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Influence of Carbons on Metal Stabilization and the Reduction in Soil Phytotoxicity with the Assessment of Health Risks

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Abstract: Despite notable achievements in the development and application of the remediation of metal-contaminated soils, the search for and study of promising immobilizing agents continues. This article presents a new approach to using brown coal and activated carbon and their application for metal stabilization. An experiment was conducted to test *Medicago falcata* L. on soils from industrial areas contaminated with varying levels of lead (Pb), cadmium (Cd), chromium (Cr), zinc (Zn), copper (Cu), and nickel (Ni) with the addition of carbons. This plant is a stress-tolerant leguminous species. In this study, the total content of metals in soil and the available forms to plants (single extractions with 0.02 M ethylenediaminetetraacetic acid, EDTA) were determined, along with metal contents in the plant. The use of carbons lowered the phytoavailable forms of metals for plants and thus, resulted in a reduction in the phytotoxicity of the soils. The contents of the tested metals in the roots and shoots were lower than in the combinations of soils with no carbon added. The activated carbon had a stronger effect on limiting the availability of metals than brown coal in relation to plants growing on soils without added carbon; the percentage of reduction for the shoots was Cr (18.2%) > Zn (11.5%) > Ni (10.7%) > Cu (10.3%) > Cd (8.9%) > Pb (2.4%) and Cu (13.3%) > Cr (12.5%) > Zn (10.5%) > Pb (9.0%) > Ni (5.7%) > Cd (4.6%) for roots. Metals reduced the growth of *Medicago falcata* L. roots from 44 to 21%, while the growth of shoots was reduced from 25 to 2%. Adding carbons to soils in all combinations resulted in a decrease in the following pollution indices: pollution index (*PI*), pollution load index (*PLI*), and non-carcinogenic (*HQ*) and carcinogenic risk factors (*ILCR*).

Keywords: environmental indices; health risks; metal stabilization; phytotoxicity; soil pollution; carbons

1. Introduction

Soil contamination, especially by metals, is recognized as a main contributor to environmental problems throughout the world [1,2]. A study on the presence of metals such as Pb, Cd, Cr, Zn, Cu, and Ni in the environment indicated that many areas associated with steel-making industries contained high concentrations of these metals [3]. Once metals are introduced into an environment, they may persist for a long time [4]. Soil is the direct pathway for the contamination of plants by metals [5]. Metals are converted into different forms [6–8]. It is assumed that in the soil's solid fraction, only some of the pollutants can negatively influence organisms. Bioavailability can be minimized through the chemical and biological stabilization of metals using a range of inorganic and organic compounds [9]. Currently, there are several remediation methods that have been implemented using stabilization approaches. The definition of the stabilization method is the immobilization of contaminants by changing their form to one that is less soluble by isolating them in the soil [10]. Metal immobilization is achievable by, e.g., adsorption and precipitation, which leads to the transfer of pollutants from the soil solution to the solid phase [11]. The stabilization method does not remove pollutants from the soil, but it affects the mobility and

Citation: Pusz, A.; Wiśniewska, M.; Kamiński, A.; Knosala, P.; Rogalski, D. Influence of Carbons on Metal Stabilization and the Reduction in Soil Phytotoxicity with the Assessment of Health Risks. *Resources* **2024**, *13*, 66. https://doi.org/10.3390/resources13050066

Academic Editor: Demetrio Antonio Zema

Received: 16 March 2024
Revised: 22 April 2024
Accepted: 3 May 2024
Published: 9 May 2024

solubility of metals and reduces their concentration in the soil solution, minimizing their potential transport to plants, microorganisms, and the soil and water environments [3,12].

For stabilization, different substances, reagents, chemical agents, etc., are added to the contaminated soil to induce physical and chemical interactions between introduced substances and pollutants to reduce their mobility [13,14]. All substances used for the immobilization method are selective towards metals by specific mechanisms: reducing leaching potential, complexation, and surface adsorption [11,15]. One of the materials used for the immobilization method that has shown a wide range of effectiveness towards the reduction in plant uptake of metals from polluted soil is carbon [16]. In this study, a method of in situ immobilization of metal forms in soils, two carbons (brown coal and activated carbon) were used. The addition of carbons may cause the stabilization of inorganic contaminants by adsorption, binding, co-precipitation, and electrostatic interactions with ion exchange. Among the properties that affect metal retention is the microporous structure of carbons [17], with activated carbons that have a specific surface area with an extensive pore system having variable pore size and active functional groups on its surface [17,18]. Carbon and carbon-based materials are effective sorbents that immobilize organic contaminants and heavy metals through various mechanisms, due to their multifunctional surface properties. The specific mechanisms are complexation, reduction, precipitation, ion exchange, π–π interactions, hydrogen bonding, and adsorption [19,20]. Brown coal features a complex of amorphous humic substances, including humins, bitumens, and humic, hymatomelanic, and fulvic acids. Brown coal enriches the soil with humus compounds, provides some nutrients needed for plant development, improves soil properties by modifying them in various ways, provides a material with a high degree of humification, and is relatively resistant to mineralization [13].

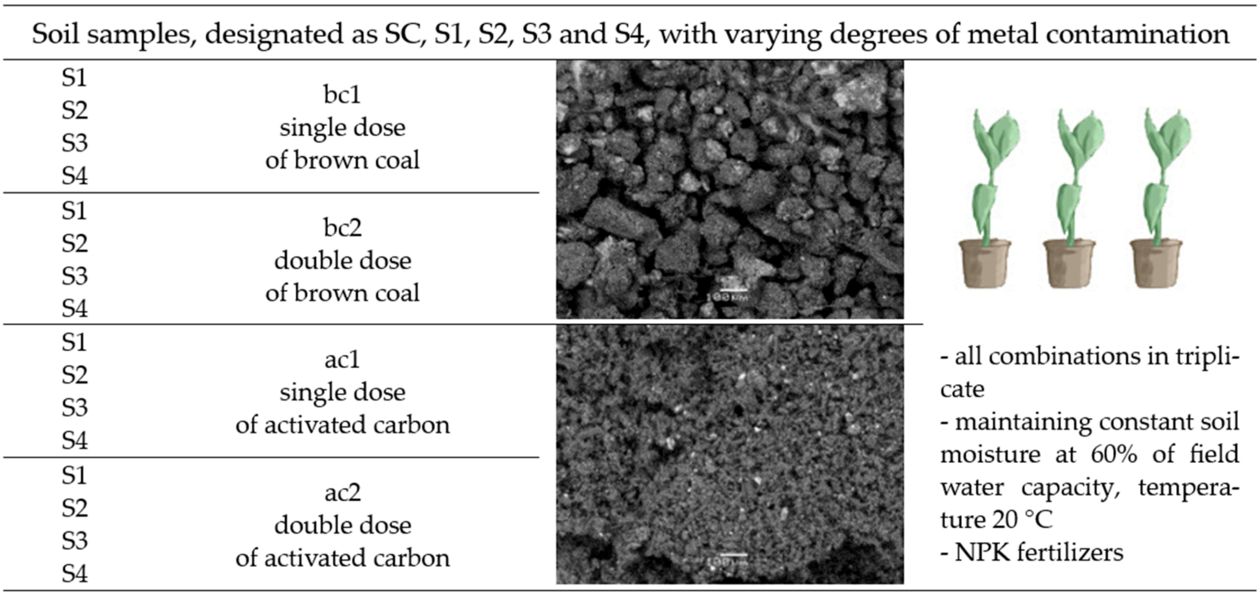
Losses of soil organic carbon occur as a result of soil processes, mainly the mineralization of organic matter and emissions of greenhouse gases into the atmosphere, i.e., carbon dioxide (CO_2) and methane (CH_4), and as a result of the migration and leaching of the dissolved form of organic carbon. In order to increase carbon sequestration in the soil, practices that increase the organic carbon content should be used. The results can be applied to polluted industrial areas or degraded soilless areas to improve the physical and chemical properties of soils, including carbon sequestration activities, which influence the organic carbon content in the soil.

This study is multifaceted; it concerns metal stabilization and the reduction in phytotoxicity in the soil after the use of carbons (brown coal and activated carbon) to reduce the mobility of metals in the soil and their accumulation in plants. An additional important aspect is the assessment of health risks based on selected indicators related to the occurrence of metals in the soil before and after the use of carbons. The use of carbons to stabilize metals in the soil is an in situ technique that does not cause any additional environmental damage. The benefits of this method include the reduced content of metal forms that are available to plants while reducing the risk of non-carcinogenic and carcinogenic effects on humans. The innovation of the method was the use of carbons, which prevent the transport of metals to the aboveground parts of the plant. This research presents the use of activated carbon for the immobilization (stabilization) of metals in the soil compared to brown coal. Often, the literature concerns only the use of brown coal. There are no comparative studies in the literature for these two carbons, especially in the context of their use in the process of stabilizing metals in soil. In this study, we used *Medicago falcata* L. This species, which belongs to the genus *Medicago*, is a deeply rooted plant with good potential to be a source of biomaterial and the ability to remove heavy metals from the soil [21]. It also has the ability to grow well in highly contaminated soils [22] and can be used as green manure [23]. *Medicago falcata* L. was chosen because of its ability to develop a root system that can reach deeper layers of soil and its ability to accumulate large amounts of metals in the roots. This plant is also characterized by high tolerance to high concentrations of metals in the soil while showing no negative effects, such as leaf necrosis or discoloration [24].

