THE EFFECT OF SULFATE AND ELEMENTAL SULFUR APPLICATION ON MODIFICATION OF CONCENTRATIONS OF MANGANESE AND LEAD IN SOIL

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A b s t r a c t

Soil acidification due to sulfur fertilization can produce an indirect result such as increased solubility and mobility of heavy metals in soil, thus affecting availability to plants of these elements derived from both natural and man-made resources. The purpose of this paper has been to explore the effect of incremental doses of sulfate and elemental sulfur on changes in the natural content of easily soluble forms of manganese and lead in two soil horizons: 0–40 and 40–80 cm. A three-year field experiment was set up on brown, acid soil with the texture of heavy loamy sand. Soil for chemical analyses was sampled in spring and autumn. Soluble forms were extracted from soil with 1 mol HCl dm^{-3} solution and their concentrations were determined with the atomic absorption spectrophometric method. Throughout the whole experiment, the dose of 40 kg ha^{-1} S-SO^{2-}_4 induced higher concentrations of manganese in soil in the 0–40 cm layer compared to the other fertilization treatments. During the three years of the field trials, the application of sulfate sulfur and elemental sulfur to soil tended to cause a small increase in the soil content of lead soluble in 1 mol HCl dm^{-1} in the 0–40 cm soil depth compared to the soil before the experiment. The concentrations of manganese and lead in soil in the 40–80 cm layer did not depend much on the form and dose of sulfur introduced to soil.

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WPŁYW STOSOWANIA SIARKI SIARCZANOWEJ I ELEMENTARNEJ NA ZMIANY ZAWARTOŚCI MANGANU I OŁOWIU W GLEBIE

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Abstrakt

Zakwaszenie gleby przez nawożenie siarką może pośrednio przyczyniać się do zwiększania rozpuszczalności i mobilności metali ciężkich w glebie, a tym samym ich dostępności dla roślin zarówno ze źródeł naturalnych, jak i antropogenicznych. Celem przedstawionej pracy było zbadanie wpływu wzrastających dawek siarki siarczanowej i elementarnej na zmiany naturalnej zawartości łatwo rozpuszczalnych form manganu i ołowiu 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. Formy rozpuszczalne ekstrahowano z gleby roztworem 1 mol HCl dm^{-3}, a ich zawartość oznaczono metodą absorpcyjnej spektrometrii atomowej. Przez cały okres trwania doświadczenia dawka 40 kg ha^{-1} S-SO$^{2-}_4$ powodowała zwiększenie koncentracji manganu w glebie w poziomie 0–40 cm w odniesieniu do pozostałych obiektów nawozowych. W ciągu 3 lat badań stosowanie siarki siarczanowej i elementarnej wpłynęło na ogół na niewielkie zwiększenie zawartości ołowiu rozpuszczalnego w 1 mol HCl dm^{-1} w glebie, w warstwie 0–40 cm, w porównaniu z glebą przed założeniem doświadczenia. Zawartość manganu i ołowiu w glebie w warstwie 40–80 cm nie zależała w większym stopniu od zastosowanej formy i dawki siarki.

Introduction

Soils under arable fields in the Province of Warmia and Mazury are characterized by moderate concentrations of trace elements, much below the average amounts in whole Poland. Usually, they have the natural (0°) content of heavy metals (TERELAK et al. 2001). However, predicting the extent of their potential mobilization is a complex problem, as the process is governed by soil-specific and environmental conditions as well as human activity. Soil reaction, for example, has an essential influence on the solubility and speciation of heavy metals, especially in soil solution (NAIDU et al. 1998, MÜHLBACHOVÁ et al. 2005). Soils that have an alkaline character and high pH are more likely to suffer from a deficit of microelements, which is manifested by poor crop yields, low effectiveness of fertilizers and high sensitivity of plants to diseases and pests (MALAKOUTI 2008). Soil acidification can stimulate the toxic nature of heavy metals and their phytoavailability (NEDERLOF and RIEMSOLIJK 1995, TEMMINGHOFF et al. 1997). KAYSER et al. (2000) as well as KAYSER et al.

(2001), who share the above view, demonstrated experimentally that when elemental sulfur had been incorporated into soil, the soil pH decreased while the solubility of heavy metals in soil increased. Among some disturbing effects of soil contamination with sulfur are the elevated solubility of manganese and mobilization of trace elements derived from both natural and anthropogenic pools (SCHWARZ et al. 2012).

