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Original scientific paper

APPLICATION OF MULTIVARIATE STATISTICAL METHODS IN DETERMINING SPATIAL DISTRIBUTION OF CHEMICAL ELEMENTS IN SOIL (POREČE REGION, NORTH MACEDONIA)

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A b s t r a c t: The purpose of this study was to determine the presence of various chemical elements in soil samples in the region of Poreče, North Macedonia. For this purpose, 88 soil samples (44 topsoil, 0-5 cm, and 44 bottom soil samples, 20–30 cm) were collected and 57 elements were analyzed, from which 18 elements (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) were analyzed by ICP-AES and additional 39 elements (B, Be, Bi, Cd, Ce, Co, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, La, Lu, Mo, Nb, Nd, Pd, Pr, Pt, Rb, Sb, Sc, Sm, Sn, Ta, Tb, Ti, Tl, Tm, W, Y, Yb and Zr) were analyzed by ICP-MS. The obtained results were statistically processed to determine possible areas with pollution of soil with heavy metals. From the results of the analyzed elements by ICP-AES, 3 association lithogenic factors [F1 (Cu-Ni-Cr-V-Zn-Fe-Mn), F2 (Sr-Ca-Mg), F3 (Li-K-Al-Ba)] were determined. The distribution of the elements which are included in the lithogenic factors are incurred as a result of geological structures present in the investigated area (schists, carbonates, sandstones, and Neogene sediments).

Key words: soil; potentially toxic elements; distribution; pollution; Poreče region; North Macedonia

INTRODUCTION

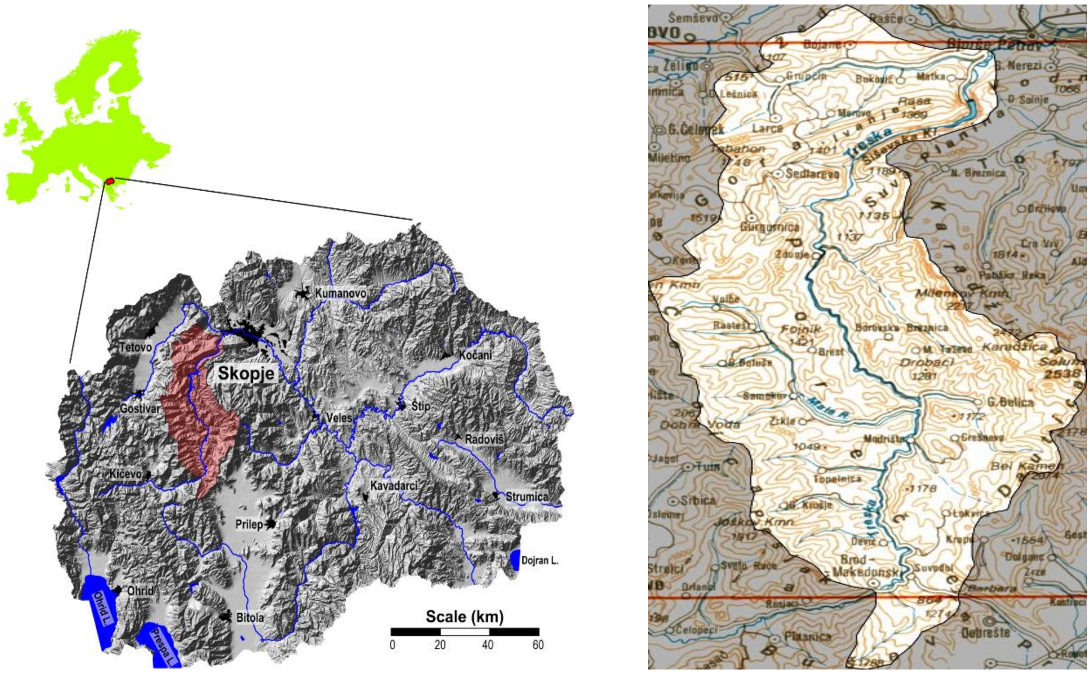
The emissions of metals into the environment occur through a wide range of processes and pathways, including into the air, surface waters, or soil (Kabata-Pendias & Mukherjee, 2007; Acton, 2013). The distribution of certain chemical elements, which at high levels represent a hazard to the environment, causes certain unwanted consequences to human health. Pollution of the environment with toxic metals has been the topic of numerous studies focusing on industrial areas, areas where the exploitation and processing of natural resources (oil, ore, etc.) take place, or highly populated areas where traffic and communal waste represent the main sources of metals (Järup, 2003). In this regard, special attention should be paid to the pollution of the environment with potentially toxic elements (PTEs) that can originate from natural and anthropogenic sources. Natural sources of PTEs include lithogenic origin (Conde et al., 2009), volcanic activity, evaporation from the sea, while anthropogenic sources of pollution are increasing with rapid industrialization and modern lifestyles include car traffic, industrial plants for manufacturing and processing, power plants, commercial activities, and waste disposal sites. PTEs can stay in the environment for hundreds of years (Kabata-Pendias & Mukherjee, 2007). Toxic elements and metals are commonly found as contaminants in soil, water, and food and are carried in the air. In recent years, environmental pollution with PTEs has been the basis for many studies (Desaules et al., 2010; Wei & Yang, 2010; Salomons et al., 2012; Wang et al., 2015; Jiménez-Ballesta et al., 2017). The pollution with PTEs of soil, water, and the air is an important part that should never be overlooked. The main cause of emission is anthropogenic sources, especially mining and metallurgical activities (Diawara et al., 2006; Stafilov et al., 2010a, 2010b; Acton, 2013). The emitted metals survive in the environment and the metal contamination that occurs as a result of ore mining persists for hundreds of years after mining has ceased (Peplow, 1999).

Our previous studies on the whole territory of North Macedonia defines the areas of soil pollution with some of the PTEs (As, Cd, Cu, Mn, Ni, Pb, Sb, Zn) due to the mining, metallurgical and urban activities (Balabanova et al., 2013; Serafimovska et al., 2013; Bačeva et al., 2014; Stafilov et al., 2010a, 2010b, 2013, 2018, 2019; Stafilov and Šajn, 2016, 2019). Therefore, within this study, the distribution of different chemical elements in the soils in the area of the Poreče region, situated in the central-northern part of the country, was determined. For that purpose, soil samples are collected from the whole area of the Skopje region with a grid of 5×5 km, from a total of 44 locations. From each location, 2 samples of soil are collected: samples of topsoil (0–5 cm) and samples from deeper layer – bottom soil (20–30 cm). The obtained results for the content of the examined elements are statistically processed by multivariate factor analysis and cluster analysis to show the associations of chemical elements. Also, the spatial distribution maps are prepared for each of the analyzed elements

MATERIAL AND METHODS

Study area description

The Poreče region is located in the central-northern part of North Macedonia and occupies the entire catchment area of the river of Treska (Figure 1a). The surface of this basin is 945 km^2 with a population of 10,000 inhabitants. In relief of Poreče mainly dominate hills and mountains, with small alluvial leveling around the Treska river. From the east, it is closed to the mountains of Suva Planina, Jakupica, Karadžica, and Dautica. It is bordered on the south by part of Mt. Buševa, on the west by Pesjak and Celoica Mts., and on the north by Mt. Suva Gora. This region includes the municipalities of Makedonski Brod, part of the municipality of Brvenica, municipality of Želino, and part of the Skopje municipalities of Saraj and Sopište. Figure 1b shows the topographic map of the study area where, in addition to the municipalities, it can be seen the names of the villages with their location as well as the flow of the river of Treska with the built artificial Lake Kozjak (Markoski, 2004).



a) b)

Fig. 1. Location of the study area in North Macedonia (a) and its topographic map (b)

Mountain of Jakupica is a natural barrier that separates the Poreče region from the Skopje and Veles valleys. The peaks of Solunska Glava (2540 m) (Figure 2), Marina Rupa (2469 m), Dautica (2178 m), and Ubava (2353 m), the spacious pastures, and the lush diverse vegetation can be especially emphasized in it. This mountainous area belongs to the protection belt as a protected area of „Jasen" and is one of the most famous ecological areas in the region. The mountainous area covers about 24,000 hectares of forested mountains, deep caves, lakes, and underground rivers (Marinoski, 2010).

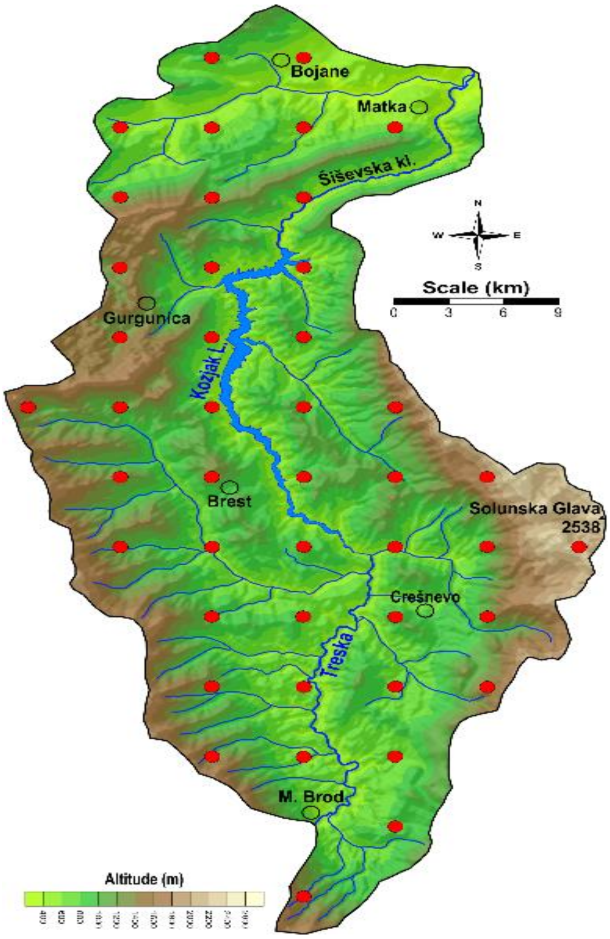


Fig. 2. Elevation map with soil sampling locations of the study area

In this region, apart from the rich forest belt, there is artificial Lake Kozjak. The lake is 32 km long, somewhere 130 m deep, and the maximum distance from one shore to another is 400 m. The lake was created in 2004 when the Kozjak hydroelectric power plant was put into operation. Cascade along the Treska river, between the hydropower plant of Kozjak and Matka, is built the hydroelectric power plant of Sveta Petka. This hydropower plant was put into operation in August 2012 (Markoski, 2004; Dimitrova et al., 2011).

Geology of the study area

The geological composition of the Poreče region is diverse and is characterized by the following types of rocks: Paleozoic and Proterozoic carbonates, Paleozoic sandstones, Proterozoic gneisses, Paleozoic shales, Quaternary alluvial sediments, Neogene clastic sediments, and magmatic rocks (Figure 3) (Petrušev et al., 2021). From the geological map (Figure 3) we can see that in the eastern, central, and whole area along the river of Treska Proterozoic carbonates predominate. In this part, there is the appearance of small areas with Neogene clastic sediments. Paleozoic and Proterozoic shales and gneisses are present in the southeastern part, but are a very small representation. In the western, southwestern, and northwestern parts, the lithology of the examined area is composed of Paleozoic shales. In this part around the village of Gurgurnica, there is the appearance of Paleozoic carbonates. Neogene clastic sediments are also present around the villages of Bojane and Matka. Quaternary alluvial sediments are present in a small part of the northern area of Poreče. The igneous rocks are present in a small area in the western part of the study area. Paleozoic sandstones also occur in the southernmost part of the area.

