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Multivariate statistical methods in determining the spatial distribution of chemical elements in soil from the Mavrovo-Rostuše region, North Macedonia

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Abstract

In this work, the contents and spatial distributions of 19 elements (Ag, Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, Zn) in the soil of the western part of North Macedonia (Mavrovo-Rostuše region) are presented. For this purpose, a total of 66 soil samples were collected from 33 locations (33 samples of topsoil, 0-5 cm, and 33 samples of subsoil, 20-30 cm). All samples were analysed 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 analysed 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 (Zn, K, Cu, Fe, and Li), Factor 2 (Cr, Ni, and Mg) and Factor 3 (Ca and Al). From the obtained data and the maps of spatial distribution, it could be concluded that the distribution of the analysed elements is related to the lithology of the region. Thus, it was found that the higher content of elements of Factor 1 occurs in the eastern and southern part of the study area (middle and lower reaches of the Radika River and along the Mala River), where Mesozoic and Paleozoic carbonates as well as Paleozoic shales and Paleogene flysch prevail. Factor 2 (Cr, Ni and Mg) also represents a lithogenic association. The highest contents of the elements in both soil layers were found in the areas where Paleozoic sandstones and shales (village of Lazaropole and the area around the Mavrovo Lake) and Paleogene flysch (Rostuše village) predominate. Factor 3 (Ca and Al) also represents lithogenic association of elements. The highest content of these elements was found in the northwestern part of the study area (village of Žirovnica and along the Berička River) and in the northeastern region above the village of Brodec where Mesozoic carbonates and Paleogene flysch dominate.

Key words: soil, heavy metals, spatial distribution, Mavrovo-Rostuše, region, North Macedonia

Introduction

Environmental pollution is usually defined as contamination by physical and biological components of the Earth/atmosphere system to an extent that excessively interferes with normal environmental processes. (Kabata-Pendias & Mukherjee 2007). Soil is rather a sensitive medium, an important natural, social and economic resource. Soils can be polluted in various ways. The anthropogenic factor is considered

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the largest and most important factor. Depending on the type of pollutant, soil pollution can be divided into two categories: organic pollution and inorganic pollution. Pollution with potentially toxic elements (PTEs) falls under the category of inorganic pollutants. The potential for pollution is higher in regions where ores and wastes are directly deposited and stored. Through rivers and streams or erosion processes, PTEs from these anthropogenic sources enter water bodies as dissolved particles or as components of suspended solids. These processes lead to bioaccumulation of PTEs in humans and animals through the food chain and cause severe health disorders (Kabata-Pendias & Mukherjee 2007). Although PTEs occur naturally in soil, anthropogenic activities increase concentrations of these elements to levels that are harmful to plants and animals. These activities include mining and metallurgical activities, fossil fuel combustion, the use of artificial fertilizers and pesticides in agriculture, the manufacture of batteries and other metal products in industry, sewage sludge and municipal waste, etc. (Järup 2003; Kabata-Pendias & Mukherjee 2007; Salomons et al. 2012).

In recent years, the results of previous studies have shown that the main emission sources of PTEs in North Macedonia are mines and drainage systems, as well as smelters located near the cities of Veles, Skopje, Tetovo, Kavadarci, Probištip, Makedonska Kamenica, and Radoviš, as well as thermoelectric power plants using lignite as fuel (Stafilov et al. 2010a, 2010b, 2018, 2019; Stafilov 2014; Stafilov & Šajn 2016, 2019; Bačeva et al. 2012, 2014; Balabanova et al. 2013; Barandovski et al. 2020).

In this study, the distribution of various chemical elements in the soil in the Mavrovo-Rostuše region was monitored and determined. The aim of this study is to determine the quality of soil in this region and identify possible sources of pollution. The contents of a total of 19 elements (Ag, Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) were determined in soil samples. For this purpose, 66 soil samples, including 33 topsoil samples (0-5 cm) and 33 subsoil samples (20-30 cm), were collected from a total of 33 sites in a 5×5 km grid. Samples were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). Element contents were statistically processed using multivariate factor and cluster analysis 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 municipality of Mavrovo-Rostuše is located in the western part of North Macedonia (Figure 1) between 41°28' and 41°43' N and 20°36' and 20°51' E. It covers an area of 682 km^2, making it one of the three largest municipalities in North Macedonia in terms of area. Of the total area of the municipality, 12 km^2 are lakes, 40 km^2 are agricultural land and 261 km^2 are pasture land. The main feature of this municipality is the high mountain structure, with 42 inhabited places – village settlements, with a relatively low population density with 5,638 inhabitants according to the 2021 census. The municipality is a real tourist attraction for the

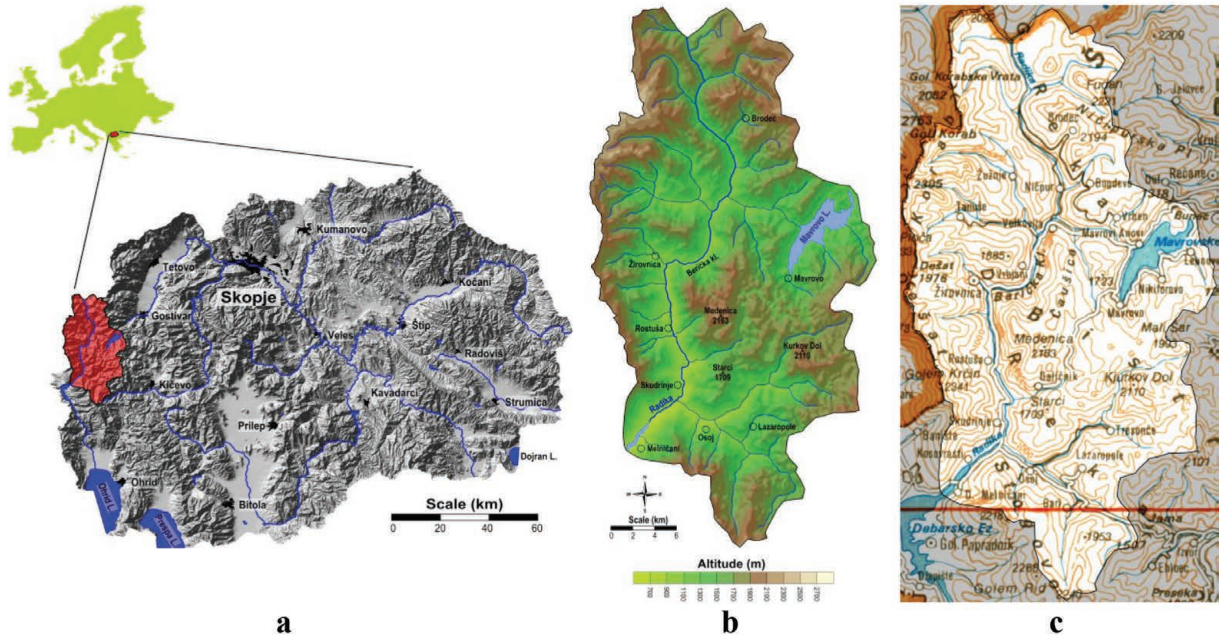


Figure 1. Location of the study area in North Macedonia (a), as well as the relief (b) and topographic maps of the study area (c)

entire region due to its terrain, climate and location, as well as its cultural and natural heritage (Mavrovo-Rostuše 2015; Popovski 2020).

