



## Article

# Bioaccumulation of Cr, Zn, Pb and Cu in *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L.

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**Abstract:** The city of Dnipro, a prominent industrial hub in Ukraine, is recognized for its particularly its significant industrial development. This study focused on two prevalent plant species, *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L., within the vicinity. Sampling was conducted at points located 12.02 km away from the emission sources associated with battery production and recycling plants in Dnipro. Analysis of heavy metal concentrations such as, Cr, Cu, Pb, and Zn was conducted using atomic emission spectrometry from the soil and plants tissues of *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L. The translocation coefficient (TF) was calculated for both plant species. The results revealed that Cu and Zn exhibited the highest bioaccumulation in the examined plants, whereas Pb demonstrated the lowest. The order of metal uptake by both plants was determined as Cu > Zn > Cr > Pb. Significantly higher concentrations of these metals were observed in the two studied plants compared to the soil ( $F_{theor} < F_{exp}$ ,  $p < 0.05$ ), suggesting the bioavailability of metals for these plants. The translocation coefficient (TF) represented the ratio of metal concentration in the shoot/the root. The TF value of *Erigeron canadensis* L. exceeded 1 for four metals. On the other hand, the TF value of *Ambrosia artemisiifolia* L. surpassed 1 for Cr, Cu, and Zn. Consequently, both species emerge as potential phytoremediators for soils contaminated with these studied metals.



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**Keywords:** metals (Cr, Cu, Pb, Zn); bioavailability; phytoremediation; phytomass; soil; *Ambrosia artemisiifolia* L.; *Erigeron canadensis* L.

## 1. Introduction

Toxic metals, such as, As, Cd, Cr, Cu, Hg, Pb, and Zn, have been widely distributed in the environment [1]. Their presence in soil has raised a major concern for human health [1,2]. Excessive amounts of heavy metals in soil can affect both the quality and quantity of functioning biota and thus ecosystems in general [3–7]. Anthropogenic activities release these toxic metals and cause environmental pollution [8–12]. The main resources are the operation of motor vehicles, energy enterprises, mining, and the production of ferrous and non-ferrous metallurgy [8–12]. These pollutants pose significant health risks to humans and the environment, with potential impacts on the skin and nervous system and increased cancer risk [13]. Dnipro is located in Ukraine. The city of Dnipro is polluted with heavy metals due to industrial activities [14,15]. This pollution has led to high concentrations of toxic elements in the soil and forests [16,17]. The need for measures to mitigate this pollution is evident, as it not only poses a threat to the environment but also has negative socio-economic consequences [15]. Nevertheless, a significant portion of these heavy metals can be taken up by plants via their root systems. Moreover, another pathway of heavy metal accumulation is absorption by leaves from atmospheric aerosols [18]. Mitigating heavy metal pollution in both soil and plants becomes crucial to investigate within this specific geographical area.

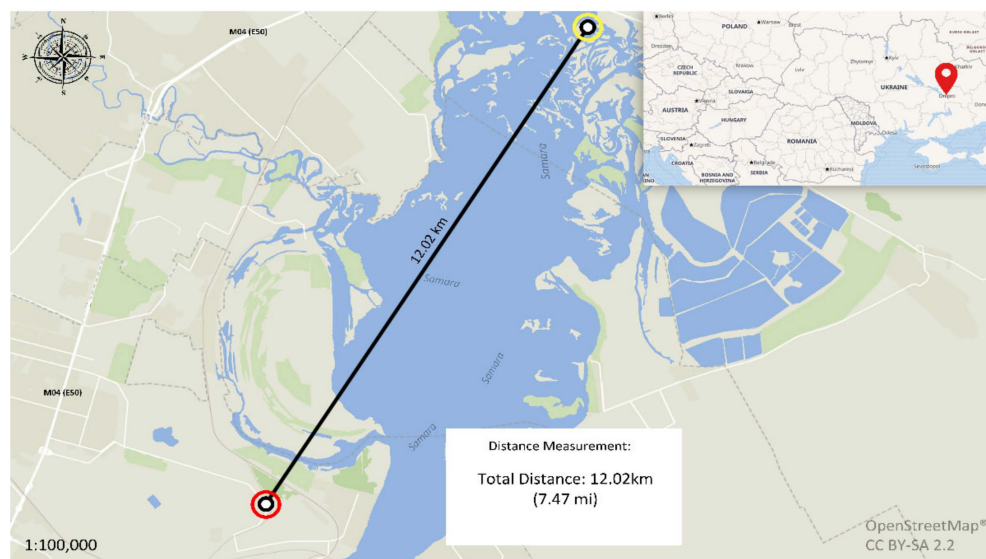
Phytoremediation has gained popularity due to its cost-effectiveness and the minimal side effects of heavy metals [19–21]. Plants can remove, degrade, or detoxify contaminants. Thus, the study of the bioavailability of metals is essential to understanding the persistent anthropogenic load in these areas. One of the main factors of environmental pollution is toxic metals, characterized by high toxicity, persistence, and bioaccumulation [22]. Bioaccumulation is dependent on different factors, such as the physical and chemical properties of the metal and its dose, soil type, and characteristics of the plant species. The concentration of available forms of toxic metals in the soil is associated with the chemical composition of technogenic emissions as well as the characteristics of soils. Metals are ubiquitous [23], for example, the anthropogenic Pb emitted into the atmosphere settles and accumulates in the topsoil. Pb is absorbed by plant roots. Pb has a long biological half-life and high bioaccumulation potential. The consequence of this is the production of foods containing Pb that are harmful to human health, especially for infants and children [24]. Available forms of lead and zinc accumulate mainly in the humus layer of the soil, while cadmium migrates to deeper soil layers [22,24]. At the same time, Zn and Cu are easily assimilated by the roots and transported to the shoots [25].

