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INFLUENCE OF LIMING AND MINERAL FERTILIZATION ON THE COPPER CONTENT IN GRAIN OF SPRING BARLEY (*HORDEUM VULGARE* L.) AND WINTER WHEAT (*TRITICUM AESTIVUM* L.) CULTIVATED ON LOESSIAL SOIL

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Abstract

The paper presents research on the copper content in grain of winter wheat and spring barley cultivated in 1986-2001, on grey-brown podzolic soils developed from loess (static fertilization experiment) underlying a field located in the Rzeszów Foothills (SE Poland). The experiment was set up by the random sub-block method, on a field under a static fertilization trial composed of a four-year crop rotation system and the NPK Mg or NPK Mg Ca fertilization system. The first variable was liming (A) and the second one consisted of different mineral fertilization variants (B). The basic level of fertilization ($N_1P_1K_1$) was 80 kg N ha^{-1}, 100 kg P_2O_5 ha^{-1} and 120 kg K_2O ha^{-1} under spring barley and 90 kg N ha^{-1}, 80 kg P_2O_5 ha^{-1}, 100 kg K_2O ha^{-1} under winter wheat. The crop rotation was the following: in 1986-1989 – potatoes, spring barley, fodder cabbage, winter wheat; in 1990-1993, 1994-1997, 1997-2001 – potatoes, spring barley, fodder sunflower, winter wheat. Mineral fertilization included NPK fertilization with constant Mg fertilization, and differentiated NPK fertilization with constant Mg and Ca (liming) fertilization. Liming was performed in 1985, 1989, 1993 and in 1997 (4 t ha^{-1} CaO). The experiment included 14 fertilization variants with 4 replications. The copper content in plants was determined by FAAS after mineralization of plant samples in a mixture of HNO_3:$HClO_4$:H_2SO_4 in the 20:5:1 ratio. Liming decreased the copper content in spring barley grain but had no statistically significant effect on the copper content in winter wheat grain. Mineral fertilization did influence the copper content winter wheat grain, but decreased it grain obtained from the plot with lower P fertilization together with NK fertilizer. However the interaction (liming x NPK fertilization) did not influence the copper content in cereal grain.

Key words: copper, liming, mineral fertilization, spring barley, winter wheat.

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WPŁYW WAPNOWANIA I NAWOŻENIA MINERALNEGO NA ZAWARTOŚĆ MIEDZI W ZIARNIE JĘCZMIENIA JAREGO (*HORDEUM VULGARE* L.) I PSZENICY OZIMEJ (*TRITICUM AESTIVUM* L.) UPRAWIANYCH NA GLEBIE LESSOWEJ

Abstrakt

Badano zawartość miedzi w ziarnie pszenicy ozimej i jęczmienia jarego uprawianych w latach 1986-2001 na glebie płowej wytworzonej z lessu, położonej na Podgórzu Rzeszowskim (południowo-wschodnia Polska). Rośliny uprawiano na stałym polu nawozowym w 4-letnim zmianowaniu z zastosowaniem nawożenia mineralnego NPK Mg i NPK Mg i Ca. Doświadczenie założono metodą bloków losowanych z podblokami. Pierwszym czynnikiem było wapnowanie (A), drugim – niezależnie od wapnowania zróżnicowane nawożenie mineralne (B). Nawożenie mineralne NPK stosowano na tle stałego nawożenia Mg oraz Mg i Ca (wapnowanie). Podstawowy poziom nawożenia ($N_1P_1K_1$) jęczmienia jarego wynosił: 80 kg N ha^{-1}, 100 kg P_2O_5 ha^{-1} i 120 kg K_2O ha^{-1}, natomiast pszenicy ozimej: 90 kg N ha^{-1}, 80 kg P_2O_5 ha^{-1} i 100 kg K_2O ha^{-1}. Doświadczenie obejmowało 4 zmianowania: w latach 1986-1989 – ziemniaki, jęczmień jary, kapustę pastewną, pszenicę ozimą, a w latach 1990-1993, 1994-1997, 1997-2001 – ziemniaki, jęczmień jary, słonecznik pastewny, pszenicę ozimą. Wapnowanie zastosowano w latach: 1985, 1989, 1993 (4 t ha^{-1} CaO). Doświadczenie obejmowało 14 obiektów nawozowych w 4 powtórzeniach. Zawartość miedzi w roślinach oznaczono metodą FAAS, po mineralizacji próbek roślin w mieszaninie HNO_3:$HClO_4$:H_2SO_4, w proporcji 20:5:1. Wapnowanie wpłynęło na zmniejszenie zawartości miedzi w ziarnie jęczmienia jarego, nie wpłynęło w sposób statystycznie istotny na zawartość miedzi w ziarnie pszenicy ozimej. Nawożenie mineralne wpłynęło na zawartość miedzi w ziarnie pszenicy ozimej, obniżając zawartość Cu w ziarnie po zastosowaniu zwiększonego nawożenia P na tle stałego nawożenia NK. Zaobserwowano, że interakcja wapnowania i nawożenia mineralnego nie wpływała na zawartość miedzi w ziarnie zbóż.

