

## **Influence of sulphur and multi-component fertilizer application on the content of Cu, Zn and Mn in different types of soil under maize**

## **Wpływ siarki i nawozu wieloskładnikowego na zawartość Cu, Zn and Mn w różnych typach gleb spod kukurydzy**

Barbara MURAWSKA<sup>1\*</sup>, Ewa SPYCHAJ-FABISIAK<sup>1</sup>, Wojciech KOZERA<sup>1</sup>, Tomasz KNAPOWSKI<sup>1</sup>, Szymon RÓŻAŃSKI<sup>2</sup>, Beata RUTKOWSKA<sup>3</sup> and Wiesław SZULC<sup>3</sup>

<sup>1</sup>Department of Agricultural Chemistry, Faculty of Agriculture and Biotechnology, UTP University of Science and Technology, Bydgoszcz, Poland, \*correspondence: [murawska@utp.edu.pl](mailto:murawska@utp.edu.pl)

<sup>2</sup>Department of Soil Science and Soil Protection, Faculty of Agriculture and Biotechnology, UTP University of Science and Technology, Bydgoszcz, Poland

<sup>3</sup>Agricultural Chemistry Department, Faculty of Agriculture and Biology, Warsaw University of Life Sciences - SGGW, Warsaw, Poland

### **Abstract**

The aim of the study was to determine the influence of the soil type and differential sulphur rates used with or without Basfoliar 36 Extra on the soil pH as well as the amount of available forms of copper, zinc and manganese based on the micro plots field experiment. Moreover, the relationship between the studied microelements was examined. The experiment was performed in two-factor design; the first-order factor was the soil type (Typic Hapludolls, Typic Hapludalfs, Typic Haplorthods, Typic Endoaquolls), while the second-order factor - fertilization with sulphur and compound fertilizer - Basfoliar 36 Extra. The plant tested was Rota cultivar maize. The use of sulphur and sulphur combined with Basfoliar 36 Extra changed the classification of the soils in terms of their pH. In the soils under study, as a result of the 10-years application of sulphur and/or foliar fertiliser with NPK fertilization as well as growing maize in monoculture showing a high uptake of macro- and micro-nutrients, there was reported a clear decrease in the content of zinc, copper and manganese, as compared with the initial content. With that in mind, one shall assume that growing maize in a 10-year monoculture is connected with an intensive use of soils, which can result in a clear deficit of the elements studied in soil.

**Keywords:** Basfoliar 36 Extra, fertilization, microelements, soil, sulphur

## Streszczenie

Celem badań było określenie wpływu typu gleby i zróżnicowanych dawek siarki stosowanych bez/lub z Basfoliarem 36 Extra na wartość pH gleby oraz zawartości dostępnych formy miedzi, cynku i manganu, w oparciu o doświadczenia mikropoletkowe. Ponadto określono zależności pomiędzy badanymi mikroelementami. Eksperyment przeprowadzono jako dwuczynnikowy: gdzie pierwszym czynnikiem był typ gleby ( $n = 4$ , czarnoziem, gleba płowa, gleba bielkowa, czarna ziemia), natomiast drugim - nawożenie siarką ( $S_1$ ,  $S_2$ ) bez/lub z Basfoliarem 36 Extra ( $n = 5$ ) oraz obiekt kontrolny. Rośliną testową była kukurydza odmiany Rota. Stosowanie siarki oraz siarki w połączeniu z Basfoliarem 36 Extra wpłynęło na zmiany klasyfikacji gleb pod względem ich odczynu. W wyniku 10-letniego stosowania siarki bez/lub z Basfoliarem 36 Extra na tle nawożenia NPK oraz uprawy kukurydzy w monokulturze charakteryzującej się dużym pobraniem makro i mikrośladników stwierdzono wyraźne obniżenie zawartości cynku, miedzi oraz manganu w stosunku do zawartości wyjściowej. W związku z powyższym należy przypuszczać, iż uprawa kukurydzy w 10-letniej monokulturze wiąże się z intensywnym użytkowaniem gleb, co powodować może wyraźny niedobór badanych pierwiastków glebie.

