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SPATIAL DISTRIBUTION OF CHEMICAL ELEMENTS IN SOILS FROM THE SOUTHEASTERN PART OF NORTH MACEDONIA (GEVGELIJA, VALANDOVO, BOGDANCI AND DOJRAN MUNICIPALITIES)

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Abstract: In this work, the contents and spatial distributions of 18 elements (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, Zn) in the soils of the southeastern part of North Macedonia (Gevgelija–Valandovo–Bogdanci–Dojran region) are presented. For this purpose, a total of 86 soil samples were collected from 43 locations (43 samples of topsoil and 43 samples of subsoil). All samples were analyzed by inductively coupled plasma – atomic emission spectrometry (ICP-AES) after complete digestion with four acids (HNO_3, HF, $HClO_4$, and HCl). The obtained results were statistically evaluated and spatial distribution maps for all analyzed elements were also prepared. Factor analysis was performed to reduce the number of data used and new synthetic variables (factors) were identified. Through the application of factor analysis, three geochemical associations were identified: Factor 1 (Fe, V, Mn, Cu, Ni, Zn, and Pb), Factor 2 (Ba, Li, and K), and Factor 3 (Mg, Al, Ca, and Sr). From the obtained data and the maps of spatial distribution, it could be concluded that the occurrence of the analyzed elements is related to the lithology of the region. Namely, it was found that the content of elements of Factor 1 is higher in soils dominated by Mesozoic volcanic rocks, Quaternary alluvial sediments, and Proterozoic gneisses and Paleozoic shales; the content of elements of Factor 2 is higher in soils in the north (where Mesozoic felsic plutonites dominate) and east (where Proterozoic gneisses and Paleozoic shales dominate) of the study area; and that elements of Factor 3 are present in soils from the area dominated by Quaternary alluvial sediments, Paleozoic carbonates and shales, and Mesozoic mafic plutonites. The only exception is the fact that the P content in the topsoil from the Gevgelija and Valandovo valleys along the Vardar and Anska rivers is higher than in the subsoil samples, which is probably due to the use of phosphate artificial fertilisers in agriculture.

Key words: soil; heavy metals; factor analysis; Gevgelija; Valandovo; Bogdanci; Dojran; municipalities; North Macedonia

INTRODUCTION

Pollution is the introduction of new and atypical substances into the environment and the inrease in the normal concentration of substances already present in the environment. Pollution includes all hazardous substances that directly or indirectly have a harmful effect on the environment and human health (Acton, 2013). This is followed by the fact that potentially toxic elements (PTEs) are also such a group of substances. The term PTEs heavy metals refers to a chemical element that is toxic even at low concentrations. The group of PTEs heavy metals includes arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin, thallium, etc. (Järup, 2003; Kabata-Pendias & Mukherjee, 2007).

Pollution with PTEs can come from a variety of sources. For example, the main sources of cadmium are phosphorus fertilizers, fuel combustion, and organic wastes. Sources of lead include coal, oil, and gas combustion. Sources of arsenic include coal, oil, gas combustion, fossil fuel combustion, geothermal power generation, phosphate fertilizers, and pesticides. Mercury is released by degassing of the Earth's crust. Sources of nickel include coal, oil, gas combustion, mining, steel production, fossil fuel combustion, oil refining, sewage sludge, and motor vehicles. Pollution is particularly pronounced in areas where there are mines, thermal power plants, and smelters. Production processes, flotation, extraction, and waste separation results in the release of heavy metals that pollute the environment (Salomons et al., 2012).

Soil is defined as the surface layer of the earth's crust composed of mineral particles, organic matter, water, air, and living organisms. Soil formation is an extremely slow process and therefore soil can be considered a non-renewable resource. Soil is a fundamental medium that serves the growth and development of plants, while it is the basis of life for animals and humans. Soil is the result of pedogenic processes caused by the continuous, joint, and interdependent action of heterogenic pedogenic factors. Soil-forming factors include relief, the presence of different climatic zones, geological formations, and the composition of the parent rock relevant to plant and animal activities (Filipovski et al., 2015).

Soil pollution is a major problem for several reasons. The long-term emission of heavy metals through water and air, due to their concentrations, causes global damage to the soil in a larger region. The high content of heavy metals negatively affects the quality of soil, which is manifested by blocking the reactivity of humic acids and anomalies in the process of formation of humic substances, leading to the destruction of soil structure and partial loss of humus, as well as a decrease in the erosion control capacity of the soil (Kabata-Pendias & Mukherjee, 2007). The effects of heavy metals on soil depend on their concentration, organic matter content, pH, redox potential, and other properties. The term "soil pollution" refers to the content interval, expressed in a certain unit of measurement, of harmful elements that in some way negatively affect the growth of plants and the development of all other ecological components. If soil pollution increases gradually, there is a possibility of permanent pollution (Ewers, 1991).

The results of previous studies on the pollution of the environment with PTEs do not show a favorable picture of North Macedonia. Thus, in our previous studies covering the whole territory of North Macedonia, soil contamination with some PTEs (As, Cd, Cu, Mn, Ni, Pb, Sb, Zn) was detected due to mining and metallurgical activities (Stafilov et al., 2010a, 2010b, 2013, 2018, 2019; Stafilov & Šajn, 2016, 2019; Balabanova et al., 2013; Bačeva et al., 2014; Serafimovski et al., 2018).

In this study, the spatial distribution of 18 chemical elements (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, and Zn) was determined in soils in the southeastern part of North Macedonia (Gevgelija, Valandovo, Bogdanci, and Dojran municipalities). For this purpose, 86 soil samples, including 43 samples of topsoil (0–5 cm) and 43 samples of subsoil (20–30 cm), were collected at a total of 43 sites with a grid of 5×5 km. Samples were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Element concentrations were statistically processed using multivariate factor analysis, and cluster analysis was performed to show relationships among chemical elements. The spatial distribution maps are provided for each element and the implications of these maps are discussed accordingly.

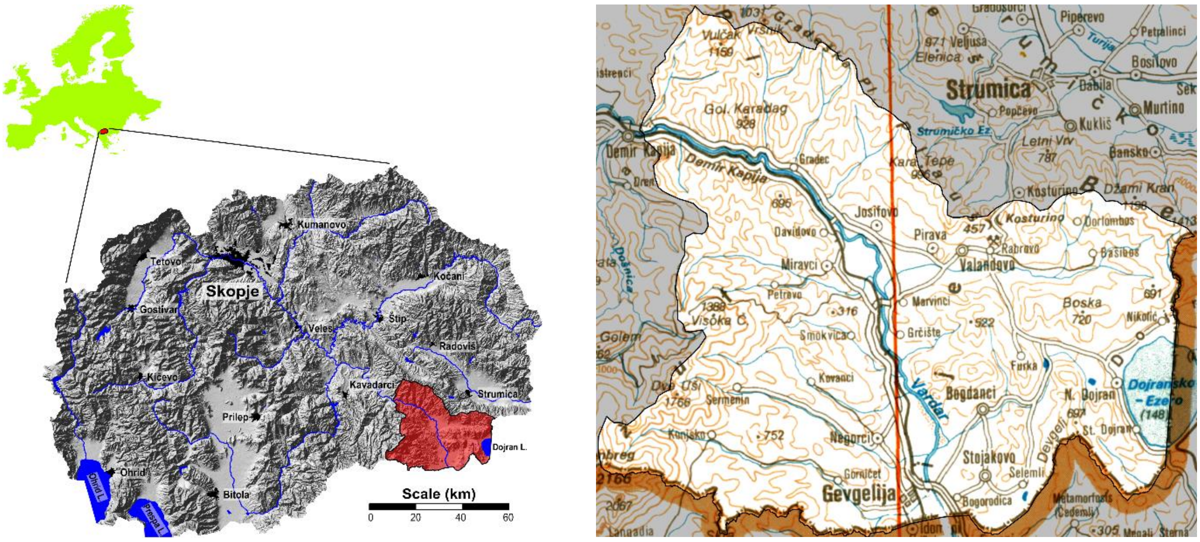
MATERIAL AND METHODS

Study area

The study area covers part of the southeastern region of North Macedonia, which includes the territory of the municipalities of Gevgelija, Valandovo, Bogdanci, and Dojran, with a total area of 1064 km^2.

The municipality of Gevgelija is located in the southeastern part of the country, bordering Greece and the municipalities of Bogdanci, Valandovo, Demir Kapija and Kavadarci (Figure 1). The municipality of Gevgelija covers an area of 485 km^2 and includes the town of Gevgelija and 16 villages (Figure 1) with a population of about 23,000 (Stojmilov & Apostolovska-Toševska, 2016).

