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CONTENT OF AVAILABLE FORMS OF SOME MICRONUTRIENTS IN SOIL AFTER LONG-TERM DIFFERENTIATED FERTILIZATION

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Abstract

The objective of this study has been to follow modifications in the content of Cu, Zn and Mn in the topmost layer of soil which had been fertilized for many years with farmyard manure and mineral fertilizers or with mineral fertilizers alone. Soil samples were collected in 2002-2005 from a trial established in 1986 on proper brown podsolic soil, according to the random block design with four replication. The first factor consisted of organic fertilization (manure applied every two years or without manure). The second factor involved different rates of mineral fertilization. Rates of nutrients in the mineral fertilizers were identical in both experimental series – with or without manure. In each year, the same crop was grown on both fields, in a crop rotation system: sugar beet (2002), spring barley (2003), maize (2004) and spring wheat (2005). Plant available forms of nutrients were extracted from soil in 1 mol HCl dm^{-3} solution. After extraction, the content of metals was determined by atomic absorption spectrophotometry. The results underwent statistical processing using analysis of variance for a two-factor experiment.

The content of available forms of copper, zinc and manganese in soil regularly amended with manure was evidently higher than analogous concentrations determined in soil receiving only mineral fertilization since 1986. Manure most strongly improved the concentration of Cu (nearly 1.7-fold), while producing the weakest influence on manganese (over 1.3-fold more). In absolute values, however, the increase in availability of manganese was the highest, reaching on average 52 mg kg^{-1} of soil. Differentiated mineral fertilization with nitrogen or potassium as well as manganese and liming to a lesser extent than manure modified the availability of Cu, Zn and Mn in soil. Among these nutrients, nitrogen most often increased the content of plant assimilable forms of metals in soil, which may have been caused by its acidifying influence.

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Key words: manure, mineral fertilizers, available forms of Cu, Zn and Mn in soil.

ZAWARTOŚĆ PRZYSWAJALNYCH FORM WYBRANYCH MIKROELEMENTÓW W GLEBIE PO WIELOLETNIM ZRÓŻNICOWANYM NAWOŻENIU

Abstrakt

Celem badań było prześledzenie zmian zawartości Cu, Zn i Mn w wierzchniej warstwie gleby po wieloletnim nawożeniu obornikiem i nawozami mineralnymi lub wyłącznie nawozami mineralnymi. Próbki gleby pobierano w latach 2002-2005 z doświadczenia założonego w 1986 r. metodą losowanych bloków, w czterech powtórzeniach, na glebie płowej typowej. Pierwszym czynnikiem było nawożenie organiczne (obornik stosowany, co dwa lata lub bez tego nawozu), drugim – zróżnicowane nawożenie mineralne. Dawki składników pokarmowych w nawozach mineralnych były takie same w obydwu seriach doświadczenia – z obornikiem i bez tego nawozu. W każdym roku uprawiano tę samą roślinę na obydwu polach w zmianowaniu: burak cukrowy (2002 r.), jęczmień jary (2003 r.), kukurydza (2004 r.) i pszenica jara (2005 r.). Przyswajalne dla roślin formy metali ekstrahowano z gleby roztworem 1 mol $HCl \cdot dm^{-3}$. Po ekstrakcji zawartość metali oznaczono metodą absorpcyjnej spektrometrii atomowej. Otrzymane wyniki opracowano statystycznie metodą analizy wariancji dla doświadczenia dwuczynnikowego.

Zawartość przyswajalnych form miedzi, cynku i manganu w glebie nawożonej regularnie obornikiem zdecydowanie przewyższała ich ilość w glebie nawożonej wyłącznie mineralnie od 1986 r. Obornik najsilniej zwiększył koncentrację Cu (prawie 1,7-krtonie), a w mniejszym stopniu manganu (ponad 1,3-krotnie). W wartościach bezwzględnych jednak wzrost dostępności manganu był największy i wynosił średnio ponad 52 $mg \cdot kg^{-1}$ gleby. Różnicowane nawożenie mineralne azotem, potasem oraz magnez i wapnowanie w mniejszym zakresie niż obornik zmieniały dostępność Cu, Zn i Mn w glebie. Spośród wymienionych wyżej składników pokarmowych azot najczęściej zwiększał zawartość przyswajalnych form metali w glebie, co mogło być spowodowane jego zakwaszającym działaniem.

Słowa kluczowe: obornik, nawozy mineralne, przyswajane formy Cu, Zn i Mn w glebie.

