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Bioaccumulation of Heavy Metals in Certain Parts of *Erigeron Annuus* l. from Contaminated Soil

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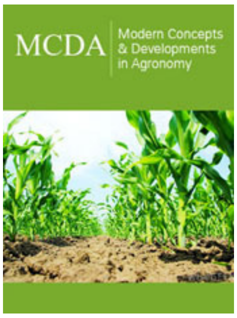

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Abstract

The objective of this study is to determine the level of heavy metals (As, Cr, Ni, and Pb) in the soil, as well as their bioaccumulation in different parts of *Erigeron annuus* L. (krasolika) plants, in the Maljen mountain area. Soil samples were taken from three locations, and the experimental part of the study was conducted through vegetation trials. The content of each element was separately determined in different parts of the plant (root, stem, and flower) in correlation with the element content in soil samples. The concentration of heavy metals was determined using atomic absorption spectrophotometry.

The examined heavy metal content in soil samples exceeded the maximum allowed amount, indicating that all analyzed sites belong to the category of contaminated soil. Furthermore, the degree of accumulation of the monitored elements in different parts of the plant varied. The highest concentrations were recorded in the stem and flower, specifically for Cd (0.785mg/L) and Co (0.805mg/L).

Pearson's product-moment correlation coefficient was used for statistical analysis of the results. The results on heavy metals (Pb, Cd, Ni, Co, and Cr) show that there is a positive correlation between soil samples, roots, stems, leaves, flowers, and fruits of krasolika grown in contaminated soil. The calculated significance level (marked as Sig. 2-tailed) suggests that the correlations calculated are statistically significant ($p > 0.05$). The data show that *Erigeron annuus* L. grown in contaminated soil exhibits phytoremediation potential significant for Ni, Cr, Cd, Cu, and Pb. The accumulation of heavy metals in plants depends not only on the total content in the soil but also on the plant's affinity and individual or interactive effects of various soil properties.

Keywords: Contaminated soil; *Erigeron annuus* L; Heavy metals; Bioaccumulation; Atomic absorption spectrophotometry

Introduction

Heavy metals are highly persistent and toxic to ecosystems, making them among the most hazardous substances in soil. These elements are toxic to plants and can accumulate in their tissues, entering food chains and persisting in ecosystems. The resulting contamination can cause phytotoxic effects and negatively impact the quality of plant products. Heavy metals are primarily of geogenic origin, originating from the lithosphere, and their concentration in soil depends on the underlying rock composition [1].

Due to their production methods, toxicity, potential uptake by plants, and incorporation into food chains, heavy metals are increasingly dominant environmental pollutants [1-3]. The mobility and accumulation of heavy metals in soil are influenced by many factors, including soil pH, organic matter content, and clay colloids [3]. The mobility and toxicity of heavy metals in soil can be influenced by multiple factors including soil moisture, calcium-carbonate content, hydrated oxides of iron and aluminum, cation exchange capacity, redox potential, and groundwater level [4].

Most toxic elements exhibit reactivity with various organic compounds, forming stable complexes with ligands that contain electron donors such as oxygen, sulfur, or nitrogen [5]. The toxic effect of these elements is derived from their irreversible binding to metabolic active sites in amino acids, polypeptides, and proteins [5]. Currently, it is widely accepted that toxic elements primarily impact the cellular membrane, with damage to intracellular enzyme systems being a secondary effect in most cases [6]. These heavy metals can enter the food chain *via* plant uptake and result in cumulative exposure in the human body, where they can accumulate in specific organs and tissues, causing harmful effects.

The intensity of metal binding in soil increases as the organic matter content and soil pH value increase. In soil, heavy metals have a tendency to strongly adsorb to the soil matrix and do not break down like organic matter does through microbial activity or chemical oxidation. The accumulation of heavy metals in soil is a major global environmental problem, with industrial activities, mining, and agricultural practices being the main sources. This accumulation can result in reduced crop yields, diseases, compromised food safety, and hinder sustainable development. Addressing locations contaminated with heavy metals using chemical or physical techniques presents a significant challenge. Heavy metals can affect plants directly and indirectly, with negative impacts on all physiological and biochemical processes of the plants. As a result, anatomical and morphological changes occur, leading to a reduction in the production of organic matter and changes in the chemical composition of the plants (Kastori, 1997).