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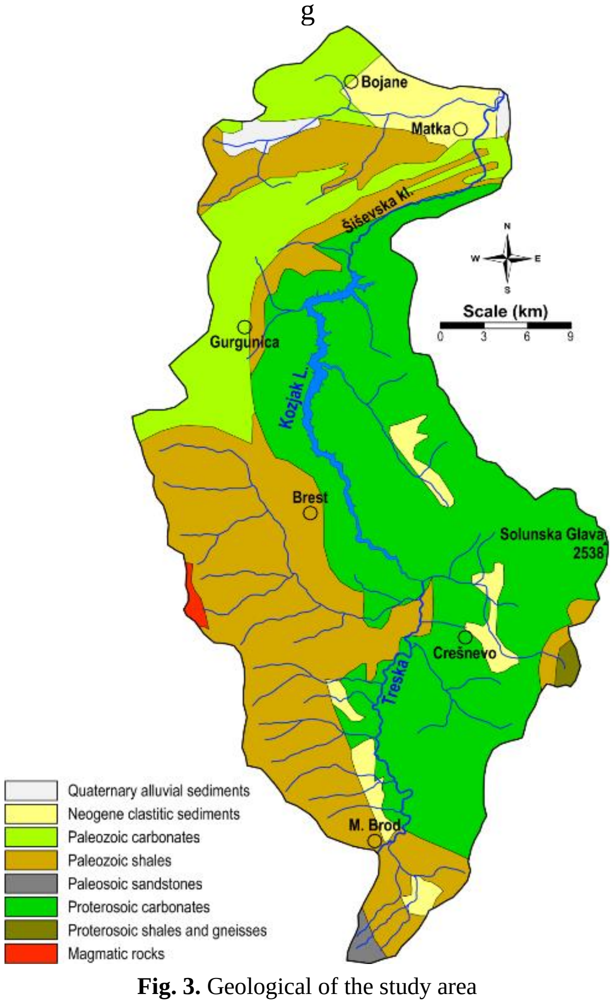

Fig. 3. Geological of the study area

Soil sampling and preparation

Samples of topsoils in the investigated area were collected according to the European guidelines and also according to our experience (Salminen et al., 2005; Stafilov et. al., 2010a,b; Stafilov & Šajn, 2016, 2019). The study area (945 km^2) was covered by the same sampling grid of 5×5 km as used for the preparation of the Geochemical Atlas of Macedonia (Stafilov & Šajn, 2016) (Figure 2). Altogether 88 soil samples were collected from 44 locations. To distinguish eventual anthropogenic pollution at the surface from the natural geochemical composition at deeper layers, samples from two intervals were collected, topsoil (0–5 cm) and subsoil (20–30 cm). To obtain representative composite samples, five subsamples from each location on a square plot of 10×10 m were collected. The soil samples brought to the laboratory were cleaned from plant material and stones and then homogenized and dried at room temperature. Subsequently, they were passed through a 2 mm sieve and ground in a porcelain mortar until reaching a final particle size below 125 μm. For the digestion of soil samples, open wet digestion with a mixture of acids was applied (HNO_3, HF, $HClO_4$, and HCl, according to ISO Standard (ISO 14869–1:2001).

Instrumentation

All samples were analyzed by ICP-AES (Varian, model 715-ES) for the elements with high contents (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, and Zn) (Balabanova et al., 2010). Trace elements ((B, Be, Bi, Cd, Ce, Co, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, La, Lu, Mo, Nb, Nd, Pd, Pr, Pt, Rb, Sb, Sc, Sm, Sn, Ta, Tb, Ti, Tl, Tm, W, Y, Yb, and Zr) were analyzed by ICP-MS measurements on a SCIEX Perkin Elmer Elan DRC II (Canada) inductively coupled plasma mass spectrometer with quadruple and single detector setup (Bačeva et al., 2012). The quality control of the two applied techniques was performed using the standard addition method, and the recovery for the investigated elements ranged from 98.2% to 100.8%. The quality control was also performed by the analysis of certified reference soil and geological samples: soil sample JSAC 0401 (The Japan Society for Analytical Chemistry) and rock CRM samples undersaturated igneous rock SARM 3 NIM-L Lujaurite (SA Bureau of Standards, Pretoria, S. Africa), rock NCS DC71306 (GBW07114) (China National Analysis Centre).

Data processing

Data analysis and the production of maps were performed on a Statistica (ver. 13), Autodesk Map (ver. 2008), QGIS (ver. 3.10), and Surfer (ver. 13) software. All field observations, analytical data, and measurements were introduced into the data matrix. Parametric and nonparametric statistical methods were used for data analysis. Box-Cox transformations were used to acquire normal distributions. Multivariate R-mode factor analysis was used to reveal associations of the chemical elements. From numerous variables, the factor analysis (FA) derives a smaller number of new, synthetic variables. The factors contain significant information about the original variables, and they may have certain meanings. Factor analysis was performed on variables standardized to a mean of zero and one unit of standard deviation (Reimann et al., 2002).

The universal kriging method with linear variogram interpolation was applied for the construction of the areal distribution maps of the analyzed elements and the obtained factor scores. Seven classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90, and 90–100.

RESULTS AND DISCUSSION

The descriptive statistics for the content of the elements in topsoil and subsoil samples are presented in Tables 1 and 2. The values for Al, Ca, Fe, K, Mg, Na, and Ti are given in %, values for Hg and In in μg/kg, while the values for the content for the remaining elements are given in mg/kg.

A comparative analysis of the contents of the analyzed elements in topsoils from the Poreče region and the soils from Macedonia (Stafilov & Šajn, 2016) and Europe (Salminen et al., 2005) is given in Table 3. It was found that the contents of many elements are different in soils from the Poreče region compared with those from Macedonian soils as well as with the European soils (Table 3) showing their dependence on the specific lithogenic origin of the rocks in the study area. Thus, due to the dominant presence of carbonate geological units, the content of Ca and Mg is significantly higher in the soils of the Poreče region (median for Ca is 4.3 mg/kg and for Mg is 1.4 mg/kg) than in the soils from the entire territory of N. Macedonia (median of 1.3 mg/kg and 0.94 mg/kg, respectively). The content of the other elements in the soils from Poreče region is similar to or lower than in the soils of the whole country. There is a characteristic decrease in the contents of Al, Ba, Cr, Mn, Na, Ni, Pb, Sr, Ce or La). Similar information is obtained when comparing the contents of the analyzed elements in the soils of the Poreče region and European soils.

