulvic acids. These compounds are responsible for the constitution of organic complexes with Zn, Mn, Cu, and Fe, which may decrease the solubility of these micronutrients and availability to plants. The constitution of these complexes explains the absence of increased nutrient levels when applied to the soil, together with humic acids, as well as a possible explanation for the reduced availability of Mn extracted by Mehlich-1 in the plots that received them humic acid treatments. It is may also suspect that Mehlich-1 was not an appropriate extractor to assess the availability of these micronutrients because it is a very acidic solution. This is because the contents extracted by Mehlich-3 were not affected. Therefore, it is extremely important to evaluate the leaf concentrations of these nutrients.

In several soils studied under no-tillage system by Moreira et al. (2006) and Moreira et al. (2016), it was observed that much of the Mn present in the soils was strongly linked to the humic substances present in soil OM.

According to Moreira et al. (2016), the Mn adsorbed by OM may be associated with its functional groups, mainly by the carboxylic and phenolic groups, in the form of external (non-specific adsorption) and internal (specific adsorption) sphere complexes. The first happen by an electrostatic attraction adsorption reaction, where one or more water molecules are interposed between the central ion and the ligands. The second happen by ionic or covalent bonding, where the central ion and the ligands form a complex with direct contact, without the interposition of water molecules. Inner sphere complexes are more stable than outer sphere complexes, which can easily exchange with other cations and anions of soil solution (SPARKS, 2003; MEURER et al., 2012).

Moreira et al. (2006), evaluating the Mn availability in four soils under no-tillage system through sequential extraction, observed that the amount of Mn in organic form reached values of up to 52% of total Mn, after supply with 48 kg ha^{-1} of Mn. Only 20% of the total Mn remained in residual form, which is the fraction that concentrates the most recalcitrant forms present in the soil, exposing the great capacity of the OM fractions in Mn adsorption on soil.

In the case of available Cu levels, the highest values were observed in treatment MAP coated by humic acids and micronutrients, compared to other sources, when extraction was performed by Mehlich-1. The increase in content was 351% compared to the control treatment without Cu supply (Table 5). MAP coated by humic acids had a 60% higher Cu content than MAP without any coating.

Cu also has high affinity for adsorption sites, both on the surface of Fe and Al oxides, and on OM functional groups in tropical soils (SODRÉ et al., 2001; LOPES et al., 2014). Strawn and Baker (2009) analyzed Cu speciation in six different soils by different methods such as near-edge X-ray absorption (XANES), extended X-ray absorption thin-structure spectroscopy (EXAFS) and synchrotron x-ray fluorescence (μ-XRF). The μ-XRF results indicated that most Cu particles in soils were not associated with calcium carbonates, Fe oxides or Cu sulfates. When analyzing data from XANES and EXAFS, they observed that Cu in all soils was mainly associated with OM.

The Cu data extracted by Mehlich-1 from this study do not endorse the results obtained by Abreu et al. (2007). According to the authors, the available Cu content may be influenced by the soil OM, and the power of complex constitution with the soil OM decreases following the order Cu> Zn> Mn. That is, Cu is the metallic micronutrient with the highest capacity for adsorption to the functional groups of OM (MOREIRA et al., 2017). However, in the present study, it was observed that the supply of fertilizer with humic acids and micronutrients (0.75 kg ha^{-1} Cu) increased the soil Cu content from low values (control treatment) to medium values (MAP + HA) and high (MAP + HA + M) according to Alvarez et al. (1999). It may be that even with micronutrient complexation reaction with the OM functional groups, part of it was still available in the soil. However, there is a need to evaluate Cu contents in the leaf.

Comparing with the values obtained from Zn and Mn, it was not expected that the treatments where the MAP was coated by humic acids and with humic acids and micronutrients would have the highest levels of Cu in the soil, mainly because according to Abreu et al. (2007) the complexation reaction power of Cu by OM is greater than that observed for Zn and Mn. It can also be inferred that the Mehlich-1 extractor is extracting amounts of Cu not available to plants, which was not observed with Mehlich-3 using.

