Carpathian Journal of Earth and Environmental Sciences August 2022, Vol. 17, No. 2, p. 351 – 363; DOI:10.26471/cjees/2022/017/227

GEOSPATIAL MAPPING OF ECOLOGICAL RISK FROM POTENTIALLY TOXIC ELEMENTS IN SOIL IN THE PANNONIAN-CARPATHIAN BORDER AREA SOUTH OF THE DANUBE

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Abstract: This study collected agricultural surface soil samples from 200 sites in the district of Braničevo, located in the Carpathian Mountains – Pannonian Basin south of the Danube River (Serbia). The main objective was to determine the soil contamination by ten potentially toxic elements (As, B, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Zn) and evaluate the associated ecological risk via different indices. The physicochemical parameters, pH, organic carbon, water content, and soil texture were also analyzed. The mean values of most metal concentrations remained below their corresponding national target values, except for Mo and Ni. The main soil texture types were silt loam (40.5 %) and silty clay loam (34.5 %). According to the mean values, pollution load index (PLI) and potential ecological risk (RI) demonstrated that the soil in the study area was exposed to moderate pollution and moderate ecological risk, while enrichment factor (EF), geoaccumulation index (I_{geo}), and contamination factor (CF) revealed very high enrichment and contamination with Mo, implying the impact of anthropogenic activities. There was a lack of strong correlations among elements and soil properties, except for Cd and C_{org}, while moderate to strong positive inter-metal relationships suggested their common sources. The chemometric analysis illustrated the classification of sampling sites into two distinct clusters of spatial similarities according to higher and lower metal concentrations. Geospatial mapping identified a few areas of considerable ecological risk.

Keywords: Agricultural soil, Metal(loid)s, Multivariate analysis, Soil texture, Risk index, GIS.

1. INTRODUCTION

The ability of the soil to ensure the development of ecosystems can be expressed through its ecological and socio-economic functions, among which there are numerous contradictions, especially in soil usage due to growing public concern about environmental hazards (Kim & Kim, 1999). As fertility and yield are of great importance for agricultural practice and are directly affected by physical and chemical properties that determine soil quality, the importance of soil preservation as a natural resource is of great interest. Most of the arable soil is intended primarily for cultivating arable crops (cereals, vegetables, stone fruits), while fertility can be increased by deep cultivation, fertilization, and protection against erosion on sloping terrain. In addition, soil fertility parameters are influenced by natural, eluvial and fluvial processes, diverse natural characteristics, and heterogeneity of soil cover. Global production and consumption have been gradually increasing in recent years and have greatly contributed to the daily contamination of the environment, resulting in severe deterioration. Thus, the geological substrate, man-made processes and human activities represent major factors that directly degrade the components of the biosphere (Saljnikov et al., 2009).

As natural constituents of the Earth's crust, the geochemical levels of potentially toxic elements (PTEs) in the soil are relatively low. The accumulation and non-biodegradable nature of PTEs could lead to detrimental effects on ecosystems and natural resources, including soil quality and productivity. Therefore, this is not only an environmental problem that can cause serious implications for biodiversity, food safety and human health but also a challenge to global socio-economic development. Furthermore, due to the growing population trend, intensified agriculture and numerous anthropogenic activities (disposal of sewage sludge, the use of agrochemicals, discharge of industrial waste and aerial fallout), the soil is increasingly affected by complex mixtures of pollutants and their elevated concentrations. This further creates habitat degradation and eutrophication problems, leading to pollution of the terrestrial environments and water bodies (Huang et al., 2017; Yüksel et al., 2022). Namely, higher concentrations of PTEs can increase toxicity and negatively affect the growth and physiological activities of many plant and animal species. PTEs such as As, Cd, Cr, Cu, Ni, Pb, and Zn are considered priority pollutants of high risk to the environment (Cai et al., 2019). An aggravating factor in determining toxicity may be the occurrence of multiple contaminations, combining the effects of potentially toxic elements with additive, synergistic or antagonistic action (Raffa et al., 2021). Therefore, identifying sources and assessing heavy metal levels can be key to controlling and preventing environmental pollution and understanding the risk (Yang et al., 2019; Alsafran et al., 2021).

Ecological risk assessment is used as an effective scientific tool for revealing the associated adverse effects of the investigated PTEs (Radomirović et al., 2020). Due to the diverse environmental conditions and sources of PTEs, numerous pollution indices are widely used to assess the anthropogenic impact of inorganic contaminants in soil samples. Indices such as enrichment factor (EF), geoaccumulation index (I_{geo}), contamination factors (CF), pollution load index (PLI), and potential ecological risk index (RI) were used to assess metal toxicity and to indicate levels of potential pollution (Håkanson, 1980; Tomlinson et al., 1980; Huang et al., 2017; Ilie et al., 2017; Gan et al., 2019; Laniyan & Adewumi, 2020; Monged et al., 2020; Radomirović et al., 2021a; Verol, et al., 2021).

This paper investigates the contamination status of agricultural soil in the district of Braničevo. Taking into account geological factors and heterogeneous soil characteristics, the main objectives of this study were mainly focused on the characterization of soil quality, pollution status, and ecological risk assessment of selected PTEs (As, B, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Zn) in the soil, and (3) identification of relationships among PTEs and their possible sources using multivariate statistical tools combined with geostatistical methods.

The results of this study can provide insight into the degrees of soil pollution and prioritize sources and potential risks, which could, directly and indirectly, affect the study area. At the same time, these findings could be helpful in taking adequate measures to protect the soil ecosystem and reduce the targeted input of PTEs into the soil.

2. MATERIAL AND METHODS

2.1. Study area and sample collection

The district of Braničevo (Serbia) is located south of the Danube river, where the southern part of the Carpathian Mountains meets with the southern part of the Pannonian Basin. It occupies a total area of 5,107 km^2, where 71.35 % of the territory represents agricultural soil. The Braničevo district consists of 8 municipalities: Požarevac, Veliko Gradište, Golubac, Kučevo, Malo Crniće, Petrovac and Žagubica with about 183,625 inhabitants in 2011. The most densely populated city in the Braničevo district is Požarevac (155 inhabitants/km^2), and the least densely populated is the municipality of Kučevo (26 inhabitants/km^2).

