296
GEOME 2
Manuscript received: July 6, 2015
Accepted: October 5, 2015

Geologica Macedonica, Vol. **29**, No. 2, pp. 155–166 (2015)
In print: ISSN 0352 – 1206
On line: ISSN 1857 – 8586
UDC: 528.94 : 550.42]:631.4(497.75)
Original scientific paper

SPATIAL DISTRIBUTION OF CHEMICAL ELEMENTS IN SOILS IN THE POLOG REGION, REPUBLIC OF MACEDONIA

Angja Ćulumoska-Gjorgjievska[1], Trajče Stafilov[1*], Robert Šajn[2]

[1]*Institute of Chemistry, Faculty of Natural Sciences and Mathematics,*
"Ss. Cyril and Methodius" University in Skopje, POB 162, Skopje, Republic of Macedonia,
[2]*Geological Survey of Slovenia, Dimičeva ulica 14, 1000 Ljubljana, Slovenia*
trajcest@pmf.ukim.mk

A b s t r a c t: The purpose of this study was to determine the presence and spatial distribution of various chemical elements in soil in the Polog region, Republic of Macedonia. For this purpose, geochemical monitoring techniques were applied for determination of 19 macro and trace elements (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn). A total of 116 soil samples (58 samples of topsoil and 58 samples of subsoil) were taken from predetermined referent locations. The collected samples were analyzed by the application of atomic emission spectrometry with inductively coupled plasma (ICP-AES). From the analyzed soil samples, 4 chemical associations were determined, from which three factors with lithogenic source (F1, F2 and F4) and one factor with mixed lithogenic and anthropogenic origin (F3). In factor 3 the anthropogenic impact is due to increased deposits of potassium in the surface soil layers in the southern parts of the Polog valley, where potassium fertilizers are used in agriculture. The elements which are included in the lithogenic factors are present in soil as a result of the geological structures in area where these elements are present (schists, carbonates, sandstones and sediments).

Key words: geochemical monitoring; soil; heavy metals; Polog; Macedonia

INTRODUCTION

The term "heavy metal" refers to any metallic element with a relatively high density, toxic or poisonous at low concentrations (Lenntech, 2004). Heavy metals are present in the composition of the Earth's crust, in free or bound state in their ores. In small quantities, they enter the human body through food, water and air. In the environment, heavy metals are emitted from natural and anthropogenic sources. The main sources of anthropogenic pollution are located in areas with mining and industrial activities. Heavy metals are emitted in their natural elemental state or in the form of organic or inorganic compounds. Mining, transport, production and use of synthetic products such as pesticides, paints, batteries, industrial waste can result in heavy metal contamination of urban and agricultural soils. Potentially contaminated surfaces may occur in industrial, mining regions and places where industrial waste has historically been deposited from various manufacturing processes. High content of heavy metals can be observed in areas with rapid industrial development that generate industrial wastewater. The processes of ore processing and tailing disposal have a major impact on the environment through their impact on the land, water and air (Kabata-Pendias & Mukherjee, 2007).

The potential for contamination is higher in the regions where ore and waste deposits are directly unloaded and stored. Through large water bodies (rivers and streams) or by erosion, metals are transported as dissolved particles in the water or as components of suspended sediments, and with the winds they are blown away from the places where they were originally deposited. The addition of additives and supplements to increase soil fertility further exacerbates the situation because many of these products contain high amounts of heavy metals which over time accumulate to dangerous concentrations. This process leads to bioaccumulation of heavy metals in humans and animals through the food chain and causes serious health disorders, which is why constant monitoring and regulation of emissions of heavy metals into the atmosphere, soil and water is necessary (Bowen, 1979; Kabata-Pendias & Mukherjee, 2007).

The Republic of Macedonia has the same problem with global pollution by heavy metals (Stafilov, 2014). Recent years the results obtained from previous studies, suggest that the most important emission sources are mines and drainage systems and smelters near the towns of Veles, Tetovo, Kavadarci and Radoviš, and some uranium deposition patterns which were described by the activity of power plants using lignite coal as fuel (Stafilov et al., 2010a, 2010b; Barandovski et al., 2012; Balabanova et al., 2010, 2011; Bačeva et al., 2012). The soil cover of the Republic of Macedonia is very heterogeneous, with great changes over small distances. Almost all relief forms, geological formations, climatic influences, plant associations and soils that appear in Europe (with the exception of podzols) are represented. More than thirty soil types are found in Macedonia (Mitkova & Mitrikeski, 2005).

The chemical analysis of the soil enables the levels of deposits of heavy metals to be determined according to the depth from which samples are taken. With correlation of different levels, information can be obtained on the differences in the concentrations of heavy metals and the potential atmospheric pollution can be determined. Within this studies the distribution of various chemical elements in the soil from the Polog region, located in the northwest part of the Republic of Macedonia, the contents of a total of 19 elements (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) was determined in soil samples collected from 58 locations. The analysis of these elements was performed using inductively coupled plasma – atomic emission spectroscopy (ICP-AES). The results on the content of elements in the tested samples were processed with bivariate statistical analysis by making matrix coefficients of correlation and multivariate factor analysis to determine associations between chemical elements. Additionally, maps of spatial distribution of the tested elements were prepared to support the identification of the locations with higher content of certain heavy metals in the investigated region.

MATERIALS AND METHODS

Study area

The Polog valley is located in the northwestern part of the Republic of Macedonia and extends in the direction of south e ast–northwest east, with length of about 55 km and width of 8–10 km (Fig. 1).

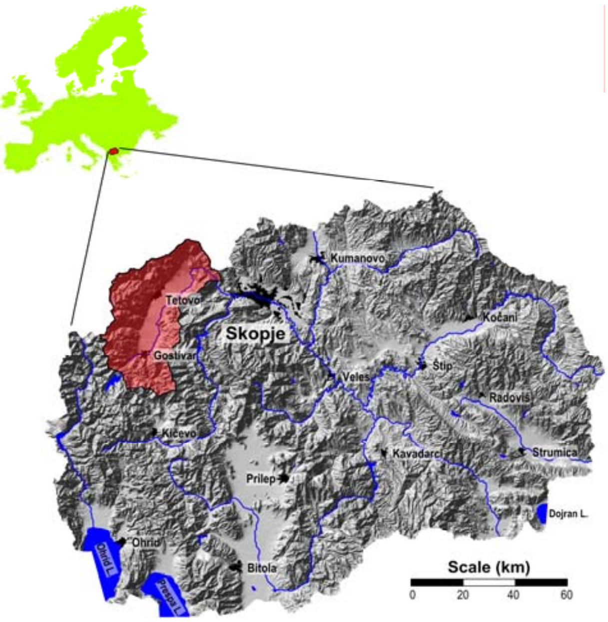

Fig. 1. Polog region

The region covers the relief units of Mt. Šara, Polog valley, Mavrovo plateau, Bistra Mt. and the part of the Radika river valley. The valley is surrounded by mountains Šara, Suva Gora and Žeden. Places with the highest population in the region are the cities of Tetovo (86,580 inhabitants) and Gostivar (81,042 inhabitants). The mountain relief has hills and mountains and is made up of the Suva Gora (1853 m.a.s.l.) and Šara (2748 m a.s.l.) mountains. Characteristic of the western mountains is the lush vegetation giving them a distinctively forest character, while the eastern mountainous areas are bare and desolate (Suva Gora, Žeden) due to the limestone composition. The Polog valley is located at 300–600 meters above sea level and has a valley relief (Emini, 2010).

