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GEOME 2
Manuscript received: September 11, 2017
Accepted: November 16, 2017

Geologica Macedonica, Vol. **31**, No. 2, pp. 117–130 (2017)
In print: ISSN 0352 – 1206
On line: ISSN 1857 – 8586
UDC: 631.416(497.742)
Original scientific paper

SPATIAL DISTRIBUTION OF CHEMICAL ELEMENTS IN SOIL FROM THE STRUMICA REGION, REPUBLIC OF MACEDONIA

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A b s t r a c t: This study presents results for the distribution of heavy metals in soil samples from the Strumica region, Republic of Macedonia. To perform this study, 132 soil samples were collected (66 from topsoil and 66 from bottom soil). Soil samples were digested by the mixture of mineral acids for total dissolution. Nineteen elements (Ag, Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) were analyzed by atomic emission spectroscopy with inductively coupled plasma (ICP-AES). The results were statistically processed and maps of spatial distribution of individual elements in the study area were prepared giving the presence of the analyzed elements in soil from the Strumica region. From the obtained results and the distribution maps it can be seen that the higher content of the elements in some areas are mainly due to their presence in the surrounding rocks. Factor analysis is performed from a number of variables providing a small number of new, synthetic variables called factors. On the basis of the spatial distribution of element patterns, comparison of basic statistical parameters, the correlation coefficient matrices, and the results of multivariate (cluster and FA) analyses, three lithogenic associations were established: F1 (Ni-Cr-Fe-V-Cu-Zn), F2 (Sr-Ca-Al-Mg) and F3 (K-Li).

Key words: soil; heavy metals; factor analysis; Strumica region; ICP-AES

INTRODUCTION

Urban and regional contamination with heavy metals in recent years has become the subject of many studies. According to the United Nations Environmental Program, the air pollution is the biggest cause of people's deaths in the world. The environmental pollution can be caused by two factors, natural and anthropogenic. These pollutants with a common name are called "primary pollutants". Apart from primary, there are also secondary pollutants that come from the primary ones. The extent and extent of the dissemination of pollutants depends on the source of the emission, its type and composition as well as on the weather conditions. Most of the emissions are located close to the source, but some can spread over thousands of kilometers. As main emission sources, there are smelters, mines, thermal power plants, metallurgical factories, etc. (Kabata-Pendias & Mukherjee, 2007).

Heavy metals are natural constituents of the Earth's crust, which are also polluting the environment because they can not be degraded or destroyed. All chemical compounds or elements released into the atmosphere cause harm to living organisms and are considered contaminants. The term "heavy metals" refers to chemical elements – metals that have relatively high density and are toxic at low concentrations. In the group of heavy metals the most present in the environment are: As, Cd, Cr, Hg, Ni, Pb, Sb or Tl (Baird, 1995; Connell, 1997; Manahan, 2000; Holdgate, 1979; Poikolainen, 2004).

Environmental pollution is pollution with the physical and biological components of the Earth's atmosphere to such an extent that the ordinary environmental processes are threatened. The intensive development of the industry is causing pollution and endangering of the environment. The particles of waste products that stand out in the atmospheric air have a wide range of sizes. Part of the particles is suspended in the atmosphere, while the other part is deposited on the soil and the surrounding vegetation (Kabata-Pendias & Mukherjee, 2007).

Soil pollution with heavy metals as a result of mining activities is a significant problem especially when the mined ore or flotation tailing are left at open landfills. Through mining activities, water bodies, soil and air are most affected to the heavy metals pollution polluted (Garbarino et al., 1995; Stafilov, 2014). Through rivers and streams, metals are transported either as dissolved species in water or as an integral part of suspended sediments.

The Republic of Macedonia has the same problem that becomes more serious as a result of the mining activities, smelting plants and thermoeectric power plants. The results of the previous studies give an indication of impaired air and soil quality in terms of presence of heavy metals and possible pollution (Barandovski et al., 2008, 2012, 2013, 2015; Stafilov, 2014). It was found high impact to the soil pollution by the Pb-Zn-Cd smelter plant in the town of Veles with several toxic elements such as As, Cd, Cu, Hg, In, Pb, Sb and Zn (Stafilov et. al., 2008, 2010).

The goal of the present study is to investigate the spatial distribution of 19 elements (Ag, Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) in soil from the Strumica region, Republic of Macedonia. For that purpose 132 soil samples were collected (66 from top soil and 66 from bottom soil). The analysis was performed by by atomic emission spectroscopy with inductively coupled plasma (ICP-AES).

MATERIALS AND METHODS

Study area

The Strumica region is situated on the south-east of the Republic of Macedonia with the biggest town of Strumica (Figure 1). The Municipality of Strumica is located on the south-western part of the Strumica region (Figure 2) and covers an area of 322 km^2 with a total population of about 55,000 inhabitants. In total the Strumica basin covers an area of 963 km^2.

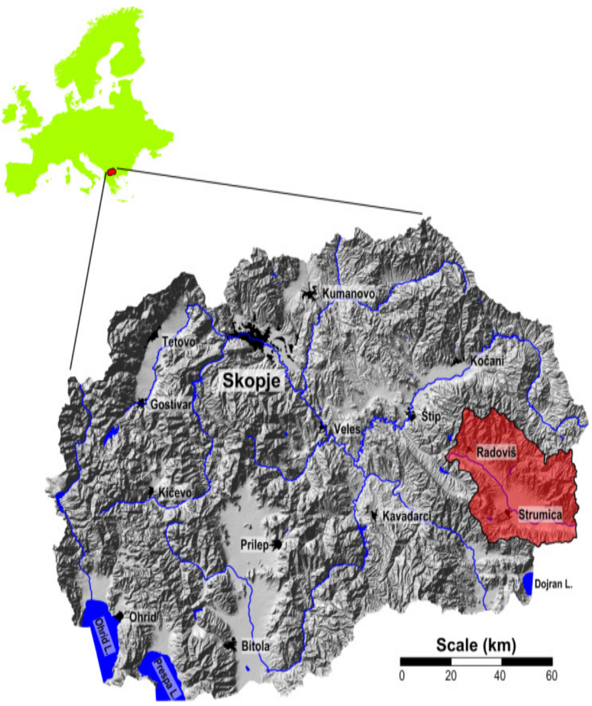

Fig. 1. Locality of the study area in the Republic of Macedonia

The entire Strumica region is divided into hilly mountains, which include scales and flatland soils, as well as alluvial, scum, rocky and carbonate soils. Most of the land (46%) is arable land and belongs to the plain relief part located at an average altitude of 250–300 m and are of primary importance for agriculture in the region.

The specific geographical and topographical position of the Strumica region is characterized by two zonal climates: sub-Mediterranean and continental. Sub-Mediterranean with long hot summers with high average daily temperatures and reduced annual rainfall, decreased winter temperatures and winds from all directions (Lazarevski, 1993).

