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Heavy metals in the land of the potential local ecological network in the city of Zenica, Bosnia and Herzegovina

ABSTRACT

In order to analyze the current state of agricultural land and assess its suitability for agricultural use within the potential local ecological network of the city of Zenica (Bosnia and Herzegovina), soil and plant samples were analyzed for the content of heavy metals (Zn, Ni, Pb, Cd, Cr, and Cu). The obtained results were evaluated against the maximum permitted concentration for agricultural soils as defined by the relevant legislation. Soil samples and selected cultivated plant species were analyzed using atomic absorption spectrometry (AAS) to determine both total and available concentrations of selected heavy metals. Bioaccumulation (BAF) and translocation (TAF) factors were calculated to assess the phytoremediation potential of selected plants. The research was conducted on agricultural plots located in settlements surrounding industrial facilities in the city of Zenica, primarily in the vicinity of the steelworks. The results revealed the highest BAF values for Cd across all investigated locations. Furthermore, the findings showed that alfalfa and corn efficiently translocated Cd, Ni, and Pb from roots to shoots. Overall, the results provide a solid basis for planning soil remediation strategies in the investigated areas using phytoremediation techniques, particularly with respect to cadmium decontamination, which proved to be feasible under by the studied conditions.

Keywords: *heavy metals, plants, agricultural soil, phytoremediation*

1. INTRODUCTION

Soil and plant contamination by heavy metals and various chemical compounds represents a major contemporary environmental problem that adversely affects human health and the safe cultivation of edible plants. Heavy metals enter soils through numerous anthropogenic activities, including steel and metal industries, biomass fuel combustion, waste disposal, agricultural practices, irrigation etc. Furthermore, heavy metals may also originate from geological sources [1, 2]. The metal sector in Bosnia and Herzegovina has a long history and significant potential, largely due to the presence of various ore deposits, established mining activities, relatively low labour costs, and industrial heritage. This sector provides considerable natural and human resources and supports the sustainable development of numerous economic activities.

Soil contamination is particularly pronounced in the industrial areas of Zenica and along major roads, where it is manifested through changes in the chemical, biological, and physical properties of arable land [2,3]. Pollution generally refers to the presence of chemical compounds at concentrations that negatively affect the environment and human health. Cultivating crops on contaminated soils poses serious health risks, as harmful substances can enter the food chain through ingestion, inhalation, or dermal contact. Growing awareness of environmental protection and public health has stimulated the development of remediation technologies aimed at restoring polluted areas to safe conditions [3, 4]. Remediation typically involves measures designed to reduce contamination to levels suitable for further land use. One environmentally friendly approach to soil decontamination is phytoremediation, which relies on plant species capable of accumulating, immobilizing, mobilizing, or transforming various chemical pollutants. Numerous studies have demonstrated that some commonly cultivated plant species possess the ability to eliminate or stabilize harmful compounds through a range of cellular

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mechanisms that confer tolerance to metal stress [3-5]. One of the main advantages of phytoremediation is its cost-effectiveness and environmental compatibility, making it one of the most affordable biotechnological approaches available [6-8]. Conventional soil remediation techniques are often expensive and may cause additional environmental disturbance. In contrast, phytoremediation offers a sustainable alternative and highlights the importance of understanding both the sources and adverse effects of heavy metals, as well as the development of innovative remediation strategies [7, 8]. Recent studies emphasize the need to integrate traditional approaches with modern analytical techniques in order to improve large-scale applicability while maintaining economic feasibility. According to Sarwar et al. [9] phytoremediation is particularly advantageous due to its efficiency and low costs [10]. Ashraf et al. [11] further describe phyto-remediation as an environmentally sustainable alternative to conventional remediation methods [9,12]. This approach contributes to the restoration of contaminated soils, supports environmental health, and enables the long-term safe use of agricultural land [13-15]. Accordingly, the present study aims to analyze the current condition of agricultural soils within the potential local ecological network of the city of Zenica and to assess their suitability for agriculture. Soil and plant samples were analyzed for the content of Zn, Ni, Pb, Cd, Cr, and Cu, and the bioaccumulation (BAF) and translocation (TAF) factors were calculated to evaluate the phytoremediation potential of selected plant species.

