ADDITION OF MICRONUTRIENTS TO NPK FORMULATION AND INITIAL DEVELOPMENT OF MAIZE PLANTS

ADIÇÃO DE MICRONUTRIENTES A FORMULADO NPK E O DESENVOLVIMENTO INCIAL DE PLANTAS DE MILHO

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ABSTRACT: Micronutrients are essential nutrients for plant growth and development; however, the micronutrient content in soil is often insufficient to ensure maximum productivity, which creates the need for their application through fertilizers. This study compared the availability of zinc, boron, manganese and copper to the soil, their absorption, accumulation and effect in developing maize plants, supplied as granules mixed with NPK granules or as powder, coating NPK granules. The experiment was conducted in a greenhouse, in a randomized block design with four replications, using a soil classified as Oxisol and maize hybrid AG1051. The formulation for fertilizers used was 4-30-10 (N- P_2O_5 -K_2O) with 0.3% zinc, 0.1% boron, 0.2% manganese and 0.2% copper applied at doses of 0, 150, 300, 600, 1200 and 2400 kg ha^{-1}, furthermore, doses of 4-30-10 without micronutrients were applied to ensure variation only for micronutrient doses. Coating NPK granules with micronutrients was better than the mixture for soil Zn content, zinc concentration and accumulation in the shoot and dry mass production. Both fertilizers presented similar behavior for soil B content, B concentration and accumulation in shoots. However, for the greatest dose, B results were better for the mixture of granules. The addition of Mn and Cu to NPK formulation resulted in no response in the soil, although the mixture resulted in greater concentration of Mn in the shoot and coating granules showed greater accumulation of Cu.

KEYWORDS: *Zea mays*. Coating granules. Zinc. Boron.

INTRODUCTION

There are seven micronutrients (B, Cl, Cu, Fe, Mn, Mo and Zn) satisfying the essentiality criteria and are, therefore, considered essential for plant development (VALE, 2000); however, the low natural levels of micronutrients in soils are insufficient to guarantee maximum yields. Hence, these elements are obtained in nature, undergo industrial purification, and then converted into commercial fertilizers (MONTEIRO FILHO, 2005).

In maize, the amounts required for a grain production of 9 t ha^{-1} are approximately 400 g Zn, 170 g B, 340 g Mn and 110 g Cu, among others (COELHO; FRANÇA, 2013). The main role of these four micronutrients in this crop include Zn as enzyme activator, precursor of amino acids and hormones and participant in tissue growth process, which means that maize is one of the crops with fastest responses to Zn application, providing gains in dry matter and grain production. Boron is essential for pollen grain germination and pollen tube formation, so the cobs of B deficient maize plants are typically curved, since the uniformity of their growth is related to the formation of the grains. Manganese acts on the synthesis of secondary metabolites and amino acids, while Cu is an important enzyme activator with vital role in photosynthesis, respiration, metabolism of carbohydrates and proteins and cell wall formation (FAVARIN et al., 2008).

Because of the small doses applied, uniformity in micronutrient application may be a problem. Thus, the supply of micronutrients aggregated to NPK formulations has become an important nutrient management practice (RESENDE, 2005). For example, mixtures of micronutrient granules with NPK granules, one of the most used forms for soil application (LOPES, 1999), presents an easy way of obtaining formulations (ABREU et al., 2007), but also has segregation problems (MORTVEDT, 1991; MORTVEDT and GILKES, 1993; LOPES, 1999).

Segregation is the separation of particles which comprise the mixture of fertilizers in order of particle size, as a result of particle size distribution and favored by the difference of particle sizes, which can occur with solid fertilizers (RODELLA, 2000). Accordingly, Carvalho (2001) showed segregation of the fertilizer components both in granule mix as the granulated mixture, having the

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most noticeable effect of chemical segregation in combination with micronutrient granules.

Knowing that segregation can be minimized with the quality control of products entering the composition of mixtures and particles having uniform size (RODELLA, 2000) to improve the micronutrient application quality, one option would be coating NPK granules with micronutrients applied as fine powder (ABREU et al., 2007). However, there is little research on micronutrient efficiency associated with NPK fertilizers in different ways, and especially evaluating the granule coating technique (VOLKWEISS, 1991; LOPES, 1999; RESENDE, 2005; ABREU et al., 2007).