The territory of the Municipality of Mavrovo and Rostuše is located in the Šar mountain group. This area includes the southern foothills of the Šar Mountains, part of the Korab Massif and the Bistra Mountains, which border the basin of the Radika River. The hydrographic characteristics of the study area are similar to those of the western part of the country with rivers, torrents, springs, and artificial reservoirs. The most significant river is the Radika, which is 67 km long and has four tributaries: Ribnica, Mavrovska, Žirovnička and Mala Rivers. On the territory of the study area there are two artificial reservoirs (Lake Mavrovo and Lake Debar). Lake Mavrovo is 10 km long, the 3-5 km width and the 50 m depth. Mavrovo Lake is an important part of the energy system (Mavrovo hydroelectric system) (Popovski 2020). The river Radika itself flows directly into the artificial Debar Lake, which provides water for the operation of the Špilje hydroelectric power plant.

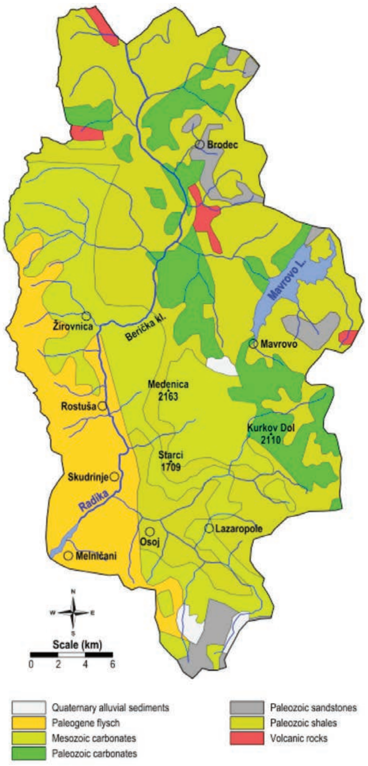


Figure 2. Geological map of the study area

The climate of the region differs according to the high mountain and valley relief. In the parts of the municipality where the altitude above sea level is more than 2000 m, the influence of the alpine climate can be observed, and therefore the number of rainy days per year is higher here. The area of Mavrovo is characterised by relatively high precipitation with an average annual precipitation of 1103 mm. The relief structure of the study area contributes to a colder climate with heavier precipitation in the form of rain and snow. The snow season usually lasts from December to March. The average annual temperature is 7.8°C. The warmest month is August, with an average multi-year air temperature of 17.5°C. In the area of Mavrovo, the winds blow mainly in a northeast-southwest direction with an average annual speed of the northeast wind of 3.1 m/s and in the southwest of 4.6 m/s C (Lazarevski, 1997).

On the territory of the municipality there is also the National Park "Mavrovo", the largest of the three national parks in the country. The area of this protected area is 72,204 ha. The altitude ranges from a minimum of 600 m to a maximum of 2,764 m. From the biogeographical point of view, the territory of Mavrovo National Park represents a pristine area where numerous oreo-tundra (arctic mountain) and northern (boreal) floristic elements develop. Besides the high species diversity, the second striking feature of the flora of the National Park "Mavrovo" is the relatively high degree of endemism with presence of more than 25 endemic plant taxa (Matevski, 2010)

From the geological point of view, the study area belongs to the West Macedonian geotectonic zone. The study area consists of ancient Paleozoic shales in the western part, Mesozoic carbonates in the central part, and Paleozoic carbonates and Paleozoic shales in the eastern part (Figure 3). In addition to the above-mentioned geological formations, small areas are covered by Quaternary alluvial sediments and Paleozoic sandstones (Arsovski 1997; Stafilov & Šajn 2016, 2019; Petrušev et al. 2021).

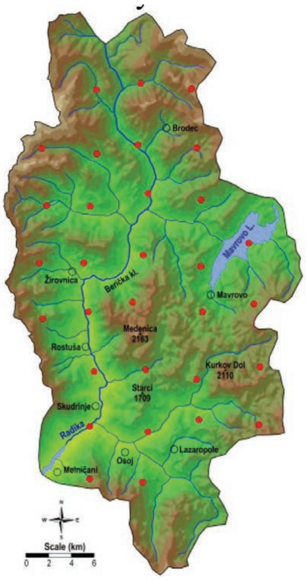


Figure 3. Study area with sampling locations

Soil sampling

Samples were collected from 33 locations in accordance with a previously established grid for the

Mavrovo region, covering the same 5×5 km sampling grid used for the preparation of the Geochemical Atlas of Macedonia (Stafilov & Šajn 2016) (Figure 3). In order to distinguish possible anthropogenic contamination at the surface from the natural geochemical composition in deeper layers, samples were collected from two intervals: topsoil (0–5 cm) and subsoil (20–30 cm). To obtain representative composite samples, five subsamples were collected from each location in a 10×10 m square area. The soil samples brought to the laboratory were cleaned of plant material and stones, homogenised and dried at room temperature or in a drying oven at 40°C. They were then sieved through a 2-mm sieve, ground in a porcelain mortar and finally sieved through a 125 µm sieve.

Digestion and analysis of soil samples

In the next stage, soil samples were digested by wet digestion using an acid mixture (HNO_3, $HClO_4$, HF and HCl) in accordance with the international standard ISO 14869-1:2001. The resulting solution is filtered through filter paper and quantitatively transferred to a 25 ml volumetric flask. The flask is filled up with distilled water. In the analysis of the soil samples, the content of a total of 19 elements (Ag, Al, Ba, Ca, Cr, Cu, B, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) was determined by using an inductively coupled plasma atomic emission spectrometer (ICP-AES), model Varian 715-ES (Balabanova et al. 2010). The method of open digestion of a soil sample with a mixture of the mentioned acids is a generally accepted method for preparing geological and soil samples for elemental analysis using ICP-AES. This method has been found to provide complete digestion even for silicate materials predominant in soil, and it is emphasised that for digestion of geological samples, HF is routinely used in combination with other mineral acids (Chao & Sanzalone 1992; Hu & Qi 2014).

Quality control was performed by analysing certified soil and geological reference 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). All elements show very low deviations from the recommended range of values, i.e., the mean value of all determined elements in the standards generally deviates from the recommended values by less than 15%. Both certified reference material and spiked samples within the laboratory were analyzed at a combined frequency of 20% of the samples. The recovery rate for spiked samples ranged from 90-110%, while the recovery rate for the certified reference material ranged from 94-108%.

Data processing and statistical analyses

Geostatistical data analysis and visualisation (mapping) was performed using the following software packages: Statistica (Stat Soft, Inc.), Autodesk MAP 3D (Autodesk, Inc.), ArcInfo (ESRI, Inc.), and Surfer (Golden Software, Inc.). Parametric and nonparametric statistical methods were used and normality tests of the data distributions were performed. Multivariate cluster and R-mode factor analyses (FA) were used to reveal relationships among chemical elements (Reimann et al. 2002). Factor analysis (FA) was performed with variables standardised to zero mean and one standard deviation. The varimax method was used for orthogonal rotation. Based on the exact number of variables, the FA provides a smaller number of new variables called factors that represent the association of the statistically significant variables. The universal kriging method with linear variogram interpolation was used to produce maps showing the spatial distribution of factor scores and maps showing the distribution of trace elements (Davis 1986). The base size of the grid cell for interpolation was 25×25 m. Seven classes of percentile values of the distribution of interpolated values were chosen as class boundaries (0–10, 10–25, 25–40, 40–60, 60–75, 75–90, and 90–100).

Results and discussion

Descriptive statistics for the content of analysed elements in a total of 33 topsoil and 33 subsoil samples (Ag, Al, B, 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 order of distribution of the concentration data of major elements Ca, Al, Fe, Mg, K, and Na, is in the following ranges: 0.18–18% Ca; 0.0.41–6,0% Al; 0.89–4.0% Fe; 0.36–2.0 K; 0.32–2.2% Mg and 0.048–0.56% Na. Major element contents are most commonly due to the predominant geologic formations of the area: Paleozoic shales, Mesozoic and Paleozoic carbonates, and Paleozoic shales.