2. EXPERIMENTAL PART

Soil samples were collected from several locations within the municipality of Zenica during the autumn in 2024, in the vicinity of the company ArcelorMittal Zenica industrial complex. The investigated surface areas were approximately 1000 m^2 each. The selected sampling locations were Podbriježje (LOC1) 44 21'17''N, 17 88'70''E, Tetovo (LOC2) 44 13'52''N, 17 53'18''E and Gradišće (LOC3) 44 24'04''N, 17 87'66''E, where alfalfa, corn, and chard were cultivated, Figure 1.

The investigated soils were classified as leptosols. Soil pH values were neutral to slightly alkaline (Table 1).

Table 1. pH values of soil samples before planting the crops

pH values	LOC1	LOC2	LOC3
pH in H_2O	8,27	8,32	8,10
pH in KCl	7,35	7,66	7,34

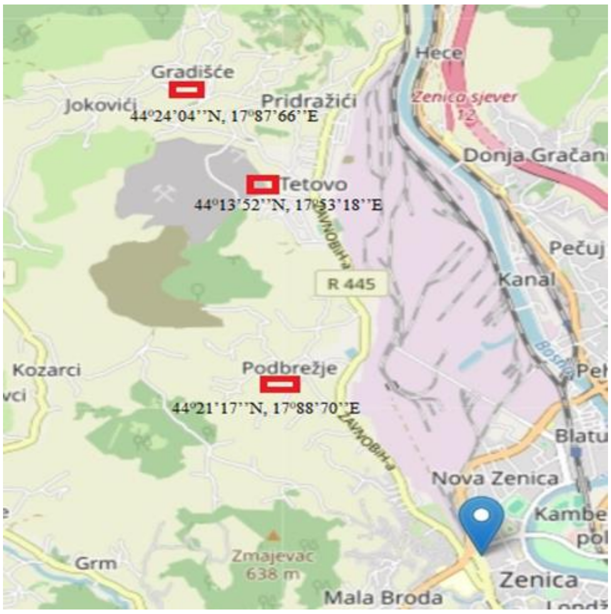

Figure 1. Sampling locations in the city of Zenica: Podriježje, Tetovo, and Gradišće

Plant samples together with the corresponding topsoil samples (more than 200 samples in total) were collected from the selected locations and analyzed for heavy metal content [3,16,17]. Plant sprouts and roots were thoroughly washed with distilled water, air-dried, and wrapped in absorbent paper. Subsequently, plant samples were oven-dried at 70 °C to constant mass and then ground to a fine powder. Approximately 5 g of powdered plant material was treated with 23 mL of 6M HNO_3 and heated at 80 °C for approximately 8 h until digestion was completed. After cooling to room temperature, the samples were filtered through Whatman filter paper and diluted with deionised water. Calibration curves were constructed using standard solutions for heavy metal determination [17]. Topsoil samples were prepared according to the procedure described by Murtic et al. [2]. The total concentrations of heavy metals (Zn, Ni, Pb, Cd, Cr, and Cu) were determined using the AAS method (PerkinElmer spectrometer 3110). Available heavy metals were batch extracted using EDTA as a strong chelating agent [18 - 20]. Chemical analyses of heavy metals were performed in accordance with ISO standard 11466 [19-21]. All measurements were conducted in accredited laboratories of the "Kemal Kapetanović" Institute, University of Zenica [22, 23].

