

# ASSESSMENT OF THE POTENTIALLY TOXIC ELEMENTS CONTAMINATION AND THEIR UPTAKE BY *AMBROSIA ARTEMISIIFOLIA* L. IN SOILS IN THE NORTHERN PART OF BOSNIA AND HERZEGOVINA

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**Abstract:** This research focused on the determination of potentially toxic elements (PTEs) distribution in different agricultural soils and *Ambrosia artemisiifolia* L. (ragweed) at seven, different locations in the northern part of Bosnia and Herzegovina (BiH). Quantification of PTEs was done using atomic absorption spectrophotometry provided after acid digestion of the air-dried samples of soil and plant material. Determined content of elements in the soils increased as follows: Cd<Pb<Cu<Zn<Cr<Ni<Mn<Fe and were under the allowed maximum for unpolluted soils, except for Ni and Cr. However, transfer of Ni and Cr from the soil to the ragweed as well as their bioaccumulation was not intensive. Established metal contents ratio from plant tissues (root and shoot) to soil for both elements, represented their bioaccumulation factors (BAF), which were extremely low in the roots, as well as in the shoots, both in average less than 0.2. On the other hand, Zn showed a tendency to accumulate in ragweed shoots (BAF=2.07). The study showed that uptake and accumulation of PTEs in the ragweed was mainly influenced by their content in the soil, as well as specific characteristics and biological role of each element. Hence, content of PTEs in the ragweed tissue could be used as the soil contamination degree indicator.

**Keywords:** ragweed, trace elements, bioavailability; invasive plants;

## 1. INTRODUCTION

Potentially toxic elements (PTEs) occur naturally in the soil environment from parent material through weathering processes at levels considered as trace in a chemical form that are rarely toxic (Kabata-Pendias, 2011). Some of these elements are essential in a small concentration (e.g. Cu, Zn, Cr, Ni), while their presence in large quantities could have harmful and chronic health impacts. On the other hand, the second group of PTEs includes toxic elements (Hg, As, Pb, Cd.) with several negative effects on the environment and human health (Hooda, 2010). In the recent years, the content of PTEs in agricultural areas has increased due to various anthropogenic activities (Li et al., 2019; Wang et al., 2021; Dhaouadi et al., 2023). Their uptake into plants involves the

movement of their ions from the solid phase in the soil solution to the root surface, entering into the roots, where they are either stored at the root system or transported to the aboveground parts (Grennan, 2009). This process is strongly influenced by soil properties such as acidity, organic matter content, clay content, redox potential, as well as soil structure and water regime (Kabata-Pendias, 2011). Moreover, PTEs translocation (transport within the plant) and bioaccumulation may vary considerably depending on plant species, total amount, nature and ionic form (Hooda, 2010; Xu et al., 2022).

Transport of PTEs from soil to plant tissues and their accumulation is studied according to various criteria, among which bioaccumulation factor (BAF) and translocation factor (TF) are the most commonly used (Avkopashvili et al., 2022; Sabir et al., 2022).

Bioaccumulation factor is established (Sychta et al., 2020) as ratio between metal content in plant tissues, roots or shoots ( $C_{PTE\ plant\ tissues}$ ) and soil ( $C_{PTE\ soil}$ ):

$$BAF = C_{PTE\ plant\ tissues} / C_{PTE\ soil} \quad (1)$$

whereas TF presented as ratio between metal content in shoots ( $C_{PTE\ shoots}$ ) and roots ( $C_{PTE\ roots}$ ):

$$TF = C_{PTE\ shoots} / C_{PTE\ roots} \quad (2)$$

Ragweed (*Ambrosia artemisiifolia* L.) is a native plant from Central and Northern America, widespread in Australia and some parts of Asia and Europe (Makra et al., 2015), particularly in Eastern and Central Europe (Vogl et al., 2008, Smith et al., 2013). It is an annual species, often found on disturbed sites such as wastelands, construction sites, areas along railways, highways and other ruderal areas, but also on cultivated agricultural land (Vogl et al., 2008). Ragweed is a worldwide invasive plant species that has multidimensional negative impacts on environment, crop production and human health (Iamónico, 2022; Global Invasive Species Database, 2023). Moreover, it is a dominant weed species in Serbia and Bosnia and Herzegovina (Kovačević et al., 2015; Rat et al., 2016). Some of recent studies revealed that ragweed can be grown on soils with high PTEs contents (Franco-Hernandez et al., 2010; Cloutier-Hurteau et al., 2014). Randelović et al., (2020) found ragweed potential for PTEs accumulation from the five sites with different level of anthropogenic pollution in Serbia. Ryzenko et al., (2022) proposed this species for phytoremediation of the soils contaminated with Zn, Cu, Cd and Cr metals.