In the north lies the municipality of Valandovo with an area of 331 km^2 and a population of about 12,000 inhabitants. Depending on the relief, the Valandovo municipality is divided into two parts: hilly-mountainous and lowland. The first one occupies 208 km^2 (63% of the territory), with the entire northern side surrounded by Plavuš Mt., the eastern side by Belasica Mt., and the southern side towards Pogana. The flat part occupies 123 km^2 (37%) and extends from the source of the Anska river at the foot of the Belasica Mt. along its entire course to the mouth of the Vardar river (Stojmilov & Apostolovska-Toševska, 2016). The average elevation of the municipality is 226 meters. Valandovo basin is located on geological and organic sediments. The Valandovo municipality is characterized by a Mediterranean climate with very hot days and mild winters, with average temperatures ranging from –5ºC to 35ºC. Annual precipitation ranges from 400 to 600 liters per square meter, most of which falls in the winter and spring months (Lazarevski, 1993).



a **b**

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

The territory of the Bogdanci municipality includes the southernmost part of North Macedonia, on the left side of the Vardar river. It covers an area of 117 km^2 and has 7400 inhabitants. The municipality consists of only four settlements, of which Bogdanci is the central place and the seat of the municipality. The other settlements are Stojakovo, Selemli, and Gjavato.

The municipality of Dojran with the Dojran Lake is located in the southeastern part of North Macedonia, about 170 km from the capital Skopje. The municipality has an area of 129 km^2 and 3080 inhabitants (Stojmilov & Apostolovska-Toševska, 2016). In the north of this natural lake extends the mountain of Belasica. The fact that this lowland opens to the south determines the Mediterranean climate, characterized by hot and dry summers and cool, humid winters. The lake itself and the pleasant climate allow the development of tourism in this municipality for most of the year.

In general, the morphological areas of these 4 municipalities are essentially flat and have very good soil quality, making them among the best agricultural areas in the country, especially for the production of early horticulture.

The climate in this region is strongly influenced by the Mediterranean climate due to the wide opening of the Vardar valley to the Thessaloniki valley (Aegean Sea). This influence is particularly pronounced in the part of the valley up to 300 m above sea level and has changed less in the hilly area up to 600 m above sea level. Mountain climate prevails only in the highest parts of the Kožuf Mountain. The most pronounced are the Vardarec and Jug (South) winds. The Vardarec come from the north and the south winds from the southeast (Lazarevski, 1993).

The study area is part of the Vardar tectonic zone (Arsovski, 1997; Blažev & Arsovski, 2001; Stafilov & Šajn, 2016, 2019; Petrušev et al., 2021). Among the geological formations, the Mesozoic mafic volcanites and plutonites are the most widespread on the Kožuf Mt. in the western part, followed by the Quaternary alluvial sediments along the Vardar river, Anska river, and near Lake Dojran, the Proterozoic gneisses and Mesozoic felsic plutonites (in the central part), and the Paleozoic shale carbonates and felsic volcanites in the eastern part of the region (Figure 2).

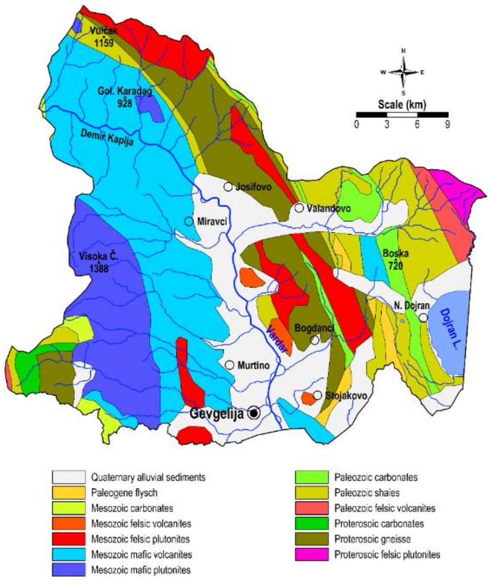


Fig. 2. The main geological units of the study area

SAMPLING AND SAMPLE PREPARATION

Soil samples were collected according to the European guidelines and also according to our experience (Stafilov et al., 2010a, 2010b; Stafilov & Šajn, 2016, 2019). The study area was covered by the same sampling grid of 5×5 km (Figure 3). A total of 86 soil samples were collected from two layers: 43 topsoil samples (0–5 cm) and 43 subsoil samples (20–30 cm). The humus layer was removed. To obtain representative composite samples, five subsamples were collected from each location (the corners and the centre) on a 10×10 m square plot. The soil samples were cleaned of plant material and stones and then homogenized and dried. They were then passed through a 2 mm sieve and ground in a porcelain mortar until they had a particle size of less than 125 μm. To complete the digestion of the soil samples, an open wet digestion was performed using a mixture of 4 acids (HNO_3, HF, $HClO_4$, and HCl) according to ISO Standard 14869–1:2001 (ISO, 2001).

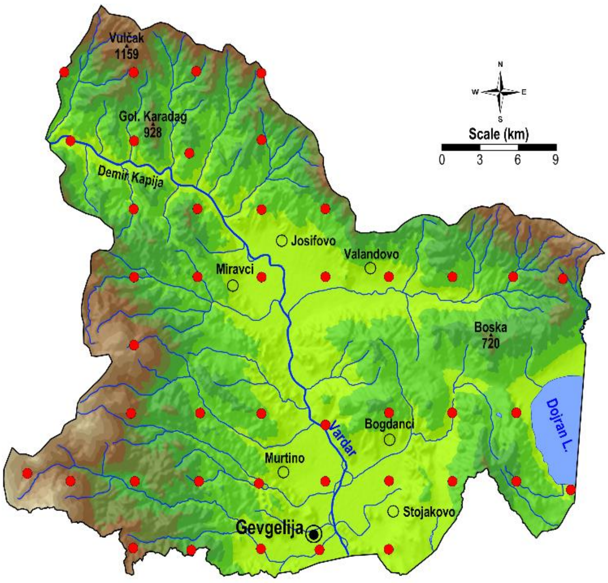


Fig. 3. Study area with sampling locations

Instrumentation

All samples were analyzed by ICP-AES (Varian, model 715-ES) for the following 21 elements: Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, and Zn (Balabanova et al., 2010). The values for As, Cd, and Co were below the detection limit and were not considered further. Quality control was performed by the standard addition method, and recoveries ranged from 98.0% to 102%. Quality control was also performed by analyzing certified reference samples of soil and geology: Soil sample JSAC 0401 (The Japan Society for Analytical Chemistry) and rock samples CRM undersaturated igneous rock SARM 3 NIM-L Lujaurite (SA Bureau of Standards, Pretoria, S. Africa) and NCS DC71306 (GBW07114) (China National Analysis Centre). The values obtained were within the standard deviation of the certified reference materials.

Data processing

Data analysis and map generation were performed using Statistica (ver. 13), Autodesk Map (ver. 2008), QGIS (ver. 3.10), and Surfer (ver. 13) programmes. Parametric and non-parametric statistical methods were used for data analysis. Box-Cox transformations were used to obtain normal distributions. Multivariate R-mode factor analyzis was used to reveal relationships among chemical elements. Factor analysis (FA) derives a smaller number of new, synthetic variables from numerous variables (Reimann et al., 2002). The universal Kriging method with linear variogram interpolation was used to construct the spatial distribution maps of the analyzed elements and the obtained factor values. Seven classes were selected with the following percentile values: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90, and 90–100.

RESULTS AND DISCUSSION

Descriptive statistics for the content of analyzed elements in topsoil and subsoil samples (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, and Zn) are presented in Tables 1 and 2. The values for Al, Ca, Fe, K, Mg and Na are given in %, while the values for the content of the other elements are given in mg/kg. The concentration ratios (FO) of the average contents (Box-Cox transformed) in topsoil and subsoil are shown in Table 3. It can be seen that the ratio is close to 1 for almost all elements, which means that there are no more significant differences in the content of the analyzed elements in the topsoil and subsoil layers. The data from the *T*, *F* and *R* tests also show that the differences are not significant. A comparative analysis of the contents of the analyzed elements in topsoils from the study area and soils from Macedonia (Mihajlov et al., 2016; Stafilov & Šajn, 2016) and

Europe (Salminen et al. 2005) is presented in Table 4. It was found that the contents of many elements in the soils of the study area differ from those in Macedonian soils and also from those in European soils. Thus, the median contents of Al, Ca, Cr, Cu, and Zn in the soils of the study area are higher than in Macedonian soils, while the contents of Ba, K, Li and Sr are lower. Similar information is obtained when comparing the contents of the analyzed elements in the soils of the study area and the European soils. Characteristics are the increased contents of Al, Ca, Cr, Cu, Mg, Mn, Na, Ni, and Zn and the lower values of Ba, K, and Sr. These differences are mainly due to the lithological peculiarities of the study area (Mesozoic volcanites and plutonites of the Kožuf Mt. and the western part of the Vardar river are enriched with the above-mentioned elements).

The degree of correlation is determined by the bivariate statistics, i.e. by the mutual relationship between the content of the analyzed elements in the soil samples. It is known that the absolute value of the correlation coefficient from 0.3 to 0.7 gives a good association, and between 0.7 and 1.0 indicates a strong correlation of the elements (Reimann et al., 2002). The content values of each element were compared with the content values of all other elements. For a better overview, all elements were presented in a matrix with the correlation coefficients of the elements (Table 5).

