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# Copper and manganese acquisition in maize (*Zea mays* L) under different P and K fertilization

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## SUMMARY

The paper demonstrates the influence of different mineral fertilization with phosphorus and potassium on the concentration of copper (Cu) and manganese (Mn) in the ear leaf of maize at the stage of flowering (BBCH 65) as well as the contents and accumulation of the nutrients studied in maize when fully ripe (BBCH 89). A single factor experiment was carried out in 5-year-cycle (2007-2011), in the randomized complete block design. The experiment was conducted as a part of a long-term stationary trial. The investigation comprised 8 different P and K treatments: the absolute control, exclusive of one of the main nutrients (P - WPN or K - WKN), reduced amount of phosphorus and potassium (to 25% - W25 and to 50% WP50, WK50) as well as recommended amounts of basic nutrients (NPKMg - W100 and NP*KMg, P* - P* as PAPR - W100 PAPR). Evaluation of the nutriational status, performed in the ear leaf of maize at flowering stage, showed that regardless of fertilization treatment applied, the concentration of copper was lower than normative values, whereas that of manganese ranged within the optimal scope. At the same time, there was found a significant relationship between the grain yield obtained and acquisition of both copper and manganese by maize at flowering stage (stronger for manganese, $r = 0.614$). The total accumulation of copper and manganese in fully ripe maize was significantly differentiated as a result of mineral fertilization. The total uptake of Cu and Mn was reduced under the conditions of 10-year lack of P fertilization. Uptake reduction was considerably more advanced when K fertilization was absent for 10 years. Regardless of the experimental factor effects, more than 50% of the total copper uptake was accumulated in grain, whereas the majority of manganese was accumulated in maize leaves (50-64% of the total uptake). Correlation analysis showed a significant relationship between maize grain yield and the total accumulation of copper, whereas that of manganese was observed only in 3 of 8 treatments tested (WPN, WP50 and W100 as PAPR).

**Key words**: micronutrient uptake, grain harvest index, unit uptake

## 1. Introduction

As maize acreage has recently shown increasing tendency all over the world including Poland, there is a need to better understand requirements of this crop for not only macronutrients such as nitrogen, phosphorus, potassium, magnesium, calcium and zinc, but also - micronutrients, such as manganese and copper. Maize is a staple crop in many parts of the word, and is often targeted for micronutrient „biofortification" (Xia et al., 2013). Suitable micronutrient concentration in crop plants is not only a crucial issue in agricultural technology, but also a key quantitative indicator in the standards of food and fodder consumption (Fageria et al., 2008; Van Campen and Glahn, 1999). As said by Quzounidou et al. (1995), maize is one of the most important cereal crops - relatively sensitive to copper. An insufficient amount of copper in the diet can be dangerous for humans and animals as well. Copper is a component of antioxidant enzymes and its deficiency can disturb functioning of the antioxidant system in human or animal body (Hänsch and Mendel, 2009). Multi-purpose utilization of maize grain draws attention to the concentration of copper and manganese in kernels. Under Poland's conditions appropriate acquisition of copper and manganese in crop plants is of key importance, since in most cases, natural micronutrient availability in soils is generally low. Recent studies carried out by the National Chemical-Agricultural Centre showed low contents of available Cu in 34% of the soils analyzed. Content of avilable manganese in the soils examined was classified as medium (Lipiński, 2013). On the other hand, in Poland's agricultural practice, there have been observed no symptoms of extreme deficiencies of copper and manganese in maize because of low nutritional requirements for Cu and Mn in this crop (from 0.5 to 1.0 kg $\cdot ha^{-1}$). Nevertheless, insufficient acquisition of these micronutrients can lead to yield deterioration and loss. Demand for fertilization with an array of micronutrients grows especially in the farmsteads oriented toward intensive plant production. Yet, little attention has been so far paid to micronutrient performance, when applied using various fertilization modes. Furthermore, the influence of soil fertility on micronutrient uptake and relocation from plant tissues to grain has not been well documented. Time and again, micronutrient deficiencies become yield limiting factors, especially under the conditions impeding micronutrient availability, e.g. light soils, inadequate soil pH (Marschner, 1995). Besides, temperature and moisture are important factors affecting micronutrient availability to plants. Additionally, not enough manure fertilization, low tillage soil cultivation, crop rotation as well high nutritional requirements of succeeding crops are the reasons behind unsatisfactory availability of micronutrients in soils (Wei et al., 2006; Fageria et al., 2002). Contemporary high-yield maize varieties tend to contain lower concentrations of micronutrients in grain, when compared to lower-yield conventional cultivars (Feil et al., 2005). Under the conditions of a long-term field experiment, different fertilization treatments may alter soil nutrients and their available concentrations, which in turn may affect soil micronutrient levels (Li et al., 2007). The influence of phosphorus on micronutrients is related to the water content in the soil. Under field conditions, application of P considerably decreases water-soluble and extractable micronutrients (Bierman and Rosen, 1994).

