
EFFECT OF LIMING AND MINERAL FERTILIZATION ON COPPER CONTENT IN POTATO TUBERS (*SOLANUM TUBEROSUM* L.) AND GREEN MATTER OF FODDER SUNFLOWER (*HELIANTHUS ANNUUS* L.) CULTIVATED ON LOESSIAL SOIL

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Abstract

The paper presents research on the copper content in potato tubers and green matter of fodder sunflower grown in 1986-2001 on podzolic soil developed from loess (static fertilization field). The plant growing experiment was established in a randomized sub-block design on a static fertilization field in a four-year rotation system with mineral NPKMg and NPKMgCa nutrition. The rotation included potato, spring barley, fodder cabbage and winter wheat in 1986-1989, and potato, spring barley, fodder sunflower and winter wheat in 1990-2001. Mineral nutrition consisted of NPK fertilization with constant Mg and varied NPK fertilization with constant Mg and Ca nutrition (liming). Liming was carried out in 1985, 1989, 1993 and in 1997 (4 t ha⁻¹ CaO). The copper content in plants was determined with the FAAS technique after digesting plant samples in a mixture of HNO₃, HClO₄, H₂SO₄ at a 20:5:1 ratio.

A reduction in the copper level in green biomass of fodder sunflower was observed. Mineral fertilization resulted in an increase of the copper content in sunflower green matter. No interaction between liming and mineral nutrition in shaping the copper content in green biomass of fodder sunflower was recorded. The copper content in potato tubers did not depend on liming, mineral nutrition or on the interaction of these treatments. Some tendency towards decreasing the copper content in potato tubers due to liming and mineral fertilization was noticeable.

Keywords: copper, liming, mineral fertilization NPKMg, potato, fodder sunflower.

**WPLYW WAPNOWANIA I NAWOŻENIA MINERALNEGO NA ZAWARTOŚĆ
MIEDZI W BULWACH ZIEMNIAKA (*SOLANUM TUBEROSUM* L.)
I ZIEŁONEJ MASIE SŁONECZNIKA PASTEWNEGO (*HELIANTHUS ANNUUS* L.)
UPRAWIANYCH NA GLEBIE LESSOWEJ**

Abstrakt

Badano zawartość miedzi w bulwach ziemniaka i zielonej masie słonecznika pastewnego uprawianych w latach 1986-2001 na glebie płowej wytworzonej z lessu (stałe pole nawozowe). Doświadczenie z uprawą roślin założono metodą podbłoków losowanych na stałym polu nawozowym w czteroletnim zmianowaniu z zastosowaniem nawożenia mineralnego NPK Mg i NPK Mg Ca. Zmianowanie obejmowało: ziemniak, jęczmień jary, kapustę pastewną, pszenicę ozimą w latach 1986-1989 oraz ziemniak, jęczmień jary, słonecznik pastewny, pszenicę ozimą w latach 1990-2001. Nawożenie mineralne obejmowało NPK na tle stałego nawożenia Mg i zróżnicowane nawożenie NPK na tle stałego nawożenia Mg i Ca (wapnowanie). Wapnowanie zastosowano w latach: 1985, 1989, 1993, 1997 (4 t ha⁻¹ CaO). Zawartość miedzi w roślinach oznaczano metodą FAAS, po mineralizacji próbek roślin w mieszaninie HNO₃, HClO₄, H₂SO₄ w proporcji 20:5:1. Zaobserwowano zmniejszenie zawartości miedzi w zielonej biomacie słonecznika pastewnego.

Nawożenie mineralne wpłynęło na wzrost zawartości miedzi w zielonej masie słonecznika. Nie stwierdzono interakcji wapnowania i nawożenia mineralnego w kształtowaniu zawartości miedzi w zielonej biomacie słonecznika pastewnego. Zawartość miedzi w bulwach ziemniaka nie zależała od wapnowania, nawożenia mineralnego i interakcji tych zabiegów. Pod wpływem wapnowania i nawożenia mineralnego wystąpiła tendencja do zmniejszania się zawartości miedzi w bulwach ziemniaka.

Słowa kluczowe: miedź, wapnowanie, nawożenie mineralne NPKMg, ziemniak, słonecznik pastewny.

