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Influence of brown coal on limit of phytotoxicity of soils contaminated with heavy metals

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Abstract

The paper gives knowledge and application values in efficiency of applying brown coal to limit uptake of heavy metals from contaminated soils by different plant species. The paper determines possibility and principles of using brown coal in reclamation of soils contaminated with heavy metals and rebuilding soils on devastated terrains like terrain in the influence zone of Copper–Smelter "Legnica". On the basis of pot experiment it was stated that increasing doses of brown coal limited phytotoxicity of soils. Results of the paper show that tested fertilizer could be applied on soils strongly contaminated with heavy metals giving long-lasting improvement of reclaimed soils.

Keywords: Heavy metal; Mobility; Contaminated soil; Brown coal; Phytotoxicity

1. Introduction

High concentrations of heavy metals such as copper, lead, zinc and cadmium, are accumulating in surface layers of soils situated, among other things, in influencing zones of industrial plants. The most contaminated with heavy metals area in Poland is in the south-west region of the country, particularly Legnicko-Głogowski district. Numerous researches conducted on areas neighbouring with Copper–Smelters "Legnica" and "Głogów" have shown the large accumulation of copper, lead, zinc and cadmium in surface layers of soils [1–5]. Maximum contents of copper and lead, measured within distance less than 1 km from the main emitter, amount to several grams per kilogram of soil. Despite considerable improvement of the air clarity in the last years, soil contamination with heavy metals in the region of mentioned smelters, does not change very much and it can be assumed that for many years it will be the potential threat to whole food chain, and also for ground and surface water and soil microorganisms [6,7].

Listed metals belong to the group of very high degree of potential threat caused in the biological environment. In the aftermath of the biological accumulation of these metals in each element of the environment, they go to the highest link in the food chain [7]. There exist a few methods of coping with this problem. One of the most popular is phytoextraction—the use of pollutant-accumulating plants to remove metals or organic pollutants from soil by concentrating them in harvestable parts [8–11], but it seems that the most efficient way to limit biological activity of heavy metals in soils is transferring them into forms hard accessible for plants. Such properties are possessed by organic matter, which can create organometallic relationships, so-called chelates, with heavy metals affecting their accessibility for plants, soil micro-organisms, as well as exerting an influence on metals potential transfer to the ground and surface water. The essential source of supplementing soils in organic matter can be brown coal or fertilizers made on its basis. The raw coal, as well as modified in different ways, delivers material with high degree of humification, relatively resistant to mineralization and with long-lasting activity [12–15]. Very important advantage of the brown coal is his large resistance to decomposition. It causes that the single use of the brown coal holds raised content of the total coal in soil more than 10 years [16].

The paper determines the possibility of using the brown coal to limit phytotoxicity of soils contaminated with heavy metals. In the research there were used soils received from the area of the Copper–Smelter "Legnica" (I and II zone) and from the Experimental Field of Warsaw Agricultural University (SGGW) in Skierniewice. The soils from I and II zone were highly contaminated with heavy metals (mostly with copper and lead) while soil from Skierniewice had their raised content. Presented paper

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contains results of the pot experiment: chosen physicochemical and chemical properties of soils and plants properties. In the experience, in order to limit transfer of heavy metals from soils to plants there was used brown coal. For the purpose of examining phytotoxicity of soils and possibility of its limitation by using different doses of brown coal, each year different species of plants were tested.

2. Materials and methods

The research was made as the pot experiment in the vegetative hall of the SGGW Experimental Field in Skierniewice in years 2001–2003. The experiment was founded in vases of the Wagner type with 5 kg capacity, with four repetitions in completely random system. The experiment included fertilization with six combinations (0, 50, 75, 100, 150, and 175) [g of brown coal pot^{-1}] for soil from I and II zone of the Copper–Smelter “Legnica” and four combinations (0, 50, 100 and 150) [g of brown coal pot^{-1}] for soil from Skierniewice. Soil in every pot was precisely mixed with appropriate dose of the brown coal, with corresponding doses 0, 30, 45, 60, 90 and 105 [t of brown coal ha^{-1}]. The same mineral fertilization with NPK (nitrogen, phosphorus and potassium) was used in each pot. Basic fertilizers were inserted into the soil before plants sowing and nitrogen also into leaves during plants vegetation. The brown coal which was used as a fertilizer had came from the Lignite Mine “Konin” in Poland. It belonged to soft brown coals, contained 20% of water and pH measured with the use of 1 M KCl was 6; it contained about 70% of humic acids fraction [17]. Basic elements in coal composition [% of dry mass] are: 70 C, 0.65 N, 3.90 Ca, 0.90 Mg, 0.07 K and 0.10 P.