The relief of this district contains hilly-mountainous, plain-hilly and lowland areas that cover its eastern, central and north-western parts, respectively. The hilly-mountainous area in the eastern part of the district is part of the lower Carpathian mountain range, including the mountains Homolje, Kučaj and Beljanica. The lowland area covers the northwest of the district and is part of the Pannonian Basin, which is surrounded by rivers: the Danube in the north, and its tributaries, the Great Morava in the west, the Pek in the east, and in the south with the river Mlava along its entire length (Štetić & Trišić, 2018). Accordingly, the district is influenced by moderate continental and mountain climate characteristics.

Sampling was conducted at 200 sites on agricultural land (arable land, pastures, orchards, vineyards, gardens), as the most frequent soil type in the district, both in natural and agricultural territories and near technogenic contaminated zones. Agriculture and food industry, mining and energy production, transport, metal processing and machinery production are this district's potential sources of pollution. A thermal power plant and an opencast lignite mine in Kostolac are the most significant industrial pollutants on the territory of the Braničevo district. Potential sources of pollution such as large industrial enterprises and traffic zones are located on the territory of neighboring districts (ironworks in Smederevo, copper industry in Bor and Majdanpek, national highway Belgrade-Niš).

Field research included the identification of cadastral parcels, while spatial sampling was undertaken using GPS technology (Trimble TDC100) to locate the geographical locations of sampling points. The study area (Figure 1) is located between latitudes (N) 44°08’01.32” – 44°48’41.04” and longitudes (E) 21°56’9.96” – 21°03’10.44”. About 1.5 – 2 kg of composite surface soil was collected at each sampling site. The upper 30 cm of soil was collected with a soil probe, placed into polyethylene bags, labeled, transported to the laboratory, and stored at 4 °C until subsequent analysis.

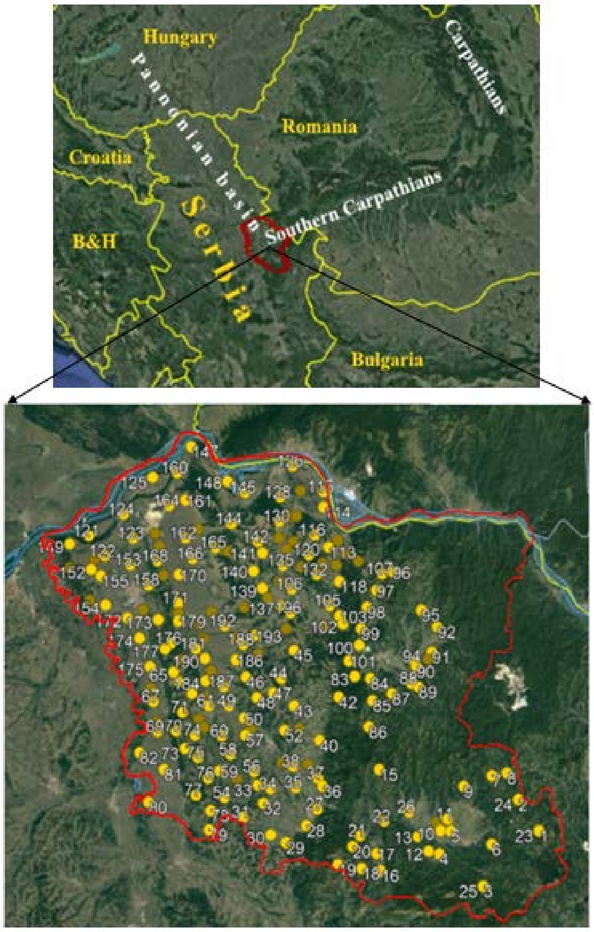

Figure 1. The study area of the Braničevo district

There is a pronounced heterogeneity of geological substrates on which the examined soils are formed. On the territory of the Braničevo district, about 78% of the soil belongs to the order of automorphic (class of undeveloped, humus-accumulative class, class of cambic and class of eluvial illuvial soils) and about 22% to the hydromorphic soils order (class of undeveloped, class of pseudogley soils and class of gleysols soils) (Mrvić et al., 2011).

2.2. Sample preparation and measurement

All digestion vessels and volumetric wares were acids washed and rinsed with reagent water before chemical analysis. Before digestion, soil samples were dried at 105°C (24 h), homogenized by grinding and passed through a 2.0-mm sieve to remove coarse particles and reduce sample variability. The soil samples were digested using aqua regia in proportion 1:3 of HNO_3 and HCl with heating and reflux. Digested soil samples were cooled, diluted (10-fold) with deionized water (⩾ 18 MΩ·cm), filtered and stored at 4 °C until analysis. Thereafter, the digested solutions were analyzed by a flame atomic absorption spectrometry (FAAS; Analyst 100, Perkin Elmer Inc., Waltham, MA, United States) to determine the concentrations of ten elements (As, B, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Zn). Working standard solutions of the analyzed PTEs were prepared by diluting the stock solution, 1000 mg/L (Merck KGaA, Darmstadt, Germany).

To estimate the pH of soil samples, the measurement was conducted at 20 ± 2°C in a solution of deionized water and soil (5:1 ratio) using a pH glass electrode (Orion model 3-Star pH-meter, Thermo Scientific). The water content was determined by the standard laboratory oven drying method ASTM D2216. Soil samples were dried at 105 ± 5°C overnight to constant weight. The experimentally obtained ratio of the mass of pore water and the mass of soil solids represents the water content, expressed in the weight percent of the dry matter.

The soil organic carbon content (C_{org}, %) was determined by the dichromate-oxidation method following the Walkley-Black procedure (Walkley & Black, 1934). In the first step, the organic matter was oxidized in 5 ml of potassium dichromate (0.2 M) - diluted sulfuric acid (1:1) solution, involving heating. Subsequently, the excess potassium dichromate used for oxidation of soil organic carbon was determined by redox titration with ammonium ferrous sulfate solution (standardized 0.1 M Mohr’s salt solution) to the terminal point. The amount of reduced chromium is equivalent to C_{org} content.

The method of determination of soil texture analysis included dispersion of soil aggregates (< 2 mm) with sodium hexametaphosphate (Biochem Chemopharma, laboratory reagent for general use, France). Particle-size distribution analysis was performed using the pipette method (Natural Resources Conservation Service, 2004), where separations of the finest soil fractions were further subdivided into different size classes based on the relative amounts of its components - sand, silt and clay.