Table 1

Descriptive statistics for the content of the elements in topsoil (0–5 cm), n=44

Elem.	Unit	X	X(BC)	Md	Min	Max	P_{25}	P_{75}	P_{10}	P_{90}	S	Sx	CV	A	E	A(BC)	E(BC)
								ICP–AES									
Ag	mg/kg	0.81	0.77	0.80	0.10	2.1	0.52	1.0	0.24	1.3	0.42	0.063	51.6	0.47	0.53	–0.03	–0.13
Al	%	2.2	1.9	2.0	0.22	6.0	1.2	2.8	0.76	4.3	14000	0.21	63.4	0.85	0.12	–0.33	–0.10
Ba	mg/kg	170	140	150	18	430	80	250	38	300	110	16	63.8	0.490	–0.586	–0.19	–0.84
Ca	%	5.7	3.0	4.3	0.057	18	0.46	11	0.097	14	54000	0.82	96.3	0.57	–1.02	–0.26	–1.45
Cr	mg/kg	52	43	46	8.6	180	23	71	11	99	38	5.7	72.2	1.345	2.280	–0.08	–0.53
Cu	mg/kg	26	20	20	6.6	74	15	32	8.9	51	16	2.4	63.4	1.200	0.872	–0.39	–0.53
Fe	%	2.3	2.2	2.3	0.36	5.6	1.4	3.4	0.41	3.7	13000	0.20	55.8	0.23	–0.50	–0.23	–0.76
K	%	0.99	0.90	1.0	0.16	2.5	0.48	1.4	0.23	1.8	5800	0.087	58.8	0.37	–0.58	–0.12	–0.97
Li	mg/kg	19	15	14	0.63	63	7.1	26	3.2	45	15	2.3	80.7	1.184	1.038	0.07	–0.34
Mg	%	2.7	1.6	1.4	0.014	10	0.61	4.3	0.31	7.3	28000	0.41	102.0	1.08	0.00	–0.15	–0.61
Mn	mg/kg	450	400	460	73	1300	240	630	140	800	270	41	60.4	0.741	0.308	–0.08	–0.82
Na	%	0.47	0.25	0.23	0.053	2.4	0.12	0.56	0.071	1.1	5400	0.082	116.4	2.04	3.98	0.04	–0.99
Ni	mg/kg	32	25	26	7.1	110	17	40	9.6	63	22	3.3	68.8	1.435	2.260	–0.27	–0.57
P	mg/kg	500	440	430	120	1500	330	610	230	950	280	43	56.4	1.596	2.772	0.02	0.38
Pb	mg/kg	11	6.8	9.0	0.50	34	0.89	18	0.50	28	10	1.5	91.0	0.630	–0.708	–0.26	–1.42
Sr	mg/kg	50	41	43	1.5	170	26	62	11	100	36	5.5	73.2	1.317	1.932	–0.12	0.21
V	mg/kg	63	57	63	12	160	36	79	23	100	34	5.1	53.5	0.790	0.640	–0.02	–0.33
Zn	mg/kg	64	56	63	23	110	43	85	27	93	25	3.8	38.9	–.030	–0.971	–0.96	–0.17
								ICP–MS									
B	mg/kg	64	39	40	0.005	230	12	110	3.6	130	65	9.7	100.5	1.158	0.585	–0.24	–0.47
Be	mg/kg	4.3	3.5	3.4	0.51	18	2.1	6.0	0.87	8.6	3.4	0.51	78.6	1.787	5.008	0.17	–0.12
Bi	mg/kg	1.4	1.1	1.1	0.42	4.8	0.71	1.7	0.47	2.9	1.0	0.16	74.7	1.838	3.164	0.39	–0.33
Cd	mg/kg	0.76	0.58	0.62	0.21	2.3	0.45	0.91	0.28	1.7	0.50	0.076	66.0	1.55	2.00	–0.51	–0.14
Ce	mg/kg	28	22	25	0.69	87	10	41	3.0	53	21	3.2	75.4	0.678	0.055	–0.34	–0.78
Co	mg/kg	12	11	11	3.2	29	6.9	17	4.8	23	6.9	1.0	55.9	0.793	–0.118	0.06	–0.83
Cs	mg/kg	3.2	2.2	2.0	0.27	16	1.2	3.9	0.75	7.8	3.1	0.47	98.0	2.199	5.747	0.29	–0.18
Dy	mg/kg	2.4	1.8	2.3	0.064	6.5	0.61	3.7	0.25	4.9	1.8	0.27	74.0	0.426	–0.716	–0.48	–0.85
Er	mg/kg	1.2	0.95	1.2	0.034	3.3	0.36	2.0	0.10	2.6	0.91	0.14	73.9	0.375	–0.923	–0.49	–0.87
Eu	mg/kg	0.73	0.57	0.74	0.024	2.0	0.22	1.0	0.11	1.4	0.52	0.079	71.5	0.55	–0.32	–0.48	–0.70
Ga	mg/kg	20	18	18	2.6	53	11	26	3.6	37	12	1.8	62.3	0.760	0.543	–0.08	–0.47
Gd	mg/kg	3.3	2.6	3.4	0.088	9.6	0.86	4.7	0.34	6.9	2.5	0.38	74.7	0.520	–0.428	–0.46	–0.81
Ge	mg/kg	1.1	0.80	0.65	0.005	4.9	0.43	1.5	0.14	2.3	1.1	0.16	100.0	1.81	3.43	0.18	0.27
Hf	mg/kg	1.7	1.4	1.5	0.084	4.8	0.65	2.6	0.34	3.5	1.2	0.18	68.7	0.667	–0.261	–0.35	–0.56
Hg	µg/kg	62	51	54	5.0	210	34	83	5.0	110	0.048	7.3	78.1	1.53	2.86	–0.02	0.11
Ho	mg/kg	0.45	0.34	0.45	0.013	1.2	0.12	0.73	0.045	0.90	0.33	0.050	74.4	0.44	–0.72	–0.46	–0.89
In	µg/kg	56	49	52	5.0	140	31	79	18	100	0.032	4.9	57.3	0.56	–0.08	–0.38	–0.33
La	mg/kg	12	9.4	11	0.11	37	3.9	19	0.96	23	9.4	1.4	76.5	0.526	–0.368	–0.40	–0.83
Lu	mg/kg	0.19	0.15	0.20	0.005	0.47	0.063	0.26	0.023	0.39	0.13	0.020	69.4	0.34	–0.77	–0.49	–0.86
Mo	mg/kg	1.3	1.1	0.98	0.38	4.8	0.72	1.5	0.61	2.2	0.83	0.13	66.2	2.35	7.36	0.32	–0.01
Nb	mg/kg	16	15	15	3.5	47	11	19	5.4	26	8.4	1.3	52.3	1.274	3.138	–0.04	0.37
Nd	mg/kg	13	10	12	0.20	37	3.7	20	1.1	25	9.5	1.4	72.8	0.447	–0.484	–0.48	–0.77
Pd	mg/kg	1.4	0.92	0.94	0.050	5.5	0.37	1.9	0.16	3.4	1.4	0.21	99.1	1.46	1.58	–0.02	–0.78
Pr	mg/kg	3.3	2.6	3.1	0.050	9.6	0.97	5.3	0.30	6.2	2.4	0.36	73.5	0.468	–0.444	–0.46	–0.80
Pt	mg/kg	0.60	0.58	0.54	0.18	1.1	0.42	0.77	0.38	0.95	0.22	0.034	37.2	0.62	–0.44	0.19	–0.34
Rb	mg/kg	70	59	67	15	220	33	88	19	120	45	6.8	64.8	1.220	1.817	0.01	–0.61
Sb	mg/kg	0.71	0.59	0.63	0.17	2.0	0.35	0.87	0.25	1.4	0.46	0.069	64.8	1.25	1.10	0.11	–0.72
Sc	mg/kg	48	16	15	2.4	700	9.1	27	6.0	60	130	19	265.5	4.528	20.477	0.28	0.90
Sm	mg/kg	2.7	2.1	2.9	0.050	7.6	0.73	3.9	0.22	5.1	1.9	0.29	73.2	0.471	–0.408	–0.49	–0.79
Sn	mg/kg	2.6	2.4	2.5	0.69	6.4	1.7	3.3	1.2	4.4	1.4	0.21	52.8	1.176	1.541	0.09	–0.08
Ta	mg/kg	1.0	0.90	0.85	0.15	2.8	0.61	1.4	0.24	1.9	0.60	0.091	58.4	0.81	0.41	–0.24	–0.29
Tb	mg/kg	0.45	0.35	0.45	0.012	1.3	0.11	0.68	0.047	0.95	0.34	0.051	74.9	0.50	–0.52	–0.46	–0.84
Ti	%	0.56	0.46	0.54	0.080	1.9	0.20	0.75	0.14	0.97	4000	0.060	71.4	1.31	2.21	–0.01	–0.58
Tl	mg/kg	0.54	0.44	0.46	0.050	1.6	0.28	0.74	0.14	1.1	0.37	0.055	68.3	1.30	1.72	–0.28	0.13
Tm	mg/kg	0.18	0.14	0.17	0.005	0.43	0.053	0.28	0.016	0.38	0.13	0.019	73.2	0.36	–0.96	–0.46	–0.89
W	mg/kg	1.5	1.3	1.5	0.25	4.9	0.77	2.0	0.35	2.5	1.0	0.16	67.9	1.531	3.326	0.04	–0.05
Y	mg/kg	11	7.7	9.3	0.11	33	3.0	17	0.66	22	8.6	1.3	79.9	0.602	–0.335	–0.48	–0.83
Yb	mg/kg	1.2	0.90	1.2	0.027	2.9	0.37	1.8	0.13	2.4	0.85	0.13	72.7	0.376	–0.889	–0.49	–0.86
Zr	mg/kg	79	67	76	4.1	210	32	110	16	160	52	7.8	65.6	0.608	–0.250	–0.31	–0.53

X = arithmetical average; X = average of Box-Cox transformed values; Md = median; Min = minimum; Max = maximum; P_{25} = 25th percentile; P_{75} = 75th percentile; P_{10} = 10th percentile; P_{90} = 90th percentile; S = standard deviation; S_x = standard deviation of transformed values; CV = coefficient of variation; A = skewness; E = kurtosis; BC = Box-Cox transformed values; BC= Box-Cox transformations

T a b l e 2

Descriptive statistics for the content of the elements in subsoil (20–30 cm); n=44

Elem.	Unit	X	X(BC)	Md	Min	Max	P_{25}	P_{75}	P_{10}	P_{90}	S	Sx	CV	A	E	A(SK)	E(SK)
ICP–AES																	
Ag	mg/kg	0.83	0.80	0.76	0.050	1.8	0.54	1.1	0.39	1.3	0.38	0.058	46.1	0.43	–0.08	–0.05	0.07
Al	%	2.2	1.8	1.8	0.33	6.2	1.0	2.6	0.72	4.9	16000	0.24	71.7	1.10	0.28	0.26	–0.72
Ba	mg/kg	160	140	120	31	330	97	220	65	300	86	13	54.7	0.69	–0.70	0.18	–0.70
Ca	%	6.2	2.8	3.7	0.024	17	0.22	13	0.084	15	62000	0.94	100.7	0.48	–1.40	–0.22	–1.60
Cr	mg/kg	53	43	47	8.4	170	22	72	14	89	37	5.6	70.4	1.17	1.39	0.00	–0.78
Cu	mg/kg	190	19	20	6.0	72	13	33	9.0	44	1100	160	580.4	6.63	43.98	0.19	1.17
Fe	%	2.4	2.3	2.4	0.35	5.3	1.2	3.6	0.76	4.2	14000	0.20	56.1	0.16	–1.20	–0.12	–1.24
K	%	1.0	0.92	1.0	0.11	2.3	0.48	1.5	0.27	1.8	5900	0.089	58.1	0.24	–1.03	–0.18	–1.06
Li	mg/kg	19	16	15	0.26	49	9.2	28	4.5	38	13	1.9	66.7	0.70	–0.24	–0.23	–0.24
Mg	%	3.0	1.6	1.5	0.033	9.9	0.35	5.5	0.17	7.9	31000	0.47	104.8	0.78	–0.95	–0.07	–1.29
Mn	mg/kg	460	400	390	66	1100	240	690	150	830	270	41	60.1	0.60	–0.64	–0.06	–0.90
Na	%	0.45	0.24	0.23	0.041	2.5	0.11	0.54	0.080	1.1	5200	0.079	115.4	2.13	5.21	0.08	–0.98
Ni	mg/kg	47	26	26	5.0	700	18	40	11	63	100	15	220.3	6.29	40.90	0.07	1.76
P	mg/kg	500	440	440	120	1300	340	550	220	910	280	42	56.1	1.53	2.29	–0.02	0.42
Pb	mg/kg	14	8.5	10	0.50	91	2.5	21	0.50	26	15	2.3	113.5	3.09	14.26	–0.07	–0.40
Sr	mg/kg	51	39	43	1.5	230	17	70	4.5	94	45	6.8	88.4	1.80	4.88	0.01	–0.19
V	mg/kg	67	60	67	10	150	34	84	22	120	38	5.7	56.7	0.65	–0.00	–0.10	–0.57
Zn	mg/kg	470	61	69	25	180	44	81	33	110	2700	400	566.4	6.63	43.98	0.34	1.93
ICP–MS																	
B	mg/kg	71	41	49	0.45	450	9.7	94	1.9	150	86	13	121.7	2.52	8.32	0.02	–0.41
Be	mg/kg	4.3	3.5	4.0	0.15	19	2.0	5.8	1.0	7.2	3.3	0.49	76.3	2.08	7.48	–0.18	0.62
Bi	mg/kg	1.7	1.3	1.3	0.12	7.4	0.76	2.2	0.55	2.9	1.4	0.21	81.8	2.17	6.08	–0.32	1.37
Cd	mg/kg	1.1	0.56	0.49	0.23	16	0.42	0.84	0.35	1.7	2.4	0.36	228.8	6.15	39.40	0.58	0.57
Ce	mg/kg	26	19	23	0.83	99	7.9	36	1.7	60	25	3.7	94.1	1.29	1.25	0.03	–0.78
Co	mg/kg	12	11	12	3.4	27	7.3	17	4.8	20	6.0	0.91	48.7	0.47	–0.43	–0.17	–0.92
Cs	mg/kg	2.7	2.0	2.0	0.11	11	1.2	3.4	0.80	6.4	2.3	0.35	85.8	1.84	3.69	–0.32	0.78
Dy	mg/kg	2.2	1.6	1.9	0.033	9.4	0.65	2.9	0.16	4.5	2.2	0.34	99.7	1.74	3.14	0.18	–0.31
Er	mg/kg	1.1	0.81	0.99	0.023	4.9	0.32	1.5	0.081	2.3	1.1	0.17	100.7	1.84	3.73	0.19	–0.30
Eu	mg/kg	0.68	0.51	0.56	0.058	2.7	0.22	0.91	0.085	1.2	0.64	0.096	93.6	1.65	2.74	0.26	–0.48
Ga	mg/kg	20	18	21	2.6	50	10	28	5.3	32	12	1.8	59.1	0.39	–0.48	–0.14	–1.02
Gd	mg/kg	3.2	2.3	2.4	0.037	14	0.91	4.4	0.17	6.1	3.2	0.48	99.8	1.70	2.88	0.15	–0.32
Ge	mg/kg	1.3	0.98	1.1	0.005	4.5	0.44	1.8	0.28	2.5	0.99	0.15	78.7	1.07	1.34	–0.46	0.10
Hf	mg/kg	1.7	1.4	1.3	0.26	5.5	0.83	2.1	0.43	4.0	1.3	0.19	74.9	1.38	1.28	0.39	–0.30
Hg	µg/kg	65	51	55	5.0	240	24	100	5.0	130	0.052	7.9	80.1	1.01	1.32	–0.16	–0.81
Ho	mg/kg	0.42	0.30	0.35	0.005	1.9	0.12	0.54	0.032	0.85	0.42	0.063	100.9	1.86	3.83	0.17	–0.24
In	µg/kg	62	51	52	5.0	260	28	80	14	110	0.051	7.7	81.7	1.98	4.91	0.19	0.58
La	mg/kg	12	8.2	10	0.073	45	3.3	16	0.56	27	11	1.6	94.7	1.29	1.45	–0.02	–0.72
Lu	mg/kg	0.18	0.14	0.14	0.014	0.68	0.058	0.25	0.024	0.30	0.15	0.023	88.2	1.53	2.44	0.24	–0.48
Mo	mg/kg	1.3	1.0	1.1	0.32	4.2	0.65	1.5	0.41	2.7	0.87	0.13	68.3	1.60	2.77	–0.13	–0.49
Nb	mg/kg	17	15	14	2.7	50	10	23	4.7	30	10	1.5	60.4	1.09	1.32	0.01	–0.16
Nd	mg/kg	12	9.0	10	0.11	56	3.4	16	0.83	27	12	1.9	98.9	1.68	3.07	0.14	–0.37
Pd	mg/kg	1.6	1.2	1.1	0.050	6.5	0.52	2.2	0.33	3.6	1.5	0.23	93.4	1.65	2.70	0.01	–0.17
Pr	mg/kg	3.1	2.2	2.6	0.021	14	0.86	4.0	0.20	6.9	3.1	0.46	97.8	1.59	2.69	0.10	–0.45
Pt	mg/kg	0.57	0.55	0.53	0.095	1.2	0.41	0.66	0.36	0.84	0.22	0.033	38.6	0.86	1.10	–0.08	1.48
Rb	mg/kg	66	56	53	8.2	210	41	77	22	140	45	6.8	68.5	1.56	2.61	–0.03	0.33
Sb	mg/kg	0.73	0.58	0.65	0.14	3.2	0.36	0.91	0.20	1.2	0.54	0.082	74.8	2.31	8.48	–0.08	–0.32
Sc	mg/kg	31	21	23	5.0	120	12	38	7.9	64	28	4.2	89.2	1.92	3.65	–0.30	–0.40
Sm	mg/kg	2.5	1.8	2.0	0.050	11	0.65	3.2	0.19	5.1	2.5	0.37	97.9	1.66	2.87	0.17	–0.41
Sn	mg/kg	2.7	2.3	2.5	0.42	7.2	1.3	3.7	0.85	4.8	1.7	0.25	61.3	0.83	0.25	–0.07	–0.76
Ta	mg/kg	1.1	0.91	0.84	0.16	3.4	0.55	1.6	0.27	2.1	0.76	0.11	70.2	1.21	1.25	0.11	–0.42
Tb	mg/kg	0.42	0.30	0.33	0.005	1.8	0.13	0.58	0.029	0.80	0.42	0.064	100.1	1.74	2.99	0.17	–0.28
Ti	%	0.54	0.45	0.49	0.062	1.6	0.27	0.73	0.13	0.90	3700	0.055	67.9	1.13	1.29	–0.09	–0.49
Tl	mg/kg	0.60	0.43	0.39	0.050	3.6	0.25	0.79	0.15	1.2	0.62	0.093	102.7	3.01	11.88	0.17	0.49
Tm	mg/kg	0.16	0.12	0.14	0.005	0.68	0.043	0.22	0.012	0.31	0.16	0.024	97.5	1.71	3.11	0.16	–0.32
W	mg/kg	1.6	1.4	1.4	0.15	5.1	0.65	2.5	0.37	3.1	1.1	0.17	69.7	0.78	0.19	–0.13	–0.86
Y	mg/kg	9.8	6.6	7.9	0.22	50	1.9	13	0.51	23	10	1.6	105.5	1.98	4.99	0.14	–0.47
Yb	mg/kg	1.1	0.79	0.92	0.063	4.5	0.32	1.5	0.099	2.0	1.0	0.15	95.0	1.64	2.78	0.22	–0.45
Zr	mg/kg	80	70	69	15	230	42	98	21	170	54	8.2	68.1	1.27	1.28	0.32	–0.20