The research was made using brown soil from clayey silt and soil from heavy silty loam at two levels of contamination with copper, lead, zinc and cadmium amounting adequately: I zone 4985 (Cu), 1236 (Pb), 294.6 (Zn), 2.82 (Cd) [mg kg^{-1}] and II zone 1008 (Cu), 413.0 (Pb), 194.5 (Zn), 1.51 (Cd) [mg kg^{-1}]. The first soil (I zone) was located about 0.1 km from main emitter and showed neutral reaction while the second soil (II zone) was located about 1 km from main emitter and showed alkaline reaction (Table 1). Soil from Skierniewice belonged to lessive type with soil separates content of heavy loamy sand. In accordance with the gradation system of chemical polluted soils worked out in The Institute of Soil Science and Plant Cultivation IUNG in Pulawy [18], this soil showed weak contamination with the zinc (154.1) and lead (72.7) and had raised content of cadmium (0.41); content of copper 12.9 [mg kg^{-1}] was natural.

During the experiment in the year 2001 there was tested mixture of grasses with following composition: 40% the perennial ryegrass (*Lolium perenne*), 35% the red fescue (*Festuca rubrics*), 15% the Italian ryegrass (*Lolium multiflorum*), 10% the meadow-grass (*Poa pratensis*). The first swath was assembled in the beginning phase of heading after 51 days of vegetation. The second swath was assembled after 48, and third after 37 days of vegetation. In the year 2002 there was tested mixture of grasses with above-mentioned composition in two swaths and the rye (*Secale cereale*). The first swath of mixture of grasses was assembled in the beginning phase of heading after 46 days of the vegetation and the second swath after 44 days. The rye was assembled in the final phase of popping in the grass-blade after 52 days of vegetation. In the year 2003 there were tested two plants: the serradella (*Ornithopus*) and the red fescue (*Festuca rubrics*). The harvest of the serradella was done in the full blooming after 71 days of vegetation and the red fescue in the beginning phase of heading after 62 days of vegetation.

In the soil samples there were determined: separates content using Casagrande’s method with modification by Prószyński, pH in H_2O and in 1 M KCl with potentiometer’s method, the content of calcium carbonate ($CaCO_3$) using Scheibler’s method, hydrolytic acidity (H_h) using Kappen’s method, content of total nitrogen ($N_{tot.}$) using Kjeldahl’s method, content of organic carbon ($C_{org.}$) using Tiurin’s method, content of exchangeable alkaline cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) in 1 M acetate of the ammonium using *ICP-AES* method. The total exchangeable sorptive capacity of soils towards cations (T) was calculated as the joint value of S and H_h and then there was established the degree of saturation of sorptive complex with alkaline cations (V). Within the framework of the paper there were established the content of heavy metals (copper, lead, zinc and cadmium) in examined soils in following ways: the digestion of soil samples in the mixture of concentrated acids HCl and HNO_3 in the ratio of 3:1 (*aqua regia*) [19] using *AAS* method – total contents; the heating in a water with $2HNO_3$ [20] using *ICP-AES* method – so-called almost total contents; the extraction with EDTA solution (0.017 M $EDTAH_4$ + 0.01135 M Ca $(CH_3COO)_2 \cdot 2H_2O$ + 0.019 M $C_3H_4(OH)(COOH)_3 \cdot H_2O + NH_3$, pH 7.3) [21] using *ICP-AES* method – forms potentially accessible for plants and the extraction with 1 M NH_4NO_3 [22] using *ICP-AES* method –

Table 1
Physicochemical and chemical properties of soils from I and II zone of Copper–Smelter “Legnica” and soil from Skierniewice before experiment