INTRODUCTION

Micronutrients play highly important biochemical roles in plant organisms, therefore it is essential to consider them when planning fertilization (SPIAK 2000). Many authors claim that good supply of plants with trace elements can only occur when fertilization is managed properly (MAZUR, MAZUR 2004, RUTKOWSKA et al. 2009). On the other hand, excessive amounts of trace elements in soil can lead to their excessive uptake by plants (MCBRIDE et al. 2004, RATTAN et al. 2005, DIATTA 2008). In view of the above considerations, it seems recommendable that trace metals in soils should be monitored because of the consequences of excess metals for agriculture (quality and quantity of yields) and environment.

The purpose of this study has been to follow the effect of mineral fertilizers and manure on the content of plant available forms of Cu, Zn and Mn in soil.

MATERIAL AND METHODS

A two-factor experiment was set up in 1986 according to the random block design with four replications on proper brown podsolic soil originating from light loam (this paper contains the results obtained from 2002 to 2005). The first-order factor included manure fertilization and the second-order factor comprised differentiated mineral fertilization (Table 1). In each year, the same crop was tested on both fields (with and without manure) in the following rotation: sugar beet, spring barley, maize, spring wheat. Manure (40 t ha^{-1}) was used under sugar beet and maize, while liming was applied under sugar beet.

Table 1

Design of mineral fertilization

No.	Treatment	Sugar beet (maize)				Spring barley (spring wheat)			
		N	P	K	Mg	N	P	K	Mg
		dose, kg ha^{-1}							
1	$N_0P_0K_0$	0	0 (0)	0 (0)	0	0 (0)	0	0	0
2	$N_1P_1K_1$	60	34.9 (26.2)	66.4 (49.8)	0	30 (40)	34.9	33.2 (24.9)	0
3	$N_2P_1K_1$	120	34.9 (26.2)	66.4 (49.8)	0	60 (80)	34.9	33.2 (24.9)	0
4	$N_3P_1K_1$	180	34.9 (26.2)	66.4 (49.8)	0	90 (120)	34.9	33.2 (24.9)	0
5	$N_2P_1K_2$	120	34.9 (26.2)	132.8 (99.7)	0	60 (80)	34.9	66.4 (49.8)	0
6	$N_2P_1K_3$	120	34.9 (26.2)	199.3 (149.7)	0	60 (80)	34.9	99.7 (74.7)	0
7	$N_2P_1K_2Mg$	120	34.9 (26.2)	132.8 (99.7)	48.2 (24.1)	60 (80)	34.9	66.4 (49.8)	18.1
8	N_2P1K_2MCa	120	34.9 (26.2)	132.8 (99.7)	48.2 (24.1)	60 (80)	34.9	66.4 (49.8)	18.1

Soil samples for chemical analyses were collected from the arable horizon (0-25 cm) after harvest. Extraction of available forms of Cu, Zn and Mn was conducted using 1 mol HCl dm^{-3}. Afterwards, the ASA method was applied for determinations of the metals. The results were processed statistically (Statistica software).

RESULTS AND DISCUSSION

In the rotation system with manure, the content of Cu in soil ranged from 1.932 to 2.299 mg kg^{-1}, and in the system with mineral fertilization alone it varied from 1.151 to 1.437 mg kg^{-1} (Table 2). These data prove univocally that manure has a considerable effect on the content of available copper in soil.

MAZUR and MAZUR (2004) as well as RUTKOWSKA et al. (2009) demonstrated empirically that copper availability improved significantly after manure was

Table 2

Content of available cupper in soil ($mg \cdot kg^{-1}$)

Factor II	Factor I		Mean
	FYM	no FYM	
$N_0P_0K_0$	2.191	1.195	1.693
$N_1P_1K_1$	2.028	1.234	1.631
$N_2P_1K_1$	2.230	1.289	1.759
$N_3P_1K_1$	2.299	1.178	1.738
$N_2P_1K_2$	2.014	1.187	1.600
$N_2P_1K_3$	1.932	1.151	1.541
$N_2P_1K_2Mg$	2.037	1.289	1.663
$N_2P_1K_2MgCa$	2.127	1.437	1.782
Mean	2.107	1.245	

$LSD_{0.05}$ for the factor I – 0.059
$LSD_{0.05}$ for the factor II – 0.088
$LSD_{0.05}$ for interaction I×II – n.s.

added to soil. Differentiated mineral fertilization did not have such a strong effect as manure on modifications in the content of plant available copper in soil. The most severe reduction in Cu availability appeared when the highest dose of potassium has been introduced to soil. Nitrogen in the treatment with manure raised the abundance of available copper in soil. In turn, when mineral fertilization was not supplemented with manure, the highest N dose reduced the availability of Cu in soil. This may have been caused by its increased uptake by crops. It is also worth noticing that liming did not limit the availability of Cu. What is more, when mineral fertilization was applied exclusively, this treatment led to a significant increase in the abundance of plant available copper in soil. Such varied influence of liming has also been reported by GONDEK (1999), SZULC et al. (2007) or RUTKOWSKA et al. (2009).

