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Features of the Phytoremediation by Agricultural Crops of Heavy Metal Contaminated Soils

Andrey Ilinskiy [1], Dmitriy Vinogradov [2], Natalia Politaeva [3], Vladimir Badenko [3,*] and Igor Ilin [3]

[1] All-Russian Research Institute for Hydraulic Engineering and Land Reclamation, 127550 Moscow, Russia
[2] Department of Agronomy and Agrotechnologies, Ryazan State Agrotechnological University Named after P.A. Kostychev, 390044 Ryazan, Russia
[3] Institute of Civil Engineering, Peter the Great Saint Petersburg Polytechnic University, 195251 Saint Petersburg, Russia
* Correspondence: badenko_vl@spbstu.ru

Abstract: The novelty of the present research consisted in the study of the features of heavy metals accumulation in the phytomass of agricultural plants under the conditions of complex heavy metals contamination of podzolized chernozem (ashy soil) in the Ryazan region (Russia). Results of the vegetation experiments conducted on four crops—oats, black beans, buckwheat, and soybeans—were analyzed, which made it possible to assess the ability of these plants to accumulate heavy metals in their phytomass depending on the level of the heavy metals contamination of the soil. Results of the study showed that the removal of copper, zinc, and lead by beans was noticeably higher than that by oats, buckwheat and soy, due to their greater tolerance and ability to form a large phytomass, which must be taken into consideration when choosing phytoremediation for soil decontamination. This made it possible to evaluate the possibility of using the analyzed plants for the biological purification of polluted soil. The results are also planned to be used in the digitalization of agricultural production.

Keywords: phytoremediation; heavy metals; soil; vegetation experiments; agricultural production

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1. Introduction

Environmentally safe crop production is one of the most important tasks of modern civilization [1–4]. Obtaining agricultural field soils of the proper quality play a key role in solving this major problem [3–8]. However, increasing anthropogenic impacts have led to the entry of many hazardous chemicals into the soils of agricultural fields. This reduces the quality of the soils and, accordingly, affects crop products, which are raw materials for the production of food for humans and domestic animals [3–6]. Heavy metals are particularly dangerous pollutants for agricultural fields. Therefore, much attention is paid worldwide to solving the problems of heavy metals removal from soils [9–11]. The content of heavy metals in soil depends on the chemical composition of parent rocks (natural landscape) and anthropogenic impacts [12–14]. The anthropogenic sources of soil pollution by heavy metals are thermal power plants (primarily coal-fired); metallurgical plants; automobile exhausts; chemical industry enterprises; and the use of mineral and organic fertilizers, pesticides and other chemicals in agriculture [11,15–19].

In the agricultural regions of Russia, the accumulation of heavy metals in the root layer of agricultural landscapes is observed to have occurred as a result of anthropogenic impacts as opposed to the origin content of heavy metals in soil-forming rocks [20,21]. Heavy metals such as copper, zinc, lead, and cadmium are the most significant polluters of agricultural soils in in the European part of Russia [22]. Earlier studies have shown that as a result of man-made load in the root-inhabited layer of the agricultural landscape of the Ryazan region, located in the southern part of the non-Chernozem zone of Russia, a complex of heavy metals (mainly copper, zinc and lead) was accumulated in quantities greater than the background content in the soil-forming rocks [23]. It should be noted that these elements may be necessary for plant growth but are toxic to plants in high concentrations. In addition, an increased concentration of heavy metals in crops creates a potential danger to human and animal health if these contaminated plants are used for food [3,8]. Therefore, the challenge of developing special measures for the detoxification and rehabilitation of contaminated soils in agricultural landscapes is relevant [23-27].

In the current ecological situation, the so-called "green" technologies, which include phytoremediation, have a special scientific interest and an essential practical importance in solving the problem of soil rehabilitation for agricultural lands contaminated by a complex of heavy metals [19,25,28–32]. Phytoremediation technologies use the features of plants to maintain their vital activity in conditions of an excess of toxic elements in the soil (or in the environment). It is also well known that these features vary from one plant to another [33–35]. Among the factors that determine the resistance of plants to heavy metals soil contamination are the low solubility of salts of these metals, the low mobility of corresponding cations in the medium surrounding plant roots, and the antagonistic effect of metal ions [36,37].

The ability of some plant species to absorb and accumulate heavy metals is used in the practical technology of phytoremediation of contaminated agricultural lands [38,39]. However, it is important to take into account, when developing such practical technologies, the internal physiological and biochemical protective mechanisms of plants that prevent the entry of heavy metals into their organs [40,41]. In addition, concentrations of heavy metals, which are toxic to plants, can vary significantly depending on soil properties [8,42]. Some plant species are able to withstand fairly high concentrations of toxic elements in the soil and absorb them during their growth and development [8,38,43]. Such tolerant plants can be used for the purification of soils from toxic elements by isolating and recycling their aboveground biomass. Thus, controversial plant characteristics can be used in phytoremediation technologies: on one hand, plants have the ability to accumulate a large amount of pollutants, which is dangerous in terms of the entry of soil pollutants into the food chains; on the other hand, the plants have resistance to increased heavy metals content in the soil [8,44].

Tolerance is not a single mechanism but includes several metabolic processes: a selective absorption of ions; a reduced membrane permeability; an immobilization of ions in roots, leaves, seeds; a removal of ions from metabolic processes by depositing them in fixed or insoluble forms in various organs and organelles; a change in the nature of metabolism; an adaptation to the replacement of a physiological element with a toxic one in an enzyme; and a removal of ions from plants during leaching through leaves, sap excretion, shedding of leaves, and an excretion through roots [37,42,45].

For the phytoremediation of polluted soils, it is advisable to use the so-called barrier-free and low-barrier tolerant plants, which are able to intensively accumulate pollutants during the formation of a large phytomass [8,36,38,46]. The most common method of phytoremediation of soils contaminated with heavy metals is phytoextraction. Phytoextraction is a subprocess of phytoremediation in which plants remove dangerous elements from soil by concentrating such elements in aboveground plant biomass followed by the removal of polluted phytomass [47,48]. Therefore, to obtain all the benefits of phytoextraction it is necessary to choose plants that have the following features: the ability to mobilize heavy metals under the influence of plant root exudates; the ability to accumulate and translocate pollutants; and resistance to their high concentrations and high biomass yield. The advantages of phytoremediation (as well as phytoextraction) should also include economic efficiency, environmental safety, aesthetic appeal, and social recognition [8,43,49,50]. Phytoextraction refers to "soft", relatively cheap, and environmentally friendly technologies and allows soil cleaning in "in situ" conditions over large areas with heterogeneous soil pollution [27,51,52]. Therefore, there is an urgent task to develop phytoextraction technologies of heavy metals polluted soils to support obtaining environmentally safe crop products. This requires expanding research on the features of the distribution of heavy metals in plant organs and tissues [49,53].

Currently, phytoremediation has significant limitations: dependence on climatic and seasonal conditions, acidity and the provision of soils with nutrients affecting plant growth, root zone depth, solubility and availability of heavy metals in soils, and the environmental consequences of metal mobilization as a result of the use of chelating agents ([54], Table 1). In the northern regions of the world, this approach is ineffective due to the low productivity in harsh climatic conditions [55,56].

Table 1. Element concentrations for different variants of experiment, mg/kg.