2. Materials and Methods

2.1. Design of the Pot Experiment

Five soil samples, designated as SC, S1, S2, S3, and S4, with varying degrees of metal contamination, were used for the pot experiment. The soils were taken from an industrial waste landfill and stored in the form of a heap in Krzemionki Opatowskie, Poland. The soils were used to clean metallurgical carts/wagons and were thus contaminated with metals. The pot experiment was conducted in the vegetation hall of the Warsaw University of Life Sciences, Poland. In the pot experiment, each Wagner-type pot (dimensions of the pot: height of 0.25 m and diameter of 0.22 m) was filled with 10 kg of soil, which was mixed thoroughly. The five combinations of soils did not contain any added carbon. To assess the efficacy of the immobilization of metal forms in the soil, we used brown coal and activated carbon. The carbons were used in different combinations: single dose, i.e., 200 g of brown coal (bc1) or activated carbon (ac1), and double dose, i.e., 400 g of brown coal (bc2) or activated carbon (ac2). In total, 21 soil combinations were obtained in triplicate (Figure 1). The carbons were introduced into the soil once, and the experiment was carried out during one vegetation period of the tested plant, from March to November. In the pot experiment, was used *Medicago falcata* L.



Soil samples, designated as SC, S1, S2, S3 and S4, with varying degrees of metal contamination

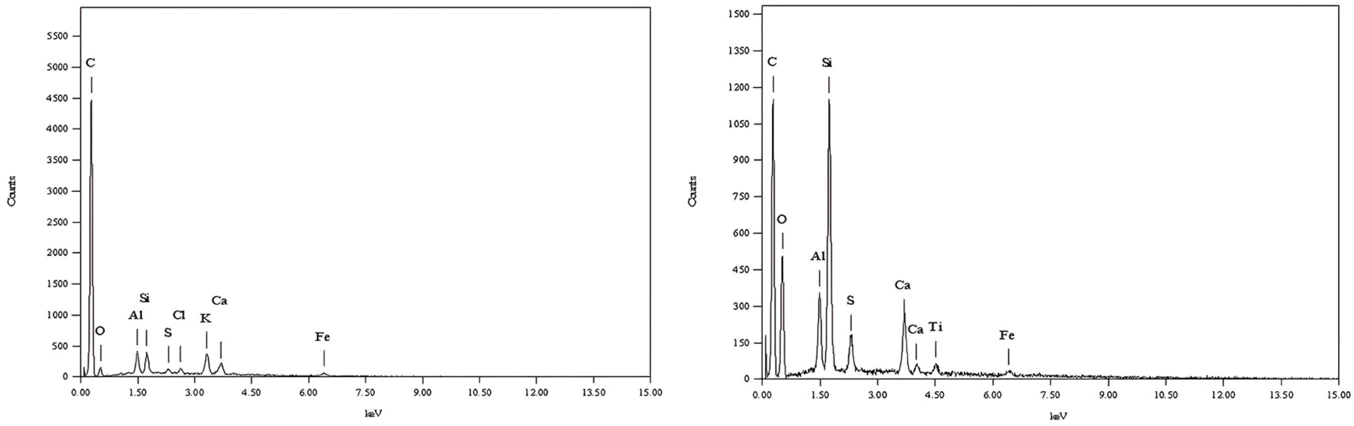
S1 S2 S3 S4	bc1 single dose of brown coal
S1 S2 S3 S4	bc2 double dose of brown coal
S1 S2 S3 S4	ac1 single dose of activated carbon
S1 S2 S3 S4	ac2 double dose of activated carbon

- all combinations in triplicate
- maintaining constant soil moisture at 60% of field water capacity, temperature 20 °C
- NPK fertilizers

Figure 1. Design of the pot experiment (photo of analyzed samples of brown coal and activated carbon).

For activated carbon, the X-ray spectrum for the sample confirmed a high content of carbon (Figure 2a). There were slight traces of silica, feldspar, clay minerals, and calcite. Unlike brown coal, K was found in the spectra of activated carbon. The analysis results for the brown coal sample show that it contained calcite, quartz, gypsum, and trace amounts of sulfur, feldspar, and clay minerals (Figure 2b).

The pot experiment was conducted under a soil moisture of 60% of field capacity and temperature of 20 °C, with the PPFD (Photosynthetic Photon Flux Density) at the plant level being around 50–70% [25]. During the vegetation period of the *Medicago falcata* L., the development phases were observed. *Medicago falcata* L. was harvested at the flowering stage (BBCH 67). The experimental research on *Medicago falcata* L., including the collection of plant material, was conducted in accordance with relevant institutional, national, and international guidelines and legislation. *Medicago falcata* L. seeds were provided by the Polish Academy of Sciences Botanical Garden—Centre for Biological Diversity Conservation in Powsin. *Medicago falcata* L. seeds can withstand desiccation (drying) and are typically able to survive long storage periods (so-called orthodox seeds).



(**a**) (**b**)

Figure 2. Dispersion energy spectra of X-rays (EDS) for certain areas of carbons: (**a**) activated carbon and (**b**) brown coal.

2.2. Methods

The following properties were determined in the soils: granulometric composition with the Casagrande method, pH in potassium chloride (1 M KCl) [26], organic carbon content (TOC) [27], carbonate content ($CaCO_3$) [28], and exchangeable alkaline cations [29]. The total concentration of metals in soils was determined after the mineralization in a concentrated perchloric acid ($HClO_4$) and nitric acid (HNO_3) mixture. The contents of metals (Cu, Pb, Zn, Cd, Cr, and Ni) in the ethylenediaminetetraacetic acid (0.02 M EDTA) extract were determined to assess metal solubility in the soil solution. The exchangeable alkaline cations and metal contents in the sample soils and plants were determined using ICP–OES (Thermo Scientific iCAP 6500 or Varian Axial Vista 720–ES spectrometer, Waltham, MA, USA). For each series of measurements, blank samples were prepared. The accuracy of the methodology was verified using the method of standard additions.

Microscopic observations of the carbons (brown coal and activated carbon) were carried out using a JJSM-6380 LA scanning electron microscope (SEM) connected to an EDS electron microprobe made by JEOL Ltd. Musashino, Tokyo, Japan.

The analyses were performed in triplicate for each sample. The standard deviation (SD) was calculated for mean values (from triplicate). The dispersion of the results did not exceed CV = 10%. All analyses, calculations, and graphical representations of the results were carried out in Microsoft® Excel® for Microsoft 365 using the Analysis ToolPak.

2.3. Phytotoxicity Tests

The modified Phytotoxkit^{TM} test made by MicroBioTest (Gent, Belgium) was used to assess the phytotoxicity of S1–S4 soils contaminated with metals to varying degrees. Very often, in practice, the Phytotoxkit^{TM} test is modified by replacing standard test plants with other species, e.g., sunflower or cucumber [30–32].

Medicago falcata L. was used as a test species in this study. The seeds were calibrated to remove small damaged seeds and rinsed three times with distilled water. After washing, the seeds were soaked in distilled water at a temperature of 25 °C. After four hours, the seeds were removed from the water and transferred to test plates containing soil. The soil was watered by determining its water-holding capacity (according to the Phytotoxkit^{TM} test). Seeds were incubated in the same conditions as standard plants (phytodetectors) and were grown vertically in a growth chamber under a night photoperiod at 25 °C for 72 h.

The germination and phytotoxicity tests were performed in three repetitions under laboratory conditions. The reaction of plants to the presence of metals was determined on the basis of the reduction in the length of roots and shoots compared to the control object. The measurements of the lengths of the roots and shoots of the tested plant were performed using ImageTool software version 3.0.

2.4. Calculation of Environmental Indices

The single-factor pollution index was used to evaluate the pollution degree of a single metal in each sample [33]. According to Lee et al. [34] and Chen et al. [35], the pollution index (PI) is defined as Equation (1) [36,37]:

$$PI = \frac{C_i}{C_{oi}} \tag{1}$$

C_i—the concentration of a given i-th element in soil samples ($\text{mg}\cdot\text{kg}^{-1}$) and

C_{oi}—the maximum standard value of the metal in the soil ($\text{mg}\cdot\text{kg}^{-1}$) [35].

To give an assessment of the overall pollution status for a sample, the integrated pollution load index (PLI) can be employed [35,38]. The PLI can be calculated using Equation (2):

$$PLI = \sqrt[n]{(PI_1 \times PI_2 \times PI_3 \times \ldots \times PI_n)} \tag{2}$$

n—the number of heavy metals [35].

The PLI is divided into seven levels to indicate the contamination degree and is described as background concentration ($PLI = 0$), unpolluted ($0 < PLI \leq 1$), unpolluted to moderately polluted ($1 < PLI \leq 2$), moderately polluted ($2 < PLI \leq 3$), moderately to highly polluted ($3 < PLI \leq 4$), highly polluted ($4 < PLI \leq 5$), or very highly polluted ($PLI > 5$) [39–41].