The geological composition of the Polog region is diverse and has the following types of rocks (Fig. 2): Quaternary and Tertiary sedimentary rocks, Paleozoic and Mesozoic carbonate rocks, Paleozoic sandstone, Precambrian and Paleozoic schists and volcanic and igneous rocks (Blažev & Arsovski, 2001). Quaternary sediments dominate in the central part of the region along the river of Vardar and are in the contact with the Paleozoic sandstones. On Šara and Bistra mountains Precambrian and Paleozoic schists are dominant geological formations where Paleozoic and Mezozoic carbonates are incorporated.

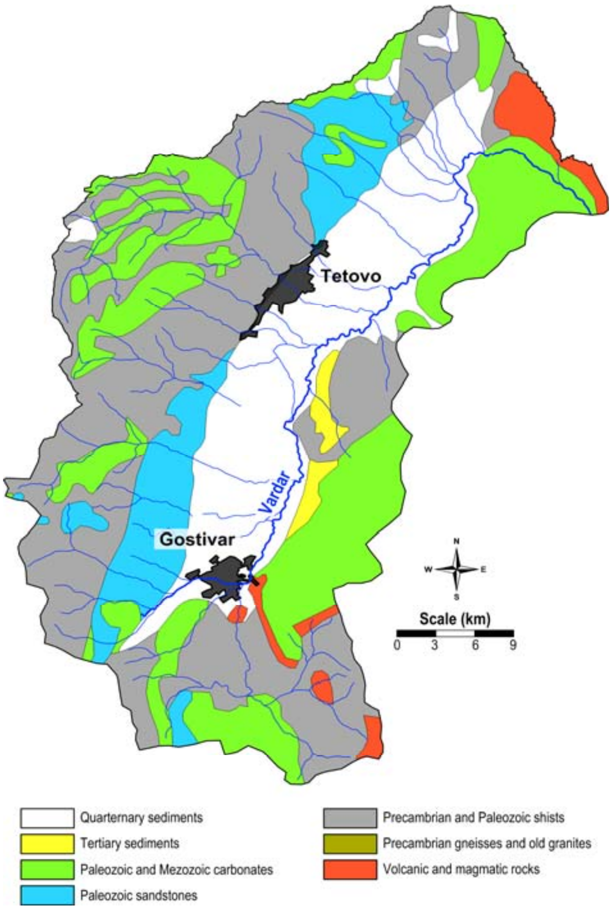

Fig. 2. Geological map of the Polog region

Types of soils found in the Polog region are the following: alluvial soils (slit, clay, sand and gravel) along the river flows, proluvial in the lowest valley part and cement soils in the wavy hills. Silicate soil types are the most present soil types of the Šara and Suva Gora mountains. There are limestone, screes and rocky places in the carbonate rocks. Above them, rankers are present in the high mountains. The composition of soil includes various minerals of which the following are primary: quartz, feldspar and feldspathoids, amphiboles or mica.

Sample collection, pre-treatment and analysis

Soil samples were collected from 58 predetermined locations (Fig. 3). From each location, topsoil (0–5 cm) and subsoil (20–30 cm) samples were taken from 5 sub-locations in radius of 10 m. The samples were stored in plastic bags, then were cleaned from external bodies (stones, debris, etc.), dried at room temperature, crushed and grinded in agate mill to obtain particles below 0.1 mm. Then, the samples were digested by wet digestion applying a mixture of acids (HNO_3, $HClO_4$, HF and HCl) in accordance with the international standards (ISO 14869-1:2001). The resulting 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 (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, Zn) with application of the atomic emission spectrometer with inductively coupled plasma (ICP-AES), model Varian 715-ES. 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 90–110%, while the recovery for the certified reference material ranges from 94–108%.

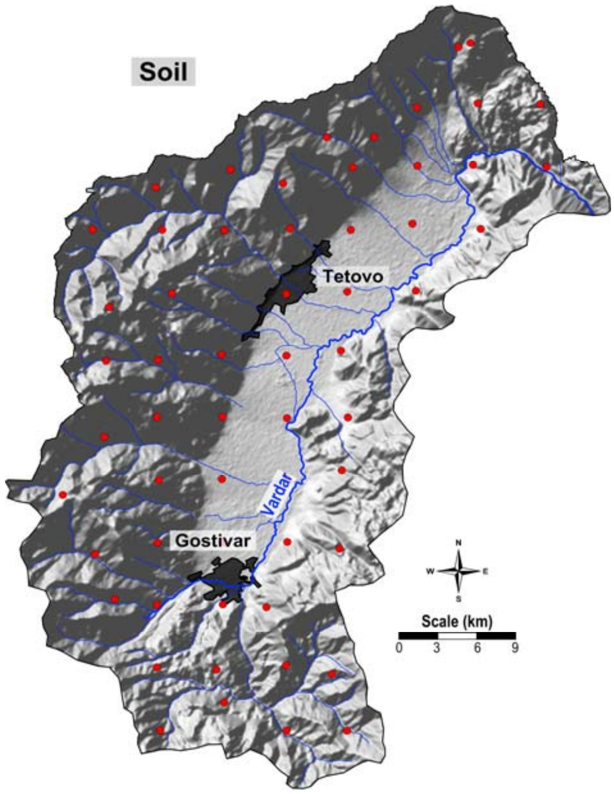

Fig. 3. Sampling locations matrix

Data processing

The methods of parametric and nonparametric statistics were used for the data analysis (Davis, 1986). On the basis of the results of the normality tests and visual inspection of the distribution histograms, logarithms of the element content for acquiring normal distribution were used for all elements. The multivariate R-mode factor analysis

(Snedecor & Cochran, 1967; 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. The factor analysis was performed on variables standardized to zero mean and unit of standard deviation (Reimann et al., 2002). As a measure of similarity between variables, the product-moment correlation coefficient (*r*) was applied. For orthogonal rotation, the varimax method was used.

The universal kriging method with linear variogram interpolation (Snedecor, 1976) 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.