**Słowa kluczowe:** Basfoliar 36 Extra, gleba, mikroelementy, nawożenie, siarka

## Streszczenie szczegółowe

W warunkach glebowo-klimatycznych Polski kukurydza, która pobiera duże ilości makro- i mikroelementów, uprawiana jest niemal na wszystkich typach gleb, z wyjątkiem terenów górskich i podgórskich. Zatem czynnikiem, który w największym stopniu decyduje o jej produktywności jest nawożenie i zasobność gleby w przyswajalne formy składników pokarmowych. Z uwagi na ograniczenie stosowania nawozów naturalnych, wprowadzenie na rynek wysokoskoncentrowanych nawozów mineralnych, jak również zmniejszenie emisji siarki do atmosfery, obserwuje się zarówno deficyt siarki, a także niski poziom mikroelementów w glebach Polski. W związku z powyższym podjęto badania, których celem była ocena, czy i na ile zróżnicowane dawki siarki aplikowane bez/lub z Basfoliarem 36 Extra determinują zawartości przyswajalnych form miedzi, cynku i manganu oraz odczyn badanych gleb. Ponadto określono zależności pomiędzy badanymi mikroelementami. Rośliną testową była kukurydza odmiany (Rota FAO 230) uprawiana w monokulturze. Doświadczenie prowadzono w betonowych cembrach w latach 2004-2015 na terenie Stacji Badawczej Uniwersytetu Technologiczno-Przyrodniczego w Bydgoszczy zlokalizowanej w Wierzchucinku ( $17^{\circ}51'E$ ,  $53^{\circ}13'N$ ). Cembry wypełniono czterema glebami, które wg systematyki amerykańskiej (Smith et al., 1999) należą do następujących typów: Typic Hapludolls, Typic Hapludalfs, Typic Haplorthods, Typic Endoaquolls zgodnie z ich profilami genetycznymi pobranymi z pól produkcyjnych regionu Pomorza i Kujaw. Doświadczenie prowadzono w układzie dwuczynnikowym, gdzie pierwszym analizowanym czynnikiem był typ gleby ( $n = 4$ ), natomiast drugim nawożenie siarką i Basfoliarem 36 Extra ( $n = 5$ : 0,  $S_1$ ,  $S_2$ ,  $S_1 +$  Basfoliar 36 Extra,

S<sub>2</sub> + Basfoliar 36 Extra) na tle stałego nawożenia NPK (150 kg N·ha<sup>-1</sup>, 34,5 kg P·ha<sup>-1</sup>, 132 kg K·ha<sup>-1</sup>). Siarkę zastosowano doglebowo w postaci siarczanu (VI) sodu przed siewem kukurydzy, w dawce 20 kg S·ha<sup>-1</sup> (S<sub>1</sub>) oraz 40 kg S·ha<sup>-1</sup> (S<sub>2</sub>) bez/lub z Basfoliarem 36 Extra.

Stwierdzono, że stosowanie siarki bez/lub z Basfoliarem 36 Extra wpłynęło na zmianę klasyfikacji badanych gleb pod względem ich odczynu, jak również na wyraźne obniżenie zawartości cynku, miedzi oraz manganu w stosunku do zawartości wyjściowej. Należy zaznaczyć, że zawartości badanych mikroelementów były zdecydowanie niższe od średniej krajowej i zależały od typu badanych gleb. Pod względem ich zawartości można uszeregować je w następującej kolejności Mn>Zn>Cu. W zawiązku z powyższym należy przypuszczać iż uprawa kukurydzy w 10-letniej monokulturze wiąże się z intensywnym użytkowaniem gleb, co powodować może wyraźny niedobór badanych pierwiastków w glebie. W konkluzji końcowej można stwierdzić, że problem zmian zawartości mikrośladników występujących w formach przyswajalnych dla roślin w różnych typach gleb użytkowanych rolniczo powinien być rozpatrywany nie tylko z uwzględnieniem nawożenia mineralnego (NPK), ale również z uwzględnieniem aplikacji siarki, mikroelementów oraz zmianowania.

