Use of multivariate statistical methods to determine spatial distributions of chemical elements in soils (Mariovo region, North Macedonia)

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Abstract. The main objective of this study is to present the distribution of different chemical elements in soil samples from the Mariovo region, North Macedonia. To determine the level of presence of chemical elements, soil samples were collected from a total of 33 locations in a 5×5 km area. From each location, two samples of soil were collected: topsoil (0–5 cm) and bottom soil (20–30 cm). The analyses of soil samples were used to assess the prevalence of the chemical elements and the presence of heavy metals in the studied area. The analysis was carried out, using two instrumental methods: atomic emission spectrometry with inductively coupled plasma (ICP-AES) for macro-elements, and mass spectrometry with inductively coupled plasma (ICP-MS) for trace elements. A factor analysis was applied to reveal the relationships between the investigated variables (chemical elements). From the obtained results, spatial distribution maps of factors for the separate groups were prepared, as well as distribution maps for the analyzed elements. It was found that the distributions of most elements follow the lithology of the examined area. Factor analysis revealed the relationships between the investigated variables and could provide dimensionality reduction based on them.

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INTRODUCTION

Potentially toxic elements (PTEs) are commonly found as contaminants in soil, water and food, and are carried in the air. In recent years, environmental pollution has often been associated with PTEs (Salminen *et al.*, 2005; Davidson *et al.*, 2006; Kabata-Pendias and Mukherjee, 2007; Reimann *et al.*, 2011; Salomons *et al.*, 2012; Wang *et al.*, 2015; Stafilov and Šajn, 2019). The pollution with PTEs of soil, water and air is an important part that should

never be overlooked. The main cause of emission are anthropogenic sources, especially mining and metallurgical activities (Peplow, 1999; Diawara *et al.*, 2006; Stafilov *et al.*, 2010a, b; Acton, 2013). For a very long time after the cessation of mining activities, 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).

On the basis of our previously obtained data from the whole territory of North Macedonia, soil pollu-

tions were found in the areas of mining, metallurgical and urban activities due to the emission of certain heavy metals (As, Cd, Cu, Mn, Ni, Sb, Zn) (Stafilev *et al.*, 2010a, b, 2013, 2018, 2019; Balabanova *et al.*, 2013; Serafimovska *et al.*, 2013; Bačeva *et al.*, 2014; Stafilev and Šajn, 2016, 2019). A need arose to determine the distributions of various chemical elements in the area of the Mariovo region, situated in the central-southern part of the country. For that purpose, soil samples were collected from the whole area of the Skopje region within a grid of 5×5 km, from a total of 33 locations. From each location, two samples of soil were collected: samples of topsoil (0–5 cm) and samples from a deeper layer, bottom soil (20–30 cm). The analyses were carried out using two instrumental methods: atomic emission spectrometry with inductively coupled plasma (ICP-AES) for macro-elements and mass spectro-

metry with inductively coupled plasma (ICP-MS) for the analysis of trace elements. A factor analysis was applied to analyze relations between a number of variables.

The obtained results for the content of the examined elements were statistically processed by multivariate factor analysis and cluster analysis and, based on them, spatial distribution maps were prepared for each of the factors.

MATERIAL AND METHODS

Study area

The Mariovo region is located in the central-southern part of North Macedonia and occupies the middle catchment area of the Crna River (Fig. 1). It is surrounded by vast mountain massifs: Nidže and

Fig. 1. Location of the studied area.

Kožuf from the south, the Selečka Mountain from the west, the Dren Mountain from the north and Kozjak with the branches of the Kožuf Mountain from the east. The borders of Mariovo mainly trace the ridges of the mentioned mountains and the region is located between 40°32'56" and 41°15'07" north latitude and 22°32'56" and 22°04'15" east longitude (Koteski, 2013). Within these borders, the Mariovo region covers an area of 1,038 km² and represents 4% of the total territory of the Republic of North Macedonia, with an average altitude of 1,090 m (Fig. 2). As shown in Fig. 2, the altitude around the catchments of the Crna River ranges from 400 m to 800 m; in the southern part, where the Nidže Mountain is located, the altitude reaches 2200 m; and in the east, where the Kožuf Mountain massif stretches, the altitude is from 1400 m to 1800 m. Most of the relief follows the Crna Riv-

er, which flows in a N-S direction. The Mariovo region has a diverse relief transitioning from high mountainous to hilly to high valley. There are three tectonic morphological units: high mountains and valleys; eruptive erosive areas; and the bottom of the Mariovo Valley, which is partially flat and intersected by watercourses (Koteski, 2013; Temovski, 2013).

According to meteorological data, Mariovo is characterized by three climatic zones (Lazarevski, 1993): modified Mediterranean climate (Crna River Valley and in a narrow belt to Tikveš) with maximum rainfall in May and November, and with a minimum in summer; the hilly and terraced part of this area has a moderate continental climate, similar to the climate in the Pelagonia valleys with maximum rainfall in November, minimum in May, and the driest months are July and August; and mountain climatic zone that occupies the area from the slopes of the mountain sides of the Nidže, Kožuf and Selečka mountains.

The Mariovo region includes various geological formations of different ages. A part of this region, together with a part of the Kozjak Mountain, is in the Vardar Zone, whereas the western areas are in the Pelagonian massif (Dumurdžanov *et al.*, 2003, 2004, 2013; Temovski, 2013; Stafilov and Šajn, 2016, Petrušev *et al.*, 2021). The southern and central parts of the region are composed of gneisses and felsic plutonites of Proterozoic age (Fig. 3). Limited occurrence of Proterozoic shales is also present. The northern part of the Mariovo region has also Proterozoic gneisses and plutonites, while in the north-eastern part Proterozoic carbonates are present. The eastern area of the region shows quite interesting geology, as it is a mixture of various geological formations. Proterozoic carbonates and gneisses are mostly present to the southeast, but Mesozoic mafic rocks and Neogene pyroclastites and volcanites also occur. In the central-eastern part, the interweaving of the following geological formations is characteristic: Neogene clastites, volcanites and pyroclastites, Paleozoic shales and Proterozoic carbonates. Proterozoic gneisses are most common along the Crna River, except for the northern part of its course, where there are Proterozoic carbonates (Fig. 3).

In terms of pedological structure, the Mariovo Valley has a heterogeneous composition that is influenced by climate, geological, biological and anthropogenic factors. The most common soil types are: ranker, regosol, cambisol, cambisol (limestone-dolomite), latosol and other (Koteski *et al.*, 2012; Filipovski *et al.*, 2015).

Fig. 2. The studied area according to the altitude.

Fig. 3. Geological map of the studied area.

Soil sampling and digestion

Samples of surface soils from the Skopje region, North Macedonia, were collected according to the European guidelines and also according to our experience (Salminen *et al.*, 2005; Stafilov *et al.*, 2010b, Stafilov and Šajn, 2019). The study area (1812 km²) was covered by a sampling grid of 5×5 km (Fig. 4). Altogether, 66 soil samples were collected from 33 locations. To distinguish possible anthropogenic pollution of the surface soil, samples from two layers 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 homogenized,

then 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 (HNO₃, HF, HClO₄ and HCl) according to the ISO Standard (ISO 14869–1:2001).