RESULTS AND DISCUSSION

The descriptive statistics of the contents of analyzed elements in soil samples are given in Table 1, in which the values have been calculated for a total of 58 topsoil and 58 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 gives data for the content of 19 elements (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn). The order of the distribution of the concentration data of major elements Al, Ca, Fe, K, Mg, Na are in the following ranges: 0.98–7.2% Al; 0.06–20% Ca; 1.4–9.7% Fe; 0.34–2.7 K; 0.47–3.9% Mg and 0.15–2.7% Na. The contents of major elements are most frequently as a result of the dominant geological formations of the area: Paleozoic and Mesozoic schist, sediments and carbonates.

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 2). 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 0.95 for B to 1.21 for Ca which shows of the absence of the significant influence of possible soil pollution from anthropogenetic activities. Also, this is confirmed by the great similarity in the spatial distribution of the investigated elements in topsoil and subsoil samples. This similarity in the contents of the analyzed elements in top- and subsoil are given in Figs. 4–8.

A comparative analysis (Table 3) was conducted based on the data of the contents of different chemical elements in the soils in Europe, provided by Salminen et al. (2005). For the comparative analysis, the values of the medians were used as a more stable parameter. The Al content is lower in relation to the data published by Salminen et al. (2005), while for the other macro-elements, including phosphorus and manganese, the values did not show significant variations. The distribution of the remaining chemical elements is characteristic correspondingly to the lithogenic origin of the rocks in the separate subregions of the area (Fig. 2). The only big difference is in the content of vanadium and zinc, which is two times bigger than European values in both, top- and subsoil samples. Similar values of the median of the investigated elements in soil from the Polog region were found with those for the soil samples collected from the whole territory of Macedonia (Mihajlov et al., 2013; Mihajlov, 2014) (Table 3). There are slightly higher content of Cr, Cu, Mg, Mn, Na, Ni, V and Zn in the Polog soils then those for Macedonian soils, and lower content for Ba and Sr which is a result of variation in the geological appearance in some parts of Macedonia (Jovanovski et al., 2012).

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 4 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 5 contains a factor analysis, i.e. the loading matrix for the dominant rotating factors, which helps to identify four factors.

T a b l e 1

Descriptive statistics of the contents of analyzed elements in soil samples (n=58)

Elem.	Unit	*N*	*X*	*X*(BC)	*Md*	min	max	P_{25}	P_{75}	P_{10}	P_{90}	*S*	*Sx*	*CV*	A	*E*	*A*(BC)	*E*(BC)
									Topsoil									
Al	%	58	3.4	3.2	3.3	0.67	7.2	2.0	4.5	1.3	5.4	1.5	0.20	45.0	0.29	–0.62	–0.26	–0.64
B	mg/kg	58	11	8.0	7.8	1.8	38	5.0	11	4.1	35	9.9	1.3	89.3	1.88	2.31	0.36	0.08
Ba	mg/kg	58	320	240	230	110	1800	170	390	130	610	270	35	83.1	3.52	16.76	0.12	–0.77
Ca	%	58	2.1	1.0	0.90	0.17	20	0.46	2.5	0.26	4.4	3.3	0.43	158.7	3.92	17.69	0.27	–0.63
Cd	mg/kg	58	2.2	2.1	2.1	0.050	11	1.5	2.5	1.1	3.5	1.4	0.19	63.8	3.55	19.20	0.67	5.63
Cr	mg/kg	58	140	99	96	15	1300	66	160	37	270	170	23	122.7	5.19	33.05	0.06	0.92
Cu	mg/kg	58	35	32	32	9.0	140	26	39	20	49	19	2.5	52.7	3.73	20.18	–0.05	3.12
Fe	%	58	3.7	3.5	3.7	1.4	9.7	3.1	4.3	1.9	5.3	1.4	0.19	37.9	1.50	5.02	0.05	1.06
K	%	58	1.5	1.4	1.5	0.39	2.7	1.0	1.9	0.76	2.4	0.56	0.074	38.2	0.37	–0.39	–0.10	–0.36
Li	mg/kg	58	34	32	32	7.9	77	22	44	17	51	14	1.8	40.2	0.54	0.57	–0.08	–0.03
Mg	%	58	1.2	1.1	1.1	0.47	3.9	0.84	1.5	0.62	1.8	0.56	0.074	46.1	2.03	7.60	0.04	0.20
Mn	mg/kg	58	1000	980	950	380	1900	770	1200	580	1600	370	49	36.1	0.67	–0.03	0.12	–0.24
Na	%	58	1.3	1.2	1.3	0.17	2.7	0.67	1.7	0.52	2.1	0.64	0.084	50.4	0.15	–0.78	–0.17	–0.80
Ni	mg/kg	58	110	52	55	7.2	2300	38	80	27	100	300	40	279.1	6.58	45.63	–0.44	4.24
P	mg/kg	58	790	760	740	350	1500	590	910	450	1300	280	36	34.9	0.67	–0.18	0.17	–0.50
Pb	mg/kg	58	44	35	31	0.47	320	23	46	15	87	46	6.0	103.4	4.15	23.03	0.28	3.57
Sr	mg/kg	58	76	61	63	12	380	42	95	26	130	60	7.9	79.0	2.94	11.84	0.11	0.50
V	mg/kg	58	110	100	100	33	310	74	130	52	170	51	6.7	46.4	1.32	3.54	0.05	0.44
Zn	mg/kg	58	120	110	110	64	530	95	130	81	150	65	8.5	52.5	4.81	28.35	0.27	1.61
									Subsoil									
Al	%	58	3.4	3.2	3.1	0.98	6.9	2.3	4.5	1.7	5.8	1.5	0.20	45.1	0.66	–0.50	0.22	–0.80
B	mg/kg	58	12	8.4	9.2	1.1	37	5.4	11	4.6	35	10	1.3	85.4	1.75	1.78	–0.38	2.00
Ba	mg/kg	58	310	230	220	83	1300	160	370	130	560	230	30	75.4	2.49	7.53	0.03	–0.48
Ca	%	58	1.9	0.84	0.80	0.063	16	0.33	2.5	0.17	4.2	2.9	0.38	152.8	3.54	14.45	–0.09	–0.64
Cd	mg/kg	58	2.1	1.9	1.9	0.18	6.2	1.4	2.5	0.66	3.7	1.2	0.15	55.4	1.12	2.15	–0.21	0.81
Cr	mg/kg	58	150	100	100	17	1100	66	180	38	260	160	20	107.2	4.55	27.29	–0.08	0.45
Cu	mg/kg	58	37	33	33	9.0	130	27	40	24	57	20	2.6	53.0	2.94	11.17	–0.05	3.09
Fe	%	58	3.9	3.7	3.8	1.7	8.8	3.1	4.6	1.9	5.7	1.5	0.19	37.6	0.97	1.87	–0.04	0.17
K	%	58	1.4	1.4	1.4	0.34	2.7	1.0	1.7	0.77	2.4	0.57	0.075	39.8	0.55	–0.22	0.05	–0.21
Li	mg/kg	58	34	33	31	10	79	24	46	18	52	14	1.9	42.2	0.56	0.29	0.02	–0.37
Mg	%	58	1.2	1.1	1.2	0.52	3.8	0.91	1.5	0.61	1.9	0.55	0.072	44.0	1.81	6.52	–0.04	0.03
Mn	mg/kg	58	1000	1000	980	330	1900	850	1200	660	1600	340	45	32.9	0.59	0.40	–0.13	0.47
Na	%	58	1.2	1.1	1.2	0.15	2.7	0.62	1.6	0.31	2.0	0.63	0.083	53.5	0.18	–0.83	–0.14	–0.91
Ni	mg/kg	58	110	55	56	12	2300	41	83	27	120	310	40	276.9	6.93	50.05	0.04	2.28
P	mg/kg	58	700	660	610	220	1500	490	880	370	1100	280	37	40.5	0.62	–0.01	–0.01	–0.49
Pb	mg/kg	58	42	37	33	6.7	110	24	55	13	89	26	3.4	62.3	0.99	0.13	0.13	–0.45
Sr	mg/kg	58	76	62	65	13	320	44	88	25	130	55	7.3	73.1	2.60	8.77	–0.12	0.62
V	mg/kg	58	110	100	110	39	230	72	130	48	190	50	6.5	44.4	0.57	–0.26	–0.08	–0.66
Zn	mg/kg	58	120	110	110	50	390	93	130	81	140	46	6.1	39.9	3.86	20.93	–0.57	3.31