The B content was not changed with any treatments used even with 750 g ha^{-1} of B supplied. Moschini e Silva (2018) studying the interaction between humic acids and B in Red-Yellow Latosol (LVA) (27% clay) and Red Latosol (LV) (71% clay), observed that in both soils, the humic acids supply decreased the availability of B when the nutrient was added. Without the addition of B, in both soils, humic acid concentrations did not affect their availability to plants. Some hypothesis presented by the authors is that the increase of humic acids concentration may have raised the soil pH and, thus, more B was adsorbed to the soil colloids, reducing its availability and that the B present in the soil may have strongly interacted with the humic acids matrix to the point that it is not available to plants. In the present study, the average pH observed was 5.7, and no significant difference was found between the pH values between treatments.

The Mehlich-3 solution was also responsible for extracting the highest available Zn and Cu contents comparing to the Mehlich-1 solution (Table 5). The highest performance of this extractor is related to the complexation reactions that happen during micronutrient extraction. Extraction promoted by Mehlich-3 involves the constitution of ethylenediaminetetraacetic acid (EDTA) complexes with metals. Its stability may vary according to reaction time, soil pH and competition from other cations. The pH of the 2.5 solution also promotes dissolution of Zn, Mn, Cu and Fe (MEHLICH 1984).

Sobral et al. (2013), when comparing Cu, Mn and Zn extraction in samples of Ultisols and Oxisols by the Mehlich-1, Mehlich-3 and DTPA methods, observed that the levels of these nutrients extracted by Mehlich-3 were higher than the levels obtained through Mehlich-1 and DTPA extractors. Similar results were found by Mylavarapu et al. (2002) for Cu and Zn in acidic Florida soils. The reason is that Mehlich-3 solution acts by both dissolving and forming metal chelates. Therefore, more of these micronutrients are extracted by Mehlich-3 solution than by Mehlich-1 and DTPA extractors. In the case of Mn, some authors have observed greater extractions by Mehlich-3 extractor than by Mehlich-1 (MYLAVARAPUET et al., 2002; NASCIMENTO et al., 2002). The results found by these authors differ from this study to Mn contents, where it was found that the Mehlich-1 extractor was the one that extracted the highest contents. Much more acidic being the extraction solution, greater are the ability to lower pH and solubility the Mn present in soils (MOREIRA et al., 2016; MOREIRA et al., 2006).

Nascimento et al. (2002) studying Mn desorption, extraction and fractionation in an oxisol using Mehlich-1, Mehlich-3, DTPA and EDTA as extraction methods, observed that Mehlich-1 was the extractor that provided the highest Mn extraction. According to the authors, this unexpected result may be due to the distribution of Mn in the soil fractions. It was found that in acid soils, after liming, much of Mn was bound to crystalline Fe oxides, which are possibly less susceptible to Mehlich-1 acid attack, decreased. While Mn bound to the amorphous Fe and Mn oxides and in the organic fraction increased. Therefore, it can be inferred that in soils with higher pH, Mn is more easily dissolved by the acid solution, but not extracted by other extractors. In corrected soils by limestone, most of Mn was linked to exchangeable forms and OM. This indicates that Mehlich-1 may be inadequate for assessing Mn availability in limed soils.

3.2 Micronutrient leaf content in corn and soybean crop

The Cu, B, Mn, and Zn contents in corn leaves were not influenced by the supply of these micronutrients together with the fertilizer in the sowing furrows, nor by the interaction of this form of supply by furrow with spraying suppy (Table 6).

On the other hand, when micronutrients were sprayed, in the growth stages V8 and V12 (eighth and twelfth fully open leaf) of corn crop, the leaf concentration in the diagnostic leaf (opposite leaf and below the first ear, collected at stage R1 (full bloom) has been modified (Table 6).

At sites with Zn supply by spraying (165 g ha^{-1} of Zn) or with Zn combined with the other micronutrients, the Zn concentration was altered. On average, there was a 33% increase over the control treatment, without supply by soil or by spraying. Zn contents found in plants that received Zn were higher than the range considered adequate to Zn leaf levels in corn, which varies from 10 to 15 mg kg^{-1}, according to Raij (2011). In plants that did not receive Zn supply by spraying, the levels found were also within the range considered adequate by Raij (2011) (Table 6), but Zn supply by spraying was important to increase leaf contents. According to Martinez et al. (1999), the reference range for leaf Zn content ranges from 20 to 70 mg kg^{-1}. To reach this reference range, we can infer that it would have been necessary to apply more than 165 g ha^{-1} of Zn. Therefore, it may be advantageous to use the extraction value of Zn rather than the export value as used in this paper.

Table 6 – Zinc (Zn), cupper (Cu) and manganese (Mn) content in corn leaves for micronutrients treatments.a UFLA, Lavras-MG, 2020.