Element	Variant 1 (Control) Zc = 1.6	Variant 2 1 APC Zc = 13.6	Variant 3 2 APC Zc = 30.1	Variant 4 4 APC Zc = 63.4	Variant 5 9 APC Zc = 146.1	APC	RBC
Cu	16.0	66	132	264	594	66	27
Zn	42.0	110	220	440	990	110	35
Pb	13.5	65	130	260	585	65	12
Cd	0.31	1	2	4	9	1	0.18

The accumulation of heavy metals in plants depends not only on the concentration and form of compounds of each metal but also on all other elements entering the plant, which usually have antagonistic and/or synergistic interactions with heavy metals. Existing studies show that, when selecting plants for phytoextraction, the following characteristics are of great importance: (1) the plant's adaptability to local soil and climatic conditions; (2) tolerance to high concentrations of heavy metals; (3) the ability to grow rapidly and produce large amounts of biomass; (4) presence of a powerful root system; (5) efficiency of transport from roots to shoots; 6) resistance to diseases and pests; and 7) the ability to undergo agrotechnical processing and harvesting [8,31,33,35,38,41–43,46–57].

The purpose of the research presented in the article was to determine the beneficial properties of agricultural plants to absorb and accumulate pollutants (heavy metals) in plant phytomass under different concentrations and combinations of metals in the soil. Results of the studies of the tolerance of agricultural crops to soil contamination with a complex of heavy metals are also presented in the article. These were obtained in the Ryazan region of Russia, taking into account the peculiarities of the soil formation process and soil properties in the region, as well as the natural and climatic features of specific heavy metal pollution in the agricultural landscapes investigated. These results are planned to be used in projects for the digitalization of agricultural production facilities.

2. Materials and Methods

The study of the tolerance of agricultural crops to soil contamination with a complex of heavy metals was carried out in model vegetation experiments on the agricultural fields of an experimental farm of the Meshchersky branch of All-Russia Research Institute of Hydraulic Engineering and Land Reclamation of A.N. Kostyakov (http://www.vniigim.ru/ 22.12.2022). The experimental farm is located on the territory of the Ryazan region in the center of the European part of the Russian Federation. The main soils in the experimental fields are podzolized and leached chernozems [54]. These soil types occupy about 800 thousand hectares of arable land in the Ryazan region. They are characterized by a high level of fertility and are located in the southern and central parts of the Ryazan region, surrounded by dark grey forest soils [58]. Organic matter content ranges from 4 to 7% in podzolized and leached chernozems; pH_{KCl} ranges from 4.5–6.0; degree of saturation with bases 85–90%; total exchangeable bases are 46–50 milligram equivalents per 100 g of soil; particles smaller than 0.01 mm fill about 39% of soil volume [59].

Previous studies of pollutant contamination of the soil cover in the Ryazan region showed that copper, zinc, lead and cadmium comprise the majority of the heavy metal pollutants in the soil [59-63]. Thus, this determined the choice for designing and conducting a series of field vegetation experiments.

Oats, buckwheat, black beans, and soybeans were selected as experimental crops for the study of plant resistance to a complex soil pollution with heavy metals and characteristics of their accumulation in plant phytomass depending on the level of soil pollution. The natural and climatic conditions of the Ryazan region are favorable for growing these crops and are widely used by regional farmers [59-63].

For the specific experiments the soil (podzolized chernozem) with the following agrochemical characteristics was used: pH_{KCl}—5.1; organic matter—5.7%; mobile soil phosphorus—235 mg/kg; exchangeable potassium—192 mg/kg of soil; cation exchange capacity (CEC)—47,4 milligram equivalents per 100 g of soil. Vegetation vessels made of chemically inert material (stabilized polyethylene) were used in the experiment, and 7 kg of soil was used in each vessel.

In the vegetative experiment, four categories of soil contamination with a complex of heavy metals (Cu, Zn, Pb, Cd) were artificially modeled according to a total pollution index from acceptable to extremely dangerous by adding aqueous solutions of salts of these heavy metals into the soil. The concentration of heavy metals was controlled by determining the total pollution index (Zc):

$$Z_c = \sum_{i=1}^{n} K_{ci} \quad (1)$$

where n is the number of pollution components; Kci—concentration coefficient of the i-th chemical, determined by the ratio of its actual content in the soil to the regional background.

To start the experiment, the soil was taken from the arable horizon, the brought soil was brought to a homogeneous state: dried, stones, roots, crop residues were selected, mixed, then sifted through a sieve with 3 mm cells.

The following structure of the experiment was used (Table 1):

1. Control with Zc = 1.6;
2. Acceptable heavy metal concentration with Zc = 13.6;
3. Moderately dangerous pollution by heavy metal with Zc = 30.1;
4. Highly dangerous pollution by heavy metal with Zc = 63.4;
5. Extremely dangerous pollution by heavy metal with Zc = 146.1.

The regional background for each substance is indicated in Table 1. The following chemically pure metal salts were used in the experiment: $Zn(CH_3COO)_2 \cdot 2H_2O$; $CuSO_4 \cdot 5H_2O$; $Pb(CH_3COO)_2$; $CdSO_4$. In Table 1, in addition to the concentrations of heavy metals for five variants of the experiment, an Approximate Permissible Concentration (APC) according to Russian regulation and a Regional Background Concentration (RBC) for each element [58] are presented.

All the test crops had been sown with germinated seeds 30 days after the introduction of pollutants into the soil. The duration of the experiment was 3 months and was executed in 4 repetitions. The study was carried out under natural lighting conditions and temperatures in an open area.

The vegetation experiment (sowing seeds, caring for plants, observing, accounting and harvesting) was carried out in accordance with methodologies used in Russian agricultural scientific and educational institutions. During the entire growing season, a soil moisture content of 0.65–0.70 of the total soil moisture capacity was provided (the total moisture capacity of the soil is the moisture content in the soil provided that all pores are completely filled with water) [64-66].

After the completion of the growing experiment, the determination of heavy metals content in plant aboveground biomass was carried out by the analysis of plant samples in a specialized laboratory using the method of atomic absorption spectrometry [61]. The efficiency of phytoextraction of heavy metals from the soil by various plant species was estimated by coefficients of biological absorption (Ax) using the following formula [62]:

$$A_x = I_x/n_x, \quad (2)$$

where I_x is the content of element x in the plant's aboveground biomass, n_x is the content of element x in the soil on which the plant had been grown.

For each element under study, third-degree polynomials were created for each culture using the standard Microsoft Office Excel program. The number of observations for each culture with fixed element under study was 20.

The determination of the removal of heavy metals with plant phytomass from the soil was determined by multiplying previously determined concentrations of metal in phytomass by the mass of plants in in the experiment, reduced to the calculated unit area of 1 km^2.

During the statistical processing of the obtained experimental data, the method of dispersion analysis, described in the works of B.A. Dospekhov [67], was used with the involvement of the computer program Excel.

3. Results

The results of determining the content of copper, zinc, lead and cadmium in the phytomass of soybean, bean, buckwheat, and oat plants in the variants of the vegetation experiment are presented in Tables 2–5. In these tables, averages are presented without absolute errors.

Table 2. Copper content in the phytomass of test crops, mg/kg.