To calculate the exposure risks of soil metals to human health, the calculation used is based on that developed by the USEPA for health risk assessment guidelines [42,43]. The dose received through ingestion and dermal absorption can be respectively estimated by Equations (3) and (4) [35,42]:

$$ADI_{ing} = C_{soil} \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{3}$$

$$ADI_{dermal} = C_{soil} \times \frac{SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{4}$$

ADI_{ing}—the daily intake from soil ingestion ($\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$),

ADI_{dermal}—the daily intake from dermal absorption ($\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$),

C_{soil}—the concentration of metal in the soil ($\text{mg}\cdot\text{kg}^{-1}$),

$IngR$—the ingestion rate of the soil ($\text{mg}\cdot\text{day}^{-1}$),

EF—the exposure frequency ($\text{day}\cdot\text{year}^{-1}$),

ED—the exposure duration (year),

BW—the body weight of the exposed individual (kg),

AT—the time period over which the dose is averaged for carcinogenic and non-carcinogenic metals (days),

SA—the exposed skin surface area (cm^2),

AF—the adherence factor ($\text{kg}\cdot\text{cm}^{-2}\cdot\text{day}^{-1}$), and

ABS—the dermal absorption factor [35,40,44].

Based on the literature [35,41,45], the values of the parameters required for the evaluation of the exposure risks to metals in the soil were used. Toxic effects are likely to ensue when the exposure dose of the target contaminant exceeds the reference dose, which is generally articulated as the non-carcinogenic risk index (HQ). The HQ can be calculated with Equation (5):

$$HQ = \frac{ADI}{RfD} \tag{5}$$

RfD—the toxicity threshold value of a specific metal ($\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$).

When the HQ value is greater than 1, it indicates that the contamination can pose a non-carcinogenic risk; for an HQ value less than 1, the non-carcinogenic risk is defined as small [41]. The carcinogenic risk of a single pollutant index (*ILCR*) is calculated with Equation (6):

$$ILCR_{ij} = ADI \times SF_{ij} \tag{6}$$

SF_{ij}—the carcinogenic tilt factor of metal i under exposure pathway j (kg·day·mg^{-1}).

To assess the total risk of the tested metals regarding the non-carcinogenic and carcinogenic effects, Equations (7) and (8) [41] were used, as follows:

$$HQ_T = \sum_{i=1}^{m} \sum_{j=1}^{n} HQ_{ij} \tag{7}$$

$$ILCR_T = \sum_{i=1}^{m} \sum_{j=1}^{n} ILCR_{ij} \tag{8}$$

If the value of the *ILCR* index is less than 1.00×10^{-4}, the metal does not pose a carcinogenic risk to human health. Otherwise, the metal has a carcinogenic risk [41,45]. Based on the classifications by the International Agency for Research on Cancer (IARC), Zn, Cu, Mn, Cr, and Cd were regarded as non-carcinogenic metals, whereas As, Cr, Ni, Cd, Co, and Pb were treated as potential carcinogenic metals [46].

3. Results

3.1. Soil and Carbon Characteristics

Five soil samples, designated as SC, S1, S2, S3, and S4, were used for the pot experiment. The examined soils were characterized by a brownish-yellow color (SC) and yellowish-brown color (S1–S4), a low content of the skeletal fraction, and an alkaline pH (Table 1).

Table 1. Chemical properties of SC and S1–S4 soils before setting up the pot experiment.

Soil	$CaCO_3$	TOC	pH KCl	Ca	Mg	K	Na	CEC
	%			cmol(+)·kg^{-1}				
SC	0.97 ± 0.04	0.97 ± 0.06	7.52–7.63	13.1 ± 1.2	0.95 ± 0.09	0.13 ± 0.02	0.86 ± 0.08	15.04
S1	8.56 ± 0.32	3.02 ± 0.21	7.58–7.62	19.1 ± 1.5	2.87 ± 0.23	0.15 ± 0.02	0.69 ± 0.06	22.81
S2	6.98 ± 0.21	1.75 ± 0.13	7.65–7.68	17.1 ± 1.6	2.35 ± 0.21	0.12 ± 0.02	0.71 ± 0.07	20.28
S3	5.86 ± 0.19	1.42 ± 0.12	7.59–7.63	14.3 ± 1.4	1.37 ± 0.12	0.11 ± 0.01	0.18 ± 0.02	15.96
S4	5.51 ± 0.16	1.26 ± 0.08	7.50–7.54	14.7 ± 1.3	0.74 ± 0.06	0.08 ± 0.01	0.09 ± 0.01	15.61

TOC—total organic carbon and CEC—cation exchange capacity.

Soil samples were taken from a depth of 0–0.25 m below ground level. The soils had different granulometric compositions: sandy loam (SC) and loamy sand (S1–S4). The total concentrations of metals in SC and S1–S4 soils are presented in Table 2. The SC soil had a low metal content. The high levels of metals in S1–S4 soils resulted from the characteristics and the soils' origins. None of the soil combinations exceeded the permissible values of Cd (15 mg·kg^{-1}), Ni (500 mg·kg^{-1}), and Cr (1000 mg·kg^{-1}), according to the relevant ordinance [47]. The permissible values were exceeded for Pb (600 mg·kg^{-1}) in all soil combinations except soil SC. In the case of Zn (2000 mg·kg^{-1}), the exceedances occurred for S1 and S2 soils. In the case of Cu (600 mg·kg^{-1}), the exceedances were only for the S1 soil.

When choosing brown coal as a soil additive, it is important to consider its pH. This relationship was confirmed by Cuske et al. [48]. In this study, the pH values (1 M KCl and demineralized water) were 5.4 and 5.9 for brown coal and 9.5 and 9.8 for activated carbon, respectively. The dry matter content was 65.69% for brown coal and 94.04% for activated carbon. Carbons are characterized by different contents of metals, which have been confirmed by numerous authors conducting research on brown coal and activated carbon [7,13,32,49]. These researchers [7,13,49,50] have observed the stabilization of soil pH in studies with brown coal on alkaline soils. Maintaining high pH values is important to reduce metal mobility and phytotoxicity. With a decrease in pH (acidic reaction), the mobility of metals in the soil and their availability to plants increases, while at higher pH values (neutral and alkaline reactions), metal immobilization and a reduction in phytotoxicity are observed. Brown coal caused a slight decrease in the pH value compared to soils without the addition of coal, which was confirmed by other authors in their studies [48,51]. The addition of activated carbon at both doses improved the reaction of the tested soils. Erdogan et al. [52] observed different sorption capacities of the tested metal ions on oxidized carbonic humic acid. The use of activated brown coal resulted in an increase in the content of exchangeable alkaline cations and an increase in the sorption capacity of the tested soils, with the highest values of sorption capacity being found for soils with both doses of activated carbon. This dependence is related primarily to the presence of humic acids, which are characterized by a very high sorption capacity for basic cations.

Table 2. Total metal concentrations in SC and S1–S4 soils.

Soil	Cu	Pb	Zn	Cd	Cr	Ni
	mg·kg^{-1} d.m.					
SC	13.1 ± 1.1	14.8 ± 1.2	49.1 ± 3.3	0.34 ± 0.08	7.51 ± 0.62	12.4 ± 1.6
S1	651 ± 35	4186 ± 126	5681 ± 237	12.9 ± 2.2	319 ± 16	139 ± 1.2
S2	406 ± 28	1892 ± 76	2469 ± 104	6.84 ± 1.17	187 ± 11	95.2 ± 6.3
S3	175 ± 11	848 ± 25	1320 ± 40	3.56 ± 0.62	135 ± 10	74.7 ± 6.1
S4	169 ± 5	697 ± 35	897 ± 36	3.21 ± 0.54	84.3 ± 4.6	54.6 ± 3.9

3.2. Total Content of Metals in Soils

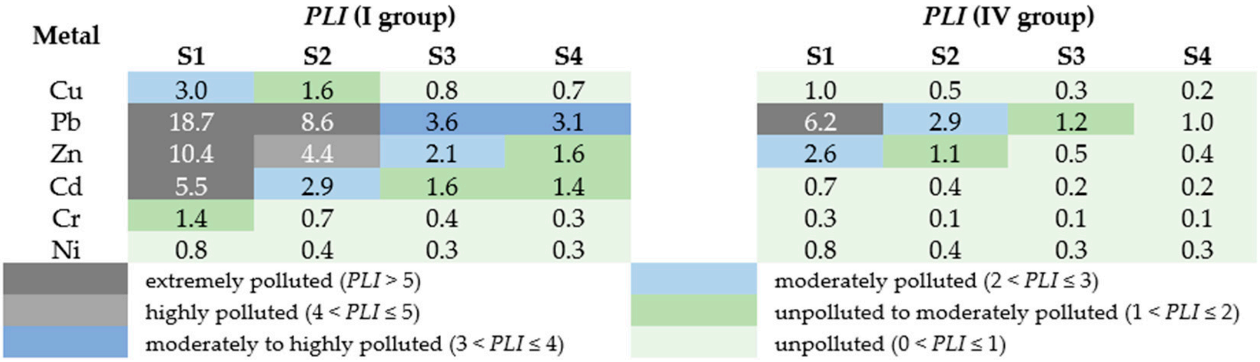
The examined soil samples originated from industrial areas, which were classified as the fourth group of land. For the SC soil, the total metal contents that were determined were Cu—17.2, Pb—23.1, Zn—61.1, Cd—0.72, Cr—10.4, and Ni—15.9 mg·kg^{-1} d.m. The limit values of the ordinance [47] were not exceeded for any of the metals in this soil (Table 3).