In view of all the above mentioned aspects, the present study was conducted with the aim to: (1) assess copper and manganese nutritional status in maize at flowering stage, and (2) to examine changes of micronutrient contents and acquisition in the organs of maize under different fertilization treatments.

## 2. Materials and methods

### 2.1. Material

A stationary field experiment was conducted within a private farm at Wieszczyczyn (52º02' N 17º05'E), during 5 consecutive growing seasons (2007-2011). The trial was a component of a long-term study, established in the year 2000, in the randomized complete block design with four replications, set up on lessive soils developed from shallow light clayey sands on glacial tills (soil quality class IIIb in the Soil Classification System of Poland).

The field trials (a single-factor design) comprised 8 treatments:

- Control - no fertilization applied;
- WPN - no phosphorus fertilization; optimal fertilization with other nutrients (nitrogen, potassium and magnesium);
- WKN - no potassium fertilization; optimal fertilization with other nutrients (nitrogen, phosphorus and magnesium);
- W25 - 25% of recommended PK dose used in optimal fertilization, optimal fertilization with N and Mg;
- WP50 - 50% of recommended P dose used in optimal fertilization, optimal fertilization with other nutrients;
- WK50 - 50% of the recommended K dose used in optimal fertilization, optimal fertilization with other nutrients;
- W100 - 100% of recommended P and K doses, optimally balanced with reference to nitrogen;
- W100 PAPR - basic set of nutrients, P applied as partially acidulated phosphoric rock.

Winter wheat was cultivated as the forecrop of the studied maize variety *Veritis* (FAO: 230-240). The rates of phosphorus and potassium fertilization were calculated every year of observation, based on the expected yield of maize grain and existing soil P and K fertility. In W100 treatment (optimally balanced with reference to nitrogen), phosphorus was applied at a rate 26 kg $P \cdot ha^{-1}$/year (except for 2007: 35 kg $P \cdot ha^{-1}$), and potassium rates ranged from 100 kg $K \cdot ha^{-1}$ to 133 kg $K \cdot ha^{-1}$. Phosphorus was applied as single superphosphate (SSP), potassium - as potassium chloride (60% $K_2O$) and magnesium - as kieserite (27% MgO). All the basic fertilizers (PKMg) were applied in autumn. In W100 PAPR treatment, phosphorus was applied in the form of partially acidulated phosphate rock (PAPR), as an alternative phosphorus source (in place of SSP).

The assessments of maize copper and manganese contents regarded different plant organs and were carried out at 2 maize growth stages: BBCH 65 (flowering – in the ear leaf) and BBCH 89 (fully ripe - in: leaves, stems, ears, cob cores, husks and grain). The calculations were performed based on dry matter (D.M.).

The concentrations of Cu and Mn were assessed with the use of atomic absorption spectroscopy (SpectraAA-250 Plus Varian).

Copper and manganese accumulation values were determined based on the concentration of a given element and D.M. of maize organs. Data on maize yields obtained is provided in the paper by Bąk and Gaj (2016).

Copper Harvest Index (CuHI) and Manganese Harvest Index (MnHI) were calculated in accordance with the algorithm defining the relationship between accumulation of a given nutrient (Cu or Mn) in maize kernels (grain) and the total nutrient accumulation in maize at the stage of physiological maturity (fully ripe).

### 2.2. Statistical analysis

The effect of the experimental factor on nutrient accumulation and concentration under differentiated mineral fertilization with P and K was tested with 2-way ANOVA (mixed-effects model). A detailed description of the model used is presented by Bąk and Gaj (2016) and Bąk et al. (2016).

