Use of brown coal as a detoxifier of soils contaminated with heavy metals

Olga S. Bezuglova [a,*], Sergey N. Gorbov [a], Svetlana A. Tischenko [a], Anastasia E. Shimko [b]

[a] Southern Federal University, Academy of Biology and Biotechnology, 344090 Rostov-on-Don, Russia
[b] Don Zonal Research Institute of Agriculture, Rassvet, Rostov Region, Russia

ABSTRACT

The main objective of the work was to study the applicability of brown coal as a sorbing and detoxifying agent of soils contaminated with heavy metals. Both laboratory experiments and field small-plot experiments on an Urbanozem contaminated with lead and zinc have been conducted. Brown coal from the Aleksandria deposit (Ukraine) has been used as a sorbent. It has been shown that brown coal has an increased capacity to sorb heavy metals due to the large specific surface area and the presence of functional groups capable of ensuring the chemosorption of contaminant cations. However, the degree of adsorption by brown coal varies among the cations. Brown coal can be recommended as an ameliorant for soils contaminated with lead, zinc, and copper. It is important to correctly calculate the application rate of the ameliorant. An empirical formula was proposed for the calculation of the ameliorant rate, which can be used for the most cost-efficient detoxification method of soils contaminated with lead, zinc, and copper.

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1. Introduction

Studies on the detoxification of soils locally contaminated with heavy metals (HMs) are of great current interest. The HM content in the topsoil exceeding the maximum permissible concentration (MPC) by tens of times can be reached in the buffer zones of motor and rail roads, mines, and industrial enterprises. HMs get with industrial waste into the sewerage system and then into the soil (Nehls et al., 2008). The wide range of HMs in waste water is typical not only for traditional dirty works (e.g., galvanic shops), where these elements are used in the technological cycle, but also for food and light industries.

The total amount of soluble metals (primarily nickel, chromium, zinc, and copper) removed with waste water and emissions from industrial factories are estimated at several tons per year (Privalenko et al., 1993; EMEP Status Report 2/06, 2006). The high load of such elements as zinc, copper, chromium, cobalt, silver, vanadium, nickel, molybdenum, and lead, on the environment is related to their concentration in solid-phase fallout. As a result, there are many areas in the world with intensive local pollution by heavy metals (Kabata-Pendias, 2011), including in many countries of Europe (Van Ginneken et al., 2007).

This is a great reason to pay more attention to the problem of remediation of heavy metal contaminated soil. No universal and sufficiently efficient technologies are yet developed for the removal of HMs from the soil profile or their fixation in a nontoxic form. All the known

methods have some of the following shortcomings: expensiveness, non-universality (suitability for certain soils), impact on elementary soil processes, or insufficient production of some ameliorants. Phytomelioration, which is an environmentally substantiated remediation method, is efficient only for the soils containing low concentrations of HMs.

Actual technologies for remediation of HM contaminated soils Gupta et al. (2000) have classified in three groups: gentle in situ remediation, in situ harsh soil restrictive measures and in situ or ex situ harsh soil destructive measures, which propose the removal of contaminated soil and removal to decontamination and/or storage.

In the first group there are adsorptive, biotechnological technical methods and phytoremediation. The most universal and accessible methods are adsorption methods based on the use of natural materials with good sorption properties.

The main goal of such methods is to reduce the bioavailability and mobility of metal. The principal requirements for sorbent is a high sorption capacity, ensuring long-term stability of immobilized heavy metal. A wide range of natural materials satisfy these requirements. It is a bentonite and composition on its basis and other clay, sapropel, brown coal, charcoal and compost, as well as mixtures of zeolites with organic matter or a mixture of poultry manure, marble chips and calcium peroxide. (Bezuglova et al., 1996; Karczewska et al., 1996; Damian and Damian, 2007; Galamboš et al., 2009; Kireicheva et al., 2009; Akbasova et al., 2012; Simonova et al., 2012; Zagrebin et al., 2012; Guerra et al., 2013; Tikhomirova et al., 2013; Beisebekov et al., 2015; Bourliva et al., 2015; Karer et al., 2015). Another material also can be used as sorbents such as lime or some salts. The mechanism of their action is not sorption

* Corresponding author at: Soil Science Department, Academy of Biology and Biotechnology, Southern Federal University, 344090 Rostov-on-Don, Russia.
E-mail address: lola314@mail.ru (O.S. Bezuglova).

but the formation of slightly mobile metal compounds (Bonee, 1986). However, as rightly noted by Wuana and Okieimen (2011), the immobilization mechanisms of heavy metals on sorbents has not been elucidated exactly. It is related to the complexity of the soil environment and the limitations of existing analytical methods.