Instrumentation

All samples were analysed by ICP-AES (Varian, model 715-ES) for the elements with high contents (Balabanova *et al.*, 2010). Trace elements were analysed 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). 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 geologi-

Fig. 4. Sample locations.

cal samples: soil sample JSAC 0401 (The Japan Society for Analytical Chemistry), rock CRM samples from undersaturated igneous rock SARM 3 NIM-L Lujaurite (SA Bureau of Standards, Pretoria, S. Africa), and rock NCS DC71306 (GBW07114) (China National Analysis Centre). The values for Al, Ca, Fe, K, Mg, Na and Ti are given in per cent, values for Cd, I, and In in $\mu\text{g/kg}$, while the values for the content of the remaining elements are given in mg/kg .

Data processing

Data analysis and maps were done on a Statistica (ver. 13), QGIS (ver. 3.14) and Surfer (ver. 20) software. All field observations, analytical data and measurements were introduced into the data matrix. Parametric and non-parametric statistical methods were used for data analysis. Box-Cox transformation was used to acquire normal distributions.

Multivariate R-mode factor analysis was used to reveal associations of the chemical elements (Faccinelli *et al.*, 2001). 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). As a measure of similarity between variables, the product-moment correlation coefficient (r) was applied. For orthogonal rotation, the varimax method was used.

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 soil samples were collected according to the 5×5 km sampling network. Each sampling point describes the following 14 parameters: ID, location, soil layer, longitude (WGS84), latitude (WGS84), region, municipality, land use, geological unit, pedological unit, altitude (m), slope ($^\circ$), exposition ($^\circ$), average annual temperature ($^\circ\text{C}$) and average annual precipitation (mm). Basic data of sampling points are presented in Table 1.

As a result of the analysis of the soil samples, data were obtained on the content of a total of 58

elements, from which 16 elements present in higher content were analyzed by ICP-AES (Al, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) and 42 trace elements by ICP-MS (Ag, As, Ba, Be, Bi, Br, Cd, Ce, Co, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, I, 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 descriptive statistics for the content of the elements in surface and bottom soil samples are presented in Tables 2 and 3, respectively.

Basic descriptive statistics were used for the statistical processing of the values obtained from this study. From the results obtained by applying descriptive statistics, it can be noticed that no serious deviation of the examined elements was found. The obtained values are within the average range, from which it can be determined that the presence of the investigated elements in the soil samples reflects the lithology. There is no significant difference between the obtained values and the geological composition (Stafilov *et al.*, 2019, Stafilov and Šajn, 2019).

Most of the elements that were analyzed are within the limits of Dutch soil standards, but some elements exceed these values. The order of the distribution of contents of the major elements (Al, Ca, Fe, K, Mg, Na and Ti) were in the following ranges: 0.48–57.6% Al; 0.29–17% Ca; 0.18–4.8% Fe; 0.03–2.4% K; 0.17–8.8% Mg, 0.03–1.9% Na and 0.01–0.73% Ti for topsoil (0–5 cm) and 0.12–2.4% Al; 0.25–18% Ca; 0.029–5.0% Fe; 0.022–2.2 K; 0.15–7.4% Mg, 0.042–1.9% Na and 0.024–0.42 Ti for bottom soil (20–30 cm). The content of major elements is most frequently a result of the dominant geological formations of the area: Proterozoic gneisses, felsic plutonites and carbonates, and Neogene felsic pyroclastites and clastic sediments (Fig. 3).

The ratio of the contents was between the topsoil and the subsoil, and is represented in Table 4. No significant differences were found, varying the ratio of 0.66 for Br to 1.36 for Pb, showing the absence of influence of possible anthropogenic activities.

A comparative analysis of the contents of the analyzed elements in topsoils from the Skopje region and the soil from the city of Skopje (urban zone), soil from North Macedonia (Stafilov and Šajn, 2016, 2019) and Europe (Salminen *et al.*, 2005) is given in Table 5. It was found that for many elements there are differences in the content in soil from the Mariovo region compared with those from Macedonian soil as well as with the European soil (Table 5), showing their dependence on the specific lithogenic origin of the rocks in the separate sub-regions of the

Table 1
Basic information about sample locations

Location	Longitude (WGS84)	Latitude (WGS 84)	Land use	Lithology unit	Chronology unit	Pedology unit	Altitude (m)
M-1	21.73750	40.96250	Forest	Metamorphic r.	Proterozoic	Cambisol	1167
M-2	21.79695	40.96222	Scrub	Metamorphic r.	Proterozoic	Ranker	2097
M-3	21.67889	41.00556	Forest	Metamorphic r.	Proterozoic	Regosol	948
M-4	21.73722	41.00723	Forest	Metamorphic r.	Proterozoic	Cambisol	1474
M-5	21.79750	41.00722	Forest	Metamorphic r.	Proterozoic	Cambisol	1471
M-6	21.61967	41.05334	Scrub	Metamorphic r.	Proterozoic	Ranker	1252
M-7	21.68250	41.05139	Forest	Metamorphic r.	Proterozoic	Regosol	687
M-8	21.73861	41.05278	Scrub	Metamorphic r.	Proterozoic	Regosol	822
M-9	21.79556	41.05222	Forest	Carbonates	Proterozoic	Cambisol	1118
M-10	21.85445	41.05222	Forest	Magmatic r.	Neogene	Cambisol	1349
M-11	21.61570	41.09836	Scrub	Metamorphic r.	Proterozoic	Ranker	875
M-12	21.67944	41.09611	Grassland	Metamorphic r.	Proterozoic	Regosol	539
M-13	21.74055	41.09722	Grassland	Metamorphic r.	Proterozoic	Vertisol	854
M-14	21.79861	41.09722	Scrub	Carbonates	Proterozoic	Cambisol	979
M-15	21.85805	41.09695	Forest	Clastites	Mesozoic	Cambisol	1278
M-16	21.62053	41.14339	Pastures	Metamorphic r.	Proterozoic	Regosol	846
M-17	21.68333	41.14306	Pastures	Metamorphic r.	Proterozoic	Regosol	602
M-18	21.73973	41.14278	Forest	Carbonates	Neogene	Ranker	716
M-19	21.79917	41.14222	Pastures	Carbonates	Paleozoic	Litosol	1051
M-20	21.85861	41.14195	Pastures	Metamorphic r.	Proterozoic	Cambisol	1249
M-21	21.68056	41.18806	Pastures	Magmatic r.	Proterozoic	Ranker	682
M-22	21.73583	41.18639	Agricultural area	Metamorphic r.	Proterozoic	Ranker	579
M-23	21.80333	41.18472		Carbonates	Mesozoic	Litosol	1108
M-24	21.85889	41.18500	Scrub	Metamorphic r.	Proterozoic	Cambisol	1060
M-25	21.68083	41.23222	Pastures	Metamorphic r.	Proterozoic	Regosol	544
M-26	21.73722	41.23416	Scrub	Metamorphic r.	Proterozoic	Ranker	783
M-27	21.80444	41.22722	Forest	Carbonates	Mesozoic	Cambisol	920
M-28	21.86001	41.23194	Forest	Metamorphic r.	Proterozoic	Regosol	1279
M-29	21.62917	41.27917	Grassland	Magmatic r.	Proterozoic	Ranker	792
M-30	21.68139	41.27805	Grassland	Metamorphic r.	Proterozoic	Regosol	682
M-31	21.74111	41.27778	Scrub	Metamorphic r.	Proterozoic	Litosol	886
M-32	21.81055	41.27000	Forest	Clastites	Mesozoic	Cambisol	319
M-33	21.62194	41.32306	Grassland	Magmatic r.	Proterozoic	Ranker	1338

