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RISKS OF HEAVY METALS ENTRANCE INTO SOIL AND PLANTS AFTER CHEMICALLY AND MECHANICALLY TREATED COAL APPLICATION

KUMULACJA METALI CIĘŻKICH W ROŚLINACH ORAZ W GLEBIE MODYFIKOWANEJ ZWIĄZKAMI WĘGLA

Abstract: The effect of chemically (solid sodium humate) and mechanically (Lignofert) treated coal application as a soil remediate substance and NPK (artificial) fertilizers, on the content of heavy metals in root, straw and grain of spring barley and in the soil have been investigated on Haplic Luvisol in the pot trial realized in vegetative cage placed on the territory of Slovak Agricultural University in Nitra (48^{o}18′ N, 18^{o}05′ E). The achieved results did not confirm the proclaimed inhibitive effect of sodium humate (SH) and Lignofert (Lig) for entrance of heavy metals into the plants. Conversely, the content of three out of eleven metals (As, Cd, Ni) in the barley grain and one (Fe) in the straw increased after SH application in a statistically significant way in comparison with the control variant. A significant decrease was demonstrated only in the content of mercury in the grain. Lignofert statistically significantly increased the content of up to four metals (Cd, Hg, Cu and Co) in the grain and one of them (Hg) in the straw. Its application did not cause the significant decrease of any heavy metal contents in the grain. The content only of one metal (Zn) decreased in the straw significantly. The application of a rational dose of NPK fertilizers in a statistically significant way increased the content of eight out of eleven investigated heavy metals in the barley corn as a result of their moderate acidification effect on the soil. The use of SH and Lig was not more risky from the viewpoint of heavy metal cumulation in spring barley than the use of NPK fertilizers. However, their application in order to inhibit the entrance of most heavy metals into the plants is not rational. At the same time both coal substances significantly simultaneously increased the content of carbon and pH value in the soil. The use of fertilizers caused a high decrease of carbon content in the soil but their effect on heavy metal level in the soil was positive, it was lower than the effect of coal substances. The overall quantities of metals in the soil of all variants were lower than allowable limit at the end of the trial.

Keywords: coal, lignite, sodium humate, heavy metals, spring barley

In Slovakia the production of organic fertilizers has decreased in the last twenty years by 55 % and compost production by 80 %. After-harvest plant remains became the main source of organic mass in the soil. They satisfy the soil needs for organic substances at

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10–70 % in dependence on the sowing methods and technologies used. Lasting decrease of carbon entrance into the soil caused deterioration of many physical, chemical, microbiological and hygienic-toxicological parameters of the soils in Slovakia.

An alternative source of carbon, that can substantially improve present unfavourable balance of organic substances in the soil, is the application of chemically and mechanically treated coal substances. There are applied chemically treated substances such as liquid sodium, potassium, calcium and ammonium humates (the salts of isolated humic acids). A lot of scientific research work deals with the liquid humates application and their effect on seed germination [1, 2], root system development [3], plant yield parameters [4, 5], on the mechanism of their direct effect on plants [6], and nutrients mobility in the soil [7]. Less papers pay their attention to solid coal substances application. They deal with physical and chemical soil parameters [8–10] but many of their results have antagonistic character.

Agricultural practice perceives the declared by many authors inhibitive effect of chemically and mechanically treated coal applications on the sorption of heavy metals by plants [11–13] as a guarantee of lower level of undesirable metals in the plants. There have appeared some papers which do not prove their inhibitive effect [14–16], therefore there was based a trial the aim of which was to identify the effect of chemically (solid sodium humate) and mechanically (Lignofert) treated coal application as a soil remediate substance and NPK (artificial) fertilizers on the content of heavy metals in the root, straw and grain of spring barley and in the soil.

Material and methods

The pot experiment was realized in 2005 and 2006 years and conducted in a vegetation cage situated in the area of the SAU in Nitra (48°18′ N, 18°05′ E). Experimental pots were filled with the mixture of 16 kg of soil (Haplic Luvisol) and 8 kg of siliceous sand, agrochemical characteristics of which are presented in Table 1 and the methods of their determination are added under Table 1. Into each pot, 100 spring barley grain (Express c.v.) was seeded. After the germination the number of the individuals was thinned out to 75 plants per pot. Moisture of the soil in the pots was maintained on the level of 60 % of full water capacity by regular irrigation. Experiment consisted of 4 treatments (0, SH, Lig, NPK). Each treatment was in four replications.

