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Influence of Zinc and Boron Interaction on Residual Available Iron and Manganese in the Soil after Corn Harvest

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Abstract: Some nutrients applied to soils remain available to plants well beyond their time of application. Efficient use of fertilizers requires better definition of these residual effects. In this study, a fertilization experiment was conducted to evaluate the effect of Zn and B application on the residual available iron (Fe) and manganese (Mn) in the soil after corn harvest in Fars Province, Iran. We used 5 concentration levels of Zn (0, 8, 16 and 24 kg ha^{-1} Zn added to the soil and Zn foliar spray with a 0.5 percent concentration) and 4 levels of B (0, 3 and 6 kg ha^{-1} B added to the soil and B foliar spray with a 0.5 percent concentration) in a completely randomized block design were set up. In all treatments, the residual Fe and Mn in the soil increased compared to its initial levels (before culture). The application of different levels of Zn and B had no significant effect on the residual available Fe and Mn contents in the soil relative to the no Zn and B levels. No treatments, showed a significant difference on the residual Mn in the soil as compared with the control. Also, no treatment except the treatment of 8 kg ha^{-1} Zn, showed no significant effect on the residual Fe in the soil relative to the control. In fact, Zn and B fertilizers had no role in the changes of residual Fe and Mn in the soil relative to the its initial levels and other factors are effective on the increasing residual Fe and Mn in the soil relative to its initial levels. The effect of Zn and B interaction on the residual Fe and Mn in the soil was insignificant.

Key words: Boron · Interaction · Iron · Manganese · Residual elements and Zinc

INTRODUCTION

Soil fertility is an important factor, which determines the growth of plant. Soil fertility is determined by the presence or absence of nutrients i.e. macro and micronutrients. The availability of micronutrients is particularly sensitive to changes in soil environment. The factors that affect the contents of such micronutrients are organic matter, soil pH, lime content, sand, silt and clay contents revealed from different research experiments. There is also correlation among the micronutrients contents and above-mentioned properties [1]. Micronutrients such as B, Zn, Fe and Mn play important physiological roles in humans and animals. Zinc and Fe deficiency are currently listed as major risk factors for human health globally [2]. Cereal grain is a good and easily accessible source of Fe and Zn and to lesser extent of B, Cu, Mn and Mo for both feed and food. Although maize is low in some micronutrients, humans and animals can obtain at least part of their nutritional requirements from maize grain [3]. Micronutrients such as Fe and Mn are needed in small amounts and there are also likely to be residual effects for some years after their application [4].

The mean amount of Zn in the lithosphere is about 80 mg kg^{-1} and that in the soil is about 10 to 300 mg kg^{-1} [5, 6]. In spite of the fact that the total soil Zn content is relatively high, but a small fraction of it is available to the plant [7]. The critical level of Fe in the soil in mg kg^{-1} by DTPA extraction, has been reported by Sims and Johnson [8] for corn to be 2.5-5, Pals and Benton [9], 2.5-5 and Agrawala [10], 2.5. The critical limit of soil Mn content is specified as 3.8 mg kg^{1} by Sims and Johnson [8] and 5.5 mg kg^{1} by Agrawala [11].

Zinc is present in the structure of the cell wall (in the pectinase component). Therefore, in its deficit, the P transfer from the superficial root cells to xylem is not controlled and the P level in airborne parts of plants increases [11, 12]. Zinc is involved in a large number of enzymes as a cofactor. For example, it is involved in activation of different enzymes such as dehydrogenase, aldolase, isomerase, transphosphorase and DNA polymerase [12]. Boron plays a very important role in vital functions of the plant, including meristem tissue cell division, petal and leaf bud formation, vascular tissue repair, sugar and hydrocarbon metabolism and their transfer, RNA and indoleacetic acid metabolism,

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membrane stability, cytokinin production and transfer, pollen budding and seed formation [13, 12].

Iron is essential in the heme enzyme system in plant metabolism (photosynthesis and respiration). The enzymes involved include catalase, peroxidase, cytochrome oxidase and other cytochromes. Iron is part of protein ferredoxin and is required in nitrate and sulfate reductions, also it is essential in the synthesis and maintenance of chlorophyll in plants and it has been strongly associated with protein metabolism [14]. Manganese primarily functions as part of the plant enzyme system, activating several metabolic functions. It is a constituent of pyruvate carboxylase. Manganese is involved in the oxidation-reduction process in photosynthesis and it is necessary in Photosystem II, where it participates in photolysis. Manganese activates indole acetic acid oxidase, which then oxidizes indole acetic acid in plants [14].

