Article

Application of Brown Coal and Activated Carbon for the Immobilization of Metal Forms in Soil, along with Their Verification Using Generalized Linear Models (GLMs)

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Abstract: Various factors can lead to the transformation of metal forms and to an increase in their solubility and, consequently, their mobility. One solution to the problem of increased solubility is the use of carbons as additives to soil in order to limit the potential migration of contaminants. The aim of this study was to determine the effect of using brown coal and activated carbon on metal forms that are available to plants. The mineral composition of the coals used in a pot experiment was analyzed. Observations were carried out with a JJSM-6380 LA scanning electron microscope (SEM) connected to an EDS electron micro-probe. The total contents of Zn, Cd, Pb and Cu in the assessed soils as well as the content of available metal forms were determined after single extractions with different reagents, namely 1 M NH$_4$NO$_3$, DTPA and 1 M HCl. Generalized linear models (GLMs) were used to evaluate the effectiveness of the stabilization methods in a long-term pot experiment. The carbons reduced the percentage of these forms relative to the total metal content in the soil. After adding brown coal, Zn, Cd, Pb and Cu forms were reduced by up to 32%, 30%, 33% and 43%, respectively. After adding activated carbon, the metal forms of Zn, Cd, Pb and Cu were reduced by up to 47%, 44%, 40% and 50%, respectively. The following order of extracted metal forms with different solutions was found: HCl: Zn > Pb > Cu > Cd; DTPA: Pb > Zn > Cu > Cd; NH$_4$NO$_3$: Zn > Cu > Pb > Cd. Eight years after setting up the pot experiment, the contents of humic substances in soils with the addition of both tested carbons were compared, and the soils with added carbons were found to have a stable content of humic fractions. The costs of remediation through the stabilization method using the tested brown coal and activated carbons do not exceed USD 75/t (taking into account the double doses of both carbons).

Keywords: metals; soil pollution; brown coal; activated carbon; in situ immobilization; generalized linear models (GLMs)

1. Introduction

Soil fulfills many different functions, such as filtering, buffering and protecting ecosystems from an excessive flow of metals to other biosphere elements. Metals can cause harmful conditions to all living organisms in the soil, including microflora and microfauna, as well as to organisms directly or indirectly related to soil, such as plants, animals and humans [1–9]. Major hazards can arise from a variety of sources, for example, industrially degraded sites that are contaminated by metals, which are often left without any remedial action. Various factors can lead to the transformation of metal forms and to an increase in their solubility and, consequently, their mobility, thus increasing their bio- and phytotoxicity and resulting in their migration to groundwater [1,3,10–13]. Particular hazards are represented by forms of metals that determine eco- and phytotoxicity and, if remaining in soil solutions, are absorbed by the plant root system and transported to the trophic chain [1,11,12,14]. Effective improvements in the environmental situation and the
reduction of risks in metal-contaminated areas can often be achieved through the use of relatively simple, fast and environmentally friendly methods [11,15]. One of these methods is the immobilization of metals in soils (stabilization). In considering this approach, one must remember that the toxicity of metals present in soil is not determined by their total content but by the forms in which these metals occur [11,16–18]. Brown coal or organic-mineral fertilizers produced on its basis can serve as a substance that binds metals into forms that are difficult for plants to access. Studies on the usefulness of brown coal and organic-mineral fertilizers from brown coal have shown that these substances significantly limit the phytotoxicity of soils contaminated by metals [16–18]. Moreover, depending on the composition, mineral fertilizers can be a source of metals [19]. One new approach may involve the use of activated carbon, produced from hard coal or wood, which has a notably higher sorption capacity than brown coal [20,21]. A comparison of soils with the addition of brown and active coal revealed that the sorption capacity increased by 26% after the use of brown coal and by 36% with activated carbon relative to soil without the addition of carbon. The difference in sorption capacity between soils after applying each of the coals was 10% [16–18].

The porous structure of carbon is due to layers that are formed by carbon atoms composed of aromatic rings connected crosswise in a random manner. In order to improve the sorption properties of the obtained products from the carbonization process and to remove decomposition products from the pores, it is subjected to additional activation. This process is carried out at a temperature of 700–1100 °C in an atmosphere of air, CO2 or water vapor [22,23]. Depending on the process conditions, micro- (<2 nm diameter), meso- (2–50 nm diameter) and macroporous (>50 nm diameter) materials can be obtained [24,25]. The process of adsorption on activated carbon occurs mainly in micropores. Mesopores are of less importance in this process, while macropores are used as flow channels through which the adsorbate travels to the interior of mesopores and to the surface of micropores. Activated carbon is characterized by a large specific surface area, reaching values as high as 2500 m²/g, and the most commonly used activated carbons have a specific surface area of 800–1500 m²/g [22,23].

The use of brown coal and activated carbon to immobilize metals in the soil is an in situ technique that does not cause any additional environmental damage [18]. The metal immobilization process is performed in a non-degrading way and has a beneficial effect on soil properties [16–18]. Another important advantage is the economic viability of this process and its immediate effect, which plays a significant role in degraded industrial areas [15,16,20].

This article presents a new approach to using brown coal and activated carbon and their application for remediation techniques. The benefits of this method include the reduced content of metal forms that are actually and potentially available to plants, thereby limiting phytotoxicity.

2. Materials and Methods

2.1. Characteristics of Soils

Two soils, designated S1 and S2, were used for the pot experiment. Soil S1 was taken from an industrial waste landfill. This soil was used to clean metallurgical carts/wagons and was therefore contaminated with metals. Soil S1 was characterized by a brown color; specific smell; alkaline pH; high carbonate, organic carbon and total nitrogen content; and a sorption complex with a high degree of saturation with exchangeable alkaline cations.

Soil S2 was taken from a heap that was formed during the construction of a steel plant. The examined soil sample was characterized by a yellow color, earthy smell and a low content of the skeletal fraction (approx. 5.0%), which consisted of fine pebbles and limestone, i.e., pieces of native rock. The chemical properties of soils S1 and S2 before setting up the pot experiment are presented in Table 1.
Table 1. Chemical properties of S1 and S2 soils before setting up the pot experiment.

| Soil | CaCO₃ [%] | TOC ± [g/kg] | TN ± [g/kg] | pH KCl | H ± [cmol(+)/kg] | Ca ± [cmol(+)/kg] | Mg ± [cmol(+)/kg] | K ± [cmol(+)/kg] | Na ± [cmol(+)/kg] | CEC ± [cmol(+)/kg] |
|------|-----------|--------------|-------------|--------|-----------------|-----------------|-----------------|-----------------|-----------------|------------------|
| S1   | 4.23 ± 0.12 | 5.28 ± 0.10  | 1.22 ± 0.09 | 8.0    | n.d.            | 25.2 ± 2.3      | 6.64 ± 0.91     | 0.15 ± 0.01     | 1.02 ± 0.03     | 33.01 ± 2.3      |
| S2   | 0.85 ± 0.05  | 0.90 ± 0.05  | 0.21 ± 0.07 | 7.6    | n.d.            | 12.2 ± 1.1      | 0.65 ± 0.43     | 0.12 ± 0.01     | 0.04 ± 0.02     | 13.01 ± 1.1      |

TOC—total organic carbon; TN—total nitrogen; H—hydrolytic acidity; n.d.—not detected.