Data on the concentration of the nutrients (Cu and Mn) tested in maize organs were compared based on the graphical representation in heat maps, where 2D variables (defining micronutrient concentrations in maize organs depending on the treatments) were represented as colors. Cluster analysis allowed for treatment grouping with reference to the concentration of a given nutrient in maize organs in such a way as to demonstrate the strongest relationships within a given group and the weakest – among the groups. The dendrograms were prepared using Ward's hierachical clustering and the Euclidean distance. Causal relationships between the concentration, uptake, unit uptake of the nutrients tested and maize grain yield were tested using correlation coefficient.

## 3. Results and discussion

### 3.1. Concentration of Mn and Cu in the ear leaf

The results of the assessment of copper and manganese concentrations in the ear leaf of maize at the stage of flowering, showed that under mineral fertilization, nutrient concentration increased when compared to the control (Table 1). Zhang et al. (2004) point out that suitable NPK fertilization can enhance availability of copper and manganese in the soil, and hence – increase the concentration of these nutrients in the plant. In maize at the stage of flowering examined in the present study, the experimental factor differentiated copper concentration more than that of manganese. In the case of copper, significant differences ($p = 0.05$) were observed both between the treatments tested and with reference to the control. In flowering maize, leaf Cu concentration values were below the normative values 5 $mg \cdot kg^{-1}$-20 $mg \cdot kg^{-1}$, (Schulte and Kelling, 2000) and fluctuated in a narrow range from 3.34 $mg \cdot kg^{-1}$ to 4.14 $mg \cdot kg^{-1}$. The results obtained indicate copper deficiency in the leaves of flowering maize. At the same time, the lack of potassium fertilization had a stronger effect on the drop of Cu contents in the ear leaf when compared to the treatment with no phosphorus fertilization. Li et al. (2007) demonstrated that the concentrations of micronutrients in soil or in crops were strongly affected by available soil P and K concentrations.

On the part of manganese, no statistical differences were found between fertilizer treatments. Regardless of the treatment tested, Mn concentration in the ear leaf was at the normative level when compared to the threshold values determined by Schulte and Kelling (2000), i.e.: 19 $mg \cdot kg^{-1}$ -75 $mg \cdot kg^{-1}$ D.M. In the majority of the world's crop plants, Mn requirements are fulfilled at tissue levels, i.e.: 20 $mg \cdot kg^{-}$- 40 $mg \cdot kg^{-1}$ D.M (Jiang, 2006). Literature data (Mahler et al., 1992; Chalmers et al., 1999) indicated prevalent Mn deficiency in crop plants all over the world, and as a result yield production has been limited.

**Table 1.** Copper and manganese concentrations in the ear leaf of maize at flowering stage (BBCH 65), $mg \cdot kg^{-1}$ D.M.

| | Control | WPN | WKN | W25 | WP50 | WK50 | W100 | W100 P as PAPR |
|---|---|---|---|---|---|---|---|---|
| Cu | 3.35 c | 4.05 ab | 3.99 ab | 3.72 abc | 4.15 a | 3.48 bc | 3.61 abc | 3.90 abc |
| Mn | 19.08 b | 26.70 a | 28.47 a | 27.84 a | 31.12 a | 28.91 a | 30.36 a | 28.10 a |

*Means with the same letter are not significantly different; $\alpha = 0.05$ (Tukey's test)

Yet, Mn shortage is difficult to manage as this nutrient applied to the soil is very susceptible to rapid oxidation (Mortveld, 1994). In the present study, the chemical form of phosphorus in the fertilizer applied had no significant effect on Cu and Mn leaf concentration in maize at flowering. Correlation analysis with regard to relationships between grain yield and Mn or Cu nutritional status in maize at BBCH 65 stage showed a significant correlation for both nutrients tested. The stronger correlation was observed for manganese ($r = 0.614$) when compared with Cu ($r = 0.420$). At this growth stage, in comparison to the control, there were observed differentiated relationships: grain yield-Mn nutritional status and grain yield-Cu nutritional status, depending on the treatment. The relationships found indicate that under the conditions of intensive production, there exists a possibility to obtain grain yields considerably higher than the national average, as long as crop plants are suitably supplied with not only macronutrients, but also – micronutrients such as copper and manganese. More information on maize yields obtained is presented in the paper by Bąk and Gaj (2016).