Soil/depth of taking	pH in		$CaCO_3$ (%)	$C_{org.}$ (%)	$N_{tot.}$ (%)	H_h (%)	Exchangeable alkaline cations [cmol(+) kg^{-1} of soil]				S_{BC} (%)	T_{CEC} (%)	V_{BS} (%)
	H_2O	1 M KCl					Ca	Mg	K	Na			
Soil from I zone of Copper–Smelter Legnica (0–30 cm)	7.30	7.05	0.84	0.94	0.091	0.44	13.8	0.91	0.46	0.090	15.3	15.7	97.2
Soil from II zone of Copper–Smelter Legnica (0–30 cm)	7.55	7.30	0.43	0.88	0.072	0.39	12.2	1.06	0.38	0.077	13.7	14.1	97.2
Soil from Skierniewice (0–25 cm)	7.15	6.30	0.27	0.91	0.070	0.94	6.45	0.50	0.55	0.068	7.57	8.51	89.0

forms actually accessible for plants. In samples there was also established total content of heavy metals after the mineralization in the mixture of acids HNO_3 and $HClO_4$—using *ICP-AES* method.

3. Results and discussion

Results received in the research showed that single use of the brown coal increasing doses improved properties of examined soils, particularly reaction, hydrolytic acidity, sorptive capacity and organic carbon. It had influence on decrease of solubility (mobility) of heavy metals compounds in soil, and consequently their phytoavailability. From the research it results that together with growth of the brown coal dose grew the sorptive capacity of examined soils (together with growth of exchangeable alkaline cations) and the degree of sorptive complex saturation with alkaline cations. These results are similar to results received by Maciejewska [15,16] and other authors examining the influence of the brown coal on sorptive properties of soils [13,14]. The use of increasing doses of the brown coal caused growth of organic carbon content in examined soils (in the case of soils from the Copper–Smelter “Legnica” it amounted from 10% to 110%, and in the case of soil from Skierniewice from 1% to 31%). Its value remained on similar level during each experiment duration. The relation of organic carbon to nitrogen in objects fertilized with the brown coal was situated in the wide range from 10 to 30, showing suitable degree of humification of the organic matter (Table 2).

The use of increasing doses of the brown coal influenced insignificantly on the decrease of total and almost total of all heavy metals contents. In the case of the extraction with *aqua regia* statistical significance of metals content decrease in tested soils has not been examined, and in the case of the heating in water with $2HNO_3$ it was insignificant. These results confirm the lack of influence of the brown coal on total metals contents in soil. For the estimation of the heavy metals solubility or soils phytotoxicity there were used soil tests based on single (simple) extractions. Using them, forms of metals solvable in two different extractive solutions (giving actual and potential accessibility of heavy metals to plants [2]) were established. The solution 1 M NH_4NO_3 extracted the most of copper in the case of soils from the Copper–Smelter “Legnica” and the most of zinc in the case of soil from Skierniewice, that is metals which were in the highest concentrations in examined soils. Highest participations of forms of copper, lead, zinc and cadmium extracted by 1 M NH_4NO_3 were noted in the case of soils with lower pH values and lower sorptive capacities, and that confirms observations made by Karczewska [2]. It points on the key role of the reaction and sorptive properties in processes of heavy metals desorption in contaminated soils. For every tested soil increasing doses of the fertilizer caused statistically significance of the decrease of heavy metals forms actually accessible for plants, what illustrates the high ability of the brown coal to limit soil phytotoxicity (Table 3).

For the purpose of single extractions there was also used EDTA solution—the reagent of greater aggressiveness with relation to 1 M NH_4NO_3 solution. It was used to estimate potential solubility and bioavailability of metals [2,23–25]. It was stated that EDTA solution extracted the most of copper forms in the case of soils from the Copper–Smelter “Legnica” and zinc forms in the case of soil from Skierniewice. Besides statistically significance of the decrease of all heavy metals forms extracted with EDTA solution together with growth of the brown coal dose were noticed. It shows favourable influence of the examined fertilizer on limitation not only forms actually accessible for plants, but also forms which are potential threat to them. During

Table 2
The influence of the brown coal on physicochemical and chemical properties of soils—average from years of experiment duration

