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Assessment of Heavy Metals (Cr, Cu, Pb, and Zn) Bioaccumulation and Translocation by *Erigeron canadensis* L. in Polluted Soil

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Abstract: This work aims to assess the bioavailability and bioaccumulation of Cr, Cu, Pb, and Zn in the soil–plant system (*Erigeron canadensis* L.) in the zone of anthropogenic impact in Dnipro city, a significant industrial and economic centre of Ukraine. Sampling was carried out at three locations at distances of 1.0 km, 5.5 km, and 12.02 km from the main emission sources associated with battery production and processing plants in Dnipro. The concentrations of heavy metals such as Cr, Cu, Pb, and Zn were analysed using atomic emission spectrometry from soil and parts of *Erigeron canadensis* L. The highest concentrations of elements in the soil, both for the mobile form and the total form, were determined to be 48.96 mg kg⁻¹ and 7830.0 mg kg⁻¹, respectively, for Pb in experimental plot 1. The general ranking of accumulation of elements in all experimental plots, both for the plant as a whole and for its parts, was as follows: Zn > Cu > Cr > Pb. Zn for plants was the most available heavy metal among all studied sites and had the highest metal content in the plant (339.58 mg kg⁻¹), plant uptake index (PUI-506.84), bioabsorption coefficient (BAC-314.9), and bioconcentration coefficient (BCF-191.94). According to the results of the study, it is possible to evaluate *Erigeron canadensis* L. as a hyperaccumulator of Zn, Cu, and Cr and recommend it for phytoextraction of soils contaminated with Zn, Cu, and Cr and phytostabilization of soils contaminated with Pb.

Keywords: metals (Cr, Cu, Pb, Zn); plant uptake; translocation; phytoremediation; soil; *Erigeron canadensis* L.



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1. Introduction

With industrialization, the consumption of heavy metals (HMs) has increased tremendously in developing countries [1–3]. As a result, HM pollution is raising concern for public attention [4]. Organic pollutants can be fully or partially transformed by various (micro)organisms or degraded by plants, but HMs do not transform and can only be changed into forms with altered toxicity and/or mobility/bioavailability [1,2]. The stability of HMs in the environment, especially in soils, sediments, and water bodies, has been confirmed [5]; for example, Pb can last up to 2000 years in soil and is unsafe for plants [6]. Thus, HM contamination is a long-term environmental and human health risk in urban and post-urban regions, including Ukraine [7–16]. The main harmful factors of HM are toxicity, toxicogenicity, and carcinogenicity [17].

For agricultural production, the accumulation of heavy metals (HMs) of anthropogenic origin leads to a decrease in productivity and a deterioration in product quality [18–20]. Several recent reports indicate that the availability of anthropogenic micronutrients to plants is significantly higher than that of naturally occurring micronutrients, regardless of their forms [21]. For example, in agricultural soils in China, 77.10% of HMs originate

from anthropogenic sources, highlighting the significant impact of this source on HM accumulation in soils [22]. Moreover, the rate of lead deposition in soil exceeds its natural removal by 20 times or more [23]. Metals are ubiquitous [24], and in the process of evolution, plants developed appropriate response mechanisms that mitigate the stress damage caused by HMs in plants, i.e., tolerance [25,26].

Phytoremediation is a method of removing accumulated toxic elements from the environment with the help of plants and associated microorganisms [27,28]. One of the main strategies of phytoremediation is phytostabilization and phytoextraction. Phytostabilization involves the use of toxic-resistant plant species to immobilize HMs in the soil, thereby reducing their bioavailability, preventing their migration into the ecosystem, and decreasing the likelihood of them entering the food chain [29–32]. Phytoextraction refers to the use of plants to absorb pollutants from soil or water, transport them, and accumulate these pollutants in their aboveground biomass [33]. Phytoextraction provides a constant solution for removing HMs from contaminated soil [34,35], making it more suitable for commercial applications [36].

Phytoremediation is an affordable and promising natural method of remediation of soils with HMs, which has received wide public recognition and has a number of advantages over other physical and chemical methods. [29,37]. At the same time, the content and impact on environmental components, in particular phytocomponents, as well as the bioaccumulation of these elements have not been sufficiently studied [38–40].

The city of Dnipro with a population of approximately 1 million residents is located in the southeastern part of Ukraine. Dnipro is polluted with HMs due to industrial activities [13,14]. The presence of an excessive amount of HMs requires measures to reduce this pollution, taking account of the danger to the environment and negative socioeconomic effects [15,16]. In our previous studies, we analysed the bioaccumulation of HMs by *Ambrosia artemisiifolia* L. in contaminated soil (1.0 km from the main sources of pollution from emission sources due to battery manufacturing and processing facilities) [41], as well as the bioaccumulation of Cr, Zn, Pb, and Cu in *Erigeron canadensis* L. and *Ambrosia artemisiifolia* L. (12.02 km from the abovementioned sources of pollution) [42]. In addition, Hg, Cr, Zn, As, Cd, Pb, and Cu were detected in the soil–plant system (*Matricaria chamomilla* L.) (0.7 km from the abovementioned pollution sources) [43].

In this research, we analysed and summarised the results of bioaccumulation and translocation of HMs (Cr, Zn, As, Cd, Pb, and Cu) in the soil–plant (*Erigeron canadensis* L.) system at all experimental plots.

Erigeron canadensis L. (or *Conyza canadensis* L.) is a genus of herbaceous plants of the aster family, one of the most common weeds that grows on all continents, but it is most common in the northern temperature zone. It is a one- or two-year erect (up to 200 cm) herbaceous plant with a branched root system, and it grows throughout Ukraine on sandy soils, garbage dumps, fields, near houses, roads, on railway embankments, in forest strips, etc. [44], and is also resistant to herbicides [45]. The flowering parts of *Erigeron canadensis* L. are used mainly as raw materials in folk medicine [46,47], and are also recommended in official medicine [48,49].

According to previous studies, *Erigeron canadensis* L. demonstrated the ability to bioaccumulate many elements under different conditions and is recognised as an effective plant for phytostabilization and phytoextraction of toxicologically polluted soils [50–55]. It is considered a promising candidate as a hyperaccumulator plant, potentially effective for the phytoremediation of contaminated soils [56].

In Ukraine, there are no regulations governing the concentration of HMs in the phytomass of medicinal plants, so our study can serve as a basis for further development of indicators of phytotoxicity and phytoavailability of plants. Given the importance and necessity of phytoremediation development as an effective, cost-effective, and environmentally friendly approach to minimizing anthropogenic environmental pollution, a more in-depth analysis of the soil–plant system is required in the future, and our results and methodology can be applied to similar soil conditions in other regions of the world. Despite

numerous studies in the field of phytoremediation, our study is the first to analyse in detail the potential of *Erigeron canadensis* L. for phytoextraction of HMs on contaminated soils of Ukraine with specific physicochemical characteristics.