Table 3. Total metal concentration in soils in mg·kg^{-1} d.m. depending on the dose of brown coal and activated carbon.

Soil	Cu	Pb	Zn	Cd	Cr	Ni
S1	615 ± 29	3912 ± 156	5415 ± 217	11.6 ± 1.4	298 ± 18	118 ± 15
S1bc1	560 ± 35	3876 ± 155	5402 ± 270	11.2 ± 1.6	239 ± 12	109 ± 8
S1bc2	573 ± 44	3566 ± 143	5242 ± 157	10.3 ± 1.5	248 ± 22	110 ± 10
S1ac1	602 ± 48	3295 ± 165	4720 ± 142	9.94 ± 1.15	247 ± 20	109 ± 7
S1ac2	605 ± 61	3211 ± 128	4350 ± 174	9.81 ± 1.49	244 ± 12	106 ± 6
S2	365 ± 25	1772 ± 71	2325 ± 93	6.11 ± 0.72	148 ± 7	67.5 ± 6.6
S2bc1	279 ± 22	1745 ± 67	2123 ± 85	5.38 ± 1.04	132 ± 11	60.4 ± 5.8
S2bc2	286 ± 11	1642 ± 66	1993 ± 80	5.41 ± 0.91	135 ± 8	58.7 ± 8.3
S2ac1	254 ± 23	1631 ± 82	2053 ± 103	5.19 ± 0.83	118 ± 9	54.7 ± 7.7
S2ac2	265 ± 11	1465 ± 73	2025 ± 101	5.06 ± 0.89	124 ± 10	54.3 ± 6.8
S3	164 ± 8	753 ± 30	1130 ± 45	3.49 ± 0.48	99.2 ± 5.1	47.1 ± 6.3
S3bc1	142 ± 12	683 ± 24	1082 ± 43	2.97 ± 0.51	72.2 ± 6.3	39.8 ± 4.3
S3bc2	145 ± 9	677 ± 27	891 ± 36	2.68 ± 0.35	75.3 ± 5.2	41.9 ± 5.9
S3ac1	141 ± 11	680 ± 19	806 ± 24	2.81 ± 0.44	68.8 ± 6.1	38.9 ± 5.3
S3ac2	134 ± 5	670 ± 29	789 ± 32	2.75 ± 0.47	72.4 ± 6.1	38.3 ± 4.2
S4	144 ± 6	650 ± 26	817 ± 41	2.97 ± 0.43	66.4 ± 6.2	45.8 ± 3.7
S4bc1	136 ± 10	576 ± 17	807 ± 32	2.71 ± 0.48	65.8 ± 4.2	41.1 ± 4.9
S4bc2	133 ± 6	582 ± 23	805 ± 24	2.82 ± 0.56	60.1 ± 5.4	40.2 ± 2.1
S4ac1	123 ± 7	529 ± 18	784 ± 39	2.79 ± 0.33	63.1 ± 5.9	40.1 ± 5.5
S4ac2	108 ± 4	544 ± 25	738 ± 22	2.78 ± 0.34	53.4 ± 3.3	40.7 ± 3.7

Compared to the limit values of the ordinance, Cu exceeded the limit (600 mg·kg^{-1} d.m.) only in the S1 soil and the combinations with activated carbon. In the case of Pb

(600 mg·kg^{-1} d.m.), the limit value was exceeded in all four soil types, and only in the case of the S4 soil, exceedance was not recorded after adding both carbons. In the case of Zn (2000 mg·kg^{-1} d.m.), exceedances were found in S1 and S2 soils, except in combination with a double dose of brown coal (S2bc2); the limit values were not exceeded in the other soils. For Cd (15 mg·kg^{-1} d.m.), Cr (1000 mg·kg^{-1} d.m.), and Ni (500 mg·kg^{-1} d.m.) in all of the tested soils, the limit values were not exceeded. The *PLI* indices were calculated (Figure 3) for the total content of metals in the soil in relation to the permissible content of metals in accordance with the relevant ordinance [47], for the residential area (group I) and industrial area (group IV).



Metal	*PLI* (I group)				*PLI* (IV group)			
	S1	S2	S3	S4	S1	S2	S3	S4
Cu	3.0	1.6	0.8	0.7	1.0	0.5	0.3	0.2
Pb	18.7	8.6	3.6	3.1	6.2	2.9	1.2	1.0
Zn	10.4	4.4	2.1	1.6	2.6	1.1	0.5	0.4
Cd	5.5	2.9	1.6	1.4	0.7	0.4	0.2	0.2
Cr	1.4	0.7	0.4	0.3	0.3	0.1	0.1	0.1
Ni	0.8	0.4	0.3	0.3	0.8	0.4	0.3	0.3

extremely polluted (*PLI* > 5)
highly polluted (4 < *PLI* ≤ 5)
moderately to highly polluted (3 < *PLI* ≤ 4)
moderately polluted (2 < *PLI* ≤ 3)
unpolluted to moderately polluted (1 < *PLI* ≤ 2)
unpolluted (0 < *PLI* ≤ 1)

Figure 3. The calculated *PLI* index values for residential and industrial areas.

For the S1 soil, the highest values of the pollution load index (*PLI*), i.e., above 5, were obtained for Pb, Zn, and Cd, which led to the soil being classified as "very highly polluted". For the S2 soil, only in the case of Pb was the *PLI* value above 5. For S3 and S4 soils, the highest *PLI* value (above 3) was found for Pb, which means "moderately to highly polluted". By analyzing the *PLI* values in relation to the values for the industrial area, it was found that the S1 soil was classified as "extremely polluted". S2 and S3 soils were classified as "moderately polluted" and "unpolluted to moderately polluted", respectively. Only the S4 soil was classified as "unpolluted" for the analyzed metals.

3.3. Metal Forms Extracted with EDTA

In order to determine phytoavailable metal forms, single extractions were carried out with the use of EDTA [53,54]. The results obtained after using the EDTA solution and non-carcinogenic risk indices are presented in Table 4. Numerous studies [55–57] have shown that the phytoassimilability of metals contained in the soil depends mainly on the pH value. Fuller et al. [58] claimed that Zn and Cd showed high mobility at pH values in the range of 4.2–6.6 and medium mobility at pH values in the range of 6.7–7.8. Simultaneously, Cu and Pb showed medium mobility in the first range of pH values and low mobility in the second range. These observations were confirmed by Brümmer and Herms [55], whose study showed that when the pH value increased, the solubility of the metals decreased in the following order: Cd > Zn > Cu > Pb. In a study conducted with brown coal on alkaline soils, the stabilization of the soil pH, a reduction in the content of the phytoassimilable forms of metals, and a decrease in their percentage share in relation to the total contents of metals in the soil were found [7,13].

Table 4. Contents of metal forms after EDTA extraction in mg·kg^{-1} d.m. and *HQ* depending on the combination.