area. It is important to note that, except in the case of Ba, the median value for all elements included in The New Dutchlist (<http://www.contaminatedland.co.uk>), are below the target values, while in some parts of the region some of the elements exceeded the target values (As, Co, Cr, Ni and Pb) or even the action values (As, Ba, Cr and Ni), which is due to the lithogenic origin of these elements in soil from the Vardar tectonic zone (Stafilov *et al.*, 2010b; Stafilov and Šajn, 2016, 2019).

To determine the degree of correlation between the elements in the samples from river sediments and soils across the whole river basin, a bivariate statistic was used, where strong correlation between the investigated elements is apparent when the absolute value of the correlation coefficient is from 0.7 to 0.9, while good correlation is found

when the correlation coefficient is between 0.5 and 0.7 (Table 6).

In factor analysis, the distribution is reduced to three synthetic variables (F1–F3). As it can be seen from the results obtained by factor analysis (Table 7), three factors (*i.e.*, associations of elements) were obtained: F1 (Fe, V, Cr, Co, Ni, Mn, Cu, Al, Sc, Ti, Li, Zn and In); F2 (Pd, As, Zr, Pt, Ag, Hf, Br and Cs); and F3 (Ga, Rb, Be, K, Na, Nb and Ge). A total of 68 elements were reduced by factor analysis to 28 elements, which had a total factor loading of 72% of the variability (Table 7). The rest of the elements were eliminated from further analysis, because they had a low share of communality or a low tendency to form independent factors. Multivariate cluster analysis was also applied to determine the significance of the factor analysis and the

Table 2

Descriptive statistics for the content of the elements in topsoil (0–5 cm), n = 33

	Unit	N	X	X _(BC)	Md	Min	Max	S	S _x	CV	A	E	A _(BC)	E _(BC)
Ag	mg/kg	33	0.72	0.64	0.51	0.12	1.9	0.48	0.083	66	0.93	0.03	0.35	–0.75
Al	%	33	2.4	2.3	2.2	0.19	5.6	1.2	0.21	2100	1.00	1.18	0.23	1.04
As	mg/kg	33	20	13	13	3.7	100	22	3.8	110	2.47	6.52	0.14	–0.58
Ba	mg/kg	33	820	760	740	52	2000	440	76	54	0.73	0.87	–0.27	0.88
Be	mg/kg	33	2.1	2.0	2.0	0.005	6.7	1.2	0.21	58	1.57	5.45	0.46	3.17
Bi	mg/kg	31	0.25	0.18	0.17	0.070	1.4	0.25	0.044	99	3.68	15.58	0.04	0.28
Br	mg/kg	31	2.4	1.5	1.5	0.005	18	3.2	0.58	130	3.69	16.66	–0.21	1.34
Ca	%	33	3.1	1.3	1.3	0.29	17	4.8	0.84	8400	2.24	3.59	0.09	0.38
Cd	µg/kg	33	100	33	35	5.0	730	140	25	140	2.84	10.85	–0.26	–1.24
Ce	mg/kg	31	37	29	27	1.1	150	33	5.8	87	2.19	5.06	–0.17	2.29
Co	mg/kg	31	7.6	5.1	5.0	1.2	36	7.9	1.4	100	2.62	6.88	–0.26	0.86
Cr	mg/kg	33	41	15	15	2.6	540	97	17	240	4.75	24.29	0.04	0.61
Cs	mg/kg	31	3.6	2.5	2.7	0.12	26	4.6	0.83	130	4.20	20.25	0.03	2.64
Cu	mg/kg	33	8.3	6.1	5.8	2.6	38	7.2	1.3	87	2.71	8.55	0.36	–0.36
Dy	mg/kg	31	2.0	2.0	2.1	0.071	3.5	0.84	0.15	41	–0.26	0.21	–0.57	0.77
Er	mg/kg	31	1.0	1.0	1.1	0.038	1.8	0.41	0.073	39	–0.44	0.59	–0.55	0.79
Eu	mg/kg	31	0.67	0.63	0.60	0.024	1.8	0.38	0.068	56	1.01	1.74	0.01	1.01
Fe	%	33	1.7	1.6	1.6	0.18	4.8	0.95	0.17	1700	1.66	4.08	0.42	2.22
Ga	mg/kg	33	12	12	11	0.24	31	5.3	0.92	45	1.05	5.61	0.75	4.95
Gd	mg/kg	31	2.7	2.6	2.7	0.10	5.9	1.3	0.24	49	0.48	0.43	–0.18	0.76
Ge	mg/kg	31	0.53	0.43	0.46	0.039	1.7	0.45	0.081	86	1.05	0.48	0.30	–0.87
Hf	mg/kg	31	0.58	0.42	0.38	0.034	2.3	0.55	0.10	97	2.10	3.68	0.17	1.48
Ho	mg/kg	31	0.38	0.38	0.39	0.013	0.66	0.15	0.027	40	–0.38	0.34	–0.60	0.76
I	µg/kg	31	45	33	34	5.0	280	51	9.2	110	3.46	14.45	0.40	1.33
In	µg/kg	31	30	28	26	5.0	75	15	2.7	50	1.20	2.24	0.08	1.38
K	%	33	1.3	1.4	1.3	0.034	2.4	0.56	0.098	980	–0.35	0.21	–0.23	0.04
La	mg/kg	31	19	16	16	0.55	51	13	2.4	69	0.57	–0.66	–0.42	–0.20
Li	mg/kg	33	17	15	14	0.53	42	10	1.8	62	0.98	0.50	–0.08	0.47
Lu	mg/kg	31	0.15	0.15	0.15	0.005	0.24	0.053	0.010	36	–0.70	1.21	–0.27	0.41
Mg	%	33	1.1	0.47	0.48	0.17	8.8	1.8	0.32	3200	3.06	9.77	0.24	–0.40
Mn	mg/kg	33	350	330	300	16	930	190	33	54	1.01	1.75	0.06	1.13
Mo	mg/kg	31	0.49	0.42	0.39	0.005	1.7	0.37	0.067	75	1.65	3.15	–0.13	1.38
Na	%	33	0.88	0.87	0.95	0.033	1.9	0.43	0.074	740	–0.16	0.35	–0.33	0.33
Nb	mg/kg	31	10	9.5	8.8	0.33	25	5.1	0.92	51	0.58	1.17	–0.17	0.93
Nd	mg/kg	31	12	11	10	0.45	30	7.0	1.3	57	0.99	0.99	–0.08	0.95
Ni	mg/kg	33	34	9.8	8.2	2.2	450	87	15	260	4.24	18.51	0.11	1.05
P	mg/kg	33	380	350	350	62	750	180	31	47	0.40	–0.57	–0.40	0.04
Pb	mg/kg	33	15	12	14	5.0	45	9.9	1.7	66	1.02	1.21	–0.26	–1.41
Pd	mg/kg	31	0.24	0.11	0.13	0.050	1.6	0.36	0.064	150	2.95	8.54	0.29	–1.20
Pr	mg/kg	31	3.2	2.9	2.6	0.12	8.2	1.9	0.35	60	1.15	1.27	–0.01	1.04
Pt	mg/kg	31	0.28	0.26	0.19	0.12	0.61	0.16	0.028	55	0.72	–0.96	0.51	–1.34
Rb	mg/kg	31	52	45	40	1.7	160	36	6.5	70	1.44	2.23	–0.09	1.03
Sb	mg/kg	31	0.28	0.21	0.21	0.071	1.6	0.27	0.049	98	3.95	18.11	0.21	1.15
Sc	mg/kg	31	3.1	2.6	2.4	0.050	7.5	1.9	0.34	62	0.82	–0.02	–0.83	1.84
Sm	mg/kg	31	2.4	2.3	2.2	0.050	5.5	1.2	0.22	51	0.69	0.86	–0.13	1.03
Sn	mg/kg	31	11	9.0	8.9	3.2	32	8.3	1.5	72	1.35	1.16	0.19	–0.88
Sr	mg/kg	33	120	96	99	32	490	88	15	76	2.70	9.42	0.57	0.43
Ta	mg/kg	31	0.76	0.74	0.73	0.050	1.7	0.39	0.070	51	0.30	0.09	–0.14	0.17
Tb	mg/kg	31	0.38	0.37	0.38	0.013	0.73	0.17	0.030	45	0.13	0.21	–0.34	0.71
Ti	%	31	0.16	0.15	0.15	0.013	0.27	0.062	0.011	110	–0.63	0.36	–1.00	1.12
Tl	mg/kg	31	0.47	0.44	0.43	0.050	1.2	0.25	0.046	55	1.25	2.25	0.28	1.46
Tm	mg/kg	31	0.15	0.15	0.15	0.005	0.26	0.056	0.010	38	–0.56	0.90	–0.55	0.88
V	mg/kg	33	40	36	33	4.9	110	23	4.1	59	1.34	1.98	0.31	0.60
W	mg/kg	31	1.4	0.93	0.88	0.29	8.2	1.6	0.29	110	3.04	10.84	0.51	0.02
Y	mg/kg	31	7.7	7.5	7.2	0.21	15	3.3	0.59	43	–0.07	0.41	–0.39	0.79
Yb	mg/kg	31	0.95	0.96	0.94	0.038	1.6	0.35	0.063	37	–0.63	1.11	–0.39	0.70
Zn	mg/kg	33	52	48	45	23	150	24	4.2	47	2.60	8.81	1.10	2.31
Zr	mg/kg	31	21	14	11	0.80	98	24	4.4	110	2.25	4.34	–0.28	2.12

