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Eva DOLEŽELOVÁ[1] and Pavel RYANT[1]

EFFECT OF FARMYARD MANURE, SEWAGE SLUDGE AND ELEMENTARY SULPHUR APPLICATION ON THE CONTENT OF HEAVY METALS IN SOIL AND WHEAT GRAIN

WPŁYW NAWOŻENIA OBORNIKIEM, OSADEM ŚCIEKOWYM ORAZ SIARKĄ ELEMENTARNĄ NA ZAWARTOŚĆ METALI CIĘŻKICH W GLEBIE I ZIARNIE PSZENICY

Abstract: In a one-year pot experiment influence of fertilisation with elementary sulphur (0.42 g per pot containing 6 kg of soil), farmyard manure and sewage sludge (both in doses of 32 g dry matter per pot) on Fe, Cu, Zn, Mn and Cd content in soil and wheat grain was studied. The experiment comprised following variants: 1) control (not fertilised), 2) farmyard manure, 3) sewage sludge, 4) elementary sulphur, 5) farmyard manure and elementary sulphur, 6) sewage sludge and elementary sulphur.

Sulphur application did not lead to any statistical increase in the heavy metals content in soil, however it resulted in a higher content of manganese and a lower content of copper in the wheat grain.

Among studied soil characteristics only Fe content was lowered after farmyard manure fertilization while the content of Fe and Mn in grain increased. Application of sewage sludge resulted in significant increase in Fe, Zn and Cu in both soil and grain and in decrease in Mn content in grain.

The cadmium content in soil was affected by interaction of organic fertilizers and sulphur. Sulphur alone caused decrease in cadmium content in soil while together with organic fertilizing led to a significant increase.

Keywords: spring wheat (*Triticum aestivum* L.), heavy metals, elementary sulphur, farmyard manure, sewage sludge

Iron is concentrated in chloroplasts. Its complexes participate in electron transfer in the photosynthetic process. Thanks to ability to change the oxidation number iron takes part in many oxidation-reduction processes. Non-heme Fe proteins are involved in the reduction of nitrates and sulphates [1].

Zinc as a key component of many enzymes interferes in metabolism of carbohydrates, proteins, auxin, RNA and phosphate [1]. In wheat zinc can alter protein composition and lower negative effect of high temperatures during the grain filling stage [2].

[1] Department of Agrochemistry, Soil Science, Microbiology and Plant Nutrition, Faculty of Agronomy, Mendel University of Agriculture and Forestry Brno, Zemědělská 1, 613 00 Brno, Czech Republic, tel. +420 545 133 102, fax +420 545 133 096, email: ryant@mendelu.cz

Thanks to the ability to change the oxidation number manganese plays an important role as a catalytic agent in many reactions. It is a specific component or can substitute for Mg in several enzymes. It is involved in oxygen-evolving system of photosynthesis and participates in the photosynthetic electron transport system [1].

Copper is involved in many physiological processes in plants including photosynthesis and respiration, carbohydrate distribution, reduction and fixation of nitrogen, protein metabolism. It controls water relationships as well as production of nucleic acids which reflects on reproduction ability of plants [1].

Plants supplied properly with zinc and copper show higher disease resistance, too [1]. Mn and Zn treated winter wheat plants were less attacked by *Drechslera tritici-repentis* (Died.) Shoem. causing the tan spot disease [3].

Mentioned elements are essential to plants. However, as heavy metals, in excessive amounts they can cause severe malfunctions and disturbances in many crucial processes [1].

Cadmium, on the other hand, is a typical non-essential element with negative effects on plants. Its fundamental characteristic is a strong affinity to sulfhydryl and phosphate groups, and ability of replacing zinc in some enzymes and consequently their inactivation [1].

Wheat does not belong among crops needing direct organic fertilising, effect differ from case to case. Some authors inform about significant increase in yield [4, 5], protein content and N, P, K, Fe, Zn, Mn uptake [5], whereas others observed significant yield decrease connected with organic fertilisers application [6, 7].

Organic fertilisers are used in crop systems to replace organic matter in soil which fell prey to mineralization. They preserve or even improve soil properties [7]. Besides, they serve as a source of microelements. In the case of sewage sludge, quite a large amount of different microelements and heavy metals is common which reflects in a higher total content of these metals in soil as well as in their higher bioavailability and consequently in an increasing content in plant tissues [4, 5, 8]. Plants supplied properly with sulphur can easily protect themselves from excessive metals using sulphur-containing phytochelatins. Therefore sulphur content in soil should be maintained at sufficient level. Especially under leaching conditions elementary sulphur is recommended as sulphur source [9]. However, it can significantly lower the soil pH value [10, 11] and thereby increase the heavy metals availability to plants [10–12].