Soil	Dose of brown coal (g pot^{-1})	pH in 1 M KCl	$C_{org.}$ (%)	$N_{tot.}$ (%)	H_h (%)	Exchangeable alkaline cations [cmol(+) kg^{-1} of soil]				S_{BC} (%)	T_{CEC} (%)	V_{BS} (%)
						Ca	Mg	K	Na			
I zone	0	6.73	0.84	0.10	0.70	12.74	0.84	0.73	0.17	14.48	15.18	95.4
	50	6.78	1.48	0.11	0.63	15.39	1.04	0.81	0.18	17.42	18.04	96.5
	75	6.94	1.69	0.11	0.55	16.47	1.19	0.87	0.19	18.72	19.27	97.2
	100	7.03	1.79	0.11	0.47	17.65	1.31	0.88	0.19	20.04	20.51	97.7
	150	7.17	2.01	0.12	0.38	18.87	1.42	0.92	0.19	21.41	21.79	98.2
	175	7.19	2.07	0.12	0.33	19.79	1.47	0.94	0.19	22.38	22.72	98.5
	LSD $\alpha = 0.05$	0.12	0.20	0.01	0.05	0.71	0.09	0.05	0.01	0.73	0.73	0.3
II zone	0	6.94	0.79	0.08	0.67	11.62	1.69	0.58	0.15	14.04	14.71	95.4
	50	7.01	1.17	0.08	0.62	13.14	1.91	0.63	0.15	15.83	16.45	96.2
	75	7.14	1.44	0.09	0.57	14.00	2.09	0.69	0.17	16.94	17.51	96.7
	100	7.19	1.57	0.09	0.49	14.82	2.21	0.69	0.17	17.90	18.39	97.3
	150	7.21	1.82	0.10	0.39	15.90	2.39	0.72	0.17	19.17	19.56	98.0
	175	7.22	1.90	0.10	0.36	16.33	2.45	0.73	0.17	19.68	20.04	98.2
	LSD $\alpha = 0.05$	0.11	0.19	0.01	0.05	0.59	0.15	0.04	0.01	0.62	0.62	0.3
Skierniewice	0	5.88	0.82	0.07	1.01	6.84	0.39	0.52	0.11	7.85	8.86	88.3
	50	6.11	1.15	0.07	0.94	7.44	0.48	0.57	0.11	8.61	9.55	89.9
	100	6.25	1.35	0.08	0.88	8.13	0.65	0.59	0.11	9.47	10.35	91.4
	150	6.33	1.55	0.09	0.85	9.12	0.94	0.65	0.12	10.82	11.67	92.7
	LSD $\alpha = 0.05$	0.14	0.17	0.01	0.05	0.38	0.05	0.04	0.01	0.38	0.39	0.6

Table 3
The influence of the brown coal on total and almost total heavy metals content and forms of heavy metals actually and potentially accessible for plants

