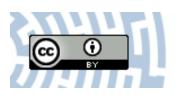


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Article The Properties of Black Locust *Robinia pseudoacacia* L. to Selectively Accumulate Chemical Elements from Soils of Ecologically Transformed Areas

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Abstract: The black locust Robinia pseudoacacia L. is a common species that originated from North America. In Europe, it is an invasive and introduced plant. Due to its low habitat requirements and ecological plasticity, this species colonizes new anthropogenically transformed areas quickly. This study investigated the chemical composition of selected tissues of Robinia pseudoacacia L. in five various habitats with different levels of anthropopression conditions in southern Poland. The presented research aimed to compare the chemical composition of black locust parts tissues (leaves, branches, and seeds) and the soil under its canopy. To determine the heavy metal contamination and enrichment in soil, the geoaccumulation index, enrichment factor, contamination factor, pollution load index, and potential ecological risk index were calculated. The results showed that all examined soils are considerably or very highly contaminated and the main heavy metals, which pollute the studied samples, are cadmium (1.3-3.91 ppm), lead (78.17-157.99 ppm), and zinc (129.77-543.97 ppm). Conducted research indicates that R. pseudoacacia leaves are the primary carrier of potentially toxic elements. Due to low bioaccumulation factor (BAF) values, it is clear that black locusts do not accumulate contaminants in such amounts that it would pose risk to its use in degraded area reclamation. The obtained results showed that *R. pseudoacacia* is able to grow in a wide range of habitats and could be applied for greening urban habitats and disturbed ecosystems caused by industry.

Keywords: *Robinia pseudoacacia;* degraded ecosystems; elemental composition; heavy metal accumulation; soil pollutions; brownfield restoration

1. Introduction

Silesia Upland is one of the most transformed areas in central Europe. This situation has been caused by the development of long-standing mining and metallurgy industries [1,2] and massive amounts of industrial waste [3]. Inept waste management has led to ecological disaster, as a result of which all elements of the natural environment have been degraded. Today, in this area, many industrial remnants, mostly coal dumps, can be found [4]. Industry development has contributed to the population's growth and the formation of the largest agglomeration in Poland and one of the largest in Europe the Katowice urban area [5]. Due to many inhabitants, Silesia Upland's area underwent transformations linked to intense human activity, such as landfills, parks, or agricultural areas [6]. All of this has led to massive soil degradation in the Silesia Upland. The most common transformations are soil contamination with heavy metals, acidification, and, in extreme cases, destruction of the soil cover [7–9]. Currently, there have been actions to rehabilitate degraded areas by reintroducing vegetation and restoring soil in areas such as dumps, landfills, etc.

Plants introduced into degraded areas must have a wide ecological tolerance to survive despite unfavorable conditions. Often, they must adapt to life in areas without soil cover.



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). One of such plants is the black locust *Robinia pseudoacacia* L. commonly used in Poland for anthropogenically the reclamation of degraded areas [10–13]. It is an invasive species that has come to Poland in the 18th century and quickly spread throughout the country [12]. Initially, this species originated from North America [14,15], but it is now considered one of the most common non-native plant species in Europe [14,16–18]. Often, it grows as tall trees (up to 20 m) or thick shrubs [19], and it is a producer of a large amount of biomass for the environment [20–22].

Plants can influence the dynamic characteristics of a community by binding nitrogen [23]. It is crucial for habitats with low nutrient content [24]. Due to rapid growth and the ability to fix nitrogen, *R. pseudoacacia* is a popular plant used in vegetation restoration in degraded areas [25,26]. It has been proven that *R. pseudoacacia* is important for the development of a better ecological surrounding [27]. Additionally, the plant litter of black locusts positively influences soil cover formation, as it enriches poor ecosystems of degraded areas in necessary micro and macro elements [12,18]. These components are mainly derived from the decaying plant litter of *R. pseudoacacia*. The critical issue is whether *R. pseudoacacia* accumulates toxic compounds and transmits them further due to biomass production included in the newly formed soils. There are sporadic investigations concerning the influence of the chemical composition of tissues of black locusts on the environment [7,12,28,29]. Due to the wide occurrence of black locusts, this matter requires research.

The main aim of this research is to compare the chemical composition of different tissues of black locust and the soil in which they grow, as well as their role in the functioning of disturbed areas. Additionally, it shows whether *R. pseudoacacia* accumulates pollutants from soils and whether this has impacted its ability to colonize adverse habitats. By the term "accumulation", we mean the enrichment of contaminants in plant tissues due to root uptake.

2. Materials and Methods

2.1. Sampling Sites

Five different locations with varying degrees of transformation were selected for testing (Table 1). The land-use classification was provided according to Corine Land Cover legend (CLC) [30]. In all localizations, soil degradation resulted from human activity. The site selection was based on different land uses. At all five sites (Figure 1), the black locust is a common plant, often forming large thickets in the form of clumps. A level of disturbance was assigned to each area. The basis of the criterion for each group was the degree of anthropogenization of the area. The areas with the highest amounts of anthropogenic artifacts are classified as extreme. As the impact of anthropogenizes on the environment decreased, the area was classified to a lower level. Among the analyzed objects, the arable field in Zawada was considered to be the least anthropogenized area. At this localization, anthropopressure consists of cultivating the land, and the soil is natural.