X – arithmetic mean, *X*(BC) – arithmetic mean obtained with the Box-Cox method, *Md* – median, min – minimum, max – maximum, P_{10} – 10 percentiles, P_{25} – 25 percentiles, P_{75} – 75 percentiles, P_{90} – 90 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.

T a b l e 2

Average of the elements contents in topsoil and subsoil and their ratio

Element	Unit	Topsoil	Subsoil	Topsoil/Subsoil
Al	%	3.2	3.2	0.98
B	mg/kg	8.0	8.4	0.95
Ba	mg/kg	240	230	1.04
Ca	%	1.0	0.84	1.21
Cd	mg/kg	2.1	1.9	1.07
Cr	mg/kg	99	100	0.96
Cu	mg/kg	32	33	0.96
Fe	%	3.5	3.7	0.95
K	%	1.4	1.4	1.03
Li	mg/kg	32	33	0.99
Mg	%	1.1	1.1	0.97
Mn	mg/kg	980	1000	0.98
Na	%	1.2	1.1	1.08
Ni	mg/kg	52	55	0.94
P	mg/kg	760	660	1.15
Pb	mg/kg	35	37	0.94
Sr	mg/kg	61	62	0.99
V	mg/kg	100	100	0.98
Zn	mg/kg	110	110	1.04

T a b l e 3

Comparison of the median values for top- and subsoil samples in the Polog region, Macedonian and European values (in mg/kg)

Element	Polog, 2012 (present work)				Europe (Salminen et al., 2005)				Macedonia, 2014 (Mihajlov et al., 2014)			
	Topsoil		Subsoil		Topsoil		Subsoil		Topsoil		Subsoil	
	Md	min– max	Md	min–max	Md	min–max	Md	min– max	Md	min–max	Md	min–max
Al	33000	6700–72000	31000	9800–69000	5800	2000–14000	6200	1100–14000	22000	7900–43000	23000	7700–51000
Ba	230	110–1800	220	83–1300	380	30–1900	390	13–2100	420	41–1600	440	66–1700
Ca	9000	1700–200000	8000	63–160000	6600	190–340000	8100	170–370000	7900	920–210000	7800	1000–210000
Cr	96	15–1300	100	17–1100	60	<3.0–6200	62	<3.0–2100	54	11–600	63	11–600
Cu	32	9.0–140	33	9.0–130	13	0.81–260	14	0.86–130	16	1.7–73	16	3.2–78
Fe	37000	14000–97000	38000	17000–88000	25000	1100–150000	26000	770–110000	25000	6300–67000	27000	7700–80000
K	15000	3900–27000	14000	3400–27000	16000	220–51000	17000	<83–50000	14000	2600–32000	15000	5200–33000
Mg	11000	4700–39000	12000	5200–38000	4700	<61–150000	6000	<61–110000	6600	1100–29000	7300	1500–31000
Mn	950	380–1900	980	330–1900	510	31–61000	470	23–4700	620	160–3200	640	99–4300
Na	13000	1700–27000	12000	1500–27000	6000	300–33000	6500	230–36000	8500	330–23000	9400	780–24000
Ni	55	7.2–2300	56	12–2300	18	<2.0–2700	22	<2.0–2400	35	2.5–530	37	5.2–530
P	740	350–1500	610	220–1500	960	83–9900	720	53–12000	450	120–1400	430	74–1300
Pb	31	0.47–320	33	6.7–110	10	5.3–970	17	<3.0–940	17	2.5–700	14	0.80–660
Sr	63	12–380	65	13–320	89	8.0–3100	95	6.0–2000	71	9.4–540	68	9.9–580
V	100	33–310	110	39–230	60	2.7–540	63	1.3–330	67	14–300	71	19–370
Zn	110	64–530	110	50–390	52	<3–2900	47	<3–3100	39	3.1–440	38	4.4–490

T a b l e 4

Correlation matrix of coefficients

Al	1.00																		
B	0.05	1.00																	
Ba	–0.17	0.37	1.00																
Ca	0.74	0.05	–0.39	1.00															
Cd	0.36	0.13	–0.03	0.29	1.00														
Cr	0.48	–0.10	–0.38	0.32	0.40	1.00													
Cu	0.34	0.27	0.07	0.15	0.47	0.39	1.00												
Fe	0.56	0.21	0.02	0.19	0.59	0.75	0.68	1.00											
K	–0.16	0.26	0.73	–0.49	–0.09	–0.14	0.17	0.14	1.00										
Li	0.02	–0.33	–0.26	0.04	0.08	0.20	0.11	–0.05	0.05	1.00									
Mg	0.65	–0.09	–0.29	0.40	0.34	0.89	0.36	0.77	–0.10	0.07	1.00								
Mn	0.19	–0.04	–0.13	0.12	0.45	0.43	0.41	0.44	–0.11	0.11	0.41	1.00							
Na	0.13	–0.31	–0.14	0.01	–0.31	0.01	–0.16	–0.09	0.05	–0.04	0.12	–0.07	1.00						
Ni	0.48	0.07	–0.26	0.35	0.57	0.89	0.51	0.78	–0.18	0.13	0.79	0.51	–0.27	1.00					
P	0.17	–0.10	–0.07	0.25	0.42	0.14	0.33	0.23	–0.05	0.26	0.14	0.51	–0.01	0.16	1.00				
Pb	–0.15	0.57	0.25	–0.06	0.09	–0.15	0.17	0.05	0.06	–0.22	–0.17	0.07	–0.46	0.03	0.14	1.00			
Sr	0.59	–0.08	–0.48	0.70	0.00	0.21	–0.02	0.08	–0.43	0.01	0.33	–0.04	0.42	0.09	0.11	–0.12	1.00		
V	0.57	0.26	0.16	0.21	0.37	0.49	0.70	0.78	0.29	0.06	0.56	0.27	0.06	0.50	0.19	0.05	0.21	1.00	
Zn	0.05	0.11	0.17	–0.02	0.51	0.23	0.51	0.42	0.17	0.17	0.19	0.51	–0.29	0.38	0.57	0.30	–0.23	0.31	1.00
Elem.	**Al**	**B**	**Ba**	**Ca**	**Cd**	**Cr**	**Cu**	**Fe**	**K**	**Li**	**Mg**	**Mn**	**Na**	**Ni**	**P**	**Pb**	**Sr**	**V**	**Zn**