Variant (*Zc*)	Experiment				
	1	2	3	4	Average
	Soybeans				
1 (1.6)	3.60	3.76	3.92	4.08	3.84
2 (13.6)	4.62	4.95	5.61	5.94	5.28
3 (30.1)	5.94	6.27	6.93	7.26	6.60
4 (63.4)	8.98	9.24	12.14	11.88	10.56
5 (146.1)	4.75	5.64	6.24	7.13	5.94
HCP_{05} = 0.72					
Black beans					
1 (1.6)	3.52	3.60	3.76	3.84	3.68
2 (13.6)	13.85	14.19	14.78	16.62	13.86
3 (30.1)	12.21	12.87	13.79	13.93	13.20
4 (63.4)	14.52	15.38	16.30	17.16	15.84
5 (146.1)	10.40	11.58	12.18	13.37	11.88
HCP_{05} = 0.67					
Buckwheat					
1 (1.6)	4.08	4.16	4.48	4.56	4.32
2 (13.6)	5.94	6.27	6.93	7.26	6.60
3 (30.1)	6.60	7.26	8.54	8.58	7.75
4 (63.4)	6.47	7.52	8.32	9.37	7.92
5 (146.1)	10.10	11.75	12.01	12.66	11.63
HCP_{05} = 0.66					
Oats					
1 (1.6)	8.40	8.56	8.72	8.88	8.64
2 (13.6)	11.55	12.21	12.87	13.53	12.54

3 (30.1)	11.81	11.88	14.52	14.59	13.20
4 (63.4)	10.24	11.22	11.52	12.54	11.38
5 (146.1)	11.04	11.25	11.29	11.47	11.26
HCP_{05} = 0.51					

Table 3. Zinc content in the phytomass of test crops, mg/kg.

Variant (*Zc*)	**Experiment**				
	1	**2**	**3**	**4**	**Average**
	Soybeans				
1 (1.6)	26.88	29.19	29.61	31.92	29.40
2 (13.6)	75.9	77.55	78.65	80.3	78.10
3 (30.1)	136.4	139.7	141.9	145.2	140.80
4 (63.4)	253.0	257.4	261.8	266.2	259.60
5 (146.1)	480.15	490.05	499.95	509.85	495.0
HCP_{05} = 3.48					
	Black beans				
1 (1.6)	34.02	35.91	36.33	38.22	36.12
2 (13.6)	106.15	107.25	108.35	109.45	107.80
3 (30.1)	185.9	191.4	195,8	201.3	193.60
4 (63.4)	215.6	226.6	231.0	242.0	228.80
5 (146.1)	227.7	252.45	262.35	287.1	257.40
HCP_{05} = 8.21					
	Buckwheat				
1 (1.6)	23.1	23.94	25.62	26.46	24.78
2 (13.6)	48.4	48.95	50.05	50.6	49.50
3 (30.1)	104.5	108.9	111.1	115.5	110.0
4 (63.4)	184.8	193.6	202.4	211.2	198.0
5 (146.1)	371.25	376.2	396.0	400.95	386.10
HCP_{05} = 4.63					
	Oats				
1 (1.6)	38.64	40.53	41.58	43.26	41.0
2 (13.6)	117.7	124,3	125.4	132.0	124.85
3 (30.1)	294.8	298.1	300.3	303,6	299.20
4 (63.4)	457.6	468.6	477.4	488.4	473.0
5 (146.1)	475.2	499.95	529.65	554.4	514.8
HCP_{05} = 9.30					

Table 4. Lead content in the phytomass of test crops, mg/kg.

Variant (*Zc*)	**Experiment**				
	1	**2**	**3**	**4**	**Average**
	Soybeans				
1 (1.6)	2.5	2.57	2.84	2.9	2.70
2 (13.6)	3.15	3.19	3.32	3.35	3.25
3 (30.1)	3.51	3.84	3.97	4.29	3.90
4 (63.4)	4.94	5.07	5.33	5.46	5.20
5 (146.1)	5.27	5.56	6.14	6.43	5.85
HCP_{05} = 0.19					
	Black beans				
1 (1.6)	1.71	1.74	1.77	1.79	1.75

2 (13.6)	1.85	1.92	1.98	2.05	1.95
3 (30.1)	2.21	2.41	2.8	2.99	2.60
4 (63.4)	2.44	2.47	2.73	2.86	2.63
5 (146.1)	2.34	2.63	3.22	3.51	2.93
HCP_{05} = 0.21					
	Buckwheat				
1 (1.6)	2.09	2.11	2.19	2.23	2.16
2 (13.6)	2.55	2.57	2.6	2.63	2.59
3 (30.1)	2.51	2.6	2.67	2.69	2.62
4 (63.4)	2.47	2.73	2.76	2.84	2.70
5 (146.1)	2.74	2.83	3.02	3.11	2.93
HCP_{05} = 0.08					
	Oats				
1 (1.6)	2.82	2.84	3.10	3.12	2.97
2 (13.6)	3.13	3.23	3.28	3.37	3.26
3 (30.1)	3.29	3.30	3.31	3.33	3.31
4 (63.4)	4.94	5.07	5.33	5.46	5.20
5 (146.1)	4.64	4.64	4.71	4.73	4.68
HCP_{05} = 0.09					

Table 5. Cadmium content in the phytomass of test crops, mg/kg.

Variant (*Zc*)	**Experiment**				
	1	**2**	**3**	**4**	**Average**
	Soybeans				
1 (1.6)	0.285	0.287	0.290	0.291	0.288
2 (13.6)	0.412	0.418	0.422	0.444	0.424
3 (30.1)	0.455	0.471	0.489	0.505	0.480
4 (63.4)	1.018	1.032	1.048	1.062	1.040
5 (146.1)	2.318	2.331	2.349	2.363	2.340
HCP_{05} = 0.01					
	Black beans				
1 (1.6)	0.183	0.192	0.220	0.211	0.202
2 (13.6)	0.210	0.215	0.225	0.230	0.220
3 (30.1)	0.370	0.380	0.383	0.387	0.380
4 (63.4)	0.536	0.572	0.628	0.664	0.60
5 (146.1)	0.981	1.044	1.116	1.179	1.080
HCP_{05} = 0.03					
	Buckwheat				
1 (1.6)	0.259	0.262	0.271	0.274	0.267
2 (13.6)	0.342	0.357	0.361	0.372	0.358
3 (30.1)	0.546	0.556	0.559	0.578	0.560
4 (63.4)	1.167	1.182	1.222	1.228	1.20
5 (146.1)	2.156	2.205	2.295	2.344	2.250
HCP_{05} = 0.03					
	Oats				
1 (1.6)	0.973	0.978	0.991	0.995	0.984
2 (13.6)	0.773	0.832	0.861	0.934	0.850
3 (30.1)	1.056	1.061	1.114	1.173	1.101
4 (63.4)	1.628	1.644	1.682	1.686	1.660

5 (146.1)	2.208	2.436	2.523	2.744	2.478

$HCP_{05} = 0.07$

The represented diagrams of scatter values of variants of vegetative experiment made on each metal (Figures 1–4) have shown representativeness of the obtained experimental data on the content of copper, zinc, lead and cadmium in phytomass of test crops from values of the total index of pollution of soil with heavy metals. In addition, statistical processing of the results of determining the content of copper, zinc, lead and cadmium in the phytomass of test crops in a growing experiment (Tables 2–5), performed on the basis of analysis of variance by calculating the least significant difference (LSD) by the method B.A. Dospekhov [67], showed the significant influence of the total soil pollution indicator on accumulation of these heavy metals in phytomass soybeans, buckwheat and oats.