Soil	Cu	*HQ* *	Pb	*HQ* *	Zn	*HQ* *	Cd	*HQ* *	Cr	*HQ* *	Ni	*HQ* *
S1	334	$7.16\cdot10^{-6}$	2440	$3.07\cdot10^{-5}$	1435	$1.23\cdot10^{-6}$	4.45	$6.87\cdot10^{-5}$	1.815	$1.33\cdot10^{-6}$	7.91	$5.65\cdot10^{-7}$
S1bc1	291	$6.24\cdot10^{-6}$	1999	$2.52\cdot10^{-5}$	1380	$1.18\cdot10^{-6}$	3.84	$5.93\cdot10^{-5}$	1.325	$9.74\cdot10^{-7}$	6.85	$4.90\cdot10^{-7}$
S1bc2	287	$6.15\cdot10^{-6}$	1817	$2.29\cdot10^{-5}$	1302	$1.12\cdot10^{-6}$	3.45	$5.33\cdot10^{-5}$	1.31	$9.63\cdot10^{-7}$	6.75	$4.82\cdot10^{-7}$
S1ac1	278	$5.96\cdot10^{-6}$	1608	$2.03\cdot10^{-5}$	1140	$9.78\cdot10^{-7}$	3.31	$5.11\cdot10^{-5}$	1.282	$9.42\cdot10^{-7}$	6.25	$4.47\cdot10^{-7}$
S1ac2	278	$5.96\cdot10^{-6}$	1510	$1.90\cdot10^{-5}$	1028	$8.82\cdot10^{-7}$	3.11	$4.80\cdot10^{-5}$	1.175	$8.64\cdot10^{-7}$	5.95	$4.25\cdot10^{-7}$
S2	218	$4.67\cdot10^{-6}$	1160	$1.46\cdot10^{-5}$	770	$6.60\cdot10^{-7}$	2.35	$3.63\cdot10^{-5}$	0.88	$6.47\cdot10^{-7}$	4.32	$3.09\cdot10^{-7}$
S2bc1	161	$3.45\cdot10^{-6}$	925	$1.17\cdot10^{-5}$	630	$5.40\cdot10^{-7}$	1.97	$3.04\cdot10^{-5}$	0.695	$5.11\cdot10^{-7}$	3.61	$2.58\cdot10^{-7}$
S2bc2	152	$3.26\cdot10^{-6}$	845	$1.06\cdot10^{-5}$	555	$4.76\cdot10^{-7}$	1.82	$2.81\cdot10^{-5}$	0.675	$4.96\cdot10^{-7}$	3.36	$2.40\cdot10^{-7}$
S2ac1	128	$2.74\cdot10^{-6}$	798	$1.01\cdot10^{-5}$	511	$4.38\cdot10^{-7}$	1.68	$2.59\cdot10^{-5}$	0.58	$4.26\cdot10^{-7}$	3.06	$2.19\cdot10^{-7}$
S2ac2	128	$2.74\cdot10^{-6}$	706	$8.90\cdot10^{-6}$	501	$4.30\cdot10^{-7}$	1.59	$2.45\cdot10^{-5}$	0.575	$4.23\cdot10^{-7}$	2.95	$2.11\cdot10^{-7}$
S3	122	$2.62\cdot10^{-6}$	650	$8.19\cdot10^{-6}$	448	$3.84\cdot10^{-7}$	1.42	$2.19\cdot10^{-5}$	0.596	$4.38\cdot10^{-7}$	3.09	$2.21\cdot10^{-7}$
S3bc1	78.5	$1.68\cdot10^{-6}$	455	$5.73\cdot10^{-6}$	397	$3.40\cdot10^{-7}$	1.12	$1.73\cdot10^{-5}$	0.398	$2.93\cdot10^{-7}$	2.35	$1.68\cdot10^{-7}$
S3bc2	68.2	$1.46\cdot10^{-6}$	422	$5.32\cdot10^{-6}$	314	$2.69\cdot10^{-7}$	0.98	$1.51\cdot10^{-5}$	0.391	$2.87\cdot10^{-7}$	2.21	$1.58\cdot10^{-7}$
S3ac1	52.2	$1.12\cdot10^{-6}$	338	$4.26\cdot10^{-6}$	274	$2.35\cdot10^{-7}$	0.96	$1.48\cdot10^{-5}$	0.346	$2.54\cdot10^{-7}$	1.98	$1.41\cdot10^{-7}$
S3ac2	47.1	$1.01\cdot10^{-6}$	324	$4.08\cdot10^{-6}$	242	$2.08\cdot10^{-7}$	0.85	$1.31\cdot10^{-5}$	0.346	$2.54\cdot10^{-7}$	1.88	$1.34\cdot10^{-7}$
S4	99.6	$2.14\cdot10^{-6}$	564	$7.11\cdot10^{-6}$	342	$2.93\cdot10^{-7}$	1.25	$1.93\cdot10^{-5}$	0.429	$3.15\cdot10^{-7}$	2.43	$1.74\cdot10^{-7}$
S4bc1	70.5	$1.51\cdot10^{-6}$	399	$5.03\cdot10^{-6}$	265	$2.27\cdot10^{-7}$	0.99	$1.53\cdot10^{-5}$	0.391	$2.87\cdot10^{-7}$	2.11	$1.51\cdot10^{-7}$
S4bc2	65.3	$1.40\cdot10^{-6}$	370	$4.66\cdot10^{-6}$	257	$2.20\cdot10^{-7}$	0.97	$1.50\cdot10^{-5}$	0.344	$2.53\cdot10^{-7}$	1.94	$1.39\cdot10^{-7}$
S4ac1	44.9	$9.63\cdot10^{-7}$	281	$3.54\cdot10^{-6}$	225	$1.93\cdot10^{-7}$	0.85	$1.31\cdot10^{-5}$	0.325	$2.39\cdot10^{-7}$	1.81	$1.29\cdot10^{-7}$
S4ac2	38.2	$8.19\cdot10^{-7}$	284	$3.58\cdot10^{-6}$	184	$1.58\cdot10^{-7}$	0.78	$1.20\cdot10^{-5}$	0.265	$1.95\cdot10^{-7}$	1.83	$1.31\cdot10^{-7}$

* *HQ*—non-carcinogenic risk index.

For the SC soil, the post-EDTA extraction metal contents were determined as follows: Cu—3.11, Pb—5.63, Zn—< 0.05, Cd—<0.005, Cr—<0.03, and Ni—<0.05 mg·kg^{-1} d.m. The percent reductions in individual metal forms after using brown coal and activated carbon are shown in Table 5.

Table 5. Percent reductions in metals forms available to plants after adding brown coal and activated carbon.

Carbon Dose	Cu	Pb	Zn	Cd	Cr	Ni
bc1	35.7%	30.0%	22.5%	21.1%	33.2%	23.9%
ac1	57.2%	50.2%	38.8%	32.4%	41.9%	35.9%
bc2	44.1%	35.1%	29.9%	31.0%	34.4%	28.5%
ac2	61.6%	50.2%	46.2%	40.1%	41.9%	39.2%

The percent reductions in the *HQ* values for metals in soils after the use of brown coal and activated carbon compared to soils without carbons are presented in Figure 4.

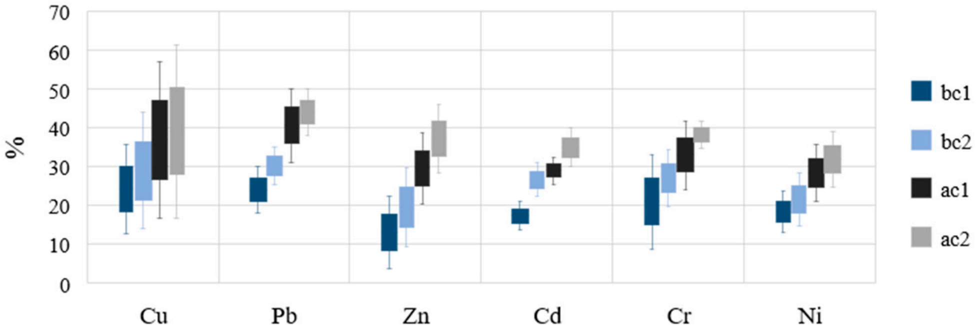


Figure 4. The boxplots of the percent reductions in the *HQ* values for individual metals in soils after the use of brown coal and activated carbon compared to soils without carbons.

The most effective reduction in the *HQ* value for Cu and Zn was observed after the addition of a double dose of activated carbon (ac2) to the least contaminated soil, i.e., S4.

For Pb, Cd, Cr, and Ni, a double dose of activated carbon (ac2) in the S3 soil was the most effective at reducing the *HQ* value. In each case, activated carbon had a higher efficiency in reducing non-carcinogenic effects. The least efficient addition at reducing the *HQ* value was a single dose of brown coal (bc1) in the most polluted soil, i.e., S1.

By analyzing the obtained values of the *ILCR* for individual metals and their sum (Table 6), it was found that none of the soil combinations or any of the elements tested exceeded a value of 1.00×10^{-4} for dermal contact.

Table 6. The values of the risk of carcinogenic effect index sum ($ILCR_T$) for the tested combinations of the carbons used in the experiment.

Soil	Cd	Cr	Ni
S1	4.19^{-9}	1.60^{-9}	2.56^{-9}
bc1/bc2	$3.62^{-9}/3.25^{-9}$	$1.17^{-9}/1.16^{-9}$	$2.22^{-9}/2.19^{-9}$
ac1/ac2	$3.12^{-9}/2.93^{-9}$	$1.13^{-9}/1.04^{-9}$	$2.03^{-9}/1.93^{-9}$
S2	2.21^{-9}	7.76^{-10}	1.40^{-9}
bc1/bc2	$1.85^{-9}/1.71^{-9}$	$6.13^{-10}/5.95^{-10}$	$1.17^{-09}/1.09^{-9}$
ac1/ac2	$1.58^{-9}/1.50^{-9}$	$5.12^{-10}/5.07^{-10}$	$9.92^{-10}/9.56^{-10}$
S3	1.34^{-9}	5.26^{-10}	1.00^{-9}
bc1/bc2	$1.05^{-9}/9.23^{-10}$	$3.51^{-10}/3.45^{-10}$	$7.62^{-10}/7.16^{-10}$
ac1/ac2	$9.04^{-10}/8.00^{-10}$	$3.05^{-10}/3.05^{-10}$	$6.42^{-10}/6.09^{-10}$
S4	1.18^{-9}	3.78^{-10}	7.88^{-10}
bc1/bc2	$9.32^{-10}/9.13^{-10}$	$3.45^{-10}/3.03^{-10}$	$6.84^{-10}/6.29^{-10}$
ac1/ac2	$8.00^{-10}/7.34^{-10}$	$2.87^{-10}/2.34^{-10}$	$5.87^{-10}/5.93^{-10}$

S1, S2, S3, and S4—soil samples with varying degrees of metal contamination; bc1—single dose of brown coal; bc2—double dose of brown coal; ac1—single dose of activated carbon; and ac2—double dose of activated carbon.

The addition of both carbons resulted in a significant reduction in metal forms that are potentially available to plants. When comparing the effect of carbons on the metal contents in different soil combinations, a stronger effect of activated carbon was observed on the reduction in metal contents compared to brown coal.

3.4. Metal Contents in *Medicago falcata* L. and Phytotoxicity

This study determined the tolerance of *Medicago falcata* L. to the contents of metals in particular soil combinations with the addition of carbons. The contents of the metals (Pb, Cd, Cr, Zn, Cu, and Ni) were determined in the roots and shoots of the tested plant (Figure 5).

