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SOIL SCIENCE

Recommendation of soil fertilization with copper and zinc for soybean crops grown in Petric Plinthosol

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ABSTRACT: *Cultivation of soybean and off-season corn is advancing in areas under restricted edaphoclimatic conditions, such as petric plinthosols, which have significant proportions of gravel and are deficiency in micro-nutrients such as copper (Cu) and zinc (Zn). The effects of Cu and Zn concentrations on soybean nutrition cultivated in petric plinthosol are unclear, and it is unknown whether the levels considered adequate for other soils are sufficient for gravely soils, or even if higher Cu and Zn rates can cause a toxic effect in soybean. The objective was to compare the response of soybean grown in petric plinthosol and ferralsol to Cu and Zn doses for identifying the changes induced by gravel soils and to evaluate the residual effect on off-season corn grown in ferralsol. Four experiments were carried out with Cu and Zn doses applied to soil with the soybean crop in ferralsol and plinthosol. The leaf tissues of soybean crops in the two soils showed the same rate of increase in Zn concentrations, for each kg·ha^{-1} of Zn applied, the increase in Zn was 0.7 mg·kg^{-1}, suggesting no difference in the effect of Zn fertilization between soils with and without gravel. The dosages of Zn and Cu Oxysulfate applied to soil did not cause residual effects in the off-season corn. The highest doses of Cu and Zn did not have any toxic effects on the plants. The main criteria for interpreting Cu and Zn in soil analysis are thus also applicable to soybean crops grown in petric plinthosol.*
Key words: *gravelly soils, nutritional toxicity, micronutrients, petroplintites.*

Recomendação de adubação de cobre e zinco via solo em soja cultivada em áreas de Plintossolo Pétrico

RESUMO: *O cultivo de soja e milho safrinha avança em condições edafoclimáticas restritivas, como nos PLINTOSSOLOS PÈTRICOS, que apresentam proporções consideráveis de cascalho no seu perfil e são deficientes em cobre (Cu) e zinco (Zn). Não se sabe os efeitos de doses de Cu e Zn na nutrição da soja cultivada em PLINTOSSOLO PÉTRICO, nem se os níveis considerados adequados para outros solos são suficientes para solos cascalhentos, ou ainda, se altas doses de Cu e Zn podem causar toxidez nas plantas de soja. O objetivo foi comparar a resposta a doses de Cu e Zn em soja cultivada em PLINTOSSOLO PÉTRICO e em LATOSSOLO, a fim de identificar alterações provocadas pelo solo com cascalho, e adicionalmente, avaliar o efeito residual da adubação feita na soja para o milho safrinha cultivado no LATOSSOLO. Quatro experimentos foram desenvolvidos com doses de Cu e Zn aplicadas via solo na cultura da soja em LATOSSOLO e em PLINTOSSOLO PÉTRICO. Houve a mesma taxa de incremento na concentração de Zn no tecido foliar da soja nos dois solos estudados, para cada kg ha^{-1} de Zn aplicado, o incremento foi de 0,7 mg·kg^{-1} demonstrando que não há diferença de um solo com ou sem cascalho para os efeitos da adubação. As doses de oxissulfato de Zn e Cu aplicadas via solo não causaram efeito residual no milho safrinha. As maiores doses de Cu e Zn não causaram efeito tóxico nas plantas. Os principais critérios de interpretação de Cu e Zn em análise do solo se aplicam para soja cultivada em PLINTOSSOLO PÉTRICO.*
Palavras-chave: *solos com cascalho, toxidez nutricional, micronutrientes, petroplintita.*

INTRODUCTION

In the agricultural frontier areas of the Brazilian Cerrado, grain cultivation is carried out in soil conditions with restrictive characteristics for agricultural exploitation. A significant portion of these areas is covered with sandy or gravelly soils, which are associated with low altitudes and high temperatures, limiting the crop productive potential and consequently, economic returns. In these

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situations, soils such as the petric plinthosols (PP), which have excess gravel, stand out as difficult to manage; however, these are currently used for grain production, without proper information and technical recommendations, resulting in environmental and economic damage. The proper management of soil in areas with large amounts of gravel has several unknowns, particularly in the management of fertilization, with regard to zinc (Zn) and copper (Cu) micronutrients.

Although Cu and Zn are micronutrients required by crops in smaller amounts compared to macronutrients, they are important for plant metabolism (SCHULTEN & KRÄMER, 2017). Cerrado soils such as petric plinthosols, are inherently deficient in micronutrients such as Zn, Cu, boron (B), and molybdenum (SOUSA et al., 2008), which has a negative impact on crop yield (TEIXEIRA et al., 2008; ZIAEYAN & RAJAIE, 2009).

Cu and Zn fertilization for plants growing in soils with low nutrient availability occurs through the soil or leaves. Application to soil provides micronutrient quantities that meet the demand throughout the crop cycle (YILMAZ et al., 1997) in a single application. However, the fertilizer doses to be administered are very low, requiring care with the distribution. If the fertilizer is broadcast, it is often necessary to mix the fertilizer with an inert material to facilitate the application. In soils with high pH or with the application of high doses of limestone, which is a common condition in the conversion of cropping areas on the Brazilian Cerrado, the efficiency of absorbing the cationic micronutrients applied to soil is low (CHAVES et al., 2009; GONÇALVES, 2018), which affects the crop yields under the low availability of micronutrients in soil. Other complicating factors include adsorption reactions with soil and the low mobility of these nutrients. Therefore, application of micronutrients to soil is often neglected in Brazil, and foliar supply is prioritized.