The geology of the investigated area is very diverse. From the geological map (Figure 2) it can be noticed that in the northern and east-northern parts prevail Proterozoic gneisses and shales. In the central part along the Strumica river prevail Quaternary alluvial sediments and Neogene clastitic sediments. In the central eastern part and in the south-eastern part magmatic rock are present, while in the south-western part prevail Paleozoic shales with the inclusion of Paleozoic carbonates (Stafilov & Šajn, 2016).

The Strumica region is reach in non-metallic mineralization. The mine of feldspar "Hamzali" is unique in the Republic of Macedonia and the Balkans. The mine of $CaCO_3$ "Memešli" is a site that is basically a marble limestone. Investigations are carried out on Mount Ogražden in the immediate vicinity of the settlement Ilovica where the copper ore was found.

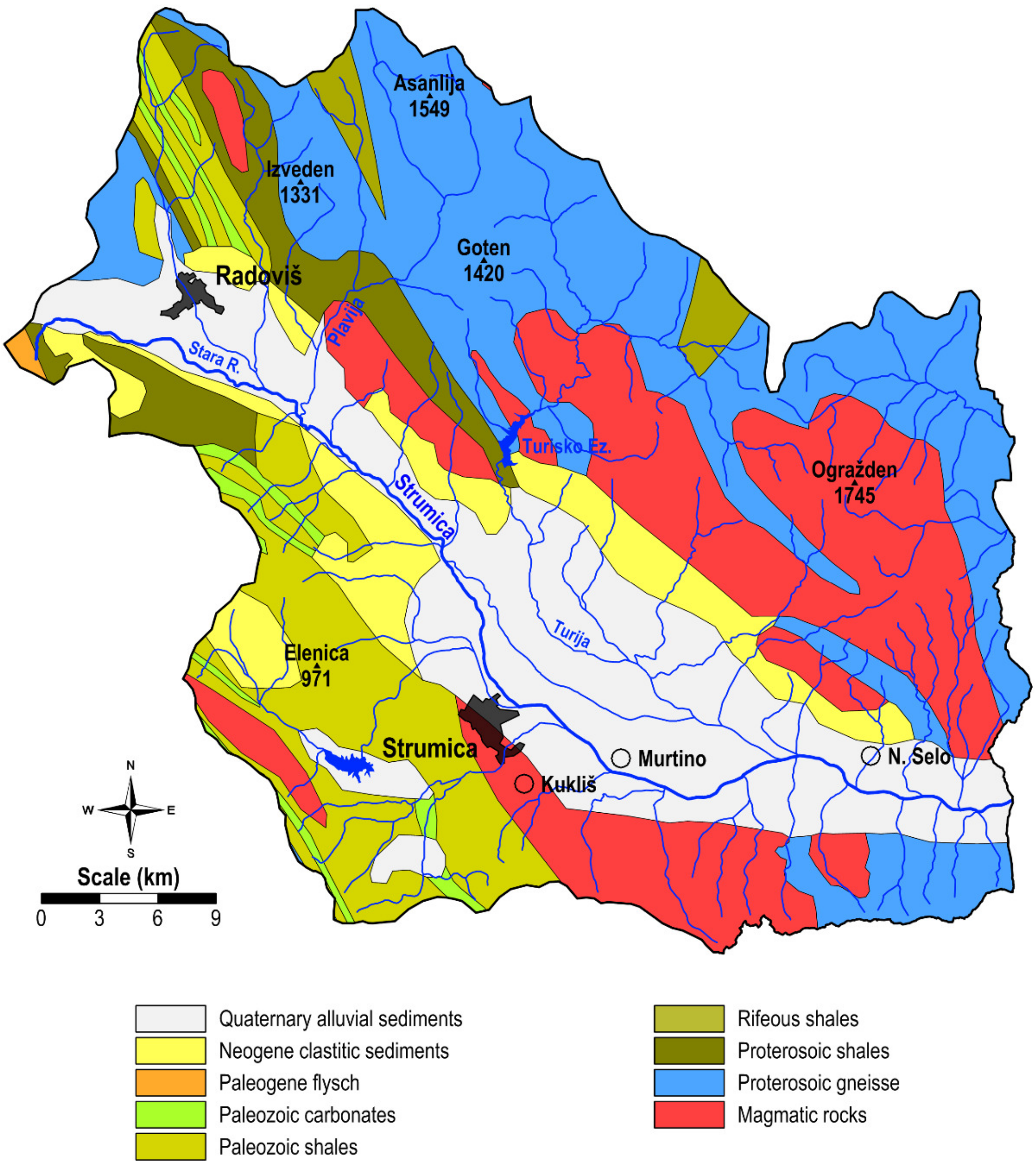

Fig. 2. Geological map of study area

Sample collection, pre-treatment and analysis

Soil samples were collected from 66 predetermined locations within networks with a density of 5 × 5 km (Figure 3). From each location, topsoil (0–5 cm) and subsoil (20–30 cm) samples were taken from 5 sublocations in radius of 10 m (Salminen et al., 2005). The samples were stored in plastic bags, then were cleaned from external bodies, dried at room temperature, crushed, sieved through 2 mm sieve and grinded in agate mill to obtain particles below 0.1 mm. Then, the samples were digested by applying a mixture of HNO_3, $HClO_4$, HF and HCl in accordance with the international standards ISO 14869-1:2001. The obtained solution is filtered through filter paper and quantitatively transferred into a volumetric flask of 25 ml. The flask is supplemented with distilled water. The analysis of the soil samples has determined the content 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) with application of the atomic emission spectrometer with inductively coupled plasma (ICP-AES), model Varian 715-ES (Balabanova et al., 2011). Both soil certified reference material (JSAC 0401) and spiked intra-laboratory samples were analyzed at a combined frequency of 20% of the samples. Recovery for spiked samples ranges from 90 to 110%, while the recovery for the certified reference material ranges from 94 to 108%.

Data processing

The multivariate R-mode factor analysis (Davis, 1986) was used to reveal the associations of the chemical elements. From numerous variables, the factor analysis (FA) derives a smaller number of new, synthetic variables. As a measure of similarity between variables, the product-moment correlation coefficient (*r*) was applied. For orthogonal rotation, the varimax method was used (Reimann et al., 2002). The universal kriging method with linear variogram interpolation (Snedecor, 1967) was applied for construction of the areal distribution maps of the particular elements and the factor scores. The basic grid cell size for interpolation was 20×20 m. For class limits the percentile values of factor scores distribution of the interpolated values were chosen. Seven classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100.