Probably the brown coal is the most complementary substance to the soil from all the above. This is not only due large internal sorption surface provided by inclusion of the clay material and the presence of developed porous structure, but also the presence of functional groups of its humic acids (HA), which increase the sorption capacity of brown coal (Perminova and Hatfield, 2005; Trusova, 2014). The HA of the brown coal provides not only the sorption of heavy metals but also their neutralization through abiotic and biotic degradation by catalysis of redox reactions. The HA can be a stimulator of plant growth and storage of nutrients (Karczewska et al., 1996; Zagrebin et al., 2012; Demin et al., 2013; Tarasova and Kudryasheva, 2013; Rogova et al., 2013).

Ladonin (1997) showed that HMs can be sorbed even in the presence of high concentrations of calcium and other cations in the soil solution, when these cations can occupy almost all exchangeable sites. This phenomenon is called specific sorption. Although the sorption of HMs is irreversible in this case, a close correlation is observed between the cation exchange capacity of separate clay minerals present in brown coal and their capacity to specifically sorb HM ions from the soil solution.

2. Objects and methods

Studies were performed with calcareous ordinary Chernozem and Urbanozems. The Chernozem was collected in the Botanical garden of the Southern Federal University of Rostov-on-Don (point #1 of the map of Fig. 1). The basic physico-chemical properties: pH – 7.9, content of organic carbon – 2.81%, the content of carbonates – 0.32%, the content of <0.01 mm particles – 56,9%. Urbanozems were sampled in the central part of Rostov-on-Don (point #3 of the map of Fig. 1), a great industrial center of southern Russia, on the plots with heavy environmental conditions: in the close vicinity of the paint, varnish, and lacquer plant (point #2 of the map of Fig. 1) or near motor roads with heavy traffic (point #4 of the map of Fig. 1). The basic physico-chemical properties: pH – 8.1, content of organic carbon – 2.54%, the content of carbonates – 0.38%, the content of <0.01 mm particles – 51,2%.

The applicability of brown coal as a sorbing and detoxifying agent was determined. Brown coal from the Aleksandria deposit (Ukraine) was used as a sorbent. Its properties: carbon content in % on ash-free substance – 51.7; nitrogen is 1.2%; pH 5.1; the ash content is 40.0%. The frame silicate from the group of zeolites – phillipsite – is dominated in the mineralogical composition (Bezuglova, 2001). Humic substances of brown coal are close to those of the soil; therefore, they do not affect the elementary soil processes. Moreover, an improvement of the humus and structural state of soil is observed at the application of brown coal (Bezuglova and Etsenkova, 1992; Bezuglova and Shevchenko, 1996; Bezuglova, 2001).