2. Materials and Methods

The concentrations of the metals (Cr, Zn, As, Cd, Pb, and Cu) in soil and *Erigeron canadensis* L. were studied at three research plots located at distances of 1.00 km, 5.5 km, and 12.02 km from the main sources of battery production and waste battery recycling facilities in Dnipro, Ukraine. Research plots 1 (P1-1.00 km) and 3 (P3-12.02 km) were presented in previous articles [52,53]. Figure 1 shows the location of the experimental plot 2.

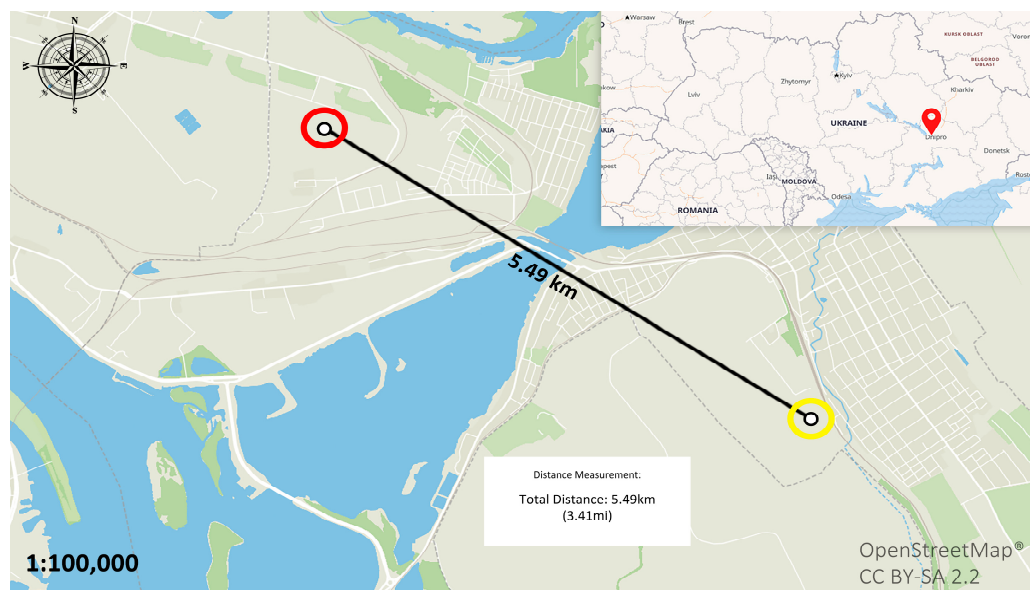


Figure 1. A map of the sampling sites. The yellow circle indicates the point-sample sites; the red circle indicates the point-enterprise location; the dark line is drawn at a distance of 5490 m from the source of pollution (enterprise for the production and processing of batteries in Dnipro city in Ukraine) to the sample site. The insert map is the Ukraine map. The red symbol indicates the city of Dnipro.

It should be noted that each study site is exposed to anthropogenic impact from several sources of pollution, except for the battery manufacturing facility and the waste battery recycling facility, which were identified as the main sources of pollution, namely, study plot 1 is located near the industrial zone “North”, which contains an enterprise for the collection and primary processing of ferrous and nonferrous scrap (0.5–1.0 km in the western direction); study plots 2 is located at a distance of 2.0–2.5 km from the slag lagoons of the Prydniprovskya Thermal Power Plant (in the southern direction); research site 3 is situated 3.3 km northwest of the Novomoskovsk Pipe Plant and 50.0 m north of the M04 (E50) highway, which could influence the concentration of HM in both soil and plants, potentially impacting the results. Future studies under realistic “field” conditions should take these factors into account and, where possible, use methods to minimise possible errors, such as the use of atmospheric transport modelling of pollutants or chemical marker analysis to identify individual sources, etc. Overall, the study area has been significantly transformed by anthropogenic activities [57].

Soil and *Erigeron canadensis* L. samples were collected in July 2021 following the requirements of Ukrainian state standards [58] (DSTU 4287:2004, DSTU ISO 10381-4-2005, DSTU ISO 10381-1:2004, DSTU 4770.3-DSTU 4770.9). Soil samples were taken from a 10 × 10 m plot (100 m²) using the “envelope” method, with four sampling points at the corners and one at the centre, totalling 5 points, and summarized in 4 replicates. The soil sampling depth was 0–20 cm, and each sample weighed between 1.0 and 1.2 kg. Twenty plant samples were separately collected from three soil sampling locations. The soil in the

study area is classified as ordinary low-humus chernozem on heavy loess loam (with a pH of 6.7 and organic matter content of 4.4% according to the Turin and Walkley–Black method). According to the American soil classification system [59], chernozems fall under the Mollisols group. The experimental results were analysed using standard statistical techniques, with statistical parameters such as standard deviation, variance, and standard errors determined in triplicate.

Soil samples (extracted using an acetate–ammonium buffer at pH 4.8) and plant samples (extracted using a mixture of concentrated acids HNO₃ and H₂SO₄) were analysed by inductively coupled plasma atomic emission spectrometry (iCAP 7000 Plus DUO, Thermo Fisher Scientific, Bremen, Germany). The limits of detection for the elements Cr, Cu, Pb, Zn, As, and Cd in soil were 1.0, 0.5, 0.2, 1.0, 0.5, and 0.2 µg kg⁻¹, respectively. In plants, the limits of detection for Cr, Cu, Pb, Zn, As, and Cd were 4.0, 2.0, 10.0, 4.0, 0.1, and 0.8 µg kg⁻¹, respectively. The measured values for Cd and As in plant tissues (except for roots) were below the limits of detection; therefore, these elements were excluded from the analysis of the research results.

The following factors were used to assess the bioavailability and phytoremediation potential of plant species:

Plant uptake index of a toxic element (PUI) [41]:

$$PUI = C_{\text{plant}}/C_{\text{soil}}, \quad (1)$$

where PUI is the plant uptake index; C_{plant} —concentration in the total plant (dry matter), mg kg⁻¹; C_{soil} —concentration of the available form in the soil, mg kg⁻¹.

Bioabsorption coefficient (BAC) [60]:

$$BAC = C_{\text{shoot}}/C_{\text{soil}}, \quad (2)$$

where BAC is the bioabsorption coefficient; C_{shoot} —concentration in the vegetative and generative parts of the plant (dry matter), mg kg⁻¹; C_{soil} —concentration of the available form in the soil, mg kg⁻¹.

Bioconcentration factor (BCF) [60]:

$$BCF = C_{\text{root}}/C_{\text{soil}}, \quad (3)$$

where BCF is the bioconcentration factor; C_{root} —concentration in the underground part of the plant (dry matter), mg kg⁻¹; C_{soil} —concentration of the available form in the soil, mg kg⁻¹.