T a b l e 5

Matrix of overload of dominant rotating factors (F)

Element	F1	F2	F3	F4	Communality.
Cr	**0.93**	0.11	–0.20	0.19	94.8
Mg	**0.90**	0.29	–0.08	0.13	91.4
Ni	**0.81**	0.11	-0.17	0.43	88.4
Fe	**0.78**	0.19	0.23	0.45	89.8
Ca	0.11	**0.86**	-0.31	0.14	87.4
Al	0.43	**0.82**	0.07	0.14	88.9
Sr	0.09	**0.81**	–0.31	–0.19	80.7
K	0.05	–0.26	**0.89**	–0.02	86.7
Ba	–0.23	–0.18	**0.86**	0.10	84.4
Zn	0.08	–0.13	0.13	**0.84**	74.5
Cd	0.23	0.20	–0.03	**0.77**	68.1
Mn	0.32	–0.10	–0.24	**0.68**	63.5
Cu	0.35	0.16	0.27	**0.64**	63.2
Prp. Totl	26.8	18.7	15.5	20.8	81.7
Expl. Var	3.48	2.42	2.02	2.70	
EigenVal	5.41	2.85	1.28	1.08	

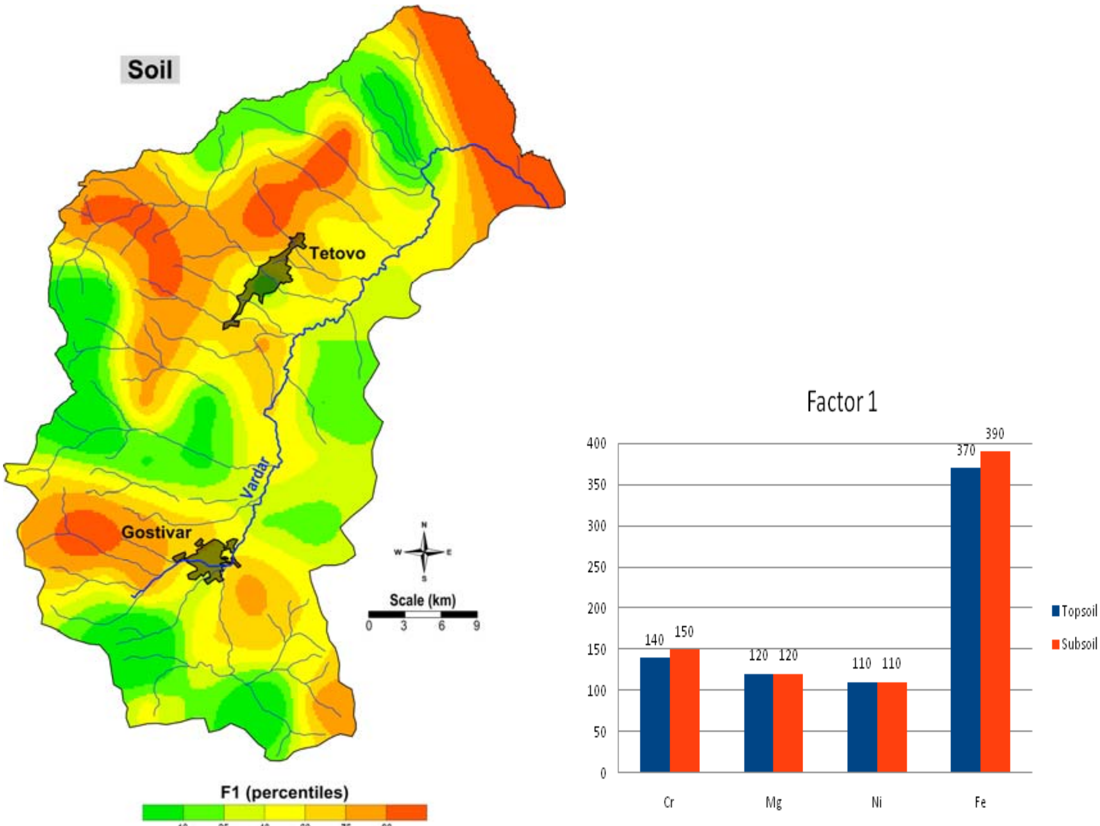

Fig. 4. Spatial distribution of factor scores of Factor 1 (Cr, Mg, Ni, Fe)