Factor analysis reduced the data to three variables (Table 6): Factor 1 (F1), which includes Fe, V, Mn, Cu, Ni, Zn, and Pb; Factor 2 (F2), which includes Ba, Li, and K; and Factor 3, which includes Mg, Al, Ca, Sr. Of the total 18 elements analyzed, the factor analysis reduces to 14, which have an overall utility of 76.5% (Table 6). The other elements (Ag, As, Na, and P) are eliminated as elements that do not contribute to the community.

The cluster grouping of the elements in the dendrogram is shown in Figure 4. In the dendrogram, the elements are divided into clusters according to their degree of correlation. The first cluster is composed of the elements Al, Ca, Mg, and Sr. These are the elements that form factor 3 of the loading matrix of the dominant rotation factors (Table 6). The second cluster is composed of the elements Cu, Ni, Fe, V, Mn, Pb, and Zn, which otherwise belong to factor 1 of the loading matrix of the dominant rotating factors (Table 6). The third cluster is composed of the elements: Ba, Li and K, which have an identical composition to factor 2 (Table 6).

Table 1

Descriptive statistics for the content of the elements in topsoil (0–5 cm), N=43

Element	Unit	X	$X_{(BC)}$	Md	Min	Max	P_{25}	P_{75}	P_{10}	P_{90}	S	S_x	CV	A	E	$A_{(BC)}$	$E_{(BC)}$
Ag	mg/kg	0.87	0.78	0.83	0.10	3.3	0.59	1.1	0.30	1.2	0.55	0.084	63	2.17	8.25	–0.09	1.85
Al	%	3.6	3.4	3.4	1.3	6.9	2.2	5.0	1.8	5.6	1.5	0.24	43	0.36	–0.93	0.07	–1.05
Ba	mg/kg	140	110	100	20	350	70	210	37	260	92	14	68	0.81	–0.34	0.05	–0.92
Ca	%	1.8	1.3	1.1	0.035	5.0	0.55	2.9	0.28	4.1	1.5	0.23	86	0.85	–0.68	–0.13	–0.66
Cr	mg/kg	120	75	77	24	800	50	100	34	150	160	24	140	3.96	15.71	0.13	0.88
Cu	mg/kg	37	29	33	7.9	110	19	45	13	62	25	3.8	68	1.27	1.27	–0.23	–0.56
Fe	%	2.9	2.8	2.9	1.1	6.0	2.1	3.6	1.6	4.0	1.0	0.16	36	0.41	0.49	–0.07	–0.14
K	%	1.0	0.85	1.1	0.075	3.1	0.33	1.6	0.23	2.1	0.82	0.12	78	0.82	–0.06	0.10	–1.09
Li	mg/kg	9.1	7.5	7.8	0.47	36	4.6	11	3.2	17	7.3	1.1	80	2.10	5.40	0.20	0.99
Mg	%	1.0	0.73	0.87	0.037	3.7	0.44	1.5	0.15	2.3	0.90	0.14	89	1.41	1.76	–0.15	–0.41
Mn	mg/kg	550	550	580	70	1100	410	730	230	800	230	35	42	–0.10	–0.14	–0.31	–0.05
Na	%	0.78	0.75	0.80	0.025	1.5	0.42	1.2	0.18	1.4	0.45	0.068	58	–0.05	–1.18	–0.29	–0.96
Ni	mg/kg	52	32	36	4.7	340	19	59	12	72	65	9.9	130	3.60	13.90	–0.34	0.65
P	mg/kg	460	370	400	51	2700	270	610	100	700	410	62	88	3.78	19.71	–0.08	1.14
Pb	mg/kg	16	13	17	1.5	48	4.6	23	1.5	31	11	1.7	72	0.56	–0.02	–0.38	–0.98
Sr	mg/kg	59	53	64	2.1	140	27	85	12	100	35	5.3	59	0.29	–0.60	–0.31	–0.68
V	mg/kg	85	74	81	16	210	46	110	34	150	47	7.2	55	0.79	0.25	–0.28	–0.40
Zn	mg/kg	94	76	78	32	460	59	90	44	140	73	11	78	3.68	15.70	0.33	1.00

N – number of samples; X – arithmetical average; $X_{(BC)}$ – 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; $A_{(BC)}$ – skewness of Box-Cox transformed values; $E_{(BC)}$ – kurtosis of Box-Cox transformations

Table 2

Descriptive statistics for the content of the elements in subsoil (20–30 cm); N=43

Element	Unit	X	$X_{(BC)}$	Md	Min	Max	P_{25}	P_{75}	P_{10}	P_{90}	S	S_x	CV	A	E	$A_{(BC)}$	$E_{(BC)}$
Ag	mg/kg	0.89	0.77	0.75	0.10	3.1	0.42	1.2	0.22	1.9	0.62	0.094	69	1.41	2.82	0.11	0.04
Al	%	3.5	3.3	3.6	1.1	7.2	1.6	4.9	1.4	5.6	1.7	0.26	48	0.10	–1.08	–0.20	–1.23
Ba	mg/kg	130	110	110	15	310	59	210	31	270	92	14	68	0.56	–1.02	–0.16	–0.95
Ca	%	1.7	1.2	1.2	0.047	5.0	0.55	2.2	0.22	4.3	1.5	0.23	89	1.03	–0.10	–0.01	–0.78
Cr	mg/kg	120	74	75	16	960	52	130	36	170	180	28	150	3.93	15.68	–0.21	1.34
Cu	mg/kg	37	28	29	9.9	170	17	49	11	58	30	4.6	83	2.62	9.16	0.26	–0.42
Fe	%	3.0	2.8	2.9	0.92	5.7	1.9	4.0	1.5	4.4	1.2	0.18	40	0.23	–0.85	–0.07	–0.98
K	%	1.1	0.87	1.0	0.047	2.8	0.25	1.6	0.15	2.0	0.76	0.12	71	0.36	–0.68	–0.39	–1.01
Li	mg/kg	9.1	7.4	6.6	0.37	33	5.3	11	1.7	21	7.0	1.1	77	1.58	2.70	–0.10	0.56
Mg	%	0.97	0.62	0.62	0.013	4.4	0.22	1.3	0.095	2.4	1.1	0.16	110	1.81	2.83	0.08	–0.31
Mn	mg/kg	550	540	600	130	1300	270	730	220	760	260	40	48	0.23	0.05	0.04	–0.28
Na	%	0.82	0.80	0.79	0.054	1.6	0.51	1.2	0.36	1.3	0.39	0.060	48	0.14	–0.89	–0.07	–0.76
Ni	mg/kg	56	32	32	7.9	440	17	57	12	88	85	13	150	3.90	15.64	0.35	0.20
P	mg/kg	410	300	320	33	2600	150	500	97	800	420	64	100	3.61	18.01	0.15	0.39
Pb	mg/kg	15	11	13	1.5	50	3.8	20	1.5	38	14	2.1	89	1.13	0.57	0.05	–0.90
Sr	mg/kg	59	53	50	1.9	150	25	83	19	110	40	6.1	67	0.71	–0.28	0.04	–0.57
V	mg/kg	86	74	74	24	230	45	110	29	180	52	7.9	61	1.01	0.21	0.22	–0.85
Zn	mg/kg	89	71	70	28	290	52	97	43	160	59	9.0	66	2.07	4.42	–0.17	0.02

N – number of samples; X – arithmetical average; $X_{(BC)}$ – 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; $A_{(BC)}$ – skewness of Box-Cox transformed values; $E_{(BC)}$ – kurtosis of Box-Cox transformations

Table 3

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
Ag	mg/kg	0.78	0.77	1.01	0.05	NS	1.25	NS*	0.72	*
Al	%	3.4	3.3	1.03	0.33	NS	1.33	NS	0.40	*
Ba	mg/kg	110	110	1.02	0.13	NS	1.13	NS	0.72	*
Ca	%	1.3	1.2	1.06	0.28	NS	1.05	NS	0.73	*
Cr	mg/kg	75	74	1.01	0.07	NS	1.25	NS	0.79	*
Cu	mg/kg	29	28	1.05	0.30	NS	1.02	NS	0.76	*
Fe	%	2.8	2.8	0.98	-0.23	NS	1.27	NS	0.81	*
K	%	0.85	0.87	0.98	-0.12	NS	1.08	NS	0.82	*
Li	mg/kg	7.5	7.4	1.01	0.07	NS	1.08	NS	0.73	*
Mg	%	0.73	0.62	1.18	0.69	NS	1.29	NS	0.68	*
Mn	mg/kg	550	540	1.01	0.11	NS	1.26	NS	0.62	*
Na	%	0.75	0.80	0.94	-0.54	NS	1.40	NS	0.66	*
Ni	mg/kg	32	32	0.99	-0.04	NS	1.09	NS	0.88	*
P	mg/kg	370	300	1.21	1.09	NS	1.24	NS	0.75	*
Pb	mg/kg	13	11	1.12	0.52	NS	1.19	NS	0.59	*
Sr	mg/kg	53	53	1.01	0.06	NS	1.17	NS	0.58	*
V	mg/kg	74	74	1.00	0.02	NS	1.02	NS	0.68	*
Zn	mg/kg	76	71	1.07	0.65	NS	1.43	NS	0.52	*