## Introduction

In Poland's soil and climate conditions, maize is cultivated on almost every type of soil, except for the mountain and piedmont areas (Książak, 2008). It uptakes large amounts of macronutrients and microelements, thus the factor determining maize productivity is soil fertilization and the soil richness in available nutrients (Barczak et al., 2009).

Till the end of the 1980's and beginning of the 1990's, sulphur appeared excessively in Poland's soils. However, at the end of the 1990's, as a result of decreased emissions of sulphur, reduced natural fertilizers usage and introducing highly concentrated mineral fertilizers to the market, sulphur and microelements deficit in Poland's soils has been observed (Szulc et al., 2004; Koncewicz-Baran and Gondek, 2010; Szulc et al., 2014). Sulphur is more often considered as an important component of fertilizers, it has been even called 'the fourth macronutrient' which can considerably determine soil quality (Oenema and Postma, 2003). In this context the research has been taken with the aim of determining the influence of the soil type and differential sulphur rates used with or without Basfoliar 36 Extra on the soil pH as well as the amount of available forms of copper, zinc, manganese and relationships between them, based on the micro-plots field experiment.

## Materials and methods

The experiment was set up in 2004 at the Experiment Station, of the University of Technology and Life Sciences in Bydgoszcz, situated at Wierzchucinek (17°51'E, 53°13'N).

The experiment was carried out in concrete wells, 0.8 m<sup>2</sup> each (micro plots), filled with four soil types according to their profile sequence of horizons, collected from the production fields of Pomerania and Kuyavian Region. The soil types examined differed in terms of their physicochemical properties (Table 1).

Table 1. Physicochemical soil properties (2004)  
Tabela 1. Właściwości fizyko-chemiczne gleby (2004)

Parameter Parametr	Unit Jednostka	Soil number Numer gleby			
		1*	2*	3*	4*
C <sub>org</sub>	g·kg <sup>-1</sup>	15.6	6.15	7.7	13.2
N <sub>t</sub>		1.3	0.63	0.81	1.25
C/N		12	10	9	11
pH <sub>KCl</sub> 2004		6.5	5.3	5.6	6.5
Soil separates <0.02 mm	%	23	8	6	26
Hh	mmol(+)-kg <sup>-1</sup>	7.2	23.5	28.4	6.8
Cu		3.44	2.02	2.88	6.97
Zn	mg·kg <sup>-1</sup>	6.23	7.57	5.07	7.92
Mn		87.22	117.89	122.4	81.96

According to Smith et al. (1999): 1\* - Typic Hapludolls, 2\* - Typic Hapludalfs, 3\* - Typic Haplorthods, 4\* - Typic Endoaquolls

Według Smith i in. (1999): 1\* - Czarnoziem, 2\* - Gleba płowa, 3\* - Gleba bielkowa, 4\* - Czarna ziemia

### Soil type and fertilization

The plant tested was Rota cultivar maize (FAO 230), cultivated in monoculture since 2004 for grain. The experiment was performed in two-factor design; the first-order factor was the soil type (n = 4: Typic Hapludolls, Typic Hapludalfs, Typic Haplorthods, Typic Endoaquolls) (Smith et al., 1999), while the second-order factor - fertilization with sulphur and Basfoliar 36 Extra (n = 5: 0, S<sub>1</sub>, S<sub>2</sub>, S<sub>1</sub> + Basfoliar 36 Extra, S<sub>2</sub> + Basfoliar 36 Extra) with fixed NPK fertilization.

Sulphur was used in a form of sodium sulphate (VI) at the rate of 20 kg S·ha<sup>-1</sup> (S<sub>1</sub>) or 40 kg S·ha<sup>-1</sup> (S<sub>2</sub>) with or without Basfoliar 36 Extra (B). The fertilizer was applied at the rate of 2 dm<sup>3</sup>·ha<sup>-1</sup>. It is a high-quality foliar compound fertilizer and provides

cereal crops, including maize, nitrogen and a full set of microelements at the following: nitrogen 36.6%, magnesium 4.3%, manganese 1.35%, copper 0.27%, iron 0.027%, boron 0.027%, zinc 0.013% and molybdenum 0.0067%.