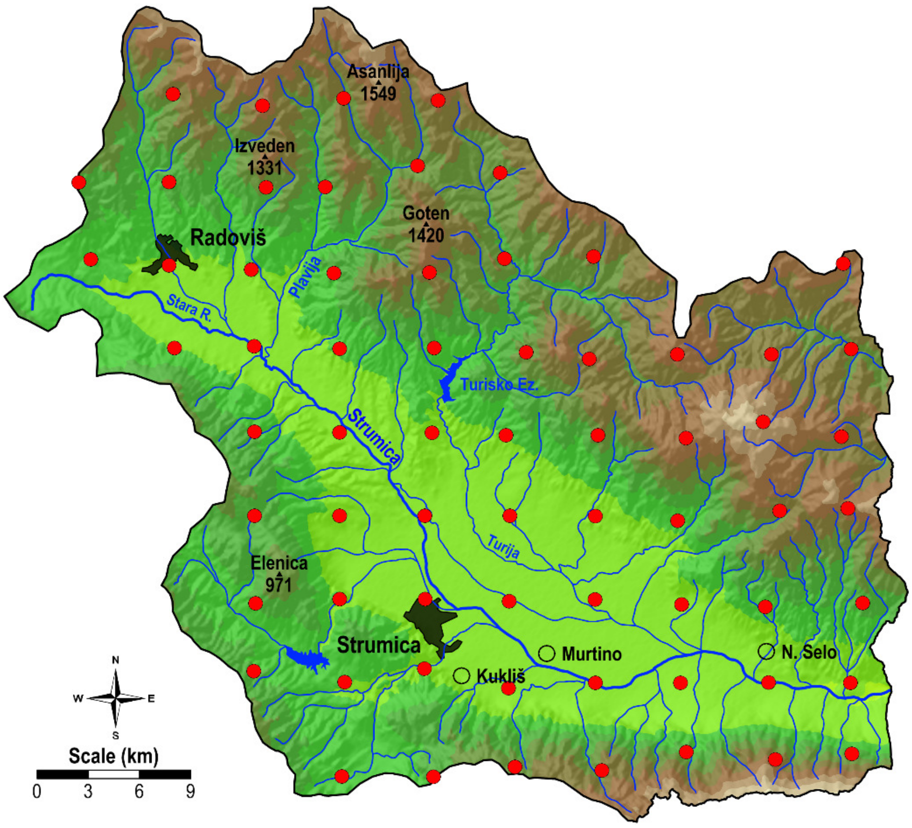

Fig. 3. Sampling location map

RESULTS AND DISCUSSIONT

he descriptive statistics of the contents of analyzed elements in soil samples are given in Tables 1 and 2, in which the values have been calculated for a total of 66 topsoil and 66 subsoil samples. Values of Al, Ca, Fe, K, Mg and Na are in %, and remaining elements in mg/kg. An analysis of the soil samples by ICP-AES gives data for the content of 19 elements (Ag, Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn). The concentrations data of major elements: Al, Ca, Fe, K, Mg and Na, are in the following ranges: 0.46–5.7% in topsoil and from 0.60 to 7.0% in subsoil for Al; 0.047–8.3% in topsoil and from 0.078 to 8.3% in subsoil for Ca; 1.0–4.6% in subsoil and from 0.78 to 5.5% in topsoil for Fe; 0.47–3.1% in subsoil and from 0.47 to 3.5% in topsoil for K; 0.057–1.2% in subsoil and from 0.099 to 0.99% in topsoil for Mg, and from 0.34 to 2.4% in subsoil and from 0.27 to 2.6% in topsoil for Na. The contents of major elements are most frequently a result of the dominant geological formations of the area: Quaternary alluvial and Neogene clastitic sediments, Paleozoic shales, Proterozoic gneisses and magmatic rocks.

T a b l e 1

Descriptive statistics for the content of analyzed elements in topsoil samples (n=66)

Element	Unit	X	X(BC)	Md	Min	Max	P_{25}	P_{75}	P_{10}	P_{90}	S	Sx	CV	A	E	A(BC)	E(BC)
Ag	mg/kg	1.3	1.0	0.93	0.040	5.9	0.61	1.5	0.40	2.8	1.1	0.13	82	1.96	4.97	–0.27	1.24
Al	%	2.4	2.2	2.0	0.46	5.7	1.4	3.1	1.2	4.2	1.2	0.14	48	0.74	–0.10	–0.17	–0.27
B	mg/kg	16	6.1	11	0.50	66	0.50	25	0.50	46	18	2.2	110	1.07	0.22	–0.18	–1.65
Ba	mg/kg	230	230	220	38	420	180	280	120	340	87	11	37	0.11	–0.09	–0.00	–0.06
Ca	%	0.96	0.60	0.63	0.047	8.3	0.33	1.1	0.24	1.8	1.2	0.15	130	4.14	21.32	–0.08	0.78
Cr	mg/kg	44	42	43	8.6	98	29	59	18.3	71	21	2.6	47	0.45	–0.18	–0.00	–0.39
Cu	mg/kg	22	20	21	5.9	58	15	28	11.4	39	11	1.3	49	1.23	1.93	0.05	0.18
Fe	%	2.6	2.5	2.6	0.78	5.5	2.1	3.1	1.2	3.4	0.84	0.10	33	0.32	1.33	–0.02	0.91
K	%	1.6	1.6	1.6	0.47	3.5	1.4	1.8	1.2	2.2	0.44	0.055	27	1.19	4.71	0.46	3.40
Li	mg/kg	16	14	12	4.0	51	8.9	20	7.0	26	9.7	1.2	60	1.52	2.44	0.21	–0.32
Mg	%	0.57	0.56	0.54	0.099	0.99	0.35	0.80	0.27	0.93	0.25	0.031	44	0.08	–1.27	–0.08	–1.16
Mn	mg/kg	530	450	450	81	2200	320	600	250	960	360	44	67	2.37	6.94	–0.11	1.62
Na	%	1.4	1.4	1.4	0.27	2.6	0.98	1.7	0.83	2.0	0.47	0.058	35	0.13	–0.05	0.05	–0.05
Ni	mg/kg	20	19	18	1.6	54	13	27	6.8	35	11	1.3	53	0.83	0.86	–0.01	0.19
P	mg/kg	530	500	510	150	1400	380	620	260	810	210	26	41	1.02	2.87	–0.08	0.69
Pb	mg/kg	20	13	17	2.5	170	7.6	23	2.5	31	25	3.1	120	4.49	23.49	–0.25	0.37
Sr	mg/kg	56	50	49	3.0	220	32	69	17.3	95	35	4.4	64	1.86	6.18	0.30	1.06
V	mg/kg	65	63	66	11	200	47	79	31.0	94	30	3.7	46	1.43	6.01	0.24	2.06
Zn	mg/kg	110	89	90	39	1200	80	110	61.6	120	130	16	120	7.74	61.79	–0.72	3.67

X – arithmetic mean, X(BC) – arithmetic mean obtained with the Box-Cox method, Md – median, Min – minimum, Max – maximum, P_{10} – 10 percentiles, P_{90} – 90 percentiles, P_{25} – 25 percentiles, P_{75} – 75 percentiles, S – standard deviation, Sx – standard deviation (standard error), CV – coefficient of variation, A – asymmetry, E – distribution, A(BC) – asymmetry obtained with the Box-Cox method, E(BC) – distribution obtained with the Box-Cox method

Table 2.