The Cu and Zn contents currently adopted as suitable for Cerrado soils based on the Mehlich 1 extraction are 0.5 mg·dm^{-3} for Cu and 1.0 mg·dm^{-3} for Zn (SOUSA & LOBATO, 2004). However, other authors have suggested different intervals as appropriate when using Mehlich 1 extraction. ALVAREZ et al. (1999) indicated that the adequate values for Cu and Zn in Cerrado soils are between 0.8–1.2 mg·dm^{-3} and 1.0–1.5 mg·dm^{-3}, respectively. GALRÃO (1999) recorded values between 0.5–0.8 mg·dm^{-3} for Cu and 1.1–1.6 mg·dm^{-3} for Zn as adequate, whereas BORKERT et al. (2002) indicated a Zn content above 2.5 mg·dm^{-3}. FAGERIA (2001) determined the adequate soil content of Cu for soybean [*Glycine max* (Merrill)] as 1 mg·kg^{-1} and that for corn (*Zea mays* L.) as 2.5 mg·kg^{-1}. The same author determined that the Cu toxicity in soils occurs at levels greater than 10 mg kg^{-1} for soybean and greater than 45 mg kg^{-1} for corn. Further, FAGERIA (2000) determined the adequate soil content of Zn for soybean cultivation to be 0.8 mg·kg^{-1} and that for corn to be 2.0 mg·kg^{-1}, with the limit of Zn toxicity at contents greater than 53 mg·kg^{-1} for soybean and at greater than 94 mg·kg^{-1} for corn.

Unlike other micronutrients such as B, which have a small limit of deficiency and toxicity (FURLANI et al., 2001), Zn and Cu have a wider gap between sufficiency and toxicity, because the toxic effects of Cu and Zn even with high doses are rare (GUPTA & KALRA 2006; TEIXEIRA et al., 2008). In the analyses of plant tissues, the concentrations of Cu and Zn that are considered adequate also vary according to the literature. According to MALAVOLTA et al. (1997) the adequate Cu content in soybean leaves is 10–30 mg·kg^{-1}, and that of Zn is 21–50 mg·kg^{-1}. GALRÃO (1999) reported an adequate soybean content of 4 mg·kg^{-1} for Cu and 20 mg·kg^{-1} for Zn. For corn, the concentration of Cu and Zn that is considered adequate in the leaves is 6.0–20.0 mg kg^{-1} of Cu and 15.0–50.0 mg kg^{-1} of Zn (MALAVOLTA et al., 1997). According to GOTT et al. (2014) the sufficiency range in corn leaves is 9.1–14.1 mg·kg^{-1} for Cu, with an optimum content of 11.6 mg·kg^{-1}, and the range for Zn is 18.0–34.1 mg·kg^{-1}, with an optimum content of 25.8 mg·kg^{-1}. FAGERIA (2001) determined an adequate concentration of Cu in the plant tissue for the cultivation of soybean and corn to be 7 mg·kg^{-1}. Studying the adequate concentration of Zn in soybean and corn crops, FAGERIA (2000) determined a concentration of 20 mg·kg^{-1} for soybean and 27 mg·kg^{-1} for corn, and reported that the Zn concentration in the plant that causes toxicity, is in the order of 187 mg kg^{-1} for soybean and 427 mg kg^{-1} for corn.

The excess of gravel from PP implies a lower volume in soil for the exploration of roots along the soil depth, which can alter the pattern of Cu and Zn supply to the cultivated plants. This raises three hypotheses: (i) The effects of the doses of fertilizers containing Cu and Zn would differ for soybean grown in ferralsol (FR) and PP (ii). The levels of these elements that are considered sufficient in other soils may be insufficient for soils with an excess of gravel, as the volume of the soil is largely occupied by inert material, which is unable to retain and exchange nutrients with the soil solution. (iii) Conversely, it is unknown whether the lower proportion of soil available to adsorb micronutrients can facilitate the absorption of these micronutrients by plants, or even propitiate the toxicity of Cu and Zn in gravel soils despite the recommended rates for other soil types.

However, little information is available on soil fertility management in areas with significant amounts of gravel. As soybean and corn crops are widely grown in these areas, a better understanding of the responses of these crops to fertilizers containing Cu and Zn is needed and will certainly contribute to the better use of nutrients and better yields. Considering these points, the objective of this study was to compare the response of soybean grown in PP and FR to Cu and Zn supplementation for identifying the changes in soybean nutrition caused by graveled soil, and to evaluate the residual effect of fertilization to soybean on the off-season corn grown in FR.

MATERIALS AND METHODS

Four experiments were conducted in Paraíso do Tocantins-TO, Brazil, (10º11'16"S and 48º40'57"W) in the 2019/2020 growing season. Experiments I and II were conducted in a plinthic ferralsol dystric soil (FOOD AGRICULTURE ORGANIZATION [FAO], 2006) or LATOSSOLO VERMELHO-AMARELO distrófico plintossólico according to the Brazilian Soil Classification System (SANTOS et al., 2018), with increasing Cu and Zn rates applied to the soil in the soybean crop. After harvesting the soybean in experiments I and II, immediate plantation of a corn crop was conducted to evaluate a possible residual effect of the fertilizer applied to the soybean crop. Experiments III and IV present the same treatments performed in experiments I and II, respectively. However, experiments III and IV were carried out in a petric plinthosol dystric soil (FOOD AGRICULTURE ORGANIZATION [FAO], 2006) or PLINTOSSOLO PÉTRICO Concrecionário típico according to the Brazilian Soil Classification System (SANTOS et al., 2018), and there was no cultivation of corn after the soybean harvest due to a high risk of crop failure caused by late sowing of the soybean crop and the low water retention capacity of this soil for off-season cultivation. Soil samples were collected before experiment implementation from each soil at a depth of 0–20 cm, with ten sampling points per sample; chemical analyses performed according to SOUSA & LOBATO (2004) are described in table 1.

The experiment used a randomized block design, with four replicates in 10 m^2 plots. In experiments I and III, the treatments comprised six increasing doses of Cu (0, 1.0, 2.5, 4.0, 5.5, and 7.0 $kg \cdot ha^{-1}$) applied to soil in the form of Cu Oxysulfate (60% soluble in CNA + H_2O) in the soybean crop. The treatments in experiments II and IV comprised six doses of Zn (0, 2.5, 5.0, 7.5, 10, and 12.5 $kg \cdot ha^{-1}$) applied to soil in the form of Zn Oxysulfate (60% soluble in $C_6H_8O_7$ at 2%). In all experiments, the fertilizer was broadcasted in the plot areas after planting, (i.e. at the sowing date). Cultivation of off-season corn in experiments I and II did not include application of these micronutrients.