		Geographical		Site	Attributes		
Site No.	Site Name	Coordination	Habitat	Level of Disturbance	Land Use Classification	Method of Restoration	Soil Type
1	Sosnowiec–Dębowa Góra	50°15′29.71″ N 19°08′56.37″ E	Dumping site with building materials and used electronic equipment	Extreme	Urban and industrial site	Spontaneous succession	Technic regosol, technic anthrosol
2	Sosnowiec–Kazimierz Górniczy	50°17′02.40″ N 19°14′24.11″ E	Spoil heap of coal mining excavation material, with a high share of fine-grained material	Very high	Mine, dump, and construction site	Spontaneous succession	Technic regosol, technic anthrosol
3	Sosnowiec-Sielec	50°17′10.43″ N 19°08′34.59″ E	Artificial surfaces, urban parks with decorative plant species	High	Green urban areas	Planting	Urbic technosol, mollic technosol
4	Rogoźnik	50°24′01.35″ N 19°02′02.82″ E	Reclaimed area with artificial plantings	Medium	Former mineral extraction sites, green urban areas	Spontaneous succession	Mollic antroposol, arenosole
5	Zawada	50°23′10.64″ N 18°40′02.71″ E	Edge of an arable field	Low	Non-irrigated arable land	Spontaneous succession	Haplic luvisols, albic luvisols

Table 1. The features of the sampling site characteristics.

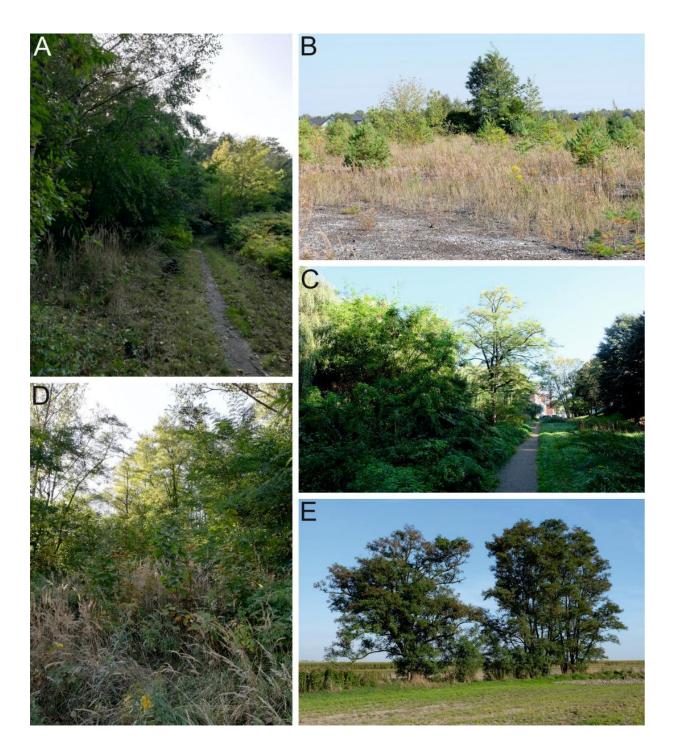


Figure 1. Sampling sites of black locust tissues and soils: (**A**) wild landfill in Sosnowiec–Dębowa Góra; (**B**) coal-mining heap in Sosnowiec–Kazimierz Górniczy; (**C**) city park in Sosnowiec–Sielec; (**D**) old sandpit area in Rogoźnik; (**E**) edge of a field in Zawada village.

All five sampling sites are located in the Silesian Upland area (southern part of Poland, Europe) (Figure 2).

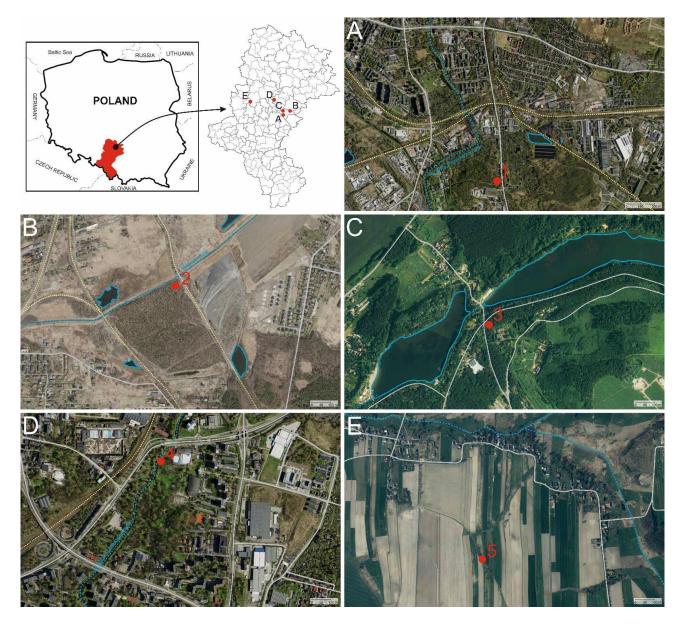


Figure 2. Location of Silesia on the background of the Polish contour map and localization of the sampling sites in the contour map of the Silesia: (**A**–**E**) satellite photos of the sampling sites. Red dot—sampling site; blue dotted line—watercourses; blue line—water reservoirs; yellow dotted line—railroads; grey lines—larger access roads.

We selected three different sites from Sosnowiec:

The first one is the Debowa Góra area, where a wild landfill has been formed (Figures 1A and 2A). Building materials and used electronic equipment have been abandoned there without any environmental protection.

The second one is the coal-waste dump formed by the KWK Kazimierz -Juliusz mine (Figures 1B and 2B). The mine was closed in 2015, but spontaneous vegetation succession started earlier as the dump was divided into two parts—the material was stored recently on only one part of the heap, where spontaneous succession is just beginning to develop. The samples of soil and *R. pseudoacacia* were taken from the part with older material, where there are developed trees.

The third site is an urban park located in the Sielec area (one of the Sosnowiec districts) (Figures 1C and 2C). It covers about 20 ha in the city center, and it is divided into an old

and new part by the Czarna Przemsza river. As it arose as a result of artificial planting, many alien and ornamental species can be found on its territory [32,33].

The fourth sampling site is located northwest of Bedzin city (Figures 1D and 2D). The samples were taken from the closed sandpit Siemonia from Rogoźnik field. In 1951–1959, sand was mined here, which led to the destruction of soil and vegetation covers [34]. Part of the sandpit was subject to the remediation processes toward the forest and park areas [34]. However, in the remaining part of the sandpit, the regeneration of biocoenosis was spontaneous [34]. The studied material was collected from the area where spontaneous vegetation succession has occurred.