Metal	Dose of brown coal (g pot^{-1})	Total contents (*aqua regia*) [mg kg^{-1} of soil]			Almost total contents (2 M HNO_3) [mg kg^{-1} of soil]			Forms potentially accessible (EDTA) [mg kg^{-1} of soil]			Forms actually accessible (1 M NH_4NO_3) [mg kg^{-1} of soil]		
		I zone	II zone	Skierniewice	I zone	II zone	Skierniewice	I zone	II zone	Skierniewice	I zone	II zone	Skierniewice
Cu	0	4968	999	12.28	6542	1242	13.44	2746	348.4	7.47	89.2	16.83	0.60
	50	4834	995	8.62	6444	1220	12.20	2511	321.5	3.98	61.8	8.08	0.48
	75	4819	992	–	6398	1199	–	2231	278.7		53.5	6.75	–
	100	4831	995	8.22	6351	1183	11.37	2103	254.1	1.85	47.4	5.15	0.38
	150	4718	989	7.95	6336	1179	10.88	1974	232.6	1.57	42.0	4.13	0.29
	175	4599	976	–	6328	1175	–	1907	227.9		37.4	3.10	–
	LSD $\alpha = 0.05$	–	–	–	281	50	2.31	87	17.6	0.47	4.2	0.88	0.08
Pb	0	1216	389.2	72.4	1182	358.9	67.6	360.0	100.2	21.0	1.09	0.11	–
	50	1198	382.5	72.4	1164	349.8	64.3	340.6	92.7	17.5	0.87	–	–
	75	1193	376.7	–	1151	344.7	–	312.7	83.6		0.57	–	–
	100	1194	368.4	72.2	1146	341.4	63.1	304.0	80.9	16.3	0.45	–	–
	150	1172	371.6	71.6	1141	335.3	63.1	285.5	74.5	15.5	0.34	–	–
	175	1153	370.2	–	1135	335.3	–	279.2	73.1		0.24	–	–
	LSD $\alpha = 0.05$	–	–	–	47	25.4	5.8	17.1	6.9	1.7	0.09	–	–
Zn	0	294.3	190.4	154.5	280.5	203.5	149.6	112.6	65.7	66.7	11.80	9.18	8.27
	50	277.8	191.5	156.0	273.2	198.0	146.9	106.5	60.0	62.1	9.95	6.55	4.09
	75	278.3	188.4	–	270.6	193.8	–	95.4	55.8		5.38	5.51	–
	100	243.5	190.2	141.7	266.1	189.6	144.3	92.5	54.8	53.5	4.58	4.58	2.33
	150	229.2	184.1	138.4	262.1	187.6	141.9	84.8	50.4	43.7	2.84	3.80	1.18
	175	233.6	183.7	–	262.1	185.9	–	83.0	49.4		2.01	2.95	–
	LSD $\alpha = 0.05$	–	–	–	23.8	17.5	10.5	5.5	3.1	4.7	0.71	0.65	0.83
Cd	0	2.81	1.49	0.41	2.42	1.29	0.38	0.78	0.40	0.15	0.18	–	–
	50	2.81	1.47	0.40	2.39	1.27	0.37	0.74	0.38	0.13	0.14	–	–
	75	2.80	1.48	–	2.32	1.26	–	0.74	0.37		0.13	–	–
	100	2.74	1.46	0.39	2.27	1.24	0.35	0.69	0.36	0.12	0.12	–	–
	150	2.71	1.47	0.39	2.26	1.23	0.35	0.67	0.35	0.12	0.10	–	–
	175	2.73	1.46	–	2.25	1.22	–	0.63	0.33		0.10	–	–
	LSD $\alpha = 0.05$	–	–	–	0.26	0.15	0.05	0.13	0.06	0.04	0.03	–	–

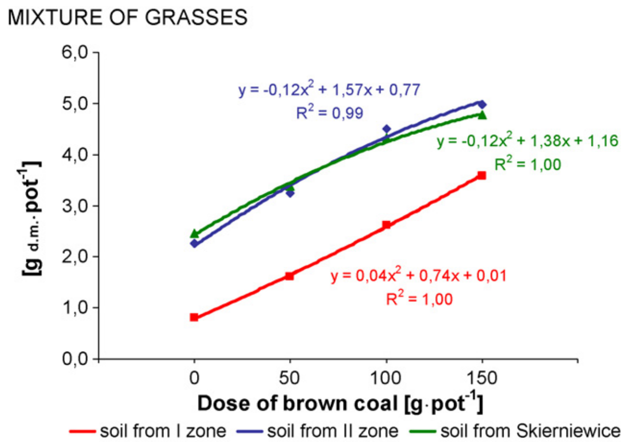

Fig. 1. The influence of the brown coal on average crop of three mixture of grasses swaths tested in the year 2001.

the time of pot experiment the distinct reaction of tested plants on the magnitude of used the brown coal dose was noticed. This results first of all from humic substances contained in used fertilizer which are source of plants growth and favourably affect their crop [13–15]. The growth of all tested plants crop after use of the brown coal was showed (even eight times bigger) (Figs. 1–3).

Analyzed contents of heavy metals in several species of plants tested on soils from I and II zone of the Copper–Smelter "Legnica" and on soil from Skierniewice with reference to the brown coal doses permits to say that used fertilizer affected decrease of heavy metals uptake from soils by plants (Table 4).