In the experiments I and II conducted in FR, the soybean crop was sown using the cultivar Bonus on 10/31/2019 with a population of 360,000 plants ha^{-1}, and the crop was harvested on 02/18/2020. In experiments III and IV conducted in PP, the soybean crop was sown using the cultivar NS8383 sown on 11/22/2019 with a population of 320,000 plants ha^{-1}, and was harvested on 03/24/2020. The fertilization applied to the soybean crop in all experiments included 20 $kg \cdot ha^{-1}$ of nitrogen (N; as asmonoammonium phosphate [MAP]), 100 $kg \cdot ha^{-1}$ of P_2O_5 (as MAP + triple superphosphate [TSP]), 98 $kg \cdot ha^{-1}$ of K_2O (as muriate of potash [MOP]), 0.075 $kg \cdot ha^{-1}$ of B (ulexite), and 1.25 $kg \cdot ha^{-1}$ of manganese (Mn; as Oxysulfate) incorporated by the seeder machine. The leaves were sprayed with 0.34 $kg \cdot ha^{-1}$ of boron (B; as boric acid) divided into two applications and 0.15 $kg \cdot ha^{-1}$ of Mn (as manganese sulfate) divided into three applications.

At the R2 stage (FEHR & CAVINESS, 1977), with full flowering of soybean, ten leaves per plot of the second or third newly expanded trefoil were collected for determining the nutritional status. The leaf tissue was ground and placed in an oven at 65 ºC for 72 h for analyses as described by MALAVOLTA et al. (1997). The concentration of N was determined by complete digestion in concentrated H_2SO_4, with subsequent distillation using the micro-Kjeldahl method (MALAVOLTA et al., 1997). The concentrations of phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), Cu, iron (Fe), Mn, Zn, and B were determined by spectrophotometric analysis of atomic absorption after digestion in HNO_3 (nitric acid) of $HClO_4$ (perchloric acid) (MALAVOLTA et al., 1997). The grain harvest was performed on 5 m^2 within the two middle 5-m long rows of each plot; grain yield was determined by mass adjustment to 13% moisture.

In the experiments involving implantation in soil classified as FR (I and II), the corn hybrid AG8700 was sown on 02/22/2020 at a population of

Table 1 - Result of analysis of samples collected in the experimental area of ferralsol and petric plinthosol, at a depth of 0–20 cm.

Soil	pH	OM	S	P*	K	Ca	Mg	H + Al	Al	CTC	V
	$CaCl_2$	$g \cdot kg^{-1}$	--------$mg \cdot dm^{-3}$------		---------------------------$cmol_c \cdot dm^{-3}$---------------------------						%
Ferralsol	5.53	27.02	14.04	31.07	0.08	2.55	1.33	3.2	0	7.16	55.3
Plinthosol	6.11	28.94	16.66	39.64	0.09	2.95	2.02	2.8	0	7.86	64.4
Soil	Sand	Silt	Clay	B	Cu	Fe	Mn	Zn	Gravel **		
	------------------$g \cdot kg^{-1}$ ----------------			---------------------------$mg \cdot dm^{-3}$-------------------------					%		
Ferralsol	98	492	410	0.38	0.83	49.82	8.22	1.49	0		
Plinthosol	280	315	405	0.12	0.8	41.53	6.91	1.35	49		

* Resin extraction. * Mehlich 1 extraction results: 5.99 for FR and 5.43 $mg \cdot dm^{-3}$ for PP; **% of gravel, by mass, of the 0–20 cm sample.

60,000 plants ha^{-1}, and was harvested on 06/16/2020. In total, 50 $kg \cdot ha^{-1}$ of N (Ammonium nitrate), 50 $kg \cdot ha^{-1}$ of P_2O_5 (MAP), and 50 $kg \cdot ha^{-1}$ of K_2O (MOP) were applied with the sowing of corn. When the corn crop presented four expanded leaves, in the V4 phase (HANWAY et al., 1966), N supplementary fertilization was carried out with 50 $kg \cdot ha^{-1}$ of N (as ammonium nitrate). At the time of corn flowering, in stage R1 (HANWAY et al., 1966), ten leaves per plot were collected below and opposite the upper ear for chemical analysis of the leaf tissue for all macro- and micronutrients. The methodology for the analysis of nutrients in the corn leaf tissue was identical to that carried out for the soybean crop. Grain harvest was performed on 5 m^2 within the two middle 5-m long rows of each plot; grain yield per hectare was determined as mass adjusted to 13% moisture.

Before statistical analysis, the data were subjected to normality and homogeneity analysis with the Box-Cox test using SAS statistical software. When necessary, the data were transformed according to indicated. The effects of applying Cu and Zn on the response variables were determined by analysis of variance (ANOVA), using the "GLM" procedure in SAS statistical software. The results regarding the response of the soybean crop to the Cu (experiments I, III) and Zn (experiments II, IV) doses in different soil types were analyzed together to verify the effect of soil in response to micronutrient application. When a difference was reported between doses, the means of each treatment were adjusted using a regression model with the best adjustment according to the "REG" procedure.

RESULTS AND DISCUSSION

Soil Zn fertilization in FR and PP

The Zn doses did not influence the soybean yield in the experiments performed in FR and PP (Table 2). Considering that the Zn contents in the studied soils were in the appropriate range according to the criteria set by SOUSA & LOBATO (2004), ALVAREZ et al. (1999), GALRÃO (1999), and FAGERIA (2000), these results indicated that these recommendations are valid even for PP. The higher doses of Zn applied to the soil in this research did not have a deleterious effect on soybean, indicating that even in PP, Zn toxicity is not a cause for concern, corroborating the observations of GUPTA & KALRA, (2006) and TEIXEIRA et al. (2008).