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 analysed elements in the topsoil and subsoil layers. Even the ratio of 0.86 for Ag and 1.05 for V, shows that there is no significant influence of possible soil pollution by anthropogenic activities. 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 analysed elements in the topsoil of the study area and

Table 1. Descriptive statistics for the content of elements in topsoil (0-5 cm), N=33

Element	Unit	N	X	$X_{(BC)}$	Md	Min	Max	P_{10}	P_{90}	P_{25}	P_{75}	S	Sx	CV	A	E	$A_{(BC)}$	$E_{(BC)}$
Ag	mg/kg	33	1.1	1.1	1.1	0.24	2.2	0.46	1.9	0.66	1.7	0.58	0.10	51	0.13	-1.16	-0.07	-1.15
Al	%	33	2.7	2.6	2.5	0.41	6.0	1.6	3.8	1.8	3.3	1.1	0.19	41	0.52	1.51	-0.03	1.10
B	mg/kg	33	23	22	23	10	37	15	29	19	26	6.3	1.1	28	0.29	0.16	-0.06	0.04
Ba	mg/kg	33	190	180	180	74	370	110	280	140	230	67	12	35	0.73	0.28	-0.16	-0.00
Ca	%	33	2.2	1.2	1.2	0.18	15	0.47	3.9	0.61	2.3	2.9	0.51	140	3.19	11.65	-0.06	-0.15
Cr	mg/kg	33	140	130	140	42	300	65	210	82	180	64	11	46	0.54	-0.04	-0.09	-0.73
Cu	mg/kg	33	37	34	36	16	64	21	52	26	46	13	2.2	34	0.25	-0.70	-0.56	-0.42
Fe	%	33	3.0	3.0	3.1	0.89	4.0	2.5	3.5	2.7	3.3	0.55	0.096	19	-1.48	5.61	0.08	1.25
K	%	33	0.88	0.79	0.73	0.36	2.0	0.47	1.5	0.55	1.1	0.41	0.071	46	1.02	0.58	0.09	-0.83
Li	mg/kg	33	29	29	28	6.8	49	21	36	25	32	7.4	1.3	26	-0.21	2.59	0.38	2.53
Mg	%	33	1.2	1.1	1.1	0.32	2.2	0.58	1.7	0.87	1.5	0.47	0.082	40	0.28	-0.38	-0.20	-0.40
Mn	mg/kg	33	720	700	690	230	1100	460	1000	600	850	210	37	29	-0.14	-0.24	-0.74	0.79
Na	%	33	0.32	0.33	0.33	0.048	0.56	0.21	0.46	0.24	0.41	0.12	0.021	37	-0.20	-0.10	-0.13	-0.17
Ni	mg/kg	33	96	79	76	24	250	34	190	51	130	58	10	61	0.80	-0.19	-0.04	-1.11
P	mg/kg	33	790	710	720	360	1500	450	1400	610	920	310	55	40	1.03	0.36	-0.24	-0.13
Pb	mg/kg	33	31	30	33	12	50	20	42	25	37	8.8	1.5	28	-0.14	-0.31	-0.65	0.23
Sr	mg/kg	23	55	46	46	16	180	32	80	38	64	33	7.0	61	2.72	9.06	-0.60	3.09
V	mg/kg	33	81	82	81	18	120	58	100	73	95	21	3.6	26	-0.59	1.66	-0.20	0.90
Zn	mg/kg	33	130	120	110	67	250	81	230	91	160	55	9.6	42	0.96	-0.20	0.09	-1.05

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 elements in subsoil (20-30 cm); N=33

Element	Unit	N	X	$X_{(BC)}$	Md	Min	Max	P_{10}	P_{90}	P_{25}	P_{75}	S	Sx	CV	A	E	$A_{(BC)}$	$E_{(BC)}$
Ag	mg/kg	33	1.3	1.3	1.3	0.45	2.5	0.60	1.9	0.91	1.7	0.51	0.090	40	0.16	-0.61	-0.05	-0.75
Al	%	33	2.7	2.6	2.4	1.5	4.3	1.6	4.0	1.9	3.5	0.89	0.15	33	0.31	-1.26	0.21	-1.32
B	mg/kg	33	23	23	23	10	41	12	33	18	29	7.6	1.3	33	0.29	-0.35	-0.03	-0.49
Ba	mg/kg	33	200	180	190	91	460	100	260	150	230	84	15	42	1.30	2.30	0.09	-0.10
Ca	%	33	2.4	1.2	1.0	0.19	18	0.56	5.3	0.64	2.6	3.5	0.61	140	3.18	11.72	0.11	-0.13
Cr	mg/kg	33	130	120	120	41	280	59	220	83	160	61	11	46	0.67	-0.02	0.00	-0.52
Cu	mg/kg	33	38	34	33	18	100	22	55	25	44	19	3.3	49	2.05	5.06	0.49	0.04
Fe	%	33	2.9	3.0	3.0	0.97	3.9	2.3	3.5	2.7	3.2	0.54	0.094	18	-1.32	4.57	0.07	1.12
K	%	33	0.87	0.79	0.76	0.39	1.9	0.47	1.4	0.59	1.1	0.37	0.065	43	0.80	-0.03	-0.04	-0.88
Li	mg/kg	33	28	28	28	8.5	39	19	37	24	32	6.8	1.2	24	-0.62	0.73	-0.32	0.07
Mg	%	33	1.1	1.1	1.1	0.56	2.2	0.73	1.5	0.87	1.4	0.36	0.062	32	0.80	0.80	0.38	0.03
Mn	mg/kg	33	730	700	690	250	1800	470	1100	560	840	310	54	42	1.55	3.89	0.42	1.52
Na	%	33	0.32	0.32	0.31	0.080	0.56	0.17	0.46	0.24	0.41	0.11	0.020	36	-0.10	-0.25	-0.04	-0.27
Ni	mg/kg	33	92	77	68	29	200	37	170	46	140	55	9.5	59	0.62	-1.01	0.04	-1.34
P	mg/kg	33	870	710	700	290	3600	460	1600	580	890	610	110	69	3.16	12.70	0.10	0.68
Pb	mg/kg	33	31	30	30	13	61	21	48	24	34	11	1.9	35	1.02	0.66	0.46	0.09
Sr	mg/kg	23	60	49	48	24	250	29	88	38	65	46	9.6	77	3.53	14.52	0.52	0.76
V	mg/kg	33	78	79	77	22	130	57	100	67	90	20	3.5	26	-0.03	1.64	0.37	1.37
Zn	mg/kg	33	140	120	120	72	420	77	210	86	160	69	12	51	2.37	7.86	0.12	-0.84

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 and *T*-, *F*- and *R*-tests