To investigate the sorbing capacity of brown coal for HMs, some experiments were set up for the determination of HM sorption parameters, during which the adsorption of zinc and lead from their solutions by brown coal was studied, and the specific surface areas of brown coal and soils were calculated from the maximum hygroscopicity. Several model experiments in the laboratory and one small field experiment were carried out during investigation. This was related to the fact that the method was designed for areas with high and superhigh levels of contamination with heavy metals; however, the necessary test integrity was difficult to attain under natural conditions, and we considered inadmissible the artificial contamination even of small soil
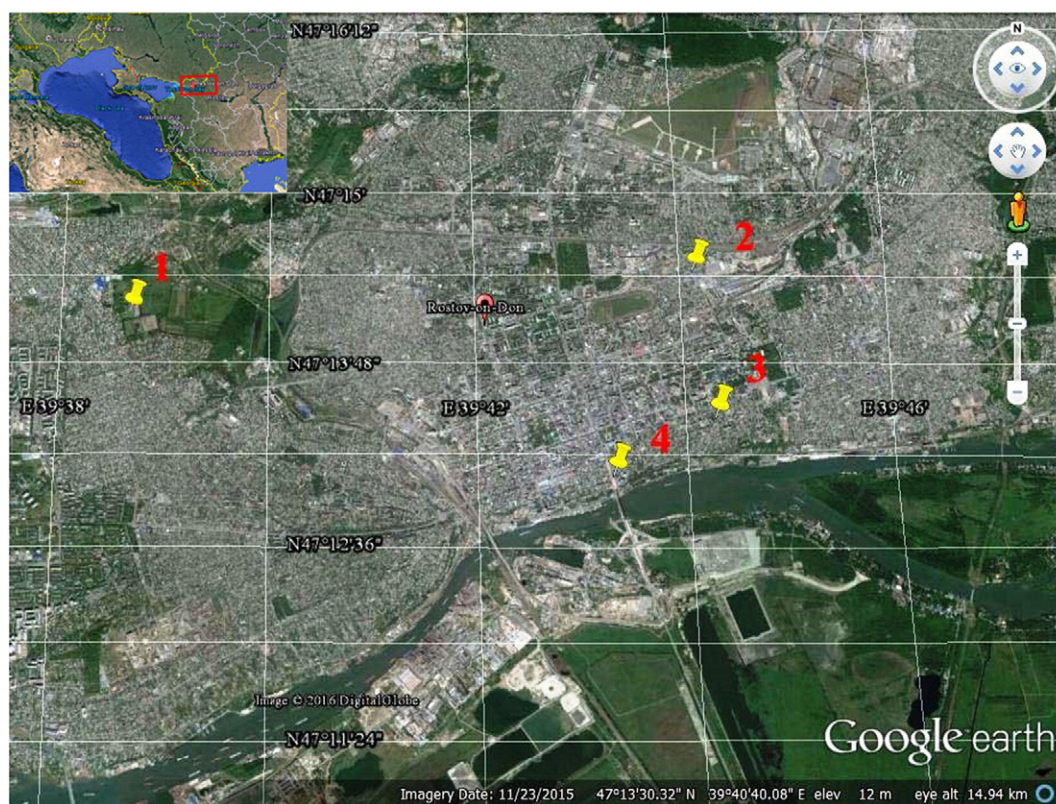

Fig. 1. Map of Rostov-on-Don city. The color points on the map indicate the places of soil sampling for research (1) Chernozem, (2) industrial center (3), Urbanozem and (4) near motor road.

areas. Under laboratory conditions, the following experimental design was used. In several experiments, HM salts were added to the soil (ordinary Chernozem sampled in the Botanic Garden of the Southern Federal university, Fig. 1 point 1) to simulate contamination with different forms and concentrations of HMs. In the other series of experiments, soil samples from the most contaminated city areas (technogenically contaminated Urbanozem, point # 2 on Fig. 1) were used. In all model experiments, the 1 kg of the soil was composted in the vessel at a humidity of 60% and a temperature of 20–22 °C. All experiments were repeated by three times.

In the first experiment, we used the soil – Urbanozem selected near the chemical plant for the production of zinc oxide (point 2 in Fig. 1). The soil was characterized by a high level of zinc contamination – >34 MPC level. Other heavy metals didn't exceed the MPC level. Brown coal was added at a dose equivalent to 1,5,25 and 50 t/ha. Brown coal was added after that the soil was moistened, and left to compost at room temperature. After 7 days soil samples were taken to determine of mobile forms of metals in it.

In the second experiment, the Chernozem contamination was modeled by introducing a variety of copper salts (acetate and sulfate), and copper oxide. Soil for this experiment was collected in the Botanical garden of Southern Federal University (point 1 in Fig. 1). Zinc was deposited only in the form of acetate. The degree of contamination was set up by using of metals concentration for soluble salts 100 mg/kg and for copper oxide 500 mg/kg. After a month of composting brown coal was added at a dose equivalent to 50 t/ha. Experimental vessels left for the 24 h and then soil samples were taken to determine of mobile forms of copper and zinc in it.

In the third experiment, we used the soil – Urbanozem were selected on the side of the Voroshilovsky Avenue at the entrance to the Rostov city from the Bataisk (point 4 in Fig. 1). This street has very high traffic and road shoulder polluted with zinc (to 1.9 MPC) and lead (3.1 MPC). Soil samples from road shoulder were composted with brown coal, which is added in amounts equivalent to 1, 5 and 10 t/ha. The content of mobile forms of zinc and lead was carried out during some period of time: on the 7th day after making brown coal, after a month and after 6 months.