To evaluate the efficiency of the plant to translocate heavy metals from the root to other parts of the plant (inflorescence, stem, leaves), the translocation factor (TF) was calculated as follows [60]:

$$TF = C_{\text{shoot}}/C_{\text{root}}, \quad (4)$$

where TF—translocation factor; C_{shoot} —concentration in the vegetative and generative parts of the plant (dry matter), mg kg⁻¹; C_{root} —concentration of metal in the root (dry matter), mg kg⁻¹.

These ratios are crucial in evaluating the effectiveness of plants for phytoextraction and phytostabilization by analysing how metals accumulate and move within the plants. To assess the contamination level of the experimental plots, the following formula was applied [61]:

$$CF = C_{i \text{ soil}}/C_{i \text{ MPC}}, \quad (5)$$

where CF is the contamination factor, $C_{i \text{ soil}}$ is the concentration of a heavy metal in the soil, mg kg⁻¹; $C_{i \text{ MPC}}$ —maximum permissible concentration of the mobile form of the respective element, mg kg⁻¹.

The mobility of HMs is an indicator that allows for the assessment of the possibility of heavy metals' transfer from total forms to mobile forms available to plants. The mobility of

HMs in the soil was evaluated using the availability ratio index (AR), calculated according to Formula [62]:

$$AR (\%) = C_{AF} \times 100 / C_{TF}. \quad (6)$$

where AR is the availability ratio index; C_{MF} —concentration of the mobile form in the soil, mg kg^{-1} ; C_{TF} —concentration of the total form in the soil, mg kg^{-1} .

3. Results and Discussion

3.1. Soil

The determined chemical characteristics of the studied soils (0–20 cm) are presented in Table 1.

Table 1. Chemical properties (mean \pm SD) of the studied soil (n = 3).

Location		pH _{salt}	OM, %	CEC, $\text{mmol } 10^{-2} \text{ g}^{-1}$
N 48°49'48.32" E 35°13'67.86"	P1 (1 km)	6.58 \pm 0.12 ^b	4.11 \pm 0.15 ^a	42.6 \pm 1.95 ^b
N 48°46'50.60" E 35°18'99.85"	P2 (5.5 km)	6.2 \pm 0.15 ^c	4.60 \pm 0.08 ^b	38.63 \pm 1.60 ^c
N 48°58'64.79" E 35°21'81.27"	P3 (12.02 km)	6.70 \pm 0.02 ^a	4.40 \pm 0.12 ^c	45.0 \pm 1.40 ^a

Different small letters indicate significant differences ($p < 0.05$) between plant parts in the concentration of elements according to Tukey's test (n = 3).

The studied soil was slightly acidic, having medium values of organic matter (OM) and cation exchange capacity (CEC), which means normal soil productivity. The highest OM content was found at the second site, which corresponds to its agricultural use (the site was not used for its intended purpose during the study). The soils at plot 1, on the border between the industrial and residential areas, had slightly lower OM content.

The CEC values indicate a moderate adsorption capacity of the studied soils, with the highest CEC values at the third site. An increase in pH values enhances the sorption of cation metals (copper, zinc, lead) and increases the mobility of anionic metals (chromium). Strengthening of oxidizing conditions increases the migration ability of metals [63,64]. The obtained results may indicate a significant level of mobility of heavy metals from soil to plants in the studied locations, as has already been shown in our previous studies [42].

The concentration of the available and total forms of TE, the availability ratio index, and the determined pollution coefficients of the experimental plots are presented in Table 2.

At plot 1, the content of mobile forms of Cd, Cr, Cu, and Zn in the soil did not exceed the established maximum permissible concentrations (MPCs), while As was below the limit of detection. However, the content of the mobile form of lead in the soil exceeded the MPC by more than eight times [65]. According to the content of the mobile form in the soil (0–20 cm), the HMs are arranged in a row: Pb > Zn > Cu > Cr > Cd.

At points 2 and 3, the content of all HMs in the soil did not exceed the established standards of maximum permissible concentrations (MPC), and Cd and As were below the limit of detection. On both experimental plots, the HMs are arranged in a row according to the content of mobile form in the soil (0–20 cm): Zn > Pb > Cr > Cu.

In general, for all the studied sites, the concentration of HMs in the soil at P2 and P3 was significantly higher than at plot 1 ($F_{\text{theor}} < F_{\text{exper}}, P_{05}$), and among the studied HMs at the studied sites, the concentrations of the mobile form of Pb and Zn were significantly higher ($F_{\text{theor}} < F_{\text{exper}}, P_{05}$).

Among the three experimental plots, the first one had the highest values of As in the total form of soil: 50.75 mg kg^{-1} (a multiple of the recommended value: 10.15), and the third site had its content below the limit of detection. The total Cd content of 0.25 mg kg^{-1} was determined only at one experimental plot, and for P2 and P3 it was below the limit of detection. The values of Cr in the total form of soil were the highest in experimental P1: $2219.0 \text{ mg kg}^{-1}$, which is significantly higher than the recommended values (the

multiplicity of exceeding the recommended value was 22.19). In our studies, the highest total Cu content in the soil: 1039.0 mg kg⁻¹-was determined at P1, with a significant excess of the recommended values (the multiplicity of the recommended value was 28.86). The results obtained in P2 and P3 correspond to the recommended values of total copper content in soils [21,66–68]. The highest values of Pb content in the total form of soil were the highest in the P1: 7830.0 mg kg⁻¹ (the multiplicity of exceeding the recommended value is 92.1). The obtained results of the total Pb content at P2 and P3 did not exceed these and recommended values, and significantly exceeded the indicative levels at P1. In our studies, the highest total Zn content in the soil: 1918.0 mg kg⁻¹ was determined in P1 (the multiplicity of exceeding the recommended value was 38.36), and for P2 and P3 it was within the permissible limits.

Table 2. Mobile concentration (C_{MF}), total concentration (C_{TF}), mobility (AR), contamination factor (CF), and degree of contamination (Cdeg) of heavy metals in the surface layer (0–20 cm) of the studied areas.