Descriptive statistics for the content of analyzed elements in subsoil samples (n = 66)

Element	Unit	X	X(BC)	Md	Min	Max	P_{25}	P_{75}	P_{10}	P_{90}	S	Sx	CV	A	E	A(BC)	E(BC)
Ag	mg/kg	1.3	1.1	0.96	0.22	5.1	0.68	1.7	0.48	2.9	1.0	0.13	77	1.67	2.50	0.61	–0.22
Al	%	2.3	2.1	2.0	0.60	7.0	1.4	2.8	1.0	4.3	1.3	0.16	54	1.33	1.91	0.15	–0.18
B	mg/kg	18	6.0	7.6	0.50	120	0.50	34	0.50	47	22	2.8	120	1.87	5.38	–0.05	–1.66
Ba	mg/kg	230	230	240	12	480	180	280	110	320	89	11	38	0.18	0.82	0.01	0.82
Ca	%	0.95	0.59	0.57	0.078	8.3	0.28	1.1	0.22	2.0	1.2	0.15	130	4.13	22.56	0.07	–0.03
Cr	mg/kg	46	44	44	10	95	33	62	17.1	76	21	2.6	45	0.24	–0.65	–0.14	–0.61
Cu	mg/kg	23	21	21	4.8	64	15	27	10.0	38	11	1.4	49	1.20	2.34	–0.05	0.15
Fe	%	2.6	2.6	2.6	1.0	4.6	2.1	3.1	1.5	4.0	0.83	0.10	32	0.27	–0.03	0.05	–0.11
K	%	1.6	1.6	1.6	0.47	3.1	1.4	1.7	1.1	2.2	0.44	0.054	28	0.48	2.02	–0.13	1.99
Li	mg/kg	16	14	14	3.3	47	9.4	21	7.6	27	9.2	1.1	57	1.46	2.53	–0.21	0.50
Mg	%	0.59	0.57	0.58	0.057	1.2	0.38	0.76	0.21	0.99	0.28	0.034	48	0.13	–0.67	–0.17	–0.56
Mn	mg/kg	520	440	440	100	2100	320	610	230	870	340	42	65	2.36	7.43	0.08	0.67
Na	%	1.4	1.4	1.4	0.34	2.4	1.1	1.6	0.86	1.9	0.42	0.052	31	–0.08	–0.36	–0.14	–0.32
Ni	mg/kg	22	20	21	3.5	48	14	28	8.7	38	11	1.3	50	0.58	–0.20	–0.01	–0.36
P	mg/kg	490	460	420	120	1100	350	630	270	780	210	26	43	0.89	0.72	0.11	0.16
Pb	mg/kg	30	15	18	1.1	780	10	23	2.5	37	95	12	320	7.92	63.75	0.19	3.69
Sr	mg/kg	55	49	50	1.5	170	31	71	19.1	96	33	4.0	60	1.02	1.57	–0.19	0.43
V	mg/kg	68	65	70	18	150	49	84	34.0	96	27	3.4	40	0.38	0.42	–0.16	–0.06
Zn	mg/kg	200	90	90	39	6400	77	110	62.3	130	780	96	400	8.05	65.21	–0.00	2.99

X – arithmetic mean, X(BC) – arithmetic mean obtained with the Box–Cox method, Md – median, Min – minimum, Max – maximum, P_{10} – 10 percentiles, P_{90} – 90 percentiles, P_{25} – 25 percentiles, P_{75} – 75 percentiles, S – standard deviation, Sx – standard deviation (standard error), CV – coefficient of variation, A – asymmetry, E – distribution, A(BC) – asymmetry obtained with the Box-Cox method, E(BC) – distribution obtained with the Box-Cox method.

In order to determine the dependence of the average contents of the analyzed elements between the topsoil and the subsoil, the ratio of the contents was calculated (Table 3).

T a b l e 3

The ration of the element average content in topsoil (TS) and subsoil (SS) samples

Element	Unit	Topsoil	Sub–soil	FO (T/S)	T (test)	Sign	F	Sign
Ag	mg/kg	1.0	1.1	0.91	–0.69	NS*	1.37	NS
Al	%	2.2	2.1	1.04	0.46	NS	1.06	NS
B	mg/kg	6.1	6.0	1.01	0.03	NS	1.09	NS
Ba	mg/kg	230	230	1.00	0.07	NS	1.06	NS
Ca	%	0.60	0.59	1.02	0.11	NS	1.01	NS
Cr	mg/kg	42	44	0.95	–0.59	NS	1.00	NS
Cu	mg/kg	20	21	0.99	–0.14	NS	1.04	NS
Fe	%	2.5	2.6	0.98	–0.43	NS	1.05	NS
K	%	1.6	1.6	1.02	0.43	NS	1.07	NS
Li	mg/kg	14	14	0.98	–0.23	NS	1.02	NS
Mg	%	0.56	0.57	0.98	–0.21	NS	1.23	NS
Mn	mg/kg	450	440	1.01	0.14	NS	1.06	NS
Na	%	1.4	1.4	0.99	–0.15	NS	1.26	NS
Ni	mg/kg	19	20	0.92	–0.92	NS	1.05	NS
P	mg/kg	500	460	1.07	0.94	NS	1.04	NS
Pb	mg/kg	13	15	0.89	–0.67	NS	1.11	NS
Sr	mg/kg	50	49	1.02	0.16	NS	1.03	NS
V	mg/kg	63	65	0.96	–0.56	NS	1.12	NS
Zn	mg/kg	89	90	0.98	–0.30	NS	1.20	NS

*NS – nonsignificant, F – ratio, FO – ratio of the concentrations topsoil/subsoil

The elements distribution should not vary significantly between the topsoil (0–5 cm) and the subsoil (20–30 cm), except if certain destructive anthropogenic or natural processes do not contribute to the variation of the concentration (Dudka & Adriano, 1997). For almost all elements, not significant differences were received for their content in the topsoil versus subsoil. Thus, this relation varies from 0.91 for Ag to 1.07 for P. For the other elements this ration is close to 1 which shows of the absence of the significant influence of possible soil pollution from anthropogenic activities. Also, this is confirmed by the great similarity in the spatial distribution of the investigated elements in topsoil and subsoil samples. The higher content of P in topsoil samples insignificant anthropogenic influence due to the usage of phosphorous fertilizers in agriculture in this area (Stafilov & Šajn, 2016).

A comparative analysis (Table 4) of the median contents of the analyzed elements in the soil from the Strumica region with those obtained for the soils in Macedonia (Mihajlov et al., 2016; Stafilov & Šajn, 2016) and Europe (Salminen et al., 2005). It could be noted that the median values are higher than the European medians for Ag, Cu, Mg, Na, Pb and Zn, lower for Ba, Ca, Cr, Mn and Sr, while for the other elements the values did not show significant variations. The median values for the Strumica region are also very similar to those for the Macedonian soils with the exception of higher values for Na and lower for Al, Ba, Ca, Cr, Li, Mg, Mn, Ni, P and Sr. Bivariate statistics has been applied in order to determine the correlation degree between the examined elements, which shows that when the absolute value of the correlation coefficient extends from 0.3 to 0.7, then it is a matter of good association of the elements, and when such values extend from 0.7 to 1.0, then we can say that there is strong connection between the examined elements.