The small field experience was placed on ordinary Chernozem (point #3 in Fig. 1) by the empirical formula proposed by us (formula 1). The experimental scheme included a treatment with manure. Manure were added at rates of 50 t/ha. The size of the experiment plots was 1 square metre. Brown coal was added to the quantity calculated weeks after the addition of ameliorants, the plots were sown with Festuca pratensis.

The specific surface areas of brown coal and the studied soils were calculated from the maximum hygroscopicity, which was determined by the Nikolaev method. The method is based on the adsorption of
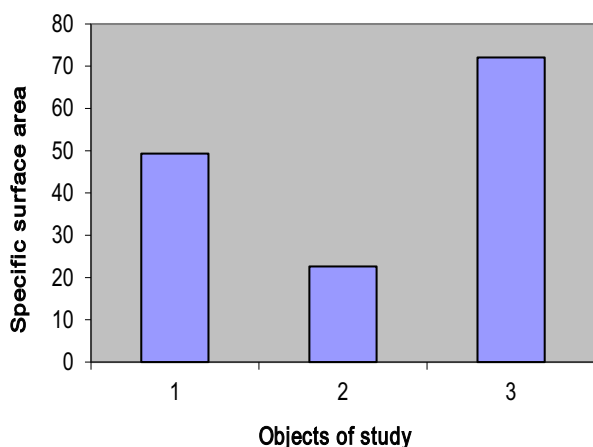
Table 1
Contents of HA functional groups, mmol/100 g.

Object	Carboxylic groups (−COOH)	Phenolic groups (−OH)	Total
Brown coal	295.7	198	495.3
Chernozem	339.5	112.7	452.4
Urbanozem	346.3	36.7	382.5

water vapor from the water-saturated air by soil particles (Vadyunina and Korchagina, 1986). To study the properties of humic acids (HAs) from brown coal, they were preparatively extracted and purified by the Orlov method (Orlov and Grishina, 1981). The purification of HAs was performed in a three-chamber electrodializer using platinum electrodes. Solutions in the side chambers were changed, when they reached a temperature of 40–50 °C. The purified HA suspension from the middle chamber was removed and centrifuged, and the precipitate was dried at 60 °C. The chemosorption capacity of HAs was studied using the methods of determining their functional groups: the total content of acid groups (carboxylic groups and phenolic hydroxyls) was determined by the rapid Dragunova method; the content of phenolic hydroxyls was determined by the Kukharenko method (Orlov and Grishina, 1981).

The content of mobile HM forms was determined in an ammonium acetate solution with pH 4.8 by the atomic absorption method (Government standard 50683-94; Government standard 50685-94; Government standard 50686-94 and Management directive 52.18.289-90) before the establishment of the experiments and after the addition of brown coal used as an ameliorant. The zinc content in the ash of plants was determined according to Government standard 27996-88.

3. Results and discussion

3.1. Studying the sorption properties of brown coal

The study of adsorption isotherms for zinc and lead was showed that satiation of Chernozems sorbing centers could become at HM concentration up to 0.05–0.1 mg/l. For the same concentration satiation of brown coal sorbing centers wasn't obtained. This fact shows that BC has a high potential for sorption of zinc and lead then Chernozem. The study of the specific surface areas of brown coal and soils showed that the specific surface area of Urbanozem is lower than that of Chernozem by 0.46 times; hence, its capacity to bind (sorb) toxic compounds, including HMs, is also lower (Fig. 2).

The determination of the number of HA functional groups (Table 1) showed that the total content of acid functional groups is maximum in HAs from brown coal and decreases in Chernozem and Urbanozem. This significant amount of HA acid functional groups promoted great chemosorption capacity of brown coal concerning of HMs.

Thus, the preliminary study of brown coal properties showed that brown coal can be used as an ameliorant: it has an increased capacity to bind HMs, because its specific surface area and, hence, sorption

Fig. 2. Specific surface areas of (1) Chernozem, (2) Urbanozem, and (3) brown coal, cm²/g.

Table 2
Effect of brown coal (BC) on the content of HM mobile forms in Urbanozem (road shoulder of the Voroshilovsky Avenue) after 7 days of composting.