Thus, this study compared the availability of Zn, Mn, B and Cu in soil, their absorption, accumulation and effect on initial maize development, from granules mixed with NPK granules or from powder coating the NPK granules.

MATERIAL AND METHODS

The experimental design was randomized blocks, as a 2 x 5 + 1 factorial, with two fertilizers with micronutrients added by different forms (granules mixed with NPK granules or powder coating NPK granules), five doses (150, 300, 600, 1200 and 2400 kg ha^{-1}) and an additional treatment with no micronutrient fertilization, with four replications. The doses were supplemented in order that all treatments would receive the equivalent to 2400 kg ha^{-1} of the formulations, and, therefore, the same dose of N, P_2O_5 and K_2O, only varying the amounts of Zn, B, Cu and Mn (Table 1).

Table 1. Type of fertilizer and amount of nutrients supplied to the soil by each treatment.

Formula NPK			Nutrients						
With micronutrients		Without micronutrients	N	P_2O_5	K_2O	Zn	B	Mn	Cu
Mixture	Coating								
kg ha^{-1}									
0	0	2400	96	720	240	0	0	0	0
150	0	2250	96	720	240	0.4	0.1	0.3	0.3
300	0	2100	96	720	240	0.9	0.3	0.6	0.6
600	0	1800	96	720	240	1.8	0.6	1.2	1.2
1200	0	1200	96	720	240	3.6	1.2	2.4	2.4
2400	0	0	96	720	240	7.2	2.4	4.8	4.8
0	150	2250	96	720	240	0.4	0.1	0.3	0.3
0	300	2100	96	720	240	0.9	0.3	0.6	0.6
0	600	1800	96	720	240	1.8	0.6	1.2	1.2
0	1200	1200	96	720	240	3.6	1.2	2.4	2.4
0	2400	0	96	720	240	7.2	2.4	4.8	4.8

The fertilizers used were NPK without micronutrients (mixture of granules), NPK with granulated micronutrients (mixture of granules) and NPK with micronutrients coating the granules. All fertilizers had the formulation 4-30-10, formulated with mono-ammonium phosphate (10% N and 54% P_2O_5), simple superphosphate (18% P_2O_5), triple superphosphate (46% P_2O_5) and potassium chloride (60% K_2O) granulated (grains with maximum 4% retained in 4-mm screen and 5% passing through 1-mm screen). The proportion of micronutrients in both fertilizers containing them was 0.3% Zn, 0.1% B, 0.2% Cu and 0.2% Mn, determined according to the production conditions at the industry and, therefore, chosen by the manufacturer.

The fertilizer containing granulated micronutrients was formulated with acidified zinc oxide (25% Zn, and 70% solubility in water), acidified ulexite (10% B, and 90% solubility in water), acidified manganese oxide (20% total Mn, and 75% solubility in water) and acidified copper oxide (2.5% Cu, and 80% solubility in water) granulated before mixing with the granules of NPK. Copper oxide and manganese oxide were granulated together, and all of them had grain size of maximum 4% retained in 4-mm screen and 5% passing through 1-mm screen.

The fertilizer coated with micronutrients was formulated with zinc oxide (80% total Zn), ulexite (15.5% total B), manganese oxide (50% total Mn) and copper oxide (25% total Cu) finely ground (100% passing through 0.15-mm screen). Adhesion of the powder to the NPK granules was done with an aggregating agent and vegetable oil.

The experiment was done in a greenhouse with soil samples obtained from the 0-20 cm layer of a soil classified as Oxisol (Soil Survey Staff, 2013.), medium texture (195 g kg^{-1} clay) (EMBRAPA, 1997), with 0.7, 0.08, 3.8 and 1.5 mg

kg^{-1} of Zn, B, Mn and Cu, respectively (RAIJ et al., 2001).