Słowa kluczowe: miedź, wapnowanie, nawożenie mineralne, jęczmień jary, pszenica ozima.

INTRODUCTION

Copper is a natural component of all soils, in which its content depends mainly on lithogenic and pedogenic factors, with the highest Cu accumulation recorded in clay sedimentary rocks (Kabata-Pendias 1996). Copper in soil can also originate from atmospheric precipitation, volcanic ash, dust created by wind erosion and from mineralization of biological substance (Nicholson et al. 2003). The copper content in soil is also shaped by anthropogenic factors. Intensive agronomy, including cultivation of high-yielding crops which require ample nutrition and fertilization, or increased yields of main and catch crops, contributes to the higher removal of copper from soils (Gembarzewski 2000, Kotecki, Kozak 2004, Nowak, Zbroszczyk 2004, Rabikowska, Piszcz 2004). As well as being an essential element for living organisms, copper is highly toxic given it appears in excess (Ruszkowska, Wojcieska-Wyskupajtys 1996). NPK and calcium fertilizers, used for soil de-acidification, are a source of trace elements (Gorlach, Gambuś 1997, Kaniuczak 1998). On the other hand, they may elevate or reduce the phytoavailability of copper by changing the pH of soil (Mercik, Stępień 2000, Bravin et al. 2009).

The uptake of copper by cereals can also be influenced by a dose and chemical form of nitrogen (Tills, Alloway 1981, Kumar et al. 1990) and phosphorus (Singh, Swarup 1982, Gunes et al. 2009) used in fertilizers. The copper content in cereal grains most often appears within a narrow range, is frequently random in character and barely depends on the Cu content in soil (Nan et al. 2002) or on soil properties – texture, organic matter, available P, K, Mg, or pH_{KCl} (Bednarek et al. 2008, Nan et al. 2002). The copper content is often more strongly correlated with a cereal species than cultivation conditions and soil management (Ciołek et al. 2012, Nambiar 1976). For example, genotypes of cereal crops with a higher protein content are more likely to present copper deficiency than those with relatively less protein in grain (Nambiar 1976).

The aim of this study has been to determine the influence of liming and mineral NPK fertilization (with constant magnesium fertilization) on the copper content in grain of spring barley and winter wheat grown in a four-crop rotation system established on podzolic soil developed from loess.

MATERIAL AND METHODS

In 1986-2001, a study on the effects of liming (A) and mineral fertilization (B) on the copper content in grain of winter wheat and spring barley grown in four-crop rotation, was carried out on a static fertilization field in Krasne near Rzeszów, in the Rzeszów Foothills (SE Poland). The podzolic soil (*Haplic luvisol*) on which the experiment was set up on was developed from loess and represented the texture of silt loam. Prior to the experiment, the soil was tested to be very acid in the plough humus layer (Ap) pH_{KCl} 3.92 and in the enrichment layer (Bt) pH_{KCl} 3.89. It was low in available phosphorus, potassium and magnesium. The total copper content of 9.10 mg kg^{-1} was within normal range, and copper forms soluble in HCl 1 mol dm^{-3} represented approximately 30% of the total copper content in soil – 2.70 mg kg^{-1} (Kaniuczak 1998).