The nitrogen fertilization was applied at the quantity of  $150 \text{ kg N}\cdot\text{ha}^{-1}$  at three rates: 1/3 pre-sowing, 1/3 top fertilization into soil, 1/3 foliar application in a form of urea solution. Phosphatic-and-potassium fertilizers were applied at the following rates and forms: as a 46% triple-superphosphate at the rate of  $34.5 \text{ kg P}\cdot\text{ha}^{-1}$  and as a 60% potassium chloride at the rate of  $132 \text{ kg K}\cdot\text{ha}^{-1}$ . Sulphur was applied to soil in form of sodium sulphate (VI) before sowing at the rate of  $20 \text{ kg S}\cdot\text{ha}^{-1}$  ( $S_1$ ) or  $40 \text{ kg S}\cdot\text{ha}^{-1}$  ( $S_2$ ) with or without Basfoliar 36 Extra (B). Agrotechnical practises, cultivation works and plant protection treatments were applied according to the maize cultivation guidelines.

### Soil analysis

Prior to the experiment in 2004 and after 10 years of research in 2015, after maize harvest, representative, composite soil samples of mixed 10 cores from 0-20 cm deep were collected from each micro plot. In the soil samples the following were determined: pH using a glass electrode in  $\text{H}_2\text{O}$  and 1M KCl (ISO 10390, 2005), Kappen's hydrolytic acidity, total nitrogen content with the Kjeldahl method after the soil sample mineralization in 95%  $\text{H}_2\text{SO}_4$  (Vapodest 50s apparatus Gerhardt, Königswinter, Germany), total organic carbon content - TOC (ISO 14235, 1998), texture by sieving and sedimentation method (ISO 11277, 2009), finally, available zinc, manganese and copper - after extraction in  $1 \text{ mol}\cdot\text{dm}^{-3}$  HCl (Rinkis method by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (apparatus: IRYS Advantage ThermoElementar Cambridge, UK).

### Statistical methods

The results were statistically analyzed with ANOVA using Statistica PL software (Tulsa, USA). To determine the effect of the experiment factors, the variance method with the Tukey's confidence intervals of half width at  $P < 0.05$ .