In our earlier study, the bioaccumulation of toxic metals in ragweed (*Ambrosia artemisiifolia* L.) in contaminated soil has been investigated by these enterprises (1000 m from the main sources of pollution) [22]. The heavy metals have been detected in *Matricaria chamomilla* L. Mercury (Hg), chromium (Cr), zinc (Zn), arsenic (As), cadmium (Cd), lead (Pb), and copper (Cu) have been found in the soil–plant system in the zone of influence (700 m from the main sources of pollution) of battery production and processing enterprises in Dnipro city [26].

*Ambrosia artemisiifolia* L. and *Erigeron canadensis* L. are widely represented in the relevant territory of the Dnipro region of Ukraine. *Ambrosia artemisiifolia* L. is an invasive type of annual herbaceous plant from the aster family, which originates from North America and accidentally came to Ukraine, where it became the main weed species in a short time, causing damage to both agriculture and human health. [19]. Metal accumulation has been intensively studied in this plant [27]. For example, high tolerance to Zn, Pb, and Cu has been detected in the colonization of *Ambrosia artemisiifolia* L. along roadsides [19,28]. *Erigeron canadensis* L. is a type of annual or biennial herbaceous flowering plant from the aster family, also native to North America, and which is used in medicine. There is evidence of its ability to bioaccumulate Cd and Zn [20]. *Erigeron canadensis* L. proves to be an effective plant for phytoextraction of lead under appropriate conditions [29]. It is one of the alternative potential candidates for the role of a hyperaccumulator plant, effective for the remediation of metal-contaminated soils [21]. Systematic studies of heavy metal contamination in *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L. are needed. Therefore, this present study aims to assess the bioavailability of Cr, Cu, Pb, and Zn for *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L. in soil potentially polluted by an enterprise for the production and processing of batteries. This can provide an opportunity to propose the studied plant species for phytoremediation, obtain data about their resistance to high metal concentrations, and get an idea of the behaviour of metals in polluted environments for control. To the knowledge of our researchers, this is the first such study for these plant species under the studied conditions. In addition, the concentration of toxic elements in the phytomass of medicinal plants is currently not regulated in Ukraine. Therefore, our research can serve as a basis for the future development of phytotoxicological indicators of plants.

## 2. Materials and Methods

The concentration of Cr, Cu, Pb, and Zn in soil and plants was investigated at a site 12.02 km away from the emission sources of battery production and waste battery recycling facilities in Dnipro, Ukraine (Figure 1).



**Figure 1.** A map of the sampling site. The yellow circle indicates the sample sites; the red circle indicates the enterprise location; the dark line is drawn at a distance of 12,020 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 a map of Ukraine. The red symbol indicates the city of Dnipro. “CC BY-SA 2.2”.

It should be noted that in the “Northern” industrial zone, which includes the enterprise for the processing of rechargeable batteries and the factory for the production of rechargeable batteries, there was also an enterprise for collecting scrap ferrous and non-ferrous metals. The other enterprise, via the exploitation processing, potentially affected the studied area. In general, the studied territory was transformed due to anthropogenic activity [30]. The research site was located at a distance of 3.3 km from Novomoskovsk Pipe Plant and 50.0 m from the M04 (E50) highway, which may affect the concentration of metals in soil and plants, and thus the results obtained.

Soil and plants of *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L. were sampled in July 2021 in compliance with the requirements of the state standards of Ukraine (DSTU 4287:2004, DSTU ISO 10381-4-2005, DSTU ISO 10381-1:2004, DSTU 4770.3—DSTU 4770.9). The soil was sampled on a  $10 \times 10$  plot ( $100 \text{ m}^2$ ) using the “envelope” method: four points in the corners and one in the center, i.e., five points that were generalized in four replicates. The depth of soil sampling ranged from 0 to 20 cm. The weight of each soil sample was 1.0–1.2 kg. Plants were collected in 20 pieces of each species at the soil sampling sites. The soil under study is ordinary low-humus black on heavy loess loams (pH salt 6.7; organ substance Turin, Walkley—Black 4.4%). According to the American soil classification system [31], chernozems belong to the “Mollisols” group. Experimental results were interpreted according to standard statistical methods. Statistic parameters such as standard deviation, variance, and standard errors were determined in three replicates.