Indicator	Plots	Cr	Cu	Pb	Zn
C_{MF} , mg kg ⁻¹	P1	1.65 ± 0.24 ^a	1.80 ± 0.19 ^{ab}	48.96 ± 4.12 ^{bc}	20.67 ± 1.88 ^a
	P2	0.17 ± 0.02 ^{bc}	0.16 ± 0.01 ^{ab}	0.53 ± 0.05 ^{bc}	0.67 ± 0.06 ^b
	P3	0.89 ± 0.17 ^{bc}	0.28 ± 0.05 ^c	2.72 ± 0.52 ^a	4.73 ± 0.91 ^c
MPC_{MF} *, mg kg ⁻¹		6.0	3.0	6.0	23.0
C_{TF} , mg kg ⁻¹	P1	2219.0 ± 39.40 ^{bc}	1039.0 ± 72.75 ^{ab}	7830.0 ± 29.77 ^a	1918.0 ± 61.90 ^a
	P2	36.51 ± 2.92 ^{bc}	15.42 ± 1.17 ^{ab}	4.53 ± 0.47 ^{bc}	14.29 ± 0.52 ^{bc}
	P3	21.21 ± 1.91 ^a	5.66 ± 0.40 ^c	10.03 ± 0.90 ^{bc}	15.11 ± 0.77 ^{bc}
Target value of soil **, mg kg ⁻¹		100.0	36.0	85.0	50.0
AR, %	P1	0.07	0.17	0.63	1.08
	P2	0.47	1.04	11.7	4.69
	P3	4.2	4.95	27.12	31.3
The contamination factor, CF	P1	22.19	28.86	92.12	38.36
	P2	0.37	0.43	0.05	0.29
	P3	0.21	0.16	0.12	0.3
The degree of contamination, Cdeg	P1		181.53		
	P2		1.14		
	P3		0.79		

Different small letters indicate significant differences ($p < 0.05$) between plant parts in the concentration of elements according to Tukey's test ($n = 3$). *—Values of maximum permissible concentrations according to the Order, regulation of 14.07.2020 № 1595 "On approval of the Hygienic Regulations for the permissible content of chemicals in soil". **—Target values are specified to indicate desirable maximum levels of elements in unpolluted soils. Source: Denneman and Robberse 1990; Ministry of Housing, Netherlands 1994.

The highest values of total soil content for Pb, Cr, Zn, Cu, and As among the experimental sites were recorded at P1 (a significant excess of the recommended values), and only the content of Cd was within the recommended limits. According to the total content in the soil (P1), the HMs can be arranged in a row: Pb > Cr > Zn > Cu > As > Cd.

In experimental P2 and P3, the values of the total HMs content in the soil did not exceed the recommended values, and the content of Cd was below the limit of detection. According to the total content in the soil (P2), the metals can be arranged in a row: Cr > Cu > Zn > Pb > As, and at P3 the row is Cr > Zn > Pb > Cu.

The determined values of the availability index were the highest at P3 for each element, namely, Cr: 4.20, Cu: 4.95, Pb: 27.12, and Zn: 31.30, where the highest pH (6.7) and CEC (45.0 mmol 10⁻² g⁻¹) and high levels of organic matter (OM-4.4%) were recorded among the studied plots. As noted by many authors and us earlier [42], the relationship between pH and organic matter content significantly affects the mobility of metals in the soil environment. A more detailed study of the physical and chemical properties of soils will provide a clearer understanding of the availability and mobility of heavy metals.

According to the methodology proposed by Hakanson, the degree of contamination of the research sites was assessed, but instead of the background content, the value of the recommended permissible concentration of the total form of metal elements was used. Thus, Hakanson [69] defines four categories of CF as follows: 1. $CF < 1$ low contamination factor \Rightarrow low level of contamination; 2. $1 < CF < 3$ moderate contamination factor \Rightarrow medium contamination; 3. $3 < CF < 6$ significant contamination factor \Rightarrow high contamination; 4. $CF > 6$ very high pollution factor \Rightarrow very high pollution.

Under to this classification by individual HM values, in our studies, we have one research site with a very high level of pollution (1.0 km from the main sources of pollution, P1) for Cr (22.19 > 6.0), Cu (28.86 > 6.0), Pb (92.12 > 6.0), and Zn (38.36 > 6.0), and two plots (P2, P3) with a low level of pollution ($CF < 1$).

The calculated values of the contamination factor CF of the total content of metals in the soil are presented in Table 2. CF is an index of a single element, and the sum of the contamination factors for all elements is determined by the degree of contamination (Cdeg) of the plot. The degree of contamination is categorized into four classes: 1. $Cdeg < 8 \Rightarrow$ low degree of contamination; 2. $8 < Cdeg < 16 \Rightarrow$ moderate degree of contamination; 3. $16 < Cdeg < 32 \Rightarrow$ significant degree of contamination; 4. $Cdeg > 32 \Rightarrow$ very high degree of pollution.

According to the total contamination index of the total content of HMs in the soil, our study identified P2 and P3 with a low degree of contamination ($Cdeg < 8$) and a site (P1) with a very high degree of contamination ($Cdeg > 32$), which corresponds to similar calculations of the mobile form of metals in the soil.

3.2. Plant

The obtained values of the content of HM in *Erigeron canadensis* L. and its parts (root, stem, leaves, inflorescence) at all research sites are presented in Supplementary Materials (Table S1).

The analysis of the obtained concentrations in plant showed different abilities of its parts to absorb HMs from soil and atmospheric air in the three experimental plots.

According to the concentration of the studied elements in the plant (dry matter), they can be placed in the following rows: P1: $Zn > Cu > Cr > Pb > As > Cd$; P2 and P3: $Zn > Cu > Cr > Pb > As$.

These accumulation series of HMs in the plant do not correspond to the accumulation series in soils (mobile and total forms), which may indicate different ways of supplying these metals to plant.

The distribution of heavy metals in different parts of plant is presented in Table 3.

Table 3. Distribution of heavy metals in *Erigeron canadensis* L. and its parts.

Plots	A Series of Heavy Metals in Order of Decreasing Concentrations in <i>Erigeron canadensis</i> L.			
	Inflorescence	Leaves	Stem	Roots
P1 (1 km)	Zn > Cu > Cr > Pb	Zn > Cu > Pb > Cr > Cd	Zn > Cu > Cr > Pb > Cd	Zn > Cu > Cr > Pb > As
P2 (5.5 km)	Zn > Cu > Cr > Pb	Zn > Cu > Cr > Pb	Zn > Cu > Cr > Pb > Cd	Zn > Cu > Cr > Pb > As
P3 (12.02 km)	Zn > Cu > Cr > Pb	Zn > Cu > Cr > Pb	Zn > Cu > Cr > Pb	Zn > Cu > Cr > Pb > As

The analysis of the data in Table 3 confirms the general trend of accumulation of toxic elements in all experimental plots both in the whole plant and in parts of *Erigeron canadensis* L., namely, $Zn > Cu > Cr > Pb$.

Arsenic is a natural part of most plants, but not much is known of its biochemical role [21]. In these studies, in all three experimental plots, As concentrations were determined only in the roots of *Erigeron canadensis* L; the values in other parts of the plant were below the limit of detection. This may indicate insignificant As contamination of the experimental plots, and/or low bioavailability of As in plant, and insignificant translocation of this element in the plant.