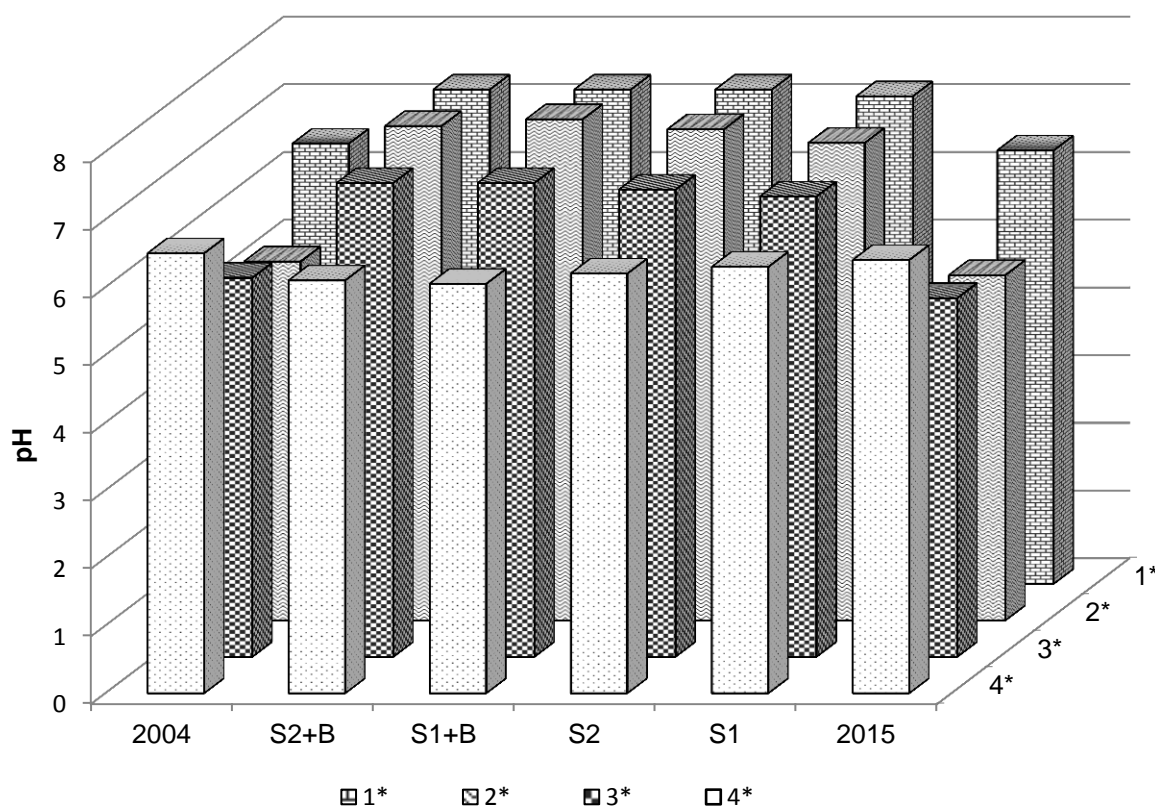
### Results and discussion

After 10 years of using sulphur and Basfoliar 36 Extra, with constant fertilization with NPK fertilizers, far going changes in soil pH have been found (Figure 1). The soil pH for Typic Hapludolls and Typic Hapludalfs changed from slightly acid to alkaline, for Typic Haplorthods from slightly acid to neutral and for Typic Endoaquolls from acid to slightly acid.

Changes in the soil pH depend on the physicochemical properties, also on the buffer properties which determine the soil resistance to acidifying factors of anthropogenic origin, including fertilization, considerably (Filipek et al., 2006). The mobility, and thus the content of microelements, e.g. copper, zinc, manganese in soil depends on the content and the quality of organic substance, soil type as well as on crop rotation

(Czekala, 2004; Gray and McLaren, 2006; Guan et al., 2011; Vodyanitskii, 2013; Rutkowska et al., 2014). It was found that the mean content of available forms of copper in the soils investigated ranged from 1.57 to 6.97 mg·kg<sup>-1</sup> (Table 2).

It was found that the contents of available copper forms in the soil samples depended on the soil type significantly. The average significantly lowest contents of that parameter were noted in Typic Hapludalfs and Typic Haplorthods; the values were 3-, 2-fold lower, as compared with the content recorded for Typic Endoaquolls, respectively. According to Domańska and Filipek (2011), acid soil pH increases the amount of copper in the soil solutions. After 10 years of fertilization there were found increased pH values of the soils, while a decrease in the Cu content only in Typic Hapludalfs and Typic Haplorthods, as compared with the initial contents. The highest contents of that microelement were noted in Typic Endoaquolls which demonstrate a high content of organic carbon (Tables 1 and 2).



1\* - Typic Hapludolls, 2\* - Typic Hapludalfs, 3\* - Typic Haplorthods, 4\* - Typic Endoaquolls  
 1\* - Czarnoziem, 2\* - Gleba płowa, 3\* - Gleba bielkowa, 4\* - Czarna ziemia

Figure 1. Changes pH<sub>KCl</sub> values of the analysed soil types  
 Rysunek 1. Zmiany wartości pH<sub>KCl</sub> badnych typów gleb

The applicable literature shows that the copper content is significantly correlated with the content of C organic and, less considerably, with the soil pH and the content of fraction <0.02 mm (Czekała, 2004, Minkina et al., 2006; Kobierski et al., 2007; Domańska and Filipek, 2011).