Material and methods

In 2005 content of five metals in spring wheat grain was studied in a pot experiment carried out in Mitscherlich pots filled with 6 kg of sandy soil (Table 1) in the vegetation hall at Mendel University of Agriculture and Forestry in Brno.

Table 1

Soil properties prior to the experiment

C_{ox} $[g \cdot kg^{-1}]$	pH/$CaCl_2$	Content of available elements $[mg \cdot kg^{-1}]$									
		P	K	Ca	Mg	$S_{water\text{-}soluble}$	Fe	Zn	Cu	Mn	Cd
0.7	7.4	112	135	1990	113	9.5	2112	9.1	4.7	204	0.21

The experiment included the following variants: 1) control (not fertilised), 2) farmyard manure, 3) sewage sludge, 4) elementary sulphur, 5) farmyard manure + + elementary sulphur, 6) sewage sludge + elementary sulphur. The cattle manure was obtained from Agro Monet Moutnice, used sewage sludge originated from wastewater treatment plant Brno in Modřice. Each variant was established in 4 replications. The chemical composition of organic materials is shown in Table 2.

Table 2

Chemical composition of applied organic materials [mg · kg^{-1} of fresh matter]

Organic material	Dry matter	N	P	K	Ca	Mg	S
	[g · kg^{-1}]	[g · kg^{-1} of fresh matter]					
Sewage sludge	907	29.5	2.1	3.4	43.8	4.3	7.8
Farmyard manure	211	4.0	1.3	7.0	5.4	1.6	0.8
Organic material	OM	Fe	Zn	Mn	Cu	Cd	C:N
	[g · kg^{-1} of fresh matter]	[mg · kg^{-1} of fresh matter]					
Sewage sludge	565.0	51800	6810	452	347	4.1	11:1
Farmyard manure	111.0	17	189	119	19	0.6	16:1

OM – organic matter.

The pH value of used soil was determined in 0.01 mol · dm^{-3} $CaCl_2$ solution, the P, K, Ca and Mg contents were determined according to the Mehlich III method, and the content of studied elements by means of AAS in a 2 mol · dm^{-3} HNO_3 extract (soil/extract ratio was 1:10). The soil reaction was alkali, the supply of available P and Ca was good, the supply of available K and Mg was suitable and the content of water-soluble S was low. According to the Decree of the Ministry for the Environment No. 13/1994 Col. [13], the copper, zinc and cadmium contents were below the limit (the standard quotes the maximum as equal to 30 mg Cu · kg^{-1}, 50 mg Zn · kg^{-1} and 0.4 mg Cd · kg^{-1} in light soils).

In late summer (24th August 2004), farmyard manure and sewage sludge were applied in dose of 32 g dry matter per pot (the dose was derived from 10 Mg per hectare) and elementary sulphur in a dose of 0.42 g per pot. All fertilisers were thoroughly mixed with the soil.

In spring (30th March 2005), 30 spring wheat grains, 'Vinjett' variety, were sown in each pot. One month later (29th April) the plants were thinned to 15 plants per pot. During vegetation the pots were watered at 60 % of the maximum water capacity, weeded and treated with the insecticide KARATE 2.5 WG and fungicide Falcon 460 EC.

The plants were harvested on 29th July in the stage of full maturity. After complete drying, the grain was threshed on the KMP 2 spike laboratory thresher. Contents of iron, zinc, manganese, copper and cadmium in grain (after mineralisation in HNO_3) and soil (in 2 mol · dm^{-3} HNO_3 extract) were determined by AAS method using the PHILIPS PU 9200 X apparatus.

Results were evaluated by multi-factor analysis of variance applying the STATISTICA version 7.1 software; successive tests were performed with Tukey's test of significance of differences.

Results

Elementary sulphur application alone had no impact on the heavy metals content in soil (in 2 mol · dm^{-3} HNO_3 extract) (Tables 3 and 4). However, the initial pH value of used soil was relatively high, so elementary sulphur could not change it to the degree that could increase the heavy metals availability.