Element	Unit	Topsoil	Subsoil	FO (T/B)	*T* (test)	Sign	*F* (ratio)	Sign	R (T/B)	Sign
Ag	mg/kg	1.1	1.3	0.86	-1.26	NS	1.38	NS	0.19	NS
Al	%	2.6	2.6	0.98	-0.19	NS	1.58	NS	0.72	*
B	mg/kg	22	23	0.98	-0.25	NS	1.43	NS	-0.07	NS
Ba	mg/kg	180	180	0.97	-0.31	NS	1.28	NS	0.83	*
Ca	%	1.2	1.2	0.94	-0.25	NS	1.01	NS	0.93	*
Cr	mg/kg	130	120	1.06	0.46	NS	1.06	NS	0.90	*
Cu	mg/kg	34	34	0.99	-0.10	NS	1.12	NS	0.72	*
Fe	%	3.0	3.0	1.02	0.51	NS	1.08	NS	0.68	*
K	%	0.79	0.79	1.00	-0.01	NS	1.08	NS	0.90	*
Li	mg/kg	29	28	1.03	0.50	NS	1.25	NS	0.74	*
Mg	%	1.1	1.1	1.02	0.16	NS	1.87	NS	0.57	*
Mn	mg/kg	700	700	1.00	-0.02	NS	1.64	NS	0.83	*
Na	%	0.33	0.32	1.02	0.18	NS	1.09	NS	0.76	*
Ni	mg/kg	79	77	1.03	0.18	NS	1.06	NS	0.88	*
P	mg/kg	710	710	1.00	0.00	NS	1.50	NS	0.90	*
Pb	mg/kg	30	30	1.00	0.04	NS	1.26	NS	0.37	*
Sr	mg/kg	46	49	0.95	-0.39	NS	1.12	NS	0.88	*
V	mg/kg	82	79	1.05	0.73	NS	1.07	NS	0.81	*
Zn	mg/kg	120	120	0.99	-0.10	NS	1.04	NS	0.61	*

Topsoil – top soil layer; Subsoil – soil under surface soil; FO(T/B) – mean values of topsoil and subsoil; R – Correlation coefficient

Table 4. Comparison of median, minimum and maximum values of the content of the analysed elements in topsoil and subsoil from the study area, North Macedonia, and Europe

		Study area				North Macedonia (Mihajlov et al. 2016; Stafilov & Šajn 2016)				Europe (Salminen et al. 2005)			
Element	Unit	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	1.1	0.24-2.2	1.3	0.45-2.5	-	-	-	-	0.27	0.01-3.15	0.25	0.02-2.07
Al	%	2.5	0.41-6.0	2.4	1.5-4.3	2.2	0.79-4.3	2.3	0.77-5.1	0.58	0.20-1.42	0.62	0.11-1.43
B	mg/kg	23	10-37	23	10-41	-	-	-	-	-	-	-	-
Ba	mg/kg	180	74-370	190	91-460	420	41-1600	440	66-1700	375	30-1870	385	13-2050
Ca	%	1.2	0.18-15	1.0	0.19-18	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	140	42-300	120	41-280	54	11-600	63	11-600	60	<3-6230	62	<3-2140
Cu	mg/kg	36	16-64	33	18-100	16	1.7-73	16	3.2-78	13	0.81-256	13.9	0.86-125
Fe	%	3.1	0.89-4.0	3.0	0.97-3.9	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	%	0.73	0.36-2.0	0.76	0.39-1.9	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	28	6.8-49	28	8.5-39	18	4.8-79	20	5.2-69	-	-	-	-
Mg	%	1.1	0.32-2.2	1.1	0.56-2.2	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	690	230-1100	690	250-1800	620	160-3200	640	99-4300	507	31-6068	468	23-4710
Na	%	0.33	0.048-0.56	0.31	0.08-0.56	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	76	24-250	68	29-200	35	2.5-530	37	5.2-530	18	<2-2690	21.8	<2-2400
P	mg/kg	720	360-1500	700	290-3600	450	120-1400	430	74-1300	560	48-5770	420	30-7250
Pb	mg/kg	33	12-50	30	13-61	17	2.5-700	14	0.8-660	10	5.32-970	17.2	<3-938
Sr	mg/kg	46	16-180	48	24-250	71	9.4-540	68	9.9-580	89	8-3120	95	6-2010
V	mg/kg	81	18-120	77	22-130	67	14-300	71	19-370	60	2.71-537	62.8	1.28-325
Zn	mg/kg	110	67-250	120	72-420	39	3.1-440	38	4.4-490	52	<3-2900	47	<3-3060

in 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 mean contents of Al, Ca, Cr, Cu and Zn are higher in the soils of the study area than in the Macedonian soils, while the contents of Ba, K, Li and Sr are lower. Similar information is obtained when comparing the contents of the analysed elements in the soils of the study area and in the European soils. Characteristic 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.

The degree of correlation is determined by the bivariate statistics, i.e. by the mutual relationship between the content of the analysed elements in the soil samples. It is known that the absolute value of the correlation coefficient from 0.3 to 0.5 gives a good association, and between 0.5 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). From Table 5, it can be seen that there is a strong correlation between the distribution of Al and Ba, Ca, K, Mg, Sr and Zn, as well as between the distribution of Ba and K, Sr and Zn; of Ca with Sr and V; Cr with Mg and Ni, Cu with Ni and Zn; Fe with K and V; K with Sr and Zn; na Sr with V.

Bivariate statistics was applied to determine the degree of correlation between the elements studied. Table 6 contains a factor analysis, i.e., the loading matrix for the dominant rotating factors, which helps to identify three lithogenic factors: Factor 1 (Zn, K, Cu, Fe, and Li), Factor 2 (Cr, Ni, and Mg), and Factor 3 (Ca and Al). In the factor analysis, of the total 19 elements analysed, those that did not contribute to the commonality were eliminated. These 3 factors include a total of 10 elements with a total share of 82.2% in commonality. The elements Ag, B, Ba, Mn, Na, P, Pb, Sr and V have low factor scores with a weak tendency to form an independent factor.

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 and Ca. 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 Cr, Ni and Mg, which otherwise belong to Factor 2 of the loading matrix of the dominant rotating factors. The third cluster is composed of the elements: Cu, K, Zn, Fe and Li, which have an identical composition to Factor 1 (Table 6).

Factor 1 (Zn, K, Cu, Fe and Li) represents a lithogenic association of elements. This factor is of greatest importance because it accounts for 35.2% of the total variability. The spatial distributions of the factor values of F1 for topsoil and subsoil and the spatial distributions of the content of elements from this factor are shown in Figure 5. The origin of the elements in this typical lithogenic association is related to the geological composition of the soil in this region. It is evident from the distribution maps that the high contents of the elements from factor 1 occur in the eastern and southern part of the study area (middle and lower reaches of the Radika River and along the Mala River), where Mesozoic and Paleozoic carbonates and Paleozoic shales and Paleogene flysch predominate.

Zinc is represented with a mean content value of 130 mg/kg for topsoil and 140 mg/kg for subsoil. The median is 110 mg/kg for topsoil and 120 mg/kg for subsoil. The zinc content in the samples from the studied area ranges from 67–250 mg/kg for topsoil and from 72–420 mg/kg for subsoil. The ratio of median zinc contents in topsoil and subsoil is 0.99, which indicates that these values are almost identical for both soil layers (Table 4), from which it can be concluded that zinc distribution is the result of lithological origin. Figure 5 shows the spatial distributions of zinc in the study area for both soil layers. From this spatial distribution it can be seen that the zinc content in the soils is highest in the same areas where the factor 1 has the highest values (the region along the course of the Radika and Mala Reka rivers).

The average value of potassium content is 0.87% for topsoil and 0.88% for subsoil, while the median value is 0.73% and 0.76% for topsoil and subsoil, respectively. The potassium content in the samples from the studied area ranges from 0.36-2.00% for the topsoil and from 0.39-1.9% for the subsoil. As can be seen from the results in Table 4, the Box-Cox transformed average contents of Zn in topsoil and subsoil are the same, i.e. their ratio is 1.00. Figure 5 shows the spatial distributions of potassium in both soil layers of the studied area. It can be seen that the highest values of K content in the soils are found in the same area where factor 1 has the highest values (the region along the Radika River and Mala Reka), where Paleogene flysch and Mesozoic and Paleozoic carbonates also dominate.