Cd is not necessary for plant metabolism. Its concentration is highest in the roots and decreases to the top of the plant [70]. It is a chemical analog of Zn, and plants may not be able to distinguish these ions [21].

In these studies, Cd in *Erigeron canadensis* L. was sporadically detected in P1 (leaves, stem) and P2 (stem), and in P3, its concentrations were below the limit of detection.

Indicators of Cr bioaccumulation and translocation in *Erigeron canadensis* L. are presented in Table 4.

Table 4. Indicators of Cr bioaccumulation and translocation in *Erigeron canadensis* L.

	PUI	BAC	BCF	TF Shoot/Root	TF Inflorescence/Root	TF Leaf/Root	TF Stem/Root
P1	4.18	2.82	1.36	2.08	0.71	0.75	0.63
P2	65.18	29.47	35.71	0.83	0.29	0.35	0.19
P3	8.3	6.98	1.33	5.26	0.64	2.74	1.88

To date, there is no clear evidence that Cr, one of the major carcinogens [71], is required for plant metabolism, and its biological function in plants is unknown [72]. It is not readily available to plants and is not easily transported by the plant [67], so it is mainly concentrated in the roots [73]. The chemical form of Cr inside the tissue influences the limited ability of Cr to translocate from roots to aboveground shoots [72].

According to our studies, the highest accumulation of Cr in plant was determined in plot 2, and the highest content among plant parts at this stage was observed in the roots ($6.07 \pm 0.49 \text{ mg kg}^{-1}$ dry matter). These levels of accumulation correspond to those known, including our previous studies [43]. According to our research on the distribution of Cr content in plant parts (dry matter), it can be presented in the following series: P1 and P2: roots > leaves > flowers > stem; P3: leaves > stem > roots > flowers. These series of Cr accumulation in the plant indicate different ways of its accumulation (root and extra-root) to *Erigeron canadensis* L. (Table S1).

In all experimental points, the PUI, BAC, and BCF were determined to be >1, which indicates the possibility of using the plant in phytoremediation strategies [42,50–52]. The highest values of PUI (65.18), BAC (29.47), and BCF (35.71) were established in the second plot with the lowest content of Cr ($0.17 \pm 0.02 \text{ mg kg}^{-1}$) in the mobile form of the soil, and the lowest value of the TFshoot/root ($0.83 < 1$) among experimental plots. The highest translocation ratio (TFshoot/root) of plant was established at P3, where the highest value of the availability ratio index (AR-4.20%) was also recorded.

In general, according to [51], the TF shoot/root of Cr ranges from 0.005 to 0.027 for vegetable plants, and from 0.1 to 0.6 for herbaceous plants, which is a relatively low TF indicator that limits the suitability of most plants in phytoremediation methods. Our obtained results of Cr in plant indicate the possibility of its use in methods of phytostabilization (PUI > 1; BCF > 1; TF < 1) and phytoextraction (PUI > 1; BAC > 1; BCF > 1; TF > 1) of soil contaminated with Cr. Wild and/or native plants are generally regarded as the most preferable phytoremediations in comparison to known metal bioaccumulates in the literature [59,72], which also reflects the properties of *Erigeron canadensis* L.

The obtained PUI values of the identified elements in *Erigeron canadensis* L. in the experimental plots are shown in Figure 2.

Indicators of Cu bioaccumulation and translocation in plant are presented in Table 5.

Plant uptake index (PUI) values for *Erigeron canadensis* L. in the experimental plots

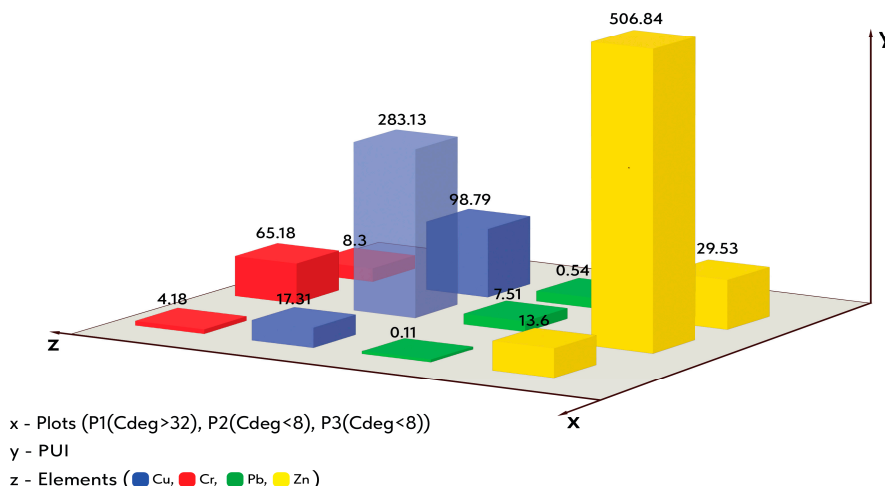


Figure 2. Plant uptake index (PUI) values for *Erigeron canadensis* L. in the experimental plots.

Table 5. Indicators of Cu bioaccumulation and translocation in *Erigeron canadensis* L.

	PUI	BAC	BCF	TF Shoot/Root	TF Inflorescence/Root	TF Leaf/Root	TF Stem/Root
P1	17.31	11.34	5.97	1.9	0.86	0.51	0.53
P2	283.13	145.31	137.81	1.05	0.47	0.37	0.21
P3	98.79	90.5	8.29	10.92	1.16	6.93	2.84

Cu is an irreplaceable trace element for plants and animals, and it plays a role in various physiological processes. However, an excessive level of copper can be toxic to soil organisms, affecting their growth and the overall soil ecosystem [67]. According to the available data, copper is not very mobile in plants and usually accumulates slowly over time, as it is strongly bound by nitrogen and proteins [21]. The onset of Cu toxicity and a decrease in productivity are detected at concentrations in shoots and leaves of 5 to 40 mg kg⁻¹ of dry matter [21], which corresponds to the results obtained by us for the Cu content in *Erigeron canadensis* L. (from 27.66 to 45.30 mg kg⁻¹, dry matter). The distribution of Cu content in parts of plant can be presented in the following series: P1: roots > flowers > stem > leaves and P2: roots > flowers > leaves > stem; P3: leaves > stem > flowers > roots. These series of accumulation of Cu indicate different ways of its arrival (root and extra-root) to the plant (Table S1).

In all our experimental plots for Cu, indexes PUI, BAC, and BCF were determined to be >1, indicating high bioavailability and bioaccumulation and, accordingly, the possibility of using the plant in phytoremediation strategies [42,50–52].

As in the case of Cr, the highest values of PUI (283.13), BAC (145.31), and BCF (137.81) were established at P2 with the lowest content of Cu (0.17 ± 0.02 mg kg⁻¹) in the mobile form of the soil, and the lowest value of the TFshoot/root (1.05) among experimental plots.