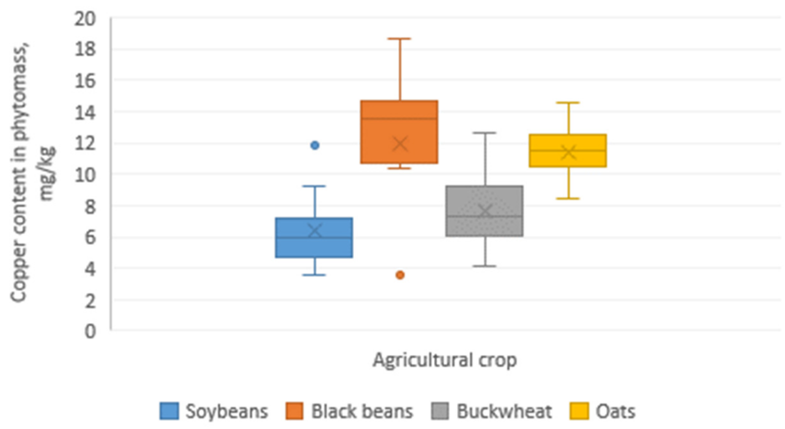

Figure 1. Diagram of copper content in the phytomass of test crops on the variants of the vegetation experiment, depending on the values of the total index of soil contamination.

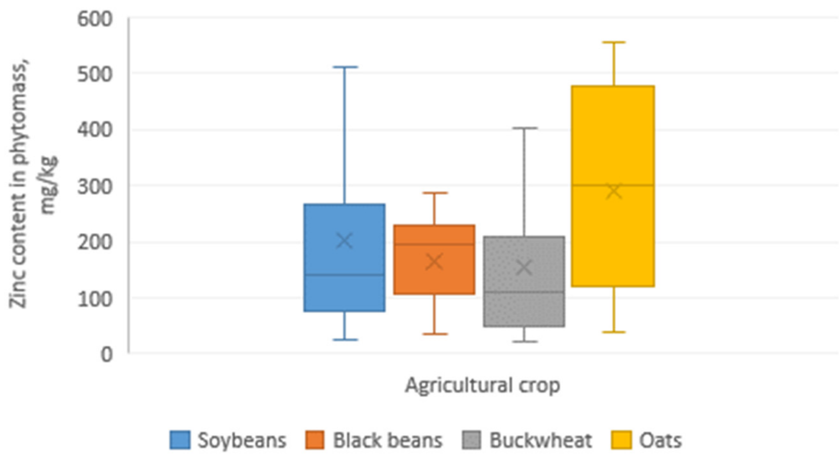

Figure 2. Diagram of zinc content in phytomass of test crops on the variants of the vegetation experiment depending on the values of the total index of soil contamination.

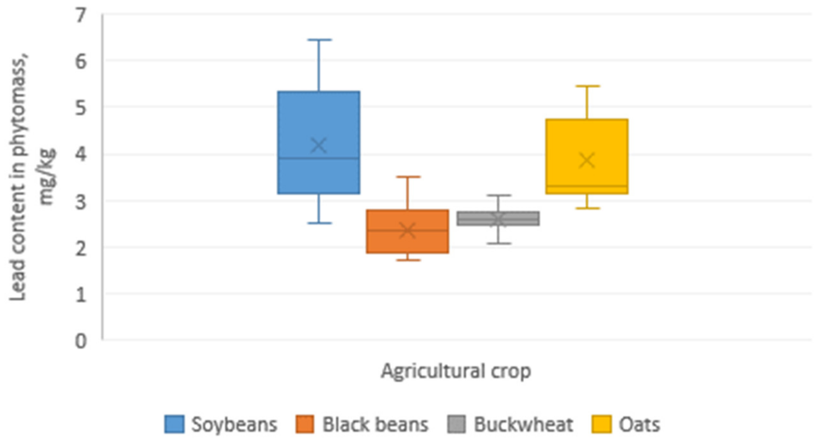

Figure 3. Diagram of lead content in the phytomass of test crops on the variants of the vegetation experiment depending on the values of the total index of soil contamination.

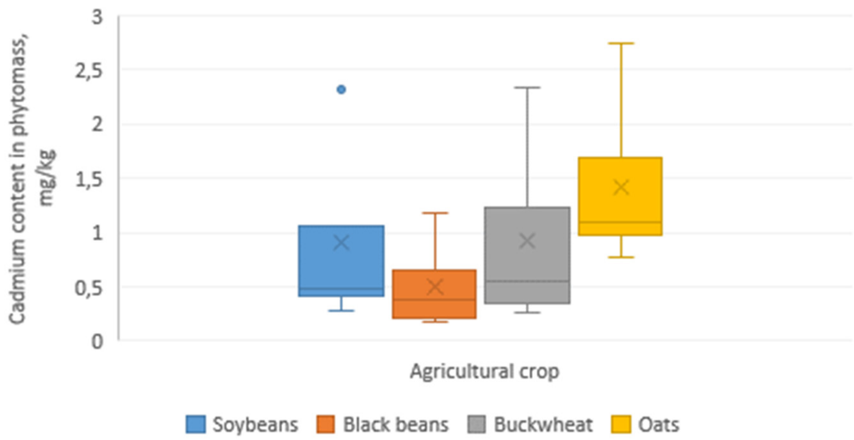

Figure 4. Diagram of cadmium content in the phytomass of test crops on the variants of the vegetation experiment depending on the values of the total indicator of soil contamination.

Analysis of the results of determining the content of heavy metals in the phytomass of test crops (Tables 2–5) depending on the total index of soil contamination revealed a number of features. Thus, at permissible, moderately hazardous, and highly hazardous levels of soil contamination (variants 2–4) copper is more actively concentrated by phytomass of beans and oats than by soybean and buckwheat, and at extremely hazardous levels of pollution (option 5)—by the phytomass of beans, buckwheat, and oats than soybean. In variant 5, in comparison with variant 4, reduction of the copper content in the phytomass of soybeans, beans and oats is noted.

It was established that at permissible and moderately dangerous levels of soil pollution (variants 2–3) zinc is more actively concentrated by the phytomass of oats and beans than by soybean and buckwheat, but at highly and extremely dangerous levels of pollution (variants 4 and 5) zinc is concentrated by phytomass of oats and soybean than by bean and buckwheat. At the same time, on all test crops, an increase of zinc content in the phytomass of plants with an increase in the value of the total index of soil contamination is noted.

The investigations show that from the permissible to extremely dangerous levels of soil pollution (variants 2–5) lead is more actively concentrated in the phytomass of soybeans and oats than in the phytomass of beans and buckwheat. The increase of lead content in the phytomass of plants is noted practically in all test crops (except for oats in variant 5) with an increase of the total index of soil contamination, although, its accumulation in the phytomass is not as active as for copper and zinc.