The average copper content is 37 mg/kg and 38 mg/kg and the median value is 36 mg/kg and 33 mg/kg in the topsoil and subsoil, respectively. The content of copper in the samples from the study area ranges from 16-64 mg/kg in the topsoil and from 18-100 mg/kg in the subsoil. The ratio of average Cu contents in topsoil and subsoil is 0.99, which indicates that the presence of copper is the same as that of the above elements and that its spatial distribution (Figure 5) in the study area is a consequence of its lithological origin. The highest copper contents are observed in areas dominated by

Table 5. Matrix of correlation coefficients of elements for topsoil and subsoil (N=66). Values in the range 0.3-0.5 (good association) are underlined and in the range 0.5-1.0 (strong association) are in bold; Box-Cox transformed values were used.

Element	Ag	Al	B	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	Sr	V	Zn
Ag	1.00																		
Al	0.41	1.00																	
B	0.08	-0.23	1.00																
Ba	0.25	**0.59**	-0.35	1.00															
Ca	0.22	**0.66**	-0.27	0.39	1.00														
Cr	-0.31	0.00	0.14	-0.39	-0.11	1.00													
Cu	0.21	0.40	0.03	0.31	0.08	0.24	1.00												
Fe	0.23	0.29	0.17	0.21	-0.23	0.24	0.58	1.00											
K	0.49	**0.58**	-0.08	**0.74**	0.17	-0.37	0.65	**0.52**	1.00										
Li	-0.01	0.15	-0.05	0.32	-0.32	0.27	0.45	0.49	0.43	1.00									
Mg	0.16	**0.59**	-0.14	0.00	0.25	**0.55**	0.22	0.24	0.01	0.16	1.00								
Mn	0.12	0.30	-0.25	0.40	0.07	0.04	0.36	0.29	0.37	0.42	0.25	1.00							
Na	0.34	0.23	-0.26	0.32	0.03	-0.42	0.00	0.06	0.28	0.08	0.19	0.43	1.00						
Ni	-0.14	0.35	-0.05	0.05	0.19	**0.79**	**0.59**	0.34	0.12	0.47	**0.55**	0.21	-0.35	1.00					
P	-0.21	0.37	-0.31	0.47	0.43	0.03	0.15	-0.16	0.14	0.22	0.10	0.36	0.07	0.26	1.00				
Pb	-0.10	-0.04	-0.19	0.35	-0.06	-0.23	0.01	0.11	0.15	0.18	-0.28	0.08	0.05	-0.14	0.42	1.00			
Sr	0.30	**0.70**	**-0.52**	**0.79**	**0.73**	-0.41	0.06	-0.30	**0.58**	0.04	0.30	0.38	**0.50**	-0.02	0.47	0.15	1.00		
V	-0.11	-0.32	0.45	-0.38	**-0.58**	0.35	0.04	**0.58**	-0.13	0.19	-0.06	-0.08	-0.21	-0.01	-0.36	0.06	**-0.69**	1.00	
Zn	0.38	**0.52**	-0.15	**0.65**	0.19	-0.29	**0.75**	0.49	**0.88**	0.41	0.03	0.42	0.26	0.21	0.26	0.23	0.49	-0.22	1.00

Mesozoic and Paleozoic carbonates and Paleogene flysch.

Table 6. Matrix of dominant rotated factor loadings. Bold values denote the factor score values for elements belonging to the corresponding factor.

Element	F1	F2	F3	Comm
Zn	**0.89**	-0.18	0.29	90.6
K	**0.89**	-0.25	0.30	93.7
Cu	**0.81**	0.30	0.13	76.1
Fe	**0.74**	0.28	-0.16	65.0
Li	**0.67**	0.34	-0.32	67.1
Cr	-0.08	**0.96**	-0.17	95.4
Ni	0.32	**0.85**	0.14	85.0
Mg	0.05	**0.74**	0.43	72.8
Ca	-0.09	0.01	**0.93**	87.0
Al	0.42	0.21	**0.82**	89.1
Prp.Totl	35.2	26.1	20.9	82.2
EigenVal	4.05	2.32	1.85	
Expl.Var	3.52	2.61	2.09	

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

Iron content has a mean of 3.0% and 2.9% and a median of 3.1% and 3.0% for topsoil and subsoil, respectively. The iron content of the samples from the studied area ranges from 0.89-4.0% in the topsoil and from 0.97-3.9% in the subsoil. The ratio between the Box-Cox transformed mean values of Fe content in the topsoil and subsoil is 1.02, which also confirms the lithogenic origin of the spatial distribution of Fe (Figure 5). Higher Fe contents are observed in the area of the villages of Brodec and Žirovnica and Skudrinje, where Paleozoic shales and Paleogene flysch dominate.

According to the factor analysis, lithium also belongs to Factor 1. It is represented with a mean value of 29 mg/kg in the topsoil and 28 mg/kg in the subsoil. The median is 28 mg/kg for topsoil and 28 mg/kg for subsoil. The content of lithium in the samples from the studied area ranges from 6.8–49 mg/kg in topsoil and from 8.5–39 mg/kg in subsoil. The spatial distributions of Li (Figure 5) in both soil layers are very similar with a ratio of mean contents of 1.03 (Table 4). It can be seen that the highest value for Li content is found in the soils of the southern part of the study area (villages Skudrinje, Osoj, Lazaropole) and Bistra Mountains, where Paleozoic shales and carbonates dominate.

According to the spatial distribution of factor scores (Figure 6), **Factor 2** (Cr, Ni and Mg) also represents a lithogenic association with the highest content in both soil layers in the areas where Paleozoic sandstones and shales (Lazaropole village and area around Mavrovo Lake) and Paleogene flysch (Rostuše village) predominate (Figure 6). Namely, the region above Lake Mavrovo belongs to the group of Old Paleozoic shales (phyllitoids) and Late Paleozoic shale metadiabases. Cretaceous flysch rocks are represented by Paleozoic shales, which are most abundant in the vicinity of Lake Mavrovo and are found to a small extent in the southernmost part of the studied area. Higher contents of these elements were also found in the western part of the studied area around the village Rostuše and for some elements in the northwestern part.

Chromium is represented by a median value of 140 mg/kg for topsoil and 130 mg/kg for subsoil. The median is 140 mg/kg for topsoil and 120 mg/kg for