X = arithmetical average; X = average of Box–Cox transformed values; Md = median; Min = minimum; Max = maximum; P_{25} – 25th percentile; P_{75} – 75th percentile; P_{10} – 10th percentile; P_{90} – 90th percentile; S = standard deviation; S_x = standard deviation of transformed values; CV = coefficient of variation; A = skewness; E = kurtosis; BC = Box–Cox transformations

T a b l e 3

Comparison of the median, minimal and maximal values of the content of the analyzed elements in topsoil from North Macedonia and Europe

Elem.	Unit	Dutchlist		Poreče region (this work)		Macedonia (Stafilov&Šajn, 2016)		Europe (Salminen et al., 2005)	
		Target	Action	Md	Min–Max	Md	Min–Max	Md	Min–Max
ICP–AES									
Ag	mg/kg			0.80	0.10–2.1	–	–	0.27	0.01–3.15
Al	%			2.0	0.22–6.0	6.6	0.090–11	5.8	0.70–14.1
Ba	mg/kg	200	625	150	18–430	430	6.0–2900	375	30–1870
Ca	%			4.3	0.057–18	1.3	0.050–35	0.66	0.019–34.3
Cr	mg/kg	100	380	46	8.6–180	88	5.0–2700	60	<3.0–6230
Cu	mg/kg	36	190	20	6.6–74	28	1.6–270	13.0	0.81–256
Fe	%			2.3	0.36–5.6	3.5	0.030–12	2.45	0.11–15.6
K	%			1.0	0.16–2.5	1.9	0.020–5.3	1.59	0.022–5.09
Li	mg/kg			14	0.63–63	26	1.8–210	–	–
Mg	%			1.4	0.014–10	0.94	0.12–0.12	0.46	<0.006–14.8
Mn	mg/kg			460	73–1300	900	17–10000	503	31–6025
Na	%			0.23	0.053–2.4	1.2	0.013–6.0	0.59	0.03–3.30
Ni	mg/kg	35	210	26	7.1–110	46	2.1–2500	18	<2–2690
P	mg/kg			430	120–1500	620	110–3900	720	62–7440
Pb	mg/kg	85	530	9.0	0.50–34	32	1.2–10000	22.6	5.32–970
Sr	mg/kg			43	1.5–170	140	21–1400	89.0	8.0–3120
V	mg/kg			63	12–160	89	<1.0–470	60.4	2.71–537
Zn	mg/kg	140	720	63	23–110	83	8.0–10000	52	<3–2900
ICP–MS									
B	mg/kg			40	0.005–230	–	–	–	–
Be	mg/kg			3.4	0.51–18	2.0	<1.0–8.0	<2.0	<2.0–18.4
Bi	mg/kg			1.1	0.42–4.8	–	–	–	–
Cd	mg/kg	0.8	12	0.62	0.21–2.3	0.30	0.01–110	0.145	<0.01–14.1
Ce	mg/kg			25	0.69–87	56	1.0–180	48.2	2.45–267
Co	mg/kg	20	240	11	3.2–29	17	0.50–150	7.78	<3.0–249
Cs	mg/kg			2.0	0.27–16	–	–	3.71	<0.5–69.1
Dy	mg/kg			2.3	0.064–6.3	–	–	3.42	0.18–44.9
Er	mg/kg			1.2	0.034–3.3	–	–	1.98	0.12–26.0
Eu	mg/kg			0.74	0.024–2.0	–	–	0.77	0.05–6.99
Ga	mg/kg			18	2.6–53	–	–	13.5	0.54–34.3
Gd	mg/kg			3.4	0.088–9.6	–	–	3.85	0.20–36.0
Ge	mg/kg			0.65	0.005–4.9	–	–	–	–
Hf	mg/kg			1.5	0.084–4.8	1.0	<0.10–6.6	5.55	<0.2–21.2
Hg	µg/kg			54	5.0–210	–	–	0.037	0.005–1.35
Ho	mg/kg			0.45	0.013–1.2	–	–	0.68	0.03–9.16
In	µg/kg			52	5.0–140	–	–	50	<10–250
La	mg/kg			11	0.11–37	25	0.60–88	23.5	1.10–143
Lu	mg/kg			0.20	0.005–0.47	–	–	0.30	<0.02–3.21
Mo	mg/kg	10	200	0.98	0.38–4.8	0.90	<0.10–51	0.62	<0.1–21.3
Nb	mg/kg			15	3.5–47	11	0.30–2000	9.68	0.45–134
Nd	mg/kg			12	0.20–37	–	–	20.8	1.14–132
Pd	mg/kg			0.94	0.050–5.5	–	–	–	–
Pr	mg/kg			3.1	0.050–9.6	–	–	5.6	0.29–31.6
Pt	mg/kg			0.54	0.18–1.1	–	–	–	–
Rb	mg/kg			67	15–220	86	0.70–390	–	–
Sb	mg/kg			0.63	0.17–2.0	0.80	<0.10–630	0.60	0.02–31.1
Sc	mg/kg			15	2.4–700	12	<1.0–39	8.21	<0.5–54.1
Sm	mg/kg			2.9	0.050–7.6	–	–	3.96	0.23–30.0
Sn	mg/kg			2.5	0.69–6.4	2.6	<0.10–680	3.00	<2.0–106
Ta	mg/kg			0.85	0.15–2.8	0.70	<0.10–30	0.68	<0.05–6.78
Tb	mg/kg			0.45	0.012–1.3	–	–	0.60	0.03–7.01
Ti	%			0.54	0.080–1.9	0.34	0.004–1.2	0.34	0.0126–3.27
Tl	mg/kg			0.46	0.050–1.6	0.70	<0.50–16	0.66	0.05–24
Tm	mg/kg			0.17	0.005–0.43	–	–	0.30	0.05–4.03
W	mg/kg			1.5	0.25–4.9	1.3	0.20–18	<5.0	<5.0–14
Y	mg/kg			9.3	0.11–33	18	0.30–110	21	<3.0–267
Yb	mg/kg			1.2	0.027–2.9	–	–	1.99	0.09–25
Zr	mg/kg			76	4.1–210	35	0.80–210	231	5.0–1060

Md – median; Min – minimum; Max – maximum

It is important to note that the element contents found in soil samples of the Poreče region (Table 3) are mainly below the target values given in The New Dutchlist, https://www.esdat.net/environmental%20standards/dutch/annexs_i2000dutch%20environmental%20standards.pdf), while in some small parts of the region some of the elements exceeded the target values (Ba, Co, Cr, Cu, and Ni) which is due to the lithogenic origin of these elements in soils from the Pelagonian massif as one of the six tectonic units in the country (Stafilov & Šajn, 2016, 2019).

To determine whether there is a significant difference in the distribution of elements in the surface and bottom soil samples, comparative statistics with a certain loading coefficient were performed by three methods [*t*–test, F–ratio and R(T/B)] (Table 4). The F–ratio, *t*–test, and R(T/B) show that there is no significant difference in the distribution of elements between the topsoil and bottom soil samples. Thus, the ratio of the content of the elements in the topsoil (T) and bottom soil (B) [R(T/B)] indicates that the difference between the distribution of the elements in the topsoil and bottom samples is insignificant (mostly close to 1) with the highest value of 1.17 for Y, which shows the absence of noticeable influence of eventual anthropogenic activities.

