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CHANGES IN THE CONCENTRATIONS OF AVAILABLE ZINC AND COPPER IN SOIL FERTILIZED WITH SULFUR

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Abstract

The concentrations of available forms of trace elements in the soil are mostly determined by their total content and soil processes. Soil organic matter and pH are the key factors affecting the content and mobility of heavy metals in soil. According to many authors, the toxicity of heavy metals and their availability to plants increase due to soil acidification caused by sulfur deposition. The direct and residual effect of sulfur fertilization on changes in the heavy metal content of soil has to be taken into account in environmental analyses in agricultural areas, including environmental impact assessments and predictions. The objective of this study was to determine the effect of increasing doses of sulfate and elemental sulfur on changes in the concentrations of available zinc and copper in soil samples collected at a depth of 0-40 and 40-80 cm. A three-year field experiment was conducted on Dystric Cambisols (FAO), of the granulometric composition of heavy loamy sand. Soil samples were collected from each plot, prior to the establishment of the trials, after each harvest and before sowing the consecutive crop. The soil samples were used to determine the concentrations: Zn and Cu in soil (extractions with 1 mol HCl dm^{-3}, the ratio between soil and extraction – 1:10) was determined by the AAS method using a Schimadzu AA apparatus. The results of the yields and chemical analysis of soil were processed statistically with the analysis of variance. The application of sulfate and elemental sulfur decreased the zinc content of 0-40 and 40-80 cm soil layers, as compared with soil sampled before the experiment. Sulfur fertilization had no effect on changes in copper concentrations in both soil horizons. The sulfur doses applied in the experiment did not affect the natural content of zinc and copper in the soil, and had no negative agricultural or environmental impacts.

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Key words: fertilizer, sulfate sulfur, elemental sulfur, available forms, zinc, copper, interaction.

ZMIANY ZAWARTOŚCI PRZYSWAJALNYCH FORM CYNKU I MIEDZI W GLEBIE NAWOŻONEJ SIARKĄ

Abstrakt

Procesy glebowe oraz ogólna zawartość metali ciężkich w glebie wpływają na zawartość ich form przyswajalnych. Materia organiczna wraz z pH gleby są najważniejszymi czynnikami kształtującymi zawartość i mobilność metali ciężkich w glebie. Nawożenie gleb siarką przez zakwaszenie może wpływać na zwiększenie toksyczności i biodostępności metali ciężkich dla roślin. Zbadanie bezpośrednich i następczych efektów nawożenia siarką na zmiany zawartości metali ciężkich w glebie ma znaczenie w ocenie skutków oraz monitorowania zmian przyrodniczych warunków na obszarach rolniczych. Celem pracy była ocena wpływu nawożenia wzrastającymi dawkami siarki siarczanowej i elementarnej na zmiany zawartości przyswajalnych form cynku i miedzi w dwóch poziomach gleby: 0-40 i 40-80 cm. Trzyletnie doświadczenie polowe założono na glebie brunatnej, kwaśnej o składzie granulometrycznym piasku gliniastego mocnego. Glebę do analiz chemicznych pobierano wiosną i jesienią. W próbkach glebowych oznaczono zawartość przyswajalnych form cynku i miedzi w wyciągu 1 mol HCl (stosunek gleby do roztworu ekstrakcyjnego wynosił 1:10) metodą absorpcyjnej spektrometrii atomowej. Wyniki analiz chemicznych gleby opracowano statystycznie metodą analizy wariancji. Po zastosowaniu siarki siarczanowej i elementarnej nastąpiło zmniejszenie zawartości Zn w glebie w poziomach 0-40 i 40-80 cm w porównaniu z glebą przed założeniem doświadczenia. Nawożenie siarką nie miało wpływu na zmiany koncentracji przyswajalnej formy miedzi w obu poziomach gleby. Wniesione dawki siarki nie zaburzyły naturalnej zawartości badanych mikroelementów w glebie w aspekcie rolniczo-przyrodniczym.

Słowa kluczowe: nawożenie, siarka siarczanowa, siarka elementarna, formy przyswajalne, cynk, miedź, interakcja.