BC rate, t/ha	HMs, mg/kg soil							
	As	Mn	Zn	Cu	Ni	Co	Cr	Cd
0	0.09	30.2	800	4.2	1.6	3.2	3.2	2.2
1	0.15	28.5	630	3.8	1.0	3.2	3.2	2.2
5	0.11	30.0	699	2.9	2.2	2.4	3.2	2.2
25	0.08	30.0	700	3.4	3.4	2.3	3.1	2.2
50	0.20	31.4	730	3.8	2.8	2.0	2.7	2.3
MPC	Non-existent	140.0	23.0	3.0	4.0	5.0	6.0	Non-existent

Table 3
Effect of different rates of brown coal (BC) on the adsorption of mobile zinc and copper from Urbanozem after 7 days of composting (Empils plant, Rostov-on-Don).

BC rate, t/ha	Zn content		t_d	Cu content		t_d
	mg/kg	% of the control		mg/kg	% of the control	
0	800	100		4.2	100	
1	630	79	**3.21**	3.8	90	0.50
5	690	86	**3.11**	2.9	69	1.46
25	700	88	**2.83**	3.4	80	1.00
50	730	91	1.98	3.8	90	0.50

Note: (t_d) Student's t-test (significance of the difference between the HM contents in the control and experimental treatments; t_{St} = 2.31 for $n_1 + n_2 = 10$, $P = 0.95$).

capacity are higher than those of Chernozem and Urbanozem by 1.5 and 3.2 times, respectively. Brown coal HAs are characterized by an elevated number of functional groups capable to ensure the chemosorption of contaminant cations.

3.2. Studying the detoxifying capacity of brown coal in model experiments

The results of determining the capacity of brown coal to uptake HMs from the soil under anthropogenic conditions are given in Table 2. Soil sample was taken on the road shoulder with very high traffic (point # 2 on Fig. 1). The data indicate that brown coal is apparently indifferent to cadmium, chromium, manganese, and arsenic, at least in the studied rate range. The differences between the results of determining the mobile forms of these metals in the treatments with the additions of brown coal and in the control are minimum (within the determination error), if any.

This fact is important for the status of trace elements in the soil. A decrease in the content of exchangeable cobalt was found only in the treatments with the high rates of brown coal: 5, 25, and 50 t/ha. However, insignificant increases in the contents of mobile arsenic, manganese, and nickel compared to the control were also observed in the treatment with the maximum application rate of HMs. These increases are statistically insignificant and inadequate to the added amounts of coal, which suggests that brown coal is not involved in the above-mentioned increase of HM concentrations.

The third group of metals includes zinc and copper (lead is probably also in this group, but its content was not determined in this experiment) (Table 2). These metals are actively and irreversibly adsorbed by brown coal, which is confirmed by the decrease in the concentrations of their mobile forms 7 days after the addition of the ameliorant. The increase in the application rate of brown coal by 10–50 times insignificantly affects the amounts of zinc, copper, and cobalt adsorbed by brown coal. It could be supposed that the addition of brown coal at high rates is inadvisable; however, the contents of most HMs were low in this case, which could be a reason for the absence of differences

in the amounts of sorbed metals among the experimental treatments. On the other hand, the prolonged effect of brown coal suggests that the complete fixation of HMs requires more than one week.

The studied soil was contaminated with zinc (the MPC was exceeded by almost 35 times) and copper (1 MPC). For zinc, the minimum experimental rate of brown coal (1 t/ha) was found to be the most efficient (Table 3). The revealed decrease in the concentration of mobile zinc was statistically significant at the high level of confidence ($P = 0.95$). The maximum decrease in the content of mobile copper was found in treatment 3, where brown coal was added at a rate of 5 t/ha. Nonetheless, it should be noted that the complete fixation and transition of toxicants to unchangeable forms were not reached during the composting time. Under longer composting, the effect of brown coal could be higher, because zinc reacts with organic matter more slowly than other metals due to its lower electronegativity (Bol'shakov et al., 1993; Ladonin and Margolina, 1997).

The results of the second model experiment, where contamination was simulated by the addition in ordinary Chernozem of different copper forms and zinc and lead acetates, partly confirmed the results of the above experiment. However, new facts of certain interest were observed (Table 4).