The control soil (SC) was characterized by a low metal content in both the roots (Cu—2.80, Pb—1.91, Zn—3.83, Cd— < 0.005, Cr—1.29, and Ni—1.34 mg·kg^{-1} d.m.) and shoots (Cu—2.62, Pb—1.75, Zn—8.89, Cd—0.224, Cr—0.93, and Ni—2.19 mg·kg^{-1} d.m.) of *Medicago falcata* L. The order of metal uptake by the plant roots is as follows: Zn > Cu > Pb > Ni > Cr > Cd. For plant shoots, the order is as follows: Zn > Cu > Ni > Pb > Cr > Cd.

The different sensitivities of plants to individual metals enable the selection of plants capable of growing in high concentrations of metals that may have toxic effects [59]. The contents of the metals in the roots and shoots were lower than in the combinations of soils with no added carbon. Their contents in the roots and shoots were as follows: Zn > Pb > Cu > Cr > Ni > Cd. In both the roots and the shoots, the addition of brown coal and activated carbon at both doses reduced the uptake of the metals by plant organs. The activated carbon had a stronger effect on limiting the availability of metals to plants than brown coal. The shoots of *Medicago falcata* L. took up greater amounts of all metals than the roots. The exception was the uptake of Pb by *Medicago falcata* L. grown in the least polluted soil (S4) with the addition of brown coal and activated carbon at both doses. In this case, the shoots of *Medicago falcata* L. took up less Pb than the roots.

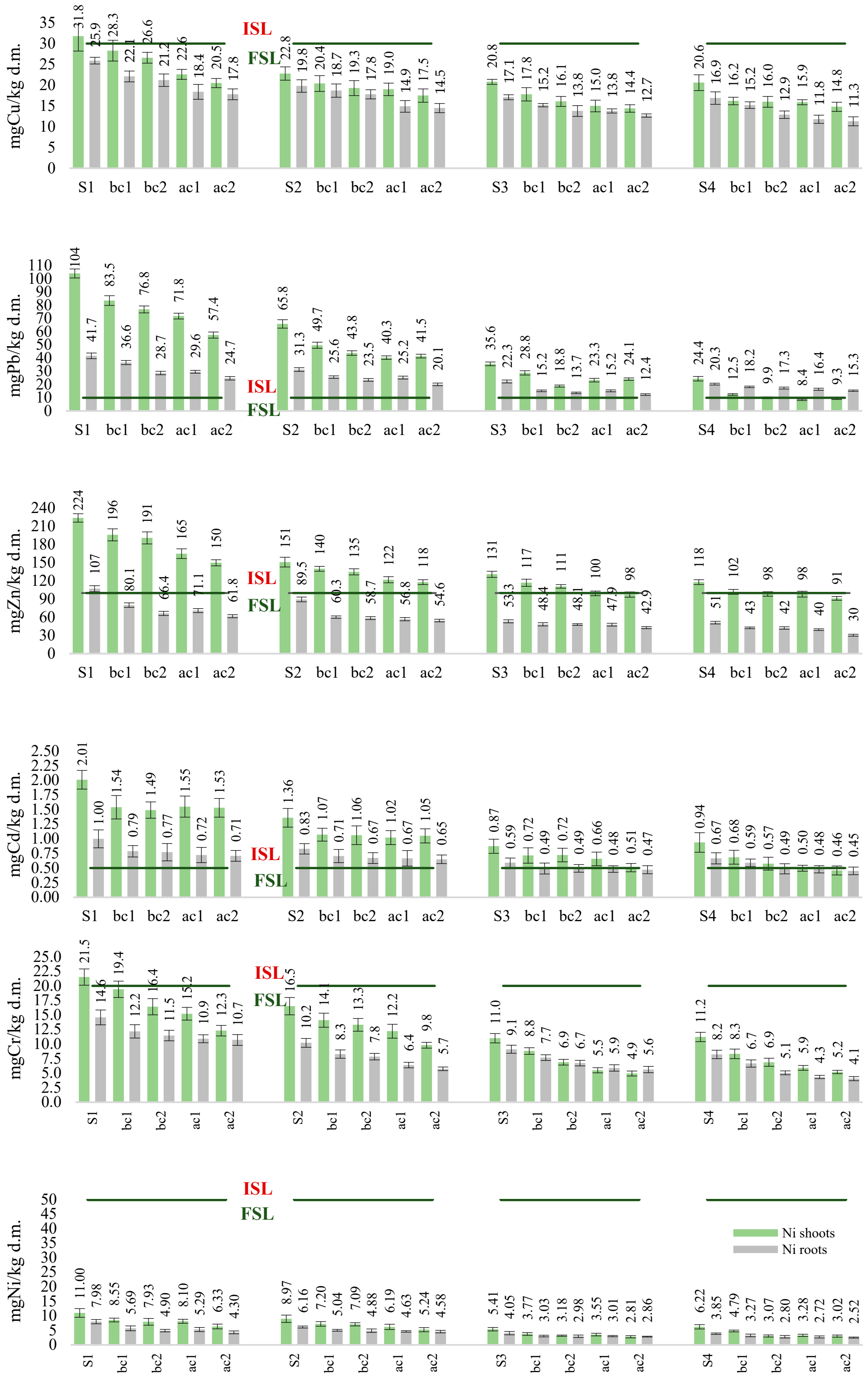


Figure 5. Metal concentrations in shoot and root dry mass of *Medicago falcata* L. depending on the combination with the forage suitability level—FSL and industrial suitability level—ISL. S1, S2, S3, and S4—soil samples with varying degrees of metal contamination; bc1—single dose of brown coal; bc2—double dose of brown coal; ac1—single dose of activated carbon; and ac2—double dose of activated carbon.

The contents of metals (Cu, Pb, Zn, Cd, Cr, and Ni) in the shoots of *Medicago falcata* L. were compared to the criteria for assessing plants in terms of their forage and industrial suitability [60] (Figure 5). The critical contents of metals were adapted for the assessment of the plants for the forage suitability level—FSL and the industrial suitability level—ISL. Only for the combination of the least polluted soil (S4) with both doses of activated carbon, the forage usefulness of *Medicago falcata* L. was found for all tested metals. It was observed, in the case of Cu and Cr, that the values of forage suitability were not exceeded, except for plants grown in the S1 soil without added carbon. For Pb, industrial suitability was found in each soil combination, except plants grown in the S4 soil with both doses of activated carbon and a double dose of brown coal. For Zn, forage suitability was found only in the case of the S4 soil with both doses of activated carbon and a double dose of brown coal and for both doses of activated carbon in the S3 soil. For the remaining combinations, industrial suitability was found. When assessing the Cd values, forage suitability was found only in the case of a combination with both doses of activated carbon for the S4 soil. For the remaining combinations, industrial suitability was found. For all the combinations, Ni did not exceed the levels for forage suitability for the tested plant.

The use of both doses of carbons limited the influence of metals in the soil on the roots and shoots of *Medicago falcata* L., minimizing their phytotoxic effects. The phytotoxicity of SC and S1–S4 soils are presented in Figure 6.