Table 4

Concentration ratios (FO) of the average contents (Box–Cox transformed) in topsoil vs. subsoil

Element	Unit	Topsoil	Subsoil	FO (T/B)	*t* (test)	Sign	F (ratio)	Sign	R (T/B)	Sign
ICP–AES										
Ag	mg/kg	0.77	0.80	0.97	–0.27	NS	0.07	NS	0.03	NS
Al	%	1.9	1.8	1.04	0.23	NS	0.05	NS	0.48	*
Ba	mg/kg	140	140	1.01	0.04	NS	0.00	NS	0.54	*
Ca	%	3	2.8	1.07	0.20	NS	0.04	NS	0.93	*
Cr	mg/kg	43	43	0.98	–0.13	NS	0.02	NS	0.93	*
Cu	mg/kg	20	19	1.01	0..10	NS	0.01	NS	0..78	*
Fe	%	2.2	2.3	0.96	–0.31	NS	0.09	NS	0.9	*
K	%	0.9	0.92	0.97	–0.20	NS	0.04	NS	0.96	*
Li	mg/kg	15	16	0.93	–0.39	NS	0.15	NS	0.88	*
Mg	%	1.6	1.6	1.03	0.10	NS	0.01	NS	0.83	*
Mn	mg/kg	400	400	0.99	–0.05	NS	0.00	NS	0.95	*
Na	%	0.25	0.24	1.02	0.08	NS	0.01	NS	0.94	*
Ni	mg/kg	25	26	0.94	–0.41	NS	0.17	NS	0.84	*
P	mg/kg	440	440	1.00	0.02	NS	0.00	NS	0.95	*
Pb	mg/kg	6.8	8.5	0.81	–0.75	NS	0.56	NS	0.2	NS
Sr	mg/kg	41	39	1.06	0.29	NS	0.08	NS	0.8	*
V	mg/kg	57	60	0.95	–0.38	NS	0.14	NS	0.96	*
Zn	mg/kg	56	61	0.92	–0.80	NS	0.65	NS	0.69	*
ICP–MS										
B	mg/kg	40	41	0.97	–0.10	NS	0.01	NS	0.4	*
Be	mg/kg	3.5	3.5	1.01	0.05	NS	0.00	NS	0.74	*
Bi	mg/kg	1.1	1.3	0.88	–0.89	NS	0.78	NS	0.1	NS
Cd	mg/kg	0.58	0.56	1.04	0.31	NS	0.10	NS	0.57	*
Ce	mg/kg	22	19	1.16	0.67	NS	0.44	NS	0.37	*
Co	mg/kg	11	11	0.98	–0.21	NS	0.04	NS	0.69	*
Cs	mg/kg	2.2	2.0	1.13	0.67	NS	0.45	NS	0.57	*
Dy	mg/kg	1.8	1.6	1.15	0.62	NS	0.39	NS	0.36	*
Er	mg/kg	0.95	0.81	1.16	0.68	NS	0.46	NS	0.38	*
Eu	mg/kg	0.57	0.51	1.13	0.58	NS	0.33	NS	0.36	*
Ga	mg/kg	18	18	0.99	–0.07	NS	0.00	NS	0.77	*
Gd	mg/kg	2.6	2.3	1.13	0.55	NS	0.30	NS	0.34	*
Ge	mg/kg	0.8	0.98	0.82	–0.89	NS	0.80	NS	0.57	*
Hf	mg/kg	1.4	1.4	0.98	–0.13	NS	0.02	NS	0.73	*
Hg	µg/kg	51	51	1.00	–0.01	NS	0.00	NS	0.59	*
Ho	mg/kg	0.34	0.30	1.16	0.65	NS	0.43	NS	0.38	*
In	µg/kg	49	51	0.97	–0.19	NS	0.04	NS	0.63	*
La	mg/kg	9.4	8.2	1.15	0.58	NS	0.34	NS	0.36	*

Element	Unit	Topsoil	Subsoil	FO (T/B)	*t* (test)	Sign	F (ratio)	Sign	R (T/B)	Sign
Lu	mg/kg	0.15	0.14	1.12	0.57	NS	0.33	NS	0.31	*
Mo	mg/kg	1.1	1.0	1.05	0.36	NS	0.13	NS	0.73	*
Nb	mg/kg	15	15	1.00	–0.02	NS	0.00	NS	0.79	*
Nd	mg/kg	10	9.0	1.14	0.59	NS	0.34	NS	0.34	*
Pd	mg/kg	0.92	1.2	0.80	–0.98	NS	0.96	NS	0.27	NS
Pr	mg/kg	2.6	2.2	1.14	0.59	NS	0.34	NS	0.34	*
Pt	mg/kg	0.58	0.55	1.05	0.64	NS	0.41	NS	0.36	*
Rb	mg/kg	59	56	1.06	0.40	NS	0.16	NS	0.67	*
Sb	mg/kg	0.59	0.58	1.02	0.11	NS	0.01	NS	0.78	*
Sc	mg/kg	16	21	0.76	–1.48	NS	2.19	NS	0.58	*
Sm	mg/kg	2.1	1.8	1.13	0.55	NS	0.30	NS	0.33	*
Sn	mg/kg	2.4	2.3	1.02	0.13	NS	0.02	NS	0.76	*
Ta	mg/kg	0.9	0.91	0.99	–0.04	NS	0.00	NS	0.8	*
Tb	mg/kg	0.35	0.30	1.14	0.60	NS	0.35	NS	0.34	*
Ti	%	0.46	0.45	1.02	0.15	NS	0.02	NS	0.87	*
Tl	mg/kg	0.44	0.43	1.01	0.05	NS	0.00	NS	0.82	*
Tm	mg/kg	0.14	0.12	1.16	0.66	NS	0.44	NS	0.36	*
W	mg/kg	1.3	1.4	0.97	–0.18	NS	0.03	NS	0.86	*
Y	mg/kg	7.7	6.6	1.17	0.62	NS	0.38	NS	0.38	*
Yb	mg/kg	0.9	0.79	1.14	0.63	NS	0.40	NS	0.35	*
Zr	mg/kg	67	70	0.96	–0.25	NS	0.06	NS	0.72	*

FO (T/B) – enrichment factor ratio of the content in topsoil and subsoil; Sign – significance, NS – nonsignificant difference;
* – significant difference

The factor analyses were performed for the major elements (analyzed by ICP–AES) including 18 elements (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, Zn) after preparation of the correlation matrix of these elements (Tables 5 and 6). Five elements (Ag, Ba, Na, P, and Pb) were eliminated from further analysis because they had low shares of communality. The total communality of the factors was 81.8%. Three geogenic factor associations (Factors) were identified: Factor 1 (F1) which includes Cu, Ni, Cr, V, Zn, Fe, and Mn, Factor 2 (F2) with Sr, Ca, and Mg, and Factor 3 (F3) including Li, K, Al, and Ba.

Table 5

Matrix of correlation coefficients of the elements determined by ICP–AES

Element	Ag	Al	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	Sr	V	Zn
Ag	1.00																	
Al	0.08	1.00																
Ba	–0.09	0.52	1.00															
Ca	0.32	0.10	–0.32	1.00														
Cr	–0.12	0.45	0.44	–0.53	1.00													
Cu	–0.03	0.28	0.33	–0.35	**0.74**	1.00												
Fe	–0.11	0.55	0.58	–0.61	**0.87**	0.66	1.00											
K	–0.24	0.33	0.58	**–0.79**	0.65	0.44	0.73	1.00										
Li	–0.06	0.38	0.59	–0.40	0.60	0.50	0.48	0.60	1.00									
Mg	0.31	0.12	–0.18	**0.87**	–0.54	–0.37	–0.56	**–0.75**	–0.27	1.00								
Mn	–0.06	0.54	0.52	–0.43	**0.75**	0.64	**0.81**	0.66	0.42	–0.55	1.00							
Na	–0.17	0.49	0.51	–0.54	0.60	0.38	**0.79**	**0.71**	0.18	–0.52	**0.72**	1.00						
Ni	–0.05	0.37	0.41	–0.41	**0.85**	**0.84**	**0.71**	0.53	0.62	–0.46	**0.71**	0.39	1.00					
P	0.18	0.44	0.37	0.06	0.39	0.42	0.45	0.19	0.25	0.03	0.42	0.31	0.42	1.00				
Pb	0.18	–0.01	0.00	0.22	0.04	0.18	–0.08	–0.11	0.16	0.10	0.00	–0.22	0.26	0.28	1.00			
Sr	0.27	0.47	0.09	**0.72**	–0.05	–0.02	–0.06	–0.35	–0.17	0.62	0.07	0.03	–0.08	0.40	0.17	1.00		
V	–0.14	0.39	0.46	–0.57	**0.92**	**0.72**	**0.90**	0.63	0.51	–0.55	**0.71**	0.61	**0.79**	0.42	0.03	–0.11	1.00	
Zn	–0.08	0.40	0.49	–0.45	**0.72**	**0.78**	**0.72**	0.61	0.58	–0.45	0.66	0.52	0.79	0.55	0.16	–0.05	0.69	1.00

*Bolded values over 0,7 show a strong association

Multivariate cluster analysis was also applied to determine the significance of the factor analysis and the stability of the new synthetic variables, that is, associations of elements. The dendrogram of the distances among the individual elements is presented in Figure 4. All of the obtained clusters correspond to the four obtained factors. The first cluster corresponds to Factor 3 including Al, Ba, K, and Li, the second cluster correspond to Factor 1 including Cr, V, Fe, Mn, Cu, Ni and Zn, and the third cluster correspond to Factor 2 additionally includes Fe and V which belongs to the Factor 1 including Ca, Mg and Sr.

T a b l e 6

Matrix of dominant rotated factor loadings ICP–AES (n = 44)

Елемент	F1	F2	F3	Comm
Cu	**0.91**	–0.06	0.07	83.0
Ni	**0.90**	–0.12	0.21	86.3
Cr	**0.86**	–0.19	0.34	88.8
V	**0.82**	–0.24	0.32	83.8
Zn	**0.78**	–0.15	0.33	74.3
Fe	**0.73**	–0.23	0.51	85.7
Mn	**0.71**	–0.12	0.47	73.4
Sr	0.06	**0.90**	0.15	84.0
Ca	–0.31	**0.89**	–0.25	94.9
Mg	–0.41	**0.83**	–0.10	86.3
Li	0.40	–0.20	**0.60**	55.3
K	0.39	–0.59	**0.62**	88.8
Al	0.33	0.44	**0.70**	80.3
Ba	0.20	–0.05	**0.87**	79.7
Prp.Totl	38.7	22.0	21.1	81.8
EigenVal	7.91	2.45	1.09	
Expl.Var	5.42	3.08	2.95	

F1, F2, F3, F4, and F5 – factor loadings of Factors 1, 2, 3, 4, and 5; Comm – communality (%); Prp.Totl – total amount of the explained system variance; Expl.Var – particular component variance; EigenVal – Eingene value

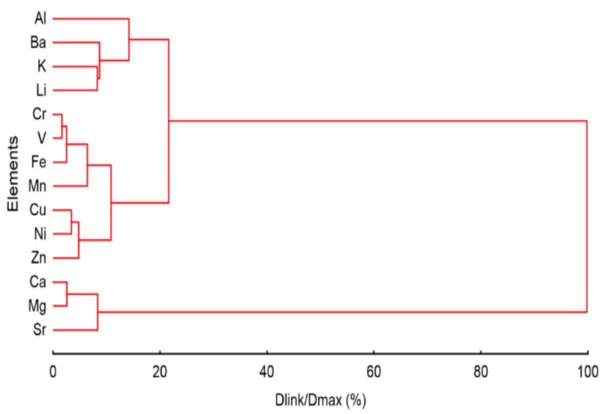

Fig. 4. Dendrogram from cluster analysis of the elements analyzed by ICP–AES analytical method

Factor 1 (Cu, Cr, Fe, Mn, Ni, V, and Zn) is a lithogenic association of elements with high values of factor loading (F > 0.78). The spatial distribution of factor score values from F1 is given in Figure 5. The origin of the elements in this spatial distribution is related to the geological composition of the soil in this region and the highest content of these elements occurs in the area with Paleozoic shales and carbonates as and neogenic clastic sediments. Figure 5 shows also the spatial distribution maps for each element of this geochemical association.