The obtained data on PTEs content in soils are compared with national regulations (Official Gazette of the Republic of Serbia, 2018) with an established list of target and intervention values.

2.3. Quality assurance/quality control

The accuracy of the analysis with scientifically acceptable results was ensured by using the standard reference material (NIST SRM Montana Soil 2711a) and reagent blank samples. SRM and reagent blanks were prepared by carrying out the entire analytical procedure and were included as quality control samples after every ten soil samples. Analytical quality was evaluated by replicate analysis, with concentrations obtained as the average of six consecutive measurements. The measurement results of studied PTEs were in the range of uncertainty of the corresponding certified values in the standard reference material. Soil concentrations were expressed in mg/kg of dry matter.

2.4. Data analysis

Descriptive statistical analysis of data was obtained using Microsoft Excel. Analysis included mean, median, skewness, kurtosis, standard deviation, maximum, minimum and Grubb's outlier tests. To estimate ecological risks, soil pollution indices such as the enrichment factor (EF), the geoaccumulation index (I_{geo}), the contamination factor (CF), the pollution load index (PLI) and risk index (RI) were calculated according to Radomirović et al., (2020). The Pearson's correlation, principal component analysis (PCA) and hierarchical cluster analysis (HCA)) were developed in order to identify the origin of PTEs. The Minitab software package was used to perform multivariate data analysis. More detail is given in Radomirović et al., (2021b). The geospatial mapping of the risk index (RI) of toxic elements was done using Golden Software Surfer. The geospatial information system (GIS) visualizes areas with high-risk index values (Miletić et al., 2020).

3. RESULTS AND DISCUSSION

3.1. Soil properties

According to the texture triangle diagram in Figure 2, samples were located mainly in the upper portion of the silt loam and the central portion of the silty clay loam. The major soil texture types in the study area were primarily silt loam (40.5%) and silty clay loam (34.5%). Several other obtained texture soil types were: loam (7%), sandy loam (7%), clay loam (6.0%), silty clay (3.0%), loamy sand (1.0%) and clay (0.5%). Most texture transitions occurred between adjacent textural classes, with 150 samples belonging to the two textural classes (silt loam and silty clay loam), representing 75% of the total analyzed soil samples.

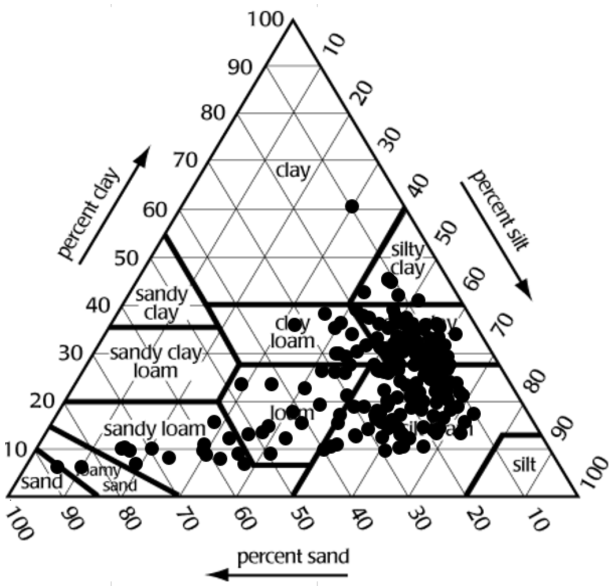

Figure 2. Soil texture triangle of investigated soil samples

3.2. Trace elements distribution

The descriptive statistics of soil properties (pH, C_{org}) and PTEs (As, B, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Zn) are presented in Table 1.

The pH values of the topsoil ranged from 4.39 to 8.12, with a mean value of 6.26. A total of 74.5% of soil samples showed slightly acidic characteristics, which regulates the solubility and thus the bioavailability of PTEs, while 25.5% of soil samples had slightly alkaline characteristics, which affected the limited availability of metals and their adsorption. Most of the soils in the study area were acidic, probably due to agricultural practices, which include the application of plant protection chemicals and fertilizers (Yang et al., 2014; Emurotu & Onianwa, 2017). The organic carbon content (C_{org}, %) in soil samples varied between 0.58 and 6.52%, with an average of 1.71. The highest C_{org} value, 6.52%, was obtained at site No. 12 (Žagubica), and the lowest at site No. 128 (Veliko Gradište). In general, the lower contents of C_{org} were obtained in the northeastern part of the district, in the municipality of Veliko Gradište and Golubac. Considering the characteristic type of soil between these two municipalities, arenosol on a sandy substrate, a minimum C_{org} content is expected at the mentioned locations. The highest contents of organic carbon (up to 6.52%) occurred mainly in the

Table 1. Descriptive statistics for the content of PTEs (mg/kg), C_{org} (%), and pH in the soil samples

	As	**B**	**Cd**	**Cr**	**Cu**	**Mn**	**Mo**	**Ni**	**Pb**	**Zn**	**pH**	**C_{org}**
C_{mean}	5.97	77.7	0.61	7.97	32.4	795.2	6.32	36.1	56.6	56.3	6.26	1.71
C_{median}	4.40	75.7	0.50	7.60	22.7	767.3	6.40	27.5	50.7	49.2	6.02	1.51
C_{skew}	6.22	0.72	1.32	1.70	9.29	2.71	0.29	2.66	2.72	1.93	0.47	2.58
C_{kurt}	53.7	1.84	3.60	8.92	105.3	14.7	-0.63	7.05	9.59	4.35	-0.86	10.1
C_{stdev}	6.95	21.3	0.40	3.97	45.1	290.4	2.80	31.2	28.7	23.9	0.94	0.79
C_{max}	74.7	171.9	2.60	32.8	572.6	2824	14.3	182.1	212.2	160.5	8.12	6.52
C_{min}	0.40	28.1	0.02	0.10	6.50	261.8	1.30	0.40	12.9	17.3	4.39	0.58
Tv[a]	29	–	0.8	9	36	–	3	35	85	140	–	–
Iv[b]	55	–	12	240	190	–	200	210	530	720	–	–
UCC[c]	4.8	17	0.09	92	28	438.6	1.1.	47	17	67	–	–

[a]Target value; [b]Intervention value (Official Gazette of the Republic Serbia, 2018);
[c]Upper continental crust value (Rudnick & Gao, 2003)

soil of the southern part of the district (Žagubica), but also in other sites such as: site No. 36 (5.18%, Petrovac), site No. 124 (3.21%, Kostolac) and site No. 172 (3.11%, Požarevac). The slightly higher content of C_{org} in agricultural soils can be attributed mainly to the use of organic and mineral fertilizers (Yang et al., 2014; Acir & Funal, 2020).