Organic materials applied as fertilisers influenced statistically significant the content of Fe, Zn and Cu (Tables 3 and 4). The highest contents of mentioned elements showed variants fertilised with sewage sludge. That can be explained by higher contents of studied metals in the used sewage sludge which was applied in the same dose as farmyard manure. While in the case of Zn and Cu the lowest content was observed on controls, the lowest content of Fe showed plots fertilised with farmyard manure.

Elementary sulphur proved to affect the content of Cu and Mn in wheat grain; it led simultaneously to a Cu content decrease and a Mn content increase (Tables 5 and 6).

Different organic materials used for fertilisation influenced significantly content of Fe, Zn, Cu and Mn in wheat grain. The highest Fe content in grain showed variants fertilised with both organic materials and elementary sulphur as well as the variant fertilised with farmyard manure alone.

In variants fertilised with sewage sludge (no matter if with or without ES application) the significantly highest Zn content and the lowest Mn content in wheat grain were detetermined (Tables 5 and 6). The highest Mn content, statistically different from the Mn content in control variants, showed the variant fertilised with sewage sludge without elementary sulphur. The Cd content in grain did not vary neither according to organic fertilization nor sulphur addition.

Discussion

In their experiment Punia and Khaterpaul [14] found out that total copper and manganese contents in wheat grain were lower on variants fertilised with organic fertilisers than on variants fertilised with mineral fertilisers. In our experiment significant differences between used organic materials were noticed. Farmyard manure application did not influence Cu content and increased Mn content in wheat grain in comparison with control variants. Sewage sludge application resulted in a significant increase of Cu and decrease of Mn content.

Among variants fertilised with garbage and mushroom composts, cattle and chicken manures and municipal sludge the latter was most effective in increasing Fe, Zn and Mn content in wheat grain [5]. In our experiment similar results were noticed for Zn content. There was no statistical difference between the influence of farmyard manure and sewage sludge in the iron content in wheat grain from our experiment and in the

Table 3

Content of monitored heavy metals in soil after harvest

Variant	Fe		Zn		Cu		Mn		Cd	
	[mg · kg^{-1}]									
	$\bar{x} \pm s_x$		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$	
Control	2239 ± 42	c	8.900 ± 0.389	a	4.228 ± 0.093	a	212.66 ± 4.12	a	0.086 ± 0.006	b
Manure	2073 ± 50	a	9.633 ± 1.199	a	4.176 ± 0.237	a	212.43 ± 8.73	a	0.071 ± 0.003	a
Sewage sludge	2394 ± 27	d	25.370 ± 2.673	b	4.934 ± 0.209	b	216.04 ± 5.29	a	0.082 ± 0.003	b
Control + ES	2174 ± 33	bc	9.960 ± 0.669	a	3.770 ± 0.218	a	203.71 ± 6.48	a	0.070 ± 0.003	a
Manure + ES	2110 ± 36	ab	10.645 ± 0.945	a	4.137 ± 0.122	a	216.27 ± 7.82	a	0.082 ± 0.005	b
Sewage sludge + ES	2396 ± 54	d	25.307 ± 1.736	b	5.027 ± 0.293	b	216.39 ± 12.73	a	0.082 ± 0.006	b

Variants marked with the same letter do not show statistically significant differences in the content of certain heavy metal ($\alpha \leq 0.05$).

Table 4

Effect of studied factors on the metals content in soil

Factor	Level of factor	Fe		Zn		Cu		Mn		Cd	
		[mg · kg^{-1}]									
		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$	
Elementary sulphur	no	2236 ± 142	a	14.637 ± 8.082	a	4.446 ± 0.400	a	213.71 ± 6.00	a	0.079 ± 0.008	a
	yes	2227 ± 133	a	15.304 ± 7.473	a	4.311 ± 0.587	a	212.12 ± 10.53	a	0.078 ± 0.007	a
Organic materials	control	2207 ± 50	b	9.433 ± 0.757	a	3.999 ± 0.290	a	208.19 ± 6.94	a	0.078 ± 0.010	a
	manure	2092 ± 45	a	10.139 ± 1.136	a	4.157 ± 0.176	a	214.35 ± 7.94	a	0.076 ± 0.007	a
	sewage sludge	2395 ± 39	c	25.338 ± 2.087	b	4.981 ± 0.241	b	216.22 ± 9.03	a	0.082 ± 0.005	a

Variants marked with the same letter do not show statistically significant differences in the content of certain heavy metal ($\alpha \leq 0.05$).