Table 5 contains a correlation matrix of coefficients from which it can be seen how the content of each element correlates with the content of all examined elements.

Table 6 contains a factor analysis, i.e. the loading matrix for the dominant rotating factors, which helps to identify four factors. The factor analysis has eliminated those elements which do not have a share in the communality, from the total of 19 analyzed elements. Those three factors include a total of 12 elements, with a total share of 78.5% in the communality. The elements Ag, B, Ba, Mn, Na, P and Pb have low factor values with a weak tendency to form an independent factor.

Figure 4 presents cluster analysis of data in which the elements are divided into clusters according to their degree of correlation. Identical results were achieved as in the case of application of factor analysis (the graphical representation is shown in Figure 4). Namely, Factor 1 (Ni, Cr, Fe, V, Cu and Zn) corresponds to cluster 2, Factor 2 (Sr, Ca, Al and Mg) to cluster 1 and Factor 3 (K and Li) corresponds to the claster 3.

T a b l e 4

Comparison of the median values for topsoil and subsoil samples from the Strumica region with Macedonian and European values

		Strumica region				Macedonia (Mihajlov et al., 2016)				Macedonia (Stafilov & Šajn, 2016)		Europe (Salminen et al., 2005)			
		Topsoil		Subsoil		Topsoil		Subsoil		Topsoil (0–30 cm)		Topsoil		Subsoil	
Element	Unit	Md	Min–Max	Md	Min–Max	Md	Min–Max	Md	Min–Max	Md	Min–Max	Md	Min–Max	Md	Min– Max
Ag	mg/kg	0.93	0.040–5.9	0.96	0.22–5.1	–	–	–	–	–	–	0.27	0.01–3.15	0.25	0.02–2.07
Al	%	2.0	0.46–5.7	2.0	0.60–7.0	2.2	0.79–4.3	2.3	0.77–5.1	6.6	0.09–11	5830	0.20–1.42	0.62	0.11–1.43
B	mg/kg	11	0.50–66	7.6	0.50–120	–	–	–	–	–	–	–	–	–	–
Ba	mg/kg	220	38–420	240	12–480	420	41–1600	440	66–1700	430	6–2900	375	30–1870	385	13–2050
Ca		0.63	0.047–8.3	0.57	0.078–8.3	0.79	0.092–21.0	0.78	0.10–21	1.30	0.10–35	6638	0.02–34.3	8136	0.17–37.1
Cr	mg/kg	43	8.6–98	44	10–95	54	11–600	63	11–600	88	5.0–2700	60	<3–6230	62	<3–2140
Cu	mg/kg	21	5.9–58	21	4.8–64	16	1.7–73	16	3.2–78	28	1.6–270	13	0.81–256	13.9	0.86–125
Fe		2.6	0.78–5.5	2.6	1.0–4.6	2.5	0.63–6.7	2.7	0.77–8.0	3.5	0.03–12	2.46	1.12–15.6	2.62	0.077–10.9
K	%	1.6	0.47–3.5	1.6	0.47–3.1	1.4	0.26–3.2	1.5	0.52–3.3	1.9	0.02–5.3	1.6	0.02–5.1	1.7	<0.01–5.0
Li	mg/kg	12	4.0–51	14	3.3–47	18	4.8–79	20	5.2–69	26	1.8–210	–	–	–	–
Mg		0.54	0.099–0.99	0.58	0.057–1.2	0.66	0.11–2.9	0.73	0.15–3.1	0.94	0.12–13	0.47	<0.006–15	0.60	<0.006–11.4
Mn	mg/kg	450	81–2200	440	100–2100	620	160–3200	640	99–4300	900	17–>10000	507	31–6068	468	23–4710
Na	%	1.4	0.27–2.6	1.4	0.34–2.4	0.85	0.033–2.3	0.94	0.078–2.4	1.2	0.013–6.0	0.6	0.03–3.3	0.6	0.02–3.5
Ni	mg/kg	18	1.6–54	21	3.5–48	35	2.5–530	37	5.2–530	46	2.1–2500	18	<2–2690	21.8	<2–2400
P	mg/kg	510	150–1400	420	120–1100	450	120–1400	430	74–1300	620	110–3900	560	48–5770	420	30–7250
Pb	mg/kg	17	2.5–170	18	1.1–780	17	2.5–700	14	0.8–660	32	1.2–>10000	10	5.32–970	17.2	<3–938
Sr	mg/kg	49	3.0–220	50	1.5–170	71	9.4–540	68	9.9–580	140	21–1400	89	8–3120	95	6–2010
V	mg/kg	66	11–200	70	18–150	67	14–300	71	19–370	89	1.0–470	60	2.71–537	62.8	1.28–325
Zn	mg/kg	90	39–1200	90	39–6400	39	3.1–440	38	4.4–490	83	8.0–>10000	52	<3–2900	47	<3–3060

T a b l e 5.

Matrix of correlation coefficients (n = 66)

Element	Ag	Al	B	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	Sr	V	Zn
Ag	1.00																		
Al	–0.13	1.00																	
B	0.14	–0.33	1.00																
Ba	–0.18	0.27	–0.21	1.00															
Ca	0.09	0.68	–0.16	0.27	1.00														
Cr	0.18	0.40	0.27	0.36	0.42	1.00													
Cu	0.15	0.44	0.03	0.23	0.41	0.60	1.00												
Fe	0.06	0.62	0.15	0.34	0.54	0.80	0.70	1.00											
K	–0.08	–0.18	–0.14	–0.14	–0.39	–0.49	–0.14	–0.37	1.00										
Li	–0.02	0.38	–0.35	0.16	0.20	0.13	0.26	0.33	0.27	1.00									
Mg	–0.07	0.68	–0.29	0.54	0.52	0.60	0.52	0.70	–0.30	0.25	1.00								
Mn	0.26	0.52	0.05	0.15	0.41	0.50	0.48	0.63	–0.26	0.27	0.44	1.00							
Na	–0.13	–0.09	–0.18	0.05	–0.03	–0.43	–0.51	–0.34	–0.11	–0.33	–0.09	–0.15	1.00						
Ni	0.20	0.36	0.26	0.27	0.33	0.94	0.61	0.75	–0.44	0.17	0.52	0.53	–0.47	1.00					
P	–0.14	0.32	0.03	0.05	0.34	0.11	0.32	0.36	–0.10	0.16	0.35	0.23	0.18	0.09	1.00				
Pb	0.24	–0.17	0.39	0.06	–0.05	0.21	0.18	0.10	0.05	–0.08	–0.08	0.18	–0.19	0.17	0.01	1.00			
Sr	0.04	0.70	–0.17	0.50	0.83	0.57	0.43	0.64	–0.48	0.31	0.66	0.49	–0.03	0.46	0.29	–0.04	1.00		
V	0.12	0.53	0.18	0.31	0.59	0.84	0.64	0.92	–0.53	0.28	0.62	0.60	–0.32	0.78	0.33	0.09	0.70	1.00	
Zn	–0.02	0.25	0.13	0.35	0.17	0.43	0.53	0.51	–0.01	0.23	0.34	0.33	–0.26	0.41	0.26	0.33	0.23	0.50	1.00