The content of each metal (copper, lead, zinc and cadmium) in tested plants decreased statistically significant together with growth of the brown coal dose. It was noticed that phytoavailability of heavy metals was the most limited in the case of highest used doses (175 g pot^{-1} of the brown coal for soils from the Copper–Smelter "Legnica" and 150 g pot^{-1} of the brown coal for soil from Skierniewice). The most significant decrease of heavy metals content in plants was obtained after use of the brown coal single dose. In examined plants the most content had zinc, then copper, lead and cadmium. The greatest uptaking of copper and zinc was noticed in serradella, for lead and cadmium—II swath of mixture of grasses from the year 2002. The least copper was uptaken by III swath of mixture of grasses in year 2001, lead by serradella, zinc by I swath of mixture of grasses from the year 2001, and cadmium by red fescue. Besides it was seen that uptaking of copper and lead by plants was a lot higher on soil from I zone of the Copper–Smelter "Legnica" than on remaining examined soils, what is connected directly with a degree of their contamination. Arranging content of metal in plants by limitation intensity of translocating heavy metals to plants under influence of the brown coal it can be stated that the greatest limitation intensity of copper and cadmium had the mixture of grasses, and for lead and zinc—a rye.

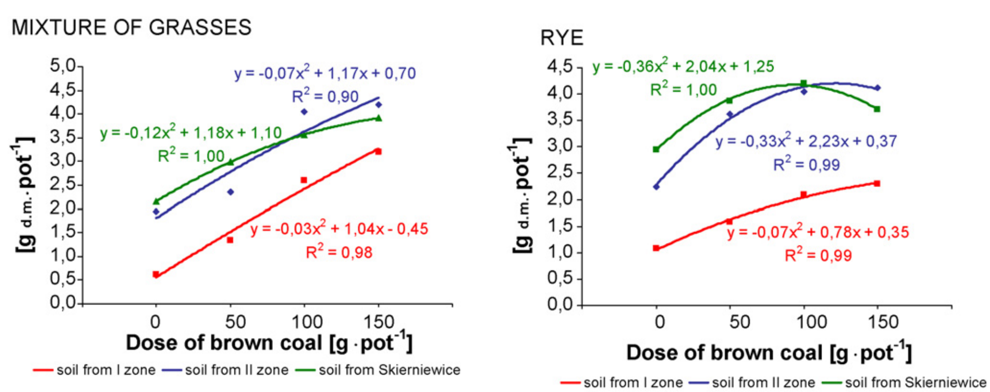

Fig. 2. The influence of the brown coal on average crop of two mixture of grasses swaths and the rye tested in the year 2002.

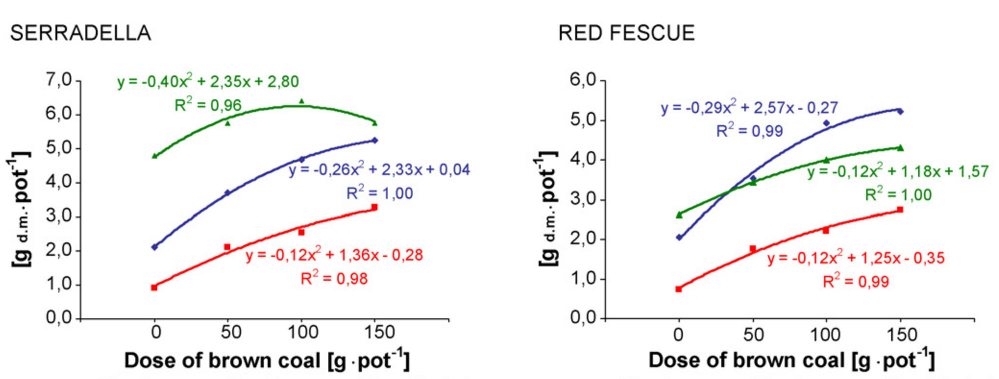

Fig. 3. The influence of the brown coal on serradella crop and the red fescue tested in the year 2003.

Table 4
The content of heavy metals in plants tested on soil from I and II zone of the Copper–Smelter “Legnica” and soil from Skierniewice depending on the brown coal dose