It is obvious that irreplaceable microelements (Zn, Cu) are present in larger quantities than toxic elements (Pb, Cd), and several previous researchers have reported the rapid translocation of Zn and Cu, and lower Pb [21]. Analysis of the translocation factor (TFshoot/root) showed that at low concentrations of heavy metals, their mobility was higher (TF > 1). The highest coefficient of Cu translocation (TF shoot/root) of *Erigeron canadensis* L. was found in P3, where the highest value of the availability index (AR-4.95%) was also recorded, indicating the importance of this parameter. According to the studies of plants, all the determined bioavailability and bioaccumulation coefficients (PUI, BAC, and BCF) for Cr, Cu, Pb, and Zn tended to decrease with increasing concentration of heavy metals in the

mobile form of soil (Tables 2 and 4–7). In addition, the translocation factor (TF_{shoot/root}) had the highest values for Cr, Cu, Pb, and Zn in experimental plot 3, which also had the highest values of the availability index (AR).

Table 6. Indicators of Pb bioaccumulation and translocation in *Erigeron canadensis* L.

	PUI	BAC	BCF	TF Shoot/Root	TF Inflorescence/Root	TF Leaf/Root	TF Stem/Root
P1	0.11	0.07	0.03	2.08	0.35	1.37	0.36
P2	7.51	3.59	3.92	0.91	0.26	0.54	0.11
P3	0.54	0.46	0.08	5.64	0.41	2.23	3

Table 7. Indicators of Zn bioaccumulation and translocation in *Erigeron canadensis* L.

	PUI	BAC	BCF	TF Shoot/Root	TF Inflorescence/Root	TF Leaf/Root	TF Stem/Root
P1	13.6	9.01	4.59	1.96	0.75	0.67	0.55
P2	506.84	314.9	191.94	1.64	0.54	0.75	0.35
P3	29.53	25.16	4.37	5.75	1.83	1.48	2.45

In general, the results obtained by us of bioavailability, bioaccumulation, and translocation of Cu in *Erigeron canadensis* L. indicate the possibility of its use in phytoextraction methods (PUI > 1; BAC > 1; BCF > 1; TF > 1) of Cu-contaminated soils.

Indicators of Pb bioaccumulation and translocation in plant are presented in Table 6.

According to the available data [21], there is no evidence of a significant role of Pb in plant metabolism, although it is naturally present in all plants. The average content of Pb determined in plants is in the range of 5–7 mg kg⁻¹ [74]. In these studies, the range of the average content of Pb in plant was 1.46–5.14 (mg kg⁻¹, dry matter).

The following series of Pb distribution between parts of plant were established at individual sites: P1: leaves > roots > stem > flowers; P2: roots > leaves > flowers > stem; P3: stem > leaves > roots > flowers. This demonstrates both routes (root and extra-root) of Pb supply to plant.

Root absorption of lead is passive and long-term, and translocation in plants is very limited; a significant part of it accumulates in roots [21]. Some experimental plants show more accumulation of Pb in stems and leaves than in their roots [75], which is associated with atmospheric precipitation that affects the level of Pb in vegetation [76–79]. Airborne Pb is absorbed by plants through leaves [6,80].

Our research established a relationship between the content of Pb in the leaves of *Erigeron canadensis* L. and its concentrations in the atmospheric air; namely, with the increase in the content of Pb in the atmospheric air (from 0.01 mg m⁻³ to 0.02 mg m⁻³), its content in the leaves of the plant decreases (from 2.28 mg kg⁻¹ to 0.49 mg kg⁻¹), which indicates the presence of a protective mechanism (tolerance strategy, avoidance strategy) in the plant regarding protection against Pb absorption from atmospheric air and can be used in phytoremediation strategies [81]. In general, the relationship between the content of toxic elements in atmospheric air and the content in vegetative parts of plants requires separate consideration and additional research.

The main factor limiting the phytoextraction potential of Pb is its low bioavailability for absorption by plants [80].

The obtained TF values of the identified elements in *Erigeron canadensis* L. in the experimental plots are shown in Figure 3.

The value of the translocation factor for *Erigeron canadensis* L. in the experimental plots

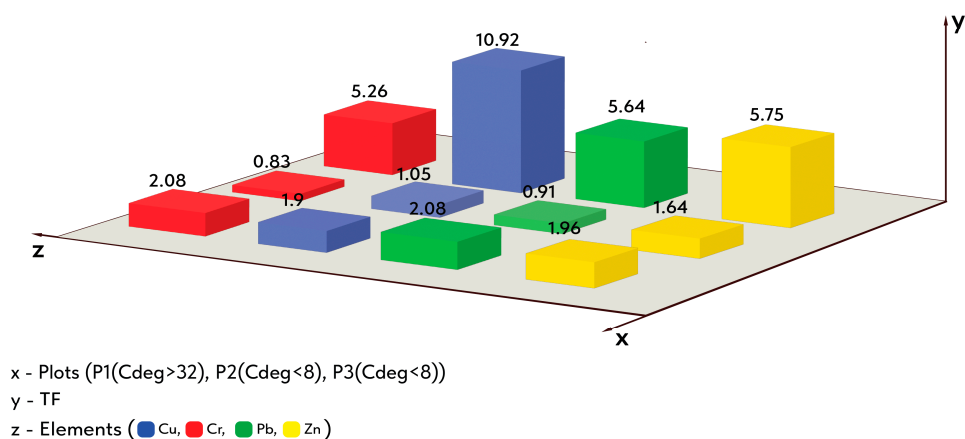


Figure 3. The value of the translocation factor for *Erigeron canadensis* L. in the experimental plots.

The highest values of PUI (7.51), BAC (3.59), and BCF (3.52) were established at P2, with the lowest content of Pb (0.53 mg kg^{-1}) in the mobile form of the soil, and the lowest value of the TFshoot/root translocation coefficient (0.91) among the experimental plots. As in the previous cases, with Cr and Cu, a sharp drop in PUI, BAC, and BCF values was determined with increasing concentrations of Pb in the mobile form of the soil (mg kg^{-1}), and the highest value of the translocation coefficient (TF-5.64) was recorded at P3 with the highest availability ratio index value (AR-27.12%).

According to the results of our research, depending on the content of Pb in the mobile form of the soil and its physical and chemical characteristics, the content of Pb in the atmospheric air, as well as climatic conditions, *Erigeron canadensis* L. demonstrated the qualities of Pb accumulation, which can be used both for phytostabilization (TF < 1) and phytoextraction (TF > 1) of soils contaminated with Pb, which corresponds to other studies [6,54,74]. In addition, taking into account current knowledge on plant bioaccumulation, the potential of plants for phytoextraction of Pb can be increased, according to specific conditions of use [6,54,82,83].