The translocation of lead in the soil environment depends on the soil texture. Typically, strong adsorption on iron hydroxides and soil colloids inhibits the mobility of lead, which nonetheless undergoes biomagnification and can easily enter a trophic chain (KABATA-PENDIAS 1992, MARTINEZ et al. 2000). KOS et al. (2003) did an experiment which proved that soil solutions either did not contain or else had very small amounts of lead forms which were directly available to plants because lead tends to form permanent complexes with soil's organic matter. Soil amendment with chelates improves the bioavailability of lead, thus increasing the phytoextractibility of this element. The presence of organic matter in soil, soil sorption properties and soil acidification are important factors which influence the sorption and desorption of lead (MA et al. 2010).

The purpose of the experiment discussed in this paper has been to investigate the effect of increasing doses of sulfate and elemental sulfur on changes in the content of lead and manganese soluble in 1 mol HCl in the soil layers 0–40 and 40–80 cm deep.

The analyzed soil samples originated from the depths of 0–40 cm and 40–80 cm because of the underlying assumption of the experiment, which was to trace the migration of lead and magnesium downwards the soil profile.

Materials and Methods

A three-year field experiment was conducted from 2000 to 2002, in North--East 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 soil samples were used to determine soil pH in 1 mol KCl (the ratio between soil and extraction –1:2.5); total sulfur (Butters, Chenery 1959) and S-SO_4^{2-} with

the turbidimetric method (the ratio between soil and extraction 1:3); N-NO$_3^-$ by colorimetry using phenyl disulphonic acid (the ratio between soil and extraction 1:5); N-NH$_4^+$ was determined using Nessler's reagent (the ratio between soil and extraction 1:5); available phosphorus and potassium was determined with Enger Riehm's method (DL) – (the ratio between soil and extraction 1:50).

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. The NPK rates depended on the crop species and soil fertility. The plants chosen for the trials demonstrate different degrees of sensitivity to sulfur deficit and excess in soil (Table 1). It was predicted that while testing the chosen doses of sulfur it would be possible to find which stimulated crop yields and which caused a demonstrably negative response of the crops.

Table 1

Applied doses of NPK in the experiment

Experimental crops	Year	kg ha^{-1}		
		N	P	K
Head cabbage *Brassica oleracea var capitata alba*	2000	200.0	52.5	180.0
Common onion *Allium cepa var. cepa*	2001	160.0	60.0	183.0
Spring barley *Hordeum sativum var nutans*	2002	90.0	80.0	111.0

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.

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. Analyzed soil samples originated from the depths of 0–40 cm and 40–80 cm because of the underlying assumption of the experiment, which was to trace the migration of lead and magnesium downwards the soil profile. The soil samples were used to determine the concentrations: Pb, Mn in soil (extractions with 1 mol HCl dm^{-3}, the ratio between soil and extraction – 1:10) according KARCZEWSKA and KABAŁA (2008), was determined by AAS method using Schimadzu AA apparatus. This method is less expensive, allows for fast, easy measuring in soil and characterized in terms of the content of micronutrients.

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.

Discussion of Results

The three-year field experiment compared the effect of sulfate and elemental sulfur, added to soil in the doses of 40, 80 and 120 kg ha^{-1}, on mobilization and changes in the natural soil content of manganese and lead. The solubility of heavy metals is markedly affected by soil reaction, hence soil acidification may increase the potential toxicity of heavy metals and their phytoavailability. In the first year of the experiment, soil was poor in sulfur, which is why the applied doses only stimulated crop yields but had negligible impact on modifications of pH_{KCl} in soil (Table 2 and Table 3). Similar results of experiments were reported by RIFFALOLI et al. (2006), who observed that a mineralized dose of elemental sulfur did not cause any significant changes in properties of analyzed soil.

Table 2

Effect of different rates and forms of sulphur on soil reaction at 0–40 cm depth

Treatments	Before cabbage sowing	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	5.30	4.84	4.89	4.54	5.51	5.39
NPK	5.40	4.93	4.70	4.37	5.36	4.50
NPK+ S_1-SO^{-2}_4	5.50	4.97	5.03	4.52	5.08	4.86
NPK+ S_2-SO^{-2}_4	5.35	5.13	4.98	4.67	4.84	4.39
NPK+ S_3-SO^{-2}_4	5.38	4.81	4.39	4.15	4.46	4.36
NPK+S_1-S^0	5.78	4.92	5.33	4.92	5.20	4.43
NPK+S_2-S^0	5.46	4.93	5.15	4.67	5.00	4.61
NPK+S_3-S^0	5.56	4.99	5.11	4.36	4.65	4.37
LSD-$_{0.05}$ *a* *b* *ab*	n.s. n.s. n.s.	n.s. n.s. n.s.	n.s. 0.209 0.295	n.s. 0.211 0.299	0.135 0.191 0.271	0.202 0.285 0.404