The soils used in this research had different granulometric compositions: loamy sand (S1) and light clay (S2). The fractions of these soils were 88% (S1) and 59% (S2) sand, 7% (S1) and 21% (S2) dust and 5% (S1) and 20% (S2) loam. The contamination concentrations in soils S1 and S2 are presented in Table 2.

Table 2. Total metal concentration in soils G1 and G2 before pot experiment settlement.

| Soil | Zn ± [mg/kg] | Cd ± [mg/kg] | Pb ± [mg/kg] | Cu ± [mg/kg] |
|------|--------------|--------------|--------------|--------------|
| S1   | 11032 ± 348  | 35.5 ± 2.5   | 9885 ± 316   | 1748 ± 71    |
| S2   | 66.1 ± 4.3   | 0.40 ± 0.05  | 15.9 ± 1.3   | 14.2 ± 1.1   |

The Soil S2 had low metals content. The high levels of metals in the S1 soil resulted from the characteristics and from the soils origin. The metals Zn, Cd, Pb and Cu were selected for their high content in soil, at the same time the S1 soil has been used as a carrier of pollutants.

2.2. Characteristics of Carbons

To assess the efficacy of the immobilization of metal forms in the soil, two substrates were used: one with the addition of brown coal and one with the addition of activated carbon. The use of activated carbon as an element of the second substrate in the pot experiment is considered a new approach to the problem of immobilizing metals in the soil. The brown coal originated from the KWB Konin brown coal mine and was among the soft lignite varieties, the so-called ground coals. The activated carbon was from a factory in Hajnówka. The pH values measured in potassium chloride solution (1 M KCl) and demineralized water (H₂O) were 5.4 and 5.9 for brown coal and 9.5 and 9.8 for activated carbon, respectively. The dry material content in air-dried samples was 65.69% for brown coal and 94.04% for activated carbon. Microscopic observations of the carbons (brown coal and activated carbon) were carried out using a JJS-6380 LA scanning electron microscope (SEM) connected to an EDS electron micro-probe made by JEOL Ltd. Musashino, Tokyo. The research was carried out at the Faculty of Geology, University of Warsaw, in the Laboratory of Electron Microscopy and Microanalysis.

2.3. Characteristic of Pot Experiment

The pot experiment was set up in 2011 in vegetation hall of Plant Physiology Department, Warsaw University of Life Sciences—SGGW in Warsaw and its been ongoing until now Figure 1.

In the pot experiment were used Wagner-type pots, each filled with 10 kg of soil. In order to obtain soils of varying degree of metal contamination, soils S1 and S2 were mixed in the following ratios 1:1; 1:3 and 1:7. Three combinations of S1 and S2 did not contain any carbons (marked as “0”). Carbons in two different doses were used in the remaining combinations: a single dose 200 g—bc1 (brown coal) or ac1 (activated carbon) and a double dose 400 g—bc2 (brown coal) or ac2 (activated carbon). In total, 15 soil combinations were obtained in triplicate in completely random system. The pot experiment was conducted under controlled conditions of soil moisture (60% of field capacity) and temperature 20 °C.
2.4. Methods

The following physical and chemical properties were determined in soils S1 and S2: granulometric composition with the Casagrande method in Prószyński’s modification, according to Polish Society of Soil Science, pH in 1 M KCl [26], organic carbon content (TOC) [27], total nitrogen (TN) [28], carbonate content (CaCO$_3$) [29], hydrolytic acidity (H) and exchangeable alkaline cations (Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$) [30].

The total metal content of the soil was established after mineralization of the samples in a 3:1 mixture of concentrated perchloric acid (HClO$_4$) and nitric acid (HNO$_3$) [31,32]. The content of metals (Zn, Cd, Pb, Cu) in the ammonium nitrate (1 M NH$_4$NO$_3$) extract, according to DIN ISO 19730 [33], was determined to assess metal solubility in the soil solution. The content of plant accessible metal forms was determined using the diethylene-triaminepentaacetic acid (0.2 M DTPA) extraction according to PN-ISO 14870: 2007P [34]. Hydrochloric acid (1 M HCl) was used for single extractions for the assessment of phytoavailable metal forms in soils (according to the procedure accepted in Agricultural and Chemical Stations in Poland) [30,35].

The metal content in the studied samples was determined by using atomic spectrometry, with the technique of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), using Thermo Scientific—iCAP 6500 or Varian Axial Vista 720-ES spectrometer (made by JEOL Ltd. Musashino, Tokyo). For each series of measurements, blank samples were prepared in parallel, and their values were included when calculating the results for the samples. Dry mass was also included in the calculations [36]. The accuracy of the methodology was verified using the method of standard additions.

Contents of fulvic acids (FA), humic acids (HA) and humins (HUM) were determined in soil samples from years 2011 and 2019 according to the method of quantitative determination of contents of the humic substances in soil recommended by IHSS.

2.5. Statistical Analysis

The analysis of variance [37–39] was used for statistical analysis of particular soil variables as well as for assessing the influence of brown coal and activated carbon on the content of actually and potentially available metal forms. If the variables did not meet the criteria their transformations were used instead, mostly logarithmic functions or inverse
values. The Least Significant Difference (LSD) for the T-student test was used as the basis for comparisons [40–42]. If the null hypothesis was rejected, HSD Tukey’s test was used for multiple comparisons among the commonly used post hoc tests [43–46] as a test supporting the inference process.

Generalized linear models (GLMs) have been increasingly used in environmental science and ecology studies. Lane in 2002 [47] presented the basic properties of different kind of the GLM models along with their advantages and disadvantages. Lane [47] discussed the model adjustment process based on the effect which fertilizer dose has on nitrogen content in soil samples. Bergsveison et al. in 2019 [48] used GLM model to show how bacterial diversity is significantly higher in surface soil within landfarm sections.

GLM models were used in this study to analyze the content of actually and poten
tially available metal forms. To assess the effectiveness of immobilization methods, by examining the effects of brown coal and activated carbon doses on the content of potentially and actually available metal forms following, respectively extraction in DTPA solution and 1 M NH$_4$NO$_3$, the following GLM model from the Gamma family was applied Equations (1)–(3):

$$\eta_i = \mu + \alpha_i$$  
$$\eta_i = \ln(E[y_i])$$  
$$\text{Var}[y_i] = \sigma^2 E[y_i]$$

where:

$\eta_i$—contents of forms of a specific metal in the given soil combination,
$\mu$—constant in the equation,
$\alpha_i$—variable corresponding to the dose of brown coal (bc) or activated carbon (ac) used.

Statistical analyses were performed in R software version 4.0.4 for Windows (R-project). The implementation of relevant tests in experimental analysis in R software is extensively discussed by Faraway [49,50] and Logan [51].