To evaluate the phytoremediation potential of plants on heavy metal-contaminated soils, enrichment factor (EF), bioaccumulation factor (BAF), and translocation factor (TAF) were calculated. The EF was used to assess the degree of soil contamination, where EF < 2 indicates minimal anthropogenic influence, EF values between 2 and 5 indicate moderate pollution, and EF values between 5 and 20 indicate significant pollution. The EF was calculated according to Equation (1) [24]:

$$EF = Cx / Co \quad (1)$$

where Cx represents the concentration of a heavy metal in contaminated soil and Co represents the concentration in control soil. The EF could serve as an indicator for soil assessment in sense of the presence and intensity of artificial contaminant deposition on topsoil. In order to determine the phytoremediation potential, calculation of bioaccumulation and translocation factors were done. The BAF was calculated as the ratio of the heavy metal concentration in the aboveground plant biomass to that in the soil [25], according to Equation (2):

$$BAF = C\ sprout / C\ soil \quad (2)$$

BAF values greater than 1 indicate the ability of a plant to accumulate or tolerate heavy metals [13]. Plants can translocate heavy metals through their roots to other parts of the plant, and this ability is expressed as the TAF [26]. This data were calculated as the ratio between the cadmium concentration in the aboveground part of the plant and the heavy metal concentration in the roots (3).

$$TAF = C\ sprout / C\ root \quad (3)$$

TAF > 1 means hyperactive translocation of elements from root to sprout.

Quality assurance procedures included the use of high-purity reagents, certified standards, and pre-cleaned laboratory equipment. All measurements were performed in triplicate.

Statistical analysis was conducted using the Pearsons correlation coefficients to assess relationships among variables. Significant differences were determined using analysis of variance (ANOVA) at a significance level of p < 0,05 [2, 3]. All statistical analyses were performed using Microsoft Excel software.

3. RESULTS AND DISCUSSION

Anthropogenic pollution resulting from long-term iron and steel production activities in Zenica renders this area particularly relevant for environmental research. Figure 2 presents the average total and available concentrations of heavy metals in soil samples collected from the investigate locations, expressed in mg/kg.

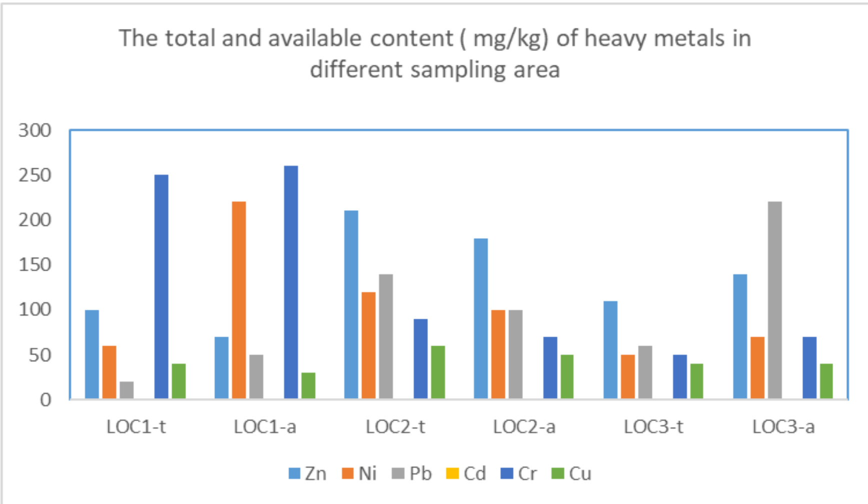

Figure 2. The heavy metals content: total and available in investigated soil samples from LOC1, LOC2 and LOC3

The average concentration ranges for Zn, Ni, Pb, Cd, Cr and Cu were 70-210, 50-220, 20-220, 1 -2, 50-260, and 30-60 mg/kg, respectively The results in Figure 2 confirm that the concentrations of most metals at all locations exceed the permissible limits defined by the Legislation of the Federation of Bosnia and Herzegovina. According to these regulations, the maximum allowable concentrations (mg/kg) for Zn, Ni, Pb, Cd, Cr, and Cu are 200, 50, 100, 1.5, 100 and 80, respectively [23]. Similar contamination patterns have been reported in previous studies conducted in the Zenica municipality and surrounding areas [2, 3, 12, 20, 22]. Correlation coefficients for heavy metal concentrations in soil samples are presented in Tables 2.