The experiment was set up in a random sub-block design with four replicates. The first variable was liming (A_2) or its absence (A_1), while the second one consisted of mineral fertilization variants (B) with constant magnesium nutrition, regardless of liming. The following crops were grown in the rotation system: potato, spring barley, fodder sunflower, and winter wheat; in the 1986-1989 rotation, fodder cabbage replaced sunflower. Four crop rotations were included in the experiment, during which winter wheat was grown in 1987, 1991, 1995 and in 1999, while spring barley was produced in 1989, 1993, 1997 and in 2001.

The basic doses of mineral fertilizers ($N_1P_1K_1$) against constant magnesium nutrition were as follows: spring barley: N_1 = 80 kg N, P_1 = 43.6 kg P, K_1 = 99.6 kg K ha^{-1}, winter wheat: N_1 = 90 kg N, P_1 = 34.9 kg P, K_1 = 83.0 kg K ha^{-1}. The constant magnesium fertilization doses applied before sowing in each experimental sub-block in 1986-1993 were: 24.1 kg Mg ha^{-1} under potato, spring barley and winter wheat, and 72.4 kg Mg ha^{-1} under the fodder crops. From 1994, the magnesium dose was reduced to 24.1 kg Mg ha^{-1}, applied under all rotation crops. Liming with 4 t CaO ha^{-1} was performed in 1985, 1989, 1993 and in 1997, i.e. prior to establishing the experiment and after the harvest of crops completing the rotation. Mineral NPK fertilizers were applied as ammonium nitrate, triple superphosphate, potassium salt KCl (58%), magnesium sulfate, and CaO or $CaCO_3$.

The copper content in the applied mineral fertilizers varied but averaged 2.6 mg kg^{-1} in ammonium nitrate, 20.0 mg kg^{-1} in triple superphosphate, 10.5 mg kg^{-1} in potassium salt and 17.0 mg kg^{-1} in calcium carbonate (Kaniuczak 1998).

Plant material samples were collected after winter wheat and spring barley harvest. In dry plant material, copper was determined with the FAAS technique, having digested the samples in a hot mixture of concentrated acids $HClO_4$, HNO_3, and H_2SO_4 (in the 20:5:1 ratio) in a Tecator digestion system.

The results were statistically processed using two-factor variance analysis (liming, mineral NPK fertilization) and calculating the Tukey's intervals (LSD) at the significance level of $p = 0.05$.

RESULTS AND DISCUSSION

The copper content in barley and wheat grain from the fertilization treatments is shown in Tables 1 and 2. The average copper content in grain of spring barley grown on limed soil (4.82 mg kg^{-1} d.m.) was statistically significantly lower than in barley from non-limed plots (5.37 mg kg^{-1} d.m.). The copper content tended to decrease in grain from cereals provided with mineral fertilization, especially with higher N and P doses. This tendency occurred both with and without liming. The available literature most frequently indicates the ability to reduce copper phytoavailability to plants by liming. Gorlach and Gambuś (1991) as well as Kabata-Pendias (1996) reported that soil liming contributed to reduced phytoavailability of copper in most of the analyzed plants, particularly on soils containing higher levels of the element than on soils with its natural quantities. In earlier research (Kaniuczak 1998), liming only slightly increased the content of total copper in soil (7.97 mg kg^{-1}) as compared to non-limed soil (7.73 mg kg^{-1}). At the same time, it also resulted in the reduction of soluble copper, which is potentially available to plants. This undesirable development in limed soil such as a lower content of soluble copper can be confirmed by lower copper concentrations in spring barley grain: the largest found in $N_2P_2K_2$ (from 5.98 mg kg^{-1} to 4.65 mg kg^{-1}) and $N_{1.5}P_{1.5}K_{1.5}$ treatments (from 5.73 mg kg^{-1} to 4.85 mg kg^{-1}). Gorlach et al. (1983) indicated that liming did not cause any major chan-

Table 1

Content of copper in grain spring barley (mg kg^{-1} d.m.) cultivated on loessial soil (mean from 4 years)