The concentrations of PTEs (mg/kg dry weight) in the soil of Braničevo district amounted: As (0.40–74.7); B (28.1–171.9); Cd (0.02–2.60); Cr (0.10–32.8); Cu (6.50–572.6); Mn (261.8–2823.5); Mo (1.30–14.3); Ni (0.40–182.1); Pb (12.9–212.2); Zn (17.3–160.5). According to Table 1, Cd had the lowest mean concentration (0.61 mg/kg), while Mn showed the highest (795.2 mg/kg). The mean values of metal concentrations decreased in the following order: Mn > B > Pb > Zn > Ni > Cu > Cr > Mo > As > Cd. The mean values of most elements (As, Cd, Mn, Cu, Mo, Pb) were higher than their respective reference values in uncontaminated soil (Rudnick & Gao, 2003).

National regulations (Official Gazette of the Republic Serbia, 2018) with an established list of target and intervention values were used to evaluate possible soil contamination, as the applied values are most similar to the Dutch guidelines for soil remediation (Dutch standards, 2000). As shown in Table 1, the mean values of most elements in the investigated soil samples did not exceed the target values, except for Mo and Ni. However, the contents of As surpassed the allowed limits in the samples at two sampling sites, No. 6 and 44 (47.2 and 74.7 mg/kg, respectively). On the other hand, many samples exceeded the permitted limits of B content. Regarding the Cd content, the highest values, 2.60 and 2.10 mg/kg were recorded at sites No. 12 (Žagubica) and 68 (Žabari), while the highest Cr content was obtained at sites No. 1 and 68 (32.8 and 26.3 mg/kg, respectively). Finally, in terms of Cu content, there is a number of samples with elevated values above the limit values, both target and intervention, especially at two sites, No. 5 (Žagubica, 572.6 mg/kg) and 100 (Kučevo, 214.3 mg/kg). A similar situation is observed for Mn with increased contents, especially at sites No. 7 and 12 (2258 and 2823 mg/kg, respectively). However, the Mo concentrations were generally above the target and below the intervention values, with their maximum in the samples at sites No. 171, 172, and 175 (13.9; 13.0 and 14.3 mg/kg, respectively).

The results showed a very similar pattern of distribution in the spatial variations of Ni, Pb, and Zn, with a high-value area located in the western part of the Braničevo district (Žabari municipality). Significantly increased Ni concentrations were obtained in several locations in Žabari, with a maximum value of 182 mg/kg at site No. 68. Moreover, the maximum levels of both Ni and B were obtained at the same sampling site, as well as elevated values of Cd, Cr, Pb, and Zn. The contents of Pb and Zn were increased in the same sites as Ni in Žabari. The highest concentrations for Pb (212 and 102.8 mg/kg) were found in Žagubica at sites No. 5, 6, and at site 37 in Petrovac na Mlavi (124.0 mg/kg), while the maximum value of Zn, 160 mg/kg, was obtained at site No. 100 (Kučevo).

Accordingly, the maximum values of the selected PTEs were above their respective target values, indicating contamination with the risk to the ecosystem. Locations with the maximum values of As and Cu (particularly Cu, which was three times higher) exceeded their intervention values and remediation is required.

The total metal contents accumulated in the studied samples of agricultural soil can be partly inherited from natural terrestrial sources (parent rock substrate) in various quantities, which are generally of little importance (Li et al., 2019); while external inputs are related to a wide range of possible anthropogenic sources such as fertilizers, soil ameliorants, plant protection chemicals, agricultural machinery, atmospheric deposition or industrial waste materials (ash, mine waste, etc.) (Barsova et al., 2019; Cai et al., 2019; Alsafran et al., 2021; Andráš et al., 2021).

Studies on the concentrations of PTEs in agricultural soils have been carried out in different regions worldwide (Table 2). Most samples of agricultural soils in the Braničevo district showed low to moderate amounts of As, Cd, Cr, and somewhat elevated levels of Cu, Mn, Mo, Ni, Pb, and Zn. The concentration ranges of investigated elements and possible soil contamination at certain locations are generally controlled by both geogenic (accumulation of eroded parent rock materials) and anthropogenic sources of PTEs (agronomic practices, atmospheric/aerial deposition, etc.) (Li et al., 2019).

Compared to the average metal contents in agricultural soils worldwide, the mean As and Cr concentrations from the soils of the Braničevo district were generally lower. The mean As content showed two times lower value than in the agricultural soils of China (Mamat et al., 2020), more than three times lower compared to the reported value in Bangladesh (Bhuiyan et al., 2010) and four times lower than in Qatar (Alsafran et al., 2021). The concentration of Cd in the study area, in general, showed approximately identical values as in the agricultural soils of Croatia (Romic & Romic, 2003), Nigeria (Emurotu & Onianwa, 2017) and southern China - Hainan island (Liao et al., 2018). The highest geometric mean value of Mn was reported in Bangladesh, while the second-highest was recorded in Serbia, with slightly higher values compared to Croatia (Romic & Romic, 2003) and Turkey (CoŞKun et al., 2006). The mean Cr and Ni contents in this research are similar to the reported mean values in agricultural soils of Iran (Hani & Pazira, 2010; Ghorbani et al., 2015), while Zn showed similar values to those reported in Spain (Micó et al., 2006; Rodríguez Martín et al., 2006). The mean Pb content in topsoil samples of the Braničevo district, 56.6 mg/kg, was at a similar level as in China, 55.14 mg/kg (Mamat et al., 2020) and was generally higher in comparison with other regions, except Poland (113 mg/kg) and Bangladesh (433 mg/kg). The analyzed results showed that the mean values of PTEs in the soils of Serbia are comparable with those published for other soils and regions worldwide.

3.3. Multivariate analysis

Correlations between the examined PTEs and selected soil properties (pH in H_2O, C_{org}) were analyzed by the Pearson's correlation matrix (Table 3). Statistically significant correlations with p-values less than 0.01, as well as $p < 0.05$ and $p < 0.1$ (moderate level) were taken into consideration for the interpretation of the data.