### 3.2. Distribution of nutrients within organs of fully ripe maize

Micronutrients differ considerably with respect to distribution within plants and remobilization from plant organs (or tissues) to developing seeds (Grusak et al. 1999). In the present study, Cu contents in maize at physiological maturity (BBCH 89) varied depending on the plant organ analyzed and the treatment applied. The highest Cu concentration was observed in the leaves (Figure 1). In other maize organs examined, Cu concentration was decreasing in the following order: grain>cob cores>stems>husks. When compared to the control, mineral fertilization increased Cu concentration only in maize leaves. In the opinion of Quzounidou et al. (1996), distribution of copper in plant tissues depends on the form in which it is present in the plant, plant species, as well as plant population involved in uptake. No explicit effect of the experimental factor was observed with respect to copper concentration in maize grain. The highest Cu concentration ($2.7 mg \cdot kg^{-1}$) was observed in grain harvested from the treatment fertilized with P and K rates reduced to 25% (W25) of the optimal dose applied in W100% treatment. Grain Cu concentration observed in W25 significantly differed from the following treatments: W100, WK50,WKN, WP50 and W100 PAPR.

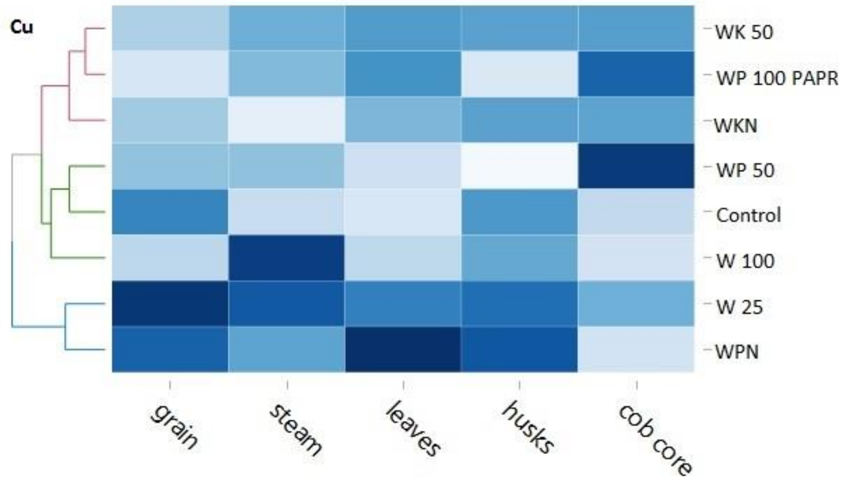


**Figure 1.** Effect of phosphorus and potassium fertilization on copper concentrations in maize parts, mg·kg$^{-1}$ D.M. (BBCH 89 - fully ripe)

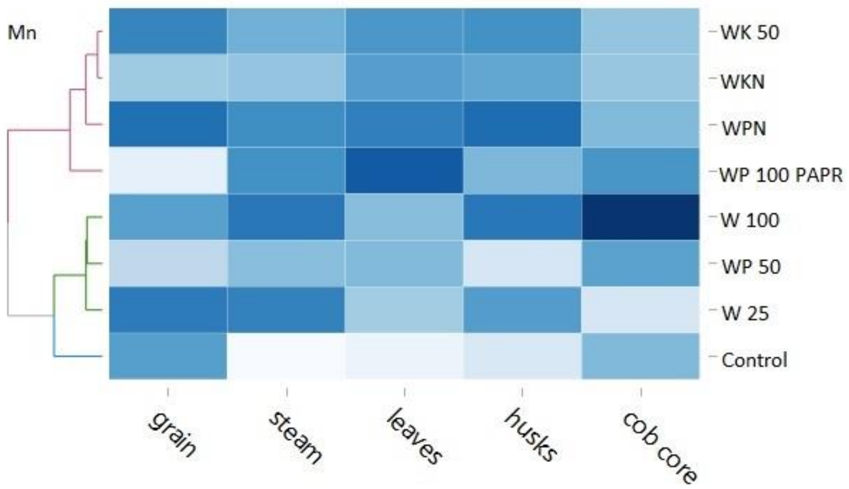


**Figure 2.** Effect of phosphorus and potassium fertilization on manganese concentrations in maize organs, mg·kg$^{-1}$ D.M. (BBCH 89 - fully ripe)