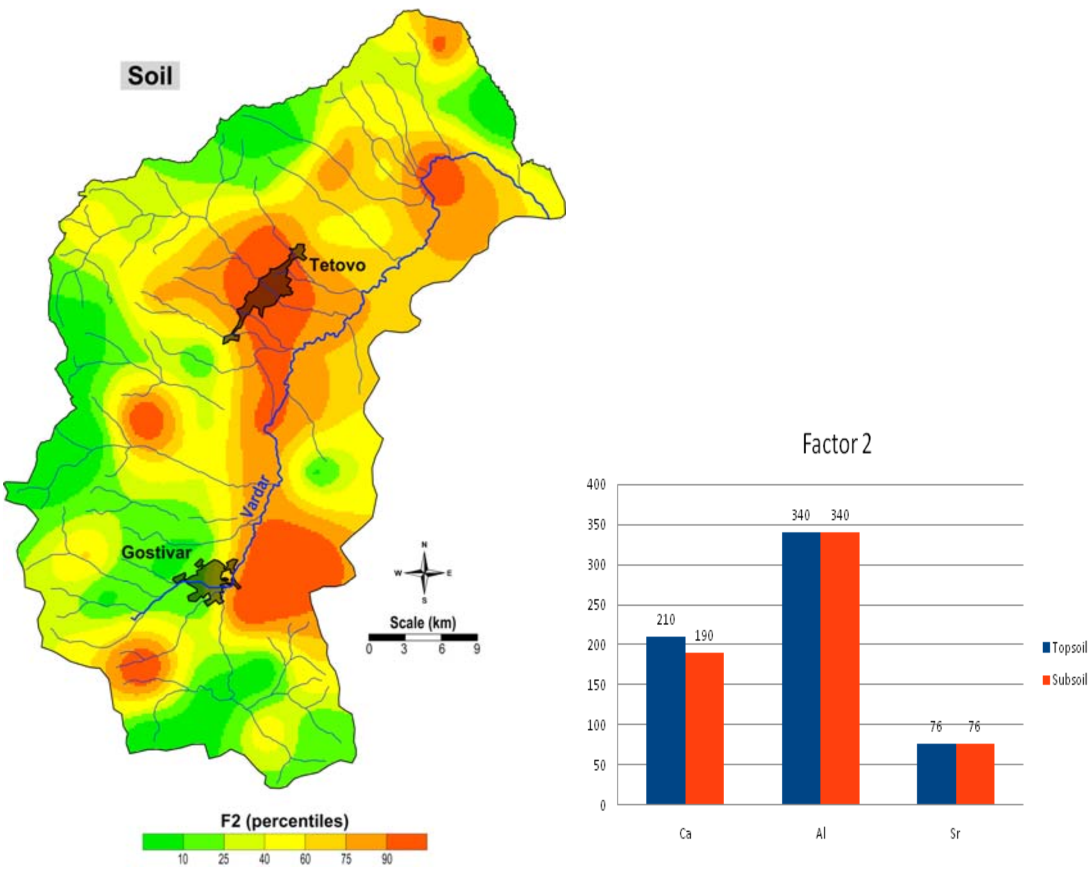

Fig. 5. Spatial distribution of factor scores of Factor 2 (Ca, Al, Sr)

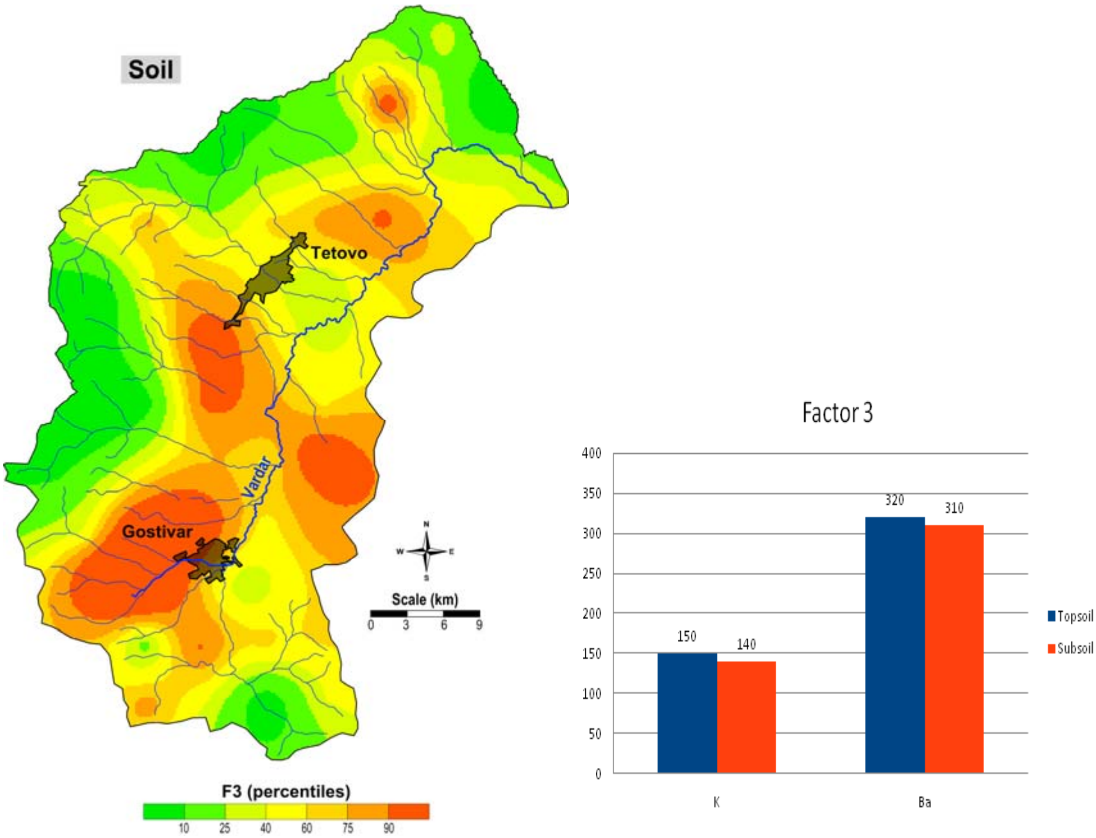

Fig. 6. Spatial distribution of factor scores of Factor 3 (K, Ba)