The soybean yield was not different when grown in PP or FR, and was, on average, 3,474 $kg \cdot ha^{-1}$ (Table 2). The concentration of macronutrients in soybean leaves was not affected by the doses of Zn applied to the soil (Table 2). However, the concentration of N, P, Ca, Mg, and S was higher in soybean grown in PP in relation to their cultivation in FR. Only the concentration of K was higher in the leaves of soybean grown in FR. The levels of P, K, and Ca in the soils were similar, but were slightly higher in PP; Mg and S contents showed a greater difference between soils, with higher concentrations in PP (Table 1). In addition to the higher macronutrient levels in the soil, these differences can be explained by the excess of gravel that occupies the soil volume in PP, with a higher proportion of inert material, which

Table 2 - Effect of Zn doses on soybean grain yield and macronutrient contents in leaves of soybean grown in ferralsol (FR) and petric plinthosol (PP), experiments II and IV, respectively.

Dose Zn (kg·ha $^{-1}$)	FR	PP	FR	PP	FR	PP	FR	PP	FR	PP	FR	PP	FR	PP
	------yield------		--------N--------		-------P-------		--------K-------		---------S-------		-------Ca-------		------Mg-----	
	kg·ha $^{-1}$		---g·kg $^{-1}$---											
0	3614	3541	44.7	48.8	2.7	4.2	26.4	20.4	2.21	3.1	6.98	13.8	4.16	5.8
2.5	3248	3136	50.4	53.0	2.4	3.8	24.1	22.8	2.11	2.9	7.51	12.9	3.99	5.3
5	3427	3211	45.7	54.6	2.6	4.9	23.3	20.9	1.99	3.3	7.36	12.1	4.02	5.5
7.5	3479	3407	44.1	50.3	2.7	5.0	28.5	21.7	2.09	3.0	7.31	11.9	4.01	5.6
10	3399	3888	49.3	52.1	2.7	4.7	20.2	21.2	1.99	3.3	6.92	13.3	4.10	5.7
12.5	3753	3580	44.6	55.7	2.6	5.1	23.9	20.2	2.12	3.3	7.02	12.3	4.16	5.6
Averages	3487	3461	46.5 b	52.4 a	2.6 b	4.6 a	24.4 a	21.2 b	2.1 b	3.2 a	7.2 b	12.7 a	4.1 b	5.6 a
	---Pr > F---													
Soil (S)	0.6962 ^{ns}		0.0013 **		< 0.0001 ***		0.0137 *		< 0.0001 ***		< 0.0001 ***		< 0.0001 ***	
Dose (D)	0.1884 ^{ns}		0.4518 ^{ns}		0.2121 ^{ns}		0.3354 ^{ns}		0.8148 ^{ns}		0.9557 ^{ns}		0.1736 ^{ns}	
S *D	0.6891 ^{ns}		0.6329 ^{ns}		0.8478 ^{ns}		0.2258 ^{ns}		0.7964 ^{ns}		0.6126 ^{ns}		0.7271 ^{ns}	
CV (%)	12.1		11.1		18.1		31.9		4.1		13.1		14.9	

Lowercase letters compare averages between columns. ns = not significant, * significant at 5% probability, ** significant at 1% probability, *** significant at 0.1% probability.

alters the dynamics of nutrients with respect to the intensity of adsorption and mobility, theoretically facilitating absorption by plants. The chemistry in soils with an excess of gravel is little studied, and there are no reports in the literature on the dynamics of nutrients in these conditions, especially for K, which among cationic macronutrients, has a lower reaction force with soil. Leaching of K below the arable layer of the soil is more marked in soils with a sandy texture with lower cation exchange capacity, compared to that in soils with a clayey texture and with higher cation exchange capacity (ROSOLEM et al., 2010); the excess of gravel in PP can potentiate this effect because it presents gravel, at an even greater fraction compared to sand.

The doses of Zn applied to soil did not influence the concentrations of Cu, Fe, and Mn in the soybean leaves (Table 3). The concentration of Fe was higher in soybean grown in PP compared their cultivation in FR (Table 3). Although, FR contains a higher Fe content in the soil analysis (Table 1), both soils have high Fe contents due to their genesis by intense weathering, resulting in a predominant ferralitization process. Acid tropical soils have high levels of Fe and a deficiency of this nutrient is unlikely (MULIMA et al., 2018). The ferruginous concretions of PP (petroplintites) can supply Fe to plants, mainly upon stimulation by the alkaline exudates of plants. According to MARTINS et al. (2018) some alkaline compounds increase the dispersion of petroplintite, which could release Fe.

The Zn concentration in the leaf tissue of soybean was increased due to the application of Zn to the two studied soils (Table 3). For each kg·ha $^{-1}$ of Zn applied to the soil, the leaves of soybean plants grown in both soils showed an increase in Zn of 0.7 mg·kg $^{-1}$ (Figure 1), which rejects hypothesis number 1 by proving that there is no difference in the effect of Zn fertilization between soils with and without gravel.

Even in the absence of Zn fertilization, the leaf concentration of Zn in soybean was 23 mg·kg $^{-3}$ in PP and 35 mg·kg $^{-3}$ in FR (Figure 1), which are values suitable for soybean cultivation (MALAVOLTA et al., 1997; GALRÃO, 1999; FAGERIA, 2000), reinforcing the justifications regarding soybean yield without the influence of Zn fertilization (Table 2),

Table 3 - Effect of Zn doses on micronutrient contents in leaves of soybean grown in ferralsol (FR) and plinthosol (PP), experiments II and IV, respectively.