However, according to our knowledge, the intensity of uptake and accumulation of PTEs by ragweed in such areas was not studied intensively in Bosnia and Herzegovina. Therefore, the main focus of this research is to establish PTEs soil contamination degree and uptake by ragweed naturally grown at the different agricultural soils in the northern part of Bosnia and Herzegovina. Moreover, it is important to understand if ragweed could be used as PTEs soil contamination bioindicator in the agricultural areas. The main objectives of this study were to: 1. determining Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn contents in soil and estimating the degree of contamination on the base of their comparison with allowed maximum for unpolluted soils; 2. estimating the PTEs uptake and accumulation by ragweed, through determination of their contents in plant tissues (root and shoot), as well as establishment of the BAF and TF, 3. assessing the main chemical properties for the tested soils and their impact of PTEs uptake and distribution in ragweed.

## 2. MATERIALS AND METHODS

The study area belongs to the central zone of the northern part of Bosnia and Herzegovina (Figure 1) and it is characterized with moderate continental climate and developed agricultural and industrial activities. The samples of ragweed and associated soils were collected at the seven locations with a different agricultural use in June 2019 (Table 1). All sampling locations are close by the most frequent roads in the sampling area (on the distance less than 800 m). The ragweed shoot and root material were carefully separated, thoroughly washed with tap water, followed by deionized water, then air dried and milled to a powder. Soil samples were taken from the top layer (depth 0-25 cm).

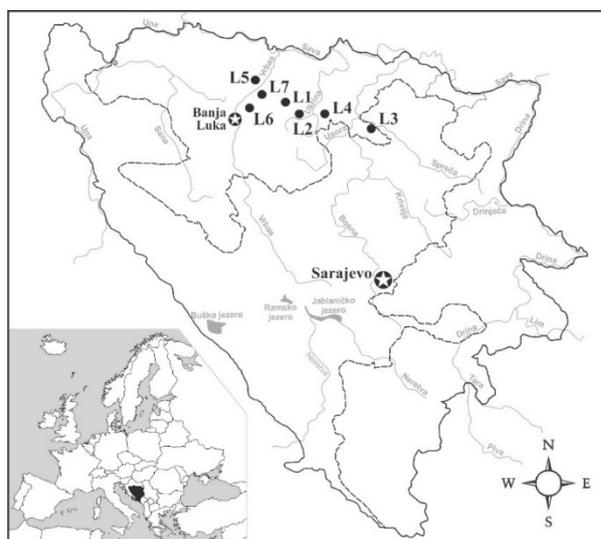


Figure 1. Map of the study area with the sampling locations

Prior to the analyses, the samples were air-dried, then grounded and sieved at 2 mm. Standard agrochemical methods were used to determine soil properties, important for PTEs mobility as soil reaction (pH), organic matter (OM) content, cation exchange capacity (CEC). The process of PTEs analysis in soil and plant material involved acid digestion and measurement of their concentrations by atomic absorption spectrophotometry (AAS) using Perkin Elmer AAnalyst 400. Soil samples were digested according to slightly modified ISO 11466 method (1995), with concentrated  $HNO_3 + HCl$  (*aqua regia*). Plant tissues destruction was obtained using concentrated  $HNO_3$  with addition of 30%  $H_2O_2$  and 70%  $HClO_4$  (Pequerul et al., 1993). After these digestion procedures, the extracts were stored at 4°C and then analyzed. The quantification of the examined elements was done by the method of atomic absorption spectrophotometry (AAnalyst 400 Perkin

Table 1. Sampling locations with agricultural usage and relevant latitude and longitude

| Location      | Used mark | Agricultural usage  | Latitude          | Longitude         |
|---------------|-----------|---------------------|-------------------|-------------------|
| Lišnja        | L1        | Vineyard            | N 44° 53' 36.40 " | E 17° 33' 56.26 " |
| Drenova       | L2        | Arable land         | N 44° 49' 42.20 " | E 17° 39' 47.11 " |
| Karanovac     | L3        | Corn field          | N 44° 41' 44.44 " | E 18° 15' 39.05 " |
| Stanari       | L4        | Medow               | N 44° 44' 43.45 " | E 17° 46' 11.18 " |
| Aleksandrovac | L5        | Barley field        | N 44° 58' 33.90 " | E 17° 18' 11.60 " |
| Trapisti      | L6        | Soybeans field      | N 44° 48' 10.80 " | E 17° 13' 13.60 " |
| Čardačani     | L7        | Chockeberry orchard | N 44° 52' 35.00 " | E 17° 19' 23.70 " |

Elmer<sup>®</sup>, USA). Standard solutions were prepared using a single element stock solution for AAS (1000 mg L<sup>-1</sup>, Perkin Elmer, USA) and an appropriate diluent extractant. The selected wavelengths of elements to be determined were as follows: Cd: 228.8 nm, Cr: 357.9 nm, Cu: 324.8 nm, Fe: 248.3 nm, Mn: 279.5 nm, Ni: 232.0 nm, Pb: 283.0 nm and Zn: 213.7 nm.