Treatments of fertilizers (B)	A_1		A_2		Mean (B)
	mean	range	mean	range	
$N_0P_0K_0$	5.50	4.4-6.5	5.07	4.7-6.3	5.29
$N_0P_1K_1$	5.65	4.7-6.1	4.82	5.0-6.3	5.24
$N_{0.5}P_1K_1$	5.60	5.1-5.8	5.02	4.4-6.9	5.31
$N_1P_1K_1$	5.45	4.4-5.7	4.67	3.9-6.3	5.06
$N_{1.5}P_1K_1$	5.30	3.9-5.8	4.50	3.5-6.4	4.90
$N_1P_0K_1$	5.50	5.0-6.1	5.02	4.5-6.9	5.26
$N_1P_{0.5}K_1$	5.20	5.3-6.1	5.27	4.2-6.7	5.24
$N_1P_{1.5}K_1$	4.33	4.5-6.1	4.75	4.0-5.8	4.54
$N_1P_1K_0$	4.83	4.0-5.4	4.82	4.0-6.3	4.83
$N_1P_1K_{0.5}$	5.36	4.1-5.6	4.62	3.9-6.1	4.99
$N_1P_1K_{1.5}$	5.20	4.6-5.6	4.70	4.1-5.9	4.95
$N_{0.5}P_{0.5}K_{0.5}$	5.50	4.4-6.6	4.70	4.0-6.7	5.10
$N_{1.5}P_{1.5}K_{1.5}$	5.73	5.0-6.0	4.85	4.1-6.8	5.29
$N_2P_2K_2$	5.98	4.6-6.2	4.65	4.2-6.9	5.32
Mean of (A)	5.37	-	4.82	-	-
LSD	A^* = 0.36, B = ns AB = ns				

A_1 – fertilization NPK + Mg constans, A_2 – fertilization NPK +Mg, Ca constans,
LSD – lowest significant difference for: A – liming, B – mineral fertilization (irrespective of liming), AB – interaction between liming and mineral fertilization, * significant at p = 0.001, ns – differences not significant

ges in the uptake of copper by grasses, although it distinctly impeded the absorption of copper by other plants. Pikuła and Stępień (2007) observed that an improved soil reaction expressed by an increase in pH in the range from 4 to 6 lowered the content of Cu in grain more strongly on sandy than on medium heavy soil. However, the Cu accumulation decline was relatively low in comparison with other heavy metals (Zn and Cd).

Mineral nutrition (B), regardless of liming, did not raise the copper content in grain, as compared to the control. However, there was a trend (at times ambiguous) for grain to have less copper in response to higher nitrogen and phosphorus fertilization rates combined with the constant nutrition using other components.

No interaction (insignificant AB LSD) appeared between liming and mineral fertilization in shaping the copper content in spring barley grain. Nevertheless, the copper content in grain was lower in all fertilized and limed plots than in non-limed ones (Table 1). An earlier experiment (Kaniuczak 1992*b*) performed on brown soil developed from loess showed some decre-

Table 2

Content of copper in grain winter wheat (mg kg^{-1} d.m.) cultivated on loessial soil (mean from 4 years)

Treatments of fertilizers (B)	A_1		A_2		Mean (B)
	mean	range	mean	range	
$N_0P_0K_0$	3.82	2.7-4.5	3.72	2.4-4.7	3.77
$N_0P_1K_1$	4.35	2.7-6.1	4.97	4.1-6.1	4.66
$N_{0.5}P_1K_1$	4.40	3.0-6.0	3.77	2.9-5.0	4.09
$N_1P_1K_1$	3.95	2.9-5.3	3.90	3.2-5.3	3.93
$N_{1.5}P_1K_1$	3.80	2.5-5.3	4.15	3.3-5.2	3.98
$N_1P_0K_1$	3.87	3.2-5.0	3.80	3.5-5.0	3.84
$N_1P_{0.5}K_1$	3.87	2.2-5.0	4.45	3.7-5.8	4.16
$N_1P_{1.5}K_1$	3.00	2.6-3.6	3.07	2.9-3.6	3.04
$N_1P_1K_0$	3.77	3.0-4.7	4.05	2.6-6.3	3.91
$N_1P_1K_{0.5}$	3.20	2.7-3.4	3.15	2.5-3.5	3.18
$N_1P_1K_{1.5}$	3.77	3.5-3.9	4.00	2.7-5.7	3.89
$N_{0.5}P_{0.5}K_{0.5}$	4.20	3.5-4.8	4.30	3.2-5.7	4.25
$N_{1.5}P_{1.5}K_{1.5}$	3.60	3.1-3.9	2.97	2.1-3.9	3.29
$N_2P_2K_2$	3.85	3.3-4.2	3.20	2.5-4.2	3.53
Mean of (A)	3.82	-	3.82	-	-
LSD	A = ns, B* = 1.51 AB = ns				