The soil was subjected to incubation for 30 days with 0.6 g $CaCO_3$ (analysis grade – A.G.) kg^{-1} soil and 0.25 g $MgSO_4$ (A.G.) kg^{-1} soil to achieve a Ca:Mg ratio around 3:1 and the base saturation around 70%. The soil was maintained near 80% field capacity by adding water at 84 mL kg^{-1} soil, complementing its initial moisture that was 87.5 mL H_2O kg^{-1} soil. This moisture (approximately 80% field capacity) was maintained during the entire period of the experiment conduction.

At sowing, the treatments were applied to the total amount of soil in each plot (5 kg), that was already dry, weighed and inside plastic 5-L pots. The water was applied at 160 mL H_2O kg^{-1} soil and 10 maize seeds (hybrid AG1051) were sown per pot. The equivalent of 80 kg ha^{-1} of S was subsequently applied using $MgSO_4$ $.7H_2O$ solution with 30.75 g L^{-1} concentration and dose of 10 mL kg^{-1} soil.

Seven days after sowing (DAS), the three best seedlings were kept in the pots. At 11 DAS and weekly thereafter, N fertilization was applied using a $(NH_4)_2SO_4$ solution with 50 g L^{-1} concentration applied at dose of 10 mL kg^{-1} soil.

Plant shoots were cut at the end of the experiment, placed in paper bags and dried in forced air circulation oven at 60º C until constant weight, which was obtained five days after harvest. Subsequently, shoots were weighed in an analytical scale.

Plant shoots were ground in a Willey mill and kept in plastic bags before analysis of Zn, B, Mn and Cu, which were determined according to Malavolta et al. (1997). Micronutrient accumulation was estimated using the results of dry matter and the contents determined. Also, with the aid of a soil sampler for pots, soil samples were collected, air dried, sieved and placed in plastic bags. Soil analyses of Zn, B, Mn and Cu were done as described by Raij et al. (2001).

Data from qualitative treatments were submitted to analysis of variance with the software ASSISTAT (SILVA; AZEVEDO, 2002). Averages were compared by Tukey's and Dunnett's tests at 0.01 and 0.05 significance, respectively. Data from the quantitative treatments were submitted to analysis of variance and regression at 0.05 significance with SISVAR software (FERREIRA, 2008).

RESULTS AND DISCUSSION

Soil micronutrients

The application of the fertilizer containing micronutrients coating the granules was able to increase the soil Zn content at 3.6 and 7.2 kg ha^{-1} Zn doses (Table 2). These doses raised the soil Zn content, moving it from "LOW" (less than 0.9 mg dm^{-3}), to "HIGH" (above 2.0 mg dm^{-3}), according to the classification proposed by Alvarez et al. (1999), which certainly favored plant development.

Regarding the sources tested, application of Zn in the form of granule coating resulted in soil Zn content greater than those obtained by their application in the form of mixture (Table 2). These results can be related to results of Galrão (1986), who states that a single broadcast application of Zn at 6.0 kg ha^{-1}, with incorporation in total area, was enough for four maize crops in a soil classified as dark-red clay oxisol. Moreover, that author observed differences between oxide, sulfate and frits as Zn sources for maize, which allows inferring that the oxide, even though having lower solubility in water, can be a good source of this micronutrient.

Table 2. Contents of Zn, B, Mn and Cu in the soil 28 days after the application of fertilizers containing them in mixture or coating NPK granules.

Dose				Zn		B		Mn		Cu	
Zn	B	Mn	Cu	M	C	M	C	M	C	M	C
kg ha^{-1}				mg dm^{-3}							
0	0	0	0	0.7		0.07		8.2		0.8	
0.4	0.1	0.3	0.3	0.7 a	1.0 a	0.08 a	0.08 a	10.9	10.5	0.9	0.9
0.9	0.3	0.6	0.6	0.7 a	1.0 a	0.06 a	0.08 a	9.1	8.9	0.9	0.8
1.8	0.6	1.2	1.2	0.7 a	0.9 a	0.09 a	0.08 a	12.3	10.7	0.8	0.9
3.6	1.2	2.4	2.4	0.7 b	2.3 * a	0.06 b	0.13 a	8.3	13.4	0.8	0.9
7.2	2.4	4.8	4.8	0.8 b	2.1 * a	0.24 * a	0.15 * b	8.7	12.8	0.8	0.9
Average				0.7	1.5	0.11	0.10	0.11 a	0.10 a	0.8 a	0.9 a

M = Mixture; C = Coating. Averages followed by different letters in the rows are different by Tukey's test at 0.01 of significance; * significant by Dunnett's test at 0.05 of significance compared to the control treatment.