*NS – not significant

Table 4

Comparison of the median, minimum and maximum values of the content of the analyzed elements in topsoil and subsoil from the study area, North Macedonia, and Europe

Element	Unit	Study area				North Macedonia (Mihajlov et al., 2016; Stafilov & Šajn, 2016)				Europe (Salminen et al., 2005)			
		Topsoil		Subsoil		Topsoil		Subsoil		Topsoil		Subsoil	
		Md	Min–Max	Md	Min–Max	Md	Min–Max	Md	Min–Max	Md	Min–Max	Md	Min–Max
Ag	mg/kg	0.83	0.1–3.3	0.75	0.1–3.1	–	–	–	–	0.27	0.01–3.15	0.25	0.02–2.07
Al	%	3.4	1.3–6.9	3.6	1.1–7.2	2.2	0.79–4.3	2.3	0.77–5.1	0.58	0.20–1.42	0.62	0.11–1.43
Ba	mg/kg	100	20–350	110	15–310	420	41–1600	440	66–1700	375	30–1870	385	13–2050
Ca	%	1.1	0.035–5.0	1.2	0.047–5.0	0.79	0.092–21.0	0.78	0.10–21.0	0.66	0.02–34.3	0.81	0.17–37.1
Cr	mg/kg	77	24–800	75	16–960	54	11–600	63	11–600	60	<3–6230	62	<3–2140
Cu	mg/kg	33	7.9–110	29	9.9–170	16	1.7–73	16	3.2–78	13	0.81–256	13.9	0.86–125
Fe	%	2.9	1.1–6.0	2.9	0.92–5.7	2.5	0.63–6.7	2.7	0.77–8.0	2.46	1.12–15.6	2.62	0.077–10.9
K	%	1.1	0.075–3.1	1.0	0.047–2.8	1.4	0.26–3.2	1.5	0.52–3.3	1.6	0.02–5.1	1.7	<0.01–5.0
Li	mg/kg	7.8	0.47–36	6.6	0.37–33	18	4.8–79	20	5.2–69	–	–	–	–
Mg	%	0.87	0.037–3.7	0.62	0.013–4.4	0.66	0.11–2.9	0.73	0.15–3.1	0.47	<0.006–15.0	0.60	<0.006–11.4
Mn	mg/kg	580	70–1100	600	130–1300	620	160–3200	640	99–4300	507	31–6068	468	23–4710
Na	%	0.80	0.025–1.5	0.79	0.054–1.6	0.85	0.033–2.3	0.94	0.078–2.4	0.6	0.03–3.3	0.6	0.02–3.5
Ni	mg/kg	36	4.7–340	32	7.9–440	35	2.5–530	37	5.2–530	18	<2–2690	21.8	<2–2400
P	mg/kg	400	51–2700	320	33–2600	450	120–1400	430	74–1300	560	48–5770	420	30–7250
Pb	mg/kg	17	1.5–48	13	1.5–50	17	2.5–700	14	0.8–660	10	5.32–970	17.2	<3–938
Sr	mg/kg	64	2.1–140	50	1.9–150	71	9.4–540	68	9.9–580	89	8–3120	95	6–2010
V	mg/kg	81	16–210	74	24–230	67	14–300	71	19–370	60	2.71–537	62.8	1.28–325
Zn	mg/kg	78	32–460	70	28–290	39	3.1–440	38	4.4–490	52	<3–2900	47	<3–3060

Md – median; Min – minimum; Max – maximum

Table 5

Matrix of correlation coefficients of the elements for topsoil and subsoils (N=86)

Element	Ag	Al	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	Sr	V	Zn
Ag	1.00																	
Al	-0.01	1.00																
Ba	0.28	0.11	1.00															
Ca	0.20	**0.58**	0.00	1.00														
Cr	0.08	0.32	-0.05	0.20	1.00													
Cu	0.23	0.37	0.01	**0.70**	0.37	1.00												
Fe	0.18	0.32	-0.09	**0.60**	0.11	**0.68**	1.00											
K	0.20	-0.15	**0.63**	**-0.58**	-0.01	-0.40	-0.46	1.00										
Li	0.15	0.16	**0.65**	-0.10	0.01	-0.01	-0.13	**0.63**	1.00									
Mg	0.17	**0.56**	0.05	**0.84**	0.10	**0.62**	**0.57**	**-0.52**	0.02	1.00								
Mn	0.18	0.32	0.25	**0.55**	0.12	**0.65**	**0.75**	-0.30	0.10	**0.55**	1.00							
Na	0.35	0.17	**0.56**	0.11	0.01	-0.04	0.00	0.39	0.11	0.06	0.02	1.00						
Ni	0.15	0.38	-0.01	**0.70**	0.45	**0.87**	0.65	**-0.50**	0.00	**0.69**	**0.65**	-0.15	1.00					
P	0.29	-0.09	**0.51**	0.20	-0.22	0.19	0.27	0.21	0.18	0.05	0.40	0.33	0.08	1.00				
Pb	0.27	0.13	0.45	0.36	-0.03	0.44	0.34	0.11	0.45	0.36	**0.55**	0.09	0.35	0.41	1.00			
Sr	0.17	**0.52**	**0.52**	**0.72**	-0.08	0.41	0.47	-0.10	0.21	**0.64**	**0.52**	**0.51**	0.36	0.42	0.45	1.00		
V	0.21	0.10	-0.13	**0.52**	0.15	**0.65**	**0.88**	-0.43	-0.31	0.39	**0.61**	0.10	**0.54**	0.28	0.24	0.38	1.00	
Zn	0.23	0.30	0.35	0.33	0.08	**0.50**	0.49	0.14	0.30	0.30	**0.58**	0.12	0.39	0.44	0.57	0.43	0.34	1.00

Values in the range 0.3–0.5 (good association) are underlined and in the range 0.5–1.0 (strong association) are bolded; Box-Cox transformed values used.

Table 6

Matrix of dominant rotated factor loadings

Element	F1	F2	F3	Comm
Fe	**0.86**	–0.13	0.27	83.7
V	**0.86**	–0.24	0.08	80.3
Mn	**0.80**	0.19	0.29	77.0
Cu	**0.77**	–0.03	0.41	75.9
Ni	**0.67**	–0.10	0.50	71.2
Zn	**0.62**	0.50	0.12	65.0
Ba	0.00	**0.88**	0.12	79.4
Li	–0.10	**0.85**	0.09	74.2
K	–0.34	**0.77**	–0.39	86.4
Pb	0.50	**0.61**	0.15	64.8
Mg	0.40	–0.06	**0.82**	83.7
Al	0.03	0.12	**0.82**	68.5
Ca	0.47	–0.12	**0.81**	89.4
Sr	0.33	0.37	**0.69**	71.6
Prp.Totl	31.9	21.3	23.4	76.5
Eingen.Val	6.39	2.98	1.35	
Expl.var	4.46	2.98	3.27	

Bold values signify the factor values for the elements belonging to the corresponding factor.
F1, F2 and F3 – Factor loadings of Factors 1, 2 and 3; Comm – Communality (%),
Prp. Totl – Total amount of the explained system variance;
Expl. Var – Particular component variance; Eigen Val – Eingene value

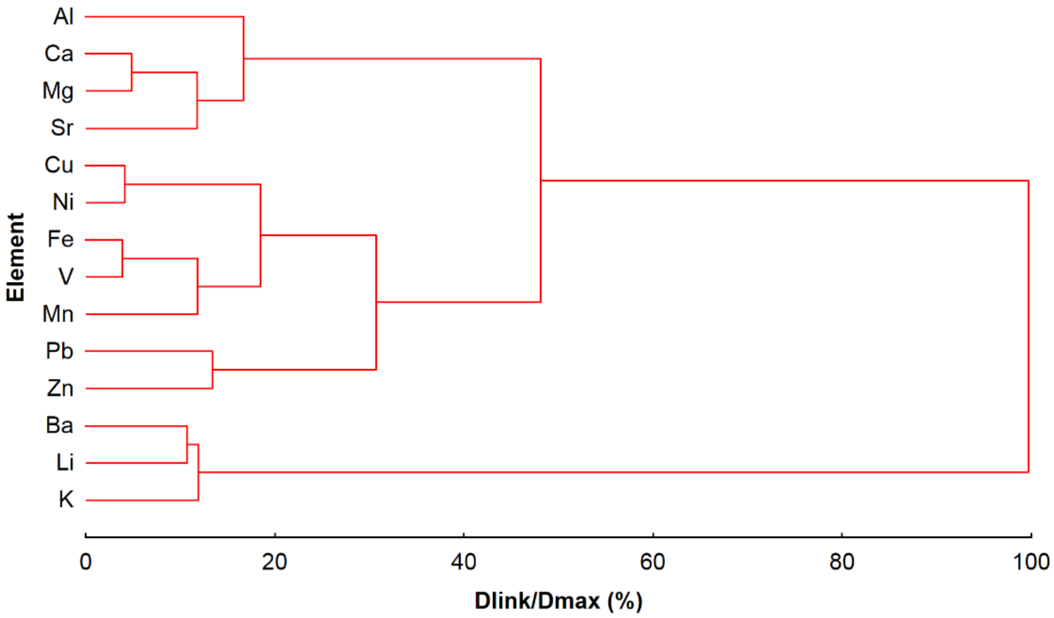


Fig. 4. Dendrogram from cluster analysis

The spatial distribution maps of factor score values of **Factor 1** for topsoil and subsoil and the spatial distribution of the contents of each element belonging to this factor (Fe, V, Mn, Cu, Ni, Zn, and Pb) are shown in Figure 5. The spatial distribution of these elements in the soil corresponds to the geological composition of the studied region. The increased content of these elements occurs in the soils from the gorge of Demir Kapija through the flat part of Valandovo Valley to the town of Gevgelija. From the distribution map it is evident that the elements of Factor 1 occur mainly in soils dominated by Mesozoic volcanic rocks, Quaternary alluvial sediments and Proterozoic gneisses and Paleozoic shales. From the results in Table 5, the values for the contents of these elements in topsoils and subsoils are very similar, indicating their lithogenic origin.