The examined elements were quantified in the air/acetylen flame with an additional deuterium background correction of signal for Cd, Ni and Zn. All analytical procedures were triplicated and made with glassware and plastic materials prewashed with 10 % HNO<sub>3</sub>. Quality control of acid digestion and PTEs quantification process was carried out by analyses of certified reference materials (ERM<sup>®</sup>-CC141, loam soil and ERM<sup>®</sup>-CD218, rye grass) with a recovery values in an acceptable range (85-105 %) for each element. The obtained results were analysed and graphically presented using the statistical softwares SPSS 22 (IBM 2013) and Origin 7.5.

### 3. RESULTS AND DISCUSSION

The determined chemical characteristics of the tested soils are presented in Table 2. The tested soils were slightly acid to acid, with exception for the locations Trapisti (L6) and Drenova (L2), which shown neutral soil reaction. The highest amount of OM was presented in Drenova (L2). A slightly lower values in OM content had the soils in Karanovac (L3) and Stanari (L4). However, soil at the other locations were poor humous. CEC values indicate low to medium adsorption capacity of the tested soils, with the highest CEC at locations Drenova (L2) and Karanovac (L3). Acid soil reaction, low CEC and low supply of OM were found for the soils in Lišnja (L1), Aleksandrovac (L5) and Čardačani (L7). These findings indicate a significant level of PTEs mobility from soils to the plant at observed locations as already shown in the studies before (Mihajlović et al., 2012; Hou et al., 2019).

Increasing order of PTEs content in the tested soils (mg kg<sup>-1</sup>) was Cd<Pb<Cu<Zn<Cr<Ni<Mn<Fe (Table 3, Figure 2). According to the study, Fe was

the most abundant element in soils, followed by Mn, which was expected due to their elevated contents in the worldwide soils (Taylor & Konhauser, 2011; Chen et al., 2019). In terms of their biological role and high naturally contents, no permissible levels in the soil have been defined for both elements.

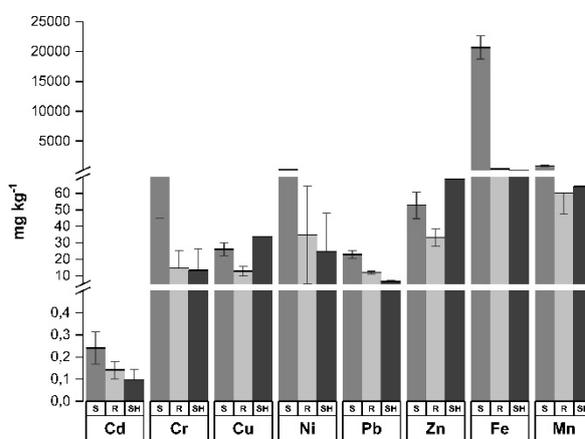


Figure 2. The content of PTEs (mg kg<sup>-1</sup>) in tested soils and ragweed, presented by element and sample material (soil, root, shoot). Soil (S) is presented in dark grey, root (R) in light grey and shoot (SH) in black colour.

With an exception of two locations (Lišnja L1, Čardačani L7), the determined Ni contents in tested soils were higher than the maximum allowed concentrations (MAC) of 50 mg kg<sup>-1</sup> for the nickel in the soil, according to the national standards of Bosnia and Herzegovina (Official Journal of the Republic of Srpska, no. 56/16; Official Journal of the Federation of Bosnia and Herzegovina, no. 96/22). The Ni content was particularly increased in Drenova (L2), Karanovac (L3) and Stanari (L4), where the determined contents were 5-10 times higher than the allowed level. For the same locations Cr contents were elevated and above the permitted maximum (80 mg kg<sup>-1</sup>).

Additionally, geological data on the examined terrain in the vicinity of these three locations (Laušević et al., 1982; Mojičević et al., 1976) indicate the presence of serpentine rocks, which contain Ni and Cr, in the geological bedrock as well as in the soil their accumulation in the ragweed will indicate soil

Table 2. The chemical properties (mean±SD) of the tested soils

| Sampling location  | pH <sub>KCl</sub>      | OM (%)                  | CEC (mmol 10 <sup>-2</sup> g <sup>-1</sup> ) |
|--------------------|------------------------|-------------------------|--|
| Lišnja (L1)        | 4.52±0.01 <sup>e</sup> | 2.39±0.26 <sup>cd</sup> | 11.76±0.49 <sup>e</sup>                      |
| Drenova (L2)       | 6.5±0.02 <sup>b</sup>  | 4.75±0.15 <sup>a</sup>  | 24.99±4.16 <sup>a</sup>                      |
| Karanovac (L3)     | 5.32±0.03 <sup>d</sup> | 2.80±0.10 <sup>bc</sup> | 24.26±0.24 <sup>a</sup>                      |
| Stanari (L4)       | 5.98±0.02 <sup>c</sup> | 3.18±0.15 <sup>b</sup>  | 18.38±1.23 <sup>b</sup>                      |
| Aleksandrovac (L5) | 4.26±0.04 <sup>f</sup> | 1.97±0.20 <sup>d</sup>  | 12.50±0.25 <sup>c</sup>                      |
| Trapisti (L6)      | 6.79±0.10 <sup>a</sup> | 2.35±0.06 <sup>cd</sup> | 17.15±1.96 <sup>b</sup>                      |
| Čardačani (L7)     | 4.34±0.02 <sup>f</sup> | 2.04±0.25 <sup>d</sup>  | 10.05±0.25 <sup>c</sup>                      |

Different small letters indicate significant differences (P<0.05) between sampling locations for pH<sub>KCl</sub>, organic matter, OM (%) and cation exchange capacity, CEC (mmol 10<sup>-2</sup> g<sup>-1</sup>) according to the Tukey test (n=3).

