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Akumulacija teških metala u listovima bokvice (*Plantago maior* L.) na području Tuzle

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SAŽETAK: Istraživanja koja su započela šezdesetih godina 20. vijeka pokazala su da zemljišta u urbanim i industrijskim područjima sadrže enormno visoke koncentracije teških metala. Biljke su najosjetljivije na industrijska zagađenja i upravo zbog toga uspješno se koriste kao indikatori procjene onečišćenja životne sredine, te uspostavu adekvatnog biomonitoringa. Cilj rada je utvrditi sadržaj teških metala u listovima bokvice (*Plantago maior* L.) na tuzlanskom području, kao i procijeniti utjecaj termoenergetskih i industrijskih postrojenja na okoliš. Istraživanje se sastojalo od terenskog rada i laboratorijske analize. Terenski rad je podrazumijevao uzorkovanje biljnog materijala na devet (9) lokaliteta na području Tuzle. Sakupljeni uzorci biljnog materijala pripremani su za hemijsku analizu u laboratoriji Prirodno-matematičkog fakulteta Univerziteta u Tuzli. Sadržaj teških metala u biljnom materijalu određen je metodom atomske apsorpcione spektrofotometrije (AAS metoda), na instrumentu „Perkin-Elmer" 3110 i grafitnoj kiveti „Perkin-Elmer" HGA-440. Interpretacija rezultata izvršena je na bazi prosječnih vrijednosti sadržaja teških metala u ispitivanim biljkama u nezagađenim područjima. Utvrđeno je da sadržaj teških metala u listu bokvice najčešće nije imao dinamiku opadanja sa povećanjem rastojanja istraživanih lokaliteta od dominantnih antropogenih izvora emisije teških metala.

Ključne riječi: *akumulacija, teški metali, Plantago maior, tuzlansko područje*

Accumulation of Heavy Metals in Leaves of Broadleaf Plantain (*Plantago maior* L.) in the Tuzla Area

ABSTRACT: Studies that began in the 60s of the 20th century have shown that soil in urban and industrial areas contains enormously high concentrations of heavy metals. Plants are most sensitive to industrial pollution and therefore they are successfully used as indicators in the assessment of environmental pollution, as well as for the establishment of adequate biomonitoring. The aim of the paper is to determine the content of heavy metals in leaves of broadleaf plantain (*Plantago maior* L.) in the Tuzla area and to estimate the effect of thermal and industrial power plants on the environment. The research consisted of fieldwork and laboratory analysis. The fieldwork included sampling of plant material at nine (9) sites in the Tuzla area. The gathered samples of plant material were prepared for chemical analysis in the laboratory at the Faculty of Natural Sciences and Mathematics, University of Tuzla. The content of heavy metals in the plant material samples was determined by atomic absorption spectrophotometry (AAS method), using "Perkin-Elmer" 3110 instrument and "Perkin-Elmer" HGA-440 graphite tube. The interpretation of the results was conducted on the basis of the average concentrations of heavy metals in the analyzed plants in unpolluted areas. It was determined that the content of heavy metals in leaves of broadleaf plantain did not generally indicate a decline with the distance increase between the investigated sites and dominant anthropogenic sources of heavy metal emissions.

Key words: *accumulation, heavy metals, Plantago maior, Tuzla area*

INTRODUCTION

Heavy metal pollution is one of the most common forms of environmental pollution in urban areas (Grzebisz et al., 2002; Yoon et al., 2006; Uvar et al., 2007; Mazur, 2015). It should be noted that heavy metals have toxic effects on living organisms, even at low concentration. Working or living near potential contaminants such as some types of industrial plants increases the risk of exposure to heavy metals (Martin and Griswold, 2009; Liu et al., 2013).

Plants are most sensitive to industrial pollution, which is why they are successfully used as bioindicators in the assessment of environmental pollution and the establishment of adequate biomonitoring. Heavy metals accumulate in plants and affect the absorption and transport of essential elements, metabolism, growth and development (Bikić et al., 2015; Mitić et al., 2013; Cheng, 2003). Broadleaf plantain (*Plantago maior* L.) is one of the most efficient bioindicators of heavy metal pollution of all herbaceous plants, which is why it is used in many studies (Djingova and Kuleff, 1999; Kurteva, 2009; Mudgal et al., 2010).