The fifth sampling site is located about 15 km north of Gliwice city, near Zawada village (Figures 1E and 2E). The samples were collected from an unprotected area of arable land, where due to human activity, vegetation is significantly transformed and differs from the original systems. Agrocenoses rich in ubiquitous species predominate. Vegetation is presented as a mosaic of natural, semi-natural, and anthropogenic communities. The samples were collected from an *R. pseudoacacia* bush growing on the edge of farmland.

2.2. Soil and Plant Sampling

Soil samples for chemical analyses were taken only in the humus horizon (A), which averaged ca. 15 cm in thickness and represents the rooting zone of *R. pseudoacacia*. In the laboratory, air-dried samples were sieved (<2 mm) and analyzed, following the standard procedures of [35]—namely, pH was measured potentiometrically in H₂O and in 1N KCl using a glass electrode, total organic C (%) according to Tiurin's method, total N content (%) using the Kjeldahl method, and hydrolytic acidity (Hh) according to the Kappen method [35].

The leaves, branches, and seeds of *R. pseudoacacia* were sampled at the end of the vegetation season in late September and early October. All plants were identified by prof. Rahmonov. The preliminary preparation of the samples for analyses involved washing of the plant material with distilled water (the use of stronger agents can remove heavy metals), drying at room temperature for two weeks, and at 105 °C for 4 h, followed by homogenization. Sampling and preparation procedures followed the instructions given by MacNaeidhe [36] and Markert [37].

Concentrations of elements in plant material and soil were measured using inductively coupled plasma optical emission spectrometry (ICP–OES). Before analyses, all samples were submitted for wet mineralization in nitrohydrochloric acid (3HCl + HNO₃). The analyses were performed in the ACME Laboratory (Vancouver, Canada) using the AQ250_EXT (soils) and VG105_EXT (plant tissues) procedures and 5 g samples. All plant tissues and soil samples were analyzed in triplicate for all the investigated parameters and mean values were calculated.

2.3. Estimating Pollutant Impact

To determine the heavy metal concentration and their enrichment in soil and *R. pseudoacacia*, we calculated chemical indexes used in similar studies [38–40]—namely, geoaccumulation index (Igeo), enrichment factor (EF), contamination factor (CF), pollution load index (PLI), potential ecological risk index (RI) and bioaccumulation factors (BAF).

2.3.1. Index of Geoaccumulation

The geoaccumulation index (Igeo) allows evaluating the degree of metal contamination or pollution in studied soil. It was calculated using an equation given by Okedeyi et al. [39], Igeo = $\log_2\left(\frac{C_n}{1.5B_n}\right)$, where C_n is the content of the element in the sample, and B_n is the concentration of the same element in the upper continental crust [41]. The use of the chemical composition of the upper continental crust as a reference value is a standard procedure used in various kinds of environmental studies [42–46]. The 1.5 factor is used to minimize the effect of possible variations in the background values [47]. Based on the

increasing value of the geoaccumulation index, the seven contamination classes can be assigned [48] as follows:

- If Igeo < 0, unpolluted;
- If 0 ≤ Igeo < 1, unpolluted to moderately polluted;
- If $1 \leq$ Igeo < 2, moderately polluted;
- If $2 \leq$ Igeo < 3, moderately to strongly polluted;
- If $3 \leq$ Igeo < 4, strongly polluted;
- If 4 ≤ Igeo < 5, strongly to very strongly polluted;
- If $5 \leq$ Igeo, very strongly polluted.

2.3.2. Enrichment Factor

The enrichment factor (EF) allows assessing the degree of metal enrichment in the soil. This method normalizes the content of metals with respect to a sample reference metal [47]. In this work, we applied Fe as reference metal, as it was successfully used before [39,49–52]. The EF was defined using the following formula: $\text{EF} = \frac{[C_{\text{metal}}/C_{\text{normalizer}}]\text{soil}}{[C_{\text{metal}}/C_{\text{normalizer}}]\text{control}}$, where C_{metal} is the content of metal, and $C_{\text{normalizer}}$ is the concentration of selected normalizer in soil and in control sample [41]. Based on the enrichment factor, the following five categories can be determined [53]:

- If EF < 2, deficiency to minimal enrichment;
- If $2 \le EF < 5$, moderate enrichment;
- If $5 \le EF < 20$, significant enrichment;
- If $20 \le EF < 40$, very high enrichment;
- If $40 \le EF$, extremely high enrichment.

2.3.3. Contamination Factor

The contamination factor (CF) can be calculated using the following formula: $CF = \frac{C_n}{B_n}$ [54], where C_n is element content in examined soil, and B_n is the background concentration of the same element [41]. It shows a degree of contamination related to the average crustal composition and can be distributed into the following four classes:

- If CF < 1, low contamination factor;
- If $1 \le CF < 3$, moderate contamination factor;
- If $3 \le CF < 6$, considerable contamination factor;
- If $6 \leq CF$, very high contamination factor.

2.3.4. Pollution Load Index

Based on the contamination factors, the pollution load index (PLI) was calculated according to the following equation: $PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times ... \times CF_n}$, where n is the number of the contamination factors [40]. To estimate PLI, we used the five highest contamination factors as suggested by Tomlinson et al. [55]. This index shows heavy metal contamination, and it can assume values <1 (absence of pollution) or 1< (existence of pollution) [55].

2.3.5. Potential Ecological Risk Index

The potential ecological risk index (RI) allows evaluating the heavy metal impact on the environment. It was calculated using the equation $RI = \sum E_r^i$, where E_r^i is the potential ecological risk factor of the specific element [40]. The E_r^i was calculated using the equation $E_r^i = T_r^i \times CF[40]$, where T_r^i is the toxic response factor of the metal given by Zhu et al. [56]. The ecological risk can be classified as follows [57]:

- If $E_r^i < 40$, low;
- If $40 \le E_r^i < 80$, moderate;
- If $80 \le E_r^i < 160$, considerable;
- If $160 \le E_r^i < 320$, high;

• If $320 \le E_r^i$, very high.