Table 3. Total contents (mean±SD) of PTEs: Cr, Cu, Mn, Ni, Pb, Zn (mg kg<sup>-1</sup>) and Fe (g kg<sup>-1</sup>) in tested soils

|    | L1                      | L2                      | L3                      | L4                      | L5                      | L6                      | L7                      | MAC* |
|----|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|------|
| Cd | 0.10±0.01 <sup>e</sup>  | 0.15±0.01 <sup>e</sup>  | 0.15±0.06 <sup>e</sup>  | 0.21±0.01 <sup>d</sup>  | 0.36±0.01 <sup>b</sup>  | 0.46±0.03 <sup>a</sup>  | 0.26±0.03 <sup>c</sup>  | 1    |
| Cr | 32.25±0.75 <sup>e</sup> | 120.0±4.29 <sup>c</sup> | 150.4±0.38 <sup>b</sup> | 236.6±16.8 <sup>a</sup> | 28.24±0.96 <sup>e</sup> | 51.59±2.14 <sup>d</sup> | 18.24±0.43 <sup>f</sup> | 80   |
| Cu | 29.11±0.0 <sup>b</sup>  | 33.78±0.95 <sup>a</sup> | 26.33±0.59              | 23.08±1.67 <sup>d</sup> | 23.15±0.25 <sup>d</sup> | 33.81±0.14 <sup>a</sup> | 13.01±0.39 <sup>e</sup> | 65   |
| Fe | 16.67±1.8 <sup>c</sup>  | 24.91±4.1 <sup>a</sup>  | 23.32±2.3 <sup>a</sup>  | 24.12±1.8 <sup>a</sup>  | 18.84±1.7 <sup>bc</sup> | 19.85±1.4 <sup>b</sup>  | 17.15±1.5 <sup>bc</sup> | -    |
| Mn | 681.7±21.3 <sup>c</sup> | 533.4±15.8 <sup>d</sup> | 1067±42.2 <sup>a</sup>  | 948.6±14.3 <sup>b</sup> | 1142±108.0 <sup>a</sup> | 1050±13.5 <sup>a</sup>  | 727.5±1.81 <sup>c</sup> | -    |
| Ni | 36.20±0.52 <sup>f</sup> | 268.6±1.51 <sup>c</sup> | 374.4±6.26 <sup>b</sup> | 597.0±16.6 <sup>a</sup> | 51.77±1.59 <sup>e</sup> | 115.1±7.11 <sup>d</sup> | 21.07±0.43 <sup>g</sup> | 50   |
| Pb | 23.49±1.18 <sup>c</sup> | 25.91±0.21 <sup>b</sup> | 18.15±0.36 <sup>d</sup> | 16.47±0.14 <sup>e</sup> | 25.43±0.23 <sup>b</sup> | 27.41±0.40 <sup>a</sup> | 23.5±1.11 <sup>c</sup>  | 80   |
| Zn | 34.8±5.29 <sup>c</sup>  | 73.15±0.91 <sup>a</sup> | 53.35±2.44 <sup>b</sup> | 37.5±0.62 <sup>c</sup>  | 49.2±2.29 <sup>b</sup>  | 68.62±3.72 <sup>a</sup> | 52.45±6.61 <sup>b</sup> | 150  |

Different small letters indicate significant differences (P <0.05) between sampling locations in content of the PTEs according to the Tukey test (n=3).

\*MAC represents the maximum allowed concentration (mg kg<sup>-1</sup>) according to national standards (Official Journal of RS no. 56/16 and Official Journal of FBiH no. 96/22)

Table 4. Determined content (mean±SD) of PTEs (mg kg<sup>-1</sup>) in the samples of ragweed