The aim of the paper is to determine the content of heavy metals in leaves of broadleaf plantain (*Plantago maior* L.) in the Tuzla area and to estimate the effect of thermal and industrial power plants on the environment.

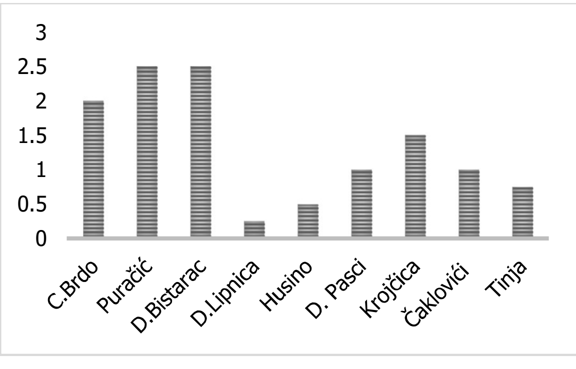
MATERIALS AND METHODS

The research consisted of fieldwork and laboratory analysis. The fieldwork included sampling of plant material at nine (9) sites in the Tuzla area. The gathered samples of plant material were prepared for chemical analysis in the laboratory at the Faculty of Natural Sciences and Mathematics, University of Tuzla. The samples were first washed with clean water and then with distilled water to remove excess dirt. The washed samples were cut into small pieces of 1-2 cm and dried at room temperature, and then in an air dryer oven at 105º C until they reached constant weight. The dried samples were ground in a mortar and pestle into particles of 1 mm and stored in hermetically sealed glass containers (vials) (Goletić, 2001).

For the chemical analysis of the plant material, 1g of the sample was weighed into 25 ml volumetric flask and digested in nitric acid (HNO3, p.a.) and hydrochloric acid (HCl, p.a.) with warming. After the sample digestion (clarification of the sample in the flask), perchloric acid (HClO4, p.a.) was added to the flask, and the sample was heated until perchloric acid vapors appeared and reached the neck of the flask. The content from the flask was cooled to room temperature. Then, distilled water was added to the flask to fill it to the mark and the content was stirred. In this way the solution was prepared for the determination of heavy metal concentrations. The contents (concentrations) of heavy metals: chromium (Cr), nickel (Ni), lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn), cobalt (Co) and manganese (Mn) in solutions of the plant material samples were determined by atomic absorption spectrophotometry (AAS method), using "Perkin-Elmer" 3110 instrument and "Perkin-Elmer" HGA-440 graphite tube. The determination of heavy metals was conducted according to ASTM E 1812-96 standard.

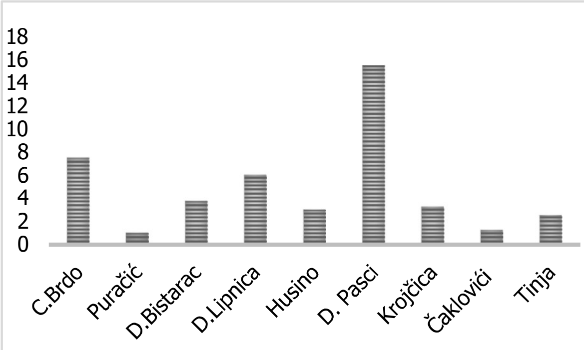
RESULTS AND DISCUSSION

The research results on heavy metal concentrations: chromium (Cr), nickel (Ni), lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn), cobalt (Co) and manganese (Mn) in broadleaf plantain are presented in graphs 1-7.



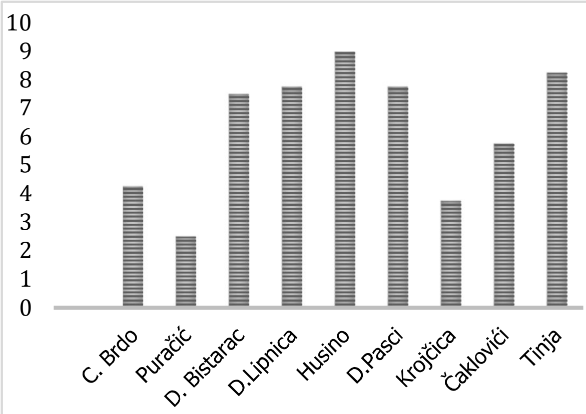
Graph 1. Chromium (Cr) content in leaves of broad leaf plantain (*Plantago maior* L.) in mg/kg of dry matter

Average chromium content in plants is in small concentrations, which vary in the range of 0.2-0.4 mg/kg of dry matter (Bogdanović et al., 1997). The determined chromium concentrations in broadleaf plantain are six times higher than the listed average values for unpolluted areas at the sites of Puračić (2.5 mg/kg) and Donji Bistarac (2.5 mg/kg) (Graph 1). Goletić (2001) notes that broadleaf plantain tends to accumulate heavy metals more intensively which is the result of genetic specificity.