Table 5

Content of monitored heavy metals in wheat grain

Variant	Fe [mg · kg^{-1}]		Zn		Cu		Mn		Cd	
	$\bar{x} \pm s_x$		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$	
Control	16.534 ± 1.598	a	20.025 ± 0.660	a	1.938 ± 0.106	a	8.768 ± 1.009	a	0.013 ± 0.001	a
Manure	22.678 ± 3.309	c	18.719 ± 0.699	a	2.035 ± 0.268	ab	11.773 ± 1.079	b	0.013 ± 0.002	a
Sewage sludge	21.901 ± 1.424	bc	25.212 ± 1.583	b	2.354 ± 0.079	b	8.322 ± 0.731	a	0.009 ± 0.003	a
Control + ES	18.543 ± 0.721	ab	19.758 ± 1.090	a	1.890 ± 0.074	a	11.496 ± 0.717	b	0.014 ± 0.001	a
Manure + ES	22.887 ± 3.006	c	18.784 ± 1.168	a	1.828 ± 0.216	a	15.344 ± 2.531	c	0.010 ± 0.001	a
Sewage sludge + ES	22.514 ± 0.673	c	26.634 ± 1.475	b	2.125 ± 0.178	ab	8.649 ± 0.818	a	0.012 ± 0.006	a

Variants marked with the same letter do not show statistically significant differences in the content of certain heavy metal ($\alpha \leq 0.05$).

Table 6

Effect of studied factors on the metals content in wheat grain

Factor	Level of factor	Fe [mg · kg^{-1}]		Zn		Cu		Mn		Cd	
		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$		$\bar{x} \pm s_x$	
Elementary sulphur	no	20.076 ± 3.562	a	21.147 ± 2.981	a	2.096 ± 0.239	b	9.556 ± 1.780	a	0.012 ± 0.002	a
	yes	20.499 ± 2.575	a	21.219 ± 3.356	a	1.931 ± 0.174	a	11.732 ± 2.693	b	0.013 ± 0.003	a
Organic materials	control	17.826 ± 1.450	a	19.853 ± 0.940	a	1.907 ± 0.086	a	10.522 ± 1.571	b	0.013 ± 0.001	a
	manure	22.782 ± 2.929	b	18.751 ± 0.892	a	1.932 ± 0.251	a	13.559 ± 2.625	c	0.011 ± 0.002	a
	sewage sludge	22.208 ± 1.082	b	25.923 ± 1.607	b	2.240 ± 0.177	b	8.486 ± 0.739	a	0.011 ± 0.004	a

Variants marked with the same letter do not show statistically significant differences in the content of certain heavy metal ($\alpha \leq 0.05$).

case of manganese variants fertilised with farmyard manure showed even statistically higher content in grain than variants treated with sewage sludge.

We also did not confirm results of Cui and Wang [10] and Cui et al [11, 12] who observed significant increase in Zn availability and uptake by plants after sulphur addition.

Our results correspond to findings of Jamil Khan et al [4], since the sewage sludge application led to an increase of Fe, Zn, Cu and Mn content in soil, although the difference from the control variants was in the case of manganese not statistically significant.

Table 7

Correlation coefficients of the heavy metals content in the soil and wheat grain

Element		Grain				Soil					
		Fe	Zn	Cu	Mn	Fe	Zn	Cu	Mn	Cd	
Grain	Fe					0.23	0.49*	0.38	0.45*	0.05	Grain
	Zn	0.30				0.72*	0.70*	0.56*	0.22	0.12	
	Cu	0.48*	0.67*			0.56*	0.59*	0.43*	0.18	0.10	
	Mn	0.48*	–0.53*	–0.27		–0.45*	–0.29	–0.28	0.27	0.03	
	Cd	–0.09	–0.11	–0.11	0.02	–0.03	–0.12	–0.02	0.10	–0.22	
		Soil									
Soil	Zn	0.86*									
	Cu	0.81*	0.89*								
	Mn	0.38	0.32	0.54*							
	Cd	0.41*	0.28	0.45*	0.33						

* Cases showing statistically significant ($\alpha \le 0.05$) correlation.

Morgounov et al [15] found a strongly positive correlation between Fe and Zn in spring wheat grain which is in contrast to our findings (r = 0.30) (Table 7). Chaudri et al [16] observed correlation between the total soil cadmium content and the Cd content in wheat grain. Neither this correlation was confirmed.

Conclusions

Elementary sulphur application did not influence the content of available forms of heavy metals in soil. The highest content of Fe, Zn and Cu in soil showed variants fertilised with sewage sludge. Different organic materials impact significantly on the Fe, Zn, Cu and Mn content in wheat grain whereas neither organic fertilization nor sulphur addition affected the Cd content in grain.