Tables 1 and 2 show that the iron content in the topsoil ranges from 1.1% to 6.0% with a median of 2.9%, while in the subsoil it ranges from 0.92% to 5.7% with a median of 2.9%. When comparing with the values for iron in Europe, it can be observed that the median of the determined values for iron in both topsoil (2.9%) and subsoil (2.9%) in the studied region is higher than the median of the determined values in Europe, which is 2.4% (Table 4). The median for the topsoil and subsoil of iron in the studied area is higher than the median of this element in the soils of N. Macedonia, while the highest determined values in both layers in the study area are lower than the Fe content in the soils from the whole area of North Macedonia. The spatial distribution of Fe in both layers is shown in Figure 5. The highest values of Fe content in both soil layers are found in the soils from the southern part of the Demir Kapija gorge, where Mesozoic mafic volcanic rocks predominate. Higher Fe contents were also found in the soils from the area of the Gevgelija town and Kožuf Mt., where Mesozoic mafic volcanic rocks predominate, and in the areas along the Vardar river and around Lake Dojran, where Quaternary alluvial sediments predominate. In the soils from the area where Mesozoic mafic plutonites and Paleozoic shales and carbonates dominate, the Fe content is lower.

The values of vanadium content in the topsoil samples range from 16 mg/kg to 210 mg/kg with a median of 81 mg/kg, and in the subsoil these values range from 24 mg/kg to 230 mg/kg with a median of 74 mg/kg. The values of manganese content in the topsoil samples range from 70 mg/kg to 1100 mg/kg with a median of 580 mg/kg and in the subsoil from 130 mg/kg to 1300 mg/kg with a median of 600 mg/kg. It was found that the median values for vanadium and manganese in both soil layers of the study area are higher compared to the soils in Europe. Compared to the soils in Macedonia, the median value for the soils of the study area is higher for V and lower for Mn than in the soils of the whole country. The spatial distribution of vanadium and manganese (Figure 5) is very similar to the distribution of iron with the highest contents in the two soil layers in the southern part of the Demir Kapija gorge and in the area of the town of Gevgelija and Kožuf Mt., where Mesozoic mafic volcanic rocks predominate. Higher contents were also found in the area along the Vardar river and near Dojran Lake, where Quaternary alluvial sediments predominate.

The values for copper content in the topsoil samples range from 7.9 mg/kg to 110 mg/kg with a median of 33 mg/kg and in the subsoil these values range from 9.9 mg/kg to 170 mg/kg with a median of 29 mg/kg. The values for nickel content in the topsoil samples range from 4.7 mg/kg to 340 mg/kg with a median value of 36 mg/kg and in the subsoil from 7.9 mg/kg to 440 mg/kg with a median value of 32 mg/kg. Figure 5 shows that the spatial distribution of copper and nickel is very similar. The highest values for copper and nickel were found in both soil layers from the contents in the topsoil and subsoil in the southwestern part of the study area along the Konjska river on Kožuf Mt. (Konjsko and Sermenin villages), where Mesozoic mafic volcanic rocks and plutonites predominate, and in the western part of the Gevgelija Valley (Gevgelija town, Negorci village), in the Valandovo Valley and at Dojran Lake, where Quaternary alluvial sediments predominate.

The distribution of lead and zinc in the soils of the study area is very similar. Values for zinc content in the topsoil samples range from 32 mg/kg to 460 mg/kg with a median of 78 mg/kg and in the subsoils these values range from 28 mg/kg to 290 mg/kg with a median of 70 mg/kg. Lead content values in the topsoil samples range from 1.5 mg/kg to 48 mg/kg with a median of 17 mg/kg and in the subsoil range from 1.5 mg/kg to 50 mg/kg with a median of 13 mg/kg. The spatial distribution of lead and zinc content in both soil layers is shown in Figure 5. The highest zinc content in the topsoil was found in the soils of the areas dominated by Mesozoic felsic plutonites and Proterozoic gneisses (Gradeška mountain and the town of Valandovo in the northern part of the study area), as well as in the area around Dojran Lake, where Paleozoic shales and carbonates and Quaternary alluvial sediments predominate.