X – arithmetic mean; BC – Box-Cox transformed values; Md – median; Min – minimum; Max – maximum; S – standard deviation; S_x – standard deviation (standard error); CV – coefficient of variation; A – asymmetry; E – distribution.

Table 3

Descriptive statistics for the content of the elements in subsoil (20–30 cm), $n = 33$

	Unit	N	X	X _(BC)	Md	Min	Max	S	S _x	CV	A	E	A _(BC)	E _(BC)
Ag	mg/kg	33	0.78	0.69	0.67	0.005	2.4	0.50	0.087	64	1.46	3.23	-0.24	1.65
Al	%	33	2.4	2.3	2.1	0.12	5.0	1.1	0.20	2000	0.64	0.35	-0.09	0.81
As	mg/kg	33	22	13	13	3.2	170	30	5.3	140	4.37	21.56	-0.09	0.70
Ba	mg/kg	33	810	740	780	77	2300	500	87	62	0.98	1.43	0.19	0.03
Be	mg/kg	33	2.1	2.0	2.1	0.005	4.1	0.97	0.17	46	-0.23	0.53	-0.86	1.24
Bi	mg/kg	31	0.24	0.17	0.17	0.067	1.8	0.30	0.054	130	5.05	27.00	-0.15	1.39
Br	mg/kg	31	3.5	2.2	2.0	0.005	32	5.8	1.0	160	4.36	20.83	0.75	4.73
Ca	%	33	3.3	1.2	1.1	0.25	18	5.3	0.92	9200	2.14	3.10	0.01	0.69
Cd	µg/kg	33	53	17	12	5.0	820	140	25	270	5.13	27.80	0.62	0.56
Ce	mg/kg	31	40	33	29	8.4	130	31	5.6	77	1.89	3.50	0.63	0.31
Co	mg/kg	31	8.8	5.8	5.9	1.9	47	11	1.9	120	3.13	9.43	0.42	1.12
Cr	mg/kg	33	48	14	13	1.8	690	130	22	260	4.54	21.83	-0.08	0.98
Cs	mg/kg	31	3.4	2.5	2.5	0.15	22	3.9	0.71	110	3.66	16.00	0.10	2.47
Cu	mg/kg	33	7.5	5.1	4.8	1.6	26	6.6	1.2	88	1.65	1.69	0.06	-0.37
Dy	mg/kg	31	2.2	2.2	2.0	0.64	5.0	0.95	0.17	43	0.68	0.93	0.47	0.50
Er	mg/kg	31	1.1	1.1	1.1	0.34	2.4	0.45	0.082	40	0.43	0.71	0.35	0.57
Eu	mg/kg	31	0.72	0.68	0.67	0.18	1.6	0.35	0.062	48	0.54	-0.14	0.12	-0.59
Fe	%	33	1.8	1.7	1.7	0.029	5.0	0.97	0.17	1700	1.38	3.44	-0.02	2.24
Ga	mg/kg	33	12	12	12	1.5	19	4.6	0.80	39	-0.64	0.20	-0.73	0.34
Gd	mg/kg	31	3.0	2.9	2.8	0.87	6.3	1.4	0.25	46	0.44	-0.55	0.19	-0.82
Ge	mg/kg	31	0.67	0.59	0.73	0.019	1.6	0.39	0.071	59	0.24	-0.02	-0.70	0.00
Hf	mg/kg	31	0.56	0.41	0.40	0.028	2.5	0.55	0.099	97	2.25	5.32	-0.08	1.34
Ho	mg/kg	31	0.42	0.41	0.40	0.12	0.92	0.17	0.031	42	0.61	1.00	0.44	0.68
I	µg/kg	31	56	41	46	5.0	240	50	8.9	89	2.19	6.10	-0.37	0.26
In	µg/kg	31	27	26	26	5.0	54	10	1.8	38	1.08	2.18	0.00	2.55
K	%	33	1.2	1.2	1.3	0.022	2.2	0.51	0.089	890	-0.62	0.13	-0.52	0.00
La	mg/kg	31	19	16	12	3.1	64	15	2.6	77	1.40	1.63	0.53	-0.46
Li	mg/kg	33	17	15	13	0.52	43	11	1.9	67	1.02	0.37	0.08	0.10
Lu	mg/kg	31	0.16	0.16	0.16	0.049	0.27	0.055	0.010	36	-0.37	-0.45	-0.18	-0.43
Mg	%	33	1.1	0.46	0.43	0.15	7.4	1.8	0.31	3100	2.70	6.67	0.11	-0.45
Mn	mg/kg	33	320	300	280	8.1	730	170	30	55	0.79	0.31	0.03	0.50
Mo	mg/kg	31	0.53	0.48	0.38	0.19	1.7	0.34	0.062	65	2.04	4.49	1.29	1.65
Na	%	33	0.81	0.80	0.91	0.042	1.9	0.43	0.075	750	-0.04	0.14	-0.19	-0.01
Nb	mg/kg	31	12	11	11	0.54	31	6.2	1.1	54	0.88	2.22	0.07	1.19
Nd	mg/kg	31	14	13	12	3.7	28	6.8	1.2	50	0.55	-0.90	0.24	-1.09
Ni	mg/kg	33	36	8.9	8.8	2.7	530	99	17	280	4.50	21.33	0.05	-0.17
P	mg/kg	33	390	350	350	74	1100	230	40	59	1.39	2.45	0.28	0.18
Pb	mg/kg	33	11	8.5	5.0	5.0	31	7.1	1.2	66	1.03	0.26	0.36	-1.61
Pd	mg/kg	31	0.25	0.12	0.14	0.050	1.4	0.33	0.060	130	2.34	5.13	0.09	-1.41
Pr	mg/kg	31	3.6	3.3	3.1	0.98	7.1	1.8	0.33	51	0.54	-0.92	0.21	-1.07
Pt	mg/kg	31	0.25	0.22	0.21	0.005	0.81	0.17	0.030	66	1.70	3.54	-0.03	2.04
Rb	mg/kg	31	47	43	45	10	160	29	5.2	62	1.93	6.58	0.32	0.99
Sb	mg/kg	31	0.23	0.18	0.18	0.054	0.82	0.17	0.030	74	2.67	7.42	-0.34	2.15
Sc	mg/kg	31	3.7	3.2	2.9	0.88	17	3.2	0.57	86	2.66	8.60	1.16	1.97
Sm	mg/kg	31	2.7	2.6	2.4	0.71	5.2	1.3	0.23	47	0.47	-0.82	0.23	-0.97
Sn	mg/kg	31	21	15	14	2.0	100	19	3.4	91	2.70	9.99	-0.39	0.59
Sr	mg/kg	33	120	93	99	11	520	95	17	81	2.70	9.48	-0.34	2.21
Ta	mg/kg	31	0.83	0.79	0.86	0.050	1.7	0.45	0.080	54	0.12	-0.77	-0.20	-0.59
Tb	mg/kg	31	0.41	0.40	0.39	0.11	0.89	0.18	0.033	44	0.55	0.09	0.31	-0.24
Ti	%	31	0.18	0.18	0.17	0.024	0.42	0.086	0.015	160	0.93	1.55	0.50	1.04
Tl	mg/kg	31	0.44	0.42	0.42	0.050	1.2	0.23	0.042	53	0.81	2.50	-0.18	0.92
Tm	mg/kg	31	0.16	0.16	0.16	0.049	0.33	0.062	0.011	39	0.29	0.57	0.30	0.58
V	mg/kg	33	44	39	41	1.4	110	27	4.7	62	0.99	0.63	-0.16	0.55
W	mg/kg	31	1.2	0.82	0.77	0.11	4.7	1.1	0.20	92	1.83	2.99	-0.37	0.78
Y	mg/kg	31	8.5	8.4	8.4	2.1	20	3.5	0.63	41	0.90	3.31	0.55	2.52
Yb	mg/kg	31	1.0	1.0	1.1	0.33	1.9	0.38	0.067	37	-0.08	0.06	0.07	0.21
Zn	mg/kg	33	48	42	42	7.8	180	30	5.2	62	2.85	11.29	-0.15	3.04
Zr	mg/kg	31	22	14	13	2.3	96	24	4.3	110	2.08	3.39	0.35	0.24

X – arithmetic mean; BC – Box-Cox transformed values; Md – median; Min – minimum; Max – maximum; S – standard deviation; S_x – standard deviation (standard error); CV – coefficient of variation; A – asymmetry; E – distribution.

Table 4

Ratio of the average contents (topsoil vs. subsoil)