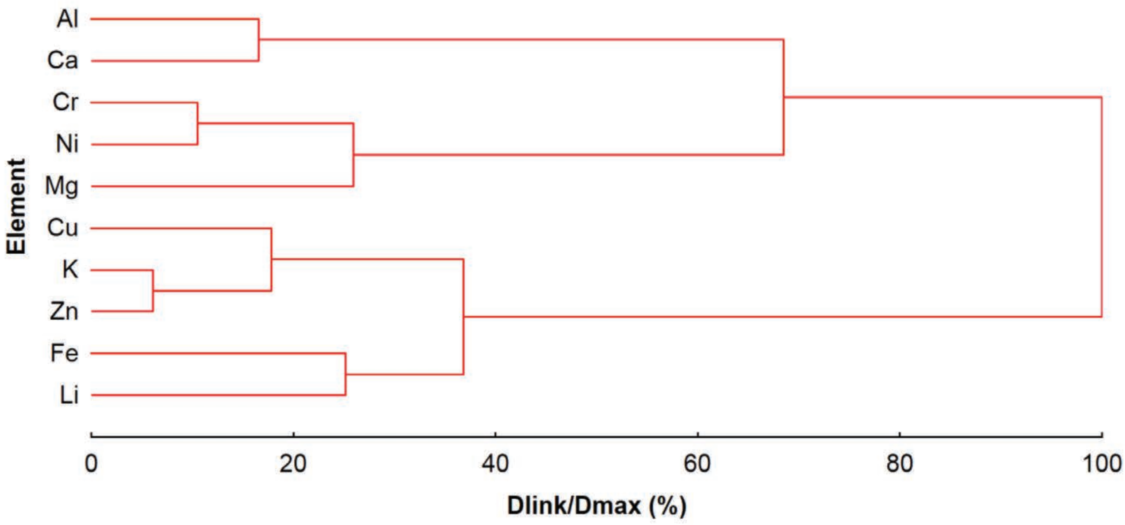


Figure 4. Dendrogram of cluster analysis

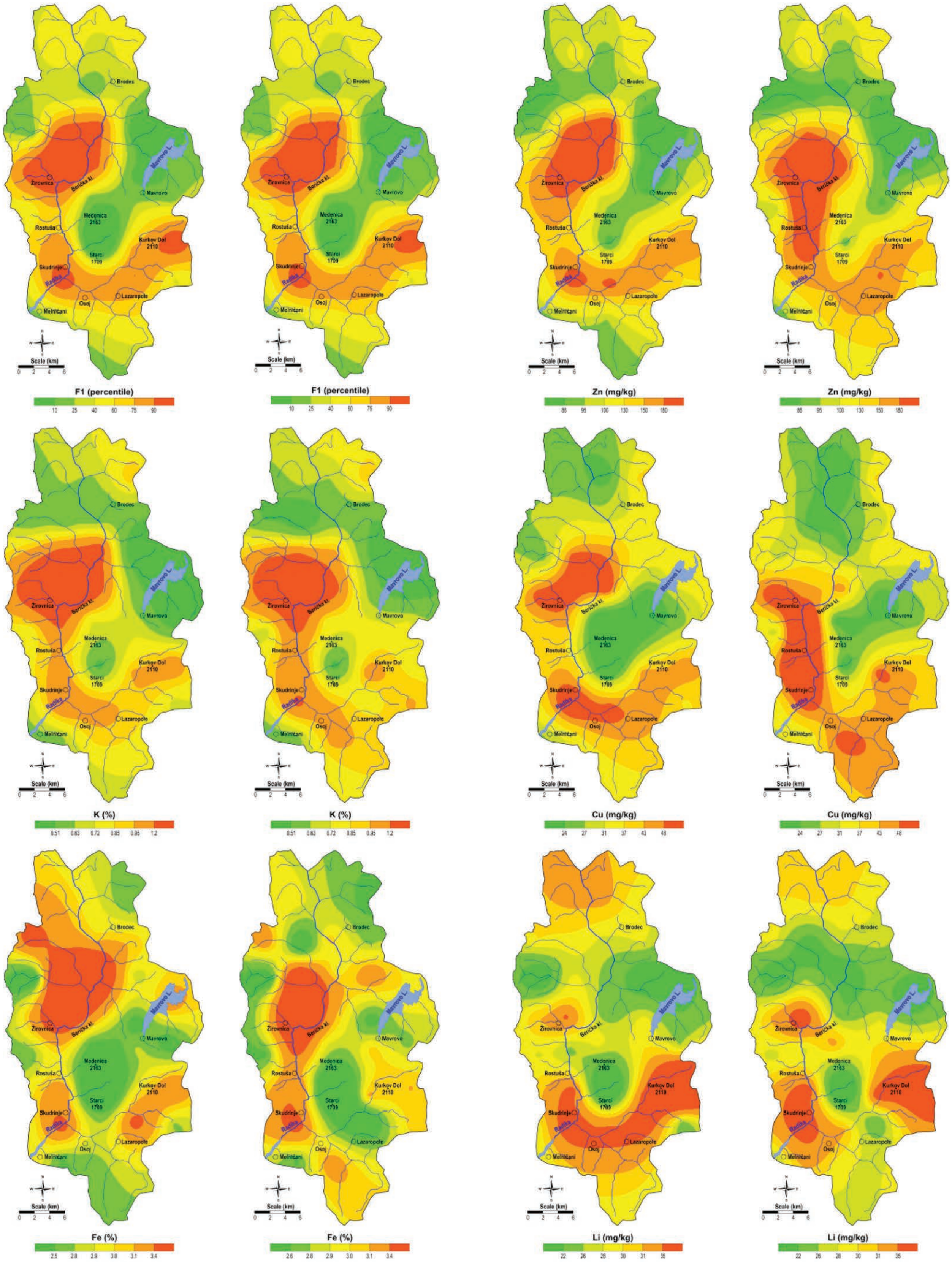
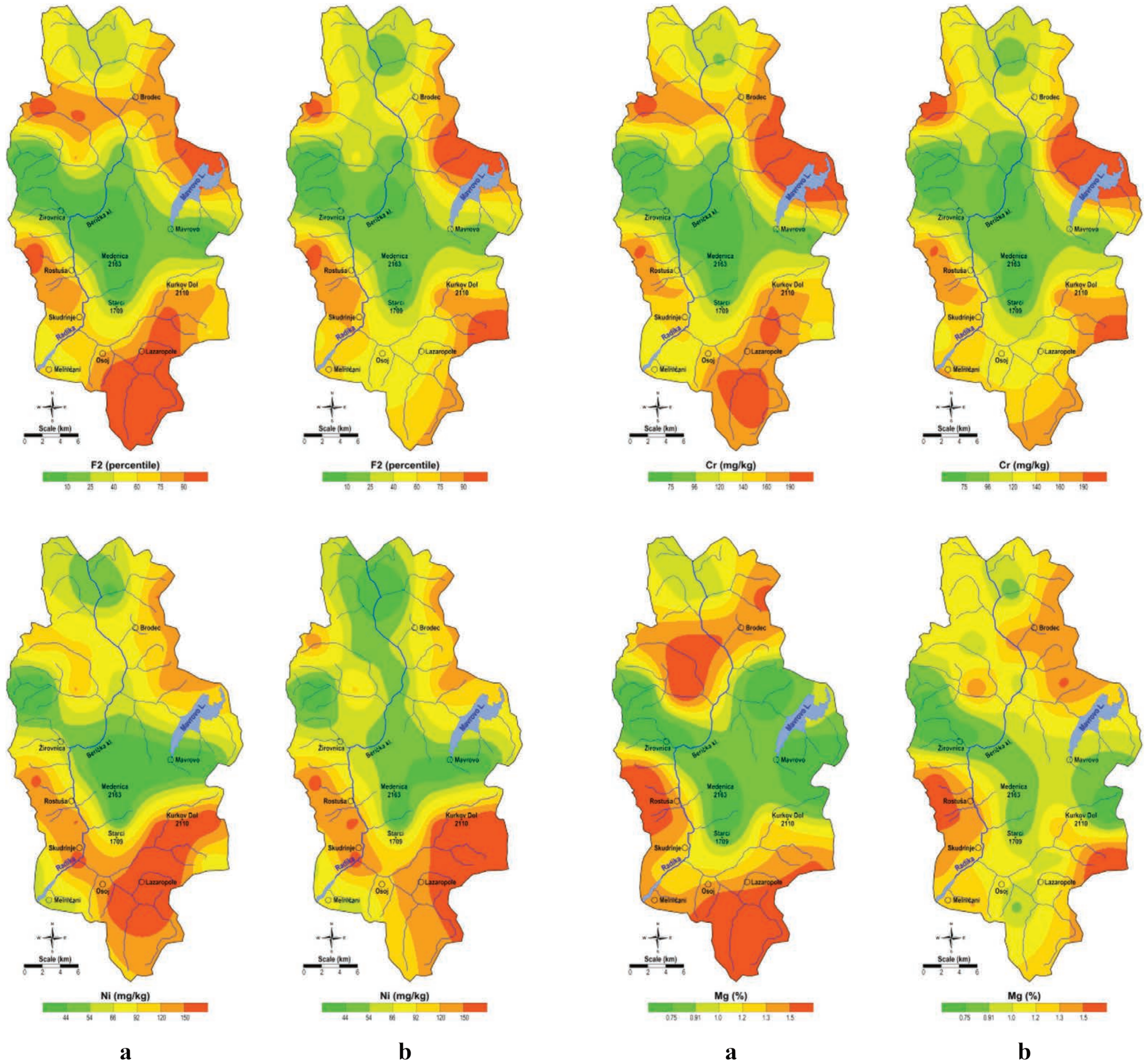


Figure 5. Spatial distribution of factor scores and content of elements in topsoil (a) and subsoil (b) of Factor 1 (Zn, K, Cu, Fe and Li)

subsoil. Chromium content in samples from the study area ranges from 42-300 mg/kg for topsoil and from 41-280 mg/kg for subsoil. The ratio between the medians of chromium contents in topsoil and subsoil is similar and is 1.06 (Table 4), which also leads to the conclusion that the distribution of chromium is a result of its lithological origin (Figure 6). The highest Cr content in both soil layers is found in the soils in the area of Lake Mavrovo, where Paleozoic shales dominate.