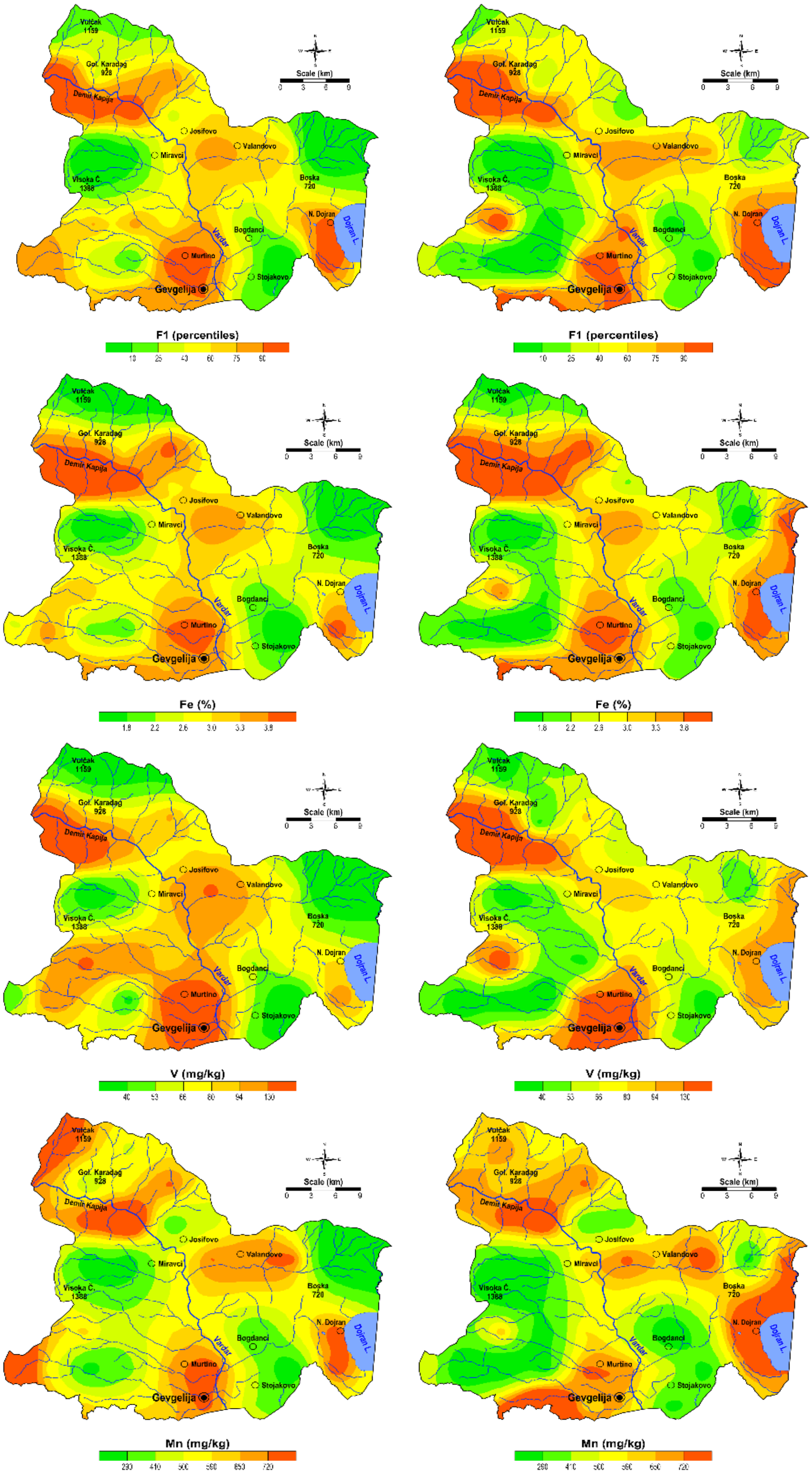
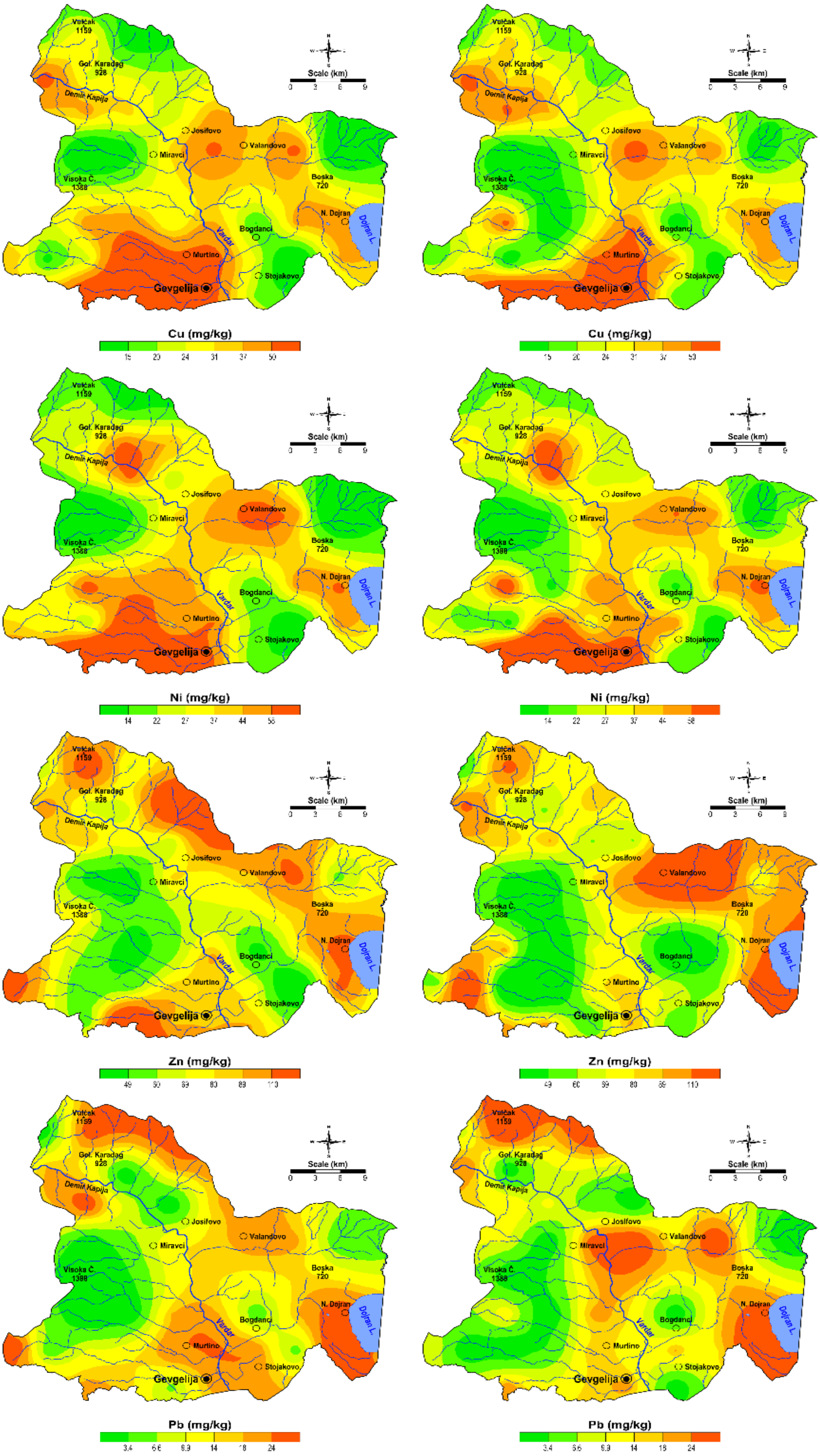

Vučak 1159
Gol. Karadag 928
Demir Kapija
Josifovo
Valandovo
Miravci
Visoka Č. 1388
Boska 720
N. Dojran
Dojran L.
Bogdanci
Vardar
Murtino
Stojakovo
Gevgelija
Scale (km)
0 3 6 9
F1 (percentiles)
10 25 40 60 75 90
Fe (%)
1.8 2.2 2.6 3.0 3.3 3.8
V (mg/kg)
40 53 66 80 94 130
Mn (mg/kg)
290 410 500 590 650 720

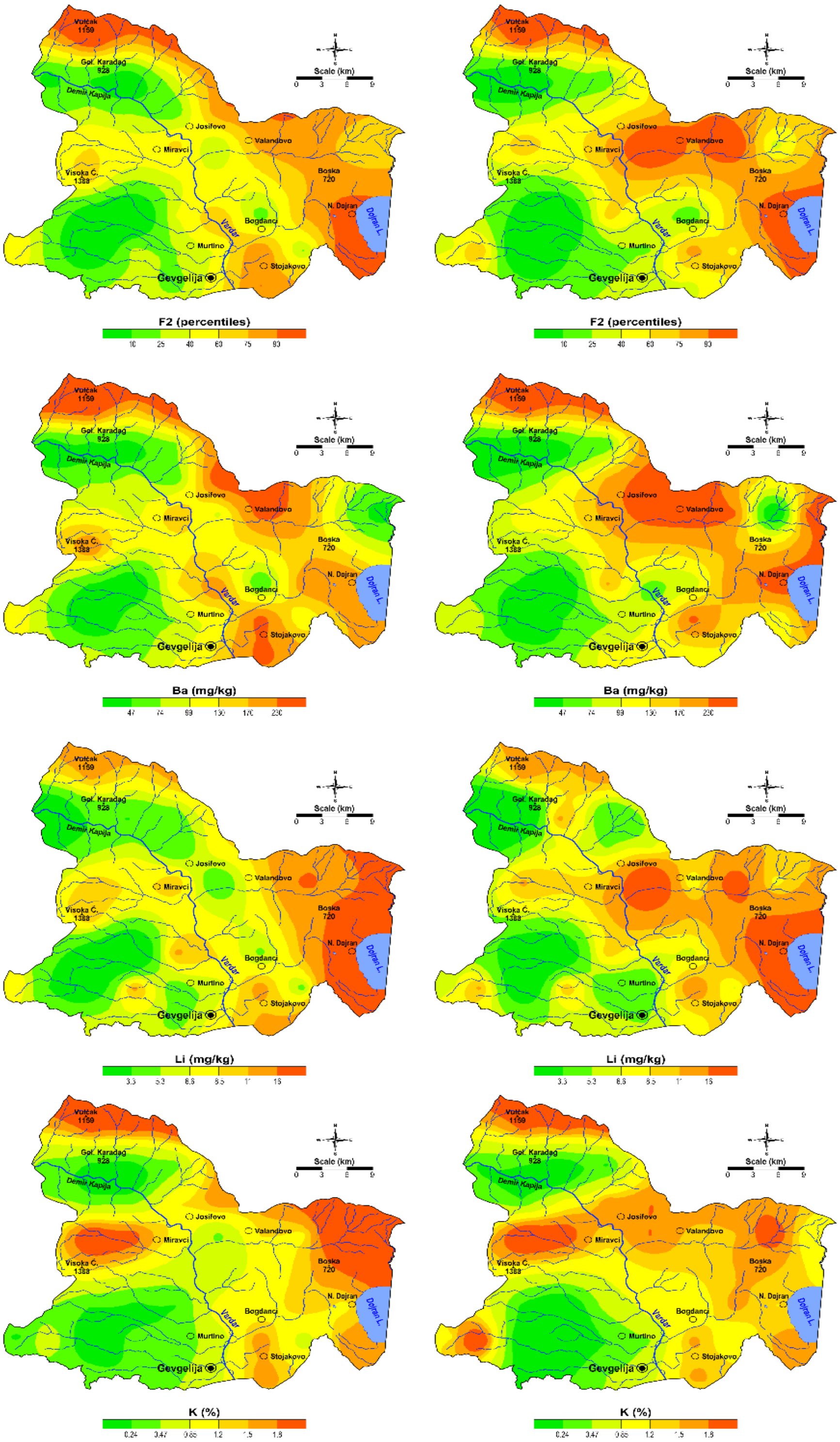
Fig. 5.



a b

Fig. 5. Spatial distribution of factor scores and of the content of the elements in topsoil (a) and subsoil (b) from the Factor 1 (Fe, V, Mn, Cu, Ni, Zn и Pb)

Factor 2 (Ba, Li, and K) is also a geogenic association. The spatial distribution maps of the factor values and the content of the elements contained in this factor in both topsoil and subsoil are shown in Figure 6. From the distribution maps, it can be generally concluded that the content of these elements is higher in soils from the northern (where Mesozoic felsic plutonites dominate) and eastern parts (where Proterozoic gneisses and Paleozoic shales dominate) of the area. The highest Li content is also found in the soils from the area around Dojran Lake in the southeastern part of the study area, where Quaternary alluvial sediments and Paleozoic shales and carbonates dominate.



a **b**

Fig. 6. Spatial distribution of factor scores and of the content of the elements in topsoil (a) and subsoil (b) from the Factor 2 (Ba, Li and K)

Barium levels in topsoil range from 20 mg/kg to 350 mg/kg with a median of 100 mg/kg, while levels in subsoil range from 15 mg/kg to 310 mg/kg with a median of 110 mg/kg. The highest barium content in the soil is found in the areas of the Gradeška Mt. and the town of Valandovo (in the northern part of the study area), where Mesozoic felsic plutonites and Proterozoic gneisses predominate. Lithium values in topsoil range from 0.47 mg/kg to 36 mg/kg with a median of 7.8 mg/kg, while values in the subsoil range from 0.37 mg/kg to 33 mg/kg with a median of 6.6 mg/kg. The highest lithium content was determined in the soil of the Star Dojran village (Dojran Lake) in the southeastern part of the study area, where Quaternary alluvial sediments and Paleozoic shales and carbonates predominate. Potassium content in topsoil ranged from 0.075% to 3.1% with a median of 1.1%, while values for the subsoil ranged from 0.047% to 5.0% with a median of 1.1%. The highest potassium content was determined in the soils of the western part of the Belasica Mt., where Paleozoic shales and Mesozoic and Proterozoic felsic volcanic rocks predominate.