|               | L1                       | L2                       | L3                       | L4                      | L5                      | L6                      | L7                       |
|---------------|--------------------------|--------------------------|--------------------------|-------------------------|-------------------------|-------------------------|--------------------------|
| <b>Roots</b>  |                          |                          |                          |                         |                         |                         |                          |
| Cd            | 0.08±0.02 <sup>de</sup>  | 0.12±0.01 <sup>c</sup>   | 0.11±0.01 <sup>cd</sup>  | 0.07±0.02 <sup>c</sup>  | 0.19±0.02 <sup>b</sup>  | 0.14±0.01 <sup>c</sup>  | 0.27±0.02 <sup>a</sup>   |
| Cr            | 8.72±0.14 <sup>c</sup>   | 6.39±0.14 <sup>c</sup>   | 7.80±0.19 <sup>d</sup>   | 56.10±0.36 <sup>a</sup> | 9.66±0.10 <sup>b</sup>  | 8.58±0.07 <sup>c</sup>  | 6.08±0.15 <sup>e</sup>   |
| Cu            | 21.61±0.51 <sup>a</sup>  | 10.26±0.20 <sup>d</sup>  | 8.16±0.04 <sup>f</sup>   | 18.24±0.11 <sup>b</sup> | 11.49±0.30 <sup>c</sup> | 8.88±0.12 <sup>e</sup>  | 10.72±0.20 <sup>d</sup>  |
| Fe            | 186.7±5.47 <sup>f</sup>  | 384.0±5.84 <sup>c</sup>  | 439.7±3.10 <sup>b</sup>  | 564.2±14.9 <sup>a</sup> | 283.0±4.43 <sup>d</sup> | 260.6±3.47 <sup>e</sup> | 285.2±3.43 <sup>d</sup>  |
| Mn            | 54.4±1.38 <sup>d</sup>   | 45.2±2.01 <sup>e</sup>   | 80.5±2.03 <sup>b</sup>   | 43.47±3.66 <sup>c</sup> | 70.14±2.53 <sup>c</sup> | 96.01±0.68 <sup>a</sup> | 31.85±0.57 <sup>f</sup>  |
| Ni            | 7.97±0.07 <sup>e</sup>   | 12.74±0.28 <sup>cd</sup> | 38.96±2.16 <sup>b</sup>  | 150.6±2.8 <sup>a</sup>  | 15.28±0.31 <sup>c</sup> | 9.99±0.18 <sup>de</sup> | 8.79±0.32 <sup>e</sup>   |
| Pb            | 13.44±0.45 <sup>a</sup>  | 10.50±0.13 <sup>c</sup>  | 12.78±0.21 <sup>ab</sup> | 13.50±0.46 <sup>a</sup> | 9.68±0.19 <sup>c</sup>  | 12.17±0.33 <sup>b</sup> | 12.02±0.33 <sup>b</sup>  |
| Zn            | 23.68±0.96 <sup>c</sup>  | 41.19±1.40 <sup>b</sup>  | 20.67±0.86 <sup>e</sup>  | 35.24±1.90 <sup>c</sup> | 31.32±0.61 <sup>d</sup> | 47.4±0.72 <sup>a</sup>  | 33.09±1.03 <sup>cd</sup> |
| <b>Shoots</b> |                          |                          |                          |                         |                         |                         |                          |
| Cd            | 0.03±0.01 <sup>c</sup>   | 0.08±0.01 <sup>bc</sup>  | 0.14±0.04 <sup>b</sup>   | 0.03±0.01 <sup>c</sup>  | 0.25±0.01 <sup>a</sup>  | 0.10±0.03 <sup>b</sup>  | 0.04±0.02 <sup>c</sup>   |
| Cr            | 9.83±0.32 <sup>b</sup>   | 1.52±0.06 <sup>e</sup>   | 7.51±0.40 <sup>c</sup>   | 65.66±1.03 <sup>a</sup> | 3.76±0.27 <sup>d</sup>  | 1.71±0.05 <sup>e</sup>  | 3.64±0.29 <sup>d</sup>   |
| Cu            | 181.2±3.5 <sup>a</sup>   | 9.80±0.16 <sup>c</sup>   | 5.68±0.16 <sup>c</sup>   | 13.95±0.13 <sup>b</sup> | 10.09±0.5 <sup>c</sup>  | 6.81±0.04 <sup>cd</sup> | 8.42±0.13 <sup>cd</sup>  |
| Fe            | 93.39±0.88 <sup>f</sup>  | 161.7±2.80 <sup>c</sup>  | 145.1±1.2 <sup>d</sup>   | 217.4±4.5 <sup>a</sup>  | 126.2±1.4 <sup>e</sup>  | 186.3±5.1 <sup>b</sup>  | 138.5±8.9 <sup>d</sup>   |
| Mn            | 48.40±3.52 <sup>ef</sup> | 51.50±1.78 <sup>e</sup>  | 68.10±3.73 <sup>c</sup>  | 59.80±4.06 <sup>d</sup> | 96.60±2.33 <sup>a</sup> | 81.80±1.16 <sup>b</sup> | 42.4±1.10 <sup>f</sup>   |
| Ni            | 7.63±0.16 <sup>d</sup>   | 10.14±0.19 <sup>c</sup>  | 20.50±0.25 <sup>b</sup>  | 116.7±1.3 <sup>a</sup>  | 11.58±0.44 <sup>c</sup> | 2.77±0.23 <sup>e</sup>  | 4.19±0.07 <sup>e</sup>   |
| Pb            | 6.39±0.03 <sup>c</sup>   | 5.87±0.51 <sup>c</sup>   | 7.42±0.19 <sup>b</sup>   | 9.08±0.16 <sup>a</sup>  | 5.61±0.38 <sup>c</sup>  | 5.65±0.40 <sup>c</sup>  | 6.45±0.48 <sup>bc</sup>  |
| Zn            | 109.7±1.9 <sup>a</sup>   | 72.32±4.23 <sup>d</sup>  | 23.14±1.36 <sup>f</sup>  | 69.11±2.34 <sup>d</sup> | 31.18±1.01 <sup>e</sup> | 94.83±1.69 <sup>b</sup> | 81.0±1.89 <sup>c</sup>   |