Nickel also belongs to Factor 2 and is represented with an average value of 96 mg/kg in the topsoil and 92 mg/kg in the subsoil. The median is 76 mg/kg for the topsoil and 68 mg/kg for the subsoil. Nickel content in the samples from the studied area ranges from 24-250 mg/kg for topsoil and from 29-200 mg/kg for subsoil. From the values given in Table 4, we can see that the medians for nickel content in topsoil and subsoil are similar and their ratio is 1.03 (Table 4). Therefore, we can conclude that the nickel contents are the result of the lithological origin. From the distribution maps (Figure 6), we can see that the highest value for nickel content is found in the soils in the southern part of the study area and near Lake Mavrovo, where Paleozoic shales and sandstones dominate.

Magnesium also belongs to factor 2 and is represented by an average value of 1.1% for topsoil and 1.1% for subsoil. The median is 1.2% for topsoil and 1.1% for subsoil. The magnesium content in the samples from the studied area ranges from 0.32-2.2% for topsoil and from 0.56-2.2% for subsoil. From the values in Table 4, the mean Mg content in the topsoil and subsoil is similar and their ratio is 1.02. The distribution maps of both layers (Figure 6) show a higher Mg content in the Moorish region for the surface and subsoil. From the distribution maps, the highest magnesium content is found in the soils in the southern and northern part of the studied area, where Paleozoic shales and sandstones dominate.



a b a b

Figure 6. Spatial distribution of factor scores and content of elements in topsoil (a) and subsoil (b) of Factor 2 (Cr, Ni and Mg)

Factor 3 (Ca and Al) also represents lithogenic association of elements (Figure 7). The highest content of these elements was found in the areas of Mesozoic carbonates and Paleogene flysch. Factor 3 of the factor analysis is the least significant factor, accounting for only 20% of the total variability. The highest occurrence of these elements is in the northwestern part of the study area (village of Žirovnica along the Berička River) and in the northeastern region above the village of Brodec. Calcium and is represented by an average value of 2.2% for topsoil and 2.4% for subsoil. The median is 1.2% for topsoil and 1.0% for subsoil. The calcium content of the samples from the studied area ranges from 0.18-15% for topsoil and from 0.19-18% for subsoil. The ratio of median values for topsoil and subsoil is 0.94, indicating a great similarity of calcium contents in the soils of both layers. The spatial distribution of calcium (Figure 6) shows that the highest calcium contents are found in the areas dominated by Mesozoic and Paleozoic carbonates. Aluminum, which belongs to factor 3 of the factor analysis, is represented with a mean of 2.5% and 2.7%, and the median is 2.5% and 2.4% for topsoil and subsoil, respectively. The content of aluminum in the samples from the studied area ranges from 0.41-6.0% for topsoil and from 1.5-4.3% for subsoil. The values for mean aluminum content are almost the same with a ratio value of 0.98. The distribution of Al is very similar to that of calcium.

Of the total 19 elements analysed, the factor analysis reduces to 10, which have a total share of 82.2% (Table 6). The other elements (Ag, B, Ba, Mn, Na, P, Pb, Sr and V) 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 average and median values of silver content in the soil of the study area are 1.1 mg/kg in the topsoil and 1.3 mg/kg, ranging from 0.24–2.2 mg/kg for the topsoil and 0.45–2.5 mg/kg for the subsoil. The spatial distribution of silver content in both (Figure 8) shows that it is similarly distributed in both soil layers. In the western part of the study area (Žirovnica and Rostuše villages), where Mesozoic carbonates and Paleogene flysch predominate, the silver content is higher.

Boron is present with a mean and median content of 23 mg/kg in both soil layers. The boron content in the samples from the studied area, ranges from 10–37 mg/kg in the topsoil and 10–41 mg/kg in the subsoil. The spatial distribution of Ba in both layers is very similar with a ratio of the average values of 0.98. In both soil layers, Ba contents are higher in the soil from the Lake Mavrovo area, where Paleozoic shales occur. In the subsoil samples, higher contents are observed in the northwestern region where Paleogene flysch and Mesozoic carbonates predominate.

The average content of barium is 190 mg/kg and 200 mg/kg while median value is 180 mg/kg and 190 mg/kg for topsoil and subsoil, respectively. The content of barium in the samples from the studied area ranges from 74-370 mg/kg for topsoil and from 91-460 mg/kg for subsoil. Figure 8 shows the spatial distribution of chromium in the topsoil and subsoil layers from the study area. From spatial distribution, it can be noted that higher content in both samples are in present in the soil from the central part the north-eastern part, which is dominated by Mesozoic and Paleozoic carbonates Paleozoic dominate.

The average content of manganese is 720 mg/kg in the topsoil and 730 mg/kg in the subsoil, and the median value is 690 mg/kg for both soil layers. The content of manganese in the samples from the studied area ranges from 230-1100 mg/kg in the topsoil and from 250-1800 mg/kg in the subsoil. The spatial distribution (Figure 8) in both layers is very similar (the ratio of average contents is 1). Similar to barium, according to the distribution maps for manganese in the topsoil and subsoil, the highest contents are observed in the northeastern part, which is dominated by Paleogene flysch and Paleozoic shales.

