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

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A b s t r a c t: The contents and spatial distributions of various chemical elements in soil in the Veles region, Republic of Macedonia, are presented. For this purpose, soil samples from two layers (0–5 cm and 20–30 cm) from 53 locations with a network of 5 × 5 km were collected. The samples were analyzed by the application of atomic emission spectrometry with inductively coupled plasma (AES-ICP) and 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) in all soil samples was determined. From the analyzed soil samples, 3 chemical associations were determined, from which two factors are characterized as lithogenic associations: F1 (Cr, Cu, Fe, Li, Mg, Mn, Ni and V) and F3 (Al and Ca), and one as anthropogenic association (F2 including Pb and Zn). From the obtained results and from the maps of spatial distribution of all analyzed elements it can be concluded that the major source of pollution of soil with Pb and Zn in the Veles region is the former lead and zinc smelter plant located in the near vicinity of the city of Veles.

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

INTRODUCTION

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 (Kemp, 1998). 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, 2011).

Contamination of the urban soils has become the subject of many studies (Plyaskina & Ladonin, 2009; Ajmone-Marsan & Biasioli, 2010; Taghipour et al., 2013). In most of the cases trace elements increased in soils of some cities and their environs as compared with surrounding soils or anthropogenic sources in Europe (Crnković et al., 2006; Argyraki & Kelepertzis, 2014; Czarnecki & Düring, 2015). It is obvious from the papers published recently that mining and metallurgical activities lead to enormous soil contamination (Douay et al., 2008; Dragović et al., 2008; Jiménez-Cárceles et al., 2008; Wilson et al., 2010; Nikolić et al., 2011; Li et al., 2014). It was also established that the most serious soil pollution was influenced by the activities of Pb-Zn mining and smelter activities (Li et al., 2005; Cappuyns et al., 2006; Cemek & Kizilkaya, 2006; Cabala et al., 2008; Rodríguez et al., 2009; Stafilov et al., 2010; Šajn et al., 2013).

The Republic of Macedonia was involved in the UNECE ICP Vegetation – *Heavy Metals in European Mosses,* for the first time in 2002 and again in 2005, 2010 and 2015, when atmospheric deposition of trace elements was studied over the entire territory of the country using moss biomonitoring. The results of these 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, 2015). The main emission sources appear to be metallurgic activities, power plants and mining activities. Therefore, special studies were performed in the areas with the highest heavy metal pollution, including air and soil pollution.

Thus, detailed study was performed to investtigated the impact to the environment of the Pb-Zn-Cd smelter plant in the city of Veles and it was found very high soil pollution with several toxic elements such as As, Cd, Cu, Hg, In, Pb, Sb and Zn (Stafilov et. al., 2008, 2010) which influence to the contamination of air with particles with high content of these metals (Pančevski, 2014) or food produced in this area (Stankovska et al., 2008; Pančevski et al., 2014a, 2014b, 2016). The impact to the water and sediment pollution of the river of Vardar was also detected (Serafimovska et al., 2013; Ilić Popov et al., 2014, 2016).

The obtained results from our previous study of spatial distribution of different chemical elements in the surface soil over of the city of Veles and its close vicinity (Stafilov et al., 2010) show that the content of elements such as As, Au, Cd, Cu, Hg, In, Pb, Sb, Se, Zn in the soil samples around the lead and zinc smelter and in the adjacent part of the town of Veles is much higher than in those collected in the surrounding areas due to the pollution from the smelter plant. The enrichment of the elements in the top soil, compared to the European (Salminen et al., 2005) and Macedonian top soil (Mihajlov et al., 2016; Stafilov & Šajn, 2016), is typical for this elemental assemblage.

It was concluded that the total pollution with heavy elements is a consequence of anthropogenic activity, more specifically, a result of operation of the lead and zinc smelter plant. The critically polluted area is of an ellipse shape (with a surface of about 7 km^2), which is a consequence of the wind rose. It is important to mention that this study includes only the SW part of the critically polluted zone. Therefore, it was important to extend the study area to determine the scope and direction of the pollution over a larger area than previously examined. The goal of the present study is to investigate the spatial distribution of various elements in the wider region of the city of Veles, including the areas of the municipalities of Veles and Čaška.