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References

[1] Kabata-Pendias A. and Pendias H.: Trace Elements in Soils and Plants. CRC Press, USA 1984.
[2] Peck A.W., McDonald G.K. and Graham R.D.: J. Cereal Sci. 2008, **47**(2), 266–274.
[3] Simoglou K.B. and Dordas C.: Crop Protect. 2006, **25**(7), 657–663.
[4] Jamil Khan M., Qasim M. and Umar M.: J. Appl. Sci. 2006, **6**(3), 531–535.
[5] Uyanöz R., Çetin Ü. and Karaarslan E.: J. Plant Nutr. 2006, **29**(5), 959–974.
[6] Tejada M. and Gonzalez J.L.: Agronom. J. 2007, **99**(6), 1597–1606.
[7] Gopinath K.A., Supradip Saha, Mina B.L., Harit Pande, Kundu S. and Gupta H.S.: Nutr. Cycl. Agroecosyst. 2008, **82**, 51–60.
[8] Bose S. and Bhattacharyya A.K.: Chemosphere 2008, **70**(7), 1264–1272.
[9] Dijksterhuis G.H. and Oenema O.: Fertilizer Res. 1990, **22**(3), 147–159.
[10] Cui Y.S., Wang Q.R. and Dong Y.T.: J. Environ. Sci. 2003, **15**(6), 836–840.
[11] Cui Y., Wang Q., Dong Y., Li H. and Christie P.: Plant Soil 2004, **261**(1–2), 181–188.
[12] Cui Y. and Wang Q.: J. Plant Nutr. 2005, **28**(4), 639–649.
[13] Decree of the Ministry for the Environment No. 13/1994 Col., http://aplikace.mvcr.cz/archiv2008/sbirka/1994/sb04-94.pdf
[14] Punia D. and Khaterpaul N.: Int. J. Food Sci. Nutr. 2008, **59**(103), 224–245.
[15] Morgounov A., Gomez-Becerra H.G., Abugalieva M.A., Dzhunusova M., Yessimbekova H., Miminjanov Yu., Zelenskiy L., Ozturk I. and Cakmak I.: Euphytica 2007, **155**(1–2), 193–203.
[16] Chaudri A., McGrath S., Gibbs P., Chambers B., Carlton-Smith C., Godley A., Bacon J., Campbell C. and Aitken M.: Chemosphere 2007, **66**(8), 1415–1423.

WPŁYW NAWOŻENIA OBORNIKIEM, OSADEM ŚCIEKOWYM ORAZ SIARKĄ ELEMENTARNĄ NA ZAWARTOŚĆ METALI CIĘŻKICH W GLEBIE I ZIARNIE PSZENICY

Abstrakt: W jednorocznym doświadczeniu wazonowym badano wpływ nawożenia siarką elementarną (0,42 g na wazon, zawierający 6 kg gleby), obornikiem i osadem ściekowym (obydwa w dawkach 32 g s.m. na wazon) na zawartość Fe, Cu, Zn, Mn i Cd w glebie i ziarnie pszenicy. Doświadczenie obejmowało następujące warianty: 1) kontrola (bez nawożenia), 2) obornik, 3) osad ściekowy, 4) siarka elementarna, 5) obornik i siarka elementarna, 6) osad ściekowy i siarka elementarna.

Zastosowanie siarki nie doprowadziło do statystycznie znaczącego wzrostu zawartości metali ciężkich w glebie, jednak skutkowało większą zawartością manganu oraz mniejszą zawartością miedzi w ziarnie pszenicy.

Spośród badanych właściwości gleby tylko zawartość Fe obniżyła się po nawożeniu obornikiem, podczas gdy wzrastała zawartość Fe i Mn w ziarnie. Stosowanie osadu ściekowego skutkowało znacznym wzrostem zawartości Fe, Zn i Cu zarówno w glebie, jak i w ziarnie oraz zmiejszeniem zawartości Mn w ziarnie.

Zawartość kadmu w glebie była uzależniona od interakcji nawozów organicznych i siarki. Stosowanie samej siarki powodowało obniżenie zawartości kadmu w glebie, podczas gdy łączne jej stosowanie z materiałami organicznymi prowadziło do znacznego wzrostu zawartości Cd.

Słowa kluczowe: pszenica jara (*Triticum aestivum* L.), metale ciężkie, siarka elementarna, obornik, osad ściekowy