Research has shown that at an admissible level of soil pollution (variant 2) cadmium is more actively concentrated by the phytomass of oats than by the phytomass of soybeans, beans and buckwheat. At a moderately dangerous level of soil pollution (variants 3) cadmium is more actively concentrated by the phytomass of buckwheat, soybeans, and beans than by phytomass of oats. At highly and extremely dangerous levels of pollution (variants 4 and 5) by the phytomass of oats, soybean, and buckwheat than by beans. At the same time, on all test crops there is an increase in the content of cadmium in the phytomass of plants with an increase in the value of the total index of soil contamination.

During experiments, interesting empirical dependences of the content of copper, zinc, lead and cadmium in the phytomass of the tested agricultural crops (y) on the total pollution index (x) (Figure 5–8) have been defined. In the next section, these results (with values of correlation coefficient R2), for different crops and substances are presented for the interval of *Zc* = [1.6–146, 1].

For oats.

$$\text{copper: } y = 3E\text{-}05x^3 - 0.0063x^2 + 0.3392x + 8.3853 \ (R2 = 0.9436);$$

$$\text{zinc: } y = 2E\text{-}05x^3 - 0.0508x^2 + 10.422x + 14.868 \ (R2 = 0.9950);$$

$$\text{lead: } y = -8E\text{-}06x^3 + 0.0013x^2 - 0.0212x + 3.0933 \ (R2 = 0.9794);$$

$$\text{cadmium: } y = -2E\text{-}06x^3 + 0.0005x^2 - 0.0089x + 0.9628 \ (R2 = 0.9952)$$

For buckwheat

$$\text{copper: } y = 2E\text{-}05x^3 - 0.0038x^2 + 0.2305x + 4.0085 \ (R2 = 0.9993);$$

$$\text{zinc: } y = 2E\text{-}05x^3 + 0.001x^2 + 2.909x + 17.036 \ (R2 = 0.9989);$$

$$\text{lead: } y = 2E\text{-}06x^3 - 0.0005x^2 + 0.0308x + 2.1555 \ (R2 = 0.9427);$$

$$\text{cadmium: } y = -1E\text{-}06x^3 + 0.0003x^2 + 0.0029x + 0.2673 \ (R2 = 1)$$

For beans

$$\text{copper: } y = 4E\text{-}05x^3 - 0.0095x^2 + 0.6295x + 3.9746 \ (R2 = 0.826);$$

$$\text{zinc: } y = 0.0004x^3 - 0.107x^2 + 8.4418x + 19.546 \ (R2 = 0.9968);$$

$$\text{lead: } y = 2E\text{-}06x^3 - 0.0005x^2 + 0.0435x + 1.6136 \ (R2 = 0.9574);$$

$$\text{cadmium: } y = -3E\text{-}07x^3 + 5E\text{-}05x^2 + 0.0047x + 0.1789 \ (R2 = 0.9968)$$

For soybeans*:*

$$\text{copper: } y = -1E\text{-}05x^3 + 0.0013x^2 + 0.0702x + 3.8425 \ (R2 = 0.9948);$$

$$\text{zinc: } y = -2E\text{-}06x^3 - 0.0056x^2 + 4.0916x + 23.054 \ (R2 = 1);$$

$$\text{lead: } y = 4E\text{-}06x^3 - 0.0011x^2 + 0.1088x + 1.7009 \ (R2 = 0.9887);$$

cadmium: $y = -9E\text{-}07x^3 + 0.0002x^2 + 0.0012x + 0.3109$ ($R2 = 0.9982$)

where: y is the metal concentration in plant phytomass (mg/kg), x is the magnitude of the impact on the affected area.

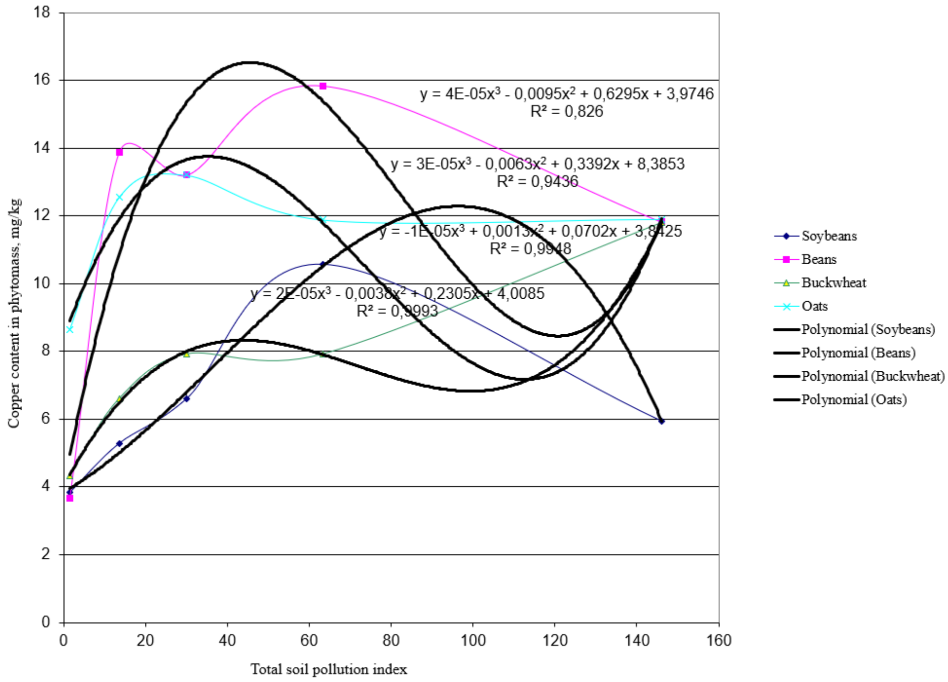

Figure 5. Dependence of copper content in plant phytomass on the level of soil pollution.

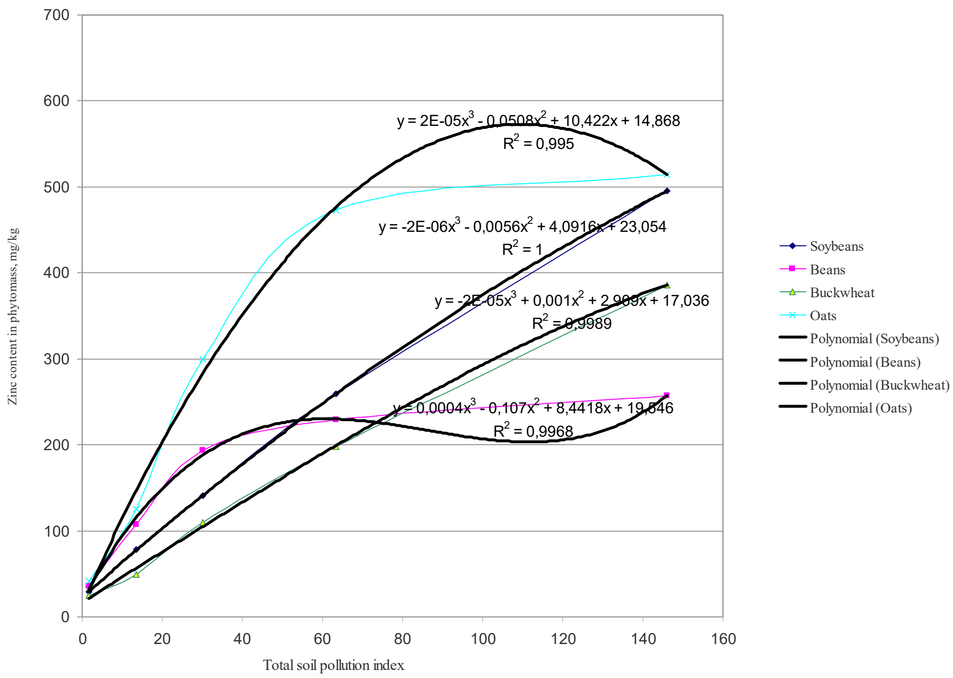

Figure 6. Dependence of zinc content in plant phytomass on the level of soil pollution.