MATERIALS AND METHODS

Study area

The study area is located in the central part of the Republic of Macedonia (Fig. 1). This area includes the municipalities of Veles and Čaška with a total of about 1,200 km^2. The city of Veles and its surroundings have a very favorable geographical position with the Vardar as a main river in the country and important crossroads. Veles valley is surrounded by several mountains: on the north is Taorska Klisura canyon and Mt. Orešnica, Mt. Klepa is on the south, while on the west of the investigated area are Jakupica and Babuna mountains. The major tributary to the river of Vardar in this area is the Babuna river. Veles is one of the major cities in the country. According to the 2002 census, this area is populated with about 60,000 inhabitants of whom about 44,000 people live in the city of Veles. The city extends to an altitude of 160–200 m. Veles climate is continental with hot summers and cold winters. The average annual temperature is 13.4°C, the average temperature in January ranges from 1.5 to 5.7°C, and in July from 23 to 42.5°C. The average annual amount of precipitations is 469 mm (Lazarevski, 1993).

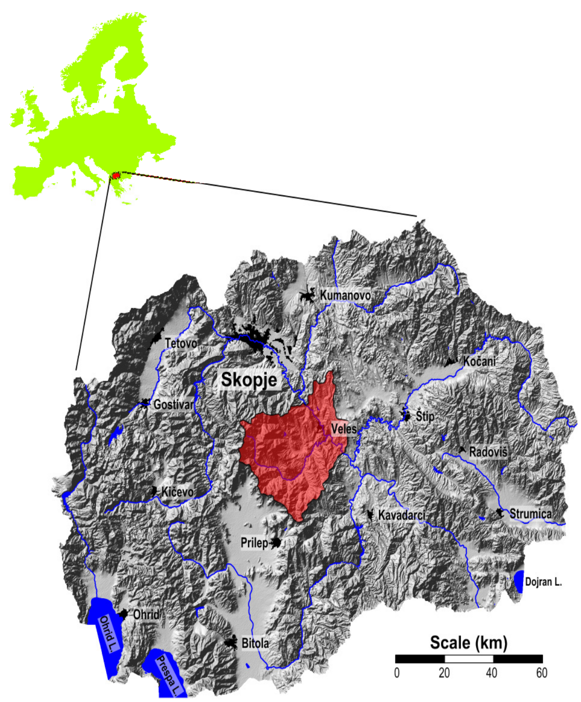

Fig. 1. Study area

Geological description

The geology of the investigated area is very diverse. From the geological map (Fig. 2) it can be noticed that in the eastern, central and the area along the river of Babuna prevail tertiary sediments. In the central eastern part, along the Vardar river, beside the tertiary sediments, volcanic and magmatic rocks, Paleozoic and Mesozoic carbonates and Precambrian and Paleozoic schists are present. In the western part of the investigated area the Precambrian gneisses and old granites are dominated with the rare occurrences of Precambrian and Paleozoic schists and Paleozoic and Mesozoic carbonates. In some parts along the Vardar, Babuna and Topolka rivers Quaternary sediments are also present. The lithology of the vicinity of the town of Veles is also very diverse. The oldest rocks of date from the Paleozoic period and belong to an internal part of the Vardar zone. This Paleozoic series is represented by green schist, feldspatized schist, biotite schist and quartz-sericite schist with layers of marble and quartzite. The following Mesozoic carbonate rocks also belong to the Vardar zone and are outspreaded on the west side of the study area. A part of this area is covered by Pliocene sand and clay. The youngest sediments are alluvial sediments of the river of Vardar and partly of the Topolka river (Stafilov et al., 2008).

Sample collection, pre-treatment and analysis

Soil samples were collected from 53 predetermined locations (Fig. 3). From each location, top soil (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 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 total content 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 by the 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 to 110%, while the recovery for the certified reference material ranges from 94 to 108%.