The content of available zinc in soil was evidently higher than that of copper (Table 3). By analogy to Cu, the abundance of available Zn rose significantly following long-term manure fertilization.

The lowest concentration of available Zn appeared in limed soil, which was certainly caused by the increased soil reaction. Similar results can be found in other reports (FILIPEK-MAZUR, GONDEK 1999, RUTKOWSKA et al. 2009). Nitrogen improved mobility of zinc by acidifying soil. This tendency appeared most clearly in soil amended with manure. In soil receiving only mineral fertilization, the highest rate of nitrogen limited the abundance of soil in available zinc.

Table 3

Content of available zinc in soil ($mg \cdot kg^{-1}$)

Factor II	Factor I		Mean
	FYM	no FYM	
$N_0P_0K_0$	10.54	6.63	8.59
$N_1P_1K_1$	10.75	7.63	9.19
$N_2P_1K_1$	11.38	8.24	9.81
$N_3P_1K_1$	12.12	7.81	9.97
$N_2P_1K_2$	10.81	7.44	9.12
$N_2P_1K_3$	10.77	7.49	9.13
$N_2P_1K_2Mg$	10.36	6.76	8.56
$N_2P_1K_2MgCa$	9.70	5.88	7.79
Mean	10.80	7.24	

$LSD_{0.05}$ for the factor I – 0.47
$LSD_{0.05}$ for the factor II – 0.49
$LSD_{0.05}$ for interaction I×II – n.s.

Manure applied every two years considerably increased the content of available magnesium in soil, on average to over 52 mg kg^{-1}, i.e. by over 33% (Table 4). The content of Mn increased as the rate of nitrogen in the treatments with manure rose. This relationship was somewhat different in the rotation system including manure. There, the lowest four-year nitro-

Table 4

Content of available manganese in soil ($mg \cdot kg^{-1}$)

Factor II	Factor I		Mean
	FYM	no FYM	
$N_0P_0K_0$	200.56	159.63	180.09
$N_1P_1K_1$	213.34	157.51	185.43
$N_2P_1K_1$	219.83	162.51	191.17
$N_3P_1K_1$	220.23	160.67	190.45
$N_2P_1K_2$	209.38	153.16	181.27
$N_2P_1K_3$	210.68	156.92	183.80
$N_2P_1K_2Mg$	200.79	150.10	175.44
$N_2P_1K_2MgCa$	193.34	148.99	171.17
Mean	208.52	156.19	

$LSD_{0.05}$ for the factor I – 6.28
$LSD_{0.05}$ for the factor II – 7.01
$LSD_{0.05}$ for interaction I×II – n.s.

gen dose (190 kg N ha^{-1}) only slightly decreased the content of Mn, but when the average dose was applied (380 kg N ha^{-1}), the content of Mn increased. Further increase in the amount of N in mineral fertilizers (from 570 kg N ha^{-1} over four years) resulted in depressed availability of magnesium, down to the level comparable to the one in the control soil. On the one hand, nitrogen may have made the soil more acidic, thus increasing the amount of manganese which was reduced to Mn^{2+}. On the other hand, however, increased solubility of manganese could have improved its uptake by plants and, possibly, raised the loss of this element caused by leaching, which could explain the relationships found in samples of soil receiving only mineral fertilization. Potassium only very slightly modified the content of Mn in soil. In turn, magnesium and calcium depressed the accumulation of available forms of manganese in soil. Both Mg and Ca are alkaline cations, which act contrary to nitrogen. Moreover, there may have been ionic antagonisms between Mg^{2+} and Ca^{2+} versus Mn^{2+}.

The elements discussed in this paper are usually present in soil in small amounts, and are available to plants as bivalent cations, which is the form that plants can assimilate. Thus, it might be expected that they will be antagonistic to one another. However, no such dependenced were verified by our results (Figures 1,2,3). The computations (regression and correlation calculations) have shown that an increase in the content of one of the metals in soil did not depress the amounts of the available forms of another metal. On the contrary, it is highly probable that changes in amounts of Cu, Zn and Mn followed the same direction.