Table 1

Agrochemical characteristics of soil used in pot trial

Year	$N\text{-}NH_4^+$	$N\text{-}NO_3^-$	N_{in}	P	K	Ca	Mg	pH_{KCl}	C_{ox}
	$[mg \cdot kg^{-1}]$								[%]
2005	12.48	0.24	12.72	41.3	242	1 310	250	5.78	0.97
2006	9.80	2.99	12.80	18.9	182	1 643	303	5.57	0.99

$N\text{-}NH_4^+$ – colorimetrically (Nessler agent); $N\text{-}NO_3^-$ – colorimetrically (phenol-2,4 disulphonic acid); N_{in} – calculated as $N\text{-}NH_4^+ + N\text{-}NO_3^-$; P – colorimetrically (Mehlich II); K – flame photometry method (Mehlich II); Mg – atomic absorption spectrophotometry (Mehlich II); C_{ox} – total carbon content (Tjurin); pH_{KCl} – 1.0 M KCl.

Applied sodium humate (SH) was of Czech origin produced by an alkalic extraction (NaOH + water) from low caloric imperfectly charred subsurface coal. Its application dose was based on respecting the knowledge of Richter and Hlusek [17] and Kovacik [10] who recommend applying dose of solid sodium humate of 300 kg · ha^{-1} in pot trials. Lignofert is ground and mechanically sorted lignite of 0.1–10 mm size of particles and was produced by a Slovak company of Bana Zahorie. In the Lignofert dose calculation (900 kg · ha^{-1}) was taken into consideration the fact that the content of humic acids in sodium humate is three times higher than in Lignofert.

Table 2 shows some agrochemical and hygienic-toxicological parameters of both materials. The contents of heavy metals of mechanically and chemically treated coal substances satisfy the criteria for the soil remediate substances of peat type.

Table 2

Some agrochemical and hygienic-toxicological parameters of sodium humate and Lignofert and limit values of heavy metals for soil additives (Slovak Law No. 577/2005)

Material	pH_{KCl}	EC* [mS · cm^{-1}]	C_{ox}	HA**	Cd	As	Hg	Cr	Ni	Pb
			[%]		[mg · kg^{-1}]					
Sodium humate (SH)	9.66	13.35	44.99	61	0.100	18.4	0.385	36.6	27	5.11
Lignofert (Lig)	5.35	2.31	30.67	22	0.087	19.9	0.110	27.6	28	4.76
Limited values of heavy metals for soil additives of peat type					2	20	1	100	50	100

* Electric conductivity, ** humic acids.

The rates of NPK nutrients were calculated on the basis of the content of N_{in} and available P and K in the soil and plant requirement for these nutrients to achieve planned yield. Nitrogen was applied in the form of DAM-390 fertilizer, P in the form of single superphosphate and potassium as 60 % KCl.

The harvest of spring barley was performed at the growth stage DC 91. The content of heavy metals – Hg, As, Cd, Pb, Cr, Zn, Cu, Co, Ni, Mn and Fe in grains, straw and roots were determined by atomic absorption spectrophotometry (AAS) using the following equipments: Hg and As – AMA 254; Cd, Pb, Cr, Zn, Cu, Co, Ni, Mn and Fe – Pye Unicam.

The total forms of metals in the soil were determined after mineralization by *aqua regia*. The heavy metal contents in the grain and in the soil have been examined in all four repetitions. In the straw only in three repetitions. In consequence of getting insufficient quantity of root phytomass (for all kinds of chemical analyses performed in the trial) the root phytomass of all four repetitions were put together and thus created one average sample.

Results and discussion

The effects of tested coal applications, sodium humate and Lignofert, on the content of heavy metals in the spring barley roots, straw and grain were similar but not identical.

Sodium humate application significantly increased the content of three (Cd, As and Ni) out of eleven monitored heavy metals in the grain (Table 3) and one (Fe) in the straw. There has been the increased content of four metals (As, Cr, Mn a Fe – Table 5) in the roots. Its declared inhibitive effect on the uptake of metals by the plants has been noticed only in Hg and Cu in grain while just the decrease of Hg content was significant. There was a decrease in the content of Cd, Pb, Zn, Mn in the straw but none of them was significant (Table 4). The level of Pb, Hg, Cu and Mn in the roots has decreased moderately (Table 5).