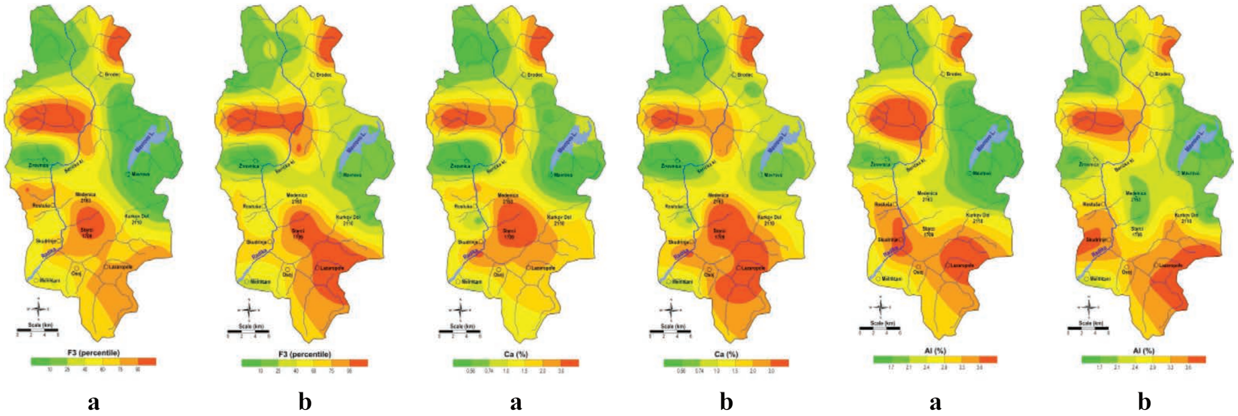
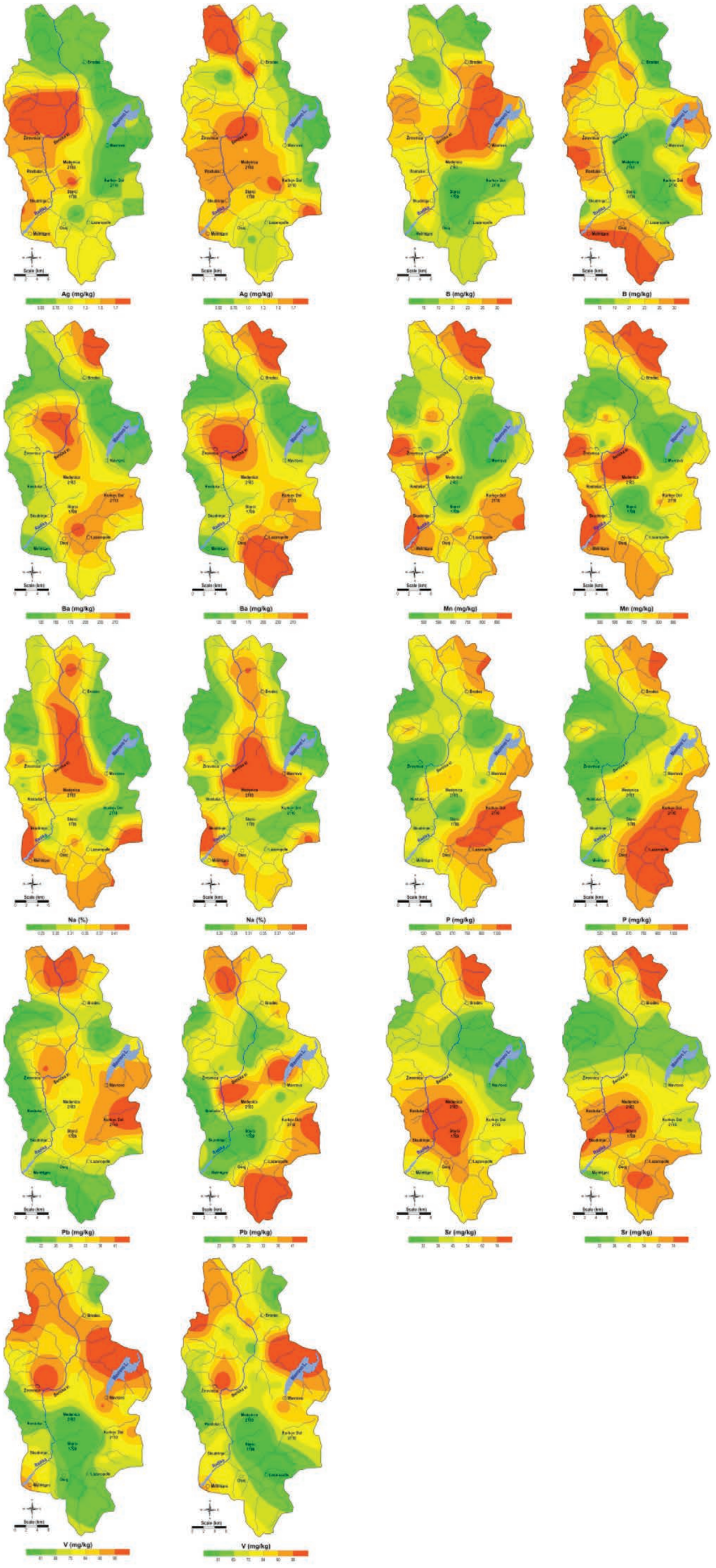


Figure 7. Spatial distribution of factor scores and content of elements in topsoil (a) and subsoil (b) of Factor 3 (Ca and Al)



a b a b

Figure 8. Spatial distribution of the content of the elements not included in the factors (Ag, B, Ba, Mn, Na, P, Pb, Sr and V) in topsoil (a) and subsoil (b)

Sodium is present in the study area with an average content of 0.32% and 0.32% and a median value of 0.33% and 0.31% in the topsoil and subsoil, respectively, ranging from 0.048-0.56% in the topsoil and from 0.080-0.56% in the subsoil. Figure 8 shows the spatial distribution of Na in both layers, from which it can be seen that the content is higher in the soils in the central and southern parts of the study area. The highest proportion, i.e. higher sodium content, is observed in the central part of the study area, where Paleozoic shales, Mesozoic carbonates and a small part of Paleozoic carbonates dominate.

The average phosphorus content is 790 mg/kg and 870 mg/kg and the median value is 720 mg/kg and 700 mg/kg in the topsoil and subsoil, respectively. The phosphorus content in the samples from the studied area ranges from 360-1500 mg/kg for the topsoil and from 290-3600 mg/kg for the subsoil. The spatial distribution of the content in both soil layers is presented in Table 8, which shows that the highest P content was found in the southeastern part of the study area (Lazaropole and Tresonče villages), where Paleozoic shales and Mesozoic and Paleozoic carbonates dominate.

Lead is represented with an average content value of 55 mg/kg in the topsoil and 31 mg/kg in the subsoil. The median value is 33 mg/kg for the topsoil and 30 mg/kg for the subsoil. The lead content in the samples from the studied area ranges from 12–50 mg/kg for topsoil and from 13–61 mg/kg for subsoil. From the spatial distribution of Pb content (Figure 8), it is evident that lead is most abundant in the soils from the northern and eastern parts, where Paleozoic shales and Paleozoic carbonates predominate. In the subsoil samples, high lead contents are also found in the southern part of the study area, where Paleozoic sandstones predominate.

Strontium is present with a mean of 55 mg/kg in the topsoil and 60 mg/kg in the subsoil. The median is 46 mg/kg and 48 mg/kg for topsoil and subsoil, respectively. The strontium content in the samples from the studied area ranges from 16-180 mg/kg in the topsoil and from 24-250 mg/kg in the subsoil. The ratio of the medians of the strontium contents in the topsoil and subsoil is approximately 1 or, more precisely, 0.95 (Table 4). The maps of spatial distribution of strontium content in topsoil and subsoil (Figure 8) show that the highest strontium contents are found in the areas dominated by Mesozoic carbonates in the central part of the study area (Medenica and Starci hills on Bistra Mountain).

The content of vanadium in the samples from the study area ranges from 18-120 mg/kg in the topsoil and from 22-130 mg/kg in the subsoil. The average contents are 81 mg/kg and 78 mg/kg with a median value of 81 mg/kg and 77 mg/kg for topsoil and subsoil, respectively. The highest V content was found in the northern part of the study area (Lake Mavrovo and Korab Mountains), where Paleozoic shales dominate.

Conclusion

The results of spatial distribution of 19 elements (Ag, Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V и Zn) in soils from the Mavrovo-Rostuše region, Republic of Macedonia are presented. The analysis of the content of the elements was performed 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. The results for the content of the analysed elements in 66 soil samples taken at 33 sites from two layers (0-5 cm and 20-30 cm) were processed using multivariate statistical methods. Factor analysis was performed and three variables (F1, F2 and F3) were identified. Factor 1 includes Zn, K, Cu, Fe and Li, factor 2 with Cr, Ni and Mg and factor 3 consists of Ca and Al. The comparison of the contents of the analysed 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 spatial distribution of the elements follows the geology of the region and that their increased contents in certain areas are of lithogenic origin.

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