Results of the calculated mean values shown in Tables 3–7 are calculated based on soil samples taken from pot experiment in years 2011–2019.

3. Results

3.1. Microscopic Analysis of Carbons

Microscopic methods were used to specify the mineral composition of the carbons used in the pot experiment (Figures 2–6). The observations were carried out with a JSM-6380 LA scanning electron microscope (SEM) connected to an EDS electron micro-probe.

Figure 2. Dispersion energy spectrum of X-rays (EDS) for certain area (1) of brown coal, (a) photo of analyzed sample of brown coal; (b) spectrum.
Figure 2. Dispersion energy spectrum of X-rays (EDS) for certain area (1) of brown coal, (a) photo of analyzed sample of brown coal; (b) spectrum.

Figure 3. Dispersion energy spectra of X-rays (EDS) for individual nuggets (2, 3, 4) of brown coal, (a) photo of analyzed sample of brown coal; (b–d) spectra in points 2–4.

Figure 4. Dispersion energy spectrum of X-rays (EDS) for certain area (1) of activated carbon, (a) photo of analyzed sample of activated carbon; (b) spectrum.

Figure 5. Dispersion energy spectra of X-rays (EDS) for certain area (2, 3, 4) of activated carbon, (a) photo of analyzed sample of activated carbon; (b–d) spectra for points 2–4.
For each sample, a collective analysis of the EDS mineral composition and a point analysis were performed to identify additional mineral phases present in the tested samples. The analysis results for the brown coal sample show that it contained calcite, quartz, gypsum and trace amounts of sulfur, silica, feldspar and clay minerals (Figures 2 and 3).

The spectrum of the activated carbon sample indicates that it was almost pure carbon. There were slight traces of silica, feldspar, clay minerals and calcite (Figures 4–6). The X-ray spectra for points 2, 3 and 4 of the samples of brown coal (Figure 3b–d) confirm the high content of silica in its structure in the general spectrum (Figure 2b), where the percentage of silica ranges from 40 to 50% relative to the highest value. It is also worth noting that at points 3 and 4 (Figure 3b–d), aluminum (0.6–47% relative to the highest value) and calcium (2–58% relative to the highest value) appear, which are not detected in high amounts in the general spectrum (Figure 2b). Additionally, a characteristic feature of brown coal in the X-ray spectrum is the presence of trace amounts of titanium, which is not evident in activated carbon.

For activated carbon, the X-ray spectra for the samples tested at points 2, 3 and 4 (Figure 5b–d) and at higher magnification at points 5, 6 and 7 (Figure 6b–d) confirm the high content of carbon, which ranges from 19 to 98% relative to the highest value in the sample of activated carbon compared with the general spectrum (Figure 4b). Contrary to brown coal, activated carbon contained potassium with a range of 29–97% relative to the highest value in the general spectrum (Figure 4b), which was also confirmed for each of the tested points (2–7) of activated carbon. The presence of potassium in activated carbon results from the carbonization process. In addition, activated carbon had a higher content of background elements than brown coal, which can be seen at higher magnification in Figure 6b–d.
Figure 6. Dispersion energy spectra of X-rays (EDS) for individual nuggets (5, 6, 7) of activated carbon, (a) photo of analyzed sample of activated carbon; (b–d) spectra for points 5–7.

3.2. Total Content of Metals in Soil

In order to determine the efficacy of immobilization methods after the application of brown coal and activated carbon, the total metal content was determined (Table 3). According to the Ordinance issued by the Polish Minister of the Environment on 1 September 2016 on the method of assessing soil contamination [52], metals are among the main environmental hazards due to the risks that they pose to the land surface. The above-mentioned Ordinance defines, among other factors, substances that create risks that are of particular concern for the protection of the land surface, as well as their permissible contents in the soil, depending on particular soil characteristics and the depths and groups of land, identified on the basis of the land use. The examined soil samples were classified as the 4th group of land, i.e., industrial areas, and the assessed layer of soil was 0–0.25 m below ground level. None of the examined soil combinations exceeded permissible values of cadmium (15 mg/kg) according to those defined in the Ordinance. The permissible values were exceeded for lead (600 mg/kg) in all soil combinations. In the case of zinc (2000 mg/kg), the permissible limits were exceeded for all soil samples in the 1:1 and 1:3 combinations, whereas exceedance for copper (600 mg/kg) was observed only in the 1:1 combinations.
Table 3. Total metal concentration in soil depending on the dose of brown coal and activated carbon.

| Combination | Total Content of Metals HNO$_3$ and HClO$_4$ (3:1) [mg/kg d.m. of Soil] | Zn (Mean ± σ, HSD) | Cd (Mean ± σ, HSD) | Pb (Mean ± σ, HSD) | Cu (Mean ± σ, HSD) |
|-------------|-----------------------------------------------------------------------|---------------------|-------------------|------------------|------------------|
| 1:1”0”      | 5095 ± 139, 12.80, 0.84, a                                           | 5225 ± 183, a       | 748.4 ± 31.5, a   |
| 1:1 bc1     | 4997 ± 123, 13.00, 0.67, a                                           | 4897 ± 104, b       | 799.5 ± 17.6, a   |
| 1:1 bc2     | 4970 ± 166, 12.05, 1.06, a                                           | 4809 ± 114, bc      | 742.1 ± 36.5, a   |
| 1:1 ac1     | 4879 ± 136, 11.90, 1.48, a                                           | 4666 ± 160, bc      | 732.0 ± 21.7, a   |
| 1:1 ac2     | 4871 ± 190, 11.95, 1.48, a                                           | 4576 ± 125, c       | 729.8 ± 28.4, a   |

LSD$_{0.95}$: 181 ± 1.37, 167 ± 33.3 |

| Combination | Total Content of Metals HNO$_3$ and HClO$_4$ (3:1) [mg/kg d.m. of Soil] | Zn (Mean ± σ, HSD) | Cd (Mean ± σ, HSD) | Pb (Mean ± σ, HSD) | Cu (Mean ± σ, HSD) |
|-------------|-----------------------------------------------------------------------|---------------------|-------------------|------------------|------------------|
| 1:3”0”      | 2522 ± 86, 6.74, 0.60, a                                             | 1892 ± 61, a        | 383.9 ± 23.3, a   |
| 1:3 bc1     | 2484 ± 82, 6.94, 0.57, a                                             | 1902 ± 63, a        | 375.3 ± 19.1, a   |
| 1:3 bc2     | 2440 ± 80, 6.47, 0.65, a                                             | 1892 ± 101, a       | 373.3 ± 24.7, a   |
| 1:3 ac1     | 2435 ± 87, 6.22, 0.43, a                                             | 1868 ± 74, a        | 365.6 ± 20.7, a   |
| 1:3 ac2     | 2401 ± 78, 6.21, 0.62, a                                             | 1858 ± 75, a        | 369.7 ± 18.1, a   |