Plant/year	Dose of brown coal (g pot^{-1})	Heavy metals content in plants tested on soils from I and II zone of Copper–Smelter Legnica and soil from Skierniewice [mg kg^{-1} d.m.]											
		Copper			Lead			Zinc			Cadmium		
		I zone	II zone	Skierniewice	I zone	II zone	Skierniewice	I zone	II zone	Skierniewice	I zone	II zone	Skierniewice
	0	158.1	56.8	16.6	30.1	15.6	4.003	223.5	199.8	145	2.69	2.10	0.815
	50	98.3	40.0	14.58	22.6	8.6	3.33	189.0	186.0	130.8	1.72	1.48	0.568
	75	74.8	30.1		16.2	7.2		167.1	154.8		1.44	1.24	
I swath of grass mixture 2001	100	59.1	23.7	14.2	14.4	6.3	2.97	162.0	147.0	121.1	1.38	1.12	0.48
	150	51.5	21.8	12.7	10.2	4.7	2.338	135.0	124.0	101.1	0.96	0.90	0.36
	175	45.6	19.5		10.3	4.3		134.2	123.6		0.95	0.87	
	LSD $\alpha = 0.05$	8.4	2.7	1.6	2.2	1.2	0.4	9.0	8.2	10.2	0.19	0.22	0.12
	0	260.0	88.0	15.3	30.1	12.4	4.513	241.0	242.5	162.5	3.22	2.35	0.918
	50	111.7	39.5	9.575	20.0	8.7	3.06	205.0	209.0	141.5	2.12	1.67	0.668
	75	83.0	36.7		17.2	7.2		191.8	194.2		1.77	1.43	
II swath of grass mixture 2001	100	57.6	32.8	9.25	16.8	6.1	2.795	183.5	189.5	134.8	1.65	1.39	0.563
	150	51.6	24.6	8.825	11.8	5.4	2.118	161.0	161.5	121.3	1.22	1.02	0.433
	175	40.4	21.6		11.8	5.0		160.2	160.1		1.19	1.02	
	LSD $\alpha = 0.05$	6.0	4.1	1.3	1.4	0.9	0.6	13.1	13.2	9.6	0.25	0.28	0.13
	0	0.0	63.9	14.68	0.00	13.3	5.803	0.0	283.5	175.8	0.00	2.40	1.045
	50	123.9	49.1	7.85	30.3	11.6	4.55	292.0	256.8	165	3.45	2.10	0.805
	75	95.1	37.8		24.0	8.8		250.8	209.5		2.61	1.57	
III swath of grass mixture 2001	100	75.5	33.0	7.875	20.0	8.3	3.105	226.0	201.0	151	2.18	1.47	0.638
	150	56.5	26.8	7.15	14.5	6.2	2.398	174.0	160.0	118	1.31	1.07	0.46
	175	48.7	26.0		12.9	6.1		162.4	158.8		1.16	1.06	
	LSD $\alpha = 0.05$	8.0	2.9	1.0	2.1	0.9	0.6	17.3	13.0	8.9	0.33	0.18	0.13
	0	284.0	96.0	17.18	41.5	19.3	4.338	289.8	270.0	173.5	3.67	2.69	1.14
	50	132.5	56.1	12.2	30.0	14.6	3.085	243.0	230.0	148	2.57	1.89	0.85
	75	101.6	40.5		22.9	8.5		215.7	205.7		1.81	1.48	
I swath of grass mixture 2002	100	92.0	32.0	11.25	21.2	7.2	2.788	206.5	193.8	131	1.43	1.41	0.53
	150	54.0	25.2	8.075	13.1	4.4	2.175	176.6	173.8	115	1.12	0.95	0.408
	175	51.7	22.6		12.9	4.3		175.7	170.5		1.09	0.93	
	LSD $\alpha = 0.05$	10.7	4.58	1.4	2.5	1.10	0.4	12.8	14.8	8.4	0.29	0.19	0.16
	0	328.0	105.0	16.58	46.6	21.0	4.538	312.0	312.0	182.7	3.72	3.20	1.24
	50	154.8	59.5	10.23	33.0	16.0	3.488	269.5	269.5	157.8	2.38	2.16	0.813
	75	108.6	39.7		22.5	9.3		223.9	223.9		1.80	1.50	
II swath of grass mixture 2002	100	82.0	29.3	9.375	19.8	8.0	2.918	210.3	210.3	128.2	1.67	1.34	0.565
	150	61.0	23.5	7.725	13.1	4.7	2.315	167.0	167.0	105	1.08	0.86	0.383
	175	52.5	20.5		13.3	4.6		165.8	166.3		1.07	0.85	
	LSD $\alpha = 0.05$	9.8	4.6	1.1	2.7	1.0	0.4	12.8	11.9	10.9	0.23	0.24	0.17
	0	246.0	99.8	16.28	45.2	19.7	3.888	300.5	276.8	186.3	2.63	1.88	0.603
	50	178.0	60.0	14.18	27.3	13.5	2.323	263.5	256.0	167	1.66	1.44	0.403
	75	118.6	45.1		23.6	9.3		224.3	223.5		1.29	1.18	
Rye 2002	100	113.0	43.0	10.33	21.8	7.6	1.883	203.0	203.0	137.5	1.20	1.09	0.303
	150	63.0	25.4	8.875	9.4	5.8	0.893	119.0	125.0	84.68	0.79	0.67	0.198