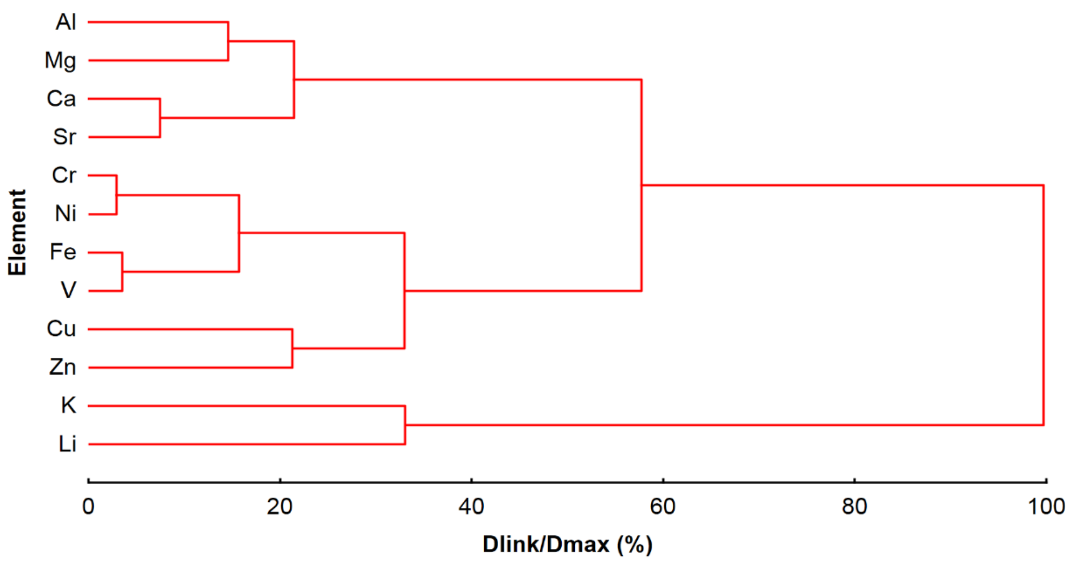

Fig. 4. Dendrogram from cluster analysis

T a b l e 6

Matrix of overload of dominant rotating factors

Elements	Factor.	F1	F2	F3	Comm
Ni	1.1	0.86	0.22	-0.22	83.7
Cr	1.2	0.85	0.32	-0.28	89.2
Fe	1.3	0.79	0.51	0.01	88.0
V	1.4	0.78	0.51	-0.16	88.8
Cu	1.5	0.75	0.28	0.18	66.9
Zn	1.6	0.72	0.00	0.31	61.4
Sr	2.1	0.29	0.88	-0.11	87.5
Ca	2.2	0.16	0.88	-0.10	80.6
Al	2.3	0.23	0.83	0.22	79.4
Mg	2.4	0.47	0.65	0.03	64.9
K	3.1	-0.26	-0.36	0.80	83.2
Li	3.2	0.19	0.35	0.72	68.0
Prp total	101	35.4	30.5	12.5	78.5
Eigen val	102	6.51	1.49	1.41	
Expl. var	103	4.25	3.67	1.50	

Factor 1 (Ni, Cr, Fe, V, Cu, and Zn) represents a lithogenous association of elements with the highest load factor values (47%). The spatial distribution of factor scores of F1 on both layers (topsoil and subsoil) is given in Figures 5 and 6. It can be seen that the spatial distribution of factor scores for the two layers is very similar which means that there is no significant difference in the presence of these elements in the surface and depth soil. The origin of the elements in this typical lithogenous association is connected to the geological composition of the soils in this region. It can be seen from the distribution maps (Figures 5 and 6) that the higher contents of the elements from Factor 1 occur in the areas of Paleozoic shales, Proterozoic gneisses and Quaternary alluvial sediments, on the western and south- and north-western part of the investigated area.

From this association of elements very characteristic is the distribution of copper. From Figures 7 and 8 it can be seen that beside in the soil from the western parts of the investigated area higher copper content is found in the region of the village of Ilovica, where opening of an open pit copper mine is planned.

The spatial distribution of the factor scores of Factor 2 (Sr, Ca, Al and Mg) is given in Figures 9 and 10, representing also lithogenous association. From the distribution maps of the factor scores for both soil layers (Figures 9 and 10) can be seen that the higher specific values of the contents of these elements were determined in soils from the central western part and eastern part of the study area with the dominant presence of Paleozoic shales and magmatic rocks.

Factor 3 (K and Li) represents the third lithogenic association of elements. The increased content of potassium and lithium is typical for the eastern part of the investigated area and the area around the town of Strumica on the dominant magmatic rocks (Figures 11 and 12).

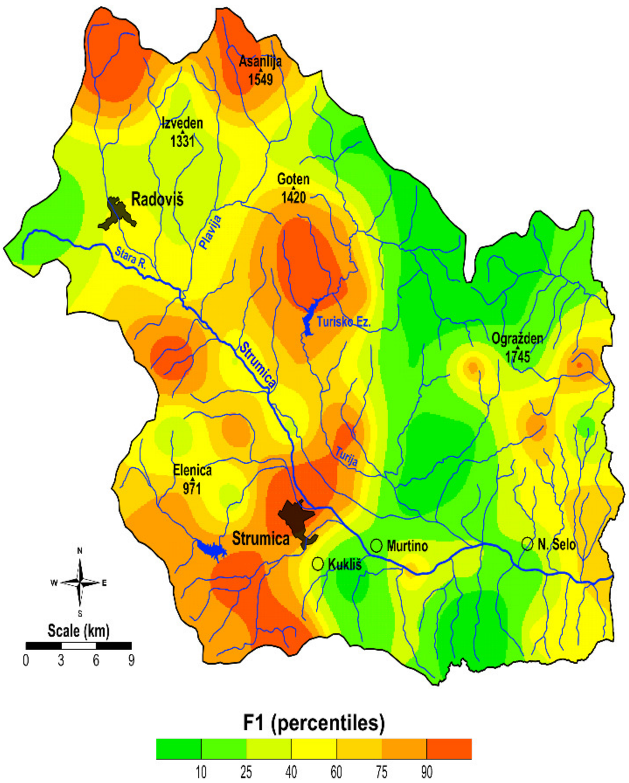

Fig. 5. Spatial distribution of factor values of Factor 1 (Ni, Cr, Fe, V, Cu and Zn) in topsoil