Zinc (Zn) deficiency is a very important nutrient problem in the world's soils. Total Zn concentration is in sufficient level in many agricultural areas, but available Zn concentration is in deficient level because of different soil and climatic conditions. Soil pH, lime content, organic matter content, amount and type of clay minerals and the amount of applied P fertilizer affect the available Zn concentration in soil [15]. Zinc deficiency rate was determined as a 30% in the world [16]. The interaction among nutrient elements is very important for plant nutrition. Boron and Zn interaction among these interactions has been curicial in the Zn deficient soils, in recent years [17]. Plant root cell membrane permeability increases in Zn deficient soils, which may lead to accumulate B and other nutrient elements in plant roots. Therefore, excess B uptakes by plants may cause B toxicity for the plants in this soil conditions [18].

Zinc and Fe are antagonistic; of course this is not always the case and even in some cases they are combined and used, they can play a useful and effective role on plant growth and increase in the harvest [19]. A negative Zn-B interaction has been seen in the plant [20]. When the corn plant is under Zn stress, it absorbs a large amount of Fe and Mn, worsening the adverse effects of Zn deficiency [21]. Moreover, an interaction exists between B and Mn; a high B content leads into appearance of signs of Mn deficiency in the plant. A Fe-B antagonism as well has been reported. Of course, in B deficiency conditions, B uptake increased by adding Fe. Also, an antagonism between B and Fe in the plant has been observed [22]. Graham *et al.* [23] reported that whenever the soil Zn content reduced, the barley plant P, K and Cu content increased while its Fe content was not affected. According to Rengel and Graham [24] report, by increase in wheat grain Zn content, Fe, Mn, Cu, B, ca, Mg, sodium, K and P contents decreased. Aref [25] reported that the presence of a high amount of Zn or B in the soil, assisted in the effect of B or Zn on increasing concentration and uptake of B in the plant. That is, a synergism was seen between the Zn and B as effecting the concentration and uptake of B in the grain.

By measuring the residual nutrients in the soil after harvesting the crop, we can use many desired relations for better management in the culture. If the amount of the residual available element in the soil is at a high level, this represents less uptake by the plant or less fixation by soil particles and if it is at a low level, this represents more uptake by the plant or more fixation by soil particles. Of course, in addition to uptake and fixation, other factors such as uptake of elements from unavailable form to available form or vice versa as well contribute to the amount of residual available element in the soil. Zinc and B deficiency play an effective role in patchiness o f the ear. Therefore, the objective of the study was examination of the effect of Zn and B on the residual available Fe and Mn in the soil after harvesting corn so that we are able to plan for Zn and B use in the next cultures.

MATERIALS AND METHODS

A field experiment was conducted at the agricultural farm of Aref in Abadeh Tashk, Fars province of Iran, on the corn (*Zea mays* L.), cultivar "Single Cross 401" during 2009 cropping season. The area is located 200 km northeast of Shiraz, at latitude 29° 43' 44" N and longitude 53° 52' 07" E and 1580 m altitude. A composite soil sample (0-30 cm) was taken from the site before the experiment was initiated. Selected soil chemical and physical characteristics for the site are presented in Table 1. This soil had a loam texture, pH of 8.2, 0.59 % organic matter, 229 mg kg^{-1} available potassium (K), 12.1 mg kg^{-1} available P, DTPA extractable Fe, Mn, Zn and Cu concentration were 1.65, 8.14, 0.32 and 0.62 mg kg^{-1} and available B with hot water extractable was 0.78 mg kg^{-1}. This experiment consisted of 20 treatments and 3 replications in the form of completely randomized block design and factorial that combinations of five Zn levels (0, 8, 16 and 24 kg ha^{-1} Zn added to the soil and Zn foliar spray with a 0.5 percent concentration) and four B levels (0, 3, and 6 kg ha^{-1} B added to the soil, and B foliar spray with a 0.3 percent concentration). Nitrogen, P and K used at 180, 70 and 75 kg ha^{-1} according to the recommendation, from sources of urea, triple super phosphate and potassium sulfate, respectively, were added to all treatments (plots). Half of the urea was used when planting and the remainder two times: At vegetative growth and when the corn ears were formed. Potassium and P used before planting. Zinc and B, from zinc sulfate and boric acid sources, respectively, were used by two methods, adding to the soil and spraying. Addition to the soil was made at the time of plantation and the sprayings were made at 0.5% Zn sulfate and 0.3% boric acid two times: one at vegetative growth stage and the other after corn ears formation. The Zn and B were both applied to the leaves with uniform coverage at a volume solution of 2500 L ha^{-1} using a knapsack sprayer. Each experimental plot was 8 m length and 3 m width, had 5 beds and 4 rows, equally spaced, and seeds 20 cm apart on the rows. At the end of the growth stage the grain yield, dry matter and the soil available Fe and Mn after corn harvest were measured.