Statistically significant positive correlations were observed for Zn-Cu, while negative correlations were detected for Zn-Cr i Pb-Cr. These results, in combination with previously reported monitoring data, provide insight into potential transport pathways of heavy metals originating from anthropogenic sources in the wider Zenica area.

Table 2. Correlation coefficients of heavy metals content in soils on investigated lands

	Zn	Ni	Pb	Cd	Cr	Cu
Zn	1					
Ni	-0.23069	1				
Pb	0.5581	-0.15602	1			
Cd	0.420389	-0.02599	0.011219	1		
Cr	-0.65859	0.520584	-0.618	-0.31332	1	
Cu	0.960114	-0.26715	0.354775	0.316228	-0.54896	1

Table 3. Correlation coefficients of heavy metals content in soils (t) and extracted from plants (a)

	Zn-t	Ni-t	Pb-t	Cd-t	Cr-t	Cu-t	Zn -a	Ni --a	Pb -a	Cd -a	Cr -a	Cu -a
Zn -t	1											
Ni -t	0.97703	1										
Pb-t	0.96862	0.893405	1									
Cd-t	-	-	-	1								
Cr-t	-0.40389	-0.19967	-0.61859	-	1							
Cu-t	0.996616	0.991241	0.944911	-	-0.32733	1						
Zn -a	0.826754	0.687881	0.940634	-	-0.84856	0.777714	1					
Ni -a	-0.40389	-0.19967	-0.61859	-	1	-0.32733	-0.84856	1				
Pb -a	-0.15053	-0.35775	0.099906	-	-0.84358	-0.23129	0.431699	-0.84358	1			
Cd -a	0.996616	0.991241	0.944911	-	-0.32733	1	0.777714	-0.32733	-0.23129	1		
Cr -a	-0.56949	-0.38125	-0.75593	-	0.981981	-0.5	-0.93326	0.981981	-0.7269	-0.5	1	
Cu -a	0.904194	0.792406	0.981981	-	-0.75593	0.866025	0.987829	-0.75593	0.286143	0.866025	-0.86603	1

Table 3 presents correlations between heavy metal concentrations in soil and those extracted from plants. Strong positive correlations were identified for several metal pairs, including Zn-t –Ni-t, Zn-t –Pb-t, Zn-t –Cu-t, Zn-t –Cd-a, Zn-t –Cu-a, Ni-t –Cu-t, Ni-t –Cd-a, Pb-t –Cu-t, Pb-t –Zn-a, Pb-t –Cd-a, Pb-t –Cu-a and Cr-t –Cr-a. Zinc naturally occurs in soil however elevated concentrations are typically associated with anthropogenic sources such as steel production, coal combustion, and waste disposal, which corresponds with the environmental conditions in Zenica [12, 20, 22]. Lead contamination is primarily linked to ironworks activity, while traffic emissions also contribute significantly. Cadmium pollution is largely attributed to atmospheric deposition from industrial and urban emissions, as well as the application of certain fertilizers, inorganic and organic moieties. Elevated concentrations of Ni and Cu are partly associated with geological background and exhibit relatively limited variation with soil depth [15]. Monitoring data from 2011-2015 and 2018-2020, together with the present findings, indicate alarmingly high concentrations of Pb and Cd in soils within the city of Zenica [15, 20, 27]. Although cadmium is not essential element for plant growth, it is readily accumulated in plants grown on contaminated soils [28, 29]. The focus of this study is therefore not solely on confirming contamination levels but on exploring feasible remediation strategies. Table 4 presents the calculated EF values.