Zn dose ($kg \cdot ha^{-1}$)	FR	PP	FR	PP	FR	PP	FR	PP	FR	PP
	----------Cu---------		-----------Fe-----------		-----------Mn-----------		------------Zn-----------		-----------B-----------	
	---mg·kg^-1---									
0	12.27	10.5	169	237.8	21.1	21	36.3	19.2	42.3	46.2
2.5	14.11	11.2	177	227.3	21.8	21.5	36	26	46.5	43.9
5	13.14	12.2	175	262.3	20	27.9	37.8	32.7	44.1	50.6
7.5	13.09	11.9	160	254.7	17.6	23.1	37.8	29.1	39.8	48.2
10	13.74	14.1	182	266	24.1	27.6	45.9	29.8	42.3	48.5
12.5	12.4	11.1	158	260.8	20.5	23.9	43.3	30.7	38.4	50.1
Averages	13.1	11.8	170 b	251 a	20.9	24.2	39.5 a	27.9 b	42.2 b	47.9 a
	---Pr > F---									
Soil (S)	0.0683 ns		< 0.0001***		0.0963 ns		< 0.0001***		< 0.0001***	
Dose (D)	0.3372 ns		0.6626 ns		0.5604 ns		< 0.0001***		0.0399*	
S*D	0.8606 ns		0.3754 ns		0.8494 ns		0.259 ns		0.0011**	
CV (%)	18		6.5		11.7		10.6		8.2	

Lowercase letters compare averages between columns. ns = not significant, * significant at 5% probability, ** significant at 1% probability, *** significant at 0.1% probability.

and indicating that the levels considered adequate for soils are sufficient to nourish soybean, even in PP, thus rejecting hypothesis number 2.

The concentration of Zn in soybean leaves was higher upon cultivation in FR compared to PP (Table 3), which can be explained by its higher content in the soil (Table 1) and the higher pH in PP, which reduces the availability of Zn for plants (GONÇALVES et al., 2018). However, the highest doses of Zn and the highest leaf concentrations measured in this study were far below the levels considered toxic, at around 187 $mg\ kg^{-1}$ (FAGERIA 2000), refuting the hypothesis that gravel soils promote greater absorption of Zn, and generating toxic effects in plants.

The concentration of B in soybean leaves was affected by the Zn doses applied to soil with significant interaction between the soil and Zn doses (Table 3). Therefore, the interaction indicated that the concentration of B in the soybean leaves showed a different pattern between soils. In FR, the concentration of B decreased at a rate of 0.45 $mg \cdot kg^{-1}$ for each $kg \cdot ha^{-1}$ of applied Zn (Figure 1). In PP, the concentration of B increased at a rate of 0.35 $mg\ kg^{-1}$ for each $kg \cdot ha^{-1}$ of applied Zn. According to ZIAEYAN & RAJAIE (2009) the leaf concentration of B decreases with an increase in the dose of Zn applied to soil. Other authors have also reported an antagonistic effect between B and Zn in the leaf concentration of one nutrient, when the supply of the other is increased (HOSSEINI et al., 2007; RAJAIE et al., 2009). The dynamics of nutrients in soils with an excess of gravel is little known and needs to be studied further to understand this contrasting effect observed in PP in relation to that observed in FR and in the literature.

The doses of Zn Oxysulfate applied to soil in the soybean crop did not cause a residual effect in the off-season corn to the point of altering the corn yield or the leaf concentration of macronutrients (Table 4). Corn was produced at an average of 9,160 $kg \cdot ha^{-1}$.

The doses of Zn applied to soil in soybean also had no effect on the leaf concentrations of Cu,

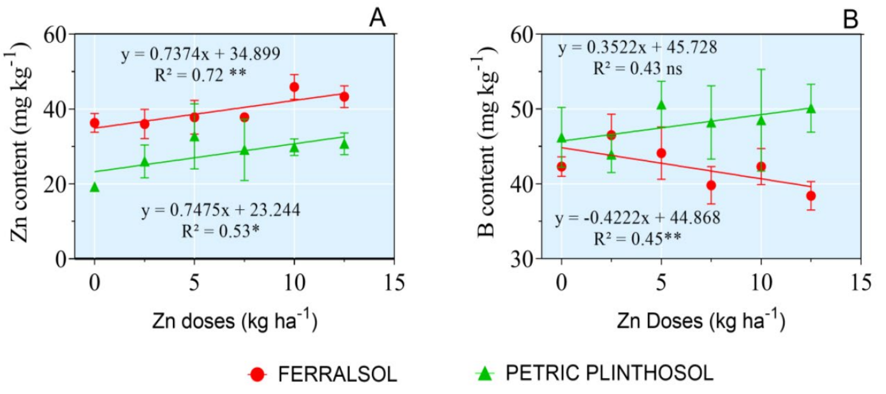

Figure 1 - Zinc (Zn) (A) and boron (B) (B) content in soybean leaves as a function of applied Zn doses. ns = not significant, * significant at 5% probability, ** significant at 1% probability. Vertical bars indicate the standard error.

Zn, and B in corn (Table 5). The concentration of Zn in corn leaves was below the appropriate range according to several authors (MALAVOLTA et al., 1997; FAGERIA, 2000; GOTT et al., 2014) and the doses of Zn applied to soybean, a predecessor crop, could not increase the Zn absorption by corn plants. Consequently, there was no increase in the corn yield, suggesting a low residual effect of Zn fertilization applied in previous crops. In this scenario, fertilization with Zn must be repeated for the cultivation of off-season corn, mainly because the corn crop has a higher demand for Zn compared to that in soybean (FAGERIA, 2000), and in this study, the content of Zn in soil (Table 1) was suitable for soybean cultivation,

Table 4 - Residual effect of Zn doses on corn grain yield and macronutrient contents in off-season corn leaves grown in ferralsol, experiment II.

Zn dose ($kg \cdot ha^{-1}$)	Yield	N	P	K	S	Ca	Mg
	$kg \cdot ha^{-1}$	$g \cdot kg^{-1}$					
0	9179	33.9	1.57	26.1	1.30	5.05	4.70
2.5	8949	33.2	1.58	27.3	1.75	4.73	4.46
5	8961	34.0	1.35	27.1	1.75	4.85	4.57
7.5	9098	33.2	1.57	26.6	1.53	5.33	4.78
10	8614	33.7	1.21	26.2	1.29	4.99	4.55
12.5	10160	34.0	1.59	27.6	1.62	4.88	4.61
Averages	9160	33.7	1.5	26.8	1.5	5.0	4.6
Pr > F	0.58 ns	0.8457 ns	0.07 ns	0.693 ns	0.3119 ns	0.4919 ns	0.3633 ns
CV (%)	13.1	3.5	13.9	6.1	23.8	8.8	4.4

ns = not significant.

Table 5 - Residual effect of Zn doses on micronutrient contents in off-season corn leaves grown in ferralsol, experiment II.