	Unit	Topsoil	Subsoil	FO(T/B)	T (test)	Sign	F(ratio)	Sign	R(T/B)	Sign
Ag	mg/kg	0.64	0.69	0.93	-0.41	NS	1.12	NS	0.28	NS
Al	%	2.3	2.3	1.01	0.09	NS	1.08	NS	0.75	*
As	mg/kg	13	13	0.94	-0.35	NS	1.13	NS	0.24	NS
Ba	mg/kg	760	740	1.02	0.13	NS	1.18	NS	0.82	*
Be	mg/kg	2	2	1.00	-0.03	NS	1.32	NS	0.63	*
Bi	mg/kg	0.18	0.17	1.05	0.40	NS	1.09	NS	0.79	*
Br	mg/kg	1.5	2.2	0.66	-1.33	NS	1.07	NS	0.15	NS
Ca	%	1.3	1.2	1.05	0.22	NS	1.13	NS	0.93	*
Cd	µg/kg	33	17	1.93	2.66	*	1.42	*	0.45	*
Ce	mg/kg	29	33	0.87	-0.69	NS	1.39	NS	0.73	*
Co	mg/kg	5.1	5.8	0.87	-0.79	NS	1.38	NS	0.84	*
Cr	mg/kg	15	14	1.08	0.30	NS	1.20	NS	0.88	*
Cs	mg/kg	2.5	2.5	1.00	-0.01	NS	1.15	NS	0.77	*
Cu	mg/kg	6.1	5.1	1.20	1.19	NS	1.65	NS	0.82	*
Dy	mg/kg	2	2.2	0.91	-0.82	NS	1.14	NS	0.57	*
Er	mg/kg	1	1.1	0.93	-0.76	NS	1.21	NS	0.57	*
Eu	mg/kg	0.63	0.68	0.92	-0.59	NS	1.30	NS	0.60	*
Fe	%	1.6	1.7	0.96	-0.27	NS	1.10	NS	0.93	*
Ga	mg/kg	12	12	0.97	-0.28	NS	1.27	NS	0.53	*
Gd	mg/kg	2.6	2.9	0.89	-0.90	NS	1.06	NS	0.58	*
Ge	mg/kg	0.43	0.59	0.72	-1.55	NS	1.26	NS	0.00	NS
Hf	mg/kg	0.42	0.41	1.04	0.17	NS	1.11	NS	0.82	*
Ho	mg/kg	0.38	0.41	0.92	-0.80	NS	1.18	NS	0.57	*
I	µg/kg	33	41	0.79	-0.97	NS	1.18	NS	0.42	*
In	µg/kg	28	26	1.07	0.56	NS	1.88	NS	0.49	*
K	%	1.4	1.2	1.13	1.19	NS	1.23	NS	0.52	*
La	mg/kg	16	16	0.99	-0.04	NS	1.24	NS	0.74	*
Li	mg/kg	15	15	1.01	0.08	NS	1.10	NS	0.93	*
Lu	mg/kg	0.15	0.16	0.96	-0.53	NS	1.17	NS	0.56	*
Mg	%	0.47	0.46	1.03	0.14	NS	1.13	NS	0.91	*
Mn	mg/kg	330	300	1.11	0.72	NS	1.08	NS	0.92	*
Mo	mg/kg	0.42	0.48	0.87	-0.78	NS	1.81	NS	0.09	NS
Na	%	0.87	0.8	1.09	0.63	NS	1.04	NS	0.61	*
Nb	mg/kg	9.5	11	0.87	-1.01	NS	1.30	NS	0.52	*
Nd	mg/kg	11	13	0.88	-0.86	NS	1.22	NS	0.65	*
Ni	mg/kg	9.8	8.9	1.10	0.47	NS	1.29	NS	0.75	*
P	mg/kg	350	350	1.02	0.13	NS	1.27	NS	0.85	*
Pb	mg/kg	12	8.5	1.36	1.89	NS	1.17	NS	0.63	*
Pd	mg/kg	0.11	0.12	0.91	-0.43	NS	1.05	NS	0.65	*
Pr	mg/kg	2.9	3.3	0.88	-0.85	NS	1.29	NS	0.66	*
Pt	mg/kg	0.26	0.22	1.17	0.97	NS	1.37	NS	0.54	*
Rb	mg/kg	45	43	1.05	0.31	NS	1.57	NS	0.48	*
Sb	mg/kg	0.21	0.18	1.15	1.02	NS	1.04	NS	0.86	*
Sc	mg/kg	2.6	3.2	0.83	-0.99	NS	1.01	NS	0.53	*
Sm	mg/kg	2.3	2.6	0.89	-0.87	NS	1.13	NS	0.63	*
Sn	mg/kg	9	15	0.60	-2.69	*	1.39	NS	-0.09	NS
Sr	mg/kg	96	93	1.03	0.16	NS	1.38	NS	0.92	*
Ta	mg/kg	0.74	0.79	0.93	-0.52	NS	1.28	NS	0.59	*
Tb	mg/kg	0.37	0.4	0.90	-0.85	NS	1.03	NS	0.56	*
Ti	%	0.15	0.18	0.88	-1.13	NS	1.57	NS	0.61	*
Tl	mg/kg	0.44	0.42	1.06	0.39	NS	1.04	NS	0.79	*
Tm	mg/kg	0.15	0.16	0.94	-0.68	NS	1.23	NS	0.54	*
V	mg/kg	36	39	0.94	-0.40	NS	1.39	NS	0.94	*
W	mg/kg	0.93	0.82	1.13	0.60	NS	1.20	NS	0.77	*
Y	mg/kg	7.5	8.4	0.90	-0.96	NS	1.01	NS	0.46	*
Yb	mg/kg	0.96	1	0.94	-0.66	NS	1.23	NS	0.52	*
Zn	mg/kg	48	42	1.14	1.14	NS	2.01	NS	0.60	*
Zr	mg/kg	14	14	0.96	-0.18	NS	1.15	NS	0.79	*

FO (T/B) – Enrichment Factor: ratio of the content in topsoil (T) and bottom soil (B); Sign – significant at $p < 0.01$; R (T/B) – ration between the results for top and bottom soil; NS – difference not significant.

Table 5

Comparison of the median, minimum and maximum values of the content of the analyzed elements in topsoil from the Mariovo region with soil from North Macedonia and Europe