Treatment	Micronutrients (mg kg^{-1})		
	Zn	Cu	Mn
Mn (g ha^{-1})	12.3 b	6.3 b	14.4 a
Zn (g ha^{-1})	16.5 a	6.0 b	13.5 b
Cu (g ha^{-1})	13.1 b	8.2 a	12.2 b
B (kg ha^{-1})	11.7 b	5.2 b	12.8 b
MZCB	16.6 a	7.0 a	15.2 a
Control	12.4 b	5.6 b	12.3 b
Average	13.8	6.4	13.4
CV(%)	37.2	41.1	21.5

The averages followed by the same lowercase letter in the column and the same capital letter in the row do not differ statistically by the Scott-Knott test at 1% probability. Mn = manganese (47 g ha^{-1}). Zn = zinc (165 g ha^{-1}). Cu = copper Cu (19 g ha^{-1}). B = Boron (2 kg ha^{-1}). MZCB = manganese (47 g ha^{-1}), zinc (165 g ha^{-1}), copper (19 g ha^{-1}) and boron (2 kg ha^{-1}). Control= Without nutrients supply. The micronutrients were supplied between V8 and V10 growth stage. The sources of Cu, Mn and Zn was EDTA and for B was ulexite.

Source: From the Author (2020).

Similar to what happened with Zn, plants that received Cu supply by spraying (19 g ha^{-1} of Cu), alone or associated with the other micronutrients, presented higher Cu leaf concentrations. When Cu was applied in combination with the other micronutrients under study, the increase was 25% compared to the control treatment. In turn, when Cu alone was applied, the increase was 46% (Table 6).

There may have been some antagonism in Cu absorption when it was applied in the blend with Mn (47 g ha^{-1} of Mn) and Zn (165 g ha^{-1} of Zn), as discussed in the literature (NGUYEN et al., 2019). The leaf contents of Cu obtained are within or very close to the range considered adequate by Raij (2011), which ranges from 6 to 20 mg kg^{-1}.

The leaf contents of Mn found followed the same trend as those of Zn and Cu. Plants that received Mn (47 g ha^{-1} of Mn) by spraying, showed 17% increase in Mn concentration on leaf in relation to the control treatment. When Mn was applied by spraying combined with Zn and Cu, was observed increasing of 24% in Mn content on leaf (Table 6).

The leaf contents of Mn found are below the appropriate range, which varies between 20 and 200 mg kg^{-1}, according to Raij (2011). These values are also outside the sufficiency range proposed by Gott et al. (2014), ranging from 22.7 to 44.2 mg kg^{-1}. Thus, although the spraying supply showed efficiency, it was not able to raise the Mn contents to adequate values. This shows the need of nutrient supply to raise the leaf value to the appropriate level.

Although the analysis of variance showed significant interaction between the factors under study for B content on leaf, the mean test did not show any difference between the sources of P factor (Table 7).

Table 7 – Boron (B) content on corn leaves for micronutrients and phosphorus treatments interaction. UFLA, Lavras-MG, 2020.

Treatment	B (mg kg^{-1})						
	Mn	Zn	Cu	B	MZCB	Control	Average
MAP	14.0 aB	8.0 aB	16.2 aA	12.2 aB	21.4 aA	9.7 aB	13.6 a
MAP + HA	15.2 aA	13.7 aA	15.2 aA	13.1 aA	14.7 bA	11.1 aA	13.8 a
MAP + HA + M	11.9 aB	14.0 aB	20.3 aA	12.0 aB	14.8 bB	11.8 aB	14.1 a
Control	9.8 aA	11.5 aA	10.6 aA	14.6 aA	13.4 bA	11.5 aA	11.9 a
Average	12.7 B	11.8 B	15.6 A	13.0 B	16.1 A	11.0 B	13.4
CV (%)	28.2						

The averages followed by the same lowercase letter in the column and the same capital letter in the line do not differ statistically by the Scott-Knott test at 5% probability. MAP = monoammonium phosphate. MAP + HA = hamster acid coated monoammonium phosphate. MAP + HA + M = Monoammonium phosphate coated with humic, zinc, manganese, copper and boron. Mn = manganese (47 g ha^{-1}). Zn = zinc (165 g ha^{-1}). Cu = copper Cu (19 g ha^{-1}). B = Boron (2 kg ha^{-1}). MZCB = manganese (47 g ha^{-1}), zinc (165 g ha^{-1}), copper (19 g ha^{-1}) and boron (2 kg ha^{-1}). Control=

Without nutrients supply. The micronutrientes were supplied between V8 and V12 growth stage. The sources of Cu, Mn and Zn were EDTA and for B was ulexite.