Dose Zn	Cu	Fe	Mn	Zn	B
(kg·ha^{-1})	----------------------------	----------------------------	mg·kg^{-1}	----------------------------	----------------------------
0	21.1	648	41.6	13.06	9.31
2.5	19.7	646	41.1	14.33	10.22
5	19.6	526	36	14.15	10.28
7.5	18.5	602	37.1	14.66	9.58
10	18.4	563	37.9	14.42	10.37
12.5	17.8	476	33.3	14.53	13.04
Averages	19.2	576	37.9	14.2	10.5
Pr > F	0.372 ^{ns}	0.0005***	0.0445*	0.4537 ^{ns}	0.7429 ^{ns}
CV (%)	25.7	14.4	22.8	8.19	22.5

ns = not significant, * significant at 5% level, ** significant at 1% level, *** significant at 0.1% level.

but not for corn, which according to FAGERIA (2000) must be 2.0 mg kg^{-1} for corn cultivation.

The concentration of Fe in the corn leaves was reduced at a rate of 11.8 mg·kg^{-1} per kg·ha^{-1} of Zn applied to soybean (Figure 2). Absorption of Fe and Zn has antagonistic effects, as increased availability of Zn reduces Fe absorption and vice versa; however, the greatest effect of one in relation to the other is observed in their translocation in the plant and not in their absorption (ADRIANO et al., 1971; ROSEN et al., 1977). In any case, Fe deficiency in weathered and acidic soils such as those in the Cerrado region is rare (MULIMA et al., 2018). This effect of reducing Fe concentration by Zn application has little effect on plant nutrition; the higher dose of Zn applied to soybean reduced the Fe in corn to 172 mg kg^{-1} compared to that in the absence of Zn application (Table 5); this represents a 26% reduction despite being a high value. The leaf concentration of Fe with Zn application at 12.5 kg ha^{-1} in soybean was 476 mg kg^{-1}, which is 190% compared to the upper limit of the appropriate range (50–250 mg·kg^{-1}) required for corn nutrition (MALAVOLTA et al., 1997).

The Mn concentration in corn leaves was reduced at a rate of 0.57 mg·kg^{-1} per kg·ha^{-1} of Zn applied to soybean (Figure 2). The flow of Mn through the roots of corn is drastically reduced by Zn (SAFAYA, 1976). This effect of reducing Mn concentrations through Zn application is important in plant nutrition; the higher dose of Zn applied to soybean reduced the Mn in corn to 8.3 mg·kg^{-1} compared to that in the absence of Zn application (Table 5), representing a 20% reduction. The Mn concentration in corn was lower than the range of 50–150 mg·kg^{-1}, which is considered adequate for the crop (MALAVOLTA et al., 1997) in all evaluated situations (Table 5).

Soil Cu fertilization in FR and PP

Copper doses did not influence soybean yield in the experiments conducted in FR and PP (Table 2). The Cu levels in soil (Table 1) were adequate according to SOUSA & LOBATO (2004), ALVAREZ et al. (1999), and GALRÃO (1999), but were below the ideal levels suggested by FAGERIA (2001). These results indicated that the recommendations for adequate Cu levels in soils suggested by SOUSA & LOBATO (2004); ALVAREZ et al. (1999); GALRÃO (1999) are valid, even for PP, which rejects hypothesis number 1. The higher doses of Cu applied to soil in this study did not exert a harmful effect on soybean, indicating that even in PP, Cu toxicity is not a cause for concern, corroborating the observations of GUPTA & KALRA, (2006) and TEIXEIRA et al. (2008), which opposes hypothesis number 3. The soybean yield was not different when grown in PP or FR, and was, on average, 3,437 kg·ha^{-1} (Table 6).

Except for Ca, the concentration of macronutrients in soybean leaves was not affected by the doses of Cu applied to soil (Table 6).

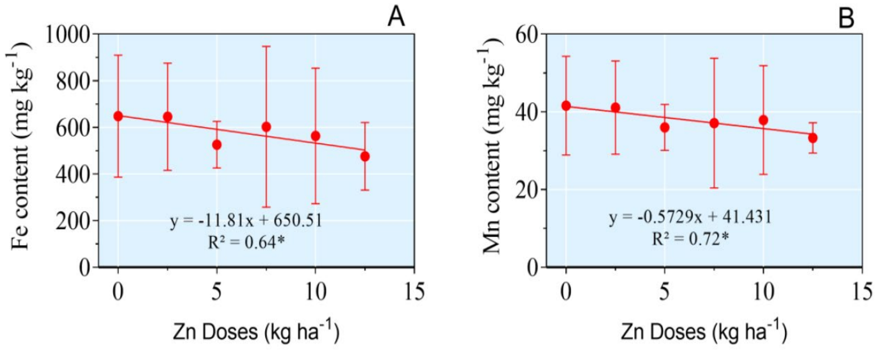

Figure 2 - Iron (Fe) (A) and manganese (Mn) (B) content in corn leaves as a function of the previously applied doses of zinc (Zn) in the soybean crop. * significant at 5% level. Experiment II. Vertical bars indicate the standard error.

However, the concentrations of P, Ca, Mg, and S were higher in soybean grown in PP compared to their cultivation in FR. The levels of P and Ca in the soils were similar, but were always slightly higher in PP; in the case of Mg and S contents, the difference was greater between soils, and was always higher in PP (Table 1). Besides higher levels in soil, these differences can be explained by the excess gravel

Table 6 - Effect of Cu doses on soybean grain yield and macronutrient contents in leaves of soybean grown in ferralsol (FR) and plinthosol (PP), experiments Iand III, respectively.