Different small letters indicate significant differences (P <0.05) between sampling locations (L) in content of the PTEs according to the Tukey test (n=3)

parent material. Most probably, due to the process of pedogenesis both elements were finally brought into the soils and therefore their contents were increased. According to Kabata-Pendias (2011) availability of PTEs to the plants depends on their forms. Metals dominantly originated from natural, geochemical sources were present in the soil in less mobile forms

than those which are the result of various anthropogenic activities (industry, traffic etc.). Hence, further analysis of the Ni and Cr content and contamination degree. Moreover, the determined contents of Cd, Cu, Fe, Mn, Pb and Zn in all tested soils did not exceed allowed levels. Therefore, it can be concluded that the tested soils were not

contaminated with these elements.

Analyses of the plant material showed that metal contents in the ragweed roots increase in the identical order as in tested soils, as follows:  $Cd < Pb < Cu < Cr < Zn < Ni < Mn < Fe$ , with exception of the Zn and Cr. Contrary to the soil, the content of Zn in the ragweed roots was higher than content of Cr. Content of metals in ragweed shoots showed similar trend as in roots:  $Cd < Pb < Cr < Ni < Cu < Mn < Zn < Fe$  (Table 4, Figure 2). The same elements were the least (Cd, Pb) and the most (Fe) abundant in different parts of plants. Moreover, Zn was the second most represented element in the ragweed shoots, which indicated a more intensive uptake and translocation of this element among others within the plant. Higher Zn content in the plant shoots compare to roots was probably connected with its obligatory functions in the plants (Sadeghzadeh, 2013).

In general, the element distribution in ragweed was more pronounced in the root compare to the shoot (Figure 2), with an exception of Zn and exception observed for Mn and Cu in some locations. Determined contents of Cu in the ragweed were below toxic values ( $20-100 \text{ mg kg}^{-1}$ , Padmavathiamma & Li, 2007), except in vineyard Lišnja (L1) which was most probably related with recent Bordeaux mixture treatment. On that location was found  $21.61 \text{ mg kg}^{-1}$  of copper in the roots, while its amount in the shoots was significantly higher ( $181.2 \text{ mg kg}^{-1}$ ).

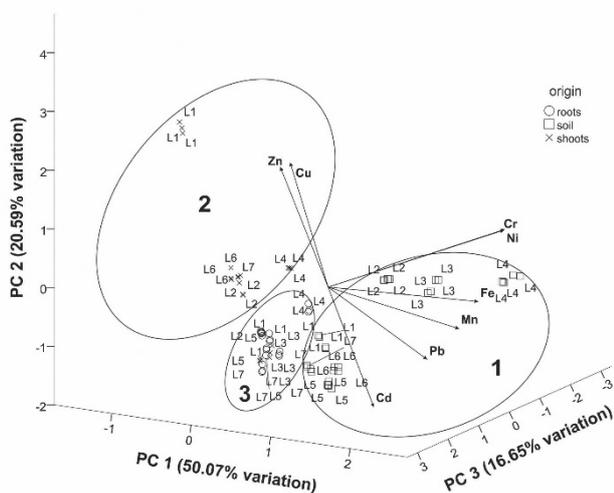


Figure 3. The principal components analysis of the PTEs contents in tested soils and ragweed

Furthermore, the analysis of the main components at the studied locations, i.e. soils and plant material (root and shoot) explained 87.32 % of total variation in data with the three principal components (Figure 3). Studied points were grouped in three distinctive groups. Group 1 consisted only of soils where all locations are grouped together

separately from measurements in plants. The levels of Fe, Mn, Pb, Cr and Ni in this group were higher than in plants, while Zn, Cu and Cd generally did not follow such a pattern. In addition, high significant correlation between Ni and Cr was observed within this group ( $r=0.998$ ,  $p<0.01$ ), most likely caused by a common origin from natural, geological sources (Hu et al., 2013). Group 2 originates from quantification of the PTEs in the shoots and is mostly effected by higher Zn and Cu contents with lower Cd contents compared to the group 3. The higher negative correlation between Zn and Cu contents on one side and Cd contents on the other side of the graph was probably caused by their different biological role and therefore of their uptake mechanisms (Arif et al., 2016). The root measurements are grouped together in the lower left part of the graph as group 3 and it was the most consistent group.