The initial level of B was "VERY LOW" (less than 0.15 mg dm^{-3}) according to Alvarez et al. (1999), resulting in an increase from 0.07 mg dm^{-3} to up to 0.24 mg dm^{-3} for the greatest doses used (Table 2). The fertilizer comparison shows that the greatest levels of soil B were obtained by applying B coated NPK granules at 1.2 kg ha^{-1} or in the mixture form at 2.4 kg ha^{-1} B (Table 2).

Soil levels of Mn and Cu, even without their application, was classified, respectively, as "GOOD" and "MEDIUM", according to Alvarez et al. (1999), which explains the lack of response to treatments (Table 2).

The study of doses, in turn, indicates that the application of increasing doses of Zn coating NPK granules increased levels of this nutrient in the soil (Figure 1). The increase in soil Zn content when applied coating NPK granules can be explained by Mortvedt (1992) stating that the granular form of Zn oxide has lower efficiency when compared to the powder form due to the lower specific surface and because it is a source with low solubility in water (MORTVEDT; GILKES, 1993).

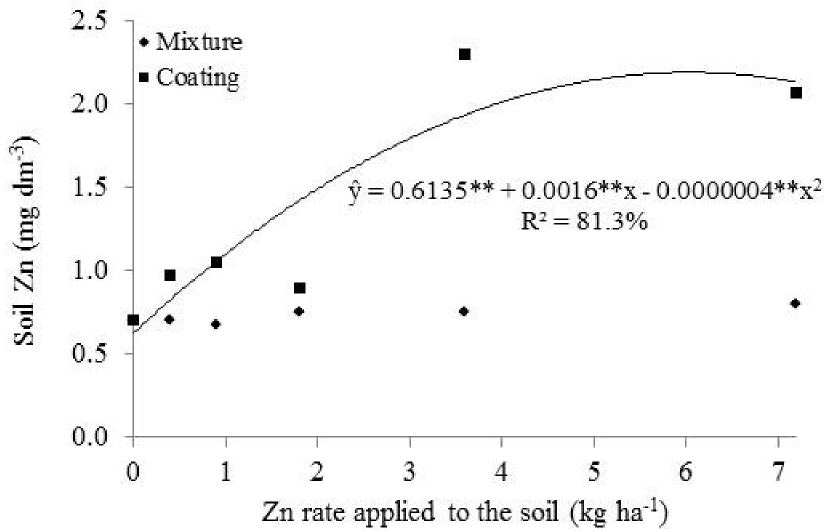

Figure 1. Zinc contents in soil 28 days after application of increasing doses of fertilizers containing it in the form of NPK granule mixture, or as a coating of NPK granules.

Also, increasing B doses resulted in increasing availability of B in the soil, regardless of its form in the fertilizer. However, only the greatest B dose applied in the form of mixture resulted in greater level in comparison to B coating NPK granules (Figure 2).

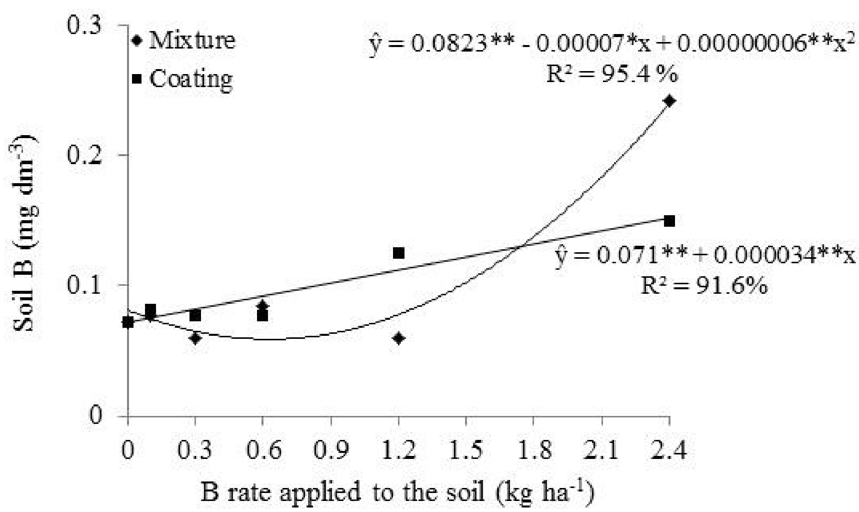

Figure 2. Boron contents in soil 28 days after application of increasing doses of fertilizers containing it in the form of NPK granule mixture, or as a coating of NPK granules.