Additionally, the risk index can be divided into the following four classes [57]:

- If RI <150, low risk;
- If $150 \le \text{RI} < 300$, moderate risk;
- If $300 \le \text{RI} < 600$, considerable risk;
- If $600 \le \text{RI}$, very high risk.

2.3.6. Bioaccumulation Factor

The bioaccumulation factors (BAF) for *R. pseudoacacia* parts were calculated using the following formula: $BAF = \frac{C_b}{C_n}$, where C_b and C_n are heavy metal concentrations in the plant parts and soil, respectively [58].

3. Results

3.1. Soil Morphology

According to the World Reference Base for Soil Resources from 2015, the analyzed soils were defined as the technic regosol, technic anthrosol, urbic technosol, Mollic technosol, arenosole, and halpic or albic luvisols. Technosol types of soils are determined based on their artificial origin and contain a large number of artifacts. Directly under the canopy of R. pseudoacacia, the organic (O) and humus (A) horizons of different thicknesses are formed.

3.2. Chemical Properties of Soils and Level of Disturbance

The particle size analysis showed the differentiation of particular samples in terms of grain size (Table 2), which allows distinguishing two types of soil.

Table 2. Soil grain size.

		Percentage Share (%)										
	>10.00	10.00-5.00	5.00-2.00	2.00-1.00	1.00-0.50	0.50-0.25	0.25-0.10	0.10-0.05	< 0.05			
Wild landfill	2.8	1.4	2.9	2.5	25.0	33.8	18.8	6.5	6.3			
Spoil heap	5.2	8.7	17.7	17.4	10.3	16.5	10.8	5.1	8.3			
Ċity park	0.0	0.0	0.0	1.2	11.0	56.9	24.5	3.8	2.6			
Old sandpit	0.0	0.0	0.7	1.3	5.4	46.1	33.9	8.7	3.9			
Fields edge	0.0	0.0	1.0	1.2	15.0	41.9	22.5	6.1	12.3			

The first one had a very diverse fractional composition with an admixture of medium (>10.0 and 5.0 < d < 10.0) and fine ($2.0 < d \le 5.0$) pebbles. This type of soil was found in the wild landfill and spoil heap. The soil from the landfill contained the coarsest ($0.5 < d \le 1.0$) and medium ($0.25 < d \le 0.5$) sand, whereas soil from the spoil heap had a content of fine pebbles, very coarse ($1.0 < d \le 2.0$), and medium sand on a similar level (about 17%) with a high amount (about 10%) of coarse and fine ($0.1 < d \le 0.25$) sand.

A completely different fractional composition was found in soils from areas with a lower degree of anthropogenization. We did not observe such differentiation in terms of soil granulation composition. They were mainly composed of medium (56.9–41.9 %) and fine (33.9–22.5%) sands. Medium pebbles were no longer present, and the fine pebbles were minor admixtures (1.0–0.0%) only. The silt and clay content did not exceed 10% in all soils, except for soil from fields, where its content was 12.3%.

Studied soils were mostly more or less acidic. The pH values were within the ranges 5.48–6.81 in H₂O and 4.70–6.37 in KCl (Table 3); hence, examined soils could be classified from very strongly acidic to neutral. The most acidic soil was found in the spoil heap, whereas pH values closest to neutral were observed for the soil from the field's edge. The highest level of hydrolytic acidity (H_h) was recorded in two sites: wild landfill (11.80 cmol(+)·kg⁻¹) and old sandpit (11.88 cmol(+)·kg⁻¹). The samples from the field had the lowest hydrolytic acidity value, at 7.48 cmol(+)·kg⁻¹. This variability is related to the fact that by colonizing the transformed areas, *R. pseudoacacia* initiates soil formation pro-

cesses on anthropogenic formations characterized by different granulometric compositions, which had a significant impact on the physicochemical properties of the soil.

	Wild Landfill	Spoil Heap	City Park	Old Sandpit	Fields Edge
pH (H ₂ O)	5.94	6.81	6.29	5.70	5.48
pH (KCl)	5.16	6.37	5.37	5.02	4.70
Loss ignition	5.72	29.67	9.53	5.01	2.83
C _{org} (%)	3.52	19.61	5.28	2.04	1.42
N _{tot} (%)	0.109	0.528	0.273	0.304	0.098
Mg _{avail} (mg/kg)	108.50	401.00	143.50	99.00	54.20
P _{avail.} (mg P ₂ O ₅)/kg)	26.77	14.30	40.81	17.27	36.10
P_{T} (mg/kg)	375.00	362.00	379.00	202.40	276.40
K_{avail} (mg/kg)	86.00	212.50	205.00	153.00	166.50
K_{avail} (mg K_2O/kg)	103.63	256.06	247.03	184.37	200.63
H_h (cmol(+)·kg ⁻¹)	11.80	7.72	8.52	11.88	7.48
Al^{3+} (cmol(+)·kg ⁻¹)	0.36	0.60	1.28	0.56	1.52
H^+ (cmol(+)·kg ⁻¹)	1.04	0.72	1.52	0.36	1.36

Table 3. The chemical properties of soils.

3.3. Element Concentration in R. pseuodacacia Leaves, Seeds, and Branches

The elemental concentrations found in soil and *R. pseudoacacia* leaves, branches, and seeds are very diverse. The detailed analysis results are presented in Tables S1 and S2 in the Supplementary Materials.