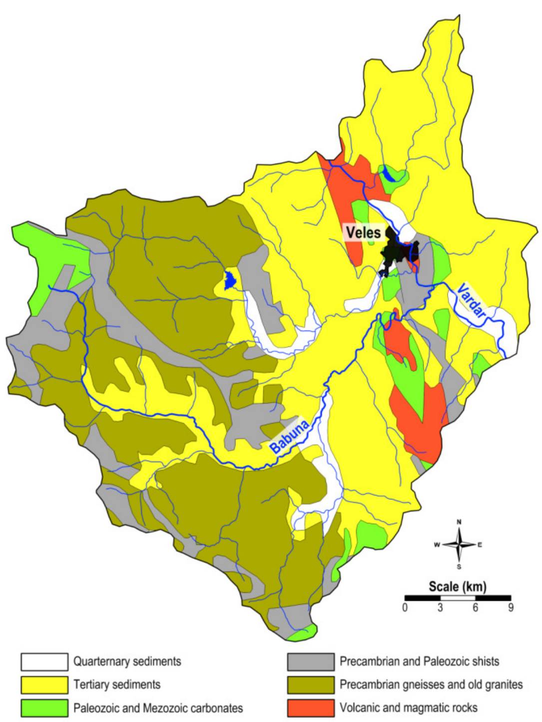

Fig. 2. Geological map of the studied area

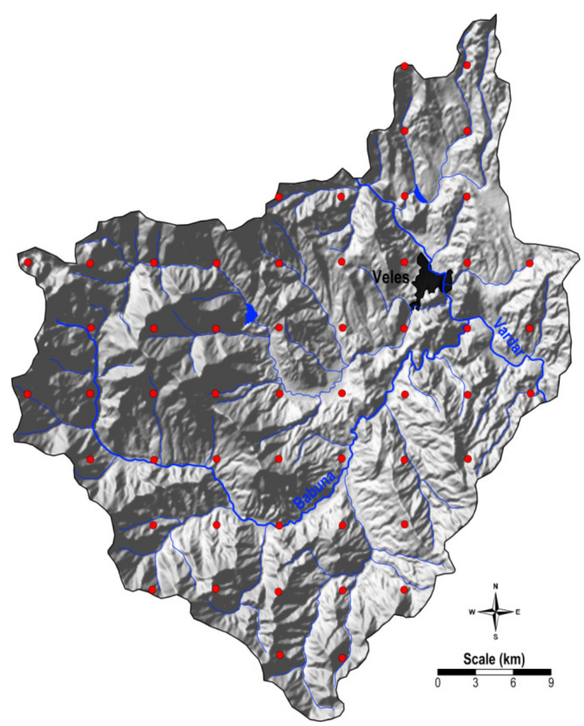

Fig. 3. Sampling location map

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, 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 Tables 1 and 2, in which the values have been calculated for a total of 53 top soil and 53 subsoil samples. Values of Al, Ca, Fe, K, Mg and Na are given in %, and remaining elements in mg/kg. An analysis of the soil samples by ICP-AES 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 and Na, are in the following ranges: 0.79 – 5.1% for top soil and from 0.87 to 5.0% in subsoil for Al; 0.28 – 11.0% for top soil and from 0.28 to 14.0% in subsoil for Ca; 0.85 – 4.6% for top soil and from 0.89 to 4.4% in subsoil for Fe; 0.77 – 2.3% for top soil and from 0.55 to 2.5% in subsoil for K; 0.10 – 1.4% for top soil and from 0.12 to 1.5% in subsoil for Mg, and from 0.27 to 2.6% for top soil and from 0.19 to 2.1% in subsoil for Na. The contents of major elements are most frequently a result of the dominant geological formations of the area: Tertiary and Quaternary sediments, Precambrian gneisses and granites and Precambrian and Paleozoic schists.

In order to determine the dependence of the average contents of the analyzed elements between the top soil and the subsoil, the ratio of the contents was calculated (Table 3). The elements distribution should not vary significantly between the top soil (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 top soil versus subsoil. Thus, this relation varies from 0.88 for Ag to 1.24 for Pb. The much higher content of Pb in top soil samples indicated anthropogenic influence due to the high pollution of soils from the city of Veles and its near vicinity (Stafilov et al., 2010). Is could be also mentioned the high ratio for phosphorpous of 1.16 also indicating the pollution of surface soil due to the usage of phosphorous fertilizers.

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 top soil and subsoil samples. However, if we consider the contents of elements in soil samples collected in the near vicinity of the town of Veles, the values for the elements defined as anthropogenic and introduced in large quantities due to the pollution from the Pb-Zn smelter in Veles it could be noted that their contents are significantly higher than in the soils from the other part of the investigated area. Thus, the average content of Pb in 6 top soil samples around the city of Veles is 81 mg/kg and in subsoil is 51 mg/kg (averages for the whole area are 30 mg/kg and 24 mg/kg, respectively) with the ratio of 1.60; and for Zn their values are 168 and 133 mg/kg (averages for whole area are 99 and 92 mg/kg), respectively, with the ratio of 1.27.