Cu dose (kg·ha^{-1})	FR	PP	FR	PP	FR	PP	FR	PP	FR	PP	FR	PP	FR	PP
	------Yield-------		--------N--------		--------P--------		------K------		--------S--------		---------Ca---------		-------Mg------	
	kg·ha^{-1}		---g·kg^{-1}---											
0	3325	3366	49.9	52.4	2.8	4.7	22.4	20.2	2.19	3.3	6.73	13.9	4.21	6.2
1	3413	3115	46.7	56.5	2.7	4.7	22.5	19.4	2.02	3.4	7.48	13.9	4.22	6.2
2.5	3339	3554	46.2	47.9	2.8	4.7	26.1	20.1	2.21	3.4	7.29	15.2	4.13	6.2
4	3446	3601	47.3	55	2.8	5.5	21.3	20.5	2.15	3.8	6.54	11.6	4.28	6
5.5	3286	3713	50.7	49.8	2.8	5.5	19	20.7	2.23	3.5	6.53	13	4.36	6.1
7	3333	3751	49	48.4	2.7	4.7	22	21.3	2.11	3.2	7.07	13.8	4.27	6.3
Averages	3357	3517	48.3	51.7	2.8 b	5 a	22.2	20.4	2.2 b	3.4 a	6.9 b	13.5 a	4.2 b	6.2 a
	---Pr > F---													
Soil (S)	0.0996 ns		0.0506 ns		<.0001***		0.1705 ns		<.0001***		<.0001***		<.0001***	
Dose (D)	0.4833 ns		0.4784 ns		0.4365 ns		0.4981 ns		0.6775 ns		0.0312*		0.1841 ns	
S*D	0.2603 ns		0.2932 ns		0.8565 ns		0.1866 ns		0.803 ns		0.9025 ns		0.0189*	
CV (%)	9.4		10.2		11.13		21.5		18		5.8		2.24	

Lowercase letters are used to compare averages between columns. ns = not significant, *significant at 5% level, **significant at 1% probability, ***significant at 0.1% level.

that occupies the soil volume in PP, with a higher proportion of inert material, which changes the dynamics of nutrients in terms of the intensity of adsorption and mobility, theoretically facilitating their absorption by plants.

Cu doses influenced the soybean leaf Ca concentrations. There are currently no reports in the literature regarding the influence of Cu on Ca absorption; in contrast, the use of limestone has been reported to reduce Cu absorption. However, this effect is due to an increase in pH, and not a direct effect of Ca (ERNANI et al., 1998). Further, the effect on the Ca concentration in soybean leaves caused by an increase in Cu doses is negligible, as the leaf Ca was reduced at a rate of 0.14 $mg \cdot kg^{-1}$ per $kg \cdot ha^{-1}$ of Cu applied in PP, and at a rate of 0.04 $mg \cdot kg^{-1}$ per $kg \cdot ha^{-1}$ of Cu applied in FR (Figure 3).

Soil fertilization with Cu doses did not influence the concentration of micronutrients in soybean leaves (Table 7). The concentrations of Fe, Mn, and B were higher in soybean grown in PP compared to their cultivation in FR (Table 7). The highest concentrations of Fe in soybean leaves grown in PP were observed similar to those in the Zn experiment (Table 3) described previously.

Despite the lower content of Mn detected in the soil analysis in PP than in FR (Table 1), the Mn concentration in corn leaves was higher in PP. An excess of gravel in the soil volume changes the dynamics of nutrients, interfering with the soil-plant relationships. Thus, more studies are needed to understand these aspects. Likewise, the dynamics of B should be better studied in graveled soils to explain the greater absorption of B in PP compared to that in FR, similar to that observed in the Zn dose experiment, wherein the absorption of B in PP occurred in a manner contrary to that in FR and that reported in literature (Figure 1-B). The higher pH of PP compared to FR (Table 1) may help explain this result, as B availability increases with increasing soil pH (PETERSON & NEWMAN, 1976).

Cu Oxysulfate fertilization did not affect the leaf Cu concentration in soybean (Table 7), and under all conditions, it was within the appropriate range (GALRÃO, 1999; FAGERIA, 2001), explaining the absence of differences in productivity in this experiment. According to KOVÁČIK & BAČKOR (2008), Cu as a redox-active metal is preferentially retained in the roots to protect shoots against oxidative damage. Similar leaf Cu concentrations with no yield

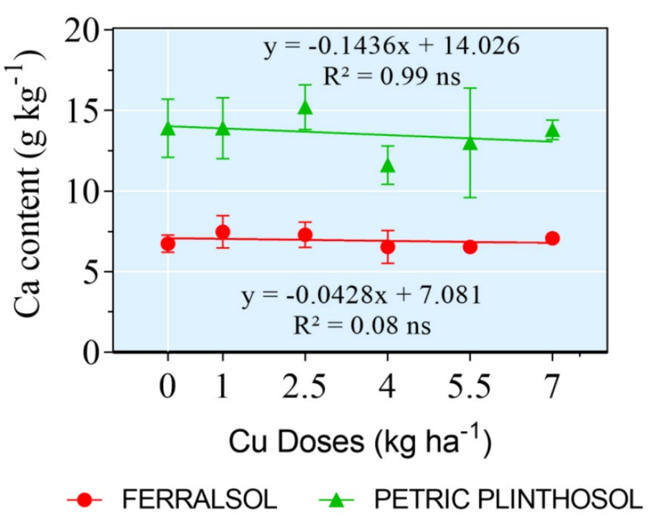

Figure 3 - Calcium (Ca) content in soybean leaves as a function of the applied copper (Cu) doses. Ns = not significant. Vertical bars indicate the standard error.

Table 7 - Effect of Cu doses on micronutrient contents in leaves of soybean grown in ferralsol (FR) and plinthosol (PP), experiments I and III, respectively.