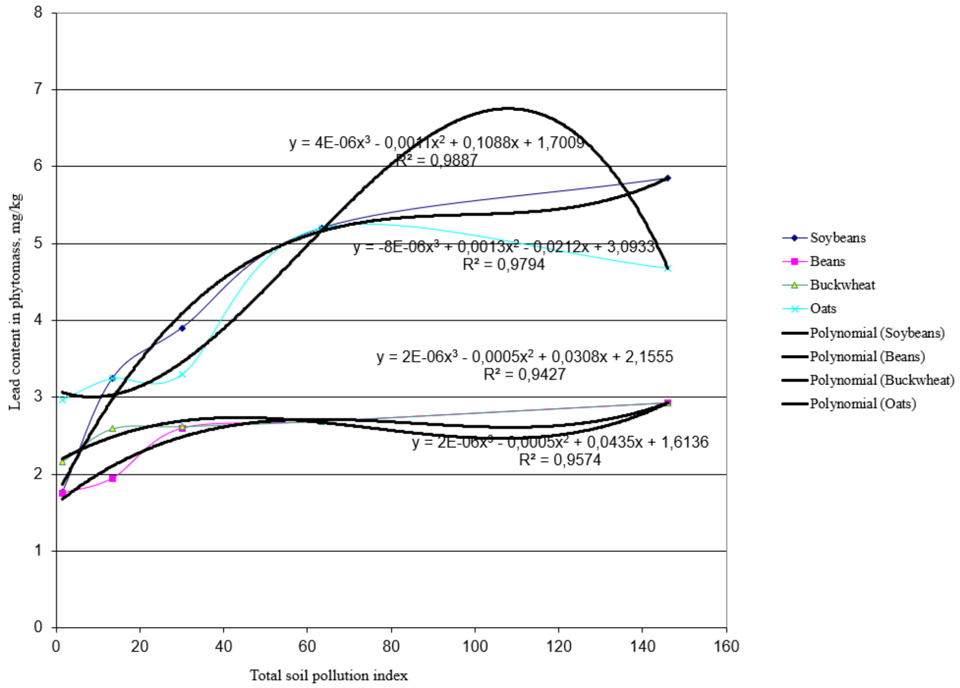

Figure 7. Dependence of lead content in plant phytomass on the level of soil contamination.

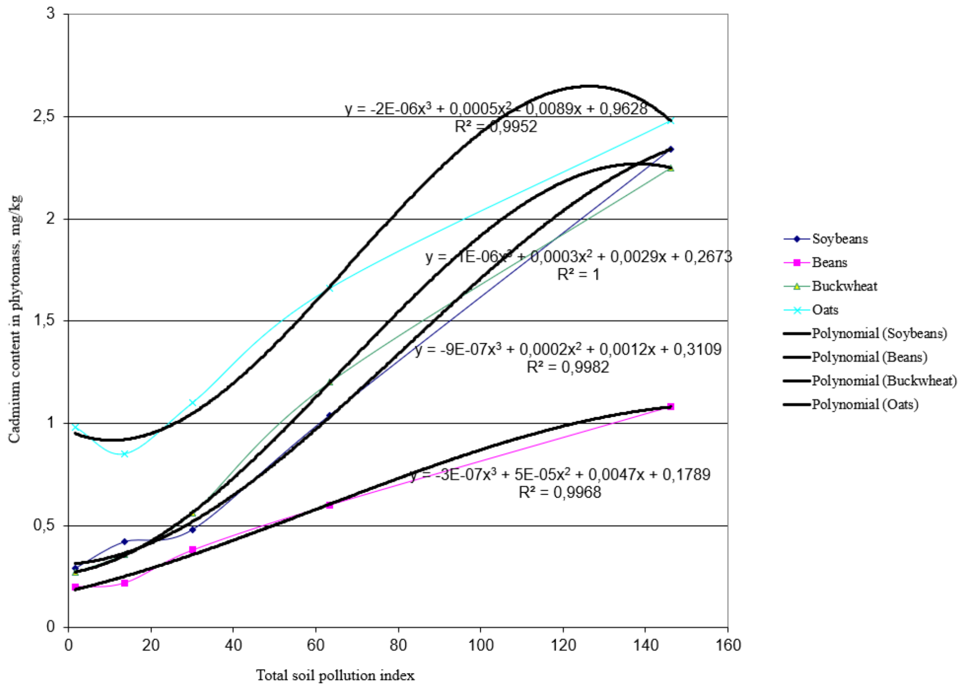

Figure 8. Dependence of cadmium content in plant phytomass on the level of soil pollution.

The results of the experiments in the form of the biological absorption coefficients of heavy metals calculated by the Equation (1) are presented in the Tables 6–9. The results for a single element (heavy metal) are presented in each table. To aid in the analysis of the results, the data from tables are presented as diagrams in Figures 9-12. When analyzing the diagrams in Figures 9–12, it should be taken into account that the scale along the axis Y (biological absorption coefficients) in all figures is different.

Table 6. The biological absorption coefficients of cadmium for all crops and the total pollution index.

Variant	*Zc*	Soybeans	Black Beans	Buckwheat	Oats
1	1.6	18.6	13	17.2	63.5
2	13.6	8.4	4.4	7.2	17
3	30.1	4.8	3.8	5.6	11
4	63.4	5.2	3	6	8.3
5	146.1	5.2	2.4	5	5.5

Table 7. The biological absorption coefficients of copper for all crops and the total pollution index.

Variant	*Zc*	Soybeans	Black Beans	Buckwheat	Oats
1	1.6	4.8	4.6	5.4	10.8
2	13.6	1.6	4.2	2	3.8
3	30.1	1	2	1.2	2
4	63.4	0.8	1.2	0.6	0.9
5	146.1	0.2	0.4	0.4	0.4

Table 8. The biological absorption coefficients of lead for all crops and the total pollution index.

Variant	*Zc*	Soybeans	Black Beans	Buckwheat	Oats
1	1.6	4	2.6	3.2	4.4
2	13.6	1	0.6	0.8	1
3	30.1	0.6	0.4	0.4	0.5
4	63.4	0.4	0.2	0.2	0.4
5	146.1	0.2	0.1	0.1	0.16

Table 9. The biological absorption coefficients of zinc for all crops and the total pollution index.