Moreover, the lowest contents among examined elements in plant and soil, were found for Cd and Pb, which was positive considering their toxicity. This could be explained with the generally accepted fact that the metal contents in the soil were dominant factor for their uptake by plants (Prabasiwi et al., 2020). In our research, this was additionally confirmed for Fe, Ni and Cr with established statistically significant correlation between contents of the same elements in the soil and roots (for Fe  $r=0.84$ ,  $p<0.05$ ; Ni  $r=0.88$ ,  $p<0.01$  and Cr  $r=0.78$ ,  $p<0.05$ ). On the other hand, determined transfer of Ni and Cr from soil to roots and shoots was not intensive. Elevated Ni and Cr contents in the tested soils did not affect primarily their content in the examined plant material. Established BAF and TF values (Table 5) for both elements ( $<1$ ) indicate a low level of their uptake, accumulation and translocation within the plant (Sychta et al., 2020). This is the most probably caused by their dominant geological origin and therefore presence of Ni and Cr in less available forms in tested soils. Moreover, due to their specific biological roles these elements are less mobile than some other PTEs, e.g. Zn and Cu (Hooda, 2010). As we mentioned before, the obtained results of the soil analyses (Table 3) indicated the soil contamination with Ni and Cr (higher contents than maximal permitted). However, their small contents in the ragweed and low bioaccumulation showed that the tested soil and plant are not polluted with these elements (Table 4 and 5).

Furthermore, Cloutier-Hurteau et al. (2014) determined PTEs presence in ragweed aboveground parts (pollen grains) with the following order:  $Zn > Mn > Cr \approx Ni \approx Pb > Cd$ . Similar order of the same elements presence was found in our research in the analyzed ragweed shoots ( $Zn > Mn > Ni > Cr > Pb > Cd$ ). This indicates a high possibility of a unique transfer mechanism for specific elements both from the soil to

Table 5. Determined bioaccumulation and translocation factors of ragweed at the study area

|   | Cd          | Cr          | Cu                       | Fe    | Mn          | Ni   | Pb   | Zn          |
|---|-------------|-------------|--------------------------|-------|-------------|------|------|-------------|
| Bioaccumulation factor (BAF) in the roots: roots/soil   |             |             |                          |       |             |      |      |             |
| Average   | 0.66        | 0.21        | 0.53                     | 0.02  | 0.07        | 0.20 | 0.55 | 0.65        |
| Minimum   | 0.30        | 0.05        | 0.26                     | 0.011 | 0.04        | 0.05 | 0.38 | 0.39        |
| Maximum   | <b>1.04</b> | 0.34        | 0.82                     | 0.023 | 0.09        | 0.42 | 0.82 | 0.94        |
| Bioaccumulation factor (BAF) in the shoots: shoots/soil |             |             |                          |       |             |      |      |             |
| Average   | 0.43        | 0.14        | 1.23 (0.40) <sup>1</sup> | 0.01  | 0.07        | 0.13 | 0.31 | <b>1.43</b> |
| Minimum   | 0.15        | 0.01        | 0.2                      | 0.006 | 0.06        | 0.02 | 0.21 | 0.43        |
| Maximum   | 0.93        | 0.30        | 6.23 (0.65)              | 0.01  | 0.10        | 0.22 | 0.55 | <b>3.15</b> |
| Translocation factor (TE): shoots/roots                 |             |             |                          |       |             |      |      |             |
| Average   | 0.71        | 0.67        | 1.89 (0.81) <sup>1</sup> | 0.47  | <b>1.12</b> | 0.65 | 0.55 | <b>2.13</b> |
| Minimum   | 0.15        | 0.20        | 0.7                      | 0.33  | 0.85        | 0.28 | 0.46 | <b>1.00</b> |
| Maximum   | <b>1.37</b> | <b>1.17</b> | 8.39 (0.96)              | 0.71  | <b>1.38</b> | 0.96 | 0.67 | <b>4.63</b> |

Values >1 are marked in bold. In the brackets are average and maximal values of BAF and TE for Cu calculated without location L1 because of unreliability caused by recent foliar fungicide treatment.