It was also found that the contents of some other anthropogenic elements (Stafilov et al., 2010) are higher in the top soil than in the subsoil in the soil around the city of Veles. Thus, the average content of Ag in 6 top soil samples around the city of Veles is 0.93 mg/kg and in subsoil is 0.86 mg/kg (average for the whole area is 0.82 and 0.93 mg/kg, respectively) with the ratio of 1.07; the average content of Cu in top soil samples around the city of Veles is 23 mg/kg and in subsoil is 21 mg/kg (average for the whole area is 15 and 14 mg/kg, respectively) with the ratio of 1.10; the average content of Mn in top soil samples around the city of Veles is 673 mg/kg and in subsoil is 602 mg/kg (average for the whole area is 500 and 450 mg/kg, respectively) with the ratio of 1.13.

T a b l e 1

Descriptive statistics for the content of analyzed elements in top soil samples (n = 53)

Element	Unit	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	1.2	0.82	0.75	0.19	8.1	0.41	2.6	0.51	1.1	1.2	0.17	108.6	3.77	18.32	0.49	0.51
Al	%	2.3	2.0	2.1	0.79	5.1	0.99	3.9	1.3	3.2	1.1	0.16	49.9	0.54	–0.77	–0.04	–1.23
B	mg/kg	2.8	1.0	1.2	0.008	17	0.05	7.3	0.28	2.8	4.3	0.59	154.7	2.49	5.68	–0.19	–0.48
Ba	mg/kg	520	360	380	110	3500	180	810	250	520	590	81.4	113.7	3.92	16.59	0.08	0.64
Ca	%	2.3	1.2	1.1	0.28	11	0.41	5.5	0.62	3.8	2.4	0.33	107.6	1.72	2.96	0.06	–1.17
Cr	mg/kg	110	92	100	37	350	47	200	69	130	61	8.4	55.6	1.65	3.91	–0.22	–0.56
Cu	mg/kg	15	14	15	3.2	39	5.8	26	8.6	19	8.3	1.1	54.1	0.74	0.37	–0.21	–0.49
Fe	%	2.2	2.1	2.2	0.85	4.6	1.2	3.2	1.5	2.6	0.82	0.11	37.3	0.75	0.67	–0.03	–0.31
K	%	1.4	1.4	1.5	0.77	2.3	0.93	1.9	1.3	1.6	0.36	0.050	25.1	0.23	–0.09	–0.06	–0.21
Li	mg/kg	14	13	12	4.8	31	7.3	24	8.9	18	6.2	0.86	45.0	0.88	0.10	0.10	–0.74
Mg	%	0.54	0.47	0.46	0.10	1.4	0.22	0.94	0.27	0.66	0.30	0.041	55.8	0.89	0.50	–0.14	–0.59
Mn	mg/kg	500	460	440	170	1500	250	760	350	580	230	31.7	46.2	1.71	4.86	0.00	0.38
Na	%	1.1	1.1	1.1	0.27	2.6	0.41	1.7	0.63	1.4	0.53	0.073	48.0	0.42	–0.11	0.04	–0.66
Ni	mg/kg	56	37	39	6.8	230	11	130	20	79	51	7.0	90.4	1.55	2.34	–0.11	–0.85
P	mg/kg	350	300	300	100	1100	150	620	240	420	210	29.0	60.2	1.82	4.06	–0.15	0.01
Pb	mg/kg	35	30	30	8.0	130	17	62	23	40	22	3.0	61.7	2.41	7.59	0.12	0.99
Sr	mg/kg	92	71	74	21	390	29	170	43	120	70	9.6	75.6	2.00	5.59	–0.04	–0.57
V	mg/kg	52	49	50	21	110	29	84	38	64	20	2.7	37.3	0.74	0.27	–0.16	–0.38
Zn	mg/kg	99	92	96	49	210	66	130	72	120	34	4.7	34.2	1.27	1.91	–0.11	–0.22

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.