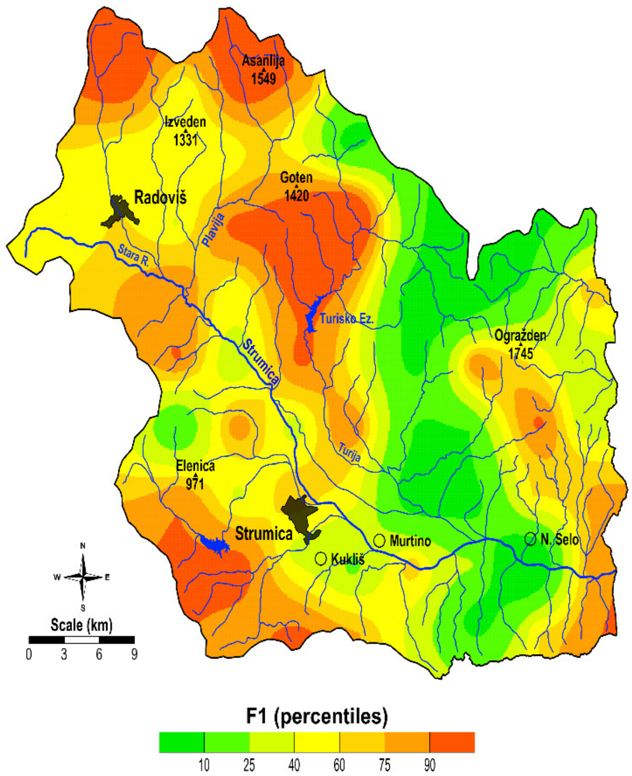

Fig. 6. Spatial distribution of factor values of Factor 1 (Ni, Cr, Fe, V, Cu and Zn) in subsoil

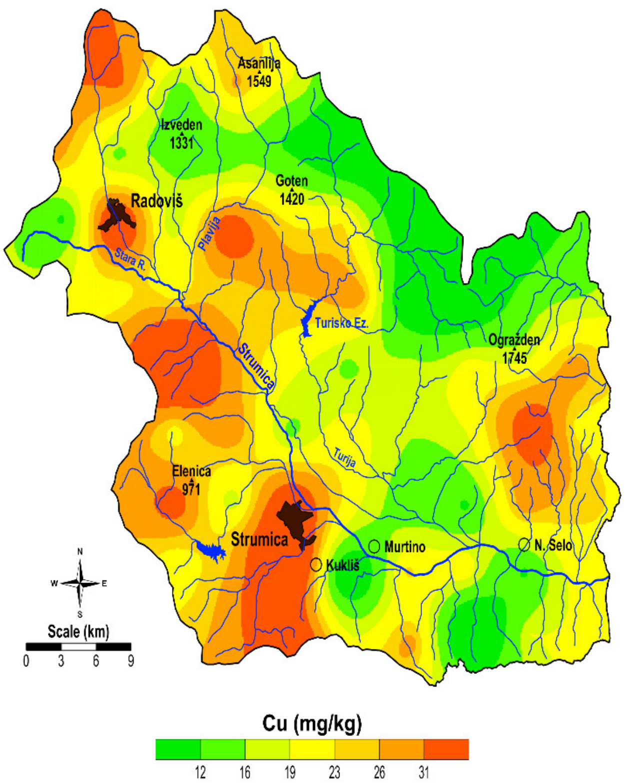

Fig. 7. Spatial distribution of copper in topsoil

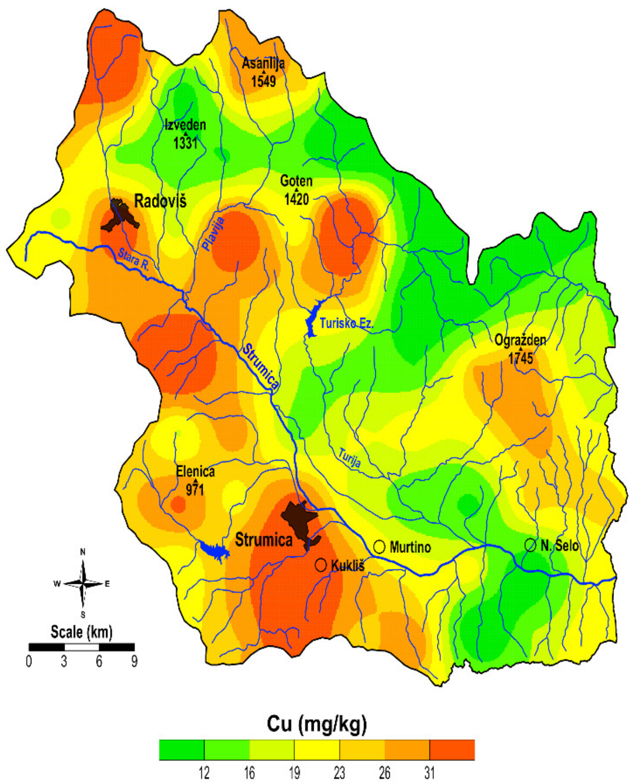

Fig. 8. Spatial distribution of copper in subsoil

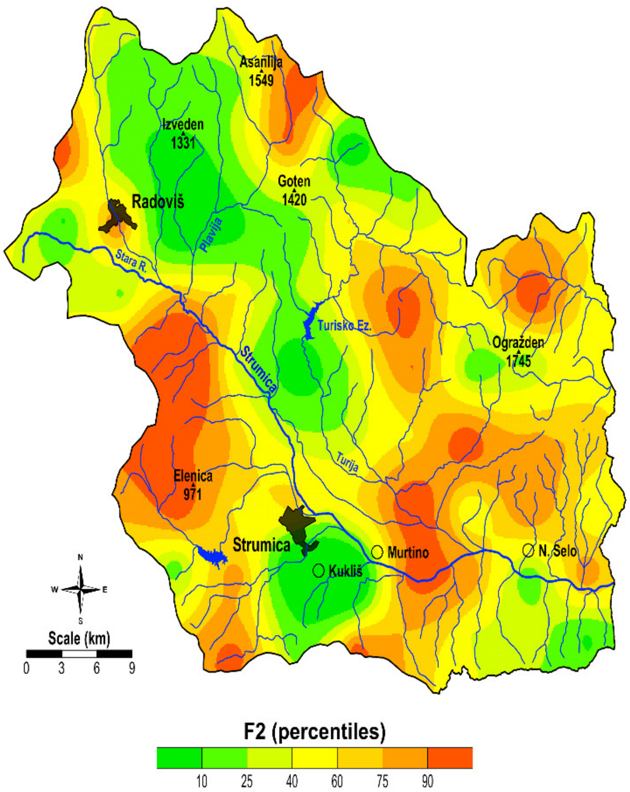

Fig. 9. Spatial distribution of factor values of Factor 2 (Sr, Ca, Al and Mg) in topsoil