The content of four metals (Cd, Hg, Cu and Co) has been in a statistically significant way increased in the barley grain and of one metal (Hg) in the straw after Lignofert application. In the roots there has been noticed higher increase of the same metals as after the sodium humate application. On the contrary, Lignofert application caused a slight, insignificant decrease of four metals (As, Cr, Zn and Mn). The contents of Cd, Pb, Zn, Cu, Ni, Mn and Fe (ie seven out of eleven metals) in the straw decreased, but only Zn decrease was significant.

The achieved results prove that the application of solid sodium humate and Lignofert into the soil before the sowing does not assure the lower uptake of heavy metals into the vegetative or generative organs. Moreover, their application can cause significant increases of metal contents in the plants. The same phenomenon has been noticed by Richter and Hlusek [17], Hlusek et al [14] who questioned generally found inhibitive humate uptake into the plants and consequently into the food chain.

The increase of heavy metal contents after the treatment by coal substances was not high, consequently the metal levels in the barley grain, except mercury, did not exceed the limits given by food code (Table 3). The Hg above limit content in variants 2 and 3 was the result of high mercury content in the control variant 1.

The application of rational dose of NPK fertilizers caused a significant increase of the contents of eight metals – out of eleven monitored – in the barley grain (Table 3). The increase in contents of up to ten metals (Table 5), have been monitored in the roots. Copper was an exception.

The trial has proved that the effect of both sodium humate and Lignofert on the increased content of heavy metals in the barley is lower than the effect of rational dose of NPK fertilizers. The reason of different effect on metal accumulation is their different effect on soil reaction. Coal substances alkalinized the soil and fertilizers did not change soil pH or they had moderately acidification effect (Table 6). Applied 300 $kg \cdot ha^{-1}$ of sodium humate and 900 $kg \cdot ha^{-1}$ of Lignofert significantly make the soil acidity lower. Many authors (Wisniowska-Kielian and Niemiec [18], Gondek and Filipek-Mazur [19], Vollmanova et al [20]) refer to a positive correlation dependence between the fertilizer dose or pH value and bio-accessibility of metals.

Common knowledge that the metals cumulate in the plants especially in their roots, less in vegetative mass and least in generative organs was confirmed in ten out of eleven analyzed metals. Zn was an exception. Its amount in the grain was comparable with its amount in the roots (Tables 3 and 5) but its amount in the straw was lower than in the roots.

The application of coal substances caused also the increase of heavy metal contents in the soil (Table 6). Sodium humate use in comparison with the control variant

Table 3

The effect of tested materials on the content of eleven metals in spring barley grain

Treatment		Cd	Pb	Hg	As	Cr	Zn	Cu	Co	Ni	Mn	Fe
Number	Designation	[mg · kg^{-1}]										
1	0	0.084a	0.956a	0.0057b	0.0083a	0.219a	33.35a	7.11b	0.215a	0.341a	15.91a	33.52a
2	SH	0.100b	1.047a	0.0007a	0.0173b	0.222a	37.12a	7.09b	0.293ab	0.546b	16.57a	35.65a
3	Lig	0.099b	1.042a	0.0074b	0.0074a	0.216a	32.78a	7.53c	0.323b	0.355a	15.38a	39.98a
4	NPK	0.136c	0.965a	0.0023a	0.0189b	0.299b	44.72b	5.63a	0.396b	0.630b	22.92b	52.14b
Limited values		0.1	1.0	0.05	0.2	4.0	—	10.0	—	3.0	—	—
$LSD_{0.05}$		0.0139	0.1623	0.00245	0.00433	0.0696	5.9929	0.277	0.1075	0.1523	1.325	8.172
$LSD_{0.01}$		0.0189	0.2200	0.00332	0.00587	0.0944	8.12107	0.375	0.1457	0.2064	1.796	11.075

LSD – Lowest Significant Difference at the level $\alpha = 0.05$ and $\alpha = 0.01$.