Soil samples (extraction with acetate-ammonium buffer pH 4.8) and plants (extraction with a mixture of concentrated acids  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ) were analyzed by inductively coupled plasma atomic emission spectrometry (iCAP 7000 Plus DUO, Thermo Fisher Scientific, Bremen, Germany). The lowest limit of detection of elements, namely Cr, Cu, Pb, Zn, As, and Cd, in the soils were 1.0, 0.5, 0.2, 1.0, 0.5, and 0.2,  $\text{mg kg}^{-1}$ , respectively. The lowest limit of detection of elements, namely Cr, Cu, Pb, Zn, As, and Cd, in the plants were 4.0, 2.0, 10.0, 4.0, 0.1, and 0.8  $\mu\text{g kg}^{-1}$ , correspondingly. The values obtained for both plants for Cd and As (except for the roots) were below the limit of detection; so, these pollutants were not included in the calculation of the research results.

The plant uptake index (PUI) was calculated as follows [3–5]:

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

where PUI is the plant uptake index;

$C_{\text{plant}}$ —concentration in the total plant (dry matter),  $\text{mg kg}^{-1}$ ;

$C_{\text{soil}}$ —concentration of the available form in the soil,  $\text{mg kg}^{-1}$ .

To evaluate the efficiency of the plant's ability to translocate toxic metals from the root to other parts of the plant (inflorescence, stem, leaves), the translocation factor (TF) was calculated as follows [23]:

$$\text{TF} = C_{\text{shoot}}/C_{\text{root}}, \quad (2)$$

where TF—translocation factor;

$C_{\text{shoot}}$ —concentration of metal in different parts of the plant (dry matter inflorescence, stem, leaves),  $\text{mg kg}^{-1}$ ;

$C_{\text{root}}$ —concentration of metal in the root (dry matter),  $\text{mg kg}^{-1}$ .

### 3. Results and Discussion

#### 3.1. Metal Concentrations in Soil and *Ambrosia artemisiifolia* L.

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 <sub>salt</sub>	OM, %	CEC, $\text{mmol } 10^{-2} \text{ g}^{-1}$
N 48°58'64.79'' E 35°21'81.27''	6.7 $\pm$ 0.02	4.4 $\pm$ 0.12	45.0 $\pm$ 1.4

The study soil was slightly acid, with moderate values of organic matter (OM) and cation exchange capacity (CEC), indicating normal soil productivity. The relationship between pH and organic matter content significantly influences metal mobility in the soil environment [32]. At slightly acidic pH levels, metals are more mobile and bioavailable, while organic matter can influence metal mobility through complexation (i.e., the formation of stable metal–organic complexes) and precipitation (i.e., chelation or adsorption of metal onto organic surfaces) [33]. The role of organic matter in metal toxicity and bioavailability is complex and depends on various factors [34]. In future, a more in-depth soil analysis will be employed in other parts of the world.

The concentration of metal in soil and *Ambrosia artemisiifolia* L. are presented in Table 2. The highest content of the available form of metals in the soil was observed for Zn, while the concentrations of As and Cd were below the limit of detection in the soil. According to the mobile form in the soil (0–20 cm), the concentration of metals was arranged in the following order: Zn > Pb > Cr > Cu. The concentration in soil was shown at the condition of acetate-ammonium buffer pH 4.8.

Statistical analysis was performed for the total phytomass and different parts of plant material. There were significant differences between Zn and Pb in the total plant compared to in parts of the plants, such as inflorescence, leaves, stem, and roots ( $p < 0.0001$ ). There were statistical differences comparing Zn to Cr and Cu in the soil ( $p < 0.05$ ).

The concentration of Zn was  $4.73 \text{ mg kg}^{-1}$  in the soil (mobile form, 0–20 cm) and  $505.52 \text{ mg kg}^{-1}$  in the total dry weight of *Ambrosia artemisiifolia* L., and was the highest among all metals and among all parts of the plant, which may indicate that it has the highest intake into the environment.