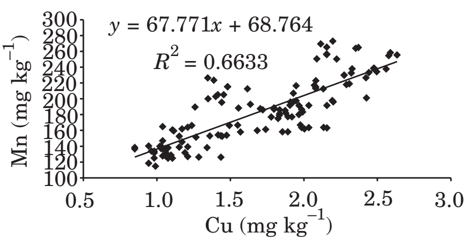

Fig. 1. Dependence between content of available forms of Cu and Mn in soil

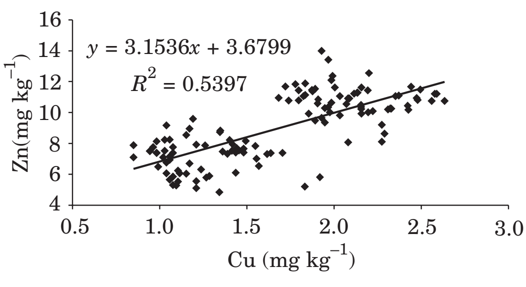

Fig. 2. Dependence between content of available forms of Cu and Zn in soil

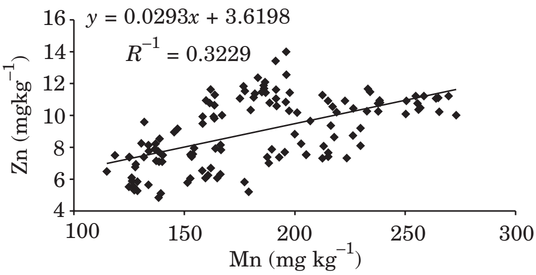

Fig. 3. Dependence between content of available forms of Mn and Zn in soil

The monitoring of the concentrations of available forms of Cu, Zn and Mn in soil is very important for two reasons. Firstly, these metals are essential for life of all living organisms, and plants must be sufficiently supplied (SPIAK 2000). Secondly, their excessive levels in soil poses a threat that plants and animals could be intoxicated (MCBRIDE et al. 2004, RATTAN et al. 2005, DIATTA 2008). The amounts of copper, zinc and manganese in soil determined in this study do not pose an ecological threat, as they range from low (Cu) to moderate (Zn and Mn) abundance. It can be hypothesised that under long-term mineral fertilization, plant may experience deficits of available copper and even regular application of FYM does not guarantee moderate abundance of soil in this element. BOWSZYS et al (2007), who investigated composted municipal waste used for fertilization, concluded that in the second year of the application of such fertilizers, zinc and magnesium in soil fell down significantly. It is worth noticing that metal elements, even when excessively accumulated in soil, do not necessarily cause their excessive accumulation in plants as organic matter strongly inhibits their uptake by plants (SAHA et al. 1999), and farmyard manure is as example of organic substance. According to GONDEK (2003), the highest differences in the content of soluble forms of trace metals are found immediately after fertilization treatments, but fertilization does not evoke their excessive mobilization. In turn, SZULC et al. (2007) found out that the concentration of available forms of Cu, Zn and Mn in soil rose under the influence of exclusive mineral fertilization, whereas manure contributed to a decrease in their soil content. In the present experiment, manure produced a stronger influence on increasing abundance of soil in Cu, Zn and Mn than mineral fertilizers, the finding that is supported by the report of MAZUR and MAZUR (2004). Nitrogen, which encourages soil acidification, can cause increased solubility of metals and their translocation to plants (DE HANN 1981). This study has demonstrated a slightly elevated content of available forms of Cu, Zn and Mn in soil under the influence of fertilization with higher nitrogen rates. However, this increase was not significant and did not create a risk of excessive uptake of the metals by plants.

CONCLUSIONS

1. Long-term fertilization with farmyard manure and mineral fertilizers or with mineral fertilizers alone does not create a risk of excessive solubility and plant availability of Cu, Zn and Mn.

2. Manure differentiated the content of available Cu, Zn and Mn in soil more strongly than mineral fertilizers.

3. Long-term mineral fertilization, which introduced to soil only macroelements can lead to soil depletion in available forms of microelements, particularly copper.

4. Manure, when was introduced to soil every other year in a long-term rotation system, it did not guarantee moderate abundance of soil in available copper.

5. Increase in the content of available forms of one of the metals (Cu, Zn or Mn) did not limit the availability of any of the other micronutrients.

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