INTRODUCTION

Soil, whose fertility depends mainly on the type of bedrock, its mineral composition, texture, humus content as well as the course and intensity of soil-typological processes, is the fundamental source of microelements for plants. Anthropogenic factors, including agriculture, as well as atmospheric deposition of gaseous and particulate substances of various origin (e.g. industry, transport) can exert some remarkable impact on the chemical composition of soil (CIEĆKO, WYSZKOWSKI 2000, GORLACH, GAMBUŚ 2000, LAVADO 2006, STRĄCZYŃSKI, STRĄCZYŃSKA 2009).

Intensive agriculture, whose aim is to ensure high yields of crops characterized by high nutritional requirements and stimulated by mineral NPK fertilization, contributes to a larger discharge of micronutrients from soils (CZUBA 2000, GEMBARZEWSKI 2000), but sometimes stimulates their accumulation owing to fertilizing agents and plant protection chemicals added to soil (GORLACH, GAMBUŚ 1997, KANIUCZAK 1998). In time, this may result in a secondary reduction of yields and alterations in the chemical composition of crops.

Copper is an essential element for ensuring good plant development, and its role is most often associated with the activation of a spectrum of

enzymes enabling specific metabolic processes. Copper deficiency reduces the plant growth and yielding; on the other hand, its excessive amounts in the environment can also lead to the abnormal functioning of organisms (KARA et al. 2004, MUSILOVÁ 2009, ROGÓZ, TRĄBCZYŃSKA 2009).

Phytoavailability of microelements depends largely on the amount of their bioavailable forms in soil, soil pH, soil chemistry as well as mineral and organic fertilization (KANIUCZAK 1992, 1998, CIEĆKO, WYSZKOWSKI 2000, GORLACH, GAMBUŚ 2000, KANIUCZAK et al. 2003, BEDNAREK et al. 2006). Under natural conditions, there is a large variation of the plant content of micro-nutrients, including copper, which depends on the species and varieties of plants, their parts, soil properties and growing conditions. Among many crops, two species were chosen for the current study: edible potato, widespread in Polish agriculture, and fodder sunflower, much rarer on Polish farms. The two species differ in economic importance in Poland. Besides, they are grown for different organs.

The aim of this study has been to determine the influence of liming and mineral NPKMg fertilization against the background of constant magnesium nutrition on the copper content in potato tubers (*Solanum tuberosum* L.) and green matter of fodder sunflower (*Helianthus annuus* L.) cultivated in rotation on loessial soil.

MATERIAL AND METHODS

In 1986-2001, the research on the effects of liming (A) and mineral nutrition (B) on the copper content in potato tubers and green matter of fodder sunflower grown in a four-year rotation was carried out on a static fertilization field in Krasne near Rzeszów, situated in the Rzeszów Foothills (*Podgórze Rzeszowskie*).

Prior to the experiment, the soil was highly acid, low in available phosphorus, potassium, boron, zinc and molybdenum, but moderately rich in available magnesium, copper and manganese. The soil was developed from podzolic-type loess (*Haplic luvisol*) and contained 0.087% total N and 0.65% organic C (KANIUCZAK 1998, KANIUCZAK et al. 2011).

The experiment was set up in a random sub-block design with four replicates. The first variable factor was liming (A_2) or its lack (A_1), while the second one consisted of different doses of mineral fertilization (B) with constant magnesium nutrition. The following crops were cultivated in the rotation system: potato, spring barley, fodder sunflower and winter wheat, but in the 1986-1989 rotation cycle fodder cabbage was cultivated instead of sunflower. Potato was grown in 1988, 1992, 1996 and in 2000, while fodder sunflower was grown in three rotations, in 1990, 1994 and 1998.