Dry matter production

Only the greatest dose of Zn, B, Mn and Cu as coating NPK granules produced maize plants with more dry matter than the control treatment (Table 3). Micronutrients coating NPK granules resulted in greater dry matter average than that found in the treatment with the mixture of micronutrients and NPK granules (Table 3).

These results differ from those found by Korndörfer et al. (1987), who tested methods of adding Zn as oxide and sulfate to the 5-30-15 fertilizer and observed similar results for both sources of Zn for dry matter production of maize shoots in a greenhouse experiment. Korndörfer et al. (1995) also found no difference in corn production for treatments without Zn and with Zn applied as oxide or in 4-30-10 formula with Zn added by FTE as mixture or incorporation.

The study of doses shows that increasing the applied amount of micronutrients coating NPK granules increased plant dry matter production, which did not occur for the micronutrients in the form of mixture (Figure 3).

Table 3. Dry matter of maize shoots 28 days after the application of fertilizers containing Zn, B, Mn and Cu in mixture or coating NPK granules.

Dose				Dry matter		Average
Zn	B	Mn	Cu	Mixture	Coating	
------ kg ha^{-1} ------				------ g pot^{-1}** ------		
0	0	0	0	26.1		
0.4	0.1	0.3	0.3	25.7	27.7	26.7
0.9	0.3	0.6	0.6	26.3	27.2	26.8
1.8	0.6	1.2	1.2	27.5	29.0	28.3
3.6	1.2	2.4	2.4	26.6	28.2	27.4
7.2	2.4	4.8	4.8	26.6	29.8 *	28.2
Average				26.5 b	28.4 a	

Averages followed by different letters in the rows are different by Tukey's test at 0.01 significance; * significant by Dunnett's test at 0.05 of significance compared to the control treatment. ** Average of five plants.

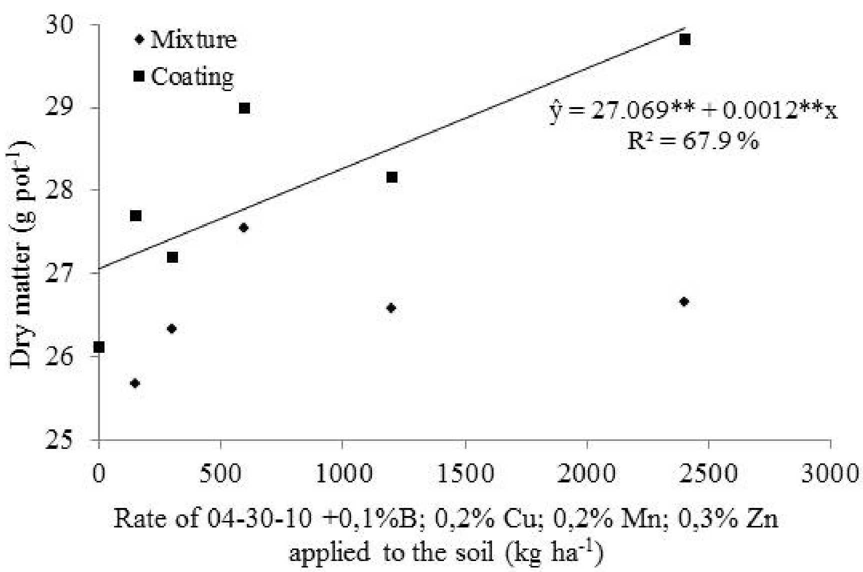

Figure 3. Dry matter of maize plants harvested 28 days after sowing as a function of the application of fertilizers containing Zn, B, Mn and Cu in the form of mixture or coating NPK granules.