The spatial distribution of factor values of **Factor 3** is shown in Figure 7. The elements Al, Ca, Mg, and Sr are included in this association. From the distribution map (Figure 7), it can be seen that the elements of Factor 3 also represent the lithogenic association. These elements belong to the group of lithophilic elements that occur naturally in the Earth's crust. They occur in soils with geological formations such as: Quaternary alluvial sediments, Paleozoic carbonates and shales, and Mesozoic mafic plutonites. The highest contents of these elements are found in the valleys of Gevgelija and Valandovo and in the area of the Demir Kapija gorge.

The values for aluminum in the topsoil samples range from 1.3% to 6.9% with a median of 3.4% and in the subsoil from 1.1% to 7.2% with a median of 3.6%. The median value for aluminum in the topsoils and subsoils of the Gevgelija-Valandovo region is lower compared to the soils in Europe. The spatial distribution of this element is shown in Figure 7. The highest value for aluminum content in topsoil and subsoil was determined in the soil collected near the village of Novo Konjsko in the Kožuf Mt. (Gevgelija municipality), where Mesozoic mafic plutonites predominate.

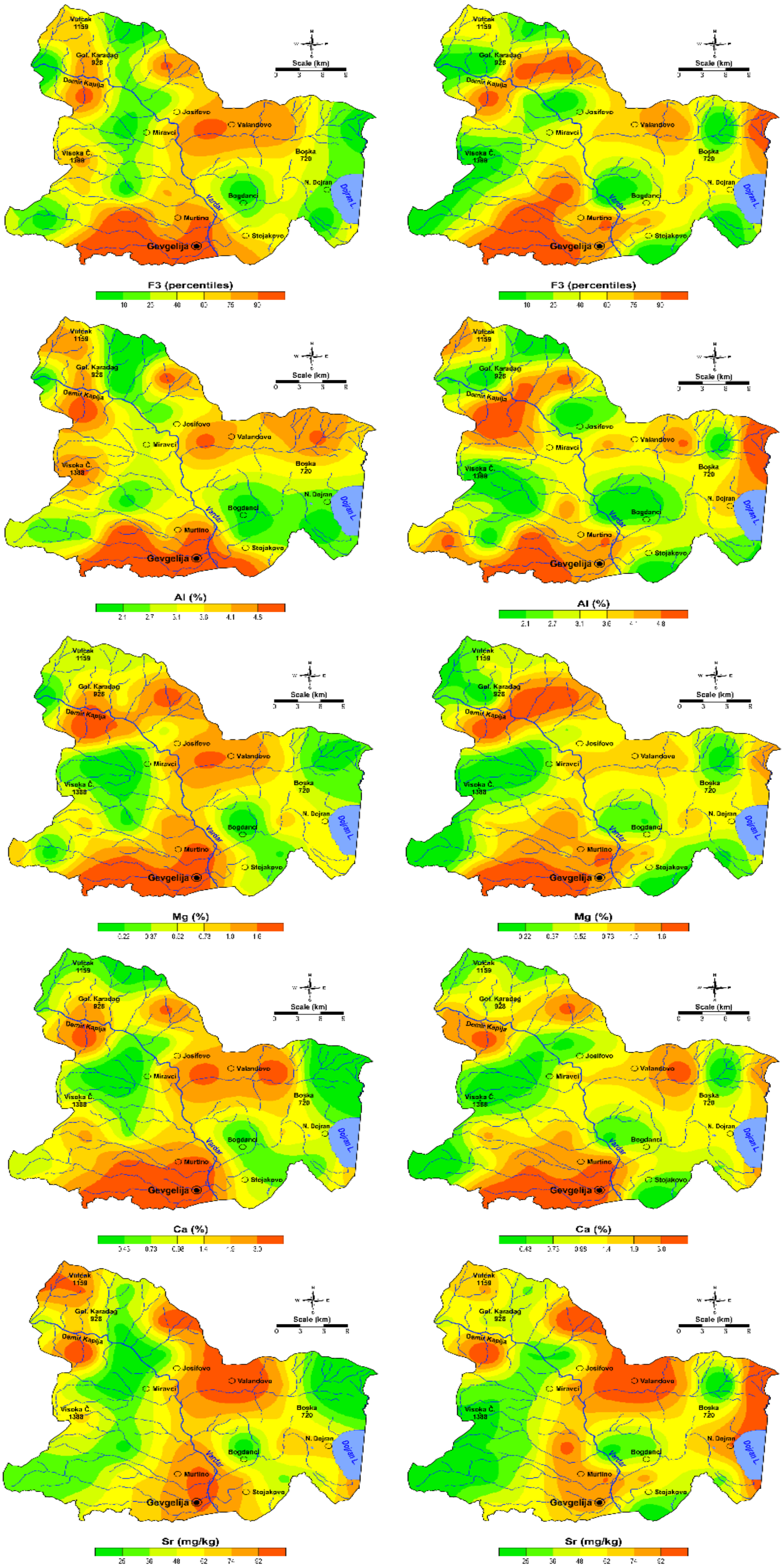
Magnesium content in the topsoil samples ranges from 0.037% to 3.7% with a median of 0.87% and in the subsoils from 0.013% to 4.4% with a median of 0.62%. The magnesium content is higher in the soils in the Demir Kapija Gorge area (Figure 7) and is most likely due to the presence of the granitoid formation, where the minerals dolomite and amphibole predominate. The highest value of the content of this element in the topsoil was determined in the soil of the Novo Konjsko village on the mountain of Kožuf.

The values of calcium content in the topsoil samples range from 0.035% to 5.0% with a median of 1.1%, and in the subsoils these values range from 0.047% to 5.0% with a median of 1.2%. The highest value of the content of this element in the topsoil and subsoil was determined in the soil of the Kožuf mountain in the southwestern part of the study (Gevgelija municipality). Higher calcium contents were also found in the valleys of Gevgelija and Valandovo, where Quaternary alluvium sediments predominate. Strontium content values in topsoil samples range from 2.1 mg/kg to 140 mg/kg with a median of 64 mg/kg, and in subsoils these values range from 1.9 mg/kg to 150 mg/kg with a median of 50 mg/kg. The distribution of strontium content is similar to that of Ca and Mg, except for its high content in the subsoils of the Belasica mountain, where Paleozoic shales and vulcanites and Proterozoic felsic plutonites predominate.

Of the total 18 elements analyzed, the factor analysis reduces to 14, which have a total share of 76.5% in the benefit (Table 6). The other elements (Ag, Cr, Na, and P) are eliminated as elements that do not contribute to the community. The spatial distribution of the content of these elements in the topsoil and subsoil samples is shown in Figure 8.