T a b l e 2

Descriptive statistics for the content of analyzed elements in subsoil samples (n = 53)

Element	Unit	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	1.3	0.93	0.98	0.11	4.3	0.48	3.3	0.63	1.2	1.0	0.14	81.7	1.63	1.60	–0.49	1.85
Al	%	2.2	2.0	2.1	0.87	5.0	1.2	3.7	1.4	2.8	0.95	0.13	43.0	0.80	0.08	0.07	–0.78
B	mg/kg	5.2	1.6	1.6	0.050	37	0.05	15	0.61	5.0	9.1	1.3	175	2.50	5.38	0.03	–0.40
Ba	mg/kg	450	360	380	130	1700	200	740	240	580	290	40.5	65.2	2.08	5.84	–0.11	–0.54
Ca	%	2.5	1.2	1.1	0.28	14	0.43	6.6	0.51	3.2	3.1	0.43	126	2.18	4.70	0.18	–1.17
Cr	mg/kg	100	84	88	36	430	48	160	58	120	70	9.6	68.1	2.64	8.89	0.28	–0.17
Cu	mg/kg	14	13	13	2.4	39	5.5	29	7.6	18	8.8	1.2	60.9	1.05	0.71	0.13	–0.53
Fe	%	2.2	2.1	2.1	0.89	4.4	1.3	3.0	1.7	2.4	0.77	0.11	35.5	0.88	1.02	0.02	0.10
K	%	1.4	1.4	1.4	0.55	2.5	0.86	2.2	1.1	1.7	0.44	0.061	30.6	0.40	–0.03	0.03	–0.09
Li	mg/kg	14	13	13	5.0	30	7.0	22	9.5	17	5.8	0.79	42.3	0.92	0.71	–0.12	–0.26
Mg	%	0.52	0.44	0.45	0.12	1.5	0.20	1.0	0.26	0.68	0.33	0.045	63.1	1.16	0.98	0.11	–0.71
Mn	mg/kg	450	400	410	130	1300	220	840	310	470	240	32.4	52.0	1.55	2.98	0.08	0.20
Na	%	1.1	1.1	1.1	0.19	2.1	0.43	1.9	0.66	1.6	0.55	0.076	48.0	0.00	–1.20	–0.27	–1.05
Ni	mg/kg	58	38	37	7.0	280	13	110	22	67	61	8.4	105	2.21	4.99	0.16	–0.47
P	mg/kg	310	250	250	78	1100	130	590	170	330	210	28.5	67.3	2.01	4.48	0.18	–0.03
Pb	mg/kg	28	24	24	5.0	120	16	46	18	30	18	2.4	62.8	3.28	14.61	–0.23	3.67
Sr	mg/kg	89	70	63	22	320	30	180	48	120	63	8.7	71.2	1.50	2.21	0.09	–0.66
V	mg/kg	51	48	48	23	130	30	69	37	58	20	2.8	39.0	1.49	3.38	0.18	0.20
Zn	mg/kg	92	86	84	50	190	63	130	72	100	29	4.0	31.7	1.43	2.41	0.13	–0.18

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 obtainned with the Box-Cox method.

Even more, if the content of cadmium in the most of the samples was bellow the detection limit (1 mg/kg), Cd average content in the top soil samples from the vicinity of Veles was 4.0 mg/kg and in the subsoil 2.6 mg/kg with the ration of 1.52 mg/kg confirming that its presence in the soil is from the former smelter plant.

Table 3

The ration of the element content in top soil (TS) and subsoil (SS) samples

Elements	Unit	Top soil	Subsoil	Ratio (TS/SS)
Ag	mg/kg	0.82	0.93	0.88
Al	%	2.0	2.0	0.99
B	mg/kg	1.0	1.6	0.63
Ba	mg/kg	360	360	1.01
Ca	%	1.2	1.2	1.02
Cr	mg/kg	92	84	1.10
Cu	mg/kg	14	13	1.08
Fe	%	2.1	2.1	1.01
K	%	1.4	1.4	1.01
Li	mg/kg	13	13	1.00
Mg	%	0.47	0.44	1.07
Mn	mg/kg	460	400	1.13
Na	%	1.1	1.1	0.97
Ni	mg/kg	37	38	0.98
P	mg/kg	300	250	**1.16**
Pb	mg/kg	30	24	**1.24**
Sr	mg/kg	71	70	1.02
V	mg/kg	49	48	1.01
Zn	mg/kg	92	86	1.06

A comparative analysis (Table 4) was conducted based on the data of the contents of different chemical elements in the soils in Macedonia (Mihajlov et al., 2016) and Europe (Salminen et al., 2005). For the comparative analysis, the values of the medians were used as a more stable parameter. It could be noted that the median values are higher than the European medians for Ca, Cr, Na, Ni, Pb and Zn, while for the other elements the values did not show significant variations. The median values for the Veles region are also very similar to those for the Macedonian soils with the exception of higher values for Pb and Zn (anthropogenic effect in the Veles region) and lower for Mg, Mn and P).