The results showed statistically significant positive correlations ($p < 0.01$) between Cd–B

Table 2. Comparison of PTEs mean concentrations (mg/kg) from agricultural soils worldwide

Location	Area	As	B	Cd	Cr	Cu	Mn	Mo	Ni	Pb	Zn	References
Qatar	Northern and central region	27.6	n.a.	0.20	35.7	25.6	n.a.	n.a.	61.9	18.2	92.4	Alsafran et al., 2021
China	31 provinces	12.21	n.a.	1.49	70.09	44.60	n.a.	n.a.	41.97	55.14	154.20	Mamat et al., 2020
China	Hainan Island	2.17	n.a.	0.60	26.5	9.43	n.a.	n.a.	8.74	22.2	39.6	Liao et al., 2018
Nigeria	Kogi State	n.a.	n.a.	0.60	n.a.	4.80	n.a.	n.a.	17.0	12.8	28.0	Emurotu & Onianwa, 2017
Iran	Golestan province	9.53	n.a.	0.18	0.68	22.99	n.a.	n.a.	36.24	13.05	70.06	Ghorbani et al., 2015
Iran	Southern Tehran	n.a.	n.a.	0.77	7.96	36.09	n.a.	n.a.	36.92	16.46	217.99	Hani & Pazita, 2010
Turkey	Thrace region	8	n.a.	0.2	173	20	600	0.6	50	33	45	CoŞKun et al., 2006
Russia	Vladimir region	n.a.	n.a.	0.13–0.36	n.a.	2.11–10.2	36–541	n.a.	.78–15.6	3.43–10.2	12.5–35.6	Selivanov & Martsev, 2019
Nepal	Bhaktapur district	n.a.	n.a.	0.08–1.52	n.a.	3.76–60.56	n.a.	n.a.	n.a.	4.67–67.43	8.67– 180.62	Kayastha, 2015
Bangladesh	Dinajpur district	17.55	n.a.	n.a.	n.a.	n.a.	1886	n.a.	n.a.	433	296	Bhuiyan et al., 2010
Poland	Olkusz district	n.a.	n.a.	2.6	n.a.	10	n.a.	n.a.	n.a.	113	1170	Miśkowiec et al., 2015
S. Korea	Central regions	.355–0.782	n.a.	.118–0.146	n.a.	.823-3.501	n.a.	n.a.	n.a.	.938–6.078	4.694–7.818	Kim & Kim, 1999
Brazil	Southwestern Amazônia	n.a.	n.a.	n.d.	47.9	18.2	n.a.	n.a.	8.7	15.3	22.4	Dos Santos & Alleoni, 2012
Colombia	Sinu River Basin	n.a.	n.a.	0.040	n.a.	1149	n.a.	n.a.	661	0.071	1365	Marrugo-Negrete et al., 2017
Spain	Alicante province	n.a.	n.a.	0.34	26.5	22.5	295	n.a.	20.9	22.8	52.8	Micó et al., 2006
Spain	Ebro Basin	n.a.	n.a.	0.42	20.3	17.3	n.a.	n.a.	20.5	17.5	57.5	Rodríguez Martín et al., 2006
Croatia	Zagreb area	n.a.	n.a.	0.66	n.a.	20.8	613	n.a.	49.5	25.9	77.9	Romic & Romic, 2003
Albania	Tirana area	n.a.	n.a.	0.30	74.2	42.7	n.a.	n.a.	305.9	19.7	95.5	Gjoka et al., 2011
Serbia	Braničevo district	5.97	77.7	0.61	7.97	32.4	795.2	5.32	36.1	56.6	56.3	This study

n.a. - not analyzed; n.d - not detected

(r=0.835), Cd–Pb (r=0.722), Pb–B (r=0.779), Zn–B (r=0.722), Pb–Zn (r=0.783), Pb–Ni (r=0.707). These strong positive correlations possibly suggest their common sources in the soil. Positive correlations at the level of $p < 0.1$ were observed between Ni–Cr (r=0.545), as they are commonly found associated, which suggests lithogenic control over their distribution (Zheng et al., 2005; Rodríguez Martin et al., 2006; Pan et al., 2016), then Ni–B (r=0.583), Ni–Pb (r=0.707), and Ni–Zn (r=0.650), while Mn showed statistically significant correlations only with Cd (r=0.566) and Cr (r=0.617). Besides, positive correlations at $p < 0.1$ level were also observed between As and Cd, Pb, as well as between Cd and Cr, Mn, C_{org}. It was also noted that Cu and Mo did not show statistically significant correlations with other elements.

The Pearson correlation analysis showed that C_{org} and Cd were positively correlated at a statistically significant level ($p < 0.1$), whereas other positive correlations with As, B, Cr, Cu, Mn, and Zn were not so high. As reported in previous studies (Gjoka et al., 2011; Mazurek et al., 2017; Raffa et al., 2021), soil organic matter is one of the main solid-phase sorbents and an influencing factor for adsorption, precipitation, complexation, and accumulation of PTEs in the soil. However, most metals tend to be available in acidic soils, except Cd, whose availability and mobility are favored at alkaline pH (Rodríguez Martin et al., 2006). Typically, the correlations between the pH and the heavy metal content in alkaline soils are not very high, while in acidic soils are higher (Rodríguez Martin et al., 2006). In this study, the pH varied between slightly acidic and slightly alkaline. Therefore, the soil pH showed relatively weak positive correlations with Mo (r=0.310), Ni (r=0.295), Zn (r=0.253), and negative correlations with Cd, Cr, and Mn. Based on this, it can be inferred that the soil pH makes a small contribution to the solubility, mobility, and bioavailability of Mo, Ni, and Zn and the retention of Cd, Cr, and Mn in the soil.

The principal component analysis was carried out to examine the sources and interpret the correlations of elements and soil parameters in the studied area. Two principal components were extracted and rotated for the maximum variance. The plot of the two dominant factors is shown in Figure 3. The associated elements were divided into two factors (F1, F2), identifying the dominant influence ascribed to lithogenic (geogenic) or anthropogenic sources.