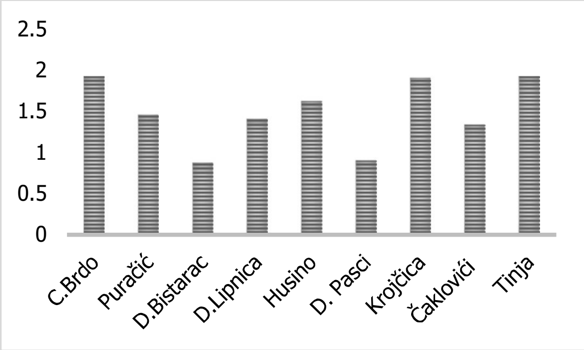
Graph 2. Nickel (Ni) content in leaves of broadleaf plantain (*Plantago maior* L.) in mg/kg of dry matter

Average nickel content in plants is 0.1-5 mg/kg of dry matter (Ward, 1995). The maximum value of nickel in leaves of broadleaf plantain was observed at the sites of Donji Pasci (three times higher than the natural average value), Crveno Brdo (7.5 mg/kg) and Donja Lipnica (6 mg/kg). The minimum value was registered at the site of Puračić (1mg/kg) (Graph 2).



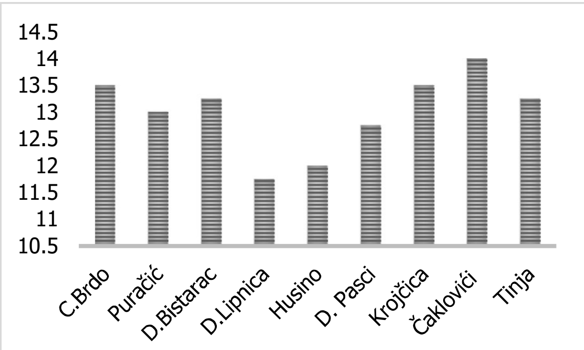
Graph 3. Lead (Pb) content in leaves of broadleaf plantain (*Plantago maior* L.) in mg/kg of dry matter

The natural lead content in plants varies in the range of 0.1-5 mg/kg (Bašić et al., 1998), and the average value is 0.1-10 mg/kg of dry matter (Bohn et al., 1985). The determined value of lead in leaves of broadleaf plantain is higher than its natural content value (0.1-5 mg/kg) in all the researched areas, but it is not higher than the threshold value (10 mg/kg). The highest concentrations of lead were observed at the site of Husino (9 mg/kg), and the lowest at the site of Puračić (2,50 mg/kg) (Graph 3). Elevated concentrations of Pb in leaves of broadleaf plantain were registered in the area of Albania and Poland (Levei et al., 2018; Buszewski et al., 2000.)



Graph 4. Cadmium (Cd) content in leaves of broadleaf plantain (*Plantago maior* L.) in mg/kg of dry matter