The soil samples were air-dried and ground to pass through a 2-mm sieve before analysis. Selected soil chemical and physical characteristics for the two sites are presented in Table 1. Analysis of the soil was carried out using common lab procedures [26]. Soil particle size distribution was determined by the hydrometer method [27], organic matter (OM) content by the Walkley-Black method [28] and pH was determined at a 1:2.5 soil:water extraction. Soil available K was determined by 1 M NH_4OAc extraction and K assessment in the extract by flame photometer [29]. Soil available P was measured by Olsen method. Available Fe, Zn, Mn and Cu in the soil were first extracted by DTPA and then were read by atomic absorption (Shimatzu Model AA-670). The soil available B was extracted by hot water and then was measured by azomethine-H colorimetric method. Statistical analysis of data was made using MSTATC and SAS software with Duncan test and regression equations via the SPSS program.

RESULT AND DISCUSSION

Soil Test Result Before Culture: Soil test results from soil samples taken before the experiment was initiated in the spring of 2009 are presented in Table 1. The soil had high clay content. The soil available K was high but soil available P was lower than the critical level suggested in scientific sources [30]. Karimian and Ghanbari [5] have reported the critical P level by the Olsen method in calcareous soils as 18 mg kg^{-1}. The soil Zn and B content was lower than the critical level. For many crops, a DTPA-extractable Zn level of 0.5-0.8 mg kg^{-1} has been regarded as a soil critical level below which crop production would be limited by Zn deficiency [31]. The soil available Mn was high but soil available Cu and Fe were lower than the critical level. Sims and Johnson (1991) have reported the critical levels of Fe, Zn, Mn and Cu by the DTPA extraction method and B by the hot water in the soil method to be 2.5-5, 0.2-2, 1-5, 0.1-2.5 and 0.1-2 mg kg^{-1}, respectively.

The Residual Available Fe Content in the Soil: The soil Fe content before culture was 1.65 mg kg^{-1} and increased after harvesting in all treatments (Table 2). Considering that Fe fertilizer was not applied to the soil, the increase in soil Fe content after harvesting was due to availability of a part of the total Fe in the form of available Fe.

Table 1: The result of soil analysis

Depth of soil (cm)	Soil texture	pH	EC (ds m^{-1})	Organic matter (%)	P	K	Fe	Mn	Zn	Cu	B
					mg kg^{-1}						
0-30	Loam	8.2	2.41	0.59	12.1	229	1.65	8.14	0.32	0.62	0.78

Table 2: The effect of Zn and B on residual available Fe in the soil after corn harvest (mg kg^{-1})*

	Zn (kg ha^{-1})					
B (kg ha^{-1})	0	8	16	24	Foliar Spray	Mean
0	4.77ab	2.63c	3.54bc	3.69bc	4.07abc	3.74a
3	3.69bc	2.91bc	3.69bc	4.11abc	4.14abc	3.71a
6	4.11abc	4.39abc	4.92ab	3.34bc	3.85bc	4.12a
Foliar Spray	4.03abc	3.42bc	4.25abc	4.15abc	5.92a	3.36a
Mean	4.15ab	3.34b	4.10ab	3.83ab	4.49a	

*Means with same letters lack a significant difference at 5% level by Duncan's test

Table 3: The effect of Zn and B on residual available Mn in the soil after corn harvest (mg kg^{-1})*