When compared to the control, significantly lower grain Cu concentration was observed in WKN treatment (no K fertilization), whereas the absence of P fertilization (WPN treatment) caused an increase of Cu and Mn in maize grain. The study by Li et al. (2007) showed an increase of Cu concentration in maize and wheat grain as well as stems under the conditions of no fertilization with P and K, respectively. Li et al. (2010) suggest that excessive availability of phosphorus or potassium in the soil decreases copper availability due to the formation of precipitates $Cu_3(PO_4)_2$ or antagonistic activity of potassium against copper, which results in Cu reduction in wheat grains. Cluster analysis performed with respect to the treatments tested and Cu contents in maize organs distinguished 3 treatment groups (3 clusters same with regard to Cu concentration): (1) control, W100, WP50; (2) WK50,WKN, W100 PAPR; (3) W25, WPN.

In fully ripe maize (BBCH 89), Mn concentration was significantly differentiated due to the effects of the experimental factor (Figure 2). Mineral fertilization caused an increase of Mn concentration in all the maize organs analyzed, except for cob cores. As in the case of copper, the highest concentration of Mn was observed in maize leaves, and the lowest – in the stem. Leaf Mn concentration ranged from 32 $mg \cdot kg^{-1}$ D.M to 55 $mg \cdot kg^{-1}$ D.M, whereas Mn concentration in maize stems was 10-fold lower. In other organs analyzed, Mn concentration decreased in the following order: husks>cob core>grain. The increase of manganese concentration in grain under P fertilization was also observed by Xia et al. (2013). Graphic illustration of Mn concentration in the examined organs of fully ripe maize depending on the experimental factor effects is presented in Figure 2. Regardless of the organ examined, the strongest relationship between the treatments with respect to analogous Mn concentrations in maize was observed in 2 treatment groups (Control, WP50, W100, W25) and (WKN, WK50, WPN, W100 PAPR).

### 3.3. Copper and manganese uptake

Total uptakes of both manganese and copper were significantly differentiated due to the effect of the experimental factor. When compared to the control treatment, mineral fertilization significantly increased accumulation of the micronutrients studied (Figure 3-4).

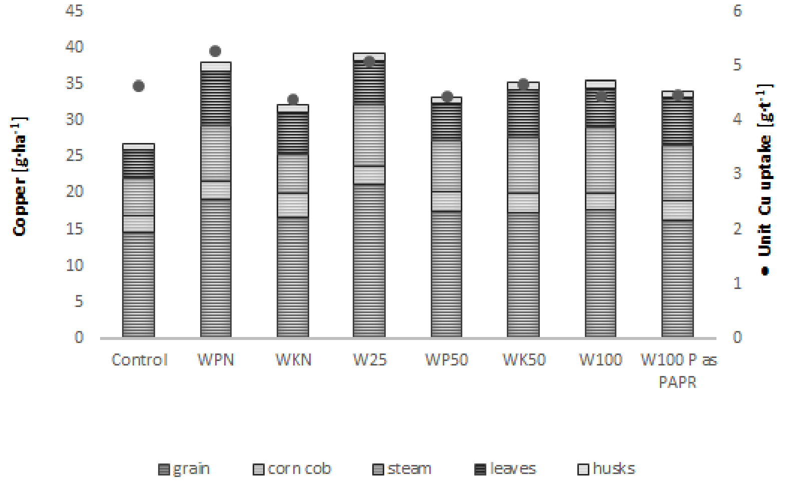


**Figure 3.** Effect of phosphorus and potassium fertilization on copper accumulation in maize organs and Cu unit uptake (BBCH 89 - fully ripe)