Basic doses of mineral fertilizers ($N_1P_1K_1$) with constant magnesium

nutrition were as follows: potato $N_1 = 120$ kg N, $P_1 = 43.6$ kg P, $K_1 = 132.8$ kg K ha^{-1} ; spring barley $N_1 = 80$ kg N, $P_1 = 43.6$ kg P, $K_1 = 99.6$ kg K; fodder sunflower $N_1 = 100$ kg N, $P_1 = 34.9$ kg P, $K_1 = 99.6$ kg K; winter wheat $N_1 = 90$ kg N, $P_1 = 34.9$ kg P, $K_1 = 83.0$ kg K ha^{-1} ; fodder cabbage; $N_1 = 120$ kg N, $P_1 = 26.2$ kg P, $K_1 = 83.0$ kg K ha^{-1} . Constant magnesium fertilization was applied before sowing in each experimental sub-block in 1986-1993 at a 24.1 kg Mg ha^{-1} dose for potato, spring barley and winter wheat, and a 72.4 kg Mg ha^{-1} dose for fodder crops. From 1994 on, the magnesium dose was reduced to 24.1 kg Mg ha^{-1} , applied for all experimental crops. Liming with a dose of 4 t CaO ha^{-1} was used in 1985, 1989, 1993 and in 1997, prior to the experiment and after the harvest of the crop last in a rotation. Mineral fertilizers were applied in forms of ammonium nitrate, triple superphosphate, potassium salt KCl (58%), magnesium sulfate and CaO or CaCO₃.

The copper content varied in the applied mineral fertilizers and 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 samples were collected after potato and fodder sunflower (at the flowering stage) harvest. In dry plant material, copper was determined with the atomic spectrophotometric absorbance technique after digesting the samples in a hot mixture of concentrated acids HClO₄, HNO₃, and H₂SO₄ (at a 20:5:1 volume proportion) in a Tecator digestion system.

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

RESULTS AND DISCUSSION

The average copper content in potato tubers was approximately 2-fold lower (Table 1) than in sunflower green matter (Table 2). For both crops, however, it ranged between 5 and 15 mg kg^{-1} d.m., which is typical for normal Cu content at plants (KABATA-PENDIAS et al. 1993, GORLACH, GAMBÚS 2000). The main EU instrument setting the maximum levels for certain contaminants in foodstuffs is Commission Regulation (EC) No 1881/2006 of 19.12.2006. However, it does not contain standard values for copper. The content of Cu in the tested plants did not exceed 20 mg kg^{-1} d.m., which – according to KABATA-PENDIAS et al. (1993) – means they are suitable for consumption.

The copper content found in our experiment is similar to the one reported by ROGÓZ and TRĄBCZYŃSKA (2009) in potato tuber samples collected from the Wieliczka Foothills. Also DOBRZAŃSKI et al. (2003) and STRĄCZYŃSKI and

Table 1

Mean values and range of copper content in potato tubers depending on liming (A) and mineral fertilization (B) (mg kg⁻¹ d.m.)

Treatments of fertilizers	A ₁		A ₂		Mean
	mean	range	mean	range	
N ₀ P ₀ K ₀	5.87	4.55-7.70	6.30	2.50-8.50	6.09
N ₀ P ₁ K ₁	5.75	3.45-8.18	5.30	2.90-6.90	5.53
N _{0,5} P ₁ K ₁	5.63	4.10-6.90	5.35	2.80-6.90	5.49
N ₁ P ₁ K ₁	6.32	3.65-8.80	5.05	2.50-7.50	5.69
N _{1,5} P ₁ K ₁	4.90	3.40-4.30	3.97	2.60-3.30	4.44
N ₁ P ₀ K ₁	5.38	3.70-8.30	5.35	3.00-7.80	5.37
N ₁ P _{0,5} K ₁	4.71	2.80-7.30	5.24	2.75-7.50	4.98
N ₁ P _{1,5} K ₁	5.29	3.80-8.10	4.80	2.20-6.20	5.05
N ₁ P ₁ K ₀	4.72	4.15-6.70	5.42	3.10-7.00	5.07
N ₁ P ₁ K _{0,5}	5.51	2.70-8.10	5.14	3.00-6.70	5.33
N ₁ P ₁ K _{1,5}	5.47	2.88-7.30	5.06	3.85-6.30	5.27
N _{0,5} P _{0,5} K _{0,5}	5.02	3.62-8.30	4.52	3.00-6.60	4.77
N _{1,5} P _{1,5} K _{1,5}	5.24	2.76-7.80	4.59	2.45-6.70	4.92
N ₂ P ₂ K ₂	4.82	2.80-7.60	4.84	3.00-6.80	4.83
Mean of A	5.33		5.07		-
LSD <i>p</i> = 0.05	LSD _A = ns; LSD _B = ns LSD _{AB} = ns				