Table 4. EF values of Zn, Ni, Pb, Cd, Cr and Cu in soils from LOC1, LOC2 and LOC3

Sampling area	EF					
	Zn	Ni	Pb	Cd	Cr	Cu
LOC1	0,7	3,6	0,7	1	1	0,8
LOC2	0,9	0,8	0,7	1	0,8	0,8
LOC3	1,3	1,4	3,7	1	1,4	1

The highest polution levels were observed in the Gradišće area, with heavy metals ranked as follows: Pb > Ni >Cr > Zn > Cd > Cu. As previously reported, alkaline soil pH conditions favour the formation of metal complexes with low solubility, thereby reducing metal availability to plants [2, 3]. Nevertheless, continued monitoring is essential to assess long-term risks associated with heavy metal accumulation in agricultural soils.

Tables 5, 6 and 7 present the calculated BAF values.

The highest BAF values were consistently observed for Cd across all investigated locations.These results indicate a strong capacity of the selected plant species to accumulate cadmium relative to its concentration in soil [4, 22, 29, 30]. Cadmium emissions in Zenica originate primarily from metallurgical processes, iron and steel production, and biomass combustion, which remains a relevant pollution source in the region [15, 22, 27]. Tables 8, 9 and 10 presents the calculated TAF values.

Table 5. BAF values for Zn, Ni, Pb, Cd, Cr and Cu transfer from soils to plants from LOC1

Plant	BAF					
	Zn	Ni	Pb	Cd	Cr	Cu
alfalfa sprout	0,033	0,117	0,05	1	0,072	0,05
alfalfa root	0,033	0,242	0,75	1	0,244	0,05
corn sprout	0,033	0,008	0,05	1	0,006	0,05
corn root	0,033	0,442	2,65	1	0,144	1,3
chard sprout	0,033	0,134	0,05	2	0,006	0,05
chard root	0,033	0,325	0,05	2	0,006	0,05

Table 6. BAF values for Zn, Ni, Pb, Cd, Cr and Cu transfer from soils to plants from LOC2

Plant	BAF					
	Zn	Ni	Pb	Cd	Cr	Cu
alfalfa sprout	0,14	0,017	0,014	**1**	0,325	0,025
alfalfa root	0,01	0,183	0,014	**1**	0,525	0,025
corn sprout	0,01	0,017	0,014	**2**	0,025	0,625
corn root	0,01	0,017	0,014	**2**	0,025	0,625
chard sprout	0,01	0,017	0,014	**3**	0,025	0,025
chard root	0,01	0,3	0,014	**3**	0,025	0,025

Table 7. BAF values for Zn, Ni, Pb, Cd, Cr and Cu transfer from soils to plants from LOC3

Plant	BAF					
	Zn	Ni	Pb	Cd	Cr	Cu
alfalfa sprout	0,017	0,4	0,025	**3**	0,033	0,033
alfalfa root	0,017	0,35	0,025	**1**	0,033	0,033
corn sprout	0,017	0,425	0,4	**1**	0,033	0,533
corn root	0,017	0,325	0,325	**1**	0,433	1,3
chard sprout	0,017	0,4	0,025	**2**	0,033	0,033
chard root	0,017	0,75	0,025	**2**	0,033	0,033

Table 8. TAF values of Zn, Ni, Pb, Cd, Cr and Cu in selected plants from LOC1

Plant	TAF					
	Zn	Ni	Pb	Cd	Cr	Cu
alfalfa	1	0,48	1	1	1	1
corn	1	0,02	0,02	**2**	0,04	0,04
chard	1	0,4	1	1	1	1

Table 9. TAF values of Zn, Ni, Pb, Cd, Cr and Cu in selected plants from LOC2

Plant	TAF					
	Zn	Ni	Pb	Cd	Cr	Cu
alfalfa	1	0,09	1	1	0,6	1
corn	1	0,02	0.02	1	0.04	1
chard	1	0,06	1	1	1	1