Table 2. Content of available copper in soil ( $\text{mg}\cdot\text{kg}^{-1}$ )  
Tabela 2. Zawartość przyswajalnej miedzi w glebie ( $\text{mg}\cdot\text{kg}^{-1}$ )

Fertilization Nawożenie	Soil type Typ gleby			
	1*	2*	3*	4*
0 (control)	3.42 <sup>Ba</sup>	1.99 <sup>Da</sup>	2.84 <sup>Ca</sup>	6.92 <sup>Aa</sup>
S <sub>1</sub>	3.68 <sup>Ba</sup>	1.66 <sup>Da</sup>	2.72 <sup>Ca</sup>	4.81 <sup>Ab</sup>
S <sub>2</sub>	3.88 <sup>Ba</sup>	1.80 <sup>Da</sup>	2.58 <sup>Ca</sup>	5.15 <sup>Aab</sup>
S <sub>1</sub> +B	3.89 <sup>Ba</sup>	1.57 <sup>Da</sup>	2.75 <sup>Ca</sup>	4.78 <sup>Ab</sup>
S <sub>2</sub> +B	3.96 <sup>Ba</sup>	1.66 <sup>Da</sup>	2.85 <sup>Ca</sup>	5.17 <sup>Aab</sup>
Mean Średnia	3.77	1.74	2.75	5.37

\* see Table 1; patrz Tabela 1

<sup>A</sup>... values denoted in the rows with the same letters do not differ significantly for  $P<0.05$

<sup>A</sup>... wartości oznaczone w wierszach tymi samymi literami nie różnią się istotnie na poziomie  $P<0.05$

<sup>a</sup>... values denoted in the columns with the same letters do not differ significantly for  $P<0.05$

<sup>a</sup>... wartości oznaczone w kolumnach tymi samymi literami nie różnią się istotnie na poziomie  $P<0.05$

The contents of available zinc in the soils varied and, on average, ranged from 4.21 to 8.76  $\text{mg}\cdot\text{kg}^{-1}$  (Table 3). A variation in the content of zinc depended both on the fertilization applied and the type of the soils which differed in physicochemical properties. On average, irrespectively of the fertilization applied, the highest contents of available zinc were noted in Typic Endoaquolls and in Typic Hapludolls, while the lowest - in Typic Haplorthods (Table 3). According to numerous authors, the Zn contents depend mostly on the content of fractions <0.02 mm and colloidal as well as organic carbon (Kabata-Pendias, 2001; Spsychaj-Fabisiak and Długosz, 2006; Gondek, 2009). The fertilization, in general, significantly lowered the contents of available forms of zinc, as compared with the content recorded for the control, except for Typic Hapludolls (Table 3).

The contents of available manganese in the soils ranged from 79.13 to 127.16 mg·kg<sup>-1</sup> (Table 4). It was found that the contents depended significantly on the soil type and the fertilization applied. Significantly higher contents were noted in Typic Hapludalfs and Typic Haplorthods, as compared with the contents assayed in Typic Hapludolls, Typic Endoaquolls.

Table 3. Content of available zinc in soil (mg·kg<sup>-1</sup>)  
Tabela 3. Zawartość przyswajalnego cynku w glebie (mg·kg<sup>-1</sup>)

Fertilization Nawożenie	Soil type Typ gleby			
	1*	2*	3*	4*
0 (control)	6.19 <sup>Ba</sup>	7.06 <sup>Aa</sup>	4.98 <sup>Cb</sup>	7.63 <sup>Ab</sup>
S <sub>1</sub>	6.7 <sup>Aa</sup>	5.98 <sup>Bb</sup>	5.94 <sup>Ba</sup>	7.09 <sup>Ac</sup>
S <sub>2</sub>	6.69 <sup>Aa</sup>	5.84 <sup>Bb</sup>	4.21 <sup>Cc</sup>	6.39 <sup>Ad</sup>
S <sub>1</sub> +B	6.47 <sup>Ba</sup>	5.03 <sup>Cc</sup>	4.46 <sup>Dc</sup>	7.25 <sup>Ac</sup>
S <sub>2</sub> +B	6.46 <sup>Ba</sup>	5.16 <sup>Cc</sup>	5.43 <sup>Cab</sup>	8.76 <sup>Aa</sup>
Mean Średnia	6.5	5.81	5	7.42

\* see Table 1; patrz Tabela 1

<sup>A</sup>... see Table 2; patrz Tabela 2

<sup>a</sup>... see Table 2; patrz Tabela 2

The fertilization (S<sub>1</sub>, S<sub>2</sub>, S<sub>1</sub> + Basfoliar 36 Extra, S<sub>2</sub> + Basfoliar 36 Extra), against the permanent NPK fertilization, also significantly modified the content of manganese in the soils (Table 4). The range of the pH value optimal for the available form of that element, ranges from 5.8 to 6.2 (Kabata-Pendias, 2001).