Table 4

The effect of tested materials on the content of eleven metals in spring barley straw

Treatment		Cd	Pb	Hg	As	Cr	Zn	Cu	Co	Ni	Mn	Fe
Number	Designation	[mg · kg^{-1}]										
1	0	0.184a	1.913a	0.0024a	0.0100a	3.27b	30.58b	12.31a	0.615a	0.953ab	31.04a	163.8a
2	SH	0.157a	1.481a	0.0069a	0.0196a	4.34b	27.73b	12.37a	0.730ab	1.168ab	30.89a	230.3b
3	Lig	0.166a	1.845a	0.0289b	0.0129a	3.50b	18.26a	10.22a	0.712ab	0.881a	24.11a	141.1a
4	NPK	0.339b	1.703a	0.0084a	0.0230a	1.38a	32.72b	9.13a	0.837b	1.214b	49.44b	181.0ab
$LSD_{0.05}$		0.0575	0.7214	0.01737	0.01359	1.629	7.345	3.517	0.2068	0.2924	7.882	65.312
$LSD_{0.01}$		0.0791	0.9969	0.02385	0.01867	2.237	10.090	4.831	0.2841	0.4017	10.827	89.714

LSD – Lowest Significant Difference at the level $\alpha = 0.05$ and $\alpha = 0.01$.

Table 5

The effect of tested materials on the content of eleven metals in spring barley roots

Treatment		Cd	Pb	Hg	As	Cr	Zn	Cu	Co	Ni	Mn	Fe
Number	Designation	$[mg \cdot kg^{-1}]$										
1	0	0.344	3.825	0.0441	0.0458	10.25	33.67	26.81	1.325	4.885	51.32	1877
2	SH	0.365	3.785	0.0383	0.5302	13.19	29.17	21.63	1.565	5.575	68.47	2609
3	Lig	0.376	4.365	0.0382	0.4587	16.48	33.74	16.22	1.925	6.140	72.14	2949
4	NPK	0.776	4.785	0.0629	0.6793	29.18	61.33	15.87	2.565	9.510	106.66	3854

Table 6

The effect of tested materials on the content of heavy metals (total forms) and some agrochemical parameters in the soil at the end of the trial

Treatment		Cd	Pb	Hg	As	Cr	Zn	Cu	Co	Ni	Mn	Fe	pH_{KCl}	C_{ox}
Number	Destination	$[mg \cdot kg^{-1}]$												[%]
1	0	0.355a	13.47a	0.031a	4.73a	16.98a	28.0a	7.68a	8.48a	14.73a	372a	11 469a	5.63a	0.954a
2	SH	0.392a	14.27a	0.030a	5.03a	18.05a	36.3b	12.97b	10.03b	16.75b	403a	12 041a	5.95b	1.107b
3	Lig	0.365a	16.25b	0.030a	4.87a	17.92a	32.4ab	12.34b	9.40ab	16.43b	419a	12 118a	5.92b	1.091b
4	NPK	0.390a	13.27a	0.028a	5.32a	17.33a	28.6a	10.05ab	8.98a	15.07a	408a	11 722a	5.60a	0.893a
BET		0.52	15.0	0.0345	5.68	19.2	34.8	11.6	9.8	18.1	412.2	14 964	5.68	0.980
Limited values		0.7	70	0.5	25	70	150	60	15	50	—	—	—	—
$LSD_{0.05}$		0.0484	1.6217	0.00683	0.767	2.614	5.733	4.325	0.980	1.3526	58.44	1 637.0	0.13	0.169
$LSD_{0.01}$		0.0665	2.2276	0.00938	1.054	3.590	7.875	5.941	1.346	1.8580	80.28	2 248.6	0.18	0.219

* Before establishing the trial, LSD – Lowest Significant Difference at the level $\alpha = 0.05$ and $\alpha = 0.01$.

significantly increased the contents of Zn, Co, Ni, Cu and Lignofert use caused the increase of Pb, Ni and Cu. On the other hand, the application of fertilizers (variant 4) did not significantly change the amounts of metals in the soil. This fact relates to the application doses of fertilizers and the contents of metals in them.