LSD$_{0.95}$: 98 ± 0.69, 90 ± 25.3 |

| Combination | Total Content of Metals HNO$_3$ and HClO$_4$ (3:1) [mg/kg d.m. of Soil] | Zn (Mean ± σ, HSD) | Cd (Mean ± σ, HSD) | Pb (Mean ± σ, HSD) | Cu (Mean ± σ, HSD) |
|-------------|-----------------------------------------------------------------------|---------------------|-------------------|------------------|------------------|
| 1:7”0”      | 1157 ± 49, 3.92, 0.48, a                                             | 1087 ± 52, a        | 258.2 ± 15.7, a   |
| 1:7 bc1     | 1017 ± 34, 3.69, 0.24, ab                                           | 997.4 ± 41.9, b     | 250.0 ± 18.1, a   |
| 1:7 bc2     | 1005 ± 41, 3.36, 0.48, abc                                          | 992.1 ± 38.3, b     | 245.9 ± 11.9, a   |
| 1:7 ac1     | 996.3 ± 44.6, 2.91, 0.25, c                                          | 971.8 ± 32.2, b     | 244.8 ± 10.0, a   |
| 1:7 ac2     | 1007 ± 33, 3.12, 0.27, bc                                           | 966.0 ± 33.6, b     | 248.9 ± 13.2, a   |

LSD$_{0.95}$: 48 ± 0.43, 47.9 ± 16.7 |

mean—mean value of the studied variable for different soil combinations and duration of the experiment in years; σ—standard deviation; HSD—differences (marked in letters) between means at significance level of 0.05 based on Tukey’s HSD test.

In the case of the 1:1 and 1:3 combinations of soils, no significant differences were found between the control soil and those treated with brown coal or activated carbon. Significant differences were noted only for the 1:7 soil combination, in which any dose of carbon (brown or activated) resulted in a significant reduction in the zinc content in the soil. For the total content of zinc in the soil, no significant differences were found between the different types of carbons or their doses. The analysis of variance for the cadmium content based on the carbon dose indicated that brown coal and activated carbon did not have a significant influence on the 1:1 and 1:3 soil combinations. Only in the 1:7 combination of soils were total cadmium contents significantly lower after the use of activated carbon. The analysis of variance for the lead content based on the carbon dose showed significant differences between the average lead content after the use of carbon in soil combinations 1:1 and 1:7. In the 1:3 combination, the differences were not significant. In all tested soil combinations, i.e., 1:1, 1:3 and 1:7, there was no reason to reject the hypothesis that the average copper content was equal between doses of both brown coal and activated carbon.

3.3. Metal Forms Extracted with 1 M HCl

Single extraction was performed with 1 M HCl, which is recommended in Poland for assessing the content of phytoavailable metal forms in soils (according to the procedure accepted by Agricultural and Chemical Stations) [30,35]. This method is used because of the high correlation between the extraction results and metal uptake by crop plants. However, these tests, as emphasized by Gembarzewski et al. [53] and by Gembarzewski and Korzeniowska [54], were carried out only on uncontaminated soils, which means that extraction with a high concentration of acid does not reflect the actual bioavailability of metals to plants [3]. This method can be used to assess the potential solubility and bioavailability of metals. In the present study, 1 M HCl extraction led to very high contents of metal forms for all metals tested. Table 4 shows the results for zinc, cadmium, lead and copper forms in different soil combinations after 1 M HCl extraction.
Table 4. Content of metal forms after 1 M HCl extraction, depending on the dose of brown coal and activated carbon.

| Combination | Content of Metal Forms after 1 M HCl Extraction [mg/kg d.m. of Soil] |
|-------------|-------------------------------------------------------------------------------------------------|
|             | Zn       | Cd     | Pb       | Cu       |
|             | Mean    | σ     | HSD Mean | σ       | HSD Mean | σ     | HSD Mean | σ     | HSD |
| 1:1“0”     | 4595    | 156   | a       | 11.50   | 0.82    | a       | 4370   | 204   | a    | 618.2  | 31.2 | a    |
| 1:1 bc1    | 4290    | 194   | b       | 10.10   | 0.81    | ab     | 4005   | 158   | b    | 584.2  | 24.7 | a    |
| 1:1 bc2    | 4100    | 144   | bc      | 8.81    | 0.93    | b       | 3627   | 234   | c    | 511.5  | 24.1 | b    |
| 1:1 ac1    | 3882    | 159   | cd      | 8.71    | 0.80    | b       | 3511   | 161   | c    | 501.8  | 18.8 | b    |
| 1:1 ac2    | 3745    | 132   | d       | 8.64    | 0.98    | b       | 3173   | 234   | d    | 498.4  | 25.7 | b    |
| LSD 0.95   | 188     | 1.03  | 207     | 30.0    |         |         |        |       |       |        |      |      |
| 1:3“0”     | 2252    | 81    | a       | 5.18    | 0.44    | a       | 1690   | 80    | a    | 347.3  | 15.4 | a    |
| 1:3 bc1    | 2147    | 65    | ab      | 4.90    | 0.62    | a       | 1548   | 62    | b    | 310.3  | 12.0 | b    |
| 1:3 bc2    | 2076    | 83    | bc      | 4.58    | 0.33    | a       | 1538   | 71    | b    | 281.3  | 17.6 | c    |
| 1:3 ac1    | 1982    | 73    | c       | 3.77    | 0.37    | b       | 1491   | 67    | b    | 313.0  | 14.0 | b    |
| 1:3 ac2    | 1956    | 79    | c       | 3.61    | 0.30    | b       | 1527   | 52    | b    | 258.2  | 16.4 | c    |
| LSD 0.95   | 91      | 0.51  | 80      | 18.1    |         |         |        |       |       |        |      |      |
| 1:7“0”     | 1045    | 40    | a       | 3.26    | 0.33    | a       | 967.0  | 45.6  | a    | 227.7  | 8.6  | a    |
| 1:7 bc1    | 877.8   | 53.2  | b       | 2.98    | 0.39    | ab      | 774.5  | 51.3  | b    | 196.7  | 7.9  | b    |
| 1:7 bc2    | 853.5   | 43.0  | bc      | 2.93    | 0.31    | ab      | 748.4  | 66.3  | b    | 153.1  | 11.1 | c    |
| 1:7 ac1    | 800.7   | 43.4  | cd      | 2.59    | 0.26    | b       | 698.9  | 47.7  | b    | 198.3  | 14.3 | b    |
| 1:7 ac2    | 731.2   | 22.4  | d       | 2.49    | 0.30    | b       | 724.5  | 48.3  | b    | 185.6  | 11.1 | b    |
| LSD 0.95   | 49.6    | 0.38  | 62.3    | 12.9    |         |         |        |       |       |        |      |      |

mean—mean value of the studied variable for different soil combinations and duration of the experiment in years; σ—standard deviation; HSD—differences (marked in letters) between means at significance level of 0.05 based on Tukey’s HSD test.