3.3.1. Major Element Concentration

The most concentrated elements found in soils and plants from all sites were Fe, Ca, P, Mg, Al, K, and S. The Fe and Al concentrations in soil (0.70–2.24% and 0.40–0.83%, respectively) were higher than in the plant parts (0.01–0.03% Fe and <0.01% Al). The Mg content varied in the soils (0.07–0.35%), and its level declined with decreasing land degradation, whereas in plant parts, its content remained at similar levels (leaves 0.10–0.25%; branches 0.04–0.13%; seeds 0.0.09–0.11%). The Ca level was highest for the leaves and branches (1.14–2.37% and 0.64–1.47%, respectively), while the most K, P, and S could be found in the seeds (K 1.23–2.20%, P 0.13–0.27%, S 0.09–0.30%) and leaves (K 0.49–1.01%, P 0.07–0.15%, S 0.09–0.17%).

In addition to the elements mentioned above, magnesium also had high concentrations in soil, exceeding contents found in plant parts. The Mn amount was high (218.00–487.00 ppm) for all the examined soil samples. In black locust samples, Mn was accumulated mainly in leaves (up to 167.67 ppm). Mn content in seeds and branches was similar (10.67–43.00 ppm for seeds and 8.33–39.33 ppm for branches), but more often, the amount in seeds was slightly higher than in branches.

3.3.2. Heavy Metal Concentration

The heavy metals concentration was higher in each examined soil than in the *R. pseudoacacia* parts (Table 4). Apart from iron, the highest heavy metal concentrations had been observed for zinc (129.77–543.97 ppm) and lead (78.17–157.99 ppm). The Zn was accumulated in each part of the black locust. The highest concentrations were present in the leaves (30.33–103.37 ppm) and branches (27.60–103.90 ppm), whereas seeds had contained reduced zinc content (23.77–60.09 ppm). The highest Zn concentration was recorded for the urban park area and landfill, while the lowest was for agricultural areas.

		Fe	Pb	Cd	Zn	Cu	Ni	Cr	As	Hg
		%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb
	Wild landfill	2.24	89.71	2.50	305.37	50.29	24.97	56.60	7.07	144.00
Ś	Spoil heap	2.07	78.17	1.30	188.03	37.11	28.27	18.73	4.23	262.33
Soils	Čity park	1.07	157.99	3.91	543.97	32.69	9.80	13.03	11.77	155.33
S	Sandpit area	0.70	152.86	3.24	200.03	9.33	7.60	8.70	8.87	47.67
	Field edge	0.79	103.06	1.41	129.77	11.24	7.27	12.80	8.97	66.67
	Wild landfill	0.03	2.70	0.58	103.37	8.47	3.17	1.40	0.23	33.67
es	Spoil heap	0.02	3.28	0.26	30.33	6.10	1.03	1.47	0.10	24.33
Leaves	Čity park	0.02	2.93	0.20	61.67	3.93	0.30	1.53	0.27	29.67
Le	Sandpit area	0.01	3.46	0.37	44.40	6.39	0.40	1.33	< 0.01	15.00
	Field edge	0.02	4.12	0.77	94.53	9.04	2.57	1.30	0.03	29.67
	Wild landfill	0.01	3.17	0.63	94.93	9.48	4.63	1.60	< 0.01	3.00
hes	Spoil heap	0.01	3.51	0.15	27.60	7.07	1.53	1.23	0.03	3.00
Branches	Čity park	0.01	1.74	0.19	80.63	7.21	0.90	1.77	0.03	2.33
3ra	Sandpit area	0.01	8.02	0.89	61.93	6.47	0.67	1.73	< 0.01	4.33
	Field edge	0.03	16.35	1.18	103.80	8.69	4.93	1.60	0.13	14.67
	Wild landfill	0.01	0.75	0.18	60.90	10.60	6.20	1.17	0.03	3.33
s	Spoil heap	0.01	0.52	0.06	23.77	6.83	3.17	1.63	< 0.01	1.67
Seeds	Ċity park	0.01	1.21	0.09	49.67	4.98	0.57	1.30	< 0.01	4.67
Se	Sandpit area	0.01	2.53	0.37	46.37	6.96	0.47	1.17	< 0.01	3.67
	Field edge	0.01	4.91	0.51	54.27	6.52	1.93	1.67	0.03	9.33

Table 4. The mean value of heavy metals concentration in studied samples.

The lead content was on a high level for all the studied areas (78.17–157.99 ppm). In the plant parts, its level is significantly lower (0.52–16.35 ppm). Other heavy metals found in both soil and plant were Cu, Ni, and Cr. In each of these cases, the soil contained more pollutants than plant parts. Its content in soil samples was variable, and it declined with the overall contamination level. The highest amounts of its content were noted in the soil from the landfill area (Cu 50.29 ppm, Cr 56.60 ppm) or coal dump (Ni 28.27 ppm), and the lowest in the sandpit (Cu 9.33 ppm, Cr 8.70 ppm) and farmland (Ni 7.27 ppm). In the plant parts, Cu and Ni contents were similar, in the 3.93–10.60 ppm range for Cu and 0.30–6.20 ppm for Ni. The Cr content in *R. pseudoacacia* elements was constant at 1.16–1.76 ppm. The As and Co were present in small amounts (As 4.23–11.77 ppm and Co 3.10–11.57 ppm), mainly in soil. In black locust samples, their content did not exceed 0.30 ppm. Additionally, in the soil chemical composition, Li and V concentrations were present only in small amounts (Li 3.47–16.27 ppm), V 10.00–31.67 ppm), and in the plant parts, they were not detected. The higher amounts of both elements were observed from the soils from degraded areas.