Indicators of Zn bioaccumulation and translocation in plants are presented in Table 7.

Most soils [21,67] exhibit a high degree of Zn mobility, and in areas that are contaminated, Zn levels can reach a high level, ranging from 443 to 1112 mg kg^{-1} [9,80], which is equivalent to the total Zn content at P1 of our study (Table 2).

The toxicity limit for Zn varies depending on the plant species, genotype, and growth stage [51]. For example, some plants, like *Thlaspi* species, are known to hyperaccumulate Zn without showing visible damage. These species can contain more than $10,000 \text{ mg kg}^{-1}$ of Zn and are used for phytoremediation of contaminated soil. However, toxic effects are typically expected when Zn concentrations exceed $300\text{--}400 \text{ mg kg}^{-1}$ [21].

Under our research, the highest content of Zn in plant was determined in P2 ($339.58 \text{ mg kg}^{-1}$, dry matter) and P1 ($281.14 \text{ mg kg}^{-1}$, dry matter), where the lowest was observed (P2) and the highest (P1) content of Zn in the mobile form of the soil (0.67 mg kg^{-1} and 20.67 mg kg^{-1} , respectively), which correlates with the above critical concentrations for the plant, and also demonstrates a wide range of bioavailable Zn for *Erigeron canadensis* L., according to which bioaccumulation is carried out. For comparison, according to our previous studies, the total content of Zn in the phytomass of *Matricaria chamomilla* L. was 5.46 mg kg^{-1} , while its concentration in the mobile form of the soil was 7.43 mg kg^{-1} [43], which emphasizes the advantages of *Erigeron canadensis* L. when used in models phytoremediation.

The results of studies of *Erigeron canadensis* L. showed a different distribution of Zn among the parts of the plant in the experimental plots: P1: roots > inflorescence > leaves > stem; P2: roots > leaves > inflorescence > stem; P3: stem > inflorescence > leaves > roots, demonstrating both root and extra-root routes of Zn uptake into the plant.

As in the cases with other heavy metals, in the experimental plots it is possible to state a rapid drop in the plant uptake index (PUI) for Zn, and, accordingly, the bioabsorption coefficients (BAC) and bioconcentration factor (BCF) with the increase in the concentration of Pb in the mobile form of the soil (mg kg^{-1}), and the highest value of the translocation ratio (TF-5.75) was recorded at experimental plot № 3 with the highest value of the availability ratio index (AR: 31.30%).

Apparently, Zn for plants turned out to be the most available heavy metal among all the studied sites, which corresponds to [84]; namely, in P2, the highest content of the element in the plant ($339.58 \text{ mg kg}^{-1}$), plant uptake index was determined for Zn (PUI-506.84), bioabsorption coefficient (BAC-314.9), and bioconcentration (BCF-191.94) (Table 7). In addition, the content of Zn in the total mass of *Erigeron canadensis* L. (dry matter) was P: 2.81%, P2: 3.4%, and P3: 1.4%, which, according to some estimates, may have economic efficiency (>3.0%) when using the plant for phytoextraction of contaminated soils [82].

In general, the concentrations of Zn and Cu were significantly higher compared to other metals in the plant and its parts across different experimental sites (Ftheor < Fexper, P₀₅). Additionally, the content of the analysed heavy metals in the plant was significantly higher than in the mobile form of soils (Ftheor < Fexper, P₀₅). This may indicate the high bioavailability of Zn and Cu in the plant, and their efficient translocation within the plant, as well as the possibility of extra-root pathways of metal absorption.

Under to the indicators of PUI, BAC, and BCF in plants, the experimental HM can be arranged in the following series in descending order of their values: P1: Cu > Zn > Cr > Pb; P2: Zn > Cu > Cr > Pb; P3: Cu > Zn > Cr > Pb, and these values for Zn, Cu, and Cr were higher than 1 in all experimental plots. These series basically correspond to similar studies [83,84].

The translocation of HM in the studied plants from roots to shoots was estimated to be quite high [1–4,6,9,21]. With the exception of Pb and Cr at P2, all TF indicators > 1 (83.7% among those studied).

Summarizing the results of our research, we can state that plants, taking into account their personal characteristics and under appropriate conditions, can be a universal candidate for use in two main phytoremediation strategies, namely, phytostabilization (PUI, BCF > 1 > TF) and phytoextraction (PUI, BAC, BCF, TF > 1), for soil contaminated with heavy metals.

Many authors [85–87] have determined that the best plants for phytoextraction of polluted soils are hyperaccumulators, which should meet the next criteria: (1) shoot-to-root ratio of elements above 1, which indicates an effective ability to translocate elements from roots to shoots; (2) shoot-to-soil concentration of elements above 1, which indicates a greater ability to absorb elements from the soil; and (3) concentration of the element of uptake above $1000.00 \text{ mg kg}^{-1}$ for Cu, Cr, and Pb, and $10,000.00 \text{ mg kg}^{-1}$ for Zn. But their use is quite limited due to many factors (physicochemical characteristics of soils, climatic conditions, time of growth and accumulation, characteristics of toxic element/s) [37,88]. According to our research, *Erigeron canadensis* L. meets only the first two criteria.

Meanwhile, the criteria proposed later [89] for identifying a hyperaccumulator plant are more flexible and are as follows: (1*) The shoot element concentration (on an oven-dry basis) should exceed 1% for Mn and Zn, 0.1% for Cu, Ni, and Pb, and 0.01% for Cd and As. (2*) The plant should efficiently transfer accumulated elements from root to shoot (aboveground), often with more than 90% efficiency. (3*) It should be capable of accumulating elements even from low external element concentrations. (4*) The plant should be fast-growing with a high rate of biomass production.

The corresponding bioaccumulate properties of *Erigeron canadensis* L. according to our studies are presented in Figure 4; in addition, the plant is estimated as fast-growing with sufficient biomass productivity [44,49].