For all soil combinations (1:1, 1:3 and 1:7), the use of carbons resulted in a significant reduction in zinc forms extracted with 1 M HCl. However, the influence of activated carbon was stronger. For cadmium, no significant reduction in the content of metal forms was found after 1 M HCl extraction, and the use of activated carbon resulted in a significant reduction in the forms of this metal. The analysis of variance showed that for all soil combinations, the use of carbons resulted in a significant reduction in extracted forms of lead with the 1 M HCl solution. Among the two types of carbons, activated carbon exerted a stronger influence, although it was not always significant. When comparing the effect of carbons using variance analysis, statistically significant differences were found between the content of copper forms in all examined soils, with the greatest reduction in copper content achieved after applying a double dose of activated carbon.

3.4. Metal Forms Extracted With DTPA

Different authors have carried out single extractions using, among other materials, complex solutions of ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) [55–58]. In order to determine phytoavailable metal forms (actually available to plants and potentially soluble forms), i.e., those that can be absorbed by plants due to changes in the soil, single extractions were carried out using different reagents (1 M NH₄NO₃ and DTPA solution). Extractions with complex reagents, e.g., EDTA and DTPA, are commonly used to evaluate the content of metals in soil that are potentially available to plants (absorbable) [59,60]. For this reason, the results obtained are overestimated relative to the phytoavailability, especially in the case of contaminated soils. The method described here is not chemical-specific, i.e., it cannot be used to determine one particular form of an element, but rather determines a certain group of forms. It has, however, been widely used in the United Kingdom and Belgium because it is relatively simple and fast, and as such, it is commonly used to assess the phytoavailability of metals. The results obtained after using the DTPA chemical solution are presented in Table 5.
Table 5. Content of metal forms after DTPA extraction, depending on the dose of brown coal and activated carbon.

| Combination | Content of Metal Forms after DTPA Extraction [mg/kg d.m. of Soil] |
|-------------|---------------------------------------------------------------|
|             | Zn     | Cd     | Pb     | Cu     |
|             | Mean  | σ     | HSD    | Mean   | σ     | HSD    | Mean  | σ     | HSD    |
| 1:1”0”      | 266.9 | 12.8  | a      | 1.95   | 0.18  | a      | 660.1 | 39.1  | a      | 110.2  | 6.1   | a      |
| 1:1 bc1     | 245.6 | 9.6   | b      | 1.87   | 0.14  | ab     | 551.8 | 39.4  | b      | 98.4   | 5.6   | b      |
| 1:1 bc2     | 225.8 | 10.9  | c      | 1.81   | 0.20  | ab     | 521.4 | 26.5  | bc     | 94.3   | 6.5   | b      |
| 1:1 ac1     | 221.1 | 9.3   | c      | 1.66   | 0.15  | b      | 480.5 | 31.4  | c      | 88.1   | 8.1   | b      |
| 1:1 ac2     | 212.8 | 14.4  | c      | 1.63   | 0.10  | b      | 467.0 | 37.9  | c      | 88.6   | 6.2   | b      |
| LSD_0.95    | 13.7  | 0.19  |        | 41.9   |       |        |        |        |        | 7.8    |       |
| 1:3”0”      | 151.7 | 10.0  | a      | 1.27   | 0.11  | a      | 461.4 | 18.1  | a      | 63.2   | 4.6   | a      |
| 1:3 bc1     | 145.4 | 8.5   | a      | 1.17   | 0.13  | a      | 420.7 | 30.8  | ab     | 54.4   | 3.6   | b      |
| 1:3 bc2     | 142.2 | 10.1  | a      | 1.14   | 0.15  | a      | 379.9 | 44.4  | b      | 50.6   | 2.2   | b      |
| 1:3 ac1     | 127.4 | 7.5   | b      | 0.87   | 0.10  | b      | 300.3 | 34.7  | c      | 45.1   | 2.0   | c      |
| 1:3 ac2     | 120.2 | 4.5   | b      | 0.77   | 0.12  | b      | 266.9 | 19.4  | c      | 42.4   | 2.3   | c      |
| LSD_0.95    | 10.0  | 0.15  |        | 36.9   |       |        |        |        |        | 3.7    |       |
| 1:7”0”      | 101.8 | 5.6   | a      | 0.83   | 0.09  | a      | 295.1 | 17.4  | a      | 36.7   | 2.5   | a      |
| 1:7 bc1     | 87.5  | 4.4   | b      | 0.76   | 0.11  | a      | 272.9 | 11.9  | a      | 32.1   | 3.0   | b      |
| 1:7 bc2     | 84.0  | 4.5   | b      | 0.73   | 0.07  | a      | 215.3 | 10.1  | b      | 28.9   | 1.2   | b      |
| 1:7 ac1     | 58.3  | 3.2   | c      | 0.53   | 0.07  | b      | 178.7 | 11.0  | c      | 22.8   | 1.5   | c      |
| 1:7 ac2     | 57.8  | 4.4   | c      | 0.48   | 0.11  | b      | 173.5 | 15.1  | c      | 21.5   | 2.6   | c      |
| LSD_0.95    | 5.3   | 0.11  |        | 15.9   |       |        |        |        |        | 2.7    |       |

Mean—mean value of the studied variable for different soil combinations and duration of the experiment in years; σ—standard deviation; HSD—differences (marked in letters) between means at significance level of 0.05 based on Tukey's HSD test.

After using the generalized linear model (GLM) to compare the effect of brown coal and activated carbon on the content of metal forms in the soil after DTPA extraction, equation coefficients were obtained. They are presented in Table 6 together with the corresponding significance levels. Activated carbon was found to have a significant effect on the contents of zinc forms in all soil combinations, whereas brown coal significantly reduced those that are potentially available to plants only in 1:1 and 1:7 soil combinations.

The greatest reduction in the content of cadmium forms after DTPA extraction was observed after the use of activated carbon. Although the use of brown coal resulted in a reduction in Cd, it was not statistically significant. Both types of carbon led to a significant reduction in metal forms that are potentially available to plants, although the effect of activated carbon was stronger. When investigating the content of lead forms that are potentially available to plants, both doses of activated carbon and brown coal had a significant effect in all cases, with a markedly stronger influence from activated carbon. When comparing the effect of different carbons on the copper content in different soil combinations, a much stronger effect of activated carbon was observed.
Table 6. GLM model parameters describing the influence of applied carbon doses on metal form concentration after DTPA extraction for a given soil combination.