3.3.3. Concentration of Minor Elements

Among the examined minor elements, several were accumulated in a greater amount in the *R. pseudoacacia* parts than in the soil. These include Ba, B, Rb, Sr, and Mo. The highest concentrations were mostly found in the leaves (Ba 13.17–79.10 ppm, B 29.33–96.33 ppm, Sr 19.87–122.53 ppm, Mo 0.14–2.01 ppm), except for Rb, which was mainly found in seeds. The highest concentration of Rb was found in the seeds from the coal dump (139.87 ppm), while in other localities, it was in the 7.70–29.30 ppm range. Boron was the only element from this group that was not found in soil at all. In the soils from all localization, the content of the other elements was generally low and on a similar level (Ba 66.40–114.50 ppm, Rb 6.33–18.70 ppm, Sr 6.83–36.17 ppm, and Mo 0.55–1.29 ppm).

The three members from the rare earth elements group were found in soils: La, Ce, and Y. Their content was the highest in the most degraded soil from the wild landfill area (La 21.67 ppm, Ce 42.70 ppm, and Y 10.29 ppm), and was gradually reduced with the decreasing degree of anthropopressure. They did not accumulate in any part of the plant.

3.3.4. Trace Elements Content

The trace elements were mainly Ag and Hg. They were found primarily in soils, and their highest content was present in the heavily degraded areas—landfill (Ag 401.67 ppb)

and coal dump (Hg 262.33 ppb). A small amount of *R. pseudoacacia* accumulated in the leaves (up to 18.00 ppb for Ag and 33.67 ppb for Hg) and branches (up to 13.67 ppb for Ag and 14.67 ppb for Hg), while the least amount was in the seeds (up to 7.67 ppb for Ag and 9.33 ppb for Hg). Other trace elements such as Au, Pd, and Pt were only found in very small amounts in soils (up to 9.57 ppb, 36.33 ppb, and 1.67 ppb, respectively). The only one trace element found only in black locust samples was Re, which occurred in leaves (up to 22.33 ppb) mostly.

3.4. The Level of Heavy Metal Contamination in Soil and Plant (Robinia pseudacacia)

The index of geoaccumulation (Igeo) shows that Cd was the element with the most significant impact on the level of contamination in all the areas studied (Table 5). It classified soils from strongly to very strongly polluted. It also showed moderate pollution of Pb and Zn in all sampled soils (Table 5). The contamination from other elements—Hg, Cu, and As—varied due to soil location from unpolluted to moderately polluted. The calculated Igeo index for Fe, Ni, and Cr had a negative or close to zero value, which indicates that these elements did not pollute tested soils.

Table 5. The geoaccumulation index (I-geo) of heavy metals within studied soils.

	Pb	Cd	Zn	Fe	Cu	Ni	Cr	Hg	As
Wild landfill	1.81	4.03	1.97	-1.05	1.23	-0.16	0.11	0.78	1.24
Spoil heap	1.61	3.09	1.27	-1.16	0.79	0.02	-1.49	1.64	0.50
City park	2.63	4.68	2.80	-2.11	0.61	-1.51	-2.01	0.89	1.97
Sandpit area	2.58	4.40	1.36	-2.73	-1.20	-1.88	-2.59	-0.82	1.56
Field edge	2.01	3.20	0.73	-2.55	-0.93	-1.94	-2.04	-0.34	1.58

The enrichment factor (Table 6) showed similar results to Igeo. All samples were characterized by notable (spoil heap), very high, or extremely high Cd enrichment, and significant to very high Pb and Zn enrichment. The obtained EF for Cu, Hg, and As indicated moderate-to-significant enrichment of these elements in studied soils. Low EF for Ni and Cr classified its content as "deficiency to minimal enrichment".

	Pb	Cd	Zn	Fe	Cu	Ni	Cr	Hg	As
Wild landfill	7.28	33.80	8.10	1.00	4.5	1.85	2.23	3.55	4.87
Spoil heap	6.86	19.02	5.40	1.00	3.87	2.27	0.80	6.99	3.16
Ĉity park	26.83	110.67	30.20	1.00	6.60	1.52	1.07	8.01	16.99
Sandpit area	39.68	140.17	16.98	1.00	2.88	1.80	1.10	3.76	19.57
Field edge	23.70	54.05	9.76	1.00	3.07	1.53	1.43	4.61	17.54

Table 6. The enrichment factor of heavy metals within sampling sites.

Calculated CF showed a very high level of contamination for Cd and very-high-toconsiderable contamination for Pb and Zn. The CF class of As and Hg varied between moderate and considerable contamination factors, whereas Fe, Cr, Ni, and Cu belonged to the low or moderate contamination class. The potential ecological risk index obtained for studied areas (Table 7) indicated that in all locations, pollution was present.

Table 7. Contamination factors for heavy metal and pollution load index for each study area.

	Pb	Cd	Zn	Fe	Cu	Ni	Cr	Hg	As	PLI
Wild landfill	5.28	24.51	5.87	0.73	3.52	1.34	1.62	2.57	3.54	7.57
Spoil heap	4.60	12.75	3.62	0.67	2.60	1.52	0.54	4.68	2.12	7.80
Ċity park	9.29	38.33	10.46	0.35	2.29	0.53	0.37	2.77	5.89	9.29
Sandpit area	8.99	31.76	3.85	0.23	0.65	0.41	0.25	0.85	4.44	7.07
Field edge	6.06	13.82	2.50	0.26	0.79	0.39	0.37	1.18	4.49	5.56

The potential ecological risk for most studied elements was low (Table 8). Higher values characterized only Hg and Cd. The potential ecological risk for mercury varied between low (sandpit area) and high (spoil heap), whereas cadmium could be classified as a very high potential ecological risk in all localizations. The risk index that assessed the contamination level showed that only soils from the edge of the field belonged to the considerable risk class. The rest of them were characterized by a very high risk index. This shows that all of the studied soils had been strongly changed as a result of human pressure. Although the element with the most significant impact on the pollution level was cadmium. The area with the highest ecological risk was the city park. Additionally, sandpit and wild landfills had very high RI values, whereas soil from the spoil heap yielded RI values not much greater than the border, between very high and considerable risk.

Table 8. Potential ecological risk factor of measured heavy metals and potential ecological risk index (RI) for each study area.