The content of copper in surface soils ranges from 6.6 mg/kg to 74 mg/kg with a median value of 20 mg/kg, while in subsoil the content ranges from 6.0 to 72 mg/kg with a median also of 20 mg/kg. The spatial distribution of copper (Figure 5) shows that the highest content of this element is in the soils of the northern part of Poreče where Paleozoic carbonates are present.

The value for the chromium content ranges from 8.4 to 180 mg/kg with a median of 43 or 47 for topsoil and subsoil samples respectively. From the map of spatial distribution (Figure 5), it can be noticed that it is mostly present in the soils around the village of Bojane, in the northern part of the study area where the Paleozoic carbonates are dominant. Chromium content is also higher in the western and southern parts where Paleozoic shales predominate.

The content of iron ranges from 0.35 to 5.6% with a median of 2.3% and 2.4% in the topsoil and subsoil respectively. Its highest contents are found in the western part of the study area where the Paleozoic carbonates and shales dominate (Fig. 5).

The value for the manganese content in the examined area ranges from 66 to 1100 mg/kg. Higher content of Mn is found mostly in soils from the northern part of the study area where Paleozoic carbonates and shales are present, as well as Quaternary alluvial sediments (Figure 5).

The value for the content of Ni ranges from 7.1 to 110 mg/kg in the topsoil and from 5 to 700 mg/kg in the subsoil, with the median value for both layers of 26 mg/kg. The highest content of nickel is found in the soils in the vicinity of the village of Brest, where Paleozoic shales are dominant (Figure 5). There are also higher nickel contents in the soils of the northern part around the villages of Bojane and Matka where the Paleozoic carbonates predominate.

The vanadium content ranges from 12 mg/kg to 160 mg/kg in topsoil and from 10 mg/kg to 150 mg/kg in the subsoil samples, while the medians are 63 mg/kg and 67 mg/kg, respectively. Vanadium is mostly found in the soils of the southern part around the town of Makedonski Brod where Proterozoic carbonates are dominant, in the northern part where Paleozoic shales and Paleozoic carbonates are most prevalent (Figure 5).

The value for the zinc content ranges from 23 to 110 mg/kg with a median of 63 mg/kg in the topsoil layer and from 25 to 180 mg/kg with a median of 69 mg/kg in the subsoil layer. The highest presence of zinc is observed in the soils from the areas where Paleozoic shales and carbonates dominate (Figure 5).

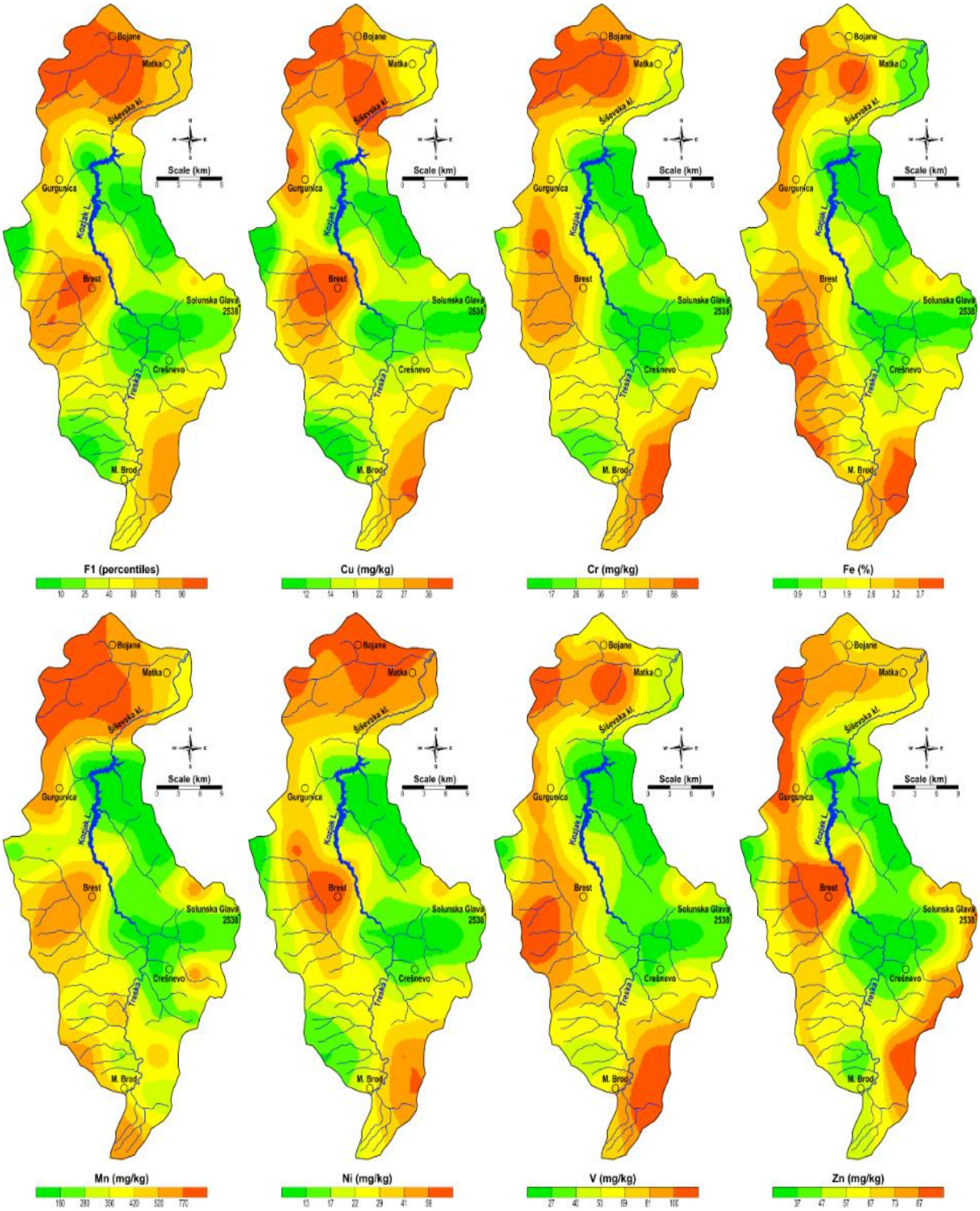

Fig. 5. Spatial distribute of factor scores of Factor 1 and the elements from F1 (Cu, Cr, Fe, Mn, Ni, V and Zn) ICP–AES analytical method

Factor 2 (Ca, Mg and Sr) is shown by the spatial distribution in Figure 6. This factor is a characteristic lithogenic association for the study area associated with the predominance of carbonate rocks. Therefore, higher contents of the elements included in this factor are observed in soils from areas dominated by Paleozoic and Proterozoic carbonates. Figure 6 shows the maps of the spatial distribution of the factor values of F2 and the spatial distribution of the contents of the elements of Factor 2. Thus, calcium and magnesium are most common in the soil in areas with dominant Proterozoic carbonates. These areas are located in the eastern and central part of the study area along the entire course of the Treska river and around the artificial Lake Kozjak (Figure 6). Values for the contents of Ca range from 0.024 to 18% with a median of 4.3% and 3.7%, and for magnesium from 0.014 to10% with a median of 1.4% and 1.5% respectively, respectively for topsoil and subsoil. The spatial distribution of strontium is similar to those of Ca and Mg, with the difference that its highest content is observed in the soil from the northern part of the study area where the Paleozoic carbonates are dominant (Figure 6). Its content ranges from 1.5 mg/kg to 230 mg/kg with a median of 43 mg/kg.

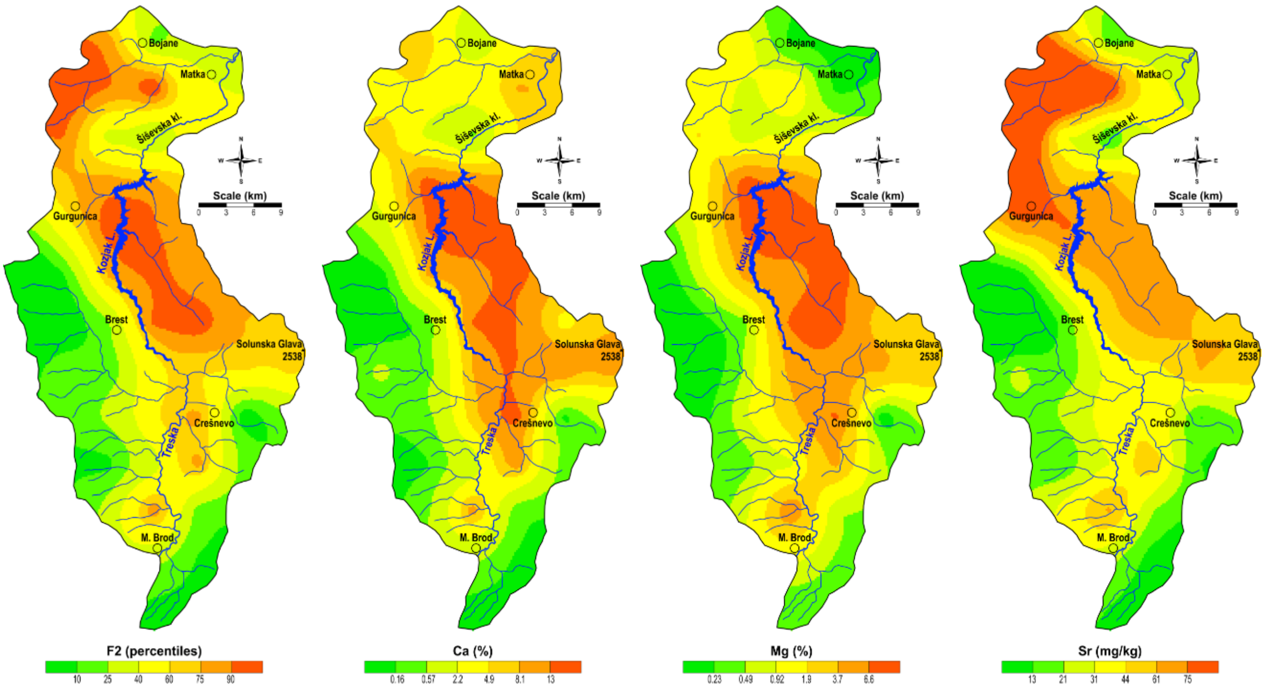

Fig. 6. Spatial distribution of Factor 2 and the elements from F2 (Ca, Mg and Sr) – ICP–AES analytical method

The map of the spatial distribution of factor scores of Factor 3 and spatial distribution of the content of the elements from this factor (Al, Ba, K, and Li) are presented in Figure 7. The content of these elements is higher in soil from the western and southwestern parts of the study area, where Paleozoic shales and Paleozoic carbonates are predominated.