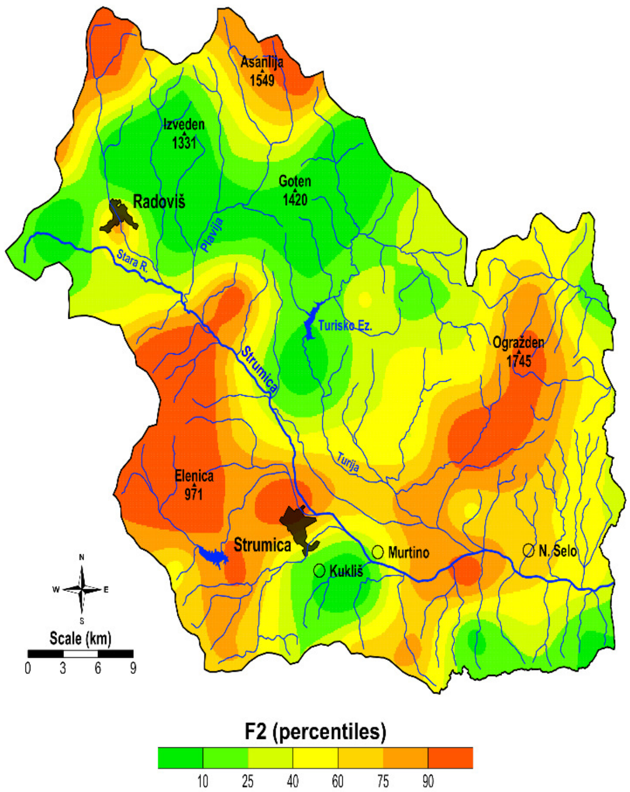

Fig. 10. Spatial distribution of factor values of Factor 2 (Sr, Ca, Al and Mg) in subsoil

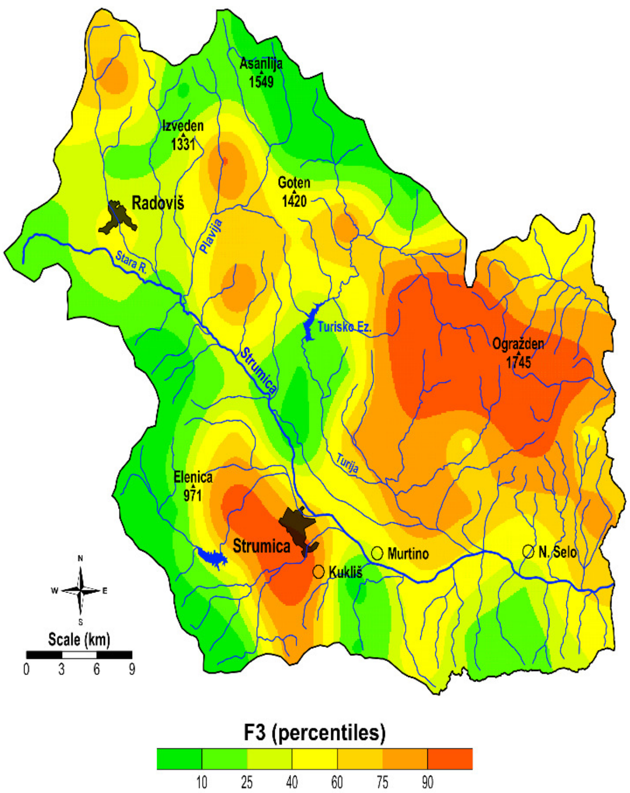

Fig. 11. Spatial distribution of factor values of Factor 3 (K and Li) in topsoil

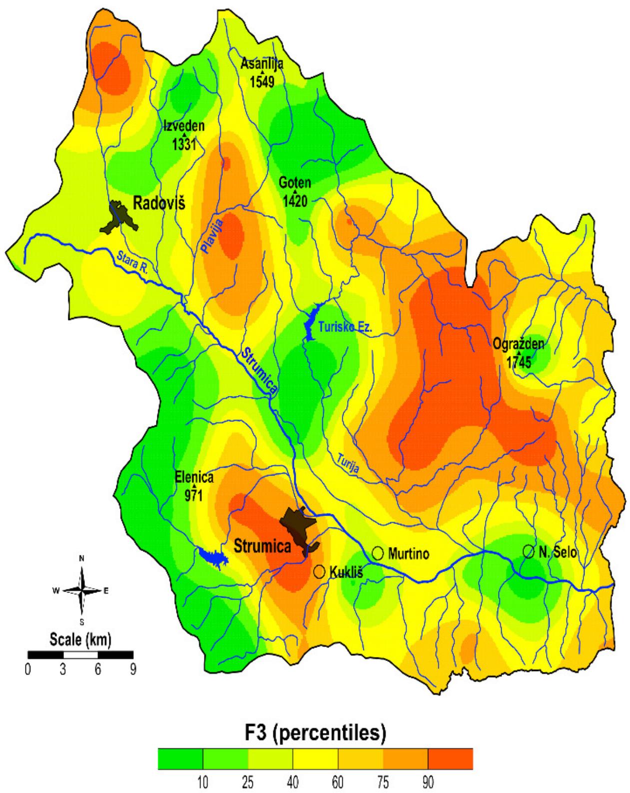

Fig. 12. Spatial distribution of factor values of Factor 3 (K and Li) in subsoil

CONCLUSION

The aim of this study is the systematic investigation of the spatial distribution of various chemical elements in surface soil over the Strumica region, Republic of Macedonia. In total 132 soil samples were collected (66 from topsoil and 66 from bottom soil). Nineteen elements (Ag, Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) were analyzed by atomic emission spectroscopy with inductively coupled plasma (ICP-AES). From the obtained results and the distribution maps of the factor scores and the analyzed elements it can be seen that the higher content of the elements in some areas are mainly due to their presence in the surrounding rocks. On the basis of the spatial distribution of element patterns, comparison of basic statistical parameters, the correlation coefficient matrices, and the results of multivariate (cluster and FA) analyses, three lithogenic associations were established: F1 (Ni-Cr-Fe-V-Cu-Zn), F2 (Sr-Ca-Al-Mg) and F3 (K-Li).

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Р е з и м е

ПРОСТОРНА ДИСТРИБУЦИЈА НА ХЕМИСКИ ЕЛЕМЕНТИ ВО ПОЧВИТЕ ОД СТРУМИЧКИОТ РЕГИОН, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: почва; тешки метали; факторна анализа; струмички регион; ICP-AES

Презентирани се податоци за дистрибуција на различни елементи во почвите во струмичкиот регионот, Република Македонија. За таа цел се земени 132 примероци од почва (66 од површинска и 66 од потповршинска почва). Примероците се разложени со смеса од минерални киселини до тотално растворање. Со примена на атомска емисиона спектрометрија со индуктивно спрегната плазма (АЕС-ИСП) вкупно се определени 19 елементи (Ag, Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn). Резултати се статистички обработени и се изработени карти на просторна дистрибуција на сите испитувани елементи, со што се добива сознание за присуството на елементите во почвите од струмичкиот регион. Од добиените резултати и од картите на дистрибуцијата може да се види дека повисоката застапеност на елементите во некои области е главно резултат на нивно поголемо присуство во околните карпи. Факторната анализа е изведена со цел од голем број променливи да се добие помал број на нови синтетички променливи, наречени фактори. Врз основа на просторната дистрибуција на елементите, споредбата на основните статистички податоци, матрицата на корелационите коефициенти и резултатите од мултиваријантните анализи (кластерна и факторна) се утврдени 3 литогени асоцијации: F1 (Ni-Cr-Fe-V-Cu-Zn), F2 (Sr-Ca-Al-Mg) и F3 (K-Li).