Explanations: SO^{-2}_4 – sulphate sulphur; S^0 – elementary sulphur; S_1 – 40 kg ha^{-1}, S_2 – 80 kg ha^{-1}, S_3 – 120 kg ha^{-1}; *a* – form of sulphur; *b* – dose of sulphur; *ab* – interaction; * n.s. – no significant difference

In the spring of 2001, the pH of the soil fertilized with 120 kg of sulfate sulfur, which had already decreased in the first year of the experiment, continued to decline (Table 2). Addition of elemental sulfur led to an increase in soil pH compared to the control treatments and plots fertilized with S-SO^{2-}_4.

In the autumn in the second year of the experiment (Table 2) the dose of 120 kg S-SO_4 ha^{-1} introduced to the 0–40 cm soil horizon caused a further decrease in the soil pH_{KCl}, similarly to the effect observed in spring. The soil reaction tended to be higher on plots with elemental sulfur than on the other plots. This dependence was not verified in the 40–80 cm layer of soil (Table 3).

Table 3

Effect of different rates and forms of sulphur on soil reaction at 40–80 cm depth

Treatments	Before cabbage sowing	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	5.30	4.82	4.32	4.29	4.40	4.47
NPK	5.01	4.83	4.66	4.46	4.47	4.55
NPK+ S_1-SO^{-2}_4	5.21	5.21	4.36	4.50	4.71	4.58
NPK+ S_2-SO^{-2}_4	5.61	5.07	4.89	4.47	4.72	4.63
NPK+ S_3-SO^{-2}_4	4.99	4.70	4.78	4.43	4.45	4.59
NPK+S_1-S^{-0}	4.89	5.14	5.02	4.53	4.56	4.60
NPK+S_2-S^{-0}	5.09	5.04	4.99	4.51	4.63	4.66
NPK+S_3-S^{-0}	5.06	5.04	4.89	4.50	4.58	4.54
LSD-$_{0.05}$ a b ab	n.s. n.s. n.s.	n.s. 0.150 0.212	n.s. n.s. n.s.	n.s. n.s. n.s.	n.s. 0.166 n.s.	n.s. n.s. n.s.

Explanations see Table 2

In the third year (in spring), the pH_{KCl} of soil in the 0–40 cm layer generally increased in all the treatments relative to the autumn 2001, especially on the plots without sulfur fertilization or with the dose of 40 kg ha^{-1} S-SO_4.

However, all the plots fertilized with sulfate sulfur and elemental sulfur demonstrated a tendency towards a lower soil reaction versus the control treatments. Sulfate sulfur was noticed to produce a stronger influence on the soil reaction, which was most profoundly lowered by the dose of 120 kg S ha^{-1} S-SO_4. Sulfate sulfur affected the soil reaction more strongly. In the experiments reported by WEI ZHOU et al. (2002), elemental sulfur did not have any significant effect on soil pH_{KCl} because only between 5.58 to 14.87% of the applied elemental sulfur was oxidized. The acidifying influence of elemental sulfur became evident in the third year of the experiment. In general, soil at

the depth of 40 to 80 cm was characterized by an almost uniform reaction, except for the plot which had received 120 kg S ha^{-1} S-SO$_4$ (Table 3).

In the autumn 2002 (Table 2), the 40 to 80 cm deep soil layer fertilized with sulfur, especially with the dose of 120 kg ha^{-1}, had a much lower pH$_{KCl}$. A similar relationship emerged in the treatments without sulfur, which may have been a consequence of the leaching of base cations from soil. In the 40–80 cm deep layer, the dose or form of sulfur fertilizer had no effect on modifications of soil pH against the control or NPK treatments (Table 3).

The concentration of manganese in soil sampled prior to the experiment from the 0–40 cm soil horizon ranged from 89.00 to 109.00 mg kg^{-1} of soil (Table 4). The Mn concentration in the 40–80 cm deep layer was much smaller. In the autumn, after cabbage harvest, the concentration of manganese in soil in the both layers (0–40 and 20–80 cm) did not depend significantly on the applied form or dose of sulfur (Table 4 and Table 5).