Micronutrients content and uptake by corn shoots

Application of Zn at 3.6 and 7.2 kg ha^{-1} coating NPK granules resulted in Zn shoot content of 30.5 and 36.7 mg kg^{-1}, respectively, results that are greater than the control (22.1 mg kg^{-1}), and also in comparison to the micronutrients as mixture of granules at the same doses (22.2 and 24.5 mg kg^{-1}, respectively) (Table 4).

Table 4. Zinc, B, Mn and Cu content in maize shoots 28 days after the application of fertilizers containing them in mixture or coating NPK granules.

Dose				Content							
				Zn		B		Mn		Cu	
Zn	B	Mn	Cu	M	C	M	C	M	C	M	C
kg ha^{-1}				mg kg^{-1}							
0	0	0	0	22.1		6.1		114		6.6	
0.4	0.1	0.3	0.3	22.4 a	21.2 a	5.7 a	7.3 a	109	97.3	6.2	7.1
0.9	0.3	0.6	0.6	23.1 a	24.6 a	6.1 a	5.6 a	112	110	6.5	7.2
1.8	0.6	1.2	1.2	23.9 a	26.2 a	10.6 a	7.4 a	119	105	6.8	6.6
3.6	1.2	2.4	2.4	22.2 b	30.5 * a	11.8 * a	11.1 a	106	99.3	6.6	6.1
7.2	2.4	4.8	4.8	24.5 b	36.7 * a	27.2 * a	16.0 * b	114	96.7	6.3	6.1
Average				23.2	27.9	12.3	9.5	112 a	102 b	6.5 a	6.6 a

M = Mixture; C = Coating. Averages followed by different letters in the rows are different by Tukey's test at 0.01 of significance; * significant by Dunnett's test at 0.05 of significance compared to the control treatment.

These results corroborate those found by Judy et al. (1964) and Allen and Terman (1966) who claim that the granular ZnO was inefficient for maize grown in the greenhouse, and bean crop grown on the field, respectively. In general, Zn absorption was high and its concentration in the shoots were above the minimum adequate level for development of maize plants (15 mg kg^{-1}), according to Büll (1993).

The results for shoot B content ranged from 5.6 to 27.2 mg kg^{-1}, and the doses of 1.2 and 2.4 kg ha^{-1} in the form of mixture and 2.4 kg ha^{-1} in the form of coating generated better results than the control (Table 4). It was also observed that the B content of 27.2 mg kg^{-1} for the highest dose, was greater for B applied as a mixture than as coating (Table 4), but both results were classified as suitable for maize (greater than 15 mg kg^{-1}) according to Büll (1993).

Manganese doses used did not affect its absorption and uptake by maize plants (Tables 4 and 5). This lack of response can be explained by the high concentration of Mn in control plants, which were within the ideal range (42 to 150 mg kg^{-1}) according to Büll (1993) (Table 4). In contrast to the doses, the method of addition of Mn to the NPK fertilizer influenced shoot Mn content, and the mixture of granules resulted in greater Mn content (112 mg kg^{-1}) compared to coating, which presented the average of 102 mg kg^{-1} (Table 4). This result differs from those obtained by Mortvedt (1991), who claimed that granulated manganese oxide was not efficient for oat, corn and soybean crops.

Copper doses, as well as its form in the fertilizer, did not affect its absorption (Table 4); however, uptake by plants treated with Cu as coating accumulated greater amounts of this element (Table 5). One possible explanation for the lack of response to Cu in the shoots could be the fact that even plants that had not received Cu application presented acceptable shoot Cu levels for maize, in the range 6-20 mg kg^{-1} (BÜLL, 1993; MARTINEZ et al., 1999).

Zinc uptake, in the form of coating of granules in the three greatest doses resulted in greater amounts (756, 855 and 1094 µg Zn pot^{-1}, respectively) as compared to plants that did not received Zn application (578 µg Zn pot^{-1}) (Table 5). The two greatest doses of this group resulted in the greatest Zn uptake compared to the same amount of Zn applied as mixture, with 589 and 654 µg Zn pot^{-1}, respectively (Table 5).