A₁ – NPK fertilization + Mg constant

A₂ – NPK fertilization + Mg constant, Ca constant

LSD – lowest significant difference for: A – liming, B – mineral fertilization (irrespective of liming), AB – interaction between liming and mineral fertilization

ns – differences not significant

STRĄCZYŃSKA (2009) determined similar quantities of Cu in potato tubers from soils with different contamination degrees caused by copper smelting, although MEDYŃSKA et al. (2009) reported a lower content. CIEĆKO and WYSZKOWSKI (2000), when examining the effects of NPK fertilization on the content of trace elements in potato tubers cultivated on sandy soil, achieved approximately half that amount of Cu in dry matter of tubers. The concentration coefficients calculated by these authors as a ratio of the Cu content in plants from contaminated soils to the metal content in plants from uncontaminated areas only slightly exceeded the value 1. The maximum concentration ratios (1.1) were calculated for plants from soils with a strong contamination degree, according to the IUNG criteria (KABATA-PENDIAS et al. 1993). This indicates a weak tendency towards accumulating the metal by potato tubers in contrast to potato aerial parts, where the concentration ratio reached 3.43, while the absolute value of Cu content appeared to be more than 4-fold higher. This trend to accumulate heavy metals in aerial plant parts is confirmed by the copper content in the fodder sunflower green matter found in the present study (9.4-17.1 mg kg⁻¹ d.m.). In addition, similar trends and concentrations were observed by other authors (LAVADO 2006, FÄSSLER et al. 2010).

Table 2

Mean values and range of copper content in green matter of fodder sunflower depending on liming (A) and mineral fertilization (B) (mg kg⁻¹ d.m.)

Treatments of fertilizers	A ₁		A ₂		Mean
	mean	range	mean	range	
N ₀ P ₀ K ₀	12.3	11.5-13.0	11.0	10.7-11.4	11.7
N ₀ P ₁ K ₁	15.3	14.3-16.2	13.3	10.6-16.2	14.3
N _{0.5} P ₁ K ₁	15.3	14.2-16.3	13.7	10.6-17.0	14.5
N ₁ P ₁ K ₁	12.1	11.2-12.9	12.6	10.6-14.7	12.4
N _{1.5} P ₁ K ₁	11.7	10.7-12.5	9.4	6.1-11.6	10.5
N ₁ P ₁ K ₁	13.4	12.3-14.6	10.8	9.2-12.4	12.1
N ₁ P _{0.5} K ₁	17.3	16.6-17.1	11.6	8.5-14.1	14.4
N ₁ P _{1.5} K ₁	13.4	12.5-14.1	10.7	9.2-12.5	12.0
N ₁ P ₁ K ₀	11.2	10.1-12.3	10.1	8.6-11.4	10.6
N ₁ P ₁ K _{0.5}	14.5	13.7-15.1	10.7	9.2-12.3	12.7
N ₁ P ₁ K _{1.5}	12.7	11.8-13.6	10.5	10.2-10.9	11.6
N _{0.5} P _{0.5} K _{0.5}	14.7	13.8-15.4	11.6	11.4-11.8	13.1
N _{1.5} P _{1.5} K _{1.5}	14.3	13.3-15.2	11.3	8.8-14.8	12.8
N ₂ P ₂ K ₂	15.2	14.2-16.1	11.0	8.4-14.4	13.1
Mean of A	13.8		11.3		-
LSD <i>p</i> = 0.05	LSD _A = 0.72; LSD _B = 3.32 LSD _{AB} = ns				

A₁ – NPK fertilization + Mg constant

A₂ – NPK fertilization + Mg constant, Ca constant

LSD – lowest significant difference for: A – liming, B – mineral fertilization (irrespective of liming), AB – interaction between liming and mineral fertilization

ns – differences not significant

The copper content in tubers of potato grown in non-limed and limed soils varied between the years in the range of 2.70-8.80 mg kg⁻¹ d.m. (Table 1). The course of weather conditions during particular years had a substantial impact on the uptake of elements by plants. The influence of this factor on the chemical composition of crops was also observed by others (PISULEWSKA et al. 2009, KRASKA 2011, GUGAŁA et al. 2012, KNAPOWSKI et al. 2012).