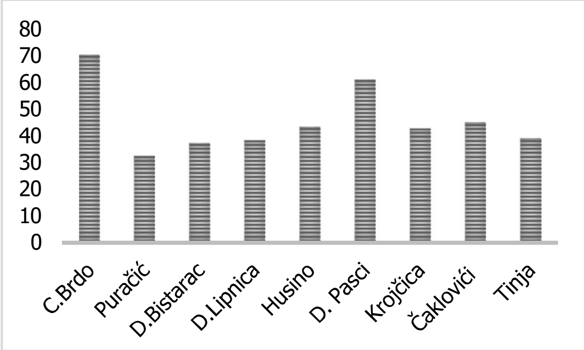
Cadmium is a significant pollutant due to its solubility in water and high toxicity to most organisms. It is the fourth most toxic element to vascular plants (Pedro et al., 2013). Cadmium content in broadleaf plantain in all the researched areas is significantly higher than its natural content which varies in the range of 0.02-0,.50 mg/kg (Ward, 1995), and its threshold value 0.1-0.8 mg/kg (Bohn et al., 1985). The highest concentrations of cadmium in broadleaf plantain were registered at the site of Crveno Brdo (2.5 times higher than the threshold value) and Tinja (2.5 times higher than the threshold value), while the lowest concentrations were determined at the site of Donji Bistarac (0.87 mg/kg) (graph 4). Many authors observe that the highest values of cadmium in plants have been determined in the vicinity of factories (Kataba-Pendias & Pendias, 1991; Yanyu et al., 1996; Markov et al., 1998; Goletić, 2001, 2003; Osmanović et al., 2014).



Graph 5. Copper (Cu) content in leaves of broadleaf plantain (*Plantago maior* L.) in mg/kg of dry matter

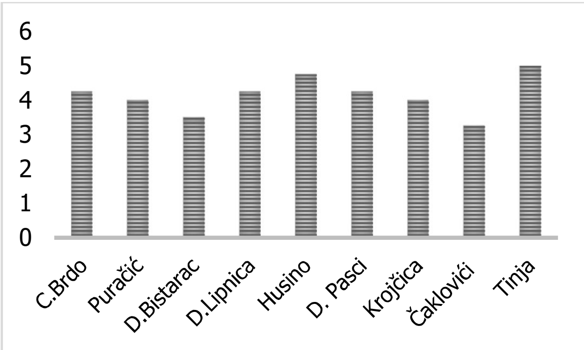
The natural content of copper in plants varies in the range of 1-15 mg/kg (Bašić et al., 1998), i.e. 1-12 mg/kg (Ward, 1995), while the average content in herbaceous plants varies between 4 and 15 mg/kg (Bohn et al., 1985), i.e. 2-20 mg/kg (Kastori, 1998) and in different plants there is mostly 0.5-30 mg/kg of dry matter (Kataba-Pendias & Pendias, 1984).

In this research, copper content in broadleaf plantain does not exceed the threshold value of 15 mg/kg of dry matter at all the sites. The highest value was determined at the site of Čaklovići (14 mg/kg), and the lowest one at the site of Donja Lipnica (11.75 mg/kg) (Graph 5).



Graph 6. Zinc (Zn) content in leaves of broadleaf plantain (*Plantago maior* L.) in mg/kg of dry matter

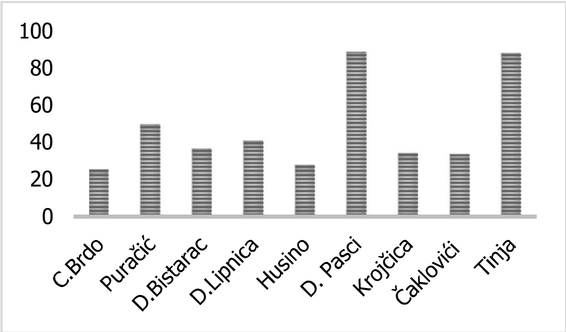
Zinc content in plants in unpolluted areas varies between 20 and 100 mg/kg (Kastori, 1998), and the average value is 30mg/kg of dry matter (Ward, 1995). In plant organs, it occurs in an amount of 2-200 mg/kg of dry matter (Gračanin & Ilijanić, 1977), and its phytotoxic threshold is 200 mg/kg (Ivetić, 1991). The harmful effects on plants occur when its content exceeds 100-300 mg/kg (Kastori, 1998). The content of zinc in broadleaf plantain is significantly higher than its natural average content in plants (30mg/kg) but considerably lower than the threshold value of 100 mg/kg of dry matter. The highest concentration was determined at the site of Crveno Brdo (70.25 mg/kg) and the lowest at the site of Puračić (32.5 mg/kg) (Graph 6).



Graph 7. Cobalt (Co) content in leaves of broadleaf plantain (*Plantago maior* L.) in mg/kg of dry matter

The natural content of cobalt in plants is in the range of 0.03-0.6 mg/kg of dry matter (Ward, 1995). The determined values in broadleaf plantain were above the natural values in all the researched areas. The maximum value was registered at the site of Tinja (eight times higher than the natural content of cobalt in plants) and the minimum value at the site of Čaklovići (3.25 mg/kg) (Graph 7).