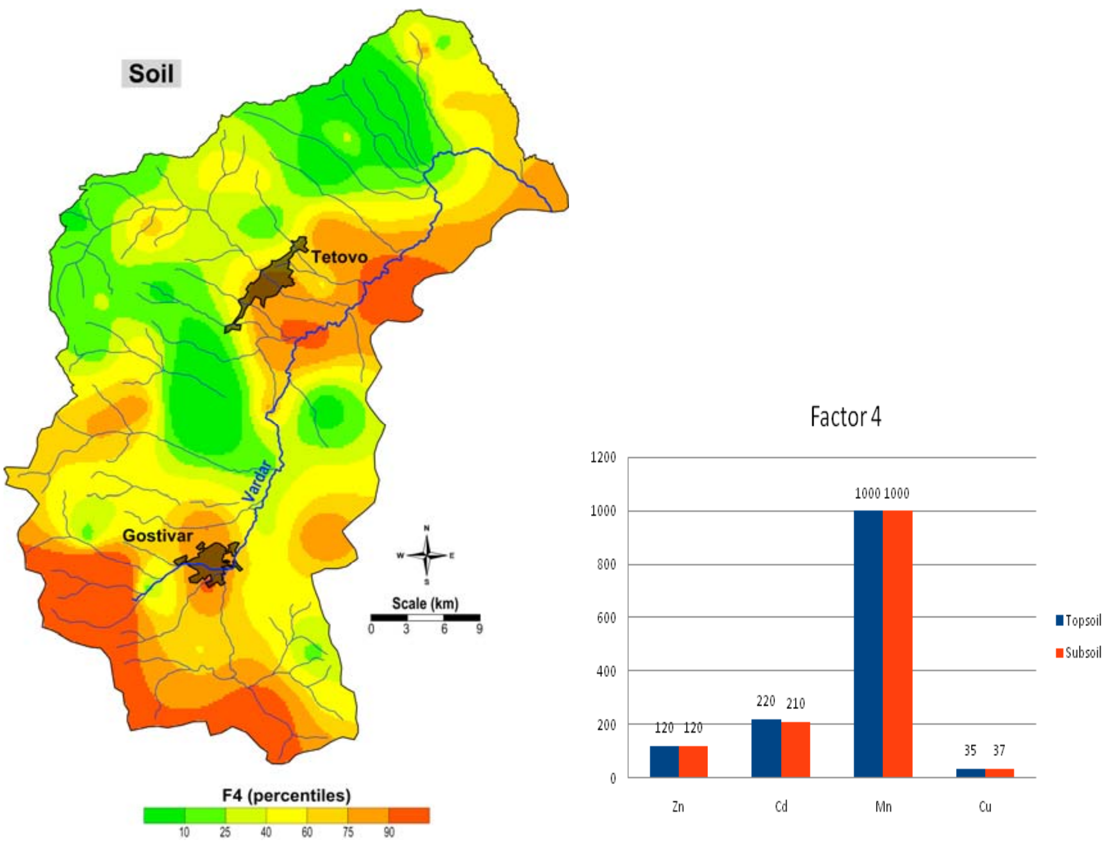

Fig. 7. Spatial distribution of Factor 4 elements (Zn, Cd, Mn, Cu)

The factor analysis has eliminated those elements which do not have a share in the communality, from the total of 19 analyzed elements. Those four factors include a total of 13 elements, with a total share of 81.7% in the communality. The elements B, Li, Na, P, Pb and V have low factor values with a weak tendency to form an independent factor.

Identical results were achieved as in the case of application of factor analysis (the graphical representation is shown in Fig. 8). Namely, Factor 1 (Cr, Mg, Ni, Fe) corresponds to Cluster 3, while Factor 2 (Al, Ca, Sr) corresponds to Claster 1. The classification of Cluster 2 (Cd, Cu, Zn, Mn) is the same of the results of Factor 4, and Cluster 4 is the same with Factor 3 (K, Ba).

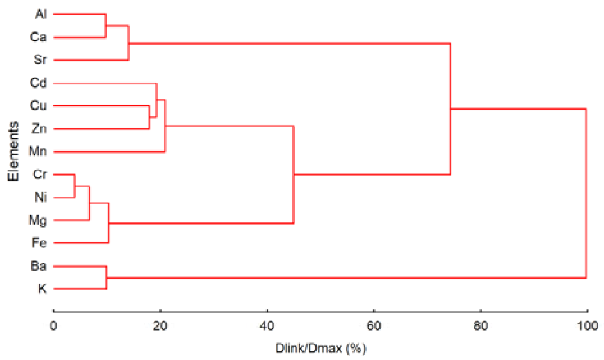

Fig. 8. Dendrogram of cluster analysis

Factor 1 (Cr, Mg, Ni, Fe) represents a lithogenous association of elements with the highest load factor values (F > 0.78). The spatial distribution of factor scores of F1 is given in Fig. 4. The origin of the elements in this typical lithogenous association is connected to the geological composition of the soil in this region. It can be seen from the distribution map (Fig. 4) that the high contents of the elements from factor 1 occur in the areas of volcanic and igneous rocks, and Paleozoic and Mesozoic schists. As it can be seen from the results given in Tables 1 and 2, and shown in Fig. 4, the values of these elements in the topsoils and subsoils are very similar. Thus, the distribution maps for the contents of these elements are prepared on the basis of the mean values for the content of each element in both layers of the soil, for each location.

According to the spatial distribution of the factor scores of **Factor 2** (Ca, Al, Sr) given in Fig. 5, represents mixed lithogenous association with the highest content in the areas of Paleozoic sediments and Paleozoic-Mesozoic carbonates. Thus, higher content of calcium in the topsoil layers can be seen in the locations reach in carbonate, while higher content of aluminum can be seen in the soil at the locations which contain sands, carbonates and igneous rocks.

Factor 3 (K, Ba) represents mixed lithogenous and anthropogenic association of elements. The content of barium and potassium is typical for the Precambrian and Paleozoic–Mesozoic schists. Fig. 6 shows the spatial distribution of factor scores of Factor 3. It can be seen that the high contents of potassium occur near the village of Šemševo on the geologic structure of Quaternary and Tertiary sedimentary rocks. It is assumed that higher content of potassium in the topsoil layers in the Polog region results also from the deposits of fertilizers as part of the agricultural activities. The highest content of barium (1800 mg/kg – topsoil, 1300 mg/kg – subsoil) was found in soil from the location near the village of Gorno Jelovce and the village of Raven. The maximum content of barium exceeds the critical limit of The New Dutch List which amounts 625 mg/kg, which points out to possible existence of rocks with increased barium mineralization

Factor 4 (Zn, Cd, Mn, Cu) represents an association of elements with lithogenous influence. It can be seen from the distribution map for the values of this factor, given in Fig. 7, that the content of these elements is connected to the presence of Paleozoic–Mesozoic carbonates and Precambrian–Paleozoic schists. In the examined area, the highest value of zinc content in the soil has been found at the location MK–647, with content of 530 mg/kg in the topsoil and 390 mk/kg in the subsoil. This is also the location with the highest content of cadmium, 11 mg/kg in the topsoil and 6.2 mg/kg in the subsoil, as well as copper with the content of 140 mg/kg and 130 mg/kg, respectively.

CONCLUSION

The aim of this study is the systematic investigation of the spatial distribution of various chemical elements in surface soils in the Polog region, Republic of Macedonia. In total 118 soil samples (from 59 locations) were collected and analyzed 19 major and trace elements (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn). Factor analysis with multivariance R-method is applied in order to show the associations of chemical elements. Four factors were obtained: Factor 1 (Cr, Mg, Ni and Fe), Factor 2 (Ca, Al and Sr), Factor 3 (K and Ba) and Facotr 4 (Zn, Cd, Mn, Cu). It was established that the distribution of these associations are mostly as a result of the complex geology and lithology of the region. The none obtained factors have not confirmed the correlation to anthropogenic influence beside the contamination with K in some fields in the valley due to the application of potassium fertilizers.

REFERENCES

[1] Bačeva, K., Stafilov, T., Šajn, R., Tănăselia, C.: Moss biomonitoring of air pollution with heavy metals in the vicinity of a ferronickel smelter plant. *Journal of Environmental Science and Health,* Part *A*, **47** (4), 645–656 (2012).

[2] Balabanova, B., Stafilov, T., Bačeva K., Šajn, R.: Biomonitoring of atmospheric pollution with heavy metals in the copper mine vicinity located near Radoviš, Republic of Macedonia. *Journal of Environmental Science and Health, Part A*, **45**, 1504–1518 (2010).