Table 4 (*Continued*)

Plant/year	Dose of brown coal (g pot^{-1})	Heavy metals content in plants tested on soils from I and II zone of Copper–Smelter Legnica and soil from Skierniewice [mg kg^{-1} d.m.]											
		Copper			Lead			Zinc			Cadmium		
		I zone	II zone	Skierniewice	I zone	II zone	Skierniewice	I zone	II zone	Skierniewice	I zone	II zone	Skierniewice
	175	62.6	25.2		9.2	5.5		117.6	123.1		0.79	0.65	
	LSD $\alpha = 0.05$	10.7	4.6	1.7	2.1	1.1	0.4	12.3	12.6	10.8	0.23	0.16	0.09
Serradella 2003	0	321.0	115.0	17.9	35.35	13.1	2.668	371.5	341.5	227.1	2.01	1.75	1.478
	50	204.0	63.0	11	21.9	10.0	1.753	310.5	302.0	203.4	1.65	1.40	1.215
	75	162.2	51.7		16.8	7.4		268.6	263.5		1.28	1.17	
	100	139.0	43.0	9.05	12.0	6.5	1.01	250.0	246.0	175.5	1.27	1.08	0.953
	150	104.0	35.0	7.925	9.5	4.9	0.973	170.0	173.0	124.5	0.85	0.89	0.673
	175	100.5	31.0		9.4	4.7		169.3	169.8		0.84	0.88	
	LSD $\alpha = 0.05$	13.8	4.0	1.7	2.1	0.8	0.3	14.1	14.9	12.0	0.16	0.20	0.17
Red fescue 2003	0	311.8	95.0	11.33	37.8	15.7	3.185	253.0	229.0	151.4	1.81	1.62	0.413
	50	250.9	70.0	8.45	28.0	9.4	2.345	223.0	201.8	134.8	1.52	1.32	0.358
	75	138.3	47.4		18.5	8.0		195.0	175.2		1.26	0.95	
	100	103.8	40.0	7.675	15.5	8.0	1.833	185.0	160.2	112.1	1.13	0.87	0.275
	150	75.6	29.0	7.45	10.4	5.5	1.758	153.0	149.0	92.7	0.62	0.61	0.165
	175	74.1	28.6		10.2	5.3		147.3	144.9		0.60	0.60	
	LSD $\alpha = 0.05$	9.9	5.6		1.9	0.98	0.3	11.0	9.7	8.3	0.17	0.12	0.04

4. Conclusions

1. The use of increasing doses of the brown coal caused following changes in chosen physicochemical properties of examined soils:
   - Stabilization of the soils reaction during experiment duration, especially visible after use of highest doses of examined fertilizer.
   - Decrease of hydrolytic acidity.
   - Improvement of the sorptive properties of soils, and particularly growth of the sorptive capacity, the sum of alkaline cations and the degree of saturation of sorptive complex.
   - Growth of the organic coal content.
2. The use of increasing doses of the brown coal leads to decreasing content of heavy metals forms actually and potentially accessible by plants.
3. The use of increasing doses of the brown coal caused statistically significant decrease of heavy metals content in plants while change of total and almost total heavy metals content in soils was statistically insignificant.
4. Profitable changes of soils properties after use of increasing doses of examined fertilizer were confirmed by magnitude of tested plants crop.
5. Results of the paper showed that the brown coal can be applied especially on soils strongly contaminated with heavy metals, and among analyzed doses of the fertilizer it is suggested to use dose of 90 [t of the brown coal ha^{-1}] (an equivalent of a dose 150 [g pot^{-1}]). It is not suggested to use dose of 105 [t of the brown coal ha^{-1}] (an equivalent of a dose 175 g pot^{-1}) because in most cases it did not cause statistically significant change of examined variable in relation to the dose of 90 [t of the brown coal ha^{-1}].

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