Boron uptake, at the the two greatest doses, resulted in greater values than in plants from the control treatment (Table 5). However, the greatest dose of B in the mixture of granules resulted in the greatest uptake compared to the coating of granules (Table 5).

The effects of doses were observed for Zn and B and, for Zn, only the application in the coating form caused an increase in shoot Zn content (Figure 4A) and uptake (Figure 4B). The greater Zn content and uptake from coating of granules, even from a water insoluble source (zinc oxide), was probably due to the availability of the nutrient as a result of the acidifying effect of superphosphates present in the formula, which causes very low pH around the granule (YOUNG, 1969; MORTVEDT; GIORDANO, 1969).

For both modes of micronutrient additon studied, increasing the dose of B resulted in greater shoot B content and greater B uptake (Figure 5), but the intensity of the increase was superior to B in the form of mixture, as seen from the third greatest dose for shoot B content (Figure 5A); however, for B uptake it was noted that from the dose of 0.6 kg ha^{-1}, for each kg ha^{-1} applied as mixture of granules, the increase in uptake of B was about 100 units greater than that found for the coating (Figure 5B).

Table 5. Zinc, B, Mn and Cu uptake by maize plants 28 days after the application of fertilizers containing them in mixture or coating NPK granules.

Dose				Uptake							
				Zn		B		Mn		Cu	
Zn	B	Mn	Cu	M	C	M	C	M	C	M	C
kg ha^{-1}				µg pot^{-1}							
0	0	0	0	578		159		2981		171	
0.4	0.1	0.3	0.3	573 a	586 a	147 a	201 a	2818	2699	159	196
0.9	0.3	0.6	0.6	608 a	665 a	160 a	152 a	2935	2987	172	195
1.8	0.6	1.2	1.2	658 a	756 * a	295 a	212 a	3253	3039	188	190
3.6	1.2	2.4	2.4	589 b	855 * a	315 * a	313 * a	2806	2792	175	171
7.2	2.4	4.8	4.8	654 b	1094 *a	722 * a	474 * b	3040	2881	168	182
Average				616	791	328	271	2970 a	2879 a	172 b	187 a

M = Mixture; C = Coating. Averages followed by different letters in the lines are different by the Tukey test at 0.01 of significance; * significant by Dunnett's test at 0.05 of significance compared to the control treatment.

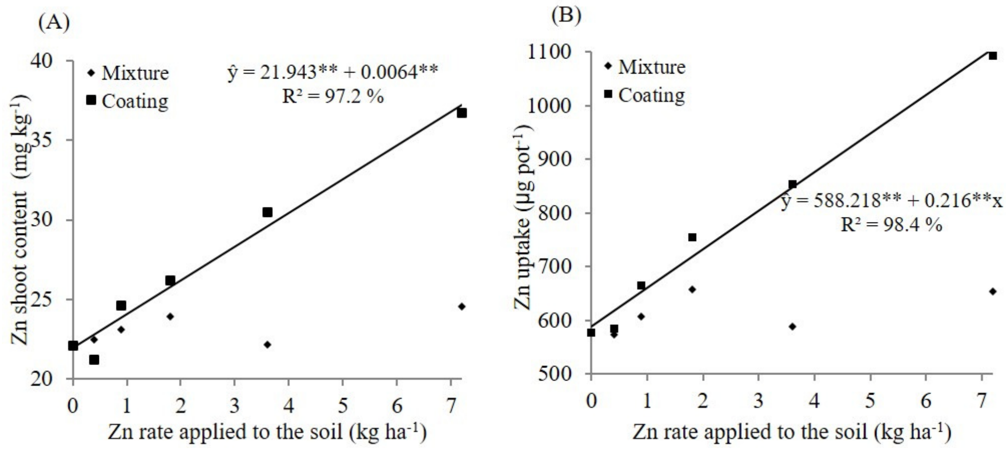

Figure 4. Zinc content (A) and uptake (B) by maize shoots 28 days after the application of increasing doses of fertilizers containing it in the form of NPK granule mixture, or as a coating of NPK granules.