INTRODUCTION

Concentrations of available forms of trace elements in soil are mostly determined by their total content and soil processes. Soil organic matter and pH are the key factors affecting the content and mobility of heavy metals in soil (Soliman et al. 1992, Martinez, Motto 2000, Borůvka, Drábek 2004, Šichorová et al. 2004, Terelak et al. 2001). Another important consideration is human activity, which contributes to soil contamination in some regions of Poland, thus leading to changes in the natural microelement content. As demonstrated by Żarczyński et al. (2011), also land management has a significant effect on the zinc and copper content of soil.

In the Province of Warmia and Mazury, average zinc and copper concentrations in agricultural soils are considerably lower than the average levels determined in other regions of Poland. The above soils have a natural (0^{o}) heavy metal content (Terelak et al. 2001).

According to many authors (NEDERLOF, RIEMSOLIJK 1995, TEMMINGHOFF et al. 1997, MOTOWICKA-TERELAK et al. 1998), the toxicity of heavy metals and their availability to plants increase due to soil acidification caused by sulfur deposition. However, some elements – including zinc and copper – precipitate as sulfides and sulfates, to produce forms that are relatively immobile in the soil profile (KABATA-PENDIAS, PENDIAS 1992).

The objective of this study was to determine the effect of increasing doses of sulfate and elemental sulfur on changes in the concentrations of available zinc and copper in soil samples collected at a depth of 0-40 and 40-80 cm.

MATERIAL AND METHODS

A three-year field experiment was conducted from 2000 to 2002, in a village in north-eastern Poland. The village is distant from larger industrial plants which emit sulfur compounds and lies far from any big cities. The concentration of sulfur in the soil were not caused by human activity.

The trial was set up on Dystric Cambisols (FAO), of the granulometric composition of heavy loamy sand. The initial soil had the following properties: $pH_{(KCl)}$ = 5.30, mineral nitrogen 24.0, sulphate sulfur 4.10, available phosphorus 34.5 and potassium 110.0 mg kg^{-1} of soil. The annual rates of sulphate sulfur (SO_4^{2-}-S) and elemental sulfur (S^{-0}-S) were: S_1 – 40, S_2 – 80 and S_3 – 120 kg ha^{-1}. Air-dry soil was passed through a 1 mm mesh sieve.

The permanent experiment was established in a random block design and consisted of eight fertilization treatments with four replications: 1) unfertilized control, 2) NPK, 3) NPK + S_1-SO_4, 4) NPK + S_2-SO_4, 5) NPK +S_3-SO_4, 6) NPK +S_1-S^0, 7) NPK +S_2-S^0, 8) NPK +S_3-S^0.

Nitrogen in the form of ammonium nitrate or ammonium sulphate, phosphorus in the form of triple superphosphate, potassium in the form of potassium salt of 60% or in the form of potassium sulphate, sulfur in the form of potassium sulphate and ammonium sulphate supplementation as well as in the form of elemental sulfur. The NPK rates (Table 1) depended on the crop species and soil fertility. The experiment did not apply the soil fertilization microelements.

Soil samples were collected from each plot, at 0-40 and 40-80 cm depths, prior to the establishment of the trials, after each harvest and before sowing the consecutive crop. Air-dry soil was passed through a 1 mm mesh sieve. The soil samples were used to determine the concentrations: Zn and Cu in soil (extractions with 1 mol HCl dm^{-3}, the ratio between soil and extraction – 1:10) was determined by the AAS method using a Schimadzu AA apparatus.

Table 1

Applied doses of NPK in the experiment

Year	(kg ha^{-1})		
	N	P	K
2000	200.0	52.5	180.0
2001	160.0	60.0	183.0
2002	90.0	80.0	111.0

The results of the yields and chemical analysis of soil were processed statistically with the analysis of variance for a two-factor experiment in a random block design, using the form of sulfur as factor a and rate of sulfur as factor b. Additional statistical analyses were performed with the software package Statistica 6.0 PL, to carry out analysis of regression with Duncan's tests with an aim of determining statistical differences between sets of data.