Factor 1 (F1) is most dependent on Mn concentration, showing strong positive factor loadings on Mn, moderate positive loadings on Cr, Cd, and negative loadings on Mo and pH. The association of Mn, Cr, and Cd in F1 may be attributed to their lithogenic source. This can be confirmed by good correlations between Mn–Cr (r=0.617) and Mn–Cd (r=0.566) (Table 3). Factor 2 (F2) contains high positive loadings on Ni, moderate positive loadings on B, Zn, and Pb, somewhat lower on Mo, pH, and negative loadings on C_{org}. Moderate loadings on Zn, B, and partially Pb were distributed in the central part of the plot, with a similar association of these elements in F1 and F2, suggesting that these elements most likely originate from mixed sources. Furthermore, it should be noted that the grouping of anthropogenic elements in F2 does not exclude the influence of natural processes. Molybdenum was scattered separately from other elements, which indicated an entirely anthropogenic influence on its concentration.

The maximum concentrations of B and Ni were reported at sampling site No. 68 and elevated levels of Pb, Zn, Cd, and Cr, while the maximum Mn, Cd, Cu, and C_{org} contents were obtained at site No. 12. Significant positive correlations between these two groups of elements confirmed the results of the PCA analysis and the close association results from elevated heavy metal concentrations at the above-mentioned locations, indicating their same and/or mixed origin.

Table 3. Pearson's correlation coefficients (r) of PTEs and chemical properties (pH, C_{org}) in soil samples

	As	**B**	**Cd**	**Cr**	**Cu**	**Mn**	**Mo**	**Ni**	**Pb**	**Zn**	**pH**
B	0.427										
Cd	**0.502**[c]	**0.835**[a]									
Cr	0.275	**0.696**[b]	**0.566**[c]								
Cu	0.240	0.288	0.343	0.066							
Mn	0.238	0.478	**0.554**[c]	**0.617**[b]	0.016						
Mo	0.073	0.293	0.273	0.111	0.132	-0.108					
Ni	0.263	**0.583**[c]	0.346	**0.545**[c]	-0.014	0.111	0.280				
Pb	**0.516**[c]	**0.779**[a]	**0.722** [a]	**0.617**[b]	0.237	0.335	0.211	**0.707**[a]			
Zn	0.438	**0.722**[a]	**0.671**[b]	**0.521**[c]	0.268	0.312	0.287	**0.650**[b]	**0.783**[a]		
Ph	0.041	0.033	-0.031	-0.064	0.008	-0.204	0.310	0.295	0.014	0.253	
C_{org}	0.238	0.352	**0.561**[c]	0.168	0.352	0.382	0.006	-0.012	0.310	0.266	-0.077

[a]Correlations significant at p < 0.01 level; [b]Correlations significant at p < 0.05 level; [c]Correlations significant at p < 0.1 level.

Although the weathering of parent rock material tends to affect the concentration of PTEs in sediment and agricultural soil (Botello et al., 2022; Radomirović et al., 2021c), metal emission is generally associated with anthropogenic activities. The most important sources that can primarily affect heavy metal concentrations distribution and accumulation in the soil include the application of organic and mineral fertilizers (Varol et al., 2021) and atmospheric PTEs inputs (transported aerosol particles) by deposition from industrial activities (coal power plant, mining) and traffic roads (Rodríguez Martin et al., 2006; Raffa et al., 2021).

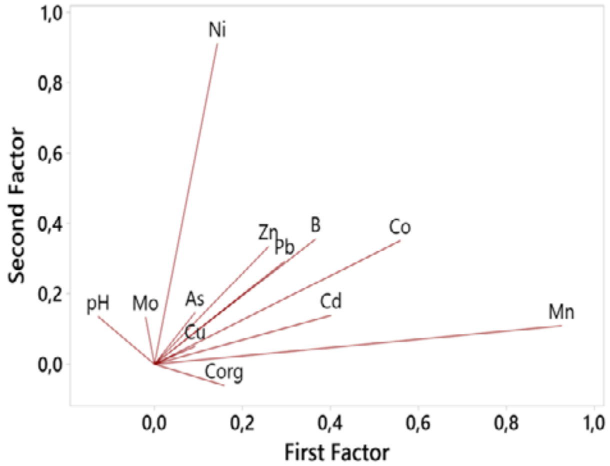

Figure 3. Loading plot of selected PTEs in agricultural soil samples

The hierarchical cluster analysis (HCA) was performed to interpret and better understand the difference and similarities of the chemical composition of soil samples with sampling sites. The dendrogram in Figure 4 was obtained using Ward's Linkage method.

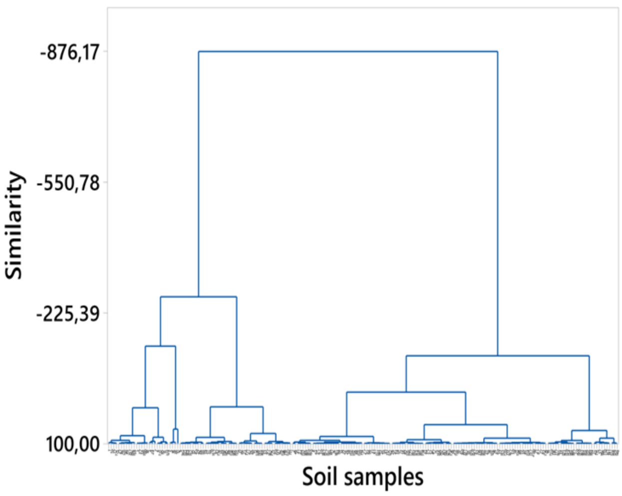

Figure 4. Dendrogram showing clustering of samples in the studied area

The groupings from hierarchical cluster analysis included soil samples at 200 sampling sites ordered in two main clusters, which were further classified into two subclusters. Each of these subclusters formed the arrangement of new subgroups. For the final grouping, a smaller distance between the existing clusters indicated their higher similarity level in the chemical content of PTEs in the investigated soil samples, denoting their class. The left grouping in Figure 4 is characterized by a high content of B, Ni, Cd, Cr, C_{org}, Mo, Pb, and Zn in soil samples at locations of defined classes. The findings from hierarchical cluster analysis showed that soil samples of each subcluster were spatially distributed at sites in the study area based on their sources and origin.

3.4. Ecological risk Assessment

To assess soil contamination in the study area and the potential ecological risk due to exposure of As, B, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Zn, three individual indices (EF, CF, I_{geo}) and two complex indices (PLI, RI) were applied. According to the purpose, CF and I_{geo} indices were employed to estimate the soil contamination level for each metal individually. The primary purpose of the EF calculation was to provide information on the origin of heavy metal pollution due to possible anthropogenic exposure. This factor is also used to estimate pollution levels based on differences between the presence of individual metals from anthropogenic, natural or mixed sources in the soil (Radomirović et al., 2020).