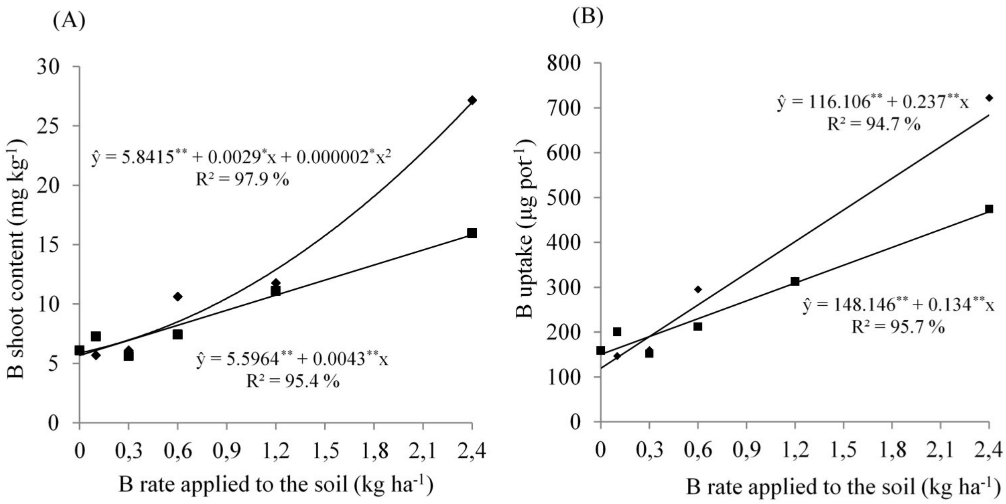

Figure 5. Boron content (A) and uptake (B) by maize shoots 28 days after the application of increasing doses of fertilizers containing it in the form of NPK granule mixture, or as a coating of NPK granules.

CONCLUSIONS

Coating of NPK granules with micronutrients was better than the physical mixture of granulated micronutrient with NPK granules for soil Zn content, shoot Zn content and uptake and the dry matter production of maize plants.

The mixture of granular micronutrients with NPK granules presented similar behavior to the coating form for soil B content, shoot B content and B uptake.

The addition of Mn and Cu to the NPK formulation did not result in increase in their soil contents, but the mixture form did result in greater shoot Mn content and the coating form showed greater Cu uptake by maize plants.

RESUMO: Os micronutrientes são essenciais às plantas porém seus teores no solo podem não ser suficientes para altas produtividades, o que gera necessidade de aplicação via fertilizantes. Objetivou-se comparar a disponibilização de zinco, boro, manganês e cobre para o solo, sua absorção, acúmulo e efeito no desenvolvimento de plantas de milho, quando aplicados granulados e em mistura com grânulos NPK ou na forma de pó, revestindo grânulos de NPK. O experimento foi conduzido em casa de vegetação, com delineamento de blocos casualizados, com quatro repetições, com amostras de solo classificado como Latossolo Vermelho distrófico típico e híbrido de milho AG1051. Os fertilizantes utilizados foram de formulação 4-30-10 (N-P_2O_5-K_2O) com 0,3 % de zinco, 0,1 % de boro, 0,2 % de manganês e 0,2 % de cobre aplicados nas doses de 0, 150, 300, 600, 1200 e 2400 kg ha^{-1}. Doses complementares de 4-30-10 sem micronutrientes foram aplicadas para que todos os tratamentos recebessem as mesmas doses de nitrogênio, fósforo e potássio, variando somente as doses dos micronutrientes. O revestimento dos grânulos de NPK com micronutrientes é superior à mistura quando se compara o teor de zinco no solo, a concentração e o acúmulo de zinco na parte aérea e a produção de massa seca das plantas de milho. A mistura de micronutrientes granulados com grânulos de NPK apresenta comportamento semelhante para os teores de boro no solo, sua concentração e acúmulo na parte aérea. A adição de manganês e cobre ao formulado NPK não resultou em resposta no solo, embora a forma de mistura tenha resultado em maior concentração de manganês na parte aérea, e o revestimento de grânulos tenha mostrado maior acúmulo de cobre pelas plantas de milho.

PALAVRAS-CHAVE: *Zea mays*. Revestimento de grânulos. Zinco. Boro.

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