A_1 – fertilization NPK + Mg constans, A_2 – fertilization NPK +MgCa constans,
LSD – lowest significant difference for: A – liming, B – mineral fertilization (irrespective of liming), AB – interaction between liming and mineral fertilization, * significant at p = 0.05, ns – differences not significant

ase in the copper content in spring barley grain, which could have resulted from increasing doses of nitrogen and phosphorus with constant PK and NK nutrition. Results achieved by Rabikowska (2000) on barley did not verify that mineral fertilizers had a consistent impact on Cu concentrations in grain.

The copper content in winter wheat grain is illustrated in Table 2. Liming did not remarkably affect the content of the element in the grain. The average copper content of 3.82 mg kg^{-1} remained on the same level both in limed and non-limed objects. Mineral fertilization (B), regardless of liming, raised the grain Cu content higher in the variant without nitrogen nutrition ($N_0P_1K_1$) than with a 1.5-fold increased dose combined with constant phosphorus fertilization NK ($N_1P_{1.5}K_1$). The highest rise in copper content, relative to the control, were observed for $N_0P_1K_1$ (up to 4.66 mg kg^{-1}) and $N_{0.5}P_{0.5}K_{0.5}$ (to 4.25 mg kg^{-1}) variants. These objects were not balanced in terms of N, P, and K doses, and in some cases phosphorus fertilization dominated over the nitrogen rate. Under such conditions, more copper was taken up by winter wheat. Although the research carried out by Gorlach and Gambuś (1997) showed no obvious dependence between the phosphorus and copper content in phosphate fertilizers, these authors suggest that phosphate fertilizers are a major source of copper (average content 13.9 mg Cu kg^{-1}, Unifoska 42.7 mg Cu kg^{-1}) to plants. The triple superphosphate used in the present experiment (Kaniuczak 1998) had an average content of copper equal 20.0 mg kg^{-1}, which was much higher than the Cu levels in ammonium nitrate (2.6 mg kg^{-1}) and potassium salt (10.5 mg kg^{-1}).

The results from an experiment run by Kaniuczak (1992*a*) on brown soil developed from loess indicate a decrease in the Cu content in winter wheat grain in plots supplied with increasing N doses (0-135 kg ha^{-1}) and constant PK fertilization, as well as an increased copper content resulting from the increasing doses of N (from 0 to 90 kg ha^{-1}) at a fixed ratio of other nutrients. In field experiments, Kotecki and Kozak (2004) demonstrated that increasing doses of phosphorus (from 0 to 78 kg P ha^{-1}) affected the copper content and its uptake by winter wheat. Singh and Swarup (1982) ran a pot experiment on winter wheat and concluded that phosphorus fertilization as well as nutrition with phosphorus and low nitrogen rates reduced the copper content in grain, because such fertilization regimes created favorable conditions for copper to bind within soil in the form of $Cu_3(PO_4)_2$. The application of higher nitrogen doses reduced the inhibitory effect of phosphorus on the accumulation of copper in grain. In the current study, the lowest copper concentrations in grain were found mostly in the plots with a dose of phosphorus higher than nitrogen ($N_1P_{1.5}K_1$).

The average copper content in the grain of wheat grown on different soils with balanced NPK fertilization and with no micronutrient nutrition varies between 2.3 and 4.6 mg kg^{-1} (Kulczycki, Grocholski 2004) and depends more strongly on a variety than on the level of mineral nutrition (Mikos, Styk 1989). Kaniuczak et al. (1996) determined the copper content in the range of 2.1-4.7 mg kg^{-1} in winter wheat grain originating from production fields situated in the region of the Rzeszów Foothills and characterized by different NPK levels. Several reserachers (Rachoń, Szumiło 2009, Ciołek et al. 2012) indicate that the Cu content is more dependent on a cereal variety than a cultivation system – organic and conventional farming (Ciołek et al. 2012). Also, conservation tillage compared to plough cultivation and stubble catch crop farming significantly raised the copper content in wheat grain (Kraska 2011).