Table 4

Effect of different rates and forms of sulphur on the content of manganese soluble in 1mol HCl dm^{-3} in soil at 0–40 cm depth [mg Mn kg^{-1} soil]

Treatments	Before cabbage sowing	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	89.00	93.00	85.29	82.50	108.20	85.75
NPK	106.25	108.25	90.17	86.97	118.54	88.66
NPK+ S$_1$-SO$^{-2}_4$	109.00	111.00	109.62	100.69	129.98	107.41
NPK+ S$_2$-SO$^{-2}_4$	101.74	100.74	89.23	92.75	120.78	91.32
NPK+ S$_3$-SO$^{-2}_4$	106.32	108.31	87.76	93.36	119.74	93.44
NPK+S$_1$-S-^{0}	101.89	102.89	96.15	80.42	112.16	93.19
NPK+S$_2$-S-^{0}	101.15	102.15	87.38	84.07	115.96	90.16
NPK+S$_3$-S-^{0}	99.74	98.74	91.00	83.54	126.94	91.80
LSD-$_{0.05}$						
a	n.s.	n.s.	3.088	5.341	n.s.	n.s.
b	n.s.	n.s.	4.367	n.s.	7.368	6.776
ab	n.s.	n.s.	6.176	10.683	10.4207	9.583

Explanations see Table 2

In the spring 2001, both the form and dose of sulfur produced significant effects on the content of manganese in soil in the 0–40 cm deep layer (Table 4). In the soil from the plots fertilized with sulfate sulfur, the concentration of manganese tended to be higher than in the soil nourished with elemental sulfur. As the dose of sulfate sulfur increased, the content of manganese in soil decreased. Similar results were reported by SOLIMAN et al. (1992). Doses of elemental sulfur produced less regular results. Compared to analogous

Table 5

Effect of different rates and forms of sulphur on the content of manganese soluble in 1 mol HCl dm^{-3} in soil at 40–80 cm depth [mg Mn kg^{-1} soil]

Treatments	Before cabbage sowing	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	41.64	42.64	–	38.66	47.10	40.02
NPK	41.32	42.31	–	27.76	51.73	32.27
NPK+ S_1-SO$^{-2}_4$	45.87	47.87	–	39.01	58.99	41.31
NPK+ S_2-SO$^{-2}_4$	43.75	44.75	–	28.60	43.74	28.96
NPK+ S_3-SO$^{-2}_4$	46.30	49.30	–	44.39	71.68	41.53
NPK+S_1-S^{-0}	33.86	37.86	–	32.00	50.35	35.45
NPK+S_2-S^{-0}	39.80	40.80	–	36.90	53.85	29.80
NPK+S_3-S^{-0}	39.45	40.45	–	38.11	53.90	26.07
LSD-$_{0.05}$ a b ab	n.s. n.s. n.s.	n.s. n.s. n.s.	–	n.s. 8.2516 n.s.	n.s. n.s. n.s.	n.s. 7.992 n.s.

Explanations see Table 2

treatments examined in the autumn 2000, the content of manganese in soil decreased (Table 4). In the autumn, after onion harvest, the concentration of manganese in the 0–40 cm deep soil layer was within 80.42 to 100.69 mg kg^{-1} of soil (Table 4). Sulfate sulfur fertilization, in particular with the dose of 40 kg ha^{-1}, affected the content of magnesium in soil by raising it above the levels found in soil treated with elemental soil. Further depletion of the manganese content in soil, first demonstrated in the spring of 2000, was observed. However, two exceptions were noted, namely the treatments with 80 and 120 kg of sulfate sulfur (Table 4). FÄSSLER et al. (2012) implied a possibility of using elemental sulfur for the sake of improved phytoextraction of metals, although they warned against excessive acidification of soil and the risk of leaching heavy metals beyond the rhizosphere. In the 40–80 cm soil horizon, significant changes in the concentrations of manganese were caused only by doses of sulfur (Table 5). The highest manganese content occurred following the application of the dose of 120 kg ha^{-1} S-SO$_4$. Fertilization with the increasing doses of elemental sulfur led to an increase in the soil content of manganese. No such tendency appeared when sulfate sulfur had been added to soil.