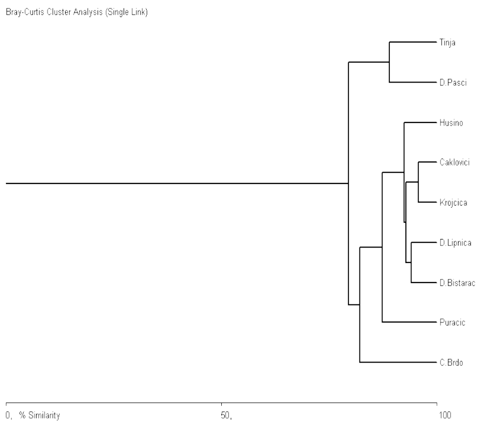
The natural content of manganese in plants is in the range of 20-240 mg/kg of dry matter (Ward, 1995). The content of manganese in broadleaf plantain is within the limits of the natural values in all the researched areas. The maximum value was determined at the site of Donji Pasci (88.75 mg/kg) and the lowest at the site of Crveno Brdo (25.25 mg/kg) (Graph 8).



Graph 8. Manganese (Mn) content in leaves of broadleaf plantain (*Plantago maior* L.) in mg/kg of dry matter

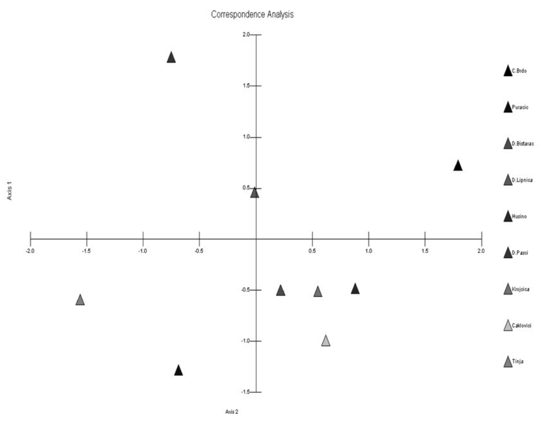
Cluster analysis of heavy metal contents in leaves of broadleaf plantain in the researched areas

The cluster analysis showed the close connection between the sites of Tinja and Donji Pasci, also between Čaklovići and Krojčica, which are further connected with the site of Husino and the sites of Donja Lipnica and Donji Bistarac (Graph 9).



Graph 9. Cluster analysis of heavy metal contents in leaves of broadleaf plantain in the researched areas

The correspondence analysis indicates the connection between the sites of Husino, Donji Pasci and Donji Bistarac, with regard to heavy metal contents in leaves of broadleaf plantain (Graph 10).



Graph 10. Correspondence analysis of heavy metal contents in leaves of broadleaf plantain in the researched areas

CONCLUSION

Based on the research results, the following conclusions are made:

The determined chromium concentrations are six times higher than the average values for unpolluted areas at the sites of Puračić and Donji Bistarac.

The maximum value of nickel was determined at the site of Donji Pasci (three times higher than the natural average value). The minimum value was registered at the site of Puračić (1mg/kg).

The determined value of lead in leaves of broadleaf plantain is higher than its natural content value in all the researched areas, but it is not higher than the threshold value.

Cadmium content in broadleaf plantain in all the researched areas is significantly higher than its natural content and its threshold value. The highest concentrations of cadmium were registered at the sites of Crveno Brdo and Tinja (2.5 times higher than the threshold value).

Copper content in broadleaf plantain does not exceed the threshold value at all the sites.

The content of zinc is significantly higher than its natural average content in plants but considerably lower than the threshold value.

The determined values of cobalt in leaves of broadleaf plantain were above the natural values in all the researched areas.

The content of manganese is within the limits of its natural values in all the researched areas.

The content of heavy metals in leaves of broadleaf plantain did not generally indicate a decline with the distance increase between the investigated sites and dominant anthropogenic sources of heavy metal emissions. The results of the cluster analysis shown by a dendrogram clearly display clustering the sites with similar characteristics (soil type, altitude, a wind rose etc.), which confirms that the complex of ecological factors of habitats affects the acquisition and accumulation of heavy metals.

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