The research conducted by Mercik et al. (2004) revealed that the copper content in winter wheat is hardly dependent on soil properties (C_{org} content and soil pH), although it could be significantly increased, up to 10.6 mg kg^{-1} (7.7 mg kg^{-1} for non-fertilized objects) after a treatment of soil nutrition with this element. Including the total copper content in soil and other physicochemical soil properties in a stepwise regression analysis leads to unsatisfactory predictions of the copper content in wheat grain (Nan et al. 2002, Właśniewski 2000).

The research carried out by Nowak et al. (2004) showed that the changeable soil moisture during the grain filling stage had a stronger influence on the copper content in winter wheat grain than the implementation of different crop protection techniques. Complete chemical protection of spring barley contributed significantly to the copper content, same as higher nitrogen nutrition; besides, significant differences between spring barley cultivars were detected (Nowak, Zbroszczyk 2004). Rabikowska and Piszcz (2004) observed a reduction in the Cu level in grain of wheat and barley due to increasing doses of mineral nitrogen, which in part may be explained by the dilution effect, i.e. higher yields under higher nitrogen doses. Tills and Alloway (1981) as well as Kumar et al. (1990) reported the effect of various nitrogen forms (NH_4^+, NO_3^- and NH_4NO_3) on the copper uptake by wheat and barley. Nitrogen fertilizers containing ammonium limited the copper accumulation more than those in the form of NO_3^- and NH_4NO_3. Singh and Swarup (1982) showed a significant effect of phosphorus (especially at low nitrogen doses) on the absorption of copper as $Cu_3(PO_4)_2$ in soil, which significantly reduced the concentration of Cu in winter wheat grain. The reduced Cu concentration in wheat due to phosphorus fertilization did not result from the dilution effect or inhibited translocation from roots to shoots, but from the reaction of positively charged Cu ions with negatively charged phosphate anions in soil (Gunes et al. 2009).

The average copper content in winter wheat grain (3.82 mg kg^{-1}) and spring barley (4.82-5.37 mg kg^{-1}) determined in our study is within the range of Cu concentrations in cereal grain found in Poland, which – according to Kabata-Pendias (1996) – is 2.6-6.5 mg kg^{-1} with an average concentration of 3.80 mg kg^{-1}, and – according to Moroń et al. (1992) – 4.1 mg kg^{-1} in wheat grain. Barley and wheat grain satisfies the requirements of food (standard 20 mg kg^{-1}) and feed cereals (25-50 mg kg^{-1}) (Kabata-Pendias et al. 1993). *The Commission Regulation (EC) No 1881/2006 of 19 December 2006* does not specify the maximum level of copper contamination in foodstuffs. High copper levels in cereals and cereal products rarely cause poisoning. In general, literature indicates serious copper deficiency in food rations, in which cereal products are an important source of Cu (Marzec 1996).

According to Moroń et al. (1992), the copper content in grain is a genetically coded trait, which is more difficult to change than in other parts of a plant. The metal is hardly released from soil; it accumulates mainly in roots of plants; in a contaminated environment, there is a slight increase in its content in grain (Bednarek et al. 2008, Kucharczyk, Moryl 2010). The monitoring studies conducted in parts of Poland affected by the copper industry, that is in the Głogów-Legnica copper district (Dobrzański et al. 2003) and around the Turów mine and power plant (Kucharczyk, Moryl 2010), show that the copper content in grain of wheat, within the range of 4.3-5.1 mg kg^{-1}, are low and do not pose any ecological of toxicological threat.

CONCLUSIONS

1. Liming did not have any statistically significant influence on the copper content in winter wheat grain; however, it decreased the copper content in spring barley grain.

2. Mineral fertilization, regardless of liming, did not significantly affect the copper content in spring barley grain, although it slightly diversified its content in winter wheat grain and markedly reduced the Cu content in grain after the application of a 1.5-fold higher phosphorus dose in combination with constant NK nutrition.

3. The interaction between liming and fertilization was not confirmed to have affected the copper content in the grain of spring barley and winter wheat. However, the copper content was generally lower in grain of spring barley originating from limed objects.

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