It is notable that zinc acetate was added to the soil so that the calculated concentration equal to 1 MPC for mobile zinc should be created. However, the composting for a month abruptly decreased the content of exchangeable zinc in the soil, and the target concentration was not reached. This indicated high absorbing properties of Chernozem and active participation of zinc cations in the metabolism of soil microorganisms. The decrease of zinc concentration was so significant that there was no need for the ameliorating effect of brown coal: the content of mobile zinc was below 1 MPC (with account for the background (5 mg/kg), 28 mg/kg of zinc should be present in the soil to reach the MPC level).

It is known that mobile zinc compounds in the soil mainly include the exchangeable zinc form bound to iron and aluminum hydroxides; carbonates also play a significant role in the fixation of zinc (Pampura, 1996; Ladonin and Margolina, 1997). The latter fact is of special importance, because the content of carbonates in the soil is high (CO_{2carb} − 1.3 ± 0.4%). However, the major part of zinc in the soil occurs in the residual fraction, which includes the metals entering into the crystal lattices of primary and secondary minerals (Pampura et al., 1993). In our experiment, after the addition of salts, the Chernozem, which is characterized by a high adsorption capacity and a significant proportion of mixed-layered minerals, was composted under optimum temperature and water content for a month; this resulted in a strong fixation of the major part of the added zinc.

Nonetheless, the obtained results indicate that the brown coal rate of 50 t/ha is capable to fix about one fourth of zinc from the exchangeable fraction at the first day after treatment (treatment 10).

Table 4
Adsorption of zinc and copper by brown coal (BC) from calcareous ordinary Chernozem under artificial contamination with different HM forms (acetate-ammonium extract, a pH of 4.8).

Treatment	Zn content		Cu content	
	mg/kg	% of the treatment without BC	mg/kg	% of the treatment without BC
1 day of composting with BC[a]				
1. Control 1: soil without BC[b] and HMs[c]	9.0	–	0.9	–
2. Control 2: soil + BC (without HMs)	5.0	–	1.0	–
3. Soil + copper acetate	4.6	–	20.0	100
4. Soil + copper acetate + BC	4.2	–	11.8	59
5. Soil + copper sulfate	3.2	–	16.2	100
6. Soil + copper sulfate + BC	4.2	–	10.6	65
7. Soil + copper oxide	2.5	–	5.6	100
8. Soil + copper oxide + BC	3.0	–	4.8	86
9. Soil + zinc acetate	22.2	100	3.6	100
10. Soil + zinc acetate + BC	17.0	76.6	0.7	19.4

[a] The soil has composted with salts of 1 month before brown coal was added.
[b] Brown coal was added at the rate corresponding to 50 t/ha.
[c] Salts were added to a concentration of 100 mg/kg, and oxides to 500 mg/kg.

Table 5

Adsorption of zinc and lead by brown coal (BC) in contaminated Urbanozem[a] (roadside at the exit from the Voroshilovskii bridge, Rostov-on-Don).

BC rate, t/ha	7 days		1 month		6 months	
	Zn[a] mg/kg	Pb[a]	Zn[a]	Pb[a]	Zn[a]	Pb[a]
0 (Urbanozem without BC)	44.0	100	44.5	106	45.3	100
1	43.0	100	42.7	90	44.2	80
5	42.0	83	43.2	**69**[b]	45.8	**53**[b]
10	41.4	**71**[b]	42.9	**49**[b]	**37.6**[b]	**31**[b]

[a] Heavy metals were extracted from soil samples using acetate-ammonium buffer (pH of 4.8).

[b] The values statistically significantly different from the control are typed in bold.

The most interesting data were obtained for the treatments in which the soil was contaminated by adding copper acetate (treatments 3–4), copper sulfate (treatments 5–6), and copper oxide (treatments 7–8) (Table 4). Similarly to the treatments with zinc addition, the concentration of copper after the composting of soil with contaminant salts for a month was significantly below the expected values.