To identify the anthropogenic impact on the content of PTEs, it is mandatory to have a reference element of lithogenic origin, which is characterized by low variability in the study area (Mazurek et al., 2017). In order to normalize the element concentrations in soil samples, Mn was used as a reference element in this study. The level of soil contamination is classified into several different categories (Jiang et al., 2019; Monged et al., 2020). The results related to soil enrichment (EF) for 10 PTEs are shown in Table 4.

The mean EFs of As, B, Cr, Cu, Ni, and Zn were lower than one, suggesting their natural origin and deficiency to no soil enrichment. Soil samples in the study area exhibited somewhat higher mean EF values for Pb but without soil enrichment, followed by moderate enrichment with Cd ($2 < EF < 5$), and significant enrichment of soil with Mo ($5 < EF < 20$). The mean EFs obtained for Cd and Mo reflect the effects of external sources, suggesting that their distribution in topsoils is affected by human activities.

Table 4. Enrichment factor (EF) and geoaccumulation index (I_{geo}) of PTEs in samples of agricultural soil in the Braničevo district

EF	As	B	Cd	Cr	Cu	Mn	Mo	Ni	Pb	Zn
EFmean	0.70	0.96	3.66	0.05	0.70	1.00	6.45	0.44	1.89	0.49
EFstdev	0.71	0.26	2.15	0.02	1.30	0.00	3.39	0.35	0.80	0.19
EFmax	7.38	2.18	15.5	0.11	17.8	1.00	21.4	1.73	5.43	1.22
EFmin	0.03	0.39	0.10	0.00	0.70	1.00	1.14	0.01	0.54	0.17
I_{geo}	**As**	**B**	**Cd**	**Cr**	**Cu**	**Mn**	**Mo**	**Ni**	**Pb**	**Zn**
I_{geo} mean	-0.83	0.09	1.71	-4.40	-0.71	0.20	2.65	-1.31	1.02	-0.94
I_{geo} stdev	1.41	0.41	1.49	1.23	0.80	0.47	0.73	1.01	0.60	0.53
I_{geo} max	3.38	1.29	4.27	-2.07	3.77	2.10	3.99	1.37	3.06	0.68
I_{geo} min	-4.17	-1.33	-3.02	-10.4	-2.69	-1.33	0.53	-7.46	-0.98	-2.54

According to the maximum EF values, soil samples showed moderate enrichment with B (2.18), while significant enrichment was noted for Pb (5.43), As (7.38), Cd (15.5), and Cu (17.8), and very high enrichment for Mo (21.4). Anthropogenic activities were likely to be the main source of these PTEs. Potential sources responsible for elevated Mo concentrations can be sewage sludges and sludges intended for land application or atmospheric deposition of fly ash and coal combustion residues (industrial pollution from the nearby power plants and lignite mine). The Mo availability may be increased by the alkaline reaction of fly ash (Kabata-Pendias & Pendias, 2001). The high EF values obtained for Cd and As reflect the influence of irregular distributions of external sources. Higher EF values of Cd, Cu, and As are probably connected with agricultural practice, as a higher percentage of the population (approx. 50 % of the municipality Žabari) is engaged in agriculture (livestock, farming, fruit growing, viticulture). Long-term pesticides, chemical (phosphate and sulfate zinc) fertilizers, and sludge on arable land eventually contaminate soils with As, Cu, and Cd (Kabata-Pendias & Pendias, 2001; Cai et al., 2019; Jiang et al., 2019). In addition, sources of As may be associated with arsenic sprays containing inorganic arsenic compounds for plant protection. Also, certain industrial activities (mine waste, metal processing, coal combustion) represent significant anthropogenic sources (Rajaković et al. 2013; Avkopashvili et al., 2017). Besides, Cu is a marker of the application of livestock manure and agricultural activities (Jiang et al., 2019), and high enrichment of Cu can be found in topsoils in the vicinity of mining areas (Kabata-Pendias & Pendias, 2001). It is assumed that the Cu source near the sampling sites in the eastern part of the district may be the result of the effluent discharge from the nearby Majdanpek copper mine (Culicov et al., 2021). Moderate soil enrichment with Pb can be ascribed to anthropogenic influence, such as combustion of fossil fuels and traffic emissions (leaded petrol and exhausts), particularly in the proximity of the highway and regional roads (Kabata-Pendias & Pendias, 2001; Rodríguez Martin et al., 2006; Li et al., 2019).

Another method applied to control soil quality and to distinguish levels of contamination with PTEs was the geoaccumulation index (I_{geo}). As shown in Table 3, the mean I_{geo} values of Pb and Cd indicated moderate soil pollution and moderate to strong pollution by Mo. The mean I_{geo} values of As, Cr, Cu, Ni and Zn were below 0, which suggested that most soil samples in the district were regarded as unpolluted by these PTEs.

Maximum I_{geo} values of As (3.38), Cu (3.77), Mo (3.99), and Pb (3.06) classified soil as strongly polluted, while in terms of Cd (4.27), some soil samples were "strongly to extremely polluted". Therefore, higher amounts of As, Cu, Mo, Pb, Cd and their accumulation in the soil is most likely related to anthropogenic sources. Although the maximum I_{geo} value for Mn (2.10) indicated moderate pollution, Mn is not considered a polluting metal in the soil and usually accumulates in the surface layers of the soil. In the case of B and Ni, the soils were moderately polluted ($1 < I_{geo} < 2$), which indicated that their accumulation in the soil could be derived from both geogenic and man-induced inputs. Although B is a deficient micronutrient in most soils, significant anthropogenic sources can be sewage sludge and fly ash, where B-rich soils can reduce crop yields in the field. The increased Ni content in the soil can usually be attributable to certain fertilizers and sludges and is often released during coal combustion or metal processing (Kabata-Pendias & Pendias, 2001).