Variant	*Zc*	Soybeans	Black Beans	Buckwheat	Oats
1	1.6	14	17.2	11.8	19.5
2	13.6	14.2	19.6	9	22.7
3	30.1	12.8	17.6	10	27.2
4	63.4	11.8	10.4	9	21.5
5	146.1	10	5.2	7.8	10.4

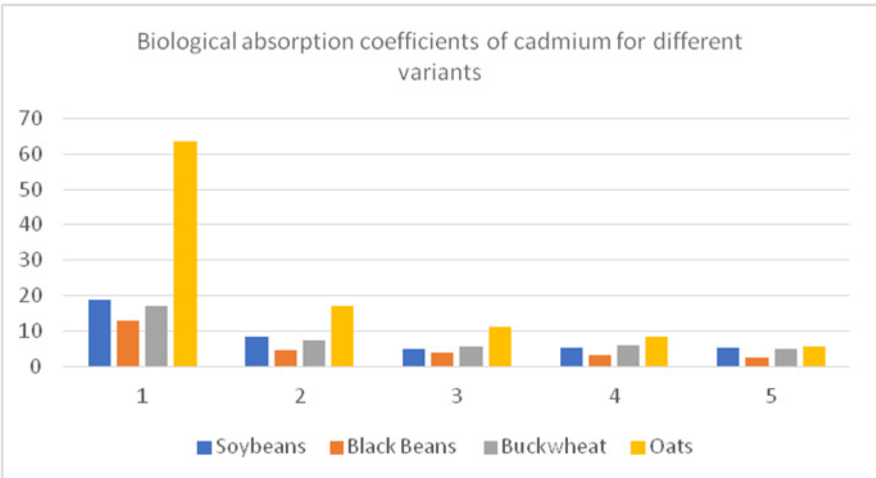

Figure 9. Values of the coefficients of biological absorption *Ax* (2) of cadmium at the different variants of the experiments (different total pollution index *Zc*).

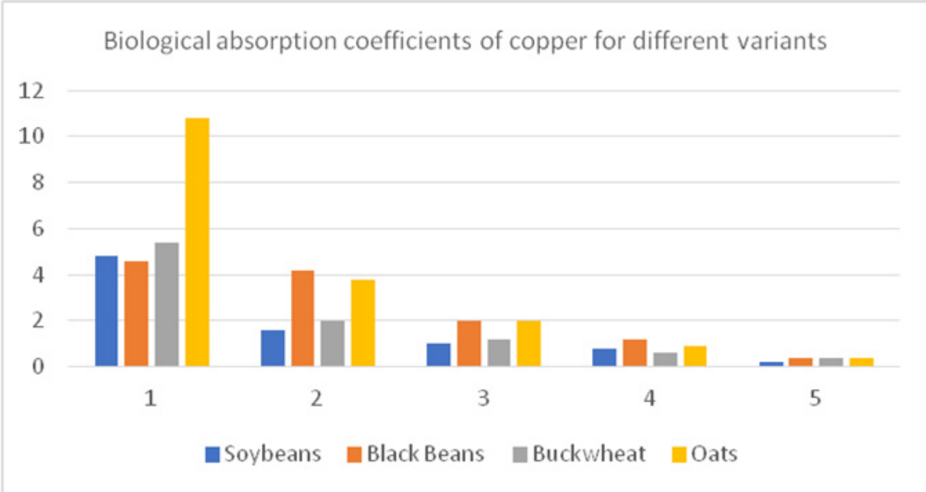

Figure 10. Values of coefficients of biological absorption Ax (2) of copper at the different variants of the experiments (different total pollution index Zc).

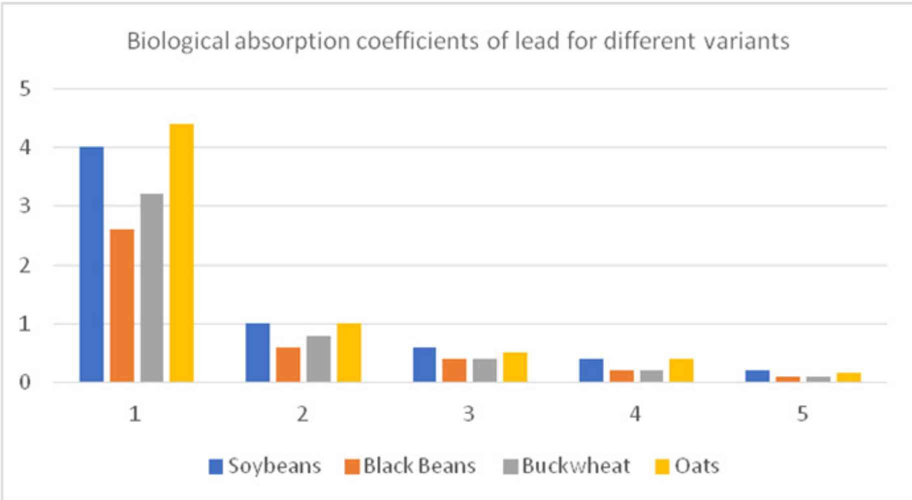

Figure 11. Values of coefficients of biological absorption *Ax* (2) of lead at the different variants of the experiments (different total pollution index *Zc*).

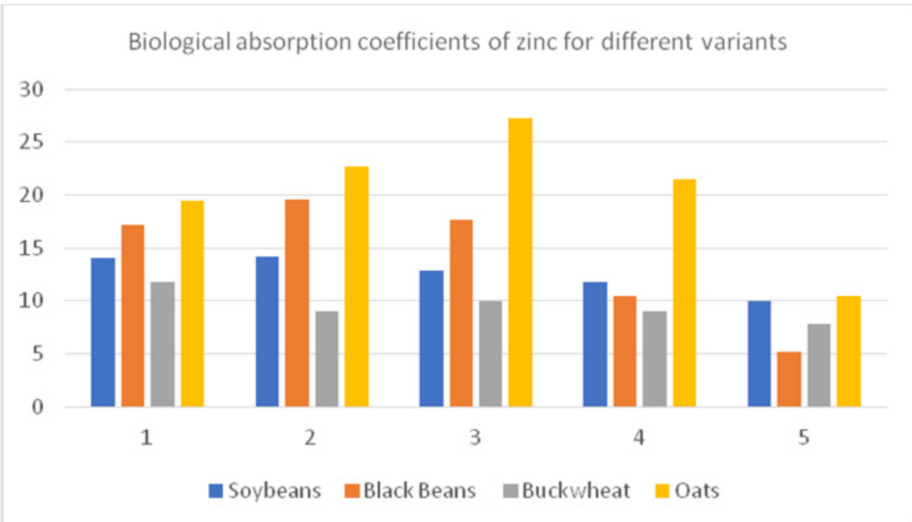

Figure 12. Values of coefficients of biological absorption Ax (2) of zinc at the different variants of the experiments (different total pollution index *Zc*).

Based on the results presented in Tables 6–9, an assessment of the phytoextraction capacity for test crops for cleaning soil (podzolized chernozem) contaminated with a complex of heavy metals was made. The results of the calculation of a specific heavy metals removal from the soil by crop phytomass of oats, buckwheat, black beans, and soybeans are presented in Table 10. It should be noted that in the last column (Sum) the total removal of all analyzed heavy metals for each crop and the total pollution index (*Zc*) are presented.

Table 10. Removal of heavy metals from soil by crop phytomass, kg/km^2.