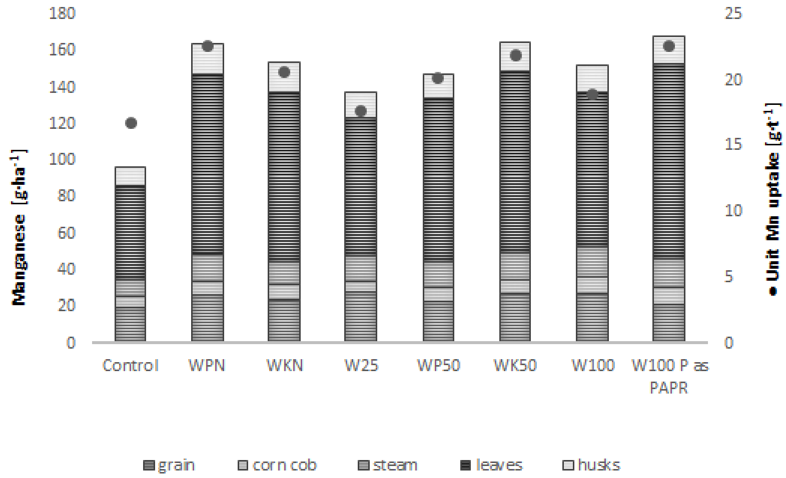


**Figure 4.** Effect of phosphorus and potassium fertilization on manganese accumulation in maize organs and Mn unit uptake (BBCH 89 - fully ripe)

However, P and K fertilization differentiated the total Cu and Mn accumulation in an ambiguous way. With respect to copper, the uppermost increase of its uptake in comparison to the control was observed in W25 treatment and amounted to 31.8%. The lowest - 23% increase of copper uptake was observed in WKN treatment. Ten-year long lack of K fertilization (WKN) reduced the total uptake both of Cu and Mn to a considerably bigger extent when compared to the lack of P fertilization (WPN). In the case of Cu, the difference (5.8 $g \cdot ha^{-1}$, i.e. 15%) between these treatments was statistically significant. WKN and WPN treatments showed no significant differences with reference to Mn uptake (9.6 $g \cdot ha^{-1}$, i.e. 5.9%). The study by Gaj et al. (2013) on triticale showed dissimilar relationships, as micronutrient accumulation in fully ripe triticale was shaped to much bigger extent by no fertilization with phosphorus or potassium. Pearson's correlation - measuring strength of association between maize grain yield and the total Cu and Mn uptake - showed significant relationships which depended on the micronutrients and treatments tested (Table 2). Statistically significant relationships between grain yield and the total accumulation of both Cu and Mn were observed in the following treatments: WPN, WP50 and W100 as PAPR. In W100 treatment, the significant relationship was observed only with respect to Cu, and in WKN, W25 and WK50 treatments – only with respect to Mn.

### 3.4. Maize grain harvest indexes

Nutrient harvest index is defined as a quotient of nutrient uptake in grain and nutrient partitioning in the crop plant. The value obtained gives indication of how efficiently the plant utilized acquired nutrients for grain production (Fageria and Baligar, 2005). Evaluation of grain harvest indexes obtained for Cu and Mn clearly indicated that regardless of the treatment tested, the majority of copper was accumulated in maize grain, whereas manganese – in the leaves (Table 3, Figures 3-4).

When compared to the control treatment, a decreasing trend was observed in copper accumulation in grain as a result of mineral fertilization. The lowest

**Table 2.** Pearson's correlation coefficients between maize grain yield and the total and partial Cu and Mn acquisition by maize organs

| Parameters | Control | WPN | WKN | W25 | WP50 | WK50 | W100 | W100 P as PAPR |
|---|---|---|---|---|---|---|---|---|
| Cu total uptake | 0.367 | 0.614* | 0.182 | 0.401 | 0.487* | 0.346 | 0.470* | 0.727* |
| Mn total uptake | 0.427 | 0.715* | 0.628* | 0.458* | 0.461* | 0.790* | 0.230 | 0.529* |
| Cu grain uptake | 0.513* | 0.694* | 0.140 | 0.589* | 0.640* | 0.318 | 0.606* | 0.833* |
| Mn grain uptake | 0.451* | 0.745* | 0.562* | 0.682* | 0.651* | 0.409 | 0.409 | 0.707* |
| Cu steam uptake | 0.055 | 0.350 | 0.142 | 0.101 | 0.076 | -0.124 | 0.139 | 0.603* |
| Mn steam uptake | -0.061 | -0.474* | -0.280 | -0.523* | -0.365 | 0.151 | -0.012 | -0.362 |
| Cu leaves uptake | 0.007 | 0.104 | 0.040 | 0.045 | -0.105 | 0.116 | 0.224 | 0.129 |
| Mn leaves uptake | 0.438 | 0.697* | 0.489* | 0.395 | 0.337 | 0.686* | 0.145 | 0.561* |
| Cu husks uptake | 0.364 | 0.187 | 0.189 | 0.150 | 0.137 | 0.301 | 0.547* | 0.510* |
| Mn husks uptake | -0.221 | -0.052 | 0.460* | -0.031 | 0.485* | 0.423 | -0.015 | -0.008 |
| Cu cob core uptake | -0.041 | 0.002 | 0.079 | 0.308 | 0.270 | 0.677* | 0.020 | -0.160 |
| Mn cob core uptake | 0.127 | -0.008 | 0.054 | 0.303 | 0.304 | 0.473* | 0.312 | -0.168 |