Source: From the Author (2020).

B contents were influenced by micronutrient spraying supply and B supply on soil. When the fertilizer at sowing was the MAP, the highest B leaf contents were observed in the plants that received Cu by spraying or the combination of all micronutrients (Cu, Mn and Zn by spraying and B by soil) being the increase 42 and 46% higher than the control treatment. The values obtained to B content on leaf are within the reference values, ranging from 10 to 25 mg dm^{-3}, according to Raij (2011). Results are also within the sufficiency range of 9.9 to 16.6 mg dm^{-3} suggested by Gott et al. (2014). However, a higher effect of B via soil was expected, as 2 kg ha^{-1} B were applied by ulexite in corn crop and in soybean crop. One hypothesis that can be raised regarding the low effect of B is related to the source used. Bardhan et al. (2017) studying the impact of B supply on corn, wheat, soybean and swithgrass (*Panicum virgatum*) growth using four sources types, including granulated ulexite, observed that this source showed slow B release to crops. Thus, possibly, after one year of supply, there was no release of the source of B to the soil to increase the contents (Table 5) or to make B available to plants.

Evaluating the micronutrient contents in soybean leaves, the responses were variable among them. In the Zn case, in general, the plants with the highest Zn levels were achieved in plants that, regardless of P source, were those that received the supply of all micronutrients together, by leaf, and in the case of B, by soil (MZCB) (Table 8). In this case, 40 g ha^{-1} of Cu, 160 g ha^{-1} of Zn, 120 g ha^{-1} of Mn were applied in growth stage V4 and 2 kg ha^{-1} of B at sowing. Plants that received 160 g ha^{-1} of Zn by spraying and P coated by humic acids also showed high levels of Zn in leaves.

This result was already expected, since it was not observed that the Zn added in MAP increased the Zn content in the soil when using the Mehlich-3 extractor. After Mehlich-1 extraction, the difference between MAP + HA + M treatment and control was only 0.2 mg dm^{-3} (Table 5).

The plants supplied by different treatments, did not show Zn leaf contents below the considered adequate range (20 to 50 g kg^{-1}), suggested by Raij (2011). The contents were within or above this range. However, no visual phytotoxicity caused by this nutrient was found.

Table 8 – Zinc (Zn), manganese (Mn), cupper (Cu) and boron (B) content in soybean leaves for micronutrients and phosphorus treatments interaction. UFLA, Lavras-MG, 2020.

	Zn (mg kg^{-1})						
	Mn	Zn	Cu	B	MZCB	Control	Average
MAP	48.2 aB	55.2 bB	46.6 aB	52.0 aB	79.7 aA	38.3 bB	53.3 a
MAP + HA	49.6 aB	75.9 aA	43.7 aB	43.5 aB	66.0 aA	43.9 bB	53.8 a
MAP + HA + M	41.7 aB	74.9 aA	45.4 aB	50.0 aB	73.8 aA	51.2 aB	56.2 a
Control	44.7 aB	49.4 bB	48.7 aB	43.3 aB	70.3 aA	52.8 aB	51.5 a
Average	46.0 C	63.9 B	46.1 C	47.2 C	72.4 A	46.6 C	53.7
CV (%)	15.4						
	Mn (mg kg^{-1})						
	Mn	Zn	Cu	B	MZCB	Control	Average
MAP	43.9 aA	32.5 aC	41.1 aA	36.9 aB	45.6 aA	29.6 aC	38.3 a
MAP + HA	37.9 bB	30.4 aC	30.1 bC	30.2 bC	43.3 aA	25.7 bC	32.9 b
MAP + HA + M	37.2 bA	26.6 aC	26.8 bC	31.8 bC	29.7 cC	32.0 aB	30.7 c
Control	33.6 bB	30.4 aC	25.9 bC	27.7 bC	38.8 bA	24.3 bC	30.1 c
Average	38.1 A	30.0 B	31.0 B	31.6 B	39.4 A	27.9 C	33.0
CV (%)	10.1						
	Cu (mg kg^{-1})						
	Mn	Zn	Cu	B	MZCB	Control	Average
MAP	9.2 aC	10.4 aC	12.2 aB	9.3 aC	16.4 aA	8.2 aC	10.9 a
MAP + HA	9.2 aB	8.1 aB	11.6 aA	9.5 aB	12.8 bA	10.2 aB	10.2 a
MAP + HA + M	8.8 aA	10.2 aA	9.42 aA	7.3 aA	9.21 cA	8.7 aA	8.9 b
Control	8.2 aB	8.5 aB	11.4 aA	8.5 aB	12.7 bA	9.5 aB	9.8 b
Average	8.8 C	9.31 C	11.2 B	8.7 C	12.8 A	9.1 C	10.0
CV (%)	16.2						
	B (mg kg^{-1})						
	Mn	Zn	Cu	B	MZCB	Control	Average
MAP	77.1 aA	75.4 aA	76.3 aA	79.7 aA	83.6 aA	68.7 bB	76.8 a
MAP + HA	81.2 aA	65.4 bB	71.6 aB	82.1 aA	85.0 aA	70.2 bB	76.3 a
MAP + HA + M	74.8 aB	73.7 aB	69.2 aB	82.1 aA	73.3 bB	80.8 aA	76.6 a
Control	74.2 aB	76.0 aB	70.1 aB	82.0 aA	74.4 bB	82.0 aA	76.4 a
Average	76.8 B	72.6 C	71.8 C	81.5 A	79.1 B	75.4 C	76.2
CV (%)	5.6						