The values for the content of aluminum range from 0.22% to 6.0% with a median value of 2.0%, in the topsoil and from 0.33% to 6.2%, and a median of 1.8% in subsoil samples.

The content of barium in the topsoil ranges from 1.8 to 430 mg/kg with a median of 150 mg/kg, while in the subsoil its content ranges from 31 to 330 mg/kg with a median of 120 mg/kg. Its highest content was observed in the soil collected in the village of Gurgurnica, in the western part of the area where Paleozoic carbonates are present/dominant, and in the southern part of the study area where Paleozoic shales and Paleozoic rocks prevail (Figure 7).

Values for potassium content range from 0.16 to 2.5% in topsoil and 0.11–2.3% in the subsoil. The median is 1.0% in both soil layers. According to the distribution map (Figure 7), its highest presence was found in the soil from the western part of the study area below the mountain of Čeloica, where the Paleozoic carbonates and shales are most present.

Values for the lithium content range from 0.63 to 63 mg/kg with a median of 14 mg/kg and from 0.26 to 49 mg/kg and a median of 15 mg/kg in the subsoil samples. It was found that its highest content in the soils is present around the village of Brest, in the western part with Paleozoic carbonates, and in the southeastern part of Makedonski Brod, where Proterozoic carbonates are predominant (Figure 7).

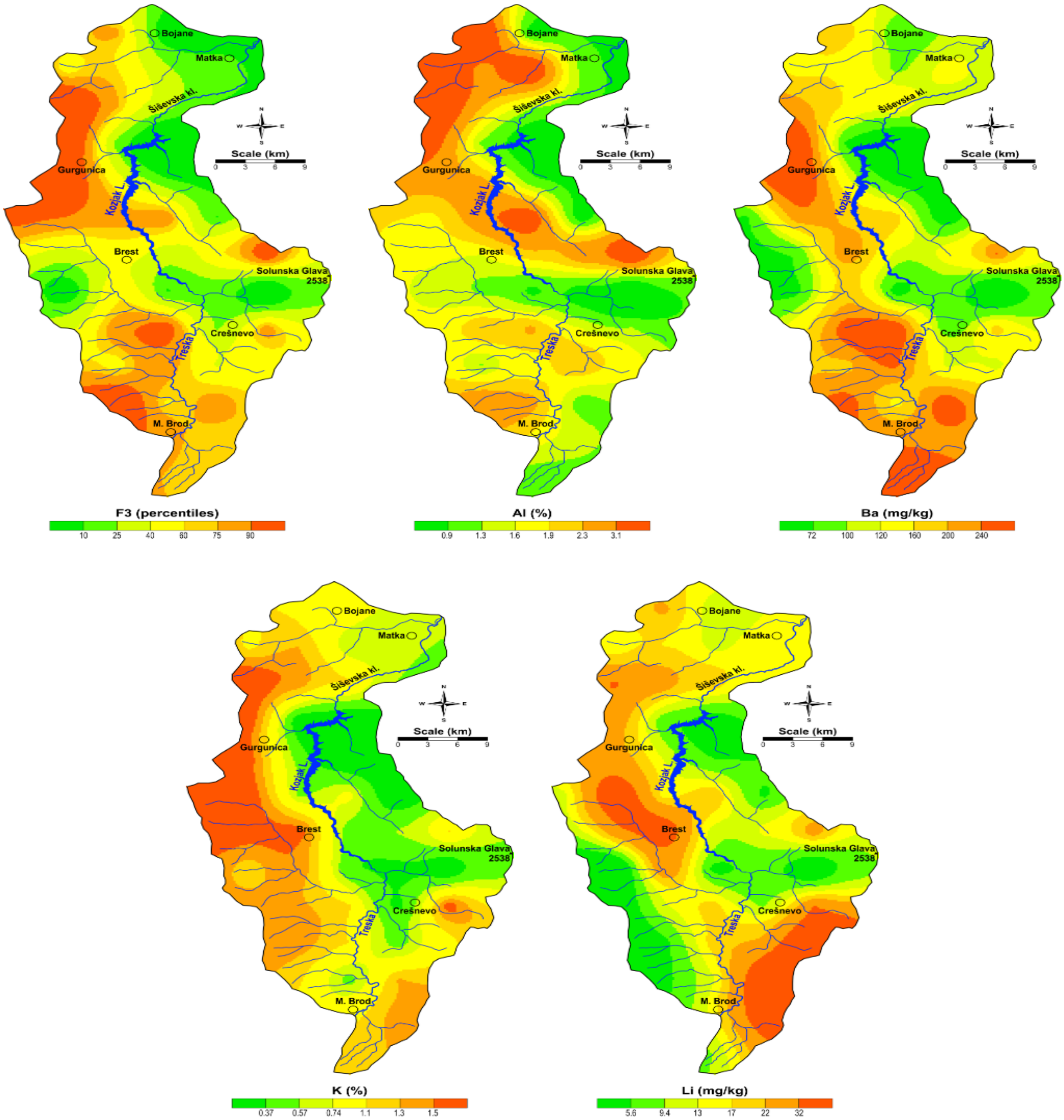

Fig. 7. Spatial distribution of factor scores of Factor 3 and the elements from F3 (Al, Ba, K, Li) – ICP–AES analytical method

In addition to these major elements, by the application of ICP–MS, additional 39 elements were analyzed (B, Be, Bi, Cd, Ce, Co, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, La, Lu, Mo, Nb, Nd, Pd, Pr, Pt, Rb, Sb, Sc, Sm, Sn, Ta, Tb, Ti, Tl, Tm, W, Y, Yb, and Zr). Table 7 shows the matrix of correlation coefficients for these elements. It can be seen a very good correlation between Ga, Hf, In, Nb, Sn, Ta, Ti, Tl, W and Zr, Co and Ti, Rb and Cs, and between Mo, Nb, Sn, Tl and W (correlation coefficient over 0.70). Their enrichment is mostly connected with the area where Paleozoic shales are dominant (Figure 8).

Along with these elements, 14 rare earth elements were analyzed (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, and Yb). The results given in Table 4 show an excellent correlation between all these elements (correlation coefficient above 0.9). Figure 8, shows the spatial distribution of rare earth elements. The spatial distribution of these elements shows that they are most present in the soils of the central part of the study area, around Lake Kozjak, where Proterozoic carbonates dominate, then in the northwestern part where Paleozoic carbonates are dominant,

T a b l e 7

Matrix of correlation coefficients of the elements determined by ICP–AES

Ele–ment	B	Be	Bi	Cd	Co	Cs	Ga	Ge	Hf	Hg	In	Mo	Nb	Pd	Pt	Rb	Sb	Sc	Sn	Ta	Ti	Tl	W	Y	Zr	RE
B	1.00																									
Be	0.34	1.00																								
Bi	0.55	0.40	1.00																							
Cd	0.29	0.34	0.28	1.00																						
Co	0.38	0.62	0.45	0.31	1.00																					
Cs	–0.10	0.53	0.02	0.24	0.14	1.00																				
Ga	0.21	**0.89**	0.25	0.14	0.67	0.48	1.00																			
Ge	0.42	0.63	0.45	0.29	0.63	–0.04	0.60	1.00																		
Hf	0.15	**0.79**	0.11	0.39	0.45	0.51	**0.75**	0.52	1.00																	
Hg	0.06	0.45	0.12	0.26	0.34	0.17	0.46	0.42	0.49	1.00																
In	0.16	**0.82**	0.31	0.25	0.62	0.42	**0.88**	0.50	0.68	0.49	1.00															
Mo	0.13	0.65	0.23	0.22	0.36	0.36	0.62	0.35	0.53	0.57	0.67	1.00														
Nb	0.14	**0.87**	0.28	0.37	0.54	0.54	**0.82**	0.53	**0.79**	0.58	**0.84**	**0.70**	1.00													
Pd	–0.13	0.41	–0.04	0.35	0.27	0.52	0.38	0.21	0.65	0.22	0.36	0.22	0.48	1.00												
Pt	0.06	0.56	0.22	0.40	0.43	0.42	0.53	0.61	0.57	0.51	0.50	0.44	0.64	0.45	1.00											
Rb	–0.05	**0.76**	0.12	0.19	0.32	**0.77**	**0.75**	0.30	**0.72**	0.40	0.69	0.61	**0.80**	0.51	0.57	1.00										
Sb	0.30	0.63	0.25	0.38	0.39	0.46	0.57	0.28	0.58	0.45	0.57	0.69	0.63	0.31	0.24	0.56	1.00									
Sc	0.19	0.59	0.25	0.04	0.60	0.02	0.67	0.69	0.52	0.34	0.53	0.31	0.53	0.20	0.42	0.43	0.28	1.00								
Sn	0.29	**0.80**	0.28	0.29	0.54	0.30	**0.83**	0.67	**0.72**	0.62	**0.78**	**0.72**	**0.86**	0.30	0.59	0.68	0.63	0.65	1.00							
Ta	0.09	**0.85**	0.23	0.27	0.52	0.48	**0.82**	0.62	**0.79**	0.60	**0.79**	0.66	**0.96**	0.48	0.69	**0.79**	0.57	0.65	**0.89**	1.00						
Ti	0.28	**0.77**	0.36	0.11	**0.83**	0.25	**0.85**	0.56	0.53	0.39	**0.79**	0.50	**0.72**	0.27	0.39	0.53	0.49	0.65	0.69	**0.70**	1.00					
Tl	0.11	**0.78**	0.18	0.26	0.32	0.58	**0.72**	0.41	**0.78**	0.53	0.66	**0.71**	**0.83**	0.42	0.48	**0.80**	**0.73**	0.48	**0.80**	**0.84**	0.49	1.00				
W	0.14	**0.82**	0.22	0.27	0.46	0.50	**0.81**	0.56	**0.77**	0.64	**0.77**	**0.80**	**0.89**	0.37	0.59	**0.78**	**0.71**	0.55	0.88	**0.90**	0.60	**0.92**	1.00			
Y	–0.29	0.27	0.08	0.12	0.26	0.47	0.29	–0.19	0.20	–0.07	0.33	–0.03	0.26	0.45	0.06	0.36	0.12	0.02	–0.04	0.18	0.36	0.11	0.06	1.00		
Zr	0.22	**0.78**	0.15	0.46	0.43	0.53	**0.71**	0.44	**0.97**	0.42	0.67	0.53	**0.76**	0.63	0.49	0.67	0.62	0.40	0.66	**0.70**	0.50	**0.72**	**0.72**	0.23	1.00	
RE	–0.29	0.33	0.11	0.17	0.30	0.55	0.32	–0.13	0.28	–0.01	0.36	0.03	0.35	0.54	0.18	0.45	0.18	0.05	0.03	0.28	0.37	0.23	0.16	**0.98**	0.29	1.00