Element	Unit	Dutchlist		Mariovo Region (this work)		North Macedonia (Stačilov and Šajn, 2019)		Europe (Salminen <i>et al.</i> , 2005)	
		Target	Action	Md	Min–Max	Md	Min–Max	Md	Min–Max
Ag	mg/kg			0.51	0.12–1.9	–	–	0.27	0.01–3.15
Al	%			2.2	0.19–5.6	1.3	0.05–35	5.8	0.70–14.1
As	mg/kg	29	55	13	3.7–100	10	1.0–720	12	0.32–562
Ba	mg/kg	200	625	740	52–2000	430	6–2900	375	30–1870
Be	mg/kg			2.0	0.005–6.7	2.0	<1.0–8.0	<2.0	<2.0–18.7
Bi	mg/kg			0.17	0.070–1.4	0.30	<0.10–15	<0.5	<0.5–9.57
Br	mg/kg			1.5	0.005–18	–	–	–	–
Ca	%			1.3	0.29–17	1.3	0.05–35	0.66	0.019–34.3
Cd	mg/kg	0.8	12	0.013	0.005–0.73	0.30	0.01–110	0.92	0.03–14
Ce	mg/kg			27	1.1–150	56	1.0–180	48.2	1.04–379
Co	mg/kg	20	240	5.0	1.2–36	17	0.50–150	8.0	<1.0–191
Cr	mg/kg	100	380	15	2.6–540	88	5.0–2700	60	<3–6230
Cs	mg/kg			2.7	0.12–26	–	–	2.71	<0.5–69
Cu	mg/kg	36	190	5.8	2.6–38	28	1.6–270	13	0.81–256
Dy	mg/kg			2.1	0.071–3.5	–	–	3.42	0.18–45
Er	mg/kg			1.1	0.038–1.8	–	–	1.98	0.12–26
Eu	mg/kg			0.60	0.024–1.8	–	–	0.77	0.05–7.0
Fe	%			1.6	0.18–4.8	3.5	0.03–12	1.34	0.049–10.6
Ga	mg/kg			11	0.24–31	–	–	13.5	0.54–34
Gd	mg/kg			2.7	0.10–5.9	–	–	3.85	0.20–36
Ge	mg/kg			0.46	0.039–1.7	–	–	–	–
Hf	mg/kg			0.38	0.034–2.3	1.0	<0.10–6.6	5.55	<0.2–21
Ho	mg/kg			0.39	0.013–0.66	–	–	0.72	0.03–9.2
I	mg/kg			0.034	0.005–0.28	–	–	3.94	0.002–70.8
In	mg/kg			0.026	0.005–0.075	–	–	0.05	0.01–0.41
K	%			1.3	0.034–2.4	1.9	0.02–5.3	1.59	0.022–5.1
La	mg/kg			16	0.53–51	25	0.60–88	23	1.10–143
Li	mg/kg			14	0.53–42	26	1.8–210	–	–
Lu	mg/kg			0.15	0.005–0.24	–	–	0.30	<0.02–3.21
Mg	%			0.48	0.17–8.8	0.94	0.12–13	0.47	<0.006–15
Mn	mg/kg			300	16–930	900	17–10000	510	31–6070
Mo	mg/kg	10	200	0.39	0.005–1.7	0.90	<0.10–51	0.61	<0.10–21
Na	%			0.95	0.033–1.9	1.3	0.007–3.7	0.6	0.03–3.34
Nb	mg/kg			8.8	0.33–25	11	0.30–2000	9.68	0.45–134
Nd	mg/kg			10	0.45–30	–	–	21	1.14–132
Ni	mg/kg	35	210	8.2	2.2–450	46	2.1–2500	18	<2–2690
P	mg/kg			350	62–750	620	110–3900	960	82–9900
Pb	mg/kg	85	530	15	5.0–45	32	1.2–10000	23	5.3–970
Pd	mg/kg			0.13	0.050–1.6	–	–	–	–
Pr	mg/kg			2.6	0.12–8.2	–	–	5.6	0.29–31.6
Pt	mg/kg			0.19	0.12–0.61	–	–	–	–
Rb	mg/kg			40	1.7–160	86	0.70–390	80	2–390
Sb	mg/kg			0.21	0.071–1.6	0.80	<0.10–630	0.60	0.02–31
Sc	mg/kg			2.4	0.050–7.5	12	<1.0–39	8.21	<0.50–54
Sm	mg/kg			2.2	0.050–5.5	–	–	3.96	0.23–30
Sn	mg/kg			8.9	3.2–32	2.6	<0.10–680	3.00	<2.0–106
Sr	mg/kg			99	32–490	140	21–1400	89	8–3120
Ta	mg/kg			0.73	0.050–1.7	0.70	<0.10–30	0.68	<0.05–6.8
Tb	mg/kg			0.38	0.013–0.73	–	–	0.60	0.03–7.0
Ti	%			0.15	0.013–0.27	0.34	0.004–1.2	0.34	0.012–3.27
Tl	mg/kg			0.43	0.050–1.2	0.70	<0.50–16	0.66	0.05–24
Tm	mg/kg			0.15	0.005–0.26	–	–	0.30	0.05–4.03
V	mg/kg			33	4.9–110	89	1.0–470	60	2.7–537
W	mg/kg			0.88	0.29–8.2	1.3	0.20–18	<5.0	<5.0–14
Y	mg/kg			7.2	0.21–15	18	0.30–110	21	<3.0–267
Yb	mg/kg			0.94	0.038–1.6	–	–	1.99	0.09–25
Zn	mg/kg	140	720	45	23–150	83	8.0–10000	52	<3–2900
Zr	mg/kg			11	0.80–98	35	0.80–210	231	5.0–1060

Md – median; Min – minimum; Max – Maximum