RESULTS AND DISCUSSION

A three-year field experiment was carried out to determine the effect of fertilization with sulfate or elemental sulfur at a dose of 40, 80 and 120 kg ha^{-1} on the zinc and copper content of the 0-40 cm and 40-80 cm soil horizons. Before the experiment, zinc concentrations ranged from 15.65 to 17.00 mg kg^{-1} in the 0-40 cm soil layer, and from 5.80 to 7.60 mg kg^{-1} in the 40-80 cm soil layer.

In the autumn, after cabbage harvest, considerable changes were noted in the zinc content of the 0-40 cm horizon, which reached 3.82-16.18 mg kg^{-1} (Table 2). The application of both sulfur forms led to a substantial decrease in zinc levels, compared with the NPK treatment. Sulfate and elemental sulfur applied at 80 kg contributed to a higher increase in the zinc content of soil, in comparison with other sulfur treatments. After cabbage harvest, zinc concentrations at the depth of 40-80 cm (Table 3) were significantly affected by sulfur form and dose. Increasing sulfur doses (in particular 120 kg ha^{-1} S-S^{-0}) led to an increase in the zinc content of soil.

In the spring, before sowing onion seeds, zinc concentrations in the 0-40 cm horizon (Table 2) decreased substantially, relative to the corresponding treatments before the experiment. The sulfur form had no significant influence on changes in the zinc content of soil. The sulfur doses applied in the experiment contributed to an increase in soil zinc concentrations, compared with the NPK treatment. The only exception was the treatment fertilized with 80 kg ha^{-1} S-S^{0}.

Table 2

Effect of different rates and forms of sulphur on the content of zinc in soil at 0-40 cm depth (mg Zn kg^{-1} soil)

Treatments	Before experiment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	17.00	7.58	6.54	4.50	8.26	2.92
NPK	16.18	16.18	4.06	7.54	6.32	2.95
NPK+ S_1-SO_4^{2-}	16.61	6.61	4.78	14.12	11.62	3.16
NPK+ S_2-SO_4^{2-}	15.65	11.65	10.46	11.28	5.36	3.44
NPK+ S_3-SO_4^{2-}	16.15	6.15	8.87	6.92	7.11	3.94
NPK+S_1-S^{-0}	15.89	5.89	9.08	4.72	6.60	3.69
NPK+S_2-S^{-0}	16.12	10.12	3.33	5.13	8.15	3.30
NPK+S_3-S^{-0}	15.82	3.82	7.25	9.17	11.81	3.99
LSD-$_{0.05}$						
a	n.s	1.4550	n.s.	1.7576	n.s.	0.2754
b	n.s.	n.s.	1.5894	2.4856	n.s.	n.s.
a x *b*	n.s.	2.9100	2.2478	3.5152	n.s.	n.s.

SO_4^{2-} – sulphate sulphur; S^0 – elementary sulphur; S_1– 40 kg h^{-1}, S_2– 80 kg ha^{-1}, S_3– 120 kg ha^{-1}; *a* – form of sulphur; *b* – dose of sulphur; *a* x *b* interaction
n.s. – non-significant difference

In the autumn, after onion harvest (Table 2), the zinc content of the 0-40 soil layer was significantly affected by the sulfur form and dose. Zinc levels increased considerably in treatments fertilized with 40 and 80 kg ha^{-1} S-SO_4^{2-}. Sulfate exerted a stronger effect than elemental sulfur.

In the 40-80 cm soil layer (Table 3), zinc concentrations increased considerably compared with the initial levels and the corresponding treatments in previous years. This trend was particularly noticeable after the application of 120 kg sulfate and elemental sulfur.

In the spring, before spring barley sowing, zinc levels tended to increase in the 0-40 cm horizon (Table 2) as a result of soil fertilization with increasing elemental sulfur doses. Neither the sulfur form nor its dose had a significant effect on the zinc content of soil. A similar trend was observed in the 40-80 cm soil layer (Table 3).