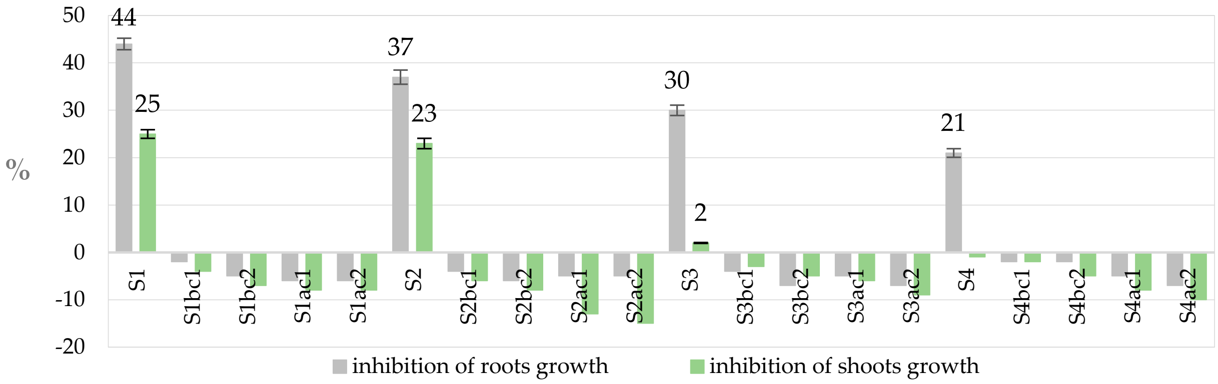


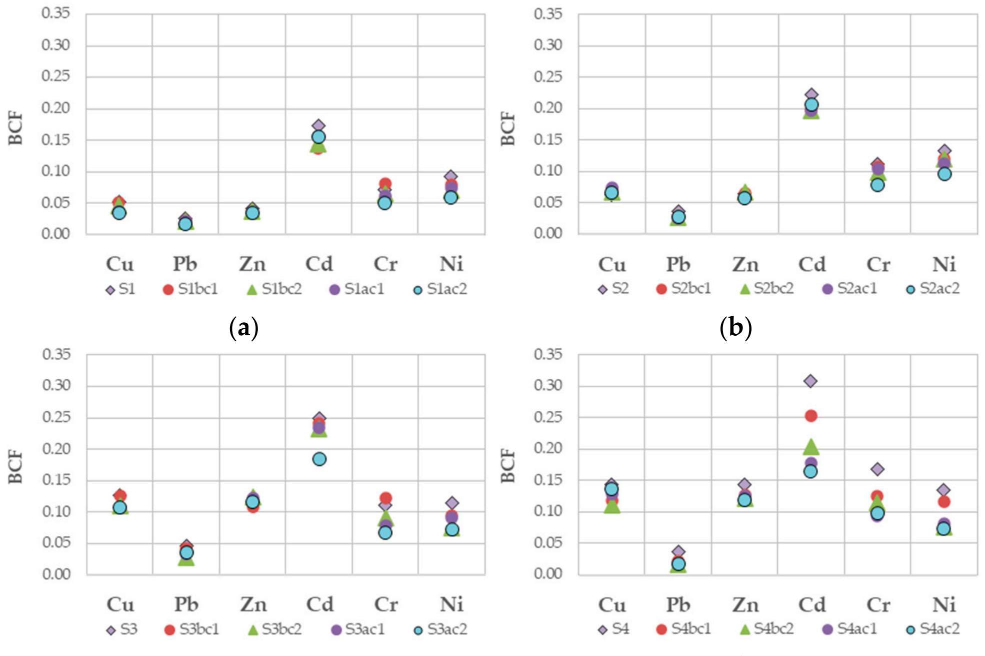
Figure 6. The germination inhibition and growth of *Medicago falcata* L. in different soils, depending on the combination.

Medicago falcata L. was characterized by a 100% germination rate. In S1, S2, S3, and S4 soils, without the addition of carbon, an inhibition of the growth of the roots and shoots of *Medicago falcata* L. was found. Only in the S4 soil without the addition of carbon, no inhibition of the growth of *Medicago falcata* L. shoots was found. In the combinations of soils with brown coal and activated carbon, there was no inhibition of seed germination and no inhibition of the growth of the roots and shoots of the tested plant.

3.5. Bioconcentration Factors (BCFs)

The BCFs were determined to evaluate the effectiveness of the applied carbons to stabilize the metals in the contaminated soils to different extents (Figure 7).

The concentration of metals in plants can vary depending on their ability to translocate from the soil to the roots or shoots [61,62]. The BCFs for the shoots of *Medicago falcata* L. grown in the SC soil were Cu—0.15, Pb—0.08, Zn—0.15, Cd—0.31, Cr—0.09, and Ni—0.14. Based on the concentration of metals collected in the shoots in relation to their contents in the soil, Ma et al. [63] divided plants into excluders (BCF < 1), accumulators (BCF 1–10), and hyperaccumulators (BCF > 10). Based on these criteria, *Medicago falcata* L. grown in the control soil (SC) and S1–S4 soil combinations qualified as an exclusion plant. According to Alloway [56], plants easily take up Cd from the soil, proportionally to its content in the environment. This relationship was confirmed in this study with regard to the metal contents in the *Medicago falcata* L. The results for the tested plant showed that the BCFs determined for the S1–S4 soil combinations obtained higher values for Cd than for the other metals. The amount of Pb taken up by plants depends on its concentration in the soil, and it increases with the increasing metal content in the soil [56]. For *Medicago falcata* L., the BCF for Pb was lower than that for other metals. The values of the BCF were influenced, among others, by the mobility of the tested metals. For Pb, which is characterized by low mobility, the BCF values were lower than for Zn and Cd, which are characterized by higher mobility compared to the other tested metals and are easily taken up by plants [8,50].



(**a**) (**b**)

(**c**) (**d**)

Figure 7. Bioconcentration factors (BCFs) of individual metals in shoots of *Medicago falcata* L. grown in different soils: (**a**) S1, (**b**) S2, (**c**) S3, and (**d**) S4.

When using the method of stabilizing metals in the soil, it is important that the mobility and bioavailability of the metals are limited. The results showed that the use of carbons reduced the BCFs in relation to the soils without added carbon in S1, S2, S3, and S4, immobilizing (stabilizing) the metals in the soil and limiting their uptake by the plants. The experiment showed lower values of BCFs in soils with both doses of activated carbon than with brown coal, which indicates its greater efficiency in immobilizing pollutants.

4. Discussion

Carbons introduced into the soil increases the content of slowly mineralizing organic compounds. To assess the efficacy of the immobilization of metal forms in the soil, two carbons were used, namely, brown coal and activated carbon. Brown coal, alone and modified in various ways, provides a material with a high degree of humification and is relatively resistant to mineralization [64]. Activated carbon designed to adsorb micropollutants has a larger number of micropores [65]. Carbons should be introduced directly into the soil once, e.g., during aeration treatments. In order to obtain the required stabilization effects, carbon should be added to the soil to a depth of approx. 0.25–0.30 m, given that metals accumulate in the surface layer, while taking into account the depth of the plant's root system.

The results indicate that the soils had a high concentration of Pb, Cd, Cr, Zn, Cu, and Ni in different combinations. These results also confirm that brown coal and activated carbon have no significant effect on the total metal concentrations in the soil, which is consistent with the results obtained by other authors [13,15,17,18,20,48,51]. The addition of brown coal resulted in a decrease in the pH value compared to soils without carbon. Therefore, when choosing brown coal as a soil additive, its reaction is important. This relationship was confirmed in their research by Cuske and Karczewska [51] and Cuske et al. [48]. The use of acidic carbon resulted in the acidification of the soil and thus, the desorption of metals into the soil solution, and increased toxicity towards microorganisms [51]. The use of slightly acidic carbon in the soil resulted in the accumulation of zinc in the tested plants, especially in their roots [66]. Studies with brown coal on alkaline soils showed a stabilization of soil pH, a reduction in the content of phytoavailable forms of metals, and a reduction in their percentage in relation to the total metal content in the soil [7,13,49,50].

In the soil environment, metals occur in various forms, which affects their phytotoxicity and phytoassimilability. On soils enriched with organic matter (e.g., peat, composts, and brown coal), the share of metal forms available to plants decreases, and thus, their toxicity to plants decreases. The durability of complex organic matter–metal connections increases with the increase in the degree of its decomposition, as well as with the increase in the pH value of the soil.

The use of brown coal is justified in soils contaminated with metals that have a neutral or alkaline reaction, while in other cases, the carbon should contain alkaline additives. In an experiment related to the immobilization of metals in the soil, Karczewska et al. [67] used, among others, brown coal mixed with lime. The contaminated soil was slightly acidic (the pH measured in 1 M KCl was 6.2), while the pH measured for brown coal was 4.8–4.9. In these studies, the immobilization process of pollutants was more effective in soil samples with the addition of carbon and lime than in the case of using carbon alone, and higher efficiency was achieved for Pb than for Cu. The authors [67] indicated that the immobilization of pollutants took place through adsorption, precipitation, as well as complexation reactions, which lead to the transfer of pollutants from the soil solution to the solid phase, limiting their bioavailability and movement in the environment [11,68]. Also, Ciecko et al. [69] used, among others, a mixture of brown coal and lime as an addition to Cd-contaminated soil. This soil was characterized by a very acidic reaction (the pH measured in 1 M KCl was 4.2). The authors [69] observed a decrease in the Cd content in triticale, and liming reduced the decline in rapeseed yields caused by Cd stress.

Darvishi et al. [70] conducted research on the use of activated carbon as an additive to alkaline soil (pH 7.65). The experiment concluded that the process of adsorption of pollutants on activated carbon significantly reduced the availability of metals in the soil to plants. Therefore, the accumulation of Pb and Cd in spinach roots and shoots was much lower than in soils without added carbon. Bezak-Mazur [71] used regenerated activated carbon during analyses. The sorbent used increased the sorption capacity of the soil; therefore, the specific adsorption of metals (Cr, Pb, and Ni) increased, and their migration in the soil was limited.

The advantage of brown coal as a substrate and fertilizer is its slow decomposition and transformation of organic matter, which contributes to the permanent enrichment of the soil with humic substances. With a larger amount of humus in the soil, very stable, sparingly soluble complexes of humic and fulvic acids with metals are formed [72]. Humic acids form much stronger complexes with metal cations than fulvic acids. Inert soil increases the durability of complex humic compounds (contained in organic matter) with metals, reducing their availability to plants [73,74], which is directly related to the mobility of metals in soil [56]. Boguta and Sokołowska [75] emphasized that for the same type of functional groups, the dissociation constant may have different values depending on the origin of the organic matter. The high sorption capacity of humic acids (HAs), in addition to their buffering capacity, also affects the bioavailability and immobilization of metals in the soil [52]. Acids interact with metal ions through ion exchange, surface adsorption, chelation, and coagulation, and with clay minerals, they form complexes that are characterized by various properties and degrees of stability [75]. Wu et al. [76] indicated that the presence of humic acids may effectively reduce the concentration of available Cu and Pb. Metals like Pb and Cu form stronger and more stable coordination bonds with humic acids than Cd. Metals are complexed with carboxyl (–COOH) and hydroxyl (–OH) functional groups [52], amine (–NH_2), and amide [77]. Spark et al. [78] emphasized that the carboxyl group is the main functional group involved in the binding of metal cations.