**Table 2.** PUI and concentrations of metals (Cr, Cu, Pb, Zn) in soil and *Ambrosia artemisiifolia* L.

Metals	mg kg <sup>-1</sup>	Concentration in the Plant, mg kg <sup>-1</sup> , Dry Matter					PUI Total
		Part of Plants					
		Total Plant	Inflorescence	Leaves	Stem	Roots	
Cr	0.89 ± 0.17	19.22 ±1.75 <sup>bc</sup>	1.13 ±0.10 <sup>bc</sup>	8.37 ±0.73 <sup>bc</sup>	1.97 ±0.17 <sup>bc</sup>	7.74 ±0.69 <sup>bc</sup>	21.69
Cu	0.28 ± 0.05	59.88 ±5.17 <sup>bc</sup>	13.56 ±1.19 <sup>bc</sup>	16.36 ±1.51 <sup>bc</sup>	4.33 ±0.37 <sup>bc</sup>	25.63 ±2.23 <sup>bc</sup>	216.73
Pb	2.71 ± 0.52	5.13 ±0.66 <sup>b</sup>	0.44 ±0.04 <sup>b</sup>	1.17 ±0.11 <sup>b</sup>	0.39 ±0.03 <sup>b</sup>	3.14 ±0.23 <sup>b</sup>	1.89
Zn	4.73 ± 0.91	505.52 ±27.33 <sup>a</sup>	127.40 ±10.70 <sup>a</sup>	171.10 ±15.57 <sup>a</sup>	58.52 ±5.09 <sup>a</sup>	148.50 ±13.22 <sup>a</sup>	106.81

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

Cu was determined at 0.28 mg kg<sup>-1</sup>, which was the lowest concentration among the four metals. The concentration of Cu in the plant was the second among all the studied metals, at 59.88 mg kg<sup>-1</sup> in total dry weight. A one-way analysis of variance (ANOVA) indicated a statistically significant difference ( $p < 0.05$ ) in the mean of concentration of plant parts in the cases of Zn, Cu, Cr, and Pb. These elements are necessary for normal plant growth. However, excessively high concentrations have a negative impact on the plants [5]. The concentration of Cd and As in plants was below the limit of detection, except for As in the roots of both plants, which may indicate a longer absorption time of this element [31].

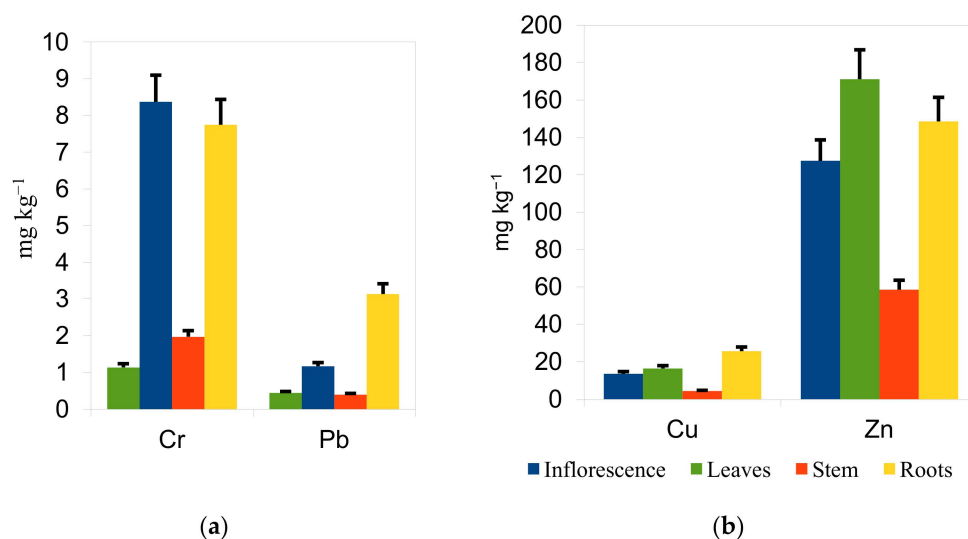
The coefficient of variation of metal concentrations in different parts of *Ambrosia artemisiifolia* L. shows that the concentration of Pb is the most variable parameter. This indicates that the distribution of Pb in different parts of the plant was very uneven ( $v > 100\%$ ). The concentrations of zinc, copper, and chromium are the most equally distributed in different parts of the plant. This may be associated with the low bioavailability of metals for roots, or it may be due to the apoplastic mechanism of element entry into the aboveground phytomass [35].

The coefficient of variation of metal concentration in different parts of *Ambrosia artemisiifolia* L. ( $v$ , %) allows us to rank the studied metals in the following descending order: Pb > Cr > Cu > Zn.

The highest concentration of Cr and Zn in plants was found in the leaves. These metals in leaves may indicate the apoplastic nature of absorption or a barrier-free mechanism of bioavailability of these elements from the soil to the roots and aboveground phytomass [36]. This is further supported by studies on metal accumulation in willow and poplar species [37], plants spontaneously inhabiting Zn-Pb waste deposits [38], and the zinc hyperaccumulator *Thlaspi caerulescens* [39]. The subcellular compartmentation of Zn in the roots and leaves of the Zn hyperaccumulator *Thlaspi caerulescens* further highlights the role of vacuoles in Zn accumulation. This was confirmed by the lowest coefficient of variation of Zn ( $v = 43.3\%$ ) of the studied metals. Pb and Cu were characterized by the largest concentration only in the roots.