Table 6
Correlation matrix of the analyzed elements, $n = 66$

[illegible]

stability of the new synthetic variables, *i.e.*, associations of elements. The dendrogram of the distances among the individual elements is presented in Fig. 5. Similar results were achieved by the application of multivariate factor analysis (Table 7). All of the obtained clusters correspond to the three obtained factors.

Factor 1 (Fig. 6) is a geogenic association composed of 13 elements: Fe, V, Cr, Co, Ni, Mn, Cu, Al, Sc, Ti, Li, Zu and In. The highest content of these elements is characteristic for the soil from the eastern (Vardar tectonic zone), southern and eastern parts (Pelagonian massif). In the eastern part of the area, Proterozoic gneisses and carbonates and Neogene felsic pyroclastites are the dominant geological formations. In the western part, the dominant geological formations are Proterozoic gneisses together with Proterozoic felsic plutonites and shales. Thus, the content of Fe reaches the highest content of 4.8% (median content is 1.6%) in the eastern part

of the region. The maximum contents of the other elements from F1 were also found in the mentioned areas of the region: 110 mg/kg for V (median value 33 mg/kg), 540 mg/kg for Cr (median 15 mg/kg), 36 mg/kg for Co (median of 5.0 mg/kg), 450 mg/kg for Ni (median of 8.2 mg/kg), 930 mg/kg for Mn (median of 300 mg/kg), 38 mg/kg for Cu (median of 5.8 mg/kg), 5.6% for Al (median of 2.2%), 7.5 mg/kg for Sc (median of 2.4 mg/kg), 0.27% for Ti (median of 0.15%), 42 mg/kg for Li (median of 14 mg/kg), 150 mg/kg for Zn (median of 45 mg/kg) and 0.075 mg/kg for Co (median of 0.026 mg/kg). Lower contents of the elements of this factor were found in soil from the central part of the region (villages of Budimirci, Staravina and Bešište, where Neogene felsic pyroclastites and volcanites are the dominant lithological formations).

Factor 2 (Fig. 7) is a geogenic association that is composed of eight elements: Pd, As, Zr, Pt, Ag, Hf, Br and Cs. The presence of these elements is char-

Fig. 5. Dendrogram from the cluster analysis (n = 28).

Table 7
Matrix of dominant rotated factor loadings ($n = 66$)

	F1	F2	F3	Assoc.
Fe	0.94	-0.03	0.12	90.1
V	0.93	-0.06	0.13	89.1
Cr	0.90	0.15	0.10	85.1
Co	0.87	0.22	0.23	86.7
Ni	0.85	0.17	0.00	76.1
Mn	0.83	0.07	0.35	81.5
Cu	0.79	0.11	-0.14	65.7
Al	0.77	0.24	0.01	65.9
Sc	0.76	0.10	0.08	59.0
Ti	0.68	0.22	0.38	66.0
Li	0.63	-0.03	0.46	61.6
Zn	0.61	0.19	0.34	52.1
In	0.59	0.02	0.46	56.8
Pd	0.23	0.89	0.09	85.0
As	-0.18	0.80	-0.27	74.4
Zr	0.44	0.78	0.13	81.8
Pt	0.19	0.72	0.30	64.8
Ag	0.14	0.72	0.31	63.7
Hf	0.47	0.71	0.06	73.4
Br	-0.35	0.69	0.06	60.0
Cs	0.44	0.64	0.38	75.2
Ga	0.20	0.09	0.87	80.7
Rb	0.14	0.41	0.82	86.5
Be	0.28	0.19	0.82	78.2
K	0.22	-0.14	0.79	69.6
Na	-0.29	-0.15	0.72	62.3
Nb	0.09	0.37	0.71	64.5
Ge	0.18	0.30	0.66	56.4
Prp. Totl	33.4	18.7	19.8	71.9
Eigen Val	12.10	4.43	3.59	
Expl. Var	9.34	5.24	5.54	