In the third year of the experiment, prior to sowing barley, the enrichment of soil (the 0–40 cm layer) with 1 mol HCl dm^{-1} soluble manganese forms was observed against the soil tested in the previous years. During the three years of the research, application of sulfate sulfur and elemental sulfur significantly

affected changes in the reaction of soil within 0–40 cm depth (from acid to very acid). In all probability, the soil acidification resulted in an increase in the content of the easily soluble forms of manganese. In a study described by ERDAL et al. (2004), the application of elemental sulfur in combination with nitrogen fertilizers led to a substantial increase in the availability of micronutrients, especially manganese, in soil. On the other hand, the research reported by ABDOU et al. (2011) suggests that sulfur has an insignificant effect on plant availability of manganese in soil. In the current study, the form of sulfur did not affect significantly changes in the content of Mn in soil (Table 4). Fertilization with sulfur, particularly with high doses of this element, generally raised the content of manganese against the control treatments. However, the applied forms and doses of sulfur had no effect on changing concentrations of manganese in the 40–80 cm soil layer of soil, although an increasing tendency appeared in the plot fertilized with the dose of 120 kg ha^{-1} S-SO$^{2-}_4$, an effect which manifested itself already in the first year of the experiment. Once the experiment was terminated, the concentration of manganese in soil at the depth of 0 to 40 cm decreased versus the same soil layer sampled in the spring of 2002. A significant effect, however, was produced only by elemental sulfur, especially its dose of 40 kg ha^{-1}. Similar regularities were detected in the deeper soil horizon, i.e. 40–80 cm, although much smaller quantities of 1 mol HCl dm^{-1} soluble manganese forms were determined (Table 5). A much higher uptake of Mn by plants induced by sulfur fertilization and its acidification has been implied by RAHMAN et al. (2011) and ISLAM (2012), who obtained similar research results. A rapid decrease of pH affects the rate at which Al and Fe are released from aluminum silicate and ferrous minerals. The harmful influence of excessive quantities of Al and Fe active forms in the environment consists in the increased bioavailability and accumulation of Mn, Cd and Pb by plants (MOTOWICKA-TERELAK, TERELAK 1998).

Concentrations of 1 mol HCl dm^{-1} soluble lead in soil prior to the experiment were evenly distributed in both soil horizons (Table 6 and Table 7), although there were twice as many such bonds in the deeper, 40–80 cm layer than in the surface soil horizon. In the autumn, after cabbage harvest, it was only the form of sulfur that affected significant modifications in the content of lead in the 0–40 cm soil layer. In general, sulfur fertilization resulted in an elevated lead concentration in soil relative to the control treatments (Table 6). Compared to sulfate sulfur, the application of elemental sulfur evoked a tendency towards an increasing content of lead in soil. The doses caused insignificant differences. In the 40–80 cm layer, the applied forms of sulfur did not have any significant influence on changes in the content of lead in soil (Table 7). In the treatments with 40 and 80 kg ha S-SO$^{2-}_4$ as well as 120 kg ha^{-1} S-S^0, the content of lead was higher than in the other treatments. This could have been

Table 6

Effect of different rates and forms of sulphur on the content of lead soluble in 1 mol HCl dm^{-3} in soil at 0–40 cm depth [mg Pb kg^{-1} soil]

Treatments	Before cabbage sowing	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	5.26	5.79	5.84	5.79	6.39	5.50
NPK	5.00	5.79	5.35	5.02	6.02	5.59
NPK+ S_1-SO^{-2}_4	5.43	6.14	6.39	5.63	7.37	5.99
NPK+ S_2-SO^{-2}_4	5.16	4.77	5.97	5.32	6.55	4.66
NPK+ S_3-SO^{-2}_4	5.55	5.95	6.11	6.29	6.68	5.95
NPK+S_1-S^{-0}	4.78	6.21	5.39	6.41	6.59	6.11
NPK+S_2-S^{-0}	4.91	5.91	5.56	5.55	6.81	5.81
NPK+S_3-S^{-0}	4.29	6.25	5.32	5.53	6.72	6.05
LSD-$_{0.05}$ a b ab	n.s. n.s. n.s.	0.2957 n.s. 0.5915	n.s. n.s. 0.6793	0.4865 n.s. n.s.	n.s. 0.5436 n.s.	0.295 n.s. 0.591

Explanations see Table 2

Table 7

Effect of different rates and forms of sulphur on the content of lead soluble in 1 mol HCl dm^{-3} in soil at 40–80 cm depth [mg Pb kg^{-1} soil]

Treatments	Before cabbage sowing	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	2.11	2.28	–	3.60	3.05	2.18
NPK	3.52	2.99	–	3.22	3.05	2.89
NPK+ S_1-SO^{-2}_4	2.41	3.24	–	2.95	2.33	3.14
NPK+ S_2-SO^{-2}_4	2.84	3.20	–	2.88	2.16	3.18
NPK+ S_3-SO^{-2}_4	2.78	2.40	–	3.84	2.54	2.38
NPK+S_1-S^{-0}	2.52	2.72	–	3.12	2.46	2.62
NPK+S_2-S^{-0}	1.64	2.70	–	2.58	1.88	2.65
NPK+S_3-S^{-0}	2.30	3.24	–	3.44	2.03	3.14
LSD-$_{0.05}$ a b ab	n.s. n.s. n.s.	n.s. 0.5725 n.s.	–	n.s. n.s. n.s.	n.s. n.s. n.s.	n.s. 0.572 n.s.