The averages followed by the same lowercase letter in the column and the same capital letter in the line do not differ statistically by the Scott-Knott test at 1% probability. MAP = monoammonium phosphate. MAP + HA = hamster acid coated monoammonium phosphate. MAP + HA + M = Monoammonium phosphate coated with humic, zinc, manganese, copper and boron. Mn = manganese (120 g ha^{-1}). Zn = zinc (160 g ha^{-1}). Cu = copper Cu (40 g ha^{-1}). B = Boron (2 kg ha^{-1}). MZCB = manganese (120 g ha^{-1}), zinc (160 g ha^{-1}), copper (40 g ha^{-1}) and boron (2 kg ha^{-1}). Control= Without nutrients supply. The micronutrientes were supplied at V4 growth stage. The sources of Cu, Mn and Zn was EDTA and for B was ulexite.

Source: From the Author (2020).

The highest Mn contents on leaf were observed when MAP was applied by spraying of leaf Mn (120 g ha^{-1}) and/or with the supply of all micronutrients (Cu , 40 g ha^{-1}; Mn, 120 g ha^{-1} and Zn, 160 g ha^{-1} by spraying on leaf and B (2 kg ha^{-1}) by soil (Table 4). This result corroborates the justification used for the reduction of soil Mn contents extracted by

Mehlich-1 in the plots that received MAP coated by humic acids. These acids may have adsorbed the Mn present in the MAP coating, reducing their availability to plants.

Looking at the Mn values in the soil, it can be inferred that the decrease of the leaf Mn content was possibly due to the decrease of Mn availability on soil (Table 1), when MAP coated by humic acids was used. Possibly, the decrease in soil contents may be compensated by the Mn spray supply, since there was an increase in Mn contents on leaves with Mn spraying. According to Raij (2011), the adequate range of Mn for soybean crop varies between 20 and 100 g kg^{-1}. Therefore, all observed Mn contents are within the sufficiency range for the crop.

In the case of Cu, it was observed that the plants that received the MAP combined with MZCB supply by spraying, showed the highest concentrations in leaves. Plants that received MAP + HA + M were expected to have the highest leaf Cu content due to the higher soil Cu content (Table 4). In the case of Cu, not all contents are within the appropriate range suggested by Raij (2011), which varies between 10 and 30 g kg^{-1}.

The B contents on leaf observed are all well above the range considered adequate by Raij (2011), which varies between 21 and 55 g kg^{-1}. Similar to Zn, no visual signs of B phytotoxicity were found in crop.

It is also noteworthy that soil supply of 2 kg ha^{-1} B in corn crop and 2 kg ha^{-1} B in soybean crop increased B levels in soybean leaves. This shows that the release of B by ulexite increased the nutrient levels on leaf, even in the plots receiving B by ulexite did not have shown the highest B contents in the soil.