Generally, lead is characterized by low bioavailability, even in contaminated soils. A total of 88.7% of the total amount of Pb in the plant can be concentrated in the roots and 11.3% in the shoots [24]. The distribution of metals in plant parts for *Ambrosia artemisiifolia* L. is presented in Figure 2.

The distribution of the studied metals by parts of *Ambrosia artemisiifolia* L. was as follows (in descending order of concentration, mg kg<sup>-1</sup>): Pb: roots > leaves > inflorescence > stem; Zn: leaves > roots > inflorescence > stem; Cu: roots > leaves > inflorescence > stem; Cr: leaves > roots > stem > inflorescence.



**Figure 2.** The concentration of Cr and Pb (a) and Cu and Zn (b) in parts of *Ambrosia artemisiifolia* L.

The coefficient of variation of metal concentration in different parts of *Ambrosia artemisiifolia* L. (v, %) indicated that the metals studied can be ranked in the following descending order: Pb > Cr > Cu > Zn.

Although Zn had the highest concentrations in soil and plants, the highest PUI value was for Cu. This result indicates its highest bioavailability and barrier-free mechanism of entry into *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L. [22]. Pb is the most harmful in the production and processing of rechargeable batteries [20], but its PUI turned out to be the lowest among the studied metals. These phenomena may indicate the resistance of the studied plants to the absorption of this pollutant [40]. According to the results of the PIU for both species, the metals may be ranked in terms of bioaccumulation intensity in the following order of decreasing intensity: Cu > Zn > Cr > Pb. This corresponds to previous studies [41]. According to the concentration of metals in different parts of both plants (*Ambrosia artemisiifolia* L. and *Erigeron canadensis* L.), the studied metals can be placed in the following rows:

Roots: Zn > Cu > Cr > Pb > As;

Inflorescence: Zn > Cu > Cr > Pb;

Leaves: Zn > Cu > Cr > Pb;

Stems: Zn > Cu > Cr > Pb.

The bioaccumulation coefficient describes the ability of a plant to accumulate metals from the soil. The optimal conditions for phytoremediation are high metal concentrations in soil and plants, as well as high bioaccumulation coefficients [42].

Phytoremediation is a cost-effective, aesthetically pleasing and accessible harmonious technology that uses plants to remediate land contaminated with toxic metals.

At the studied site, the concentration of metals in the atmospheric air was analyzed. The results showed that the concentrations of metal in the air were as follows: Cr—0.13 mg/m<sup>3</sup> (the daily average maximum permissible concentration (MPC) in the air was  $1.5 \times 10^{-3}$  mg/m<sup>3</sup>, which exceeds the MPC by 84.5 times), Cu—0.05 mg/m<sup>3</sup> (daily average maximum permissible concentration (MPC) in atmospheric air—0.001 mg/m<sup>3</sup>, exceeding the MPC by 50.1 times), Pb—0.02 mg/m<sup>3</sup> (daily average maximum permissible concentration (MPC) in atmospheric air— $0.3 \times 10^{-3}$  mg/m<sup>3</sup>, exceeding the MPC by 69.8 times), and Zn—0.117 mg/m<sup>3</sup> (daily average maximum permissible concentration (MPC) in atmospheric air—0.05 mg/m<sup>3</sup>, exceeding the MPC by 2.33 times) [43]. The majority of the elements are taken by plants through their roots, and some are absorbed by leaves from atmospheric aerosols [44]. Many studies have shown that atmospheric deposition mainly affects the level of Pb in vegetation [44–46].

The results obtained on the concentration of metals in the atmospheric air and its impact on *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L. require additional research.

The highest PUI values for different parts of *Ambrosia artemisiifolia* L. for all investigated metals, except for Cu, are noted in the leaf, which may also indicate the foliar route of its entry into the plant [47]. For Cu, the highest PUI was recorded in the root, which may indicate a barrier mechanism for the uptake of this element.

Overall, the concentration of all metals studied in the plant was significantly greater than in the soil ( $F_{\text{theor}} < F_{\text{exper}}$ ,  $p < 0.05$ ). However, the concentration of zinc was significantly higher among the individual parts of *Ambrosia artemisiifolia* L. ( $F_{\text{theor}} < F_{\text{exper}}$ ,  $p < 0.05$ ), which indicates the highest bioavailability of Zn for *Ambrosia artemisiifolia* L.

### 3.2. The Metals Concentrations in Soil and *Erigeron canadensis* L.

The concentrations of metals in the soil and *Erigeron canadensis* L. plants are presented in Table 3. As with *Ambrosia artemisiifolia* L., the largest concentration of available forms of metals in the soil was observed for Zn, while the concentrations of As and Cd were lower than the limit of detection in the soil. By the concentration of mobile form in the soil (0–20 cm), the metals are in the following ranking: Zn > Pb > Cr > Cu.