Explanations see Table 2

caused by the soil acidification due to sulfur and mobilization of forms of lead soluble in 1 mol HCl dm^{-1}. The influence of soil reaction on mobility of heavy metals is elucidated by the solubility product, where a decrease in the soil pH by one unit is associated with a 100-fold decrease in the potential solubility

of heavy metals. When soil is polluted with several metals, the so-called 'salt effect' appears. The presence of one ion enhances the activity of other ions, which promotes the bioavailability of heavy metals (MOTOWICKA-TERELAK, TERELAK 1998).

In the spring of the second year, before sowing onion, the content of lead in the 0–40 cm deep soil layer did not depend significantly on either the form or the dose of sulfur (Table 6). The concentration of lead in soil from sulfate sulfur fertilized treatments was higher than in soil from analogous treatments analyzed in the first year of the experiment. In contrast, a small decline in the concentration of lead was determined in soil with added elemental sulfur. In the autumn of the second year, the form of sulfur, especially elemental sulfur, rather that its dose, had a significant effect. In general, concentrations of lead in the 0–40 cm soil layer on sulfur fertilized and control plots were on an approximately identical level (Table 6). Sulfur fertilization did not tend to have a significant effect on changes in the lead content in the 40–80 cm soil layer (Table 7). The content of lead in this soil horizon was much smaller than in the 0–40 cm layer of soil fertilized with sulfur. Similar results were obtained by ŠICHOROVÁ et al (2004), who concluded that the concentration of lead decreased with the depth of the soil profile.

In the spring of the third year, a slight increase was noticed in the content of 1 mol HCl dm^{-1} soluble lead form in all the experimental treatments versus the analogous plots from the preceding years (Table 6). However, significant effects were produced only by the higher doses of sulfur, and especially 40 kg ha^{-1} of sulfate sulfur. The application of sulfur to soil caused an increase in the concentration of lead in soil compared to a plot fertilized with NPK alone. The form of sulfur did not have significant impact. In the deeper soil layer, 40–80 cm, the content of lead was smaller than in the analogous plots in the autumn or in soil sampled from the topmost soil horizon.

When the experiment was terminated, the content of lead in soil from the 0–40 cm deep layer was within 4.66 to 6.11 mg kg, and depended significantly on the form of sulfur. More lead was found in soil from the treatments with elemental than sulfate sulfur. In the soil fertilized with elemental sulfur, the content of lead forms soluble in 1 mol HCl dm^{-1} was higher than in the other fertilized treatments. In general, soil was slightly richer in lead than before the experiment had commenced, especially when plots were fertilized with elemental sulfur. In the autumn 2002, after harvest, the soil from the 0–4–0 cm layer contained less lead than the soil sampled before sowing barley. TERELAK et al. (1996) claim that when soils are polluted with sulfur, the bioavailability and accumulation of Mn, Cd and Pb in crops increase. Similar results were achieved by HOLAH et al. (2010), who concluded that the content and uptake of lead by plants increased significantly in response to growing doses of elemental

sulfur, which led to a decreasing content of Pb in soil. In the deeper soil horizon, i.e. 40–80 cm, the concentration of lead was much smaller than in soil samples collected from the 0–40 cm layer, and depended only on the dose of sulfur (Table 6 and Table 7).

Conclusions

1. Throughout the whole experiment, the dose of 40 kg ha^{-1} S-SO$^{2-}_4$ caused higher concentrations of manganese in soil within the 0–40 cm layer than in the other fertilized treatments.

2. During the three years of the experiment, the application of sulfate and elemental sulfur caused small increases in the content of lead soluble in 1 mol HCl dm^{-1} in soil in the 0–40 cm layer compared to soil before the experiment was set up.

3. The content of manganese and lead in soil, within the 40–80 cm layer, did not depend much on the applied form or dose of sulfur.

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