It is clear that a higher content of manganese was recorded for Typic Hapludalfs and Typic Haplorthods with lower pH values, as compared with the content recorded in Typic Endoaquolls and Typic Hapludolls the pH values of which ranged from pH 6.9 to 7.4. The deficit of manganese occurs due to its immobilisation in organic soils and those including carbonates. Gray and McLaren (2006) report on the amount of Mn<sup>2+</sup> increasing in the soils with a lower pH value, a high microbiological activity, mostly under anaerobic conditions which enhance the reduction processes.



The statistical analysis demonstrated significant positive correlations between the content of zinc in the soils and the content of copper ( $r = 0.65$ ). Significant negative coefficients of correlation, on the other hand, were shown for the relationship between Mn and Cu, as well as the content of Mn and Zn which were:  $r = -0.78$  and  $r = -0.45$ , respectively. Similarly there were also calculated the equations of linear regression for the above relationships presented in a graphic form in Figure 2.

The strongest relationship was found between the copper content and the content of manganese in the soils. One can calculate that an increase in the content of copper by 1 unit, namely  $1 \text{ mg}\cdot\text{kg}^{-1}$ , decreases the content of manganese in soil by about  $9.3 \text{ mg}\cdot\text{kg}^{-1}$  of soil (Niesiobędzka, 2004).

Table 4. Content of available manganese in soil ( $\text{mg}\cdot\text{kg}^{-1}$ )  
Tabela 4. Zawartość przyswajalnego magnezu w glebie ( $\text{mg}\cdot\text{kg}^{-1}$ )

Fertilization Nawożenie	Soil type Typ gleby			
	1*	2*	3*	4*
0 (control)	86.55 <sup>Ca</sup>	115.54 <sup>Bb</sup>	119.39 <sup>Aa</sup>	79.56 <sup>Da</sup>
S <sub>1</sub>	89.15 <sup>Ca</sup>	105.07 <sup>Bc</sup>	113.02 <sup>Ab</sup>	79.53 <sup>Db</sup>
S <sub>2</sub>	83.02 <sup>Cb</sup>	127.16 <sup>Aa</sup>	98.37 <sup>Bc</sup>	79.13 <sup>Db</sup>
S <sub>1</sub> +B	86.66 <sup>Ca</sup>	116.84 <sup>Ab</sup>	98.51 <sup>Bc</sup>	80 <sup>Db</sup>
S <sub>2</sub> +B	80 <sup>Cc</sup>	118.93 <sup>Ab</sup>	93.77 <sup>Bd</sup>	79.35 <sup>Cb</sup>
Mean Średnia	85.08	116.71	104.61	79.51