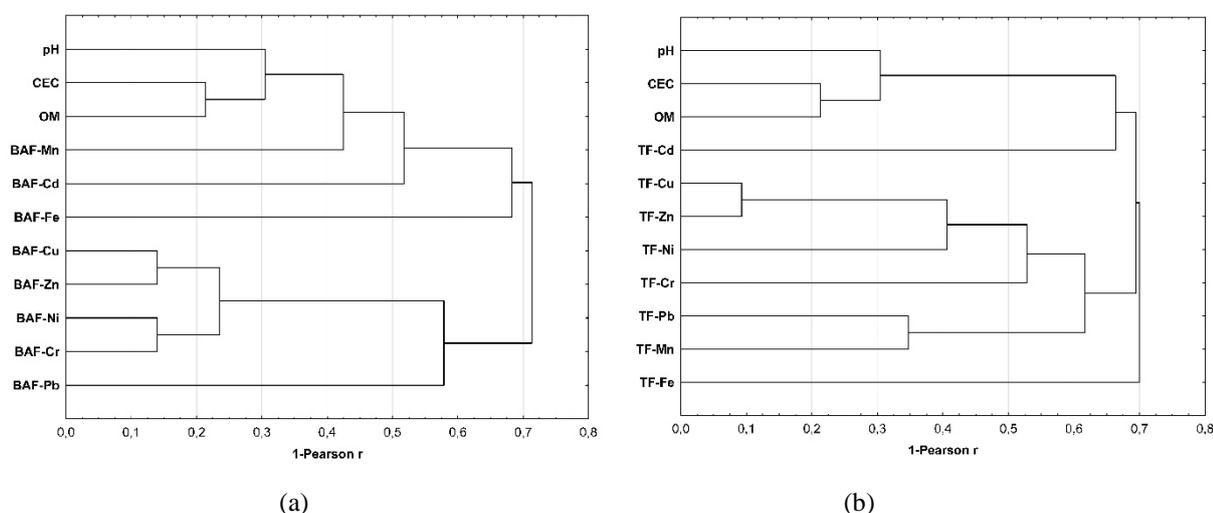


Figure 4. The cluster analysis between soil characteristics and PTEs: a) bioaccumulation factor (BAF) in the shoots and b) translocation factor (TF)

the roots of the plant and from the roots of the plant to the aboveground part of the plant.

Established BAF values were lower than 1 at all locations, with exception of Cu in the before mentioned vineyard in Lišnja (L1), with the determined value for bioaccumulation factor in the shoots BAF=6.23, what was the most probably consequence of recent pesticide treatment.

Average TF values for investigated PTEs, except Zn and Mn, were less than 1, that indicates small intensity of their transfer through the plant. As was stated before, translocation of Zn is intensive in the tested plants at all localities. Besides, TF values for Mn were higher to 1 in the ragweed at four locations, while on the other three locations were between 0.85 and 0.89 (Table 5). On the other hand, transfer of this element from the soil to the plants was very low (mean BAF<sub>roots</sub>=0.07; BAF<sub>shoots</sub>=0.07). During the research in Serbia, in the soils highly contaminated with PTEs Randelović et al. (2012) found similar Mn uptake and translocation into ragweed, with BAF<sub>roots</sub><0.1 and

BAF<sub>shoots</sub><0.5, while TF values for Mn were between 1-10 and for Cd between 1-5. Here was also found the absence of Ni, Cr and Pb accumulation in ragweed. On the other hand, in our research were also found TF for Cd and Cr slightly higher than 1 at two different locations for both elements.

Additionally, cluster analysis (Figure 4) showed that translocation and bioaccumulation of PTEs in the ragweed generally were not dominantly determined with soil reaction, CEC and OM contents. Furthermore, correlation analyses showed statistically significant ( $p<0,05$ ) and negative correlation between bioaccumulation factor in the shoots for Ni and soil reaction ( $r=-0.79$ ) and CEC ( $r=-0.78$ ), as well as BAF<sub>shoots</sub> for Cr and CEC ( $r=-0.64$ ). Decrease of the soil adsorption capacity leads to the higher Ni and Cr mobility and accessibility to the plants. For Ni, this process was also encouraged with higher soil acidity (lower pH values). Between the bioaccumulation factors in the shoots for other elements and main soil characteristics were not found

significant correlation. Cloutier-Hurteau et al. (2014) found that Cd, Pb and Zn contents in pollen grains were not related to soil pH or adsorptive capacity (CEC, OM content), while content of Ni was slightly but not significantly affected with OM content.

#### 4. CONCLUSIONS

Taking into account all the obtained results, we can conclude that tested soil were not polluted with Cd, Cu, Fe, Mn, Pb and Zn. However, contamination with Ni and Cr was found at several locations. The presence of serpentine rocks near the study locations, highly significant correlation between their soil contents ( $r=0.998$ ,  $p<0.01$ ) and low level of the Ni and Cr uptake by ragweed indicated dominant origin of both elements from natural, geological sources and therefore the absence of pollution. The most abundant elements in the tested soils and ragweed were Fe and Mn, while the most mobile among examined elements was Zn. In general, transfer of examined elements into ragweed favored roots over shoots, with exception of Zn. Average value of bioaccumulation factor in the shoots for Zn was 1.43, while translocation factor for the same element was 2.13. This indicates intensive translocation of this element into the ragweed and good potential for use of this plant in phytoextraction of Zn. Determined results indicated also similar possibility in the case of Mn, Cd and Cr, which needs to be further investigated.

According to our findings, soil properties such as pH, CEC and OM content, did not significantly affect the uptake of the tested PTEs by ragweed. Only in conditions of reduced soil adsorption potential (CEC) was observed an increased mobility, and thus the bioavailability of Ni and Cr.

The uptake and accumulation of PTEs in ragweed from the tested soils were mainly influenced by their content in the soil, the mobility and specific characteristics of each element (biological role, toxicity, etc.). Therefore, the content of PTEs in ragweed could be an indicator of the degree of soil contamination. In addition, the established ability to accumulate Zn in ragweed, even in uncontaminated soils, could serve as a prerequisite for strategies to manage its use in phytoextraction and prevent PTEs dispersion in the environment. This is particularly interesting due to the fact that ragweed is an invasive species that grows spontaneously in both ruderal and cultivated areas.

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Received at: 06. 09. 2023

Revised at: 06. 11. 2023

Accepted for publication at: 17. 11. 2023

Published online at: 20. 11. 2023