	Pb	Cd	Zn	Fe	Cu	Ni	Cr	Hg	As	– RI
T_r^{i1}	5	30	1	1	5	5	2	40	10	- 10
Wild landfill	26.39	735.29	5.87	0.73	17.58	6.71	3.23	102.86	35.35	934.01
Spoil heap	22.99	382.35	3.62	0.67	12.96	7.60	1.07	187.38	21.15	639.80
City park	46.47	1150.00	10.46	0.35	11.43	2.63	0.74	110.95	58.85	1391.88
Sandpit area	44.96	952.94	3.85	0.23	3.26	2.04	0.50	34.05	44.35	1086.18
Field edge	30.31	414.71	2.50	0.26	3.93	1.95	0.73	47.14	44.85	546.38

¹ Toxic response factor adopted from Zhu et al. [43].

3.5. Comparison of Heavy Metal Content in the Soil–Plant–Soil System

The bioaccumulation factors for *R. pseudoacacia* parts are listed in Table 9. The accumulation factors can be listed in descending order as follows:

- For leaves: Cu > Zn > Hg > Cd > Mn > Ni > Cr > Pb > Fe,Co,As;
- For branches: Cu > Zn > Cd > Ni > Cr > Hg > Pb > Mn > Co > Fe, As;
- For seeds: Cu > Zn > Ni > Cd > Cr > Mn, Hg > Pb > Co, Fe.

Table 9. Bioaccumulation factors (BAF) values for heavy metals in examined *R. pseudoacacia* parts.

	Cu	Pb	Ni	Со	As	Cd	Cr	Hg	Zn	Mn	Fe
Leaves	0.39	0.03	0.12	0.02	0.02	0.23	0.10	0.26	0.31	0.19	0.02
Branches	0.41	0.06	0.22	0.02	0.01	0.31	0.11	0.07	0.34	0.05	0.01
Seeds	0.37	0.02	0.15	0.01	0.00	0.12	0.09	0.06	0.21	0.06	0.01

According to the ranges for bioaccumulation factors provided by Sekabira et al. [58], *R. pseudoacacia* should be considered as a low or moderately heavy metal accumulator plant. The highest BAF value in all plant parts was recorded for Cu and Zn. The *R. pseudoacacia* leaves were average accumulators for Hg compared with branches, which were better accumulators for Cd and Ni. Seeds had the lowest value of BAF. Except for Cu and Zn, they were low accumulators for heavy metals. Only Ni and Cd could be regarded on the low and moderate borderline.

4. Discussion

Today, *R. pseudoacacia* is one of the most planted tree species in different countries due to its effectiveness in greening [59,60]. In Europe, this species is mainly planted along road-sides, in urban and rural areas, as it is resistant to environmental pollution [61]. *R. pseudoacacia* is widely employed in vegetation restoration in many degraded areas [7], attributable to its rapid growth and its proficiency at fixing nitrogen from the atmosphere [25,26].

The impact of *R. pseudoacacia* on the natural environment can be assessed in two ways. On the one hand, it is an invasive plant that displaces native species and reduces biodiversity. On the other hand, it is a species that positively influences the degraded areas, as it can initiate soil-forming processes [12]. Due to the high fallout in the annual cycle of the black locust leaves and its fast decomposition, it is a good source of organic matter [12]. R. pseudoacacia, as a nitrogen-fixing plant, can affect the dynamic characteristics of the community, particularly for those habitats with poor nutrient surroundings [24]. The annual black locust biomass production (mainly plant litter: leaves, pods) enriches the poor or initial soil with mineral and organic matter, on which pedogenesis often depends. In the chemical composition of *R. pseudoacacia* leaves, substantial contents of Ca (1.14–2.38%), K (1.30–1.49 %), Mg (0.10–0.26%), and P (0.14–0.16%) can be observed. After decomposition, the elements return to the soil as potential nutrients. It is one of the most important sources of nutrients for plants. It contributes to the rapid formation of the humus level and creates improved conditions for more demanding species. Previous works suggest that besides nutritional substances, black locust also accumulates heavy metals [15]. We examined R. pseudoacacia from five different localizations with various changes in the intensity of anthropogenic processes.

Comparing the results presented in this paper with data from the Geochemical Atlas of the Upper Silesia [62], it can be seen that the content of heavy metals in the tested samples is similar to the range of the same elements in surrounding soils. Due to Regulation of the Minister of the Environment on 5 September 2016 regarding the assessment method of the pollution of the earth's surface (*Journal of Laws*, 2016, item 1395), the results obtained do not exceed the group IV standards, including communication, industrial, and mining areas.

In all of the sites, heavy metals were present at different concentrations in the soil. The calculated chemical indices show that all studied soils are contaminated by heavy metals, especially cadmium, zinc, lead, and mercury. The presence of these elements is connected with urbanization and causes soil degradation and contamination [37]. The element with the greatest impact on the level of pollution is undoubtedly cadmium. The source of cadmium is most probably connected with industrialization—mining, coal combustion, or using phosphate fertilizers [63]. All of this occurred in the Silesian agglomeration and may contribute to soil pollution.

Despite the different degrees of anthropopressure, all studied soils were characterized by heavy metal values not exceeding the maximum allowable concentrations in agricultural soils in Poland provided by Kabata–Pendias [64]. However, comparing them with the limits on heavy metals in soil for other countries found by Okedeyi et al. [39], it can be derived that both Pb and Zn exceeded given standards. The rest of the heavy metals practically did not exceed the limit values. This shows that all examined soils were not strongly phytotoxic.