Cu dose	FR	PP	FR	PP	FR	PP	FR	PP	FR	PP
(kg·ha^{-1})	-----------Cu------------		------------Fe-----------		--------------Mn--------------		------------Zn-------------		-------------B-----------	
	----------mg·kg^{-1}----------									
0	14.9	10.1	194	266	22.8	27.5	39.9	22.0	45.8	53.9
1	14.8	9.8	182	264	22.7	27.3	39.0	21.9	44.3	54.5
2.5	14.4	9.3	182	261	22.3	31.6	41.0	19.8	43.5	52.7
4	13.4	8.3	184	268	21.6	32.5	35.4	27.7	44.0	57.5
5.5	13.9	9.8	194	266	25.0	32.5	40.5	24.7	45.6	58.5
7	14.3	10.7	186	247	22.6	25.4	37.4	24.6	44.3	54.1
Averages	14.3 a	9.7 b	187 b	262 a	22.8 b	29.5 a	38.9 a	23.5 b	44.6 b	55.2 a
	----------Pr > F----------									
Soil (S)	< 0.0001***		< 0.0001***		< 0.0001***		< 0.0001***		< 0.0001***	
Dose (D)	0.4563 ns		0.6131 ns		0.3851 ns		0.949 ns		0.2847 ns	
S*D	0.9416 ns		0.7844 ns		0.4975 ns		0.1427 ns		0.5564 ns	
CV (%)	14.6		7.6		17.8		15.8		6.8	

Lowercase letters compare averages between columns. ns = not significant, ** significant at 1% probability, *** significant at 0.1% probability.

reduction reinforces the idea that the levels considered suitable for soils (SOUSA & LOBATO 2004; ALVAREZ et al., 1999; GALRÃO, 1999) are sufficient to nourish soybean, including those in gravelly soil, and the observed high Cu concentrations without yield reduction contradict the hypothesis that gravel may act as an inert material, enhancing the absorption of Cu and promoting toxic effects.

The higher absorption of Cu by soybean in FR than in PP can be explained by the higher Cu content in the soil in the FR, and higher pH of soil in the PP (Table 1), as Cu availability decreases with increasing soil pH (ALVA et al., 2000).

As in the Zn dose experiment, the Cu concentration in soybean leaves was higher when cultivated in FR compared to that in PP (Table 7), which can be explained by the higher Cu content in soil (Table 1) and the higher pH in PP, which reduces the availability of Cu for plants (GONÇALVES et al., 2018).

The corn yield or macronutrient concentrations in corn leaves were not affected by the doses of Cu applied to soybean grown before the off-season corn crop (Table 8). Corn was produced on average, at 9,315 kg·ha^{-1} (Table 8). The reduction in Ca absorption due to the increase in the Cu dose observed in soybean (Figure 3), was not observed in corn, indicating a non-significant effect.

Similar to soybean, the Cu doses applied to soybean did not increase the leaf concentration of Cu in the subsequently grown off-season corn (Table 9), demonstrating that there was no residual effect of fertilization on soybean in corn. The leaf concentration of Cu in corn was on average 17.7 mg·kg^{-1}, within the range considered ideal, or even above it (MALAVOLTA et al., 1997; FAGERIA, 2001; GOTT et al., 2014), which explains the lack of response in this experiment. Even high doses of Cu did not affect the absorption of the other micronutrients.

CONCLUSION

In conclusion, our results indicate that the official criteria for interpreting Zn in soil analysis are applicable to soybean grown in petric plinthosol. Soil fertilization with zinc oxysulfate is efficient and has the same effect in ferralsol and petric plinthosol, as it

Table 8 - Residual effect of Cu doses on grain yield and macronutrient contents in off-season corn leaves grown in ferralsol, experiment I.

Cu dose	Yield	N	P	K	S	Ca	Mg
(kg·ha^{-1})	kg·ha^{-1}	----------g·kg^{-1}----------					
0	8770	33.7	1.5	25.8	1.3	5.0	4.6
1	9846	33.5	1.6	26.3	1.3	5.1	4.9
2.5	9579	34.1	1.3	25.9	1.3	5.0	4.7
4	9229	34.1	1.4	24.8	1.4	5.1	4.7
5.5	9480	34.2	1.5	25.8	1.4	4.9	4.8
7	8990	32.8	1.5	24.6	1.3	5.4	5.0
Averages	9315	33.7	1.5	25.5	1.3	5.1	4.8
Pr > F	0.6572 ^{ns}	0.899 ^{ns}	0.49 ^{ns}	0.6959 ^{ns}	0.9877 ^{ns}	0.4562 ^{ns}	0.2559 ^{ns}
CV (%)	10.5	5.4	14	6.9	17	20.2	4.5

ns = not significant.

increased the concentration of Zn in soybean leaves by 0.7 mg kg^{-1} of Zn for each kg·ha^{-1} of Zn applied, in both soils. High doses of Zn, up to 12.5 kg·ha^{-1} in a single annual application, did not cause a toxic effect in soybean grown in petric plinthosol. Although, there was no residual effect of Zn Oxysulfate applied to soybean on off-season corn, the concentration of Mn in the corn leaves was reduced at a rate of 0.57 mg·kg^{-1} per kg·ha^{-1} of Zn applied to soybean.

The official criteria for interpreting Cu in soil analysis are applicable to soybean grown in petric plinthosol. Cu doses did not influence soybean

Table 9 - Residual effect of Cu doses on the micronutrient contents in off-season corn leaves grown in ferralsol, experiment I.

Cu dose	Cu	Fe	Mn	Zn	B
(kg·ha^{-1})	----------mg·kg^{-1}----------				
0	16.4	367	24.7	12.8	11.2
1	19.1	391	23.9	13.5	12.5
2.5	17.1	372	24.7	13.4	12.3
4	17.2	374	23.7	12.1	11.0
5.5	19.1	390	25.1	12.8	8.8
7	17.3	367	24.1	12.0	10.9
Averages	17.7	377	24.4	12.8	11.1
Pr > F	0.4 ^{ns}	0.7 ^{ns}	1.0 ^{ns}	0.29 ^{ns}	0.2 ^{ns}
CV (%)	11.6	18.0	18.8	8.6	22.4

ns = not significant.

productivity or the leaf concentration of N, P, K, Mg, S, and micronutrients in the experiments conducted in ferralsol and petric plinthosol. Similarly, Cu Oxysulfate applied to soybean had no residual effect on the subsequently grown off-season corn. Further, high doses of Cu, up to 7 kg·ha^{-1}, in a single annual year application, did not have a toxic effect on the soybean grown in petric plinthosol.

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DECLARATION OF CONFLICT OF INTEREST

The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

AUTHORS' CONTRIBUTIONS

All authors contributed equally for the conception and writing of the manuscript. All authors critically revised the manuscript and approved of the final version.

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