	Zn (kg ha^{-1})					
B (kg ha^{-1})	0	8	16	24	Foliar Spray	Mean
0	12.20abc	8.05c	11.75abc	12.03abc	12.63ab	11.33a
3	12.83ab	12.01abc	11.20abc	11.93abc	10.55abc	11.70a
6	13.41a	12.57ab	11.81abc	10.47bc	11.31abc	11.92a
Foliar Spray	8.49c	10.85abc	12.91ab	12.12abc	12.55ab	11.39a
Mean	11.73a	10.87a	11.92a	11.64a	11.76a	

*Means with same letters lack a significant difference at 5% level by Duncan's test

Root secretions and reactions was carried out in the soil by activities such as irrigation and climate changes during the growing season leads into availability of a part of the total Fe in the form of available Fe. Also, by adding zinc sulfate fertilizer can increase available Fe content in the soil by replacement of Zn instead of Fe. Therefore, in addition to the presence of total Fe in the soil can meet the plant needs, also, some amount of the total soil Fe content be available to the plant after culture and operations on the soil. Of course, with the elapse of time the total available Fe content in the soil decrease to the unavailable form. Iron and Mn oxides soil minerals are important sinks for these two elements in soil [32].

Different Zn levels had no significant effect on the residual available Fe content in the soil relative to the no Zn level, but Zn spraying increased residual available Fe content as compared with the 8 kg ha^{-1} Zn level. There was a relation between the leaf Fe content and the residual Fe content. The study of the effect of Zn and B on the leaf Fe content and residual Fe content in the soil showed that Zn application at all levels had no significant effect on the leaf Fe content, thus the amount of Fe uptake from the soil did not change and thereby, Zn application had no significant effect on the residual available Fe content in the soil relative to the no Zn level.

The main effect of B on the soil residual available P content in the soil was insignificant at 5% level. Also, B application in any Zn levels had no significant effect on the residual available Fe content. At zero B level, only the use of 8 kg ha^{-1} Zn significantly decreased residual Fe content in the soil from 4.77 to 2.63 mg kg^{-1} (44.86 percent decrease as compared with no Zn use at this B level), but at other B levels, Zn use had no significant effect on the residual available Fe content in the soil. The lowest and the highest soil P content after harvesting, 5.92 and 2.63 mg kg^{-1}, were observed by joint use of Zn and B spraying and 8 kg ha^{-1} Zn (24.11 and 44.86 percent decrease as compared with the control with a residual Fe content of 4.77 mg kg^{-1}). Except the treatment with the lowest soil Fe content, all treatments showed no significant effect on the residual available Fe content in the soil as compared with the control. Because Zn and B application at all levels had no significant effect on the residual Fe content in the soil relative to the Zn and B level and also, almost all treatments showed no significant difference from the control, therefore increasing the residual Fe content in the soil depend on the many factors such as soil tillage, irrigation, root secretions and NPK fertilizers.

The Residual Available Mn Content in the Soil: The available Mn content in the soil before culture was 8.14 mg kg^{-1} and increased after harvesting in all treatments (Table 3). The increase in available Mn after harvesting was due to availability of a part of the total Mn in the form of available Mn by root secretions, weather and operations carried out on the soil. Iron and Mn distributions among metal fractions were generally dependent on total metal content, soil properties and degree of chemical weathering [33]. The main effect of Zn and B on the residual Mn in the soil was insignificant at 5% level. The Zn-B interaction effect on residual available Mn in the soil showed that only at 8 kg ha^{-1} Zn level, the use of 6 kg ha^{-1} B increased available Mn after harvesting from 8.05 to 12.57 mg kg^{-1} (56.15% increase), but at other Zn levels, B application had no significant effect on the available Mn content in the soil.

Zn application at high B levels (6 kg ha^{-1} B) decreased soil Mn content and at B spraying level increased soil Mn content after harvesting, but at other B levels showed no significant effect on the soil Mn content after harvesting. At 6 kg ha^{-1} B level, only the use of 24 kg ha^{-1} Zn decreased soil Mn content after harvesting from 13.41 to 10.47 mg kh^{-1} (21.92% decrease relative to the no Zn use at this B level). At B spraying level, the use of 16 kg ha^{-1} and Zn spraying increased available Mn content in the soil from 8.49 to 12.91 and 12.55 mg kg^{-1}, respectively (52.06 and 47.82 percent increase as compared with no Zn use at this B level). Any treatments showed no significant effect on the residual available Mn content in the soil relative to the control (no Zn and B use).