[3] Balabanova, B., Stafilov, T., Šajn, R., Bačeva, K.: Distribution of chemical elements in attic dust as reflection of lithology and anthropogenic influence in the vicinity of copper mine and flotation. *Archives of Environmental Contamination and Toxicology*, **61** (2), 173–184 (2011).

[4] Barandovski, L., Frontasyeva, M. V., Stafilov, T., Šajn, R., Pavlov, S., Enimiteva, V.: Trends of atmospheric deposition of trace elements in Macedonia studied by the moss biomonitoring technique. *Journal of Environmental Science and Health, Part A*, **47** (13), 2000–2015 (2012).

[5] Battarbee, R., Anderson, N., Appleby, P., Flower, R. J., Fritz, S., Haworth, E., Higgit, S., Jones, V., Kreiser, A., Munro, M. A., Natkanski, J., Oldfield, F., Patrick, S. T., Richardson, N., Rippey, B., Stevenson, A. C.: *Lake Acidification in the United Kingdom*. ENSIS, London, 1988.

[6] Blažev, K., Arsovski, M.: *Basic Geology*. Faculty of Mining and Geology, Štip, 2001 (in Macedonian).

[7] Bowen H. T. M.: *Environmental Chemistry of the Elements*. Academic Press, London, 1979.

[8] Davis, J. C.: *Statistic and Data Analysis in Geology*. Willey and Sons, New York, 1986, p. 651.

[9] Dudka, S., Adriano, C. D.: Environmental impacts of metal ore mining and processing: A review. *Journal of Environmental Quality*, **26**, 590–602 (1997).

[10] Emini, A.: *Program for development of the Polog mountain region*. Center for Development of the Polog Mountain Region, Tetovo, 2010 (in Macedonian).

[11] Jovanovski, G., Boev, B., Makreski, P.: *Minerals from the Republic of Macedonia with an Introduction to Mineralogy.* Macedonian Academy of Sciences and Arts, Skopje, 2012.

[12] Kabata-Pendias, A., Mukherjee, A. B.: *Trace Elements from Soil to Human.* Springer, Heidelberg, 2007.

[13] *Lenntech Water Treatment and Air Purification*. Water Treatment, Lenntech, Rotterdamseweg, Netherlands, 2004.

[14] Mihajlov, M., Barandovski, L., Šajn, R., Stafilov, T.: Spatial distribution of heavy metals in soils from the Republic of Macedonia. *10th Congress of Pure and Applied Chemistry for the Students of Macedonia with International Participation, 17–19 October 2013, Skopje*, Book of Abstracts, Z. Noneska, D. Stanoeva-Gogovska (Eds.), 2013, p. 24.

[15] Mihajlov, M.: *Distribution of Heavy Metals in Soils in the Republic of Macedonia*. MSc thesis, Faculty of Natural Sciences and Mathematics, Ss Cyril and Methodius University in Skopje, 2014.

[16] Mitkova, T., Mitrikeski, J.: *Soils of the Republic of Macedonia: Present Situation and Future Prospects*. European Soil Bureau, Research Report No. 9, 2005.

[17] Nriagu, J. O.: A global assessment of natural sources of atmospheric trace metals. *Nature*, **338**, 47–49, (1989).

[18] Reimann, C., Filzmoser, P., Garrett, R. G.: Factor analysis applied to regional geochemical data: problems and possibilities. *Applied Geochemistry*, **17**, 185–206 (2002).

[19] Salminen, R., Batista, M. J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Jordan, G., Klayer, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P. J., Olsson, S. Å., Ottesen, R. T., Petersell, V., Plant, J. A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T.: *Geochemical Atlas of Europe,* Part 1*, Background Information, Methodology and Maps.* Geological Survey of Finland, Espoo, 2005, p. 526.

[19] Snedecor, G. W., Cochran, W. G.: *Statistical Methods*. The Iowa State University Press, Ames, Iowa, 1967, 575 p.

[20] Stafilov, T., Šajn, R., Pančevski, Z., Boev, B., Frontasyeva, M. V., Strelkova, L. P.: Heavy metal contamination of surface soils around a lead and zinc smelter in the Republic of Macedonia. *Journal of Hazardous Materials*, **175**, 896–914 (2010).

[21] Stafilov, T., Šajn, R., Boev, B., Cvetković, J., Mukaetov, D., Andreevski, M., Lepitkova, S.: Distribution of some elements in surface soil over the Kavadarci region, Republic of Macedonia. *Environmental Earth Sciences*, **61** (7): 1515–1530 (2010).

[22] Stafilov, T.: Environmental pollution with heavy metals in the Republic of Macedonia. *Contribution, Section of Natural, Mathematical and Biotechnical Sciences,* MASA*,* **35** (2), 81–119 (2014).

Р е з и м е

ПРОСТОРНА ДИСТРИБУЦИЈА НА ХЕМИСКИ ЕЛЕМЕНТИ ВО ПОЧВИТЕ ВО ПОЛОШКИОТ РЕГИОН, РЕПУБЛИКА МАКЕДОНИЈА

Анѓа Ќулумоска-Ѓорѓиевска[1], Трајче Стафилов[1]*, Роберт Шајн[2]

[1]*Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј“ во Скопје, п. фах 162, Скопје, Р. Македонија*
[2]*Геолошки завод на Словенија, Димичева 14, 1000 Љубљана, Словенија*
trajcest@pmf.ukim.mk

Клучни зборови: геохемиски мониторинг; почви; тешки метали; Полог; Македонија

Целта на ова истражување е определување на присуството и просторната дистрибуција на различни хемиски елементи во почвите од полошкиот регион, Република Македонија. За таа цел е спроведен геохемиски мониторинг за определување 19 макроелементи и елементи во траги (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V и Zn). Земени се вкупно 116 примероци почва (58 примероци од површинска и 58 примероци од потповршинска почва) од претходно утврдени референтни локации. Земените примероци се анализирани со примена на атомската емисиона спектрометрија со индуктивно спрегната плазма (ICP-AES). Извршена е статистичка обработка на добиените резултати со цел да се утврдат областите со евентуално загадување со тешки метали. Во анализираните примероци почва се утврдени 4 хемиски асоцијации (фактори), од кои три фактори се од литогено потекло (F1, F2 and F4), а еден фактор (F3) е мешан фактор од литогено и антропогено потекло. Факторот 3 се смета и за антропоген поради зголемената содржина на калиум во одредени области од Полошката Котлина, што е резултат на употреба на калиумови ѓубрива во земјоделието. Елементите кои се вклучени во литогените фактори се присутни во почвите како резултат на геолошките структури во областите во кои овие елементи се присутни (шкрилци, карбонати, песочници и орогени седименти).