\* see Table 1; patrz Tabela 1

<sup>A</sup>... see Table 2; patrz Tabela 2

<sup>a</sup>... see Table 2; patrz Tabela 2

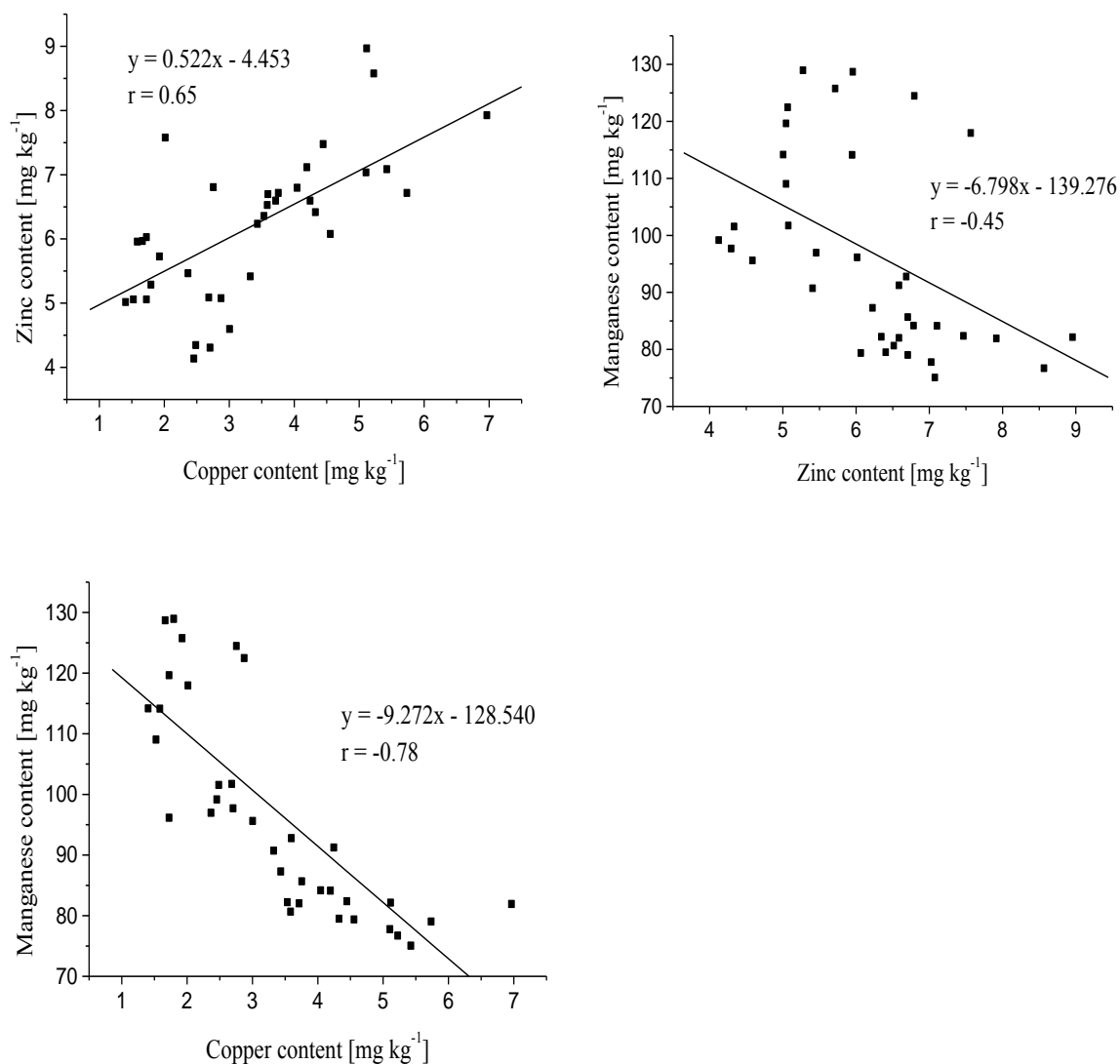


Figure 2. Relationships between the microelements

Rysunek 2. Zależności pomiędzy badanymi mikroelementami

## Conclusions

The research results show that the problem of changes in the content of available micro-nutrients (Cu, Zn, Mn) in various soil types under agricultural use where maize was grown in monoculture depended not only on mineral fertilization (NPK) but also on the application of sulphur, microelements (Basfoliar 36 Extra). The use of sulphur and sulphur combined with Basfoliar 36 Extra changed the classification of the soils in terms of their soil pH. After 10 years of research Typic Hapludalfs, Typic Hapludolls and Typic Endoaquolls can be classified as the soils with neutral and alkaline reaction, while Typic Haplorthods – slightly acid soils. In the soils under study, as a result of the 10-years application of sulphur and/or foliar fertiliser with

NPK fertilization as well as growing maize in monoculture showing a high uptake of macro- and micro-nutrients, there was reported a clear decrease in the content of zinc, copper and manganese, as compared with the initial content. The differences were, on average, 63.4%, 43.6%, 22.14%, respectively. One shall note that the content of the microelements were definitely lower than the national average and they depended on the soil type. In terms of their content, one can put them in the following order: Mn>Zn>Cu. With that in mind, one shall assume that growing maize in a 10-years monoculture is connected with an intensive use of soils, which can result in a clear deficit of the elements studied in soil.

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