**Table 3.** PUI and the concentration of metals (Cr, Cu, Pb, and Zn) in soil and *Erigeron canadensis* L.

Metals	mg kg <sup>-1</sup>	Concentration in Plant, mg kg <sup>-1</sup> , Dry Matter					PUI Total
		Part of Plants					
		Total Plant	Inflorescence	Leaves	Stem	Roots	
Cr	0.89 ± 0.17	7.39 ±0.60 <sup>bc</sup>	0.76 ±0.07 <sup>bc</sup>	3.23 ±0.29 <sup>bc</sup>	2.22 ±0.20 <sup>bc</sup>	1.18 ±0.10 <sup>bc</sup>	8.34
Cu	0.28 ± 0.05	27.66 ±3.34 <sup>bc</sup>	2.70 ±0.24 <sup>bc</sup>	16.07 ±1.37 <sup>bc</sup>	6.58 ±0.60 <sup>bc</sup>	2.32 ±0.20 <sup>bc</sup>	100.12
Pb	2.7 ± 0.52	1.46 ±0.14 <sup>b</sup>	0.09 ±0.01 <sup>b</sup>	0.49 ±0.04 <sup>b</sup>	0.66 ±0.06 <sup>b</sup>	0.22 ±0.02 <sup>b</sup>	0.54
Zn	4.73 ± 0.91	139.68 ±7.29 <sup>a</sup>	37.79 ±3.44 <sup>a</sup>	30.56 ±2.57 <sup>a</sup>	50.65 ±4.31 <sup>a</sup>	20.68 ±1.80 <sup>a</sup>	29.51

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

Statistical analysis was performed for the entire phytomass and its various parts. As in the previous case, significant differences between Zn and Pb were found both in the whole plant and in individual plant parts, such as inflorescence, leaves, stem, and roots ( $p < 0.001$ ). There was a statistical difference between Zn, Cu, and Cr in the soil ( $p < 0.05$ ).

The metal concentrations in soil and *Erigeron canadensis* L. are presented in Table 3. The concentration in soil is shown at the condition of acetate-ammonium buffer pH 4.8.

The concentration of Zn was 139.68 mg kg<sup>-1</sup> in the total dry weight of *Erigeron canadensis* L. and was the highest among all metals and among all plant parts, which may indicate its highest intake into the environment. The Cu was determined as 0.28 mg kg<sup>-1</sup> which was the lowest concentration among the four metals. The concentration of Cu in the plant was the second among all the studied metals, at 27.66 mg kg<sup>-1</sup> in total dry weight. These elements are necessary for normal plant growth, but in excessive concentrations, they have a negative impact [5]. Concentrations of Cd and As in plants were below the limit of detection, except for As in the roots, which may indicate a longer absorption time for this element [35]. A one-way analysis of variance (ANOVA) indicated a statistically significant difference ( $p < 0.05$ ) in the mean concentration of metal in plant parts among Zn, Cu, Cr, and Pb.

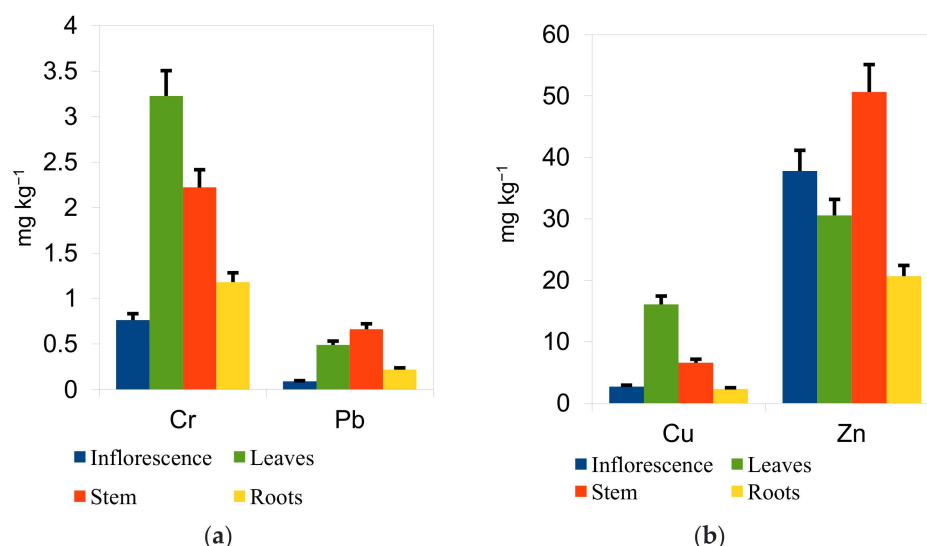
As in the case of ragweed, Pb had the lowest values in *Erigeron canadensis* L., both in the whole plant (1.46 mg kg<sup>-1</sup>) and in individual parts, which most likely indicates its lowest bioavailability.