The presence of elevated levels of PTEs in relation to the reference values was estimated using the contamination factor (CF), which further defined the degree of soil pollution. The CF values of selected PTEs were in the following range: As (0.08–15.6), B (0.60–3.66), Cd (0.19–28.9), Cr (0.00–0.36), Cu (0.23–20.5), Mn (0.60–6.44), Mo (2.17–23.8), Ni

(0.01–3.87), Pb (0.76–12.5) and Zn (0.26–2.40). These values suggested low to very high levels of soil contamination. Based on the mean CF values in Table 5, metals followed the ascending order: Cr < Ni < Zn < Cu < As < B < Mn < Pb < Cd < Mo. The mean CFs of selected PTEs were indicative of low contamination by Cr, Ni, Zn, moderate contamination by B, Cu, Mn, followed by considerable contamination of Pb, and very high contamination by Cd and Mo. Based on the CF results, the general observation is that Mo is one of the priority PTEs in the analyzed soil.

The pollution load index, PLI, was calculated based on the CFs of the ten selected PTEs. PLI ranged from 0.24 to 3.67, whereas the mean value of 1.37 indicated moderate soil pollution. According to the maximum PLI value (3.67), obtained at site No. 68 in the western part of the district, the soil was characterized as strongly polluted. Generally increased PLI values were observed in the western (sites No. 68, 69, 80, 175) and southern parts of the district (sites No. 5, 6, 12). The results of a comprehensive pollution assessment using the pollution load index (PLI) highlighted that 21.5 %, 67.5 %, and 11 % of sampling sites had unpolluted, moderately and strongly polluted levels. Thus, the preceding discussion suggested that most soil samples were classified as moderately polluted.

Following the RI criteria (Radomirović et al., 2020), the soil quality and potential ecological risk were assessed due to ecological sensitivity and exposure to toxic PTEs from soil (Håkanson, 1980). The obtained RI values ranged from 17.6 to 933, with a mean value of 243, indicating a moderate ecological risk to the soil ecosystem. As seen in Fig. 5, RI values related to the soil at the investigated sampling sites showed predominantly moderate ecological risk, except in the southern and western parts of the district. The maximum RI value (933) indicated a very high ecological risk (RI > 600) at location No. 12, Žagubica. Other sites whose RI values represent a very high ecological risk (RI > 600) were observed in the southern (sites no. 2, 5, 6, 7, 12) and western (sites no. 68, 69) parts of the district. According to the RI index, 20 % of soil samples in the study area were characterized by low ecological risk, 52 % moderate, 24 % significant, and 3% very high ecological risk.

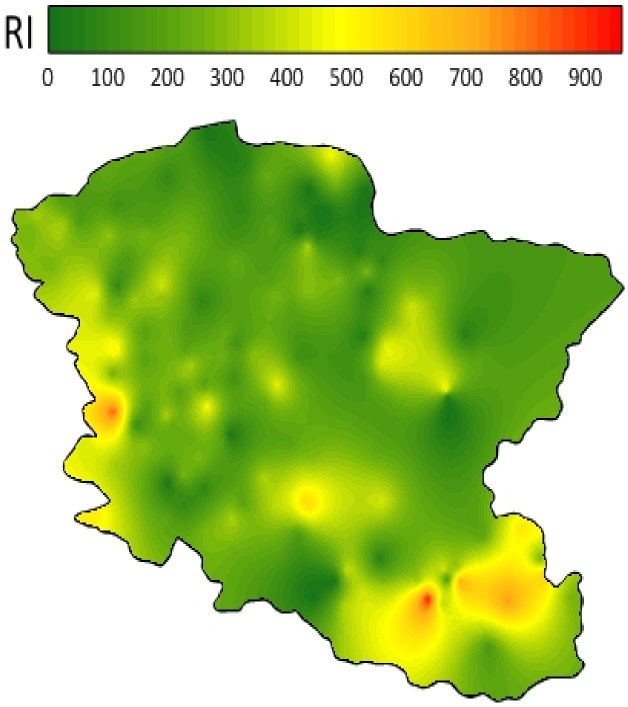

Figure 5. Spatial distribution of risk index (RI) values related to sampling sites in the study area.

4. CONCLUSION

The results of the analysis showed that the average metal concentrations decreased in the following order: Mn > B > Pb > Zn > Ni > Cu > Cr > Mo > As > Cd. The mean values of most metal concentrations remained below the corresponding target values, except for Mo and Ni. The influence of soil textural composition on the content of the tested metals is insignificant. The results showed that the study area soils were slightly acidic to slightly alkaline.

The pollution load index (PLI) results emphasized that 67.5 % and 11 % of sampling sites showed moderately and strongly polluted degrees, respectively, while the potential ecological risk index (RI) showed that 52.5 %, 24 %, and 3% of soil samples were under moderate, significant, and very high ecological risk, respectively. In addition, the mean values of enrichment factor (EF), geoaccumulation index (Igeo) and contamination factor (CF) highlighted strong contamination with Mo, which implied the influence of external anthropogenic sources.

Table 5. Contamination factor (CF) of the investigated PTEs in soil samples and pollution load index (PLI)

CF	CF_{As}	CF_{B}	CF_{Cd}	CF_{Cr}	CF_{Cu}	CF_{Mn}	CF_{Mo}	CF_{Ni}	CF_{Pb}	CF_{Zn}	PLI
CF mean	1.24	1.65	6.78	0.09	1.16	1.81	10.5	0.77	3.33	0.84	1.37
CF stdev	1.45	0.45	4.41	0.04	1.61	0.66	4.67	0.66	1.69	0.36	–
CF max	15.6	3.66	28.9	0.36	20.5	6.44	23.8	3.87	12.5	2.40	3.67
CF min	0.08	0.60	0.19	0.00	0.23	0.60	2.17	0.01	0.76	0.26	0.24

The hierarchical cluster analysis showed the grouping of sampling sites into two distinctive clusters according to higher and lower metal concentrations. Multivariate statistical analysis and spatial distribution illustrated high-risk locations and unpolluted areas.

In summary, this study provides essential information on the quality of agricultural soil in the study area in terms of distribution of heavy metal content and pollution control, with estimated ecological risk in the Braničevo district.

Acknowledgment: This research was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants 451-03-68/2022-14/200287 and 451-03-68/2022-14/200135).

Author contributions AM: methodology, software, investigation: MR: writing - original draft, validation; AĐ: conceptualization, project administration, funding acquisition; ML: visualization; JB: formal analysis, resources; AO: supervision, writing - review and editing.

Availability of data and materials: The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation to any qualified researcher.

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Received at: 16. 06. 2022
Revised at: 21. 07. 2022
Accepted for publication at: 24. 07. 2022
Published online at: 28. 07. 2022