F – load factor values; F1, F2 and F3 – load factor values for each appropriate factor 1, 2 and 3; Assoc. – association (%); Prp. Totl – total variance of the system; Eigen Val – Engene values; Expl. Var – variance of the special component.

acteristic of the central part of Mariovo, around the village of Bešište, and the eastern part around Nidže. This factor is geogenic because the distribution is related to geology, *i.e.*, the highest contents of these elements are observed in the areas of Proterozoic plutonites and gneisses, Neogene felsic pyroclastites, sediments and volcanites, Proterozoic gneisses and carbonates. Thus, the content of Pd reaches its highest content of 1.6 mg/kg (median content is 0.13 mg/kg) in the eastern part of the region. The maximum contents of the other elements from F2 were also found in the mentioned areas of the region: 100 mg/kg for As (median value 13 mg/kg), 98 mg/kg for Zr (median 11 mg/kg), 0.61 mg/kg for Pt (median of 0.19 mg/kg), 1.9 mg/kg for Ag

Fig. 6. Spatial distribution of factor scores of Factor 1 (Fe-V-Cr-Co-Ni-Mn-Cu-Al-Sc-Ti-Li-Zn-In).

Fig. 7. Spatial distribution of factor scores of Factor 2 (Pd-As-Zr-Pt-Ag-Hf-Br-Cs).

Fig 8. Spatial distribution of factor scores of Factor 3 (Ga-Rb-Be-K-Na-Nb-Ge).

Fig. 9. Spatial distribution of rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sm, Tb, Tm and Yb).

(median of 0.51 mg/kg), 2.3 mg/kg for Hf (median of 0.38 mg/kg), 18 mg/kg for Br (median of 1.5 mg/kg) and 26 mg/kg for Cs (median of 2.7 mg/kg). Lower distributions of the elements from F2 are in the south-western part of Mariovo, in the samples from the area where Proterozoic gneisses and felsic plutonites are the dominant geological formations.

Factor 3 represents the geogenic association that includes Ga, Rb, Be, K, Na, Nb and Ge. The spatial distribution maps of the factor scores of Factor 3 are given in Fig. 8. The presence of elements in higher contents is mostly in the soil samples from the southern part of the region and from the small area of the northern part with Proterozoic and Mesozoic carbonates and Proterozoic shales, gneisses and felsic plutonites. The maximum median content of Ga from these areas is 31 mg/kg

(median of 11 mg/kg), Rb is 160 mg/kg (median 40 mg/kg), Be is 6.7 mg/kg (median 2.0 mg/kg), K is 2.4% (median 1.3%), Na is 1.9% (median 0.95%), Nb is 25 mg/kg (median 40 mg/kg) and Ge is 1.7 mg/kg (median 0.46 mg/kg).

Fourteen rare-earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sm, Tb, Tm, and Yb) were also determined by ICP-MS (Fig. 9). It can be noted that the highest values exist in the areas dominated by Neogene clastic sediments, Proterozoic shales and felsic plutonites in the western part of the Mariovo region, which is a part of the Pelagonian massif known for increased contents of REEs (Stačilov and Šajn, 2016, 2019). Potential deposits of REEs in mineral ore deposits can be divided into primary and secondary. Primary deposits are those formed by magmatic, hydrothermal and/or metamorphic

Fig. 10. Spatial distribution maps of the potentially toxic elements not included in the factors (Bi, Cd, Pb, Sb, Sn and Tl).

processes. REEs in soils are predominately concentrated in minerals, such as fluorocarbonates, phosphates, silicates and oxides (Al-Ani *et al.*, 2018).

As previously mentioned, from a total of 68 analyzed elements, the factor analysis reduced them to 28 elements; 14 elements are associated with the

group of rare earth elements (REEs), while the remaining 16 elements (Ba, Bi, Ca, Cd, I, Mg, Mo, P, Pb, Sb, Sn, Sr, Ta, Tl, W and Y) were eliminated due to their lack of participation in the association. Spatial distribution maps of the potentially toxic elements not included in the factors (Bi, Cd, Pb, Sb,

Sn and Tl) are given in Fig. 10. Especially noteworthy is the increased content of As, Sb and Tl in the southwestern part of the studied area, the western part of Mount Nidže and the western parts of Mount Kožuf, where the Allchar mine operates, known for its large reserves of arsenic, antimony and thallium mineralization. This reflects the increased content of As up to 100 mg/kg (increasing the action value to almost 2×), of Sb 1.6 mg/kg and of Tl up to 1.2 mg/kg in the surrounding soils (Bačeva *et al.*, 2014; Stafilov and Šajn, 2016, 2019; Jovanovski *et al.*, 2018, 2019).

CONCLUSION

Examination of the distribution of 58 chemical elements in soil samples from the Mariovo region, North Macedonia, was performed. Soil samples collected from 60 locations were analyzed by using two spectroscopic techniques: 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 and their spatial distributions showed that their occurrences are geologically determined. In factor analysis, the distribution is reduced to three synthetic variables (F1–F3): F1 (Fe, V, Cr, Co, Ni, Mn, Cu, Al, Sc, Ti, Li, Zn and In); F2 (Pd, As, Zr, Pt, Ag, Hf, Br and Cs); and F3 (Ga, Rb,

Be, K, Na, Nb and Ge). Factor 1 is a geogenic association composed of 13 elements: Fe, V, Cr, Co, Ni, Mn, Cu, Al, Sc, Ti, Li, Zn and In. Their highest content was found in soil from the eastern part of the region, which belongs to the Vardar tectonic zone, and southern and eastern parts, which belong to the Pelagonian massif where Proterozoic gneisses and carbonates and Neogene felsic pyroclastites are the dominant geological formations. In the eastern part, the dominant geological formations are Proterozoic gneisses together with Proterozoic felsic plutonites and shales. Factor 2 is a geogenic association composed of eight elements (Pd, As, Zr, Pt, Ag, Hf, Br and Cs). Their presence is characteristic of the central part of Mariovo and their highest contents were observed in the areas of Proterozoic plutonites and gneisses, Neogene felsic pyroclastites, sediments and volcanic rocks, and Proterozoic gneisses and carbonates. Factor 3 represents the geogenic association that includes Ga, Rb, Be, K, Na, Nb and Ge. The presence of elements in higher contents is mostly in the soil samples from the southern part of the region and the small area of the northern part with Proterozoic and Mesozoic carbonates, and Proterozoic shales, gneisses and felsic plutonites.

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