| Parameter | Zn           | Cd           | Pb           | Cu           |
|-----------|--------------|--------------|--------------|--------------|
|           | Est | p       | Est | p       | Est | p       | Est | p       |
| 1:1 µ     | 5.59 | <0.001 | 0.67 | <0.001 | 6.49 | <0.001 | 4.70 | <0.001 |
| 1:1 bc1   | −0.08 | 0.008 | −0.04 | 0.400 | −0.18 | <0.001 | −0.11 | 0.010 |
| 1:1 ac1   | −0.19 | <0.001 | −0.17 | 0.003 | −0.32 | <0.001 | −0.22 | <0.001 |
| 1:1 bc2   | −0.17 | <0.001 | −0.08 | 0.147 | −0.24 | <0.001 | −0.16 | <0.001 |
| 1:1 ac2   | −0.23 | <0.001 | −0.18 | 0.001 | −0.35 | <0.001 | −0.22 | <0.001 |
| 1:3 µ     | 5.02 | <0.001 | 0.24 | <0.001 | 6.13 | <0.001 | 4.15 | <0.001 |
| 1:3 bc1   | −0.04 | 0.222 | −0.08 | 0.261 | −0.09 | 0.083 | −0.15 | <0.001 |
| 1:3 ac1   | −0.17 | <0.001 | −0.38 | <0.001 | −0.43 | <0.001 | −0.34 | <0.001 |
| 1:3 bc2   | −0.06 | 0.071 | −0.10 | 0.170 | −0.19 | <0.001 | −0.22 | <0.001 |
| 1:3 ac2   | −0.23 | <0.001 | −0.50 | <0.001 | −0.55 | <0.001 | −0.40 | <0.001 |
| 1:7 µ     | 4.62 | <0.001 | −0.18 | 0.006 | 5.69 | <0.001 | 3.60 | <0.001 |
| 1:7 bc1   | −0.15 | <0.001 | −0.10 | 0.277 | −0.08 | 0.037 | −0.13 | <0.001 |
| 1:7 ac1   | −0.56 | <0.001 | −0.45 | <0.001 | −0.50 | <0.001 | −0.48 | <0.001 |
| 1:7 bc2   | −0.19 | <0.001 | −0.13 | 0.146 | −0.32 | <0.001 | −0.24 | <0.001 |
| 1:7 ac2   | −0.57 | <0.001 | −0.56 | <0.001 | −0.53 | <0.001 | −0.54 | <0.001 |

Est—estimated value of coefficient in the GLM model; p—significance level of the coefficient.

The parameters of the model clearly indicate that activated carbon had a stronger effect than brown coal on reducing the metal content. The differences in the content of zinc forms after the application of various carbon doses in different ratios of contamination in soil are also shown in Figure 7a (1:1 ratio), Figure 7b (1:3 ratio) and Figure 7c (1:7 ratio). The graphical presentation of the results (Figures 7 and 8 have been presented purposely in different scales to make more visible differences between doses of carbons) was also obtained using R software.

Figure 7. Influence of brown coal and activated carbon on zinc concentrations (after DTPA extraction) in soils, (a) 1:1 ratio; (b) 1:3 ratio; (c) 1:7 ratio.

Figure 8. Influence of brown coal and activated carbon on zinc concentrations (after 1 M NH₄NO₃ extraction) in soils, (a) 1:1 ratio; (b) 1:3 ratio; (c) 1:7 ratio.
The analysis shows that both the lower and higher doses of activated carbon significantly reduced metal forms that are potentially available to plants. In each case, activated carbon had a stronger effect than that achieved with the corresponding dose of brown coal for all tested ratios presented in Figure 7a–c.

### 3.5. Metal Forms Extracted with 1 M NH\(_4\)NO\(_3\)

Ammonium nitrate (1 M NH\(_4\)NO\(_3\)) was used in the experiment for the extraction of metals from soils due to the characteristics of the used soils and the common use of this method (e.g., standardization in Germany). The results are presented in Table 7. Numerous authors [61–63] have asserted that in order to assess the solubility of metals in a soil solution, it is best to use inert salt solutions as extraction solutions.

Table 7. Content of metal forms after 1 M NH\(_4\)NO\(_3\) extraction, depending on the dose of brown coal and activated carbon.

| Combination | Content of Metal Forms after 1 M NH\(_4\)NO\(_3\) Extraction [mg/kg d.m. of Soil] |
|-------------|--------------------------------------------------------------------------------|
|             | Zn | Cd | Pb | Cu |
|             | mean | σ | HSD | mean | σ | HSD | mean | σ | HSD | mean | σ | HSD |
| 1:1 “0”     | 146.9 | 8.5 | a | 1.10 | 0.07 | a | 6.68 | 0.59 | a | 77.4 | 5.9 | a |
| 1:1 bc1     | 133.3 | 8.3 | b | 0.97 | 0.11 | a | 6.12 | 0.33 | a | 60.4 | 3.4 | b |
| 1:1 bc2     | 92.5 | 6.2 | c | 0.81 | 0.07 | b | 5.13 | 0.27 | b | 51.4 | 3.4 | c |
| 1:1 ac1     | 74.8 | 2.8 | d | 0.82 | 0.08 | b | 3.90 | 0.32 | c | 49.3 | 2.9 | c |
| 1:1 ac2     | 59.3 | 3.0 | e | 0.56 | 0.07 | c | 3.50 | 0.29 | c | 34.9 | 3.1 | d |
| LSD 0.95    | 7.5 | 0.10 | | 0.45 | 0.05 | | 4.6 | 0.10 | |
| 1:3 “0”     | 68.5 | 2.7 | a | 0.51 | 0.08 | a | 2.52 | 0.30 | a | 37.2 | 2.9 | a |
| 1:3 bc1     | 61.2 | 2.6 | b | 0.41 | 0.04 | b | 1.87 | 0.15 | b | 18.9 | 2.2 | b |
| 1:3 bc2     | 40.3 | 2.7 | c | 0.23 | 0.04 | c | 1.58 | 0.15 | bc | 9.2 | 0.7 | c |
| 1:3 ac1     | 38.0 | 1.8 | cd | 0.25 | 0.03 | c | 1.28 | 0.13 | cd | 7.6 | 0.8 | c |
| 1:3 ac2     | 35.7 | 2.2 | d | 0.21 | 0.02 | c | 1.58 | 0.15 | bc | 9.2 | 0.7 | c |
| LSD 0.95    | 2.9 | 0.05 | | 0.22 | 0.05 | | 2.0 | 0.05 | |
| 1:7 ”0”     | 31.0 | 1.8 | a | 0.29 | 0.04 | a | 2.50 | 0.20 | a | 9.4 | 0.8 | a |
| 1:7 bc1     | 19.0 | 0.9 | b | <det. | - | - | 1.52 | 0.18 | b | 7.9 | 0.6 | b |
| 1:7 bc2     | 12.2 | 0.9 | c | <det. | - | - | 1.30 | 0.17 | b | 7.3 | 0.5 | b |
| 1:7 ac1     | 10.3 | 0.8 | d | <det. | - | - | <det. | - | - | 5.9 | 0.7 | c |
| 1:7 ac2     | 10.1 | 0.6 | d | <det. | - | - | <det. | - | - | 5.4 | 0.4 | c |
| LSD 0.95    | 1.3 | - | - | 0.7 | - | - | - | - | - | - | - | - |

mean—mean value of the studied variable for different soil combinations and duration of the experiment in years, σ—standard deviation; HSD—differences (marked in letters) between means at significance level of 0.05 based on Tukey’s HSD test. <det—below detection limit (Cd < 0.2 mg/kg; Pb < 1 mg/kg; Cu < 2 mg/kg).

As a result of using the GLM to compare the effect of brown coal and activated carbon on the content of metal forms in the soil after 1 M NH\(_4\)NO\(_3\) extraction, equation coefficients were obtained, along with the corresponding significance levels. These are presented in Table 8.