Table 10. TAF values of Zn, Ni, Pb, Cd, Cr and Cu in selected plants from LOC3

Plant	TAF					
	Zn	Ni	Pb	Cd	Cr	Cu
alfalfa	1	1,14	1	3	1	1
corn	1	1,08	1,23	1	0,08	0,4
chard	1	0,5	1	1	1	1

The TAF represents the relationship between the mass fraction of a metal in the aboveground part of the plant and its proportion in the roots, and is used to determine the efficiency of metal translocation, particularly cadmium, from roots to aboveground plant parts. Hyperaccumulative plants are characterized by TAF values greater than 1.0 [3, 5, 31, 32]. The results showed that alfalfa and corn efficiently translocated Cd, Ni, and Pb from roots to sprouts, which is consistent with findings reported in similar studies on agricultural plants, where TAF values were calculated for Cd, Cr, Zn and Pb [1, 2, 5]. Numerous studies have investigated cadmium accumulation mechanisms in plants, however, available data remain limited and current knowledge is still inconsistent. Cadmium uptake in roots is not yet fully understood due to complexity of chemical detection and quantification, particularly of organometallic complexes. Furthermore, identifying reactive sites in the soil solid phase is necessary to accurately predict cadmium solubility products [33].

4. CONCLUSIONS

The study highlights the potential for remediation of heavy metal-contaminated soils in the city of Zenica through phytoremediation using commonly cultivated plant species. The highest bioaccumulation factors were observed for Pb, Cd, and Cu, while the highest translocation factors were recorded for cadmium (Cd) in all investigated plants. These findings demonstrate the phytoaccumulation and translocation capacity of alfalfa, corn, and chard under local environmental conditions. Given that certain areas of Zenica are classified as critical with regard to Cd contamination, the presented results provide valuable information for future soil remediation planning. The use of selected cultivars with high accumulation potential represents a feasible and environmentally sustainable approach to soil decontamination.

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IZVOD

TEŠKI METALI U ZEMLJIŠTU POTENCIJALNE LOKALNE EKOLOŠKE MREŽE U GRADU ZENICA, BOSNA I HERCEGOVINA

U cilju analize trenutnog stanja poljoprivrednog zemljišta i procene njegove pogodnosti za poljoprivrednu proizvodnju u okviru potencijalne lokalne ekološke mreže grada Zenice (Bosna i Hercegovina), izvršena je analiza uzoraka zemljišta i biljaka na sadržaj teških metala (Zn, Ni, Pb, Cd, Cr i Cu). Dobijeni rezultati upoređeni su sa maksimalno dozvoljenim koncentracijama za poljoprivredna zemljišta propisanim važećom zakonskom regulativom. Uzorci zemljišta i odabrane gajene biljne vrste analizirani su metodom atomske apsorpcione spektrometrije (AAS) radi utvrđivanja ukupnih i pristupačnih koncentracija odabranih teških metala. U cilju procene fitoremedijacionog potencijala odabranih biljnih vrsta izračunati su faktori bioakumulacije (BAF) i translokacije (TAF). Istraživanje je sprovedeno na poljoprivrednim parcelama smeštenim u naseljima u okruženju industrijskih postrojenja na području grada Zenice, pretežno u neposrednoj blizini železare. Rezultati su pokazali najviše vrednosti BAF za kadmijum (Cd) na svim ispitivanim lokalitetima. Takođe je utvrđeno da lucerka i kukuruz efikasno translokuju Cd, Ni i Pb iz korena u nadzemne delove biljke. U celini posmatrano, dobijeni rezultati predstavljaju pouzdanu osnovu za planiranje strategija remedijacije zemljišta na ispitivanim područjima primenom fitoremedijacionih tehnika, naročito u pogledu dekontaminacije kadmijuma, za koju je potvrđeno da je izvodljiva u uslovima obuhvaćenim predmetnim istraživanjem.

Ključne reči: *Teški metali, biljke, poljoprivredno zemljište, fitoremedijacija*

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