At the end of the study, zinc concentrations in the 0-40 cm soil layer ranged from 2.92 to 3.99 mg kg^{-1}, irrespective of sulfur doses, and they were generally considerably lower than in the corresponding treatments in the first and second year of the study. This could be due to increased bioavailability of zinc. KAYSER et al. (2001) demonstrated that the application of elemental sulfur increased zinc solubility in the soil and utilization by plants. KAYA et al. (2009) found that the application of elemental sulfur and sulfur-

Table 3

Effect of different rates and forms of sulphur on the content of zinc in soil at 40-80 cm depth (mg Zn kg^{-1} soil)

Treatments	Before experiment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	6.72	5.72	-	6.00	1.30	1.94
NPK	6.51	3.51	-	6.80	1.80	2.32
NPK+ S_1-SO_4^{2-}	6.12	3.12	-	6.91	1.13	2.08
NPK+ S_2-SO_4^{2-}	5.99	5.99	-	6.00	1.30	1.75
NPK+ S_3-SO_4^{2-}	5.80	5.30	-	10.27	1.66	1.69
NPK+S_1-S^{-0}	7.50	6.77	-	7.42	1.59	1.57
NPK+S_2-S^{-0}	6.30	7.30	-	8.68	1.36	1.79
NPK+S_3-S^{-0}	7.60	9.60	-	18.54	1.70	1.65
LSD-$_{0.05}$						
a	n.s	1.046		1.640	n.s.	0.210
b	n.s.	1.479		2.319	n.s.	n.s.
a x *b*	n.s.	2.092	-	3.280	n.s.	n.s.

Explanations see Table 2

containing waste resulted in a decrease in soil pH, but it also increased the concentrations of nutrients available to plants, such as Zn, Cu and Mn. Different results were reported by MODAISHSH et al. (1989) and ABDOU et al. (2011) who did not observe an increase in zinc availability to plants as a result of elemental sulfur fertilization.

Zinc concentrations in soil samples collected at the depth of 40-80 cm were significantly affected only by a sulfur dose. Sulfate (in particular at 40 kg ha^{-1}) exerted a stronger effect than elemental sulfur on the soluble zinc content of soil. Zinc depletion was noted in comparison with soil samples collected before the experiment and after the first and second year of the study.

Before the experiment, the copper content of the 0-40 cm soil layer was similar in all treatments and tended to increase in the treatment with a single dose of elemental sulfur. In the 40-80 cm horizon, copper levels ranged from 1.00 to 1.26 mg kg^{-1}. In the autumn, after cabbage harvest, the copper content of the 0-40 cm soil layer remained at a stable level in all treatments (Table 4). Neither the sulfur form nor its dose had a significant effect on changes in copper concentrations, which tended to increase in the treatment with a single dose of elemental sulfur. The experimental factors had no significant influence on changes in copper concentrations in the 40-80 cm horizon (Table 5).

Table 4

Effect of different rates and forms of sulphur on the content of copper in soil at 0-40 cm depth (mg Cu kg^{-1} soil)

Treatments	Before experiment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	1.80	1.63	1.82	1.72	1.62	1.71
NPK	1.90	1.65	1.59	1.44	1.61	1.62
NPK+ S_1-SO_4^{2-}	1.90	1.75	1.98	1.80	1.82	1.56
NPK+ S_2-SO_4^{2-}	1.80	1.77	1.85	1.82	1.87	1.78
NPK+ S_3-SO_4^{2-}	1.76	1.76	1.57	1.60	1.70	1.56
NPK+S_1-S^{-0}	2.00	1.97	1.86	1.66	1.71	1.53
NPK+S_2-S^{-0}	1.50	1.61	1.55	1.72	1.66	1.58
NPK+S_3-S^{-0}	1.60	1.54	1.67	1.64	1.68	1.7
$LSD_{0.05}$ *a* *b* *a* x *b*	 n.s n.s. 0.299	 n.s. n.s. 0.299	 0.091 n.s. 0.183	 n.s. 0.147 0.208	 n.s. 0.102 0.144	 n.s. n.s. n.s.