Soil contamination with heavy metals is not easy to determine and varies among different types of soil. The presence of a certain compound, in a certain quantity, may not disturb plant production in one type of soil, but its presence in another type of soil may reduce the quality and quantity of the yield. In phytoremediation, plants are used to remove pollutants from the environment. Plants act as bioreactors, as their roots show unique and selective abilities to take up pollutants, while the shoot is a site for translocation, bioaccumulation, and degradation of pollutants.

Erigeron annuus (L.) Pers. is an annual herbaceous plant from the Asteraceae family. The stem is upright, branched in the upper part and up to 150cm tall. The root is spindle shaped. The leaves are simple, alternately located on short petioles or sessile, narrow and oblong in shape, up to 10 cm long, covered with sparse hairs. The flowers are small, clustered in flower heads with a diameter of about 2 cm at the tips of the stems, and numerous such heads form a cluster of flowers. Blooms from June to September. The fruit is an achene with a hairy pappus.

The critical concentrations of metals in plants, which cause a 10% reduction in dry matter, depend on the plant species, variety or genotype, as well as the characteristics of the heavy metal. The aim of this work was to determine the level of heavy metals in non-carbonate alluvial (fluvial) soil (As, Cr, Ni and Pb), taken from the Maljen mountain, and their accumulation in wild and cultivated *Erigeron annuus* L. Correlation analysis established the connection between the content of heavy metals in plant material and some soil properties.

Materials and Methods

The soil was taken from Mount Maljen, the location of the air spa Divčibare. According to the research data of Novaković Vujović & Eremija [7]. Mount Maljen, where the air spa Divčibare is located, from which the samples of soil were taken, is naturally composed of serpentine rocks that naturally contain heavy metals [8] (Figure 1).

Figure 1: Soil sampling site.

The surface area of the tested area was 1ha (100 × 100m). The soil samples were mixed. In four experiments, each with 2kg of soil, *Erigeron annuus* L were sown. From that, 1.0000g of soil was taken and digested with aqua regia to determine the total metal concentration (pseudo-total), 1,00g of soil was digested with a mixture of nitric and hydrochloric acid (1:3) for 5 hours in a water bath at 85 °C. The plant samples, after being weighed out (0.5g), were transferred to Teflon vessels. To each vessel, 7ml of 65% nitric acid (HNO_3) and 1ml of 30% hydrogen peroxide (H_2O_2) were added. Digestion was carried out according to the following program:

temperature was increased to 200 °C for 10 minutes and then held at 200 °C for 15 minutes [9].

Atomic absorption spectrophotometry was used to determine the metal content absorbed by this plant from the soil. For the statistical analysis of the results, the Pearson product moment correlation coefficient was used. The data will be presented in both tabular and graphical formats.

Result and Discussion

The Table 1 shows the number of heavy metals in contaminated and uncontaminated *Erigeron annuus* L in each of the observed items: soil, root, stem, leaf and flower with fruit. The goal of correlation analysis is to determine if there is a quantitative agreement (correlation) between the observed variations and, if so, to what extent [10]. A scatterplot provides great help in this regard.

Table 1: Parameters for the presence of heavy metals in sunflower soil.

Metals (mg/L)	Soil	Root	Stem and Leaf	Flower with Fruit
Pb	0,243	0,223	0,519	0,523
Cd	0,018	0,004	0,785	0,462
Ni	0,404	0,265	1,204	1,111
Co	0,960	0,184	0,805	0,458
Cr	0,195	0,210	0,646	0,640

The results on heavy metals (Pb, Cd, Ni, Co, Cr) indicate that there is a correlation between the soil, roots, stems, leaves, flowers, with fruits of *Erigeron annuus* L grown in contaminated conditions [11,12] (Table 2). When interpreting statistical results, it is important to calculate the level of significance (indicated by Sig. 2 tailed), which indicates the degree of confidence with which we can consider the obtained results. In this case, the calculated p-value is 0.714, which is greater than the commonly used significance level of 0.05. Therefore, we can conclude that the correlation calculated is not statistically significant [13] (Figure 2).

Table 2: Pearson correlation coefficient.