*Bolded values over 0,7 show a strong association

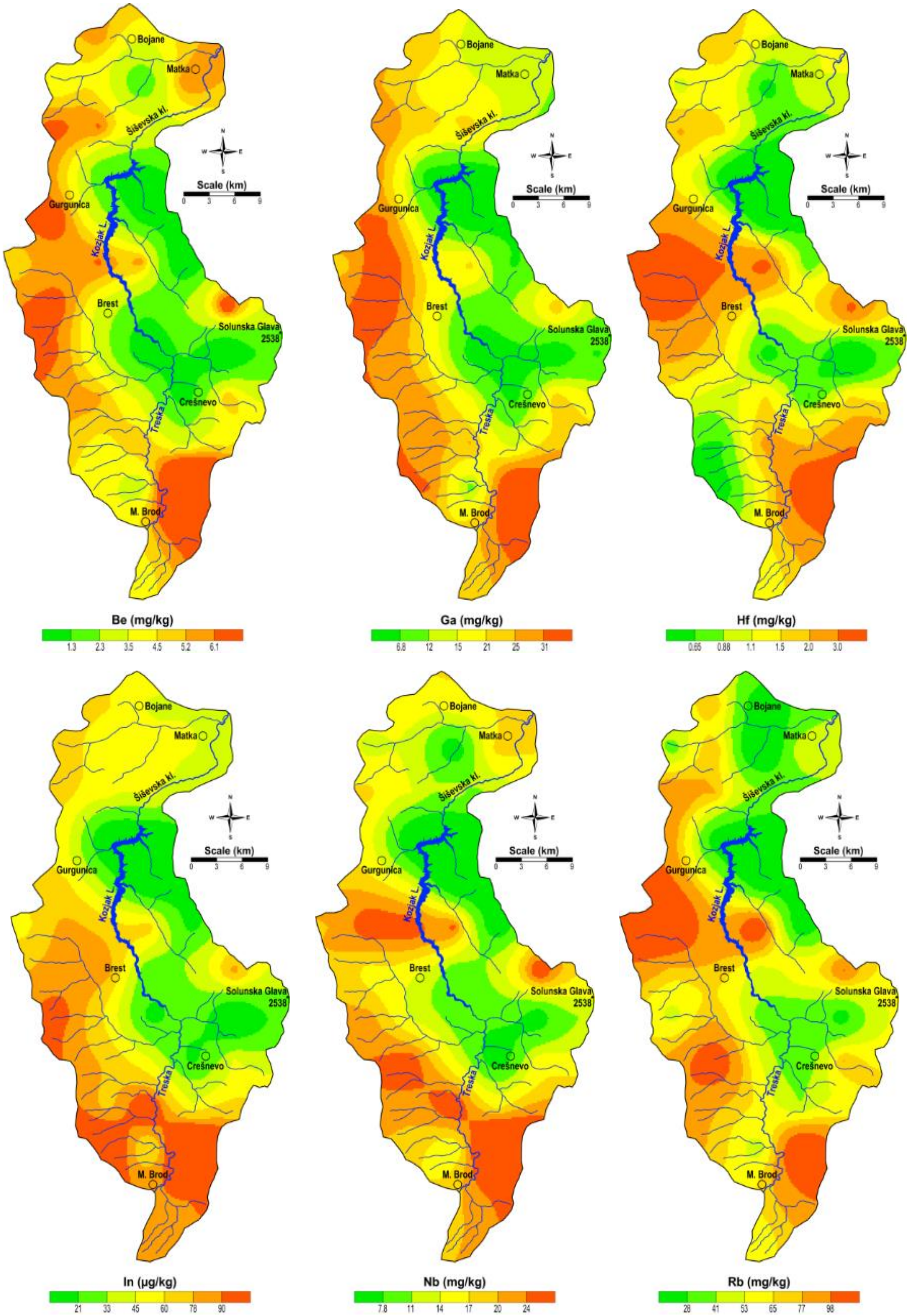
Bojane
Matka
Šiševska kl.
N
W
E
S
Scale (km)
0 3 6 9
Gurgunica
Kozjak L.
Brest
Solunska Glava
2538
Crešnevo
Treska
M. Brod
Be (mg/kg)
1.3 2.3 3.5 4.5 5.2 6.1
Ga (mg/kg)
6.8 12 15 21 25 31
Hf (mg/kg)
0.65 0.88 1.1 1.5 2.0 3.0
In (µg/kg)
21 33 45 60 78 90
Nb (mg/kg)
7.8 11 14 17 20 24
Rb (mg/kg)
28 41 53 65 77 98

Fig. 8a

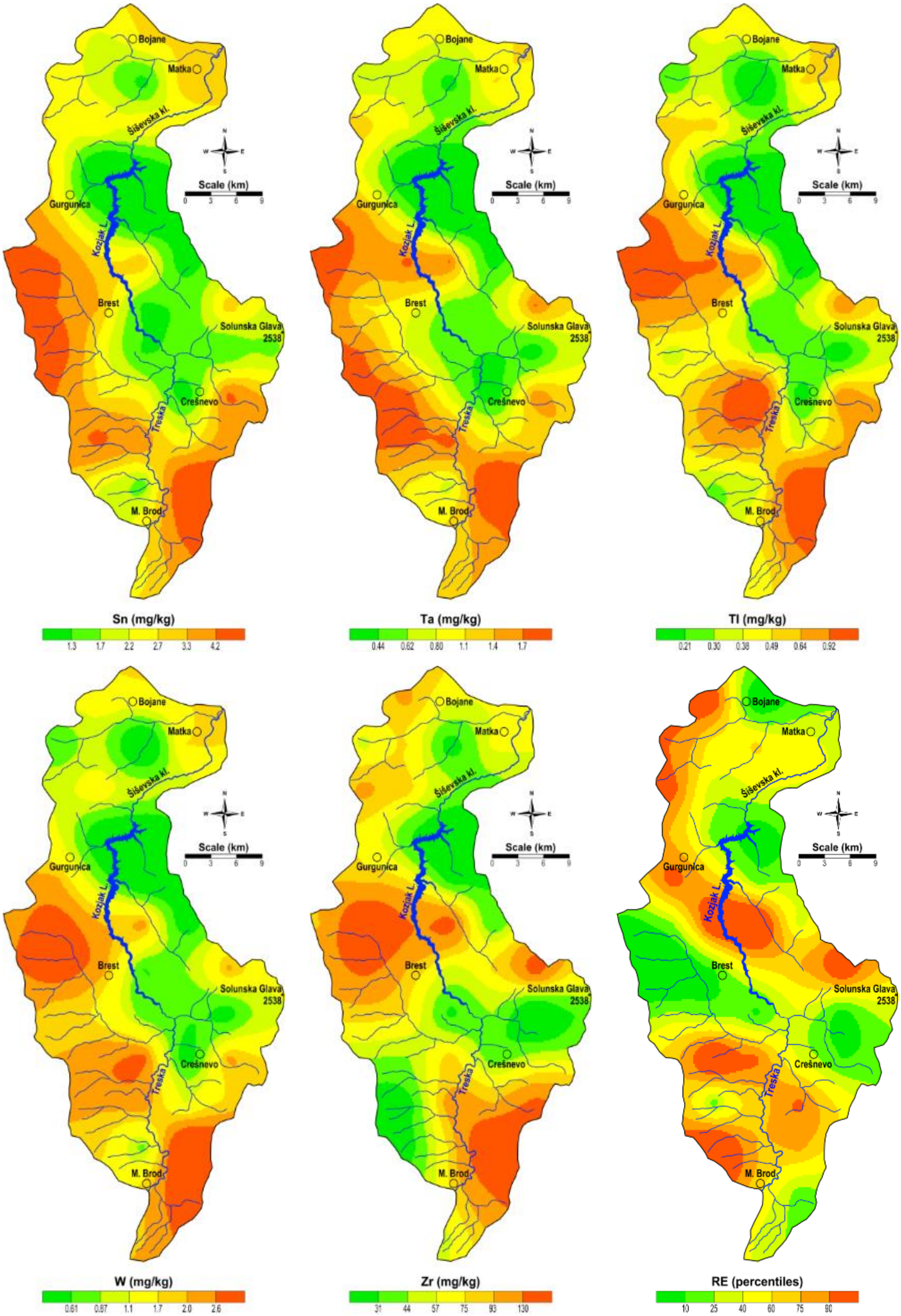

Fig. 8b

Fig. 8. Spatial distribution of trace elements with the highest correlation and spatial distribution of rare earth elements

CONCLUSION

Examination of the distribution of 57 chemical elements in soil samples from the Poreče region, North Macedonia, was performed. Soil samples collected from 44 locations were analyzed by using inductively coupled plasma – atomic emission spectrometry (ICP–AES) for major elements and inductively coupled plasma – mass spectrometry (ICP–MS) for trace elements. Factor analysis of the major elements gives three geogenic factors [F1 (Cu–Ni–Cr–V–Zn–Fe–Mn), F2 (Sr–Ca–Mg), F3 (Li–K–N–Ba)] and their spatial distribution showed that the distribution of the elements occurs as a result of lithogenic origin. The deposits of the elements from the lithogenic factors are formed as a result of the atmospheric dispersal of the represented geological structures in this region which are dominated by the corresponding elements (shales, carbonates, sandstones, and Neogene sediments). By the application of ICP–MS 39 elements were analyzed (B, Be, Bi, Cd, Ce, Co, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, La, Lu, Mo, Nb, Nd, Pd, Pr, Pt, Rb, Sb, Sc, Sm, Sn, Ta, Tb, Ti, Tl, Tm, W, Y, Yb, and Zr). The matrix of correlation coefficients shows a very good correlation between Ga, Hf, In, Nb, Sn, Ta, Ti, Tl, W, and Zr, which shows that their enrichment is connected with the area where Paleozoic shales are dominant. Rare earth elements were analyzed (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, and Yb) showing an excellent correlation between all elements. The spatial distribution of RREs shows that they are most present in the soils of the central part of the study area where Proterozoic carbonates and shales are dominant.

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Р е з и м е

ПРИМЕНА НА МУЛТИВАРИЈАНТНИ СТАТИСТИЧКИ МЕТОДИ ВО ОПРЕДЕЛУВАЊЕТО НА ПРОСТОРНАТА РАСПРЕДЕЛБА НА ХЕМИСКИ ЕЛЕМЕНТИ ВО ПОЧВАТА (ОБЛАСТА ПОРЕЧЕ, СЕВЕРНА МАКЕДОНИЈА)

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Клучни зборови: почва; потенцијално токсични елементи; дистрибуција; загадување; регион Порече; Северна Македонија

Целта на ова истражување беше да се утврди присуството на различни хемиски елементи во примероците од почвата во регионот на Порече, Република Северна Македонија. За таа цел беа собрани 88 примероци почва (44 примероци површинска почва, 0–5 cm, и 44 примероци длабочинска, 20–30 cm) и беа анализирани 57 елементи, од кои 18 елементи (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V и Zn) беа анализирани со ICP–AES, а дополнителни 39 елементи (B, Be, Bi, Cd, Ce, Co, Cs , Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, La, Lu, Mo, Nb, Nd, Pd, Pr, Pt, Rb, Sb, Sc, Sm, Sn, Ta, Tb , Ti, Tl, Tm, W, Y, Yb и Zr) беа анализирани со ICP–MS. Добиените резултати беа статистички обработени за да се утврдат можни подрачја со загадување на почвата со тешки метали. Од резултатите на анализираните елементи со ICP–AES, беа утврдени 3 асоцијативни литогени фактори [F1 (Cu–Ni–Cr–V–Zn–Fe–Mn), F2 (Sr–Ca–Mg), F3 (Li–K–Al–Ba)]. Распределбата на елементите кои се вклучени во литогените фактори настанува како резултат на геолошките структури присутни во истражуваното подрачје (шкрилци, карбонати, песочници и неогени седименти).