The mean copper content in potato tubers grown on non-limed soil ranged from 4.71 to 6.32 mg kg⁻¹ d.m., with an overall average content of 5.33 mg kg⁻¹ d.m. In general, liming decreased the metal content in potato tubers; an overall average Cu content was 5.07 mg kg⁻¹ ranging from 3.97 to 6.30 mg kg⁻¹ (Table 1); however, the differences between mean values were statistically insignificant. The difference between the average Cu content in green matter of fodder sunflower harvested from fields treated (11.3 mg kg⁻¹) and not treated with lime (13.8 mg kg⁻¹) was bigger and statistically significant (Table 2). Nevertheless, the copper content in green matter of fodder sunflower grown on non-limed and limed soils was somewhat less varied between years, ranging between 10.1-17.1 and 6.1-17.0 mg kg⁻¹, respectively (Table 2). The effect of soil pH and therefore liming on the content of metal elements at plants was emphasized by many authors (GORLACH, GAMBUŚ

2000, BEDNAREK et al. 2006, BRAVIN et al. 2009, MERCIK et al. 2004, ROGÓZ, TRĄBCZYŃSKA 2009). Most studies show a decline in the copper content in plants with an increasing soil pH, e.g. ROGÓZ and TRĄBCZYŃSKA (2009) found a reduction in the average copper content in potato tubers from 6.8 mg kg⁻¹ d.m. to 4.7 mg kg⁻¹ d.m. along the soil pH increasing from 5.5 to 6.5. This is the consequence of higher solubility and bioavailability of copper as the soil pH becomes lower (BRAVIN et al. 2009). CHAIGNON et al. (2002) observed better copper bioavailability at higher soil pH values around the rhizosphere in acid soils.

Both BRAVIN et al. (2009) and CHAIGNON et al. (2002) point to the influence of fertilization with nitrogen fertilizers on soil pH and copper bioavailability to plants; although usually fertilization with nitrates increases the pH of the rhizosphere, the introduction of ammonium nitrate into soil enhances its acidification and consequently copper absorption, hence the accumulation of copper in plants increases (with the exception of strongly acid soils). In the present study, limited nitrogen fertilization together with a constant dose of phosphorus and potassium (regardless of liming) resulted in a slight increase in the copper content in potato tubers (N₁ dose), while the highest dose (N_{1,5}) caused a significant decrease in the content of this element, although the differences between the mean values were statistically insignificant (Table 1). Similarly, fertilization of fodder sunflower with N_{1,5}P₁K₁ resulted in a remarkable (and statistically significant compared to N₀P₁K₁ and N_{0,5}P₁K₁ fertilization variants) reduction of yields of aerial plant parts (Table 2). It is worth noting that the highest content of Cu was characterized by potato tubers grown in the control variant (without NPK fertilization, regardless of liming) - an average of 6.09 mg kg⁻¹ d.m. Phosphorus nutrition (at constant fertilization with N₁ and K₁) as well as potassium fertilization (at regular N₁ and P₁ fertilization) did not result in any statistically significant differences in the copper content of potato tubers or green matter of fodder sunflower. Also, the use of increasing NPK doses at a constant N:P:K ratio did not univocally affect the Cu content in the yields of the two crops, although a slight decrease in the Cu content in potato tubers (Table 1) as well as an increase Cu content in the aerial parts of sunflower (Table 2) could be noticed, as compared to the variant without fertilization. CIECKO and WYSZKOWSKI (2000) and TRAWCZYŃSKI (2009) found no effect of NPK fertilization on the copper content in potato tubers. However, phosphorus fertilization is a way to immobilize heavy metals in soil and to reduce their bioavailability (GORLACH, GAMBUS 2000). This was confirmed by the research performed by GUNES et al. (2009), who reported that the concentrations of Cu and Zn in the analysed plants (including sunflower) were reduced due to phosphorus fertilization.

CONCLUSIONS

1. The copper content in potato tubers did not depend on liming, mineral nutrition or the interaction of these treatments. Under the influence of liming and mineral fertilization, a trend to reduce the copper content in potato tubers was observed.

2. There was no interaction of liming and mineral fertilization in the shaping of the content of copper in green biomass of fodder sunflower.

3. Liming significantly reduced the copper content in green biomass of fodder sunflower, whereas mineral fertilization caused an increase in the copper content in green matter of fodder sunflower.

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