Based on the coefficient of variation of the concentration of metals in various parts of *Erigeron canadensis* L., Cu is characterized by the highest variability. This indicates that the distribution of this metal in various parts of the plant seemed to be very uneven ( $v = 96.5\%$ ). The concentrations of Zn, Cr, and Pb are most evenly distributed across various parts of the plant. This may be related to the low bioavailability of Pb and Cr for roots (in terms of Pb and Cr, the rate of metal uptake by plants is the lowest among other plant parts), and, as in the case of *Ambrosia artemisiifolia* L., may be due to the barrier-free mechanism of element entry into the aboveground part of the plant.

According to the coefficient of variation of the concentration of metals in various parts of *Erigeron canadensis* L. ( $v, \%$ ), the analyzed metals were placed in the following descending order:  $\text{Cu} > \text{Pb} > \text{Cr} > \text{Zn}$ .

In total, for all metals analyzed, the concentration in plant parts was significantly lower than in soil ( $F_{\text{theor}} < F_{\text{exper}}, p < 0.05$ ), and the concentrations of Cu and Pb were significantly higher among individual parts of *Erigeron canadensis* L. ( $F_{\text{theor}} < F_{\text{exper}}, p < 0.05$ ), indicating the root and foliar pathways of heavy metals and the highest bioavailability of Cu and Pb to *Erigeron canadensis* L.

The distribution of metals in plant parts for *Erigeron canadensis* L. is presented in Figure 3.



**Figure 3.** Cr and Pb (a) and Cu and Zn (b) content in parts of *Erigeron canadensis* L.

The distribution of the studied metals by parts of *Erigeron canadensis* L. was as follows (in descending order of content,  $\text{mg kg}^{-1}$ ): Pb: roots > stem > leaves > inflorescence; Zn: stem > inflorescence > leaves > roots; Cu: leaves > stem > inflorescence > roots; Cr: leaves > stem > roots > inflorescence.

Usually, the metal content in different parts of plants decreases in the following order: roots > leaves > stem > inflorescence > seeds [47]. In our studies, only Pb distribution in plant parts corresponded to this sequence in *Erigeron canadensis* L. This may indicate the barrier-free (or foliar) character of metal penetration into plants [48,49], as well as general anthropogenic environmental pollution in the study area [50].

Despite the fact that the highest concentration of metal was Zn in soil and plants, the highest PUI value was Cu. This indicates its highest bioavailability and barrier-free mechanism of entry into *Erigeron canadensis* L. [22]. Pb is the most harmful element produced in the production and processing of rechargeable batteries [40], but its PUI value was the lowest among the studied metals, which may indicate the resistance of the studied plants to the absorption of this pollutant [41].

Following the results of the PUI for both species, the metals in terms of bioaccumulation intensity can be placed in the following row in decreasing order:  $\text{Cu} > \text{Zn} > \text{Cr} > \text{Pb}$ .



According to the concentration of metals in various parts of both plants (*Ambrosia artemisiifolia* L. and *Erigeron canadensis* L.), the studied metals can be placed in the following row: roots: Zn > Cu > Cr > Pb > As; inflorescence: Zn > Cu > Cr > Pb; leaves: Zn > Cu > Cr > Pb; stems: Zn > Cu > Cr > Pb.

The highest values of PUI for various parts of *Erigeron canadensis* L. for all investigated metals, except for Cu, are noted in the leaf (Cr and Cu) and the stem (Pb and Zn), which may also indicate a possible apoplastic method of entry.

### 3.3. Translocation Factor (TF)

The translocation coefficient shows the plant's efficiency in translocation metals from the roots to the vegetative part of the plant. The metal ratio between roots and plant parts is an important parameter for selecting a model plant species for phytoremediation, and a ratio above 1 means that metals accumulate more in shoots than in roots [51]. For Pb, for example, plants with a transfer coefficient above 1 are classified as hyperaccumulators, while plants with a transfer coefficient less than 1 are called lead non-accumulators [52], and this classification is also true for zinc [53].

Hyperaccumulation is understood as the process of absorption, translocation, and accumulation of metals in concentrations greater than those found in the environment in various parts of the plant. [54]. In general, plants that accumulate metals are classified as hyperaccumulators (accumulating more than 1000 µg/g) or non-hyperaccumulators (accumulating < 500 µg/g). The hyperaccumulators accumulate metals in the shoots above the roots [55]. According to another definition, hyperaccumulator plants include plants in which the absorption of metals is more than 100 times higher than in ordinary plants, and in which the correlation of the content of metals in the leaves to the roots is >1 [56].

The ratios of PUI and TF are presented in Table 4. The total and ratio of root/soil were calculated in PUI. Shoot, inflorescence, leaf, and stem were divided by root. The ratio of each TF is listed in this table.