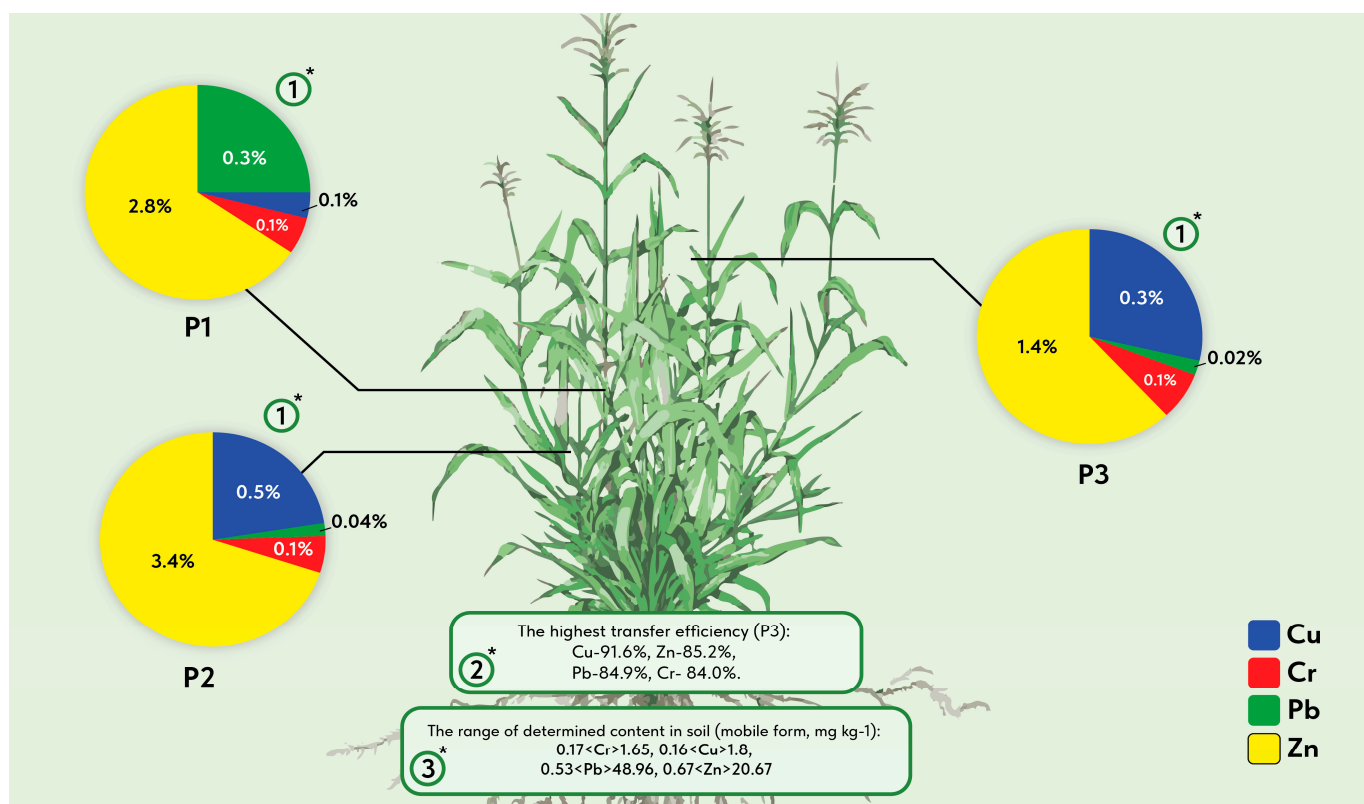


Figure 4. Bioaccumulative properties of *Erigeron canadensis* L.

Therefore, according to the obtained research results, it is possible to evaluate *Erigeron canadensis* L. as a Zn, Cu, and Cr hyperaccumulator plant, and to recommend it for phytoextraction of Zn-, Cu-, and Cr-contaminated soils, and phytostabilization of Pb-contaminated soils, i.e., immobilization of HMs in the soil, reducing their bioavailability, which prevents migration of metals into the ecosystem and reduces the risk of metals entering the food chain [90].

The results obtained confirm the properties of *Erigeron canadensis* L. as a phytoremediator and suggest new ways to use phytoremediation in solving heavy metal pollution problems. This research may provide a basis for further studies on the application of phytoremediation in other similar environments.

Biota demonstrates the potential for developing tolerance to anthropogenic pressure on ecosystems, and wild and/or native plants are generally considered to be better phytoremediators than metal bioaccumulators known from the literature and do not need regular irrigation, pesticide treatment, etc. [59,91]. In the meantime, it is clear that in reality, a single approach is not possible and insufficient for effective remediation of soils contaminated with HMs. A combination of different approaches, such as genetic engineering, microbiological, and chelating approaches, is important for highly effective and comprehensive phytoremediation in the future [37].

4. Conclusions

According to the obtained research results, it is possible to evaluate *Erigeron canadensis* L. as a Zn, Cu, and Cr hyperaccumulator plant and recommend it for phytoextraction of soils contaminated with Zn, Cu, and Cr, and phytostabilization of soils contaminated with Pb.

The highest concentrations of heavy metals in the soil, both for the mobile form and for the total form, were determined for Pb at P1 (48.96 mg kg⁻¹ and 7830.0 mg kg⁻¹, respectively). In general, for all the studied sites, the concentration of metals in the soil at P2 and P3 was significantly higher than at P1 ($F_{\text{theor}} < F_{\text{exper}}$, P_{05}), and among the tested metals, the concentrations of the mobile form of Pb and Zn at the experimental sites were significantly higher ($F_{\text{theor}} < F_{\text{exper}}$, P_{05}). Availability index (AR) values were highest at P3 for each metal (Cr: 4.20, Cu: 4.95, Pb: 27.12, and Zn: 31.30).

According to Hakanson's method, the degree of pollution in terms of the total content of HMs for the experimental areas was estimated as two areas with a low level of pollution ($CF < 1$, P2 and P3) and an area with very high pollution (P1), and both according to individual values (Cr (22.19 > 6.0), Cu (28.86 > 6.0), Pb (92.12 > 6.0), and Zn (38.36 > 6.0)), as well as by the total pollution index ($C_{\text{deg}} > 32$), which corresponds to similar calculations of the mobile form of metals in the soil.

The general tendency of accumulation of HMs in all experimental plots, both for the plant as a whole and for its parts, was as follows: Zn > Cu > Cr > Pb.

Zn for plants turned out to be the most available heavy metal among all the investigated sites and toxic elements; namely, in P2, the highest content of the metal in the plant was determined for Zn (339.58 mg kg⁻¹), plant uptake index (PUI: 506.84), bioabsorption coefficient (BAC: 314.9), and bioconcentration coefficient (BCF: 191.94). In addition, the Zn content in the total mass of plant had values that demonstrated economic efficiency (>3.0%) in the case of using the plant for phytoextraction of Zn-contaminated soils.

In general, the concentrations of Zn and Cu were significantly higher among other metals in *Erigeron canadensis* L. and its parts in different experimental plots ($F_{\text{theor}} < F_{\text{exper}}$, P_{05}), and the content of the analysed heavy metals in plant was significantly higher than in the mobile form of soils ($F_{\text{theor}} < F_{\text{exper}}$, P_{05}), which may indicate high bioavailability of Zn and Cu in the plant and their better translocation in the plant, as well as possible root and foliar pathways of heavy metals absorption, which is also true for Pb and Cr.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pollutants4030029/s1>, Table S1. Concentrations of heavy metals (mean \pm SD) in *Erigeron canadensis* L. and its parts (root, stem, leaves, inflorescence) in experimental plots.

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