*p<0.05

CuHI value was obtained in W100 PAPR treatment. A significant correlation between maize grain yield and Cu accumulation was found in most of the treatment studies, except for WKN and WK50 (Table 3).

Manganese acquisition in grain expressed as harvest index MnHI ranged from 13.7 (W100 PAPR) to 20.9 (control). MnHI values obtained in the present study were analogous to those reported by other authors (Xia et al., 2013, Li et al., 2007). In the present study, a considerable portion of manganese (50 - 64% of the total uptake) was accumulated in maize leaves, which indicates low mobility of this nutrient within the plant (Figure 4). In other words, the results clearly

**Table 3.** Copper and manganese accumulation index depending on phosphorus and potassium fertilization

| Treatments | CuIH | MnIH |
|---|---|---|
| Control | 53.95 a | 20.86 a |
| WPN | 49.12 ab | 16.05 cd |
| WKN | 51.28 ab | 15.47 cd |
| W25 | 53.30 ab | 19.81 ab |
| WP50 | 51.63 ab | 15.45 cd |
| WK50 | 48.65 b | 16.28cd |
| W100 | 49.16 ab | 17.78 cd |
| W100 P as PAPR | 48.07 b | 13.69 d |

*Means with the same letter are not significantly different; $\alpha = 0.05$ (Tukey's test)

demonstrated that Mn cannot be mobilized from the leaves of maize, even though Mn is lacking in grain. The above relationship was also confirmed by Person and Rengel (1994, 1995) in the study on wheat. The question still remains whether Mn immobility in the leaves of some plant species is attributable to no exchangeable incorporation of this nutrient into high-molecular-weight compounds or structures within the cell or to the requirement for chelates in phloem loading. In the present study, significant relationships between grain yield and manganese accumulation in the leaves of fully ripe maize were found in 4 of 8 tested treatments (Table 3).

The unit uptakes of copper and manganese were differentiated by the experimental factor (Figures 3-4). When compared to the control, in all the fertilizer treatments tested, Mn unit uptake was increased and ranged from 16.7 $g \cdot t^{-1}$ to 22.7 $g \cdot t^{-1}$. At the same time, copper unit uptake ranged from 4.4 $g \cdot t^{-1}$ to 5.3 $g \cdot t^{-1}$. Of all the treatments applied, only W25 and WPN showed a significant increase of Cu unit uptake in comparison to the control. Higher values of the unit uptake of both copper and manganese were obtained in the treatment with neglected phosphorus fertilization (WPN). The form of phosphorus applied as the fertilizer significantly differentiated only manganese unit uptake – higher values of this parameter were obtained in the treatment with partially acidulated phosphate rock.

## 4. Conclusions

- The assessment of the nutritional status carried out in the ear leaf of maize at flowering (BBCH 65), showed that regardless of the treatment tested, copper concentration was below the normative values and that of manganese was in the range of the optimal values.
- The significant correlation was found between maize grain yield and copper and manganese concentrations observed in the ear leaf of maize at BBCH 65.
- In fully ripe maize (BBCH 89), of all the plant organs examined, the highest contents of copper and manganese were observed in the leaves, and the lowest - in the stems.
- Mineral fertilization significantly increased the total uptake of Cu and Mn. Regardless of the effect of the experimental factor, Cu was mainly accumulated in maize grain (50% of the total accumulation) and manganese in the leaves (50-64%).
- Ten-year-long absence of fertilization with potassium reduced the total uptake of copper and manganese to a considerably bigger extent when compared to no phosphorus fertilization within the same period of time.

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