In the case of zinc, the influence of both activated carbon and brown coal was found to be significant in all soil combinations, and the influence of activated carbon on more polluted soils was stronger. Differences in the content of zinc forms after using different carbon doses are shown in Figure 8. The carbons significantly reduced the cadmium content, with activated carbon having a stronger effect than brown coal. For lead and copper, the immobilization effect of activated carbon was considerably higher than that of brown coal.

The analysis clearly demonstrates that both carbons are beneficial for the reduction of metal forms that are actually available to plants in the tested soils, with activated carbon being more effective.
Table 8. GLM model parameters describing the influence of applied coal doses on metal form concentration after 1 M NH$_4$NO$_3$ extraction for a given soil combination.

| Parameter | Zn       | Cd * | Pb * | Cu *       |
|-----------|----------|------|------|------------|
|           | Est      | p    |      | Est        | p    |      | Est        | p    |      | Est        | p    |      | Est        | p    |      |
| 1:1 μ     | 4.99     | <0.001 | 0.09 | 0.026 | 1.90       | <0.001 | 4.35 | <0.001 | 4.35 | <0.001 | 4.35 | <0.001 | 4.35 | <0.001 |
| 1:1 bc1   | −0.10    | 0.006 | −0.13 | 0.034 | −0.09       | 0.048 | −0.25 | <0.001 | −0.25 | <0.001 | −0.25 | <0.001 | −0.25 | <0.001 |
| 1:1 ac1   | −0.67    | <0.001 | −0.30 | <0.001 | −0.54       | <0.001 | −0.45 | <0.001 | −0.45 | <0.001 | −0.45 | <0.001 | −0.45 | <0.001 |
| 1:1 bc2   | −0.46    | <0.001 | −0.30 | <0.001 | −0.26       | <0.001 | −0.41 | <0.001 | −0.41 | <0.001 | −0.41 | <0.001 | −0.41 | <0.001 |
| 1:1 ac2   | −0.91    | <0.001 | −0.67 | <0.001 | −0.65       | <0.001 | −0.80 | <0.001 | −0.80 | <0.001 | −0.80 | <0.001 | −0.80 | <0.001 |
| 1:3 μ     | 4.23     | <0.001 | −0.68 | <0.001 | 3.62        | <0.001 |      |      |      |      |      |      |      |      |
| 1:3 bc1   | −0.11    | 0.001 | −0.21 | 0.011 | 0.68        | <0.001 |      |      |      |      |      |      |      |      |
| 1:3 ac1   | −0.59    | <0.001 | −0.70 | <0.001 | 1.60        | <0.001 |      |      |      |      |      |      |      |      |
| 1:3 bc2   | −0.53    | <0.001 | −0.78 | <0.001 | 1.40        | <0.001 |      |      |      |      |      |      |      |      |
| 1:3 ac2   | −0.65    | <0.001 | −0.88 | <0.001 | 1.75        | <0.001 |      |      |      |      |      |      |      |      |
| 1:7 μ     | 3.43     | <0.001 |      |      | 2.24        | <0.001 |      |      |      |      |      |      |      |      |
| 1:7 bc1   | −0.49    | <0.001 |      |      | 0.17        | 0.002 |      |      |      |      |      |      |      |      |
| 1:7 ac1   | −1.10    | <0.001 |      |      | 0.47        | <0.001 |      |      |      |      |      |      |      |      |
| 1:7 bc2   | −0.93    | <0.001 |      |      | 0.25        | <0.001 |      |      |      |      |      |      |      |      |
| 1:7 ac2   | −1.12    | <0.001 |      |      | 0.55        | <0.001 |      |      |      |      |      |      |      |      |

Est—estimated value of coefficient in the GLM model; p—significance level of the coefficient; * Cd, Pb, Cu were tested on selected combinations

3.6. Percentage of Metal Forms

The percentage of metal forms of the total contents after 1 M HCl extraction decreased after the use of carbons. This effect was clearly noticeable in the case of activated carbon, especially after using a double dose. The effectiveness of the carbons used in the pot experiment was evaluated by determining the percentage of the total contents of metal forms extracted with the DTPA solution and 1 M NH$_4$NO$_3$. When comparing the results of the extractants, a higher solubility in the DTPA solution was observed for zinc, cadmium, lead and copper (especially for the lead content). The presented results indicate that the solubility of metal forms in different combinations, including their potential availability to plants, can be expressed with the following series: Cu ~ Pb ~ Cd > Zn, whereas the actual availability to plants can be expressed with the following series: Cu > Cd > Zn > Pb (starting with the most soluble and ending with the least soluble).

3.7. Content of Humic Substances in Soils

For the determination of humic fractions in the studied soils, tests were carried out to analyze the content of humic substances, namely, fulvic acids (FA), humic acids (HA) and humins (HUM). These tests were conducted for soils that were most contaminated (1:1) and least contaminated (1:7) with metals, as well as for the uncontaminated soil sample, with single and double doses of brown coal and activated carbon (Figures 9 and 10). In these tests, soil samples from 2011 (before setting up the pot experiment) and from 2019 (eight years after adding the brown coal and activated carbon to the pots) were used.
With the addition of carbons, the contents of FA in soils in 2019 were similar to those on the day that the pot experiment was set up (in 2011). The addition of carbons caused an increase in the contents of HA and HUM. The duration of the experiment did not cause an increase in the contents of HUM, as their quantities in soils with brown coal and activated carbon did not change significantly.

4. Discussion

In accordance with the Regulation of the Minister of the Environment [52], the total content of metals is used as a basis to assess the degree of soil contamination. Many methods are used to determine the content of metals; for example, metals can be determined directly in solid samples using X-ray fluorescence spectrometry or by using ICP-OES methods (although they do not enable us to determine all metal forms, especially those
of lithogenic origin). Kabata-Pendias [2] argued that, despite the incomplete dissolution of aluminosilicate minerals in aqua regia, most cations, especially trace ones, are leached, primarily from clay minerals and micas. Aqua regia easily decomposes organic matter, as well as carbonates, phosphates and sulfides. On the other hand, Karczewksa [3] indicated that compounds that are not susceptible to acid mixtures are of no practical significance for the assessment of environmental hazards. The results of the present study indicate that the studied soils had a high content of all tested metals (Zn, Cd, Pb and Cu) in different combinations and ratios. These results also confirm that brown coal and activated carbon have no significant effect on the total metal content in the soil, which is in line with the results obtained by other authors [2,16].