Calculated indices show that the most polluted soil came from the park in Sosnowiec. The reason can be related to its location—in the city center with numerous pollution sources. An interesting observation is the low pollution of soil, which was formed at a coal dump. This can be caused by a lack of fertilizers, which impact the level of cadmium. Similar results from soils formed at post-mining waste were presented before from Poland [65–67] and other countries, such as China [68]. The obtained results show that soils formed at coal dumps were not heavily enriched in heavy metals and did not exceed the pollution level specified by Polish law. Therefore, these soils should be regarded as non-phytotoxic similar to all other tested soils. This also explains why the succession was similar to that in other anthropogenically transformed areas. The lack of phytotoxicity in these soils is also indicated by the level of accumulated heavy metals in the *R. pseudoacacia* tissues [68]. The results obtained through the analysis of the content of heavy metals in the tested waste material, compared with the standards in force in Poland, industry guidelines, and studies in the literature, do not indicate their increased content. The content of almost all heavy metals in collected *R. pseudoacacia* leaves was within the proposed amounts for normal

concentrations in mature leaf tissues [69]. Only Cd exceeded the range listed for normal concentrations but did not reach the ranges listed for toxic amounts.

Analyses of the chemical composition of the *R. pseudoacacia* parts show that the highest content of almost all metals was accumulated in the plant leaves. This confirms the conclusions from previous works [15], which also indicate leaves as carriers of the highest amounts of pollutants. The only exceptions were K, Si, and Rb, which were accumulated in higher amounts in the seeds, and Zn, which was accumulated in high amounts in the branches. Additionally, the BAF values show that leaves and branches were the most pollutant-accumulating tissues. The lowest bioaccumulation factors were observed for seeds. Low heavy metal content in the *R. pseudoacacia* and low BAF values indicate that there was no relation between the content of heavy metals in the environment and the plant parts. Analyses reveal that high amounts of alkali metals (K, Ca, Na) in black locust tissues are potential enrichment materials for the habitats. This is important due to fact that the content of available elements in the soil was low, indicating a poor soil nutrient index, which is related to the particle size composition of the analyzed material, dominated by coarse and medium sands.

Compared with approximate concentrations of trace elements in leaves for various species provided by Kabata-Pendias [64], the heavy metal content was below average and should not be considered toxic. The only element with a higher amount was Cd in the leaves collected from the farmland area. However, the concentration of heavy metals in the plant tissue exceeded the content recommended for edible plants listed by World Health Organization [39].

The results obtained from *R. pseudoacacia* branches in terms of Cd content (0.15–1.18 ppm) were significantly lower than the results from post-industrial areas (2.48 ppm) found by Palowski et al. [15]. Low heavy metals content was also observed in the case of Pb (1.74–16.35 ppm) and Cu (6.47–9.48 ppm) concentrations in branches in comparison with other works, where the content of these elements was for Pb, 29 ppm, and for Cu, 9.69 ppm. Similar observations were made for the content of heavy metals in *R. pseudoacacia* leaves. Additionally, Samecka-Cymerman et al. [61] have found similar results. They stated that the bark of R. pseudoacacia is a good bioindicator of long-term cumulative traffic pollution, whereas leaves are good indicators of short-term seasonal accumulation trends. In the studied areas, the obtained heavy metal contents are Zn: 129.77–543.99 ppm; Pb: 78.17–157.99.2 ppm; Cd: 1.30–3.91 ppm; Ni: 7.60–24.97 ppm; Cu: 9.33–50.29 ppm. The results of research on soils on which R. pseudoacacia develops conducted by Samecka–Cymerman et al. [61] are characterized by lower ranges of the content of the following elements: Zn: 132–381 ppm; Pb: 30–99 ppm; Cd: 0.6–1.9 ppm; Ni: 8.9–17.8 ppm; Cu: 14–37 ppm. Nevertheless, the results of heavy metal content in leaves obtained by us are similar (Zn, Cr) or lower (Pb, Cd, Cu, Ni) than values presented by Samecka–Cymerman et al. [61].

The issue worth considering is whether the totality of our results is related to root uptake only. Research on the effectiveness of leaf washing shows that distilled water does not entirely remove surface contamination [70]. This may indicate that some heavy metals come from soil dust depositions. However, this does not affect the conclusions of our work.

All of our results show that regardless of the content of heavy metals, black locust is a moderate or low accumulator of heavy metals from soil. This indicates that *R. pseudoacacia* can be introduced into extremely polluted environments without affecting the condition of the plant. Despite the lack of significant amounts of nutritional products, black locust successfully colonizes areas with a minimum content of humus and minerals. Due to black locust plants' ability to adapt to very diverse ecological conditions, rapid growth rate, significant production of plant fallout, and non-accumulation of heavy metals, it is a suitable species for the reclamation of areas with degraded soils.

5. Conclusions

- By colonizing the transformed areas, *R. pseudoacacia* initiates soil formation processes on anthropogenic substrates characterized by different granulometric compositions, which significantly impacts the soil's physicochemical properties;
- Clear differentiation in terms of the main elements (Fe, Ca, P, Mg, Al, K, S) content was found in the chemical composition of black locust leaves, branches, seeds, and soil materials. These elements in the initial stages of ecosystem development are important nutrients for invading organisms. The results reveal a significant influence of *R. pseudoacacia* on the restoration of disturbed habitats;
- The content of heavy metals concentration was higher in soil than in the *R. pseudoacacia* analyzed tissues. In the case of plant tissues, the highest concentrations were in the leaves and branches, whereas seeds contained reduced zinc content;
- Based on the index of geoaccumulation (Igeo), it was determined that the content of Cd had the most significant impact on the level of contamination of the studied soils. This statement also confirmed the results of the enrichment factor (EF) and contamination factor (CF);
- Despite the anthropogenic character of soil material and location within the investigated urban region, the potential of ecological risk for most studied elements was low—higher values were only found for Hg and Cd;
- BAF analysis indicates that *R. pseudoacacia* is a weak accumulator of heavy metals. Within the analyzed elements, Cu and Zn accumulated the most.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/f13010007/s1, Table S1: Chemical composition of soils, Table S2: Chemical composition of *Robinia pseudoacacia* parts.

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