According to Resende (2004), it is necessary to consider the interpretation of leaf contents, as it is possible that the nutrient levels found in the leaves have no direct relationship with the yields obtained. The effects of leaf nutrient dilution or concentration due to higher or lower vegetative growth (Jarrel; Beverly, 1981) are frequent causes of misconceptions about the nutritional status of plants subjected to treatments that allows differences in yield biomass. In addition, leaf nutrient levels may not correlate with soil availability, since absorption is affected by several other factors (Martinez et al., 1999; Oliveira, 2002). Among these factors, climatic conditions, soil moisture, antagonisms and synergisms between nutrients and varietal differences possibly influenced the results observed in the present study.

The correlation coefficients between the levels extracted by Mehlich-1 and Mehlich-3 solutions for Zn, Mn and Cu were 0.17, 0.04 and 0.01, respectively, and all nonsignificant ($p > 0.05$). There were also no significant positive correlations between Mehlich-1 nutrient contents and their respective leaf contents and soybean yield (Table 9).

Table 9 – Pearson correlation between the available Zinc (Zn), Manganese (Mn) and Copper (Cu) contents on soil extracted by Mehlich-1 (M1) and their respective Mehlich-3 (M3) contents, leaf contents and soybean yield. UFLA, Lavras-MG, 2020.

	Zn (M3)	**Mn (M3)**	**Cu (M3)**	**Zn (L)**	**Mn (L)**	**Cu (L)**	**Yield**
Zn (M1)	0.17^{ns}			0.04^{ns}			-0.05^{ns}
Mn (M1)		0.04^{ns}			-0.11^{ns}		-0.02^{ns}
Cu (M1)			0.01^{ns}			0.14^{ns}	-0.07^{ns}

^{NS}: not significant. n=96.

Source: From the Author (2020).

The correlation coefficients between the contents extracted from Zn, Mn, Cu and B by the Mehlich-3 solution and the content of these nutrients in leaves were 0.46, 0.25, 0.31 and 0.09, respectively. Only the correlation for B was not significant ($p > 0.05$). The absence of correlation coefficients equal to or greater than 0.70 were also not found for the correlations between the levels of these nutrients determined by Mehlich-3 and their respective leaf contents and productivity (Table 10).

Table 10 – Pearson correlation between the available zinc (Zn), manganese (Mn), copper (Cu) and boron (B) contents on soil extracted by Mehlich-3 (M3) and their leaves contents (L) and soybean grain yield. UFLA, Lavras-MG, 2020.

	Zn (L)	**Mn (L)**	**Cu (L)**	**B (L)**	**Yield**
Zn (M3)	0.39**				0.24^{ns}
Mn (M3)		0.22**			0.22^{ns}
Cu (M3)			0.27**		0.27^{ns}
B (HW)				0.00^{ns}	0.00^{ns}

**, ^{NS}: significant by F test by 1% and not significant, respectively. n=96.

Source: From the Author (2020).

The results found in the present study differ from those found by Silva et al. (2009). The authors observed that Mehlich-1 showed a good correlation with Mehlich-3 extractor to Zn, Cu, Mn and Fe contents. It also diverges from the results found by Heinrichs et al. (2006) where Mehlich-1, Mehlich-3 extractors showed positive and significant correlations with the Mn and Zn levels found in the leaves used for diagnosis in soybean cultivated in a Red Latosol.

The lack of correlation between Mn contents extracted by Mehlich-1 and Mehlich-3 was also observed by Aspiazú (2004) after evaluating Mn extraction in fifteen soils of Minas Gerais and Bahia.

Menezes et al. (2010), when comparing Mehlich-1, Mehlich-3 and DTPA extractors in Minas Gerais soils with a clay content range from 140 g kg^{-1} to 820 g kg^{-1}, concluded that soil Zn contents extracted by extractors showed correlations with Zn content on leaves and can be used to evaluate soil Zn availability.

Leaf contents of Zn and Cu significantly correlated with their respective soil contents available from Mehlich-1 and Mehlich-3. The correlation between leaf content and available soil content of Mn determined by both extractors was low in the experiment by Sobral et al. (2013).

4 CONCLUSIONS

The B, Cu, Mn and Zn contents used in the MAP coating do not increase the leaf contents of these micronutrients in soybean leaves.

The B supply by soil and Cu, Mn and Zn by spraying provides increase of leaf contents of these nutrients in corn and soybean crop, regardless of the use of phosphate fertilizer coated with these micronutrients.

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