The addition of brown coal favored a significant decrease in the content of mobile copper in the Chernozem, by 41% at the contamination with copper acetate (treatment 4), by 35% at the addition of copper sulfate (treatment 6), and only by 14% at the addition of copper oxide. The observed difference in the fixation of zinc and copper by brown coal is easy to explain. According to Pampura et al. (1993), the exchangeable and carbonate-bound fractions of copper in the soil are almost not detected; >9% of copper is bound in the most conservative residual fraction, the fraction bound to organic matter is the second largest. Copper has one unpaired electron on the outer energy level; however, the second-from-outer level can also lose electrons; therefore, copper easily donates two electrons to form divalent cations. This explains the increased activity of this metal in reactions with HAs and the high stability of the resulting complexes, which were experimentally confirmed in some works (Stevenson, 1976; Schnitzer and Kerndorff, 1981; Orlov, 1992; Ladonin and Margolina, 1997; Zhorobekova, 1997). An additional amount of HAs was added together with brown coal to the reaction area, which explains the significant decrease in the content of copper extractable by ammonium acetate buffer.

In the third model experiment, we studied the anthropogenically contaminated soil sampled at one of the most contaminated sites in the city (point #2 of the map of Fig. 1), as in the first model experiment. The mobile zinc and lead forms extractable by ammonium acetate solution with pH 4.8 were determined (Table 5).

The results showed that a decrease in the lead content was observed in all treatments with brown coal. In the treatments with brown coal rates of 5 and 10 t/ha, lead was relatively actively absorbed, in spite of the high contamination level (16 MPC for mobile forms). After the first composting period, only the difference between the control and the treatment with the maximum rate of brown coal (10 t/ha) was statistically significant ($t_d = 2.46$; $t_{St} = 2.23$). The sorption of lead continued under further composting. The differences between the control and the treatments with the rates of 5 and 10 t/ha were statistically significant after the second ($t_d = 2.75$ and 5.25, respectively, at $t_{St} = 2.23$) and

the third ($t_d = 6.08$ and 11.00, respectively, at $t_{St} = 2.26$) composting periods.

The adsorption of zinc was significant only for the third composting period in the treatment with a brown coal rate of 10 t/ha ($t_d = 3.31$; $t_{St} = 2.57$). In the studied soil, the content of zinc is below 2 MPC. It is known (Bol'shakov et al., 1993) that zinc is significantly worse sorbed by organic matter than lead. The brown coal rate of 10 t/ha could be insufficient for the complete detoxification of urbanozem at this level of contamination.

3.3. Determination of the optimum rate of ameliorant

In the analysis of the above experimental results, the rate of brown coal necessary for binding metals at a specific contamination level should be known. We propose a formula to calculate doses of brown coal required to clean contaminated soils by heavy metals. Probably, this rate can be calculated from the equation

$$D = 0.0001 \cdot S \cdot H \cdot d \sum_{i=1}^{4n} C_i \cdot K_i \qquad (1)$$

where D is the amount of brown coal (t); S is the contaminated area (m^2); H is the contaminated level depth (cm); d is the soil density (g/cm^3); C_i is the concentration of the i-th mobile HM extracted by an ammonium acetate solution with pH 4.8 (mg/kg) determined by atomic absorption spectrometry; and K_i is the corresponding empirical coefficient. It was found that K_i is 0.0044 for lead and copper and 0.0052 for zinc. The value of K_i probably depends on the electronegativity (EN) of HM ions: at EN > 1.75, K_i = 0.0044; at EN < 1.75, K_i = 0.0052. If brown coal with different properties (contents of HAs, ash, etc.) is used, the value of K_i will obviously be different; nonetheless, the rate of brown coal necessary for the detoxification of soil contaminated with HMs can be approximately calculated from Eq. (1). The value of K_i cannot be exactly calculated, because HMs arrive to the soil as different compounds (sulfites, sulfates, arsenites, etc.), which are differently absorbed by brown coal.

In the soil contaminated with HM salts in the laboratory experiment, the sorption–desorption processes can proceed differently than in the anthropogenically contaminated soil. Therefore, an experiment with technogenically contaminated Urbanozem was set up. From the data of atomic absorption spectrometry, Urbanozem (point #3 on Fig. 1) contained 1133 mg/kg of mobile zinc and 109 mg/kg of mobile lead. Brown coal was added to this soil at a rate of 191 t/ha, which was calculated from Eq. (1). After three weeks of composting in pots, the contents of zinc and lead decreased to 565 and 59.5 mg/kg, respectively, which corresponded to about half of their initial amounts. After five weeks of composting, the content of zinc decreased to 371 mg/kg, and the concentration of lead remained on the same level.