The minimum and the maximum available Mn content in the soil after harvesting, 8.05 and 13.41 mg kg^{-1}, were seen by the use of 8 kg ha^{-1} Zn and 6 kg ha^{-1} B, respectively; showing 34.02 and 9.91 percent increase relative to the control, with a residual available Mn content of 12.12 mg ka^{-1}.

The correlation between the residual available P and Zn in the soil with other variables The correlation coefficients (r) between different variables by the Pearson method and the relevant equations were obtained by the step by step method using the SPSS software. One can use each of the following equations depending on what are the variables measured and r and r^2, but the last equation derived, is the most complete equation containing dependent and independent variables and we must measure more variables to derive that equation. The symbols * and ** in equations and correlation coefficients (r or r^2), are significance at 5% ($\alpha = 0.05$) and 1% ($\alpha = 0.01$) levels.

The Residual Available Fe Content in the Soil: There was a positive correlation between soil Fe content after harvesting and soil P content ($r = 0.50^*$), Mn content ($r = 0.45^*$) and Cu content ($r = 0.84^{**}$), leaf Fe content (r = 0.38), grain N content ($r = 0.61^{**}$) and B content (r = 0.34), N uptake by the grain (r = 0.31), ear weight (r = 0.33), grain weight in the ear (r = 0.42), the percentage of grain in the ear ($r = 0.69^{**}$), grain protein content ($r = 0.61^{**}$) and a negative correlation with the leaf P content (r = -0.39) and Mn content ($r = -0.50^*$), Cu concentration in the grain ($r = -0.52^*$), Cu uptake by the grain (r = - 0.43) and 1000-grain weight (r = - 0.31). The relevant equations were:

- $FeS = 0.356 + 4.537\ CuS\ r = 0.84^{**}$
- $FeS = -2.984 + 3.854\ CuS + 2.286\ NG\ r^2 = 0.82^{**}$
- $FeS = -2.306 + 3.681\ CuS + 2.618\ NG - 0.00492\ ZnUG\ r^2 = 0.88^{**}$
- $FeS = -2.546 + 2.536\ CuS + 4.744\ NG + 0.0101\ ZnUG + 0.301\ BL\ r^2 = 0.93^{**}$
- $FeS = -3.21 + 2.389\ CuS + 4.324\ NG - 0.0109\ ZnUG - 0.0269\ BL + 0.00716\ GW\ r^2 = 0.96^{**}$

FeS, CuS, NG, ZnUG BL and GW are available Fe content in the soil (mg kg^{-1}), available Cu content in the soil (mg kg^{-1}), N concentration in the grain (%), Zn uptake by the grain (g ha^{-1}), grain B content (mg kg^{-})^{1} and grain weight in the ear (g).

The Residual Available Mn Content in the Soil: The soil Mn content after harvesting showed a positive correlation with available Fe content in the soil ($r = 0.45^*$) and available B content in the soil (r = 0.37), leaf B content (r = 0.39), grain N content ($r = 0.51^*$), grain protein content ($r = 0.51^*$), percentage of grain in the ear (r = 0.38) and a negative correlation with 1000-grain weight ($r = -0.49^*$). The equation of which was:

$$MnS = 0.602 + 6.46\ NG\ r = 0.51^*$$

MnS and NG denote residual available Mn content in the soil (mg kg^{-1}) and N concentration in the grain (%).

CONCLUSION

In all treatments, the residual available Fe and Mn content in the soil increased after harvesting relative to the its initial levels. The use of different levels of Zn and B on the soil Fe and Mn content after harvesting was insignificant relative to the no Zn and no B levels. No treatments, had no significant effect on the soil Mn content after harvesting relative to the control. Also, except for the treatment of 8 kg ha^{-1} Zn, other treatments showed no significant effect on the residual available Fe content in the soil as compared with the control. Therefore, Zn and B fertilizers had no significant effect on the changes of residual available Fe and Mn content in the soil relative to the its initial level. In fact, many factors such as soil tillage, irrigation, root secretions and NPK fertilizers affect on the residual available Fe and Mn content in the soil relative to the its initial.

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