Variant	*Zc*	Crops	Cu	Zn	Pb	Cd	Sum
1	1.6	Oats	0.27	2.10	0.09	0.018	2.478
		Buckwheat	1.76	10.19	0.88	0.111	12.941
		Black beans	1.71	16.96	0.85	0.095	19.615
		Soybeans	1.08	8.46	0.76	0.080	10.380
2	13.6	Oats	0.40	3.99	0.11	0.027	4.527
		Buckwheat	2.33	18.20	0.91	0.132	21.572
		Black beans	8.30	66.40	1.11	0.138	75.948
		Soybeans	1.98	30.40	1.22	0.160	33.76
3	30.1	Oats	0.34	7.77	0.08	0.029	8.219
		Buckwheat	2.72	39.66	1.02	0.205	43.605
		Black beans	8.52	124.07	1.36	0.243	134.193
		Soybeans	1.58	37.63	1.13	0.130	40.470
4	63.4	Oats	0.22	9.00	0.09	0.031	9.341
		Buckwheat	2.95	70.30	1.12	0.423	74.793
		Black beans	8.86	124.82	1.53	0.333	135.543
		Soybeans	2.47	60.38	1.00	0.240	64.090
5	146.1	Oats	0.18	7.29	0.07	0.035	7.575
		Buckwheat	1.91	77.93	0.64	0.463	80.943
		Black beans	3.42	93.44	1.04	0.412	98.312
		Soybeans	1.65	95.17	1.45	0.480	98.750

4. Discussion

The features of accumulation of heavy metals in the phytomass of test crops depending on the values of the total index of soil contamination have been discovered. These features are largely related to both the specificity of soil contamination with copper, zinc, lead and cadmium, and the species features of the test crops. Also, it must be noted that these substances are inherent antagonistic interaction when entering the plants. As noted by A. Kabata-Pendias and H. Pendias [68], zinc acts as a powerful antagonist in the absorption of copper, lead and cadmium by plants from the soil solution. In our experiment, with an increase degree of complex soil contamination with these metals, zinc accumulation in the phytomass of test crops is more actively observed in comparison with the accumulation of copper, lead and cadmium. This confirms the data of O.A. Sokolov, V.A. Chernikov [69] and T.M. Guseva [70] on the accumulation of copper, zinc, lead and cadmium in oat phytomass at different levels of complex pollution of sod-podzolic loamy sand soil with heavy metals.

As noted by A. Kabata-Pendias and H. Pendias [68], there is mutual competition between cations of copper and zinc in their absorption by the root system, which results in their content in the phytomass of plants. This trend was clearly manifested in our experiment when studying the content of copper in the phytomass of test crops at extremely dangerous levels of soil contamination (option 5). The same authors point out the antagonism between zinc, lead and cadmium cations in the process of their absorption by roots and transfer into the phytomass of plants, which is confirmed by the data of our experiment on a fairly gradual increase in lead and cadmium content in the phytomass of test crops.

In the range of [1.6–146.1] values of the total indicator of soil pollution, it was found that:

– copper is more actively concentrated in beans, followed by oats. At $Zc \geq 60$, the copper concentration in soybean phytomass begins to decrease. In buckwheat phytomass, unlike other crops, copper concentration continues to increase at $Zc \geq 60$;
– zinc is more actively concentrated in oats, followed by soybean. At $Zc \geq 60$, the increase in the concentration of zinc in the bean phytomass significantly slows down;
– lead is more actively concentrated in soybeans, followed by oats. Lead is much less concentrated in the biomass of buckwheat and beans;
– cadmium is more actively concentrated in the biomass of oats, followed by buckwheat and soybean. Much less cadmium is concentrated in the biomass of beans.

The obtained values of the approximation reliability show that the proposed polynomial dependencies quite accurately allow predicting the concentration of copper, zinc, lead, and cadmium in the phytomass of the tested plant species, depending on the value of the total indicator of soil pollution by heavy metals.

The results in Tables 6–9 and Figures 1–4 have shown that oats are characterized by the highest biological absorption coefficients at an acceptable ($Zc = 13.6$), moderately ($Zc = 30.1$) and highly dangerous ($Zc = 63.4$) degree of soil contamination with heavy metals. If the soil contamination by heavy metals is of a moderately dangerous ($Zc = 30.1$) and highly dangerous ($Zc = 63.4$) degree, buckwheat and soybeans absorb cadmium more intensively than black beans. Black beans, in turn, absorb copper and zinc more intensively. Soybeans absorb lead more intensively than other studied crops.

Based on the analysis of the values of the coefficients of biological absorption of heavy metals, an empirical series of their accumulation by the phytomass of the studied crops were discovered: Zn > Cd > Cu > Pb. An analysis of the empirical series of heavy metal absorption showed that the tested agricultural plants absorb zinc and cadmium from the soil more intensively. Lead and copper are more firmly retained by the soil absorbing complex, so their translocation into plants is less active, which is also confirmed by the studies of T.M. Guseva, performed by a similar method on sod-podzolic soil [68]. At the same time, copper, being a trace element, is more intensively absorbed from the soil by plants than lead. The data obtained are fully consistent with the biological absorption series of A.I. Perelman [56,62], according to which Zn and Cd belong to the series of intense and medium accumulations, and Cu and Pb to the series of weak accumulations and strong capture and are also fully consistent with the results of Yu.A. Mazhaysky [63].

The results have shown that the total removal of Cu, Zn, Pb, Cd, depending on the type of a phytoremediator, at a moderately hazardous degree of soil pollution ($Zc = 30.1$), were: for oats 8.2 kg/km^2; for buckwheat: 43.6 kg/km^2; for black beans 134.2 kg/km^2; for soybean 40.5 kg/km^2. With a highly dangerous degree of soil pollution ($Zc = 63.4$) it was: for oats 9.3 kg/km^2; for buckwheat: 74.8 kg/km^2; for black beans 135.5 kg/km^2; for soybean 64.1 kg/km^2.

It has been discovered that the removal of copper, zinc and lead by black beans is noticeably higher than that of oats, buckwheat and soybeans due to greater tolerance and the ability to form a large phytomass, which must be taken into account when choosing a phytoremediator for the removal of any contaminant from soil, which is also confirmed by N. A. Chernykh, N.Z. Milashchenko, V.F. Ladonin performed at different levels of contamination of sod-podzolic soil with cadmium, lead and zinc [71].

5. Conclusions

Empirical dependences of the content of copper, zinc, lead and cadmium in the phytomass of the tested agricultural crops on the value of the total indicator of soil pollution in the range from 1.6 to 146.1 were obtained.

The vegetation experiments carried out showed a high tolerance of the tested crops to the contamination of the soil investigated (podzolized chernozem) with a complex of heavy metals: Cu, Zn, Pb, Cd. During the experiments, oats, buckwheat, soybeans and black beans have demonstrated the ability to accumulate a fairly high amount of pollutants in the phytomass. This result allows us to conclude that these crops are effective as phytoremediation plants in the purification of any contaminated soil from heavy metals under the conditions of moderately dangerous pollution. In general, the results of the study are a good basis for creating digital models of plant phytoextraction as a part of a digitalization process of agricultural production objects in the center of the European part of Russia.

As one of the possible options for the disposal of a contaminated phytomass we consider the preparation of fertilizer mixtures based on ash from phytoremediators and peat with mandatory control over the content of heavy metals [16,19,22,25,26,30,56,63]. The practical significance of the work lies in the possibility of using phytoremediation in the rehabilitation of heavy metals-contaminated (under conditions of moderately dangerous pollution) agricultural land soils in the center of the European part of the Russian Federation.

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