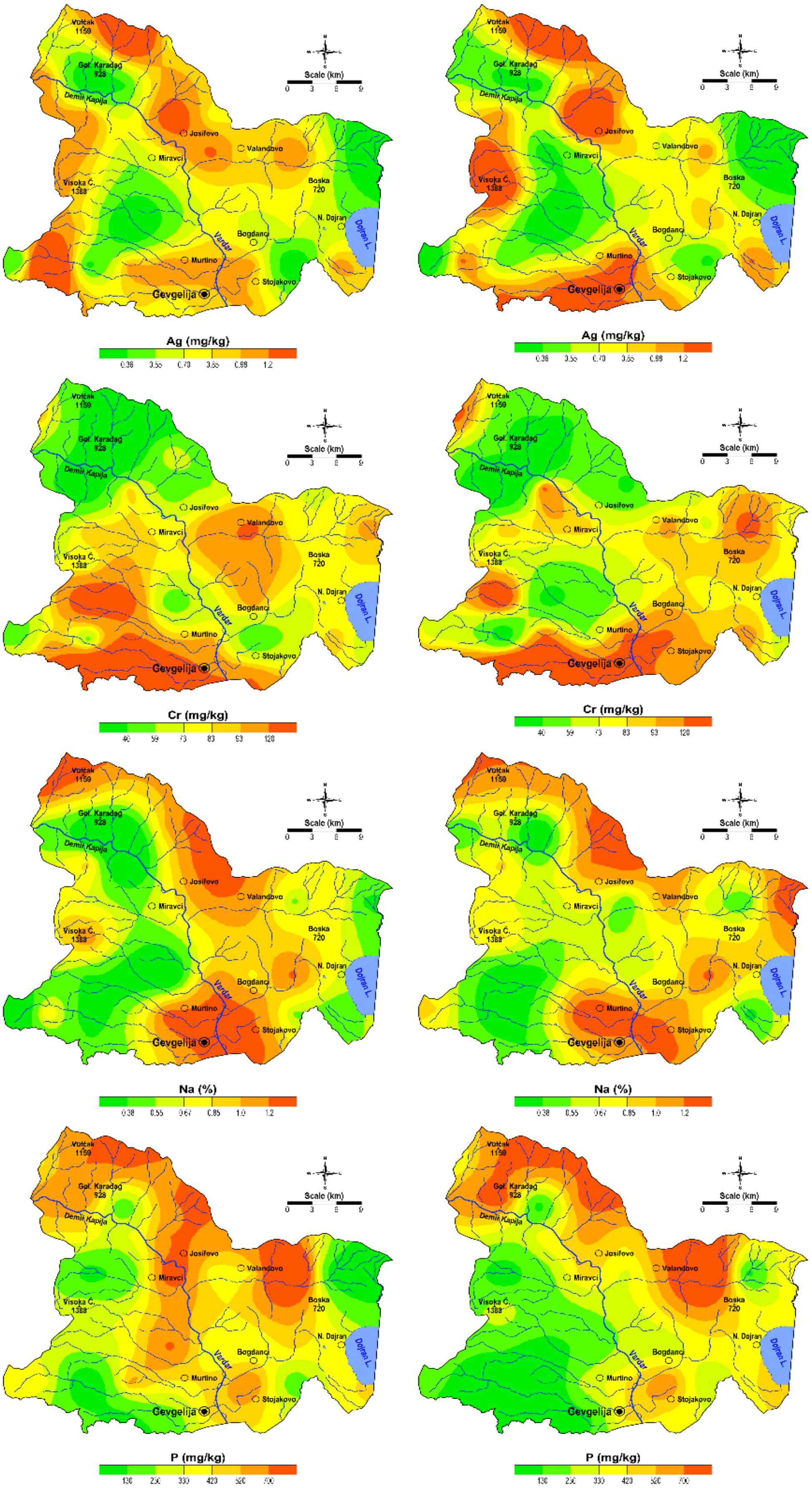
The minimum value of silver content in topsoil samples ranges from 0.10 mg/kg to 3.3 mg/kg, the average value is 0.87 mg/kg and the median is 0.83 mg/kg. very similar data were also obtained for subsoil: values range from 0.10 to 3.1 mg/kg, with an average of 0.89 mg/kg and a median of 0.75 mg/kg. It can be concluded that the Ag content is higher in the soils from the southwestern part (Kožuf Mt.) and the northern part of the study area, where Proterozoic gneisses and Mesozoic felsic plutonites predominate (Figure 8).

Chromium content in the topsoil and subsoil is also very similar, ranging from 24 to 800 mg/kg and 16 to 960 mg/kg, respectively, with mean values of 120 and 74 mg/kg and median values of 77 and 75 mg/kg. From the distribution maps for both strata (Figure 8), it can be concluded that the chromium content is higher in the soils from the southwestern part of the study area (Kožuf Mt. and the area of the town of Gevgelija), since this area consists mainly of Mesozoic mafic volcanic rocks and plutonites and Quaternary alluvial sediments.



a b

Fig. 7. Spatial distribution of factor scores and of the content of the elements in topsoil (a) and subsoil (b) from the Factor 3 (Al, Mg, Ca and Sr)



a **b**

Fig. 8. Spatial distribution of the content in topsoil (a) and subsoil (b) of the elements not included in the factors (Ag, Cr, Na and P)

The minimum value of sodium content in soil samples is 0.025% and 0.054%, the maximum content is 1.5% and 1.6%, the average content is 0.78 and 0.82%, and the median value is 0.80% and 0.79% in topsoil and subsoil, respectively. The minimum value of phosphorus content in the topsoil samples ranges from 51 mg/kg to 2700 mg/kg, the average value is 370 mg/kg and the median is 400 mg/kg. Very similar data were also obtained for the subsoil: values range from 33 to 2600 mg/kg, with an average value of 410 mg/kg and a median of 320 mg/kg. From the spatial distribution of P content (Figure 8), it can be concluded that its distribution is very similar to that of silver, with a higher content in soils from the southwestern part (Kožuf Mt.) and the northern part of the study area, where Proterozoic gneisses and Mesozoic felsic plutonites predominate. Figure 8 also shows that the P content in the topsoil from the Gevgelija and Valandovo valleys along the Vardar and Anska rivers is higher than in the subsoil samples, which is probably due to the use of phosphate fertilizers in agriculture.

CONCLUSION

In this work, the results of spatial distribution of 18 elements (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V и Zn) in soils from the southeastern part of North Macedonia (Gevgelija, Valandovo, Bogdanci and Dojran municipalities) are presented. The analysis of the content of the elements was carried out by atomic emission spectrometry with inductively coupled plasma (ICP-AES). The results were processed with special statistical programs and distribution maps were prepared for each element separately. Multivariate statistical methods were used to process the results for the content of the analyzed elements in 86 soil samples. Factor analyzis was performed and three variables (F1, F2 and F3) were identified: F1 includes Fe, V, Mn, Cu, Ni, Zn and Pb, F2 includes Ba, Li and K and F3 consists of Mg, Al, Ca and Sr. The comparison of the contents of the analyzed elements in the topsoil and subsoil showed that they are very similar (the ratio of the values is about 1 for all elements). This indicates that there is no anthropogenic soil pollution in the study area and that the distribution of the elements follows the geology of the region and that their elevated contents in certain areas are of lithogenic origin. The only exception is the fact that the P content in the topsoil from the Gevgelija and Valandovo valleys along the Vardar and Anska rivers is higher than in the subsoil samples, which is probably due to the use of phosphate artificial fertilizers in agriculture.

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Резиме

ПРОСТОРНА ДИСТРИБИУЦИЈА НА ХЕМИСКИ ЕЛЕМЕНТИ ВО ПОЧВИТЕ ОД ЈУГОИСТОЧНИОТ ДЕЛ НА СЕВЕРНА МАКЕДОНИЈА (ОПШТИНИТЕ ГЕВГЕЛИЈА, ВАЛАНДОВО, БОГДАНЦИ, ДОЈРАН)

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Клучни зборови: почви; тешки метали; општини; Гевгелија; Валандово; Богданци; Дојран; Северна Македонија

Презентирани се резултатите од истражувањата на содржината и просторната дистрибуција на 18 елементи (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V и Zn) во почвите од југоисточниот дел на Северна Македонија (регионот на општините Гевгелија, Валандово, Богданци и Дојран). За таа цел, од 43 локации се земени вкупно 86 примероци почва (43 примероци површинска и 43 примероци длабочинска почва). Сите примероци се анализирани со индуктивно спрегната плазма – атомска емисиона спектрометрија (ICP-AES) по нивна целосна дигестија со 4 киселини (HNO_3, HF, $HClO_4$ и HCl). Добиените резултати се обработени статистички, подготвени се и карти на просторна дистрибуција на сите анализирани елементи. Факторната анализа е применета за да се редуцира бројот на податоци, со што се идентификувани нови синтетички променливи (фактори). Со примената на факторната анализа идентификувани се три геохемиски асоцијации: фактор 1 (Fe, V, Mn, Cu, Ni, Zn и Pb), фактор 2 (Ba, Li и K), и фактор

3 (Mg, Al, Ca и Sr). Од добиените податоци и од картите на просторна дистрибуција, може да се заклучи дека појавата на анализираните елементи е поврзана со литологијата на регионот. Имено, утврдено е дека содржината на елементите кои се вклучени во фактор 1 е повисока во почвите од областа во која се доминантни мезозојските вулкански карпи, квартерни алувијални седименти, протерозојски гнајсеви и палеозојски шкрилци; содржината на елементите од фактор 2 е повисока во почвите од северниот (каде се доминантни магматските плутонити) и источниот дел на испитуваната област (каде се доминантни протерозојските гнајсеви и палеозојските шкрилци); додека елементите вклучени во фактор 3 се присутни повеќе во области со доминантни квартерни алувијални седименти, паеозојски карбонати и шкрилци и мезозојски базични плутонити. Единствен исклучок е фактот што содржината на фосфорот во површинските почви од Гевгелиската и Валандовската Долина, по текот на реките Вардар и Анска Река, е повисока отколку во длабочинските почви, што е најверојатно резултат на примената на вештачки ѓубрива во земјоделието.