**Table 4.** PUI and TF for *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L.

Metals	Ratio vs. Root					
	PUI		TF			
	Total Root/Soil		Shoot	Inflorescence	Leaf	Stem
<i>Ambrosia artemisiifolia</i> L.						
Cr	21.69	8.74	1.48	0.15	1.08	0.25
Cu	216.70	92.76	1.34	0.53	0.64	0.17
Pb	1.89	1.15	0.64	0.14	0.37	0.13
Zn	106.81	31.38	2.40	0.86	1.15	0.40
<i>Erigeron canadensis</i> L.						
Cr	8.34	1.33	5.26	0.65	2.74	1.88
Cu	100.12	8.38	10.94	1.17	6.94	2.84
Pb	0.54	0.08	5.66	0.41	2.23	3.02
Zn	29.51	4.36	5.75	1.83	1.48	2.45

In summary, the determination of a hyperaccumulator has to meet the following parameters: (1) a shoot-to-root metal concentration ratio higher than 1, which signifies an efficient ability to translocate metals from roots to shoots [57]; (2) a shoot-to-soil metal concentration greater than 1, which indicates a greater ability to uptake metals from the soil [58]; and (3) a shoot metal concentration higher than 1000.00 mg kg<sup>-1</sup> for Cu, Cr, and Pb, and 10,000.00 mg kg<sup>-1</sup> for Zn [59].

According to the TF translocation coefficient shoot/root indicator in *Ambrosia artemisiifolia* L., values above 1 were determined for Cr, Cu, and Zn. The highest TF shoot/root was Zn at 2.4. This indicates the highest phytoavailability of this metal.

The value of bioaccumulation index PUI of four metals was above 1 in *Ambrosia artemisiifolia* L. The highest value of the PUI was Cu. The PUI values were 216.7 and 92.76

in the total plant mass and root/soil, respectively. The lowest value of the PUI was Pb. The PUI values were 1.89 and 1.15 in the total plant mass and root/soil, respectively. This distribution indicates its lowest bioavailability. The concentrations of metals in *Ambrosia artemisiifolia* L. plants are lower than the recommended levels for hyperaccumulators, i.e., two out of the three criteria for hyperaccumulation are met [59]. At the same time, given the PUI and TF results, *Ambrosia artemisiifolia* L. can be proposed for phytoremediation of soils contaminated with Cu, Zn, and Cr due to their negative impacts on human health.

In *Erigeron canadensis* L., the translocation coefficient (TF) exhibited values above 1 for four metals, with Cu having the highest shoot/root ratio at 10.9. Notably, both Cu and Zn demonstrated TF values exceeding 1 in both the entire plant and its components.

The values of the PUI bioaccumulation index of Zn, Cu, and Cr were found to be above 1 in *Erigeron canadensis* L. The highest value of the PUI was for Cu. The PUI values were 100.12 and 8.38 in the total plant mass and root/soil, respectively. The value of the PUI bioaccumulation index was determined below 1 for Pb in *Erigeron canadensis* L. This indicates its lowest bioavailability. The concentrations of metals in *Erigeron canadensis* L. are below the recommended levels for hyperaccumulators, i.e., two out of the three criteria for hyperaccumulation are met [59]. At the same time, taking into account the PUI and TF results, *Erigeron canadensis* L. can be proposed for the phytoremediation of soils contaminated with Cu, Zn, and Cr.

#### 4. Conclusions

The largest metal concentrations in *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L. were determined for Zn and Cu. According to the concentration in different parts of *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L., the metals can be placed in the following rows: for roots: Zn > Cu > Cr > Pb > As; for inflorescences: Zn > Cu > Cr > Pb; for leaves: Zn > Cu > Cr > Pb; for stems: Zn > Cu > Cr > Pb. For all analyzed metals, the content in *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L. was significantly higher than in the soil ( $F_{\text{theor}} < F_{\text{exper}}$ ,  $p < 0.05$ ), which may indicate a high bioavailability of metals by studied plants, as well as possible foliar pathway of metal uptaking. Zn concentration was significantly higher among other metals in some (leaves, stem and inflorescence) parts of *Ambrosia artemisiifolia* L. ( $F_{\text{theor}} < F_{\text{exper}}$ ,  $p < 0.05$ ). The contents of Cu and Pb were significantly higher in some (leaves, stem) parts of *Erigeron canadensis* L. ( $F_{\text{theor}} < F_{\text{exper}}$ ,  $p < 0.05$ ). These facts could indicate the best translocation of Zn, Cu, and Pb in the studied plant species. For the studied species, Cu was characterized by the highest bioaccumulation, while Pb by the lowest. Under the PUI, the metals can be ranked in descending order: Cu > Zn > Cr > Pb. The translocation of metals in the studied plants from roots to shoots was estimated to be quite high. Based on the shoot/root TF index for *Ambrosia artemisiifolia* L., values above 1 were identified for Cr, Cu, and Zn. For *Erigeron canadensis* L., the values of TF shoot/root were higher than 1 for Cr, Cu, Pb, and Zn.

Thus, both *Ambrosia artemisiifolia* L. and *Erigeron canadensis* L. can be recommended as plants for phytoremediation of soils polluted with Cu, Zn, and Cr.

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