		Soil	Root	Stem and Leaf	Flower with Fruit
Soil	Pearson Correlation	1	,387	,227	-,035
	Sig. (2-tailed)		,520	,714	,955
	N	5	5	5	5
Root	Pearson Correlation	,387	1	,194	,592
	Sig. (2-tailed)	,520		,755	,293
	N	5	5	5	5
Stem and Leaf	Pearson Correlation	,227	,194	1	,796
	Sig. (2-tailed)	,714	,755		,107
	N	5	5	5	5
Flower and Fruit	Pearson Correlation	-,035	,592	,796	1
	Sig. (2-tailed)	,955	,293	,107	
	N	5	5	5	5

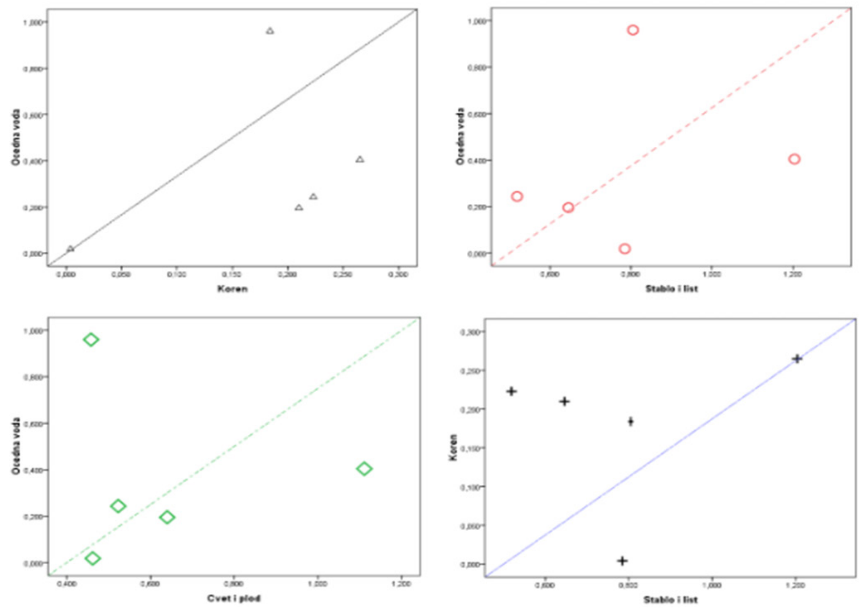

Figure 2: Scatter diagram.

Pearson correlation indicates a direct relationship between variables as assumed by scatter plot analysis. The coefficient of Pearson's correlation between root and stem and leaf is 0.194, between root and flower with fruit 0.592. A positive value of the Pearson correlation indicates a direct relationship between the variables as presented by the analysis of the scatter diagram. Also, in the conducted analysis, there is a linear positive small correlation between the two variables (r=0.194), which suggests that the linear relationship between them is weak .

Observing the calculated level of significance (indicated by Sig. 2 tailed) is the data that shows with how much confidence the obtained results should be observed. In this case, p=0.955> 0.05, so we conclude that the calculated correlation is not significant. The increased concentration of these heavy metals in the roots and the low value of translocation to the aerial parts indicated their suitability for phytostabilization [14].

Based on the obtained results (Table 1), the elements Pb, Cd and Cr showed a significant translocation from the roots of the plant to the stem, which is a prerequisite for efficient phytoextraction and accumulation of metals in the above-ground parts [15].

The Maximum Allowed Concentration (MAC) of heavy metals in the soil in Serbia is defined by the Regulation on permitted quantities of hazardous and harmful substances in the soil and methods of their testing, published in the Official Gazette of the Republic of Serbia (23/94) [16]. However, this regulation defines MAC only for agricultural land, while for other types of land (industrial land, playgrounds, parks, etc.) there is no legally prescribed maximum content of heavy metals [17].

Conclusion

Observing the calculated level of significance (marked with Sig. 2 tailed) is the data that shows how much confidence should be observed in the obtained results, we can conclude that the calculated correlations are not statistically significant (p> 0.05), which gives us the right to state the hypothesis (H1): The results on heavy metals (Pb, Cd, Ni, Co, Cr+6) indicate that there is a correlation between the soil, root, leaf, flower and fruit in *Erigeron annuus* L that grew in contaminated conditions, we cannot adopt completely.

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