Metal forms in the soil solution largely determine the phytotoxicity and phytoavailability of metals, which is conditioned by the activity of free ions in the soil solution [64]. Soil tests, usually based on single (simple) extracts, are used to determine the solubility of metals or the phytotoxicity of soils. Such tests can be used to determine soluble metal forms in various extraction solutions, which determine the actual or potential availability of metals to plants [3]. Inert salt solutions are the best extraction solutions to assess the solubility of metals, which largely determines their assimilation by plants. Many authors have successfully used 1 M NH$_4$NO$_3$ as an extractant for both contaminated and uncontaminated soils [61–63,65]. The determination of the content of metal forms carried out through 1 M NH$_4$NO$_3$ extraction in this study indicates that the studied eluent varied in efficiency for different metals. The 1 M NH$_4$NO$_3$ solution used in this study was most effective in extracting zinc, regardless of the soil combination, followed by copper and lead. For each of the tested soils, increasing the carbon doses resulted in a statistically significant reduction in the forms of all tested metals that are actually available to plants. This illustrates the significant ability of brown coal and activated carbon to limit soil phytotoxicity, with activated carbon being more effective in each case.

For single extractions, a DTPA solution was also used. This is a more aggressive reagent compared with the 1 M NH$_4$NO$_3$ solution and is often used to assess the potential solubility and bioavailability of metals [3,59,60,66–69]. Research has shown that the DTPA solution extracts more of the total contents of metal forms than forms that are actually available to plants. Alloway [1] indicated that these forms may change into actually available forms under conditions such as lower pH values. Based on the results obtained in the present study, the DTPA solution extracted the largest number of lead forms, followed by zinc and copper, in all soil combinations. Our analysis shows that both doses of activated carbon significantly reduced the forms that are potentially available to plants, with the effect of activated carbon being stronger than that of brown coal in each case. This demonstrates a beneficial effect of the studied carbons, as they help to reduce not only forms that are actually available to plants but also those that pose a potential threat.

The effectiveness of the tested carbons can be determined on the basis of the percentage of metal forms that are actually and potentially available. A higher solubility of copper, cadmium and lead in DTPA was observed, as well as a higher solubility of copper, cadmium and zinc in the 1 M NH$_4$NO$_3$ solution. The greatest difference was found in the case of lead, where the percentage of potentially available forms of the total values was among the highest of the tested metals and, at the same time, the lowest among the percentages of actually available forms of the total values. Increasing the doses of both brown coal and activated carbon reduced these percentages in the tested soils for all metals studied. This means that the organic matter contained in the tested carbons bound metals into forms that are not easily soluble and, as such, less available to plants.

The present study found a relationship between the content of different metals extracted using different extraction solutions, namely, 1 M HCl, DTPA and 1 M NH$_4$NO$_3$, which are dependent primarily on the total content of these metals in the soil. The concentration of metals in the soil solution is contingent not only on the maximum content of metal forms that are susceptible to desorption and mobilization via other processes but also on the balance of sorption–desorption processes at the boundary of the solid phase...
and the soil solution. Despite the potentially high susceptibility of specific metal forms to mobilization, desorption can be negligible under natural conditions if the balance of this process is shifted towards sorption [3,32,70]. Under natural conditions, with a very narrow ratio of soil solution to soil mass, the reaction equilibrium is likely to be shifted towards sorption. In single extractions, based on mixing soil samples with extraction solutions, the equilibrium of these processes depends on the ratio of the solid phase to the solution and is reached within different shaking times. If the solution exceeds the solid phase, the equilibrium is shifted towards desorption, whereas in the absence of shaking, in soil under natural conditions, the equilibrium is likely to be shifted towards sorption. Despite the high potential solubility, this leads to a situation in which metal forms are not activated, which further reduces the leaching of metals from the soil and reduces their bio- and phytoavailability. This is especially true for the so-called least active metals. The present study found a high percentage of metal forms, especially zinc forms, that are susceptible to extraction not only with highly potent reagents (DTPA solution, 1 M HCl) but also with a solution of inert salts (1 M NH$_4$NO$_3$).

Klucakova and Pavlikova [71] claimed that brown coal has a high content of humic acids. Regardless of time, their contents remained similar to those in soils with amendments. The only exception was for the 1:7 soil with a double dose of activated carbon, in which a high increase in HA contents was observed after 8 years of the pot experiment. The results of this study indicate that the tested carbons can be used particularly in degraded industrial areas contaminated with metals, as well as serve as a basis for developing specific technological solutions.

Studies conducted over the years confirm the presence of metals in the 0–0.25 m soil layer, especially in Lower Silesia, which is the main mining area in the country. Industrial branches such as metal processing, landfills, urban and post-industrial areas are associated with the problem of exceeding permissible contents in soil. The immobilization of metals in soil is an effective method, especially in terms of ecological risk reduction, resulting in the improvement of the physical and chemical properties of soil.

Soil remediation with the method of immobilization (stabilization) can be carried out with the use of many materials, characterized by various physical and chemical properties and structures. All of these factors, as well as the dose of the sorbent used and the type and size of the contamination, affect the effectiveness and efficiency of remediation. Wang et al. [72] reported that the costs of stabilizing inorganic pollutants in the soil are 75–205 USD/t. The costs of remediation through the stabilization method using the tested brown coal and activated carbon do not exceed USD 75/t (taking into account the double doses of both carbons), assuming that the carbons are mixed with the contaminated soil to a depth of approx. 25 cm, i.e., to the average depth of plant roots.

5. Conclusions

1. The dispersive X-ray energy spectra of selected areas of samples of both activated carbon and brown coal reveal that activated carbon has a lower content of metals than brown coal and trace amounts of silica, feldspar, clay minerals and calcite. For the dispersive energy spectra for selected areas of the sample of brown coal, higher contents of calcite, quartz, and gypsum, and trace amounts of sulfur, silica, feldspar and clay minerals were detected compared with activated carbon.

2. The content of phytoavailable metal forms in the soil was divided into those that are actually available to plants (after extraction in 1 M NH$_4$NO$_3$) and those that are potentially available to plants (after extraction in the DTPA solution or 1 M HCl). The use of both brown coal and activated carbon reduced the content of metal forms that are actually and potentially available to plants and also reduced the percentage of these forms relative to the total metal content in the soil.

3. Extraction with a strong acid at a relatively high concentration (1 M HCl) does not reflect the actual availability of metals to plants in highly contaminated soils because
the quantities of metals extracted with this eluent are highly overestimated relative to availability.

4. The carbons reduced the percentage of these forms relative to the total metal content in the soil. After adding brown coal, Zn, Cd, Pb and Cu forms were reduced by up to 32%, 30%, 33% and 43%, respectively. After adding activated carbon, the metal forms of Zn, Cd, Pb and Cu were reduced by up to 47%, 44%, 40% and 50%, respectively. When comparing the content of metal forms (from the highest to the lowest content) with extractions using HCl, DTPA and NH₄NO₃, the following order was found:
   a. HCl: Zn > Pb > Cu > Cd; DTPA: Pb > Zn > Cu > Cd; NH₄NO₃: Zn > Cu > Pb > Cd.

5. Eight years after setting up the pot experiment, the contents of humic substances in soils with the addition of both tested carbons were compared, and those with added carbons were found to have a stable content of humic fractions.

6. The use of brown coal or activated carbon helps to reduce the solubility of metal forms in contaminated soils from industrial areas, which leads to their immobilization and the reduction in bio- and phytoavailability and, as a result, can serve as a quick and effective method of in situ remediation (immobilization) in degraded industrial areas.
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