To determine the solubility of metals or phytotoxicity of soils, single extracts are generally used. Soil tests, usually based on single extracts, can be used to determine soluble metal forms in various extraction solutions, which determine the potential availability of metals to plants [32]. For single extractions, an EDTA solution was used, as a common reagent for assessing the potential solubility and bioavailability of metals [79,80]. The EDTA solution extracted the largest number of Pb forms, followed by Zn and Cu, in all soil combinations. Both doses of carbons reduced the forms that are potentially available to plants. In the soils with activated carbon, with single and double doses, the concentrations of the available forms of metals were lower than in the soils with brown coal. Similar results for brown coal and activated carbon were obtained by other authors [49,50,81]. The tested coals reduced the availability of metals in relation to their high and low contents. They can be used for alkaline soils. The studies confirmed that EDTA is an effective reagent for determining phytoavailable metals and is a useful tool for providing information about their potential mobility [82].

Dermal absorption of metals is the main exposure pathway for As, Cd, Cr, Cu, Ni, and Hg, while ingestion is a more common exposure pathway for Pb and Zn [45]. Based on the obtained results, it was found that the use of brown coal and activated carbon at both doses not only allowed one to reduce the bioavailability of metals but also allowed one to reduce the *HQ* and the *ILCR* indices for potential non-carcinogenic and carcinogenic risks, respectively. These results are consistent with the findings of Zhang et al. [83] and Li et al. [45], who analyzed environmental pollution and related health effects due to Pb/Zn mining and smelting activities. Metals entering the human body can cause kidney damage, cancer, and other diseases [45,84]. Pollution and risk indices (*PI*, *PLI*, *HQ*, and *ILCR*) were used for the evaluation of contamination levels [85]. The calculated soil pollution indices *PI* and *PLI* showed that all soil combinations are polluted to varying degrees (from moderate to extreme pollution) depending on the metal. The calculated indices for non-carcinogenic and carcinogenic risks showed no risk for all soil combinations for each of the metals.

One of the tests used to evaluate the toxic effects on plants is the Phytotoxkit^{TM} test, which is part of the toxicity test [86]. Phytotoxicity tests do not reflect the specific levels of environmental contamination by individual toxic substances and do not indicate which substance causes toxicity to the test plant [87,88]. However, they can be used to signal the problem of ecotoxicological risks in an investigated area or investigated facility and may also indicate the need for detailed research [7–9,14,32,49,50]. Małachowska-Jutsz et al. [32] believe that the performance of phytotoxicity tests during remediation works allows for a quick and reliable assessment of the degree of soil toxicity and also provides an opportunity to assess the progress of such works. In the combinations of soils with brown coal and activated carbon, there was no inhibition of seed germination and no inhibition of the growth of the roots and shoots of the tested plant. The use of carbons at both doses limited the influence of metals in the soil on the roots and shoots of *Medicago falcata* L., minimizing their phytotoxic effects. This was observed in the example of the most polluted soil (S1) without the addition of carbons, for which growth inhibition was found at a level of 44% for the roots and 25% for the shoots of *Medicago falcata* L. The addition of brown coal and activated carbon reduced the phytotoxicity of the soils.

In this study, the contents of metals in *Medicago falcata* L. depended on their concentrations in the soil, which was confirmed by several authors [89–91]. Ghelich et al. [92] found a linear relationship between the Pb concentration in the soil and its concentration in *Medicago falcata* L. roots during the growing season. In the shoots of *Medicago falcata* L., higher contents of all metals were found than in its roots; similar results were obtained by Peralta et al. [89]. The exception was *Medicago falcata* L. grown in the least polluted soil (S4) with both doses of brown coal and activated carbon for Pb. In this case, the shoots of *Medicago falcata* L. accumulated less Pb than the roots; similar results for Pb were obtained by Ghelich et al. [92]. The addition of brown coal and activated carbon reduced the uptake of metals by *Medicago falcata* L., as well as the reduction in the BCF for the roots and shoots in relation to soils without carbons. The uptake of metals in the roots and shoots of *Medicago falcata* L. grown in soils with brown coal and activated carbon occurred sequentially, as follows: Zn > Pb > Cu > Cr > Ni > Cd. The exception was in the roots of the plants grown in the S4 soil with the addition of carbons at both doses, where the dependence of metal uptake by *Medicago falcata* L. was as follows: Zn > Cu > Pb > Cr > Ni > Cd. Rezaeian et al. [91] observed a similar distribution of metals in *Medicago falcata* L.: Zn > Cu > Pb > Cr > As > Cd. Peralta et al. [89] and Rezaeian et al. [91] observed that *Medicago falcata* L. took up the highest amounts of Zn. The contents of Zn in the parts of the plants grown in the most polluted soils with brown coal and activated carbon in relation to soils without carbon addition were reduced by the following: for roots: 25% (bc1), 38% (bc2), 33% (ac1), and 42% (ac2) and for shoots: 13% (bc1), 15% (bc2), 26% (ac1), and 33% (ac2). The addition of carbons to the soil reduced phytotoxicity and the risk of including metals in the trophic chain. This was confirmed by the results obtained for the least polluted soil (S4) with both doses of activated carbon, where the suitability of *Medicago falcata* L. was classified as forage according to Kabata-Pendias et al. [60] and the regulations on the contents of substances causing risk in forage suitability [93].

In the study by Semenyuk et al. [94], activated carbon was used in the form of granules on forest soils contaminated with diesel oil. The use of carbon made the contaminated soil less bio- and phytotoxic for both plants (*Medicago falcata* L.) and microorganisms. Therefore, the yield of *Medicago falcata* L. was higher in soils with added carbon than in soils without added carbon, and the bioremediation process was faster and more effective in soils with added carbon. According to Cuske and Karczewska [51], the use of brown coal is justified for soils contaminated with metals that have a neutral or alkaline reaction, while in other cases, the carbon should contain alkaline additives. The use of brown coal and activated carbon reduced the concentration of metal forms that are potentially available to plants and reduced the non-carcinogenic and carcinogenic effects. The results of this study indicate that the tested carbons can be used to limit the phytotoxicity of soils, particularly in degraded industrial areas contaminated with metals.

5. Conclusions

1. Added carbons lowered potential carcinogenic and non-carcinogenic risk effects in comparison to soils without carbons.
2. The activated carbon had a stronger effect on limiting the availability of metals than brown coal in relation to plants grown in soils without added carbon; the percentage of reduction for shoots was Cr (18.2%) > Zn (11.5%) > Ni (10.7%) > Cu (10.3%) > Cd (8.9%) > Pb (2.4%) and Cu (13.3%) > Cr (12.5%) > Zn (10.5%) > Pb (9.0%) > Ni (5.7%) > Cd (4.6%) for roots. For the combinations of the least polluted soils with both doses of activated carbon, the forage suitability of *Medicago falcata* L. was found.
3. Higher contents of all tested metals (Cu, Pb, Zn, Cd, Cr, and Ni) were found in the shoots compared to the roots of *Medicago falcata* L. Only for Pb, a higher content was found in the roots than in the shoots of the plant in the least polluted soil with the addition of carbons.
4. The use of carbons at both doses limited the influence of the metals in the soil on the roots and shoots of *Medicago falcata* L., minimizing phytotoxic effects, and at the same time, it allowed for a better-quality yield than in the case of soils without the addition of carbons. The metals reduced the growth of *Medicago falcata* L. roots from 44 to 21%, while the growth of shoots was reduced from 25 to 2%.
5. The lower values of the BCFs in soils with activated carbon at both doses compared to those with brown coal indicate greater efficiency in immobilizing metals. The highest values for the BCFs were for Cd, which was accumulated in greater amounts in comparison to the other tested metals.
6. The use of brown coal is justified in soils contaminated with metals that have a neutral or alkaline reaction, while in other cases, the carbon should contain alkaline additives.

The use of activated carbon requires additional research on its use on acidic soils, taking into account both environmental and economic issues.

Author Contributions: Conceptualization, A.P. and M.W.; methodology, A.P. and M.W.; validation, A.P., M.W., A.K., P.K. and D.R.; formal analysis, A.P. and D.R.; investigation, A.P.; resources, A.P.; writing—original draft preparation, A.P. and M.W.; writing—review and editing, A.P., M.W., A.K., P.K. and D.R.; visualization, A.P.; supervision, A.P.; funding acquisition, A.P. and M.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the following projects: "An attempt to determine the effectiveness of methods of remediation/detoxification of soils contaminated with metals for the reclamation of degraded industrial and post-mining areas" (504M/1110/0001) and "Assessment of effectiveness of stabilization methods soils contaminated with metals" (504/02097), financed by the Warsaw University of Technology.

Data Availability Statement: All data are available in the manuscript.

Acknowledgments: The authors would like to thank the director of the Polish Academy of Sciences Botanical Garden—Centre for Biological Diversity Conservation in Powsin, Arkadiusz Nowak, who agreed to provide the seeds of *Medicago falcata* L., and Konrad Woliński, who was responsible for the formal identification of the plant material used in this study.

Conflicts of Interest: Author Arkadiusz Kamiński was employed by the company Environmental Protection Department, ORLEN S.A., Chemików 7, 09-411 Plock, Poland. Author Peter Knosala was employed by the company BHU Umwelttechnik GmbH: Environmental Technology-Water and Sludge, Einsteinstrasse 57, D71229 Leonberg, Denmark. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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