Explanations see Table 2

Table 5

Effect of different rates and forms of sulphur on the content of copper in soil at 40-80 cm depth (mg Cu kg^{-1} soil)

Treatments	Before experiment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	1.20	1.15	-	1.07	1.12	0.76
NPK	1.00	1.00	-	0.93	1.04	1.15
NPK+ S_1-SO_4^{2-}	1.11	1.05	-	1.00	0.88	0.76
NPK+ S_2-SO_4^{2-}	1.15	1.15	-	0.86	0.96	0.71
NPK+ S_3-SO_4^{2-}	1.20	1.18	-	1.16	1.28	0.89
NPK+S_1-S^{-0}	1.26	1.21	-	0.95	1.13	1.13
NPK+S_2-S^{-0}	1.04	0.96	-	0.85	0.89	0.70
NPK+S_3-S^{-0}	1.00	1.00	-	0.94	1.01	0.76
$LSD_{0.05}$ *a* *b* *a* x *b*	 n.s n.s. n.s.	 n.s. n.s. n.s.	 -	 n.s. n.s. n.s.	 n.s. n.s. n.s.	 n.s. n.s. n.s.

Explanations see Table 2

In the spring, before sowing onion seeds, only the sulfur form had a significant effect on changes in the copper content of the 0-40 cm soil layer. Sulfate, compared with elemental sulfur, caused a significant increase in copper concentrations. This could have resulted from changes in soil pH. Sulfur decreases soil pH and increases the solubility, availability and mobility of heavy metals (Tichý et al. 1997, Seidel et al. 1998, Kayser et al. 2000, Cui et al. 2004, Martinez et al. 2000). The effect of soil pH on heavy metal mobility can be expressed as a solubility product – a decrease in soil pH by one unit causes a 100-fold increase in the potential solubility of heavy metals. In soils contaminated by several heavy metals, the so-called salt effect is observed – the presence of one ion enhances the activities of the remaining ions, thus increasing the bioavailability of heavy metals (Motowicka-Terelak, Terelak 1998).

In the autumn, after onion harvest, sulfur fertilization increased the copper content of the 0-40 cm soil layer, compared with the NPK treatment. $S\text{-}SO_4^{2-}$ applied at 40 and 80 kg ha^{-1} led to an increase in copper concentrations, in comparison with the remaining sulfur doses. Sulfur form had no significant influence on copper levels. Increasing doses of sulfate and elemental sulfur had no significant effect on the copper content of soil samples collected at a depth of 40-80 cm (Table 5).

In the spring of the third year of the study, copper concentrations in the 0-40 cm horizon ranged from 1.61 to 1.87 mg kg^{-1}, regardless of sulfur forms (Table 4). The copper content of soil fertilized with 40 and 80 kg ha^{-1} $S\text{-}SO_4^{2-}$ increased, similarly as in the first year of the experiment. The application of different forms and doses of sulfur had no significant impact on copper concentrations in the 40-80 cm soil layer (Table 5), which increased slightly relative to the corresponding treatments in the fall of 2001.

At the end of the experiment, copper concentrations in the 0-40 cm soil layer were comparable, irrespective of sulfur forms and doses. A minor decrease in the copper content was noted compared with soil samples collected before the experiment. A similar trend was observed in the 40-80 cm horizon, which could have been due to the copper uptake by plants. (Skwierawska et al. 2008b). Kaya et al. (2009) reported that increased application of elemental sulfur led to a significant increase in the average copper content of plants. In our study, sulfur fertilization had no significant effect on changes in the copper content of soil at the depths of 0-40 and 40-80 cm throughout the experiment.

CONCLUSIONS

1. The application of sulfate and elemental sulfur decreased the zinc content of the 0-40 and 40-80 cm soil layers, as compared with soil sampled before the experiment.

2. Sulfur fertilization had no effect on changes in copper concentrations in both soil horizons.

3. The sulfur doses applied in the experiment did not affect the natural content of zinc and copper in the soil, and had no negative agricultural or environmental impacts.

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