However, the application of these large amounts of brown coal is not necessary, because all calculations for the model experiments in this work were made for the contaminated layer depth of 25 cm (i.e., the depth used for calculating the rate of fertilizers per ha of Chernozems). In practice, the upper 10-cm thick layer was taken, because the soils are

Table 6

Effect of brown coal (BC) on the concentrations of mobile zinc and lead in ordinary Chernozem and Urbanozem.

Treatment	Zn			Pb		
	mg/kg	% of the control		mg/kg	% of the control	
		1	2		1	2
Ordinary Chernozem (control 1: uncontaminated soil without BC)	16.8	100	–	1.9	100	–
Urbanozem (control 2: without BC)	740.3	4406.5	100	87.2	4589.5	100
Urbanozem + manure	674.7	4016.1	91.1	68.5	3463.2	78.6
Urbanozem + BC	24.9	148.2	3.3	1.2	63.1	1.4

Table 7
Effect of brown coal (BC) on the contents of zinc and lead in the aboveground part of *Festuca pratensis*.

Treatment	Ash, %	Zn			Pb		
		mg/kg	% of the control		mg/kg	% of the control	
			1	2		1	2
Ordinary Chernozem (control 1: uncontaminated soil without BC)	4.8	24.5	100	–	8.6	100	–
Urbanozem (control 2: without BC)	6.2	155.0	419.2	100	48.4	433.3	100
Urbanozem + manure	5.8	116.0	392.2	80	19.7	188.9	43.6
Urbanozem + BC	4.9	27.9	111.8	22.8	5.4	61.1	14.1

most contaminated with HMs from the surface. Thus, the mean contents of zinc and lead in the 25-cm thick layer of this Urbanozem and, hence, the calculated rate of brown coal should be lowered. It should be also noted that such a high contamination level of soil cover is rare.

In spite of the efficiency of brown coal, the use of its high rates at such a high contamination level is economically inadvisable. In addition, according to our studies, brown coal added at rates higher than 50 t/ha inhibits bacteria of the genus *Azotobacter*, at least at the first stages of composting.

3.4. Verification of laboratory results in a field small-plot experiment

The results of laboratory experiments were tested under field conditions. An experiment was set up on the soil extremely contaminated with zinc. The contaminated plot was located near the chemical plant (point 3, Fig. 1). The content of mobile zinc (ammonium acetate buffer solution, pH 4.8) before the beginning of the experiment was 874.5 mg/kg soil, which exceeded the maximum permissible level for this metal in soils by >35 times; the content of lead was 100 mg/kg (about 18 MPC). Uncontaminated ordinary Chernozem was used as a control (point 1, Fig. 1). The experimental scheme included a treatment with manure. The recommended reclaiming rates of manures are 20–80 t/ha (Obukhov and Efremova, 1988). In this experiment manure were added at rates of 50 t/ha; the brown coal rate was determined using Eq. (1) from the significantly lower thickness of the reclaimed layer (10 cm). Two weeks after the addition of ameliorants, the plot was sown with meadow fescue (*Festuca pratensis*). In fall, the contents of HMs in the soil and aboveground plant organs were determined after harvest. The results are given in Tables 6 and 7. It can be seen that the application of manure decreases the content of mobile zinc by only 9% and that of mobile zinc by 21.4%. In the treatment with brown coal, the content of mobile zinc decreased to a level corresponding to an uncontaminated soil, and the content of lead was even lower than in the control.

Very high concentrations of zinc and leads were found in the aboveground part of plants in the treatment with Urbanozem (Table 7). No MPC for forage grasses is available in the literature. However, Tserling (1990) found that the mean content of zinc in the aboveground part of meadow fescue is 16 mg/kg dry matter, and the almost 10-fold excess of this value can abruptly decrease the forage value of the crop. The application of manure as an ameliorant significantly decreases the input of HMs to plants; however, their content remains very high. In the treatment with brown coal, the input of zinc to plants decreases almost to the control level. The content of lead in meadow fescue grown on the soil with the addition of brown coal is even lower than in the control.

4. Conclusions

Brown coal can be recommended as a detoxifier of soils contaminated with lead, zinc, and copper. It is important to correctly calculate the rate of the ameliorant. The equation proposed for the calculation of ameliorant rate can be used for the most cost-efficient method of detoxification of HM-contaminated soil. The fact that brown coal is a good ameliorant of the soil humus status is of importance for increasing the fertility of soils.

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