Compared amounts of metals in the soil before and at the end of the trial showed the decrease of the Cd, Hg, As, Cr, Ni and Fe contents in all variants. Application of sodium humate caused increased contents of Zn, Cu and Co and used Lignofert increased the contents of Pb, Cu and Mn. Both substances positively effected on the increase of carbon in the soil. The contents of heavy metals and C_{ox} in the variant where fertilizers were not used (variant 1) and in the variant with the application of NPK fertilizers (variant 4) were lower than before the trial. The lowest amount of carbon was in variant 4 as a result of higher mineralization of organic substances in the soil after fertilizers application.

The amounts of the metals at the end of the trial showed lower values than the allowable limit amounts are.

Conclusions

The achieved results did not confirm the inhibitive effect of sodium humate (SH) and Lignofert (Lig) for uptake of heavy metals into the plants. Conversely, the content of three out of eleven metals (As, Cd and Ni) in the barley grain and one (Fe) in the straw increased after SH application in a statistically significant way in comparison with the control variant. A significant decrease in content of mercury was demonstrated only in the grain. Lignofert statistically significantly increased the content of up to four metals (Cd, Hg, Cu and Co) in the grain and one of them (Hg) in the straw. Its application did not cause the significant decrease of any heavy metal contents in the grain. The content only of one metal (Zn) decreased in the straw significantly.

The application of a rational dose of NPK fertilizers in a statistically significant way increased the content of eight out of eleven investigated heavy metals in the barley grain as a result of their moderate acidification effect on the soil.

The use of SH and Lig was not more risky from the viewpoint of heavy metal cumulation in spring barley than the use of NPK fertilizers. However, their application in order to inhibit the entrance of most heavy metals into the plants is not rationale. Both coal substances simultaneously increased significantly the content of carbon and pH value in the soil

The use of fertilizers caused a high decrease of carbon content in the soil but their effect on heavy metal level in the soil was positive, it was lower than the effect of coal substances.

The overall quantities of metals in the soil of all variants were lower than allowable limit at the end of the trial.

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KUMULACJA METALI CIĘŻKICH W ROŚLINACH ORAZ W GLEBIE MODYFIKOWANEJ ZWIĄZKAMI WĘGLA

Abstrakt: Badano wpływ aplikacji chemicznie (humian sodu) i mechanicznie (Lignofert) modyfikowanego węgla wraz z nawozami sztucznymi na zawartość metali ciężkich w korzeniach, pędach oraz ziarnie jęczmienia. Badania prowadzono w glebie płowej z lessu w eksperymencie donicowym. Eksperyment przeprowadzono w Słowackim Uniwersytecie Rolniczym w Nitrze (48°18′ N, 18°06′ E). Uzyskane wyniki nie potwierdziły zakładanego hamującego wpływu humianu sodu (SH) i Lignofert (Lig) na pobieranie metali ciężkich z gleby przez rośliny. Przeciwnie odnotowany został statystycznie istotny wzrost zawartości trzech (As, Cd, Ni) spośród 11 badanych metali w ziarnie jęczmienia oraz jednego (Fe) w pędach tej rośliny po dodaniu SH w porównaniu z kontrolą. Lignofert spowodował statystycznie istotny wzrost zawartości czterech metali (Cd, Hg, Cu i Co) w ziarnie oraz jednego (Hg) w pędach. Zawartość cynku w pędach zmniejszyła się w sposób statystycznie istotny. Zastosowanie nawozów sztucznych spowodowało wzrost zawartości 8 spośród 11 badanych metali w ziarnie jęczmienia. Było to związane z zakwaszeniem gleby przez stosowane nawozy. Użycie SH i Lig nie stanowiło większego zagrożenia w aspekcie kumulacji metali w młodych pędach roślin niż zastosowanie nawozów sztucznych. Jednakże stosowanie SH i Lig w celu ochrony roślin przed gromadzeniem metali ciężkich nie jest racjonalne. Obydwa stosowane związki węglowe powodowały wzrost pH i zawartości węgla w glebie. Aplikacja nawozów sztucznych była przyczyną silnego zmniejszenia zawartości węgla w glebie. Zawartość metali ciężkich w glebie we wszystkich przeprowadzonych próbach była mniejsza niż ustanowione limity.

Słowa kluczowe: węgiel kamienny, węgiel brunatny (lignit), humian sodu, metale ciężkie, jęczmień