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 four factors include a total of 12 elements, with a total share of 81.1% in the communality. The elements Ag, B, Ba, K, Na, P and Sr 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 (Cr, Cu, Fe, Li, Mg, Mn, Ni, V) corresponds to Cluster 2, while Factor 2 (Pb, Zn) and Factor 3 (Al, Ca) corresponds to subclusters 1 and 2 of the Claster 1.

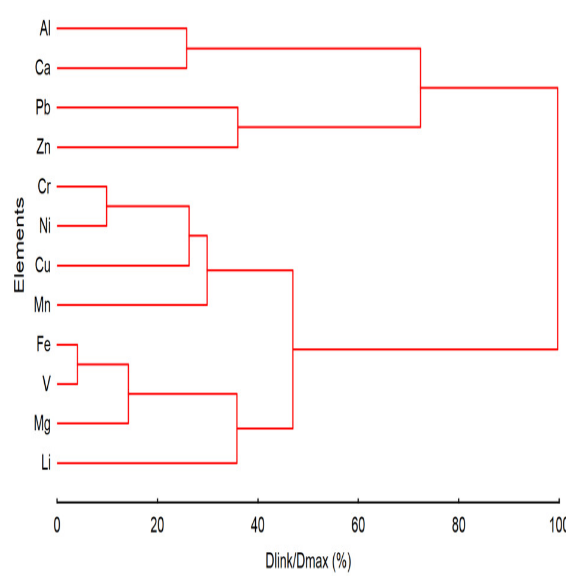

Fig. 4. Dendrogram from cluster analysis

Table 4

Comparison of the median values for topsoil and subsoil samples in the Veles region, Macedonian and European values (in mg/kg)

Element	Polog, 2012 (present work)				Europe (Salminen et al., 2005)				Macedonia (Mihajlov et al., 2016)			
	Top soil		Subsoil		Top soil		Subsoil		Top soil		Subsoil	
	Md	Min–Max	Md	Min–Max	Md	Min– Max	Md	Min– Max	Md	Min–Max	Md	Min– Max
Al	21000	7900–81000	21000	8700–50000	5800	2000–14000	6200	1100–14000	22000	7900–43000	23000	7700–51000
Ba	380	110–3500	380	130–1700	380	30–1900	390	13–2100	420	41–1600	440	66–1700
Ca	11000	2800–110000	11000	2800–140000	6600	190–340000	8100	170–370000	7900	920–210000	7800	1000–210000
Cr	100	37–350	88	36–430	60	<3.0–6200	62	<3.0–2100	54	11–600	63	11–600
Cu	15	3.2–39	13	2.4–39	13	0.81–260	14	0.86–130	16	1.7–73	16	3.2–78
Fe	22000	8500–46000	21000	8900–44000	25000	1100–150000	26000	770–110000	25000	6300–67000	27000	7700–80000
K	15000	7700–23000	14000	5500–25000	16000	220–51000	17000	<83–50000	14000	2600–32000	15000	5200–33000
Mg	4600	1000–14000	4500	1200–15000	4700	<61–150000	6000	<61–110000	6600	1100–29000	7300	1500–31000
Mn	440	170–1500	410	130–1300	510	31–61000	470	23–4700	620	160–3200	640	99–4300
Na	11000	2700–26000	11000	1900–21000	6000	300–33000	6500	230–36000	8500	330–23000	9400	780–24000
Ni	39	6.8–230	37	7.0–280	18	<2.0–2700	22	<2.0–2400	35	2.5–530	37	5.2–530
P	300	100–1100	250	78–1100	960	83–9900	720	53–12000	450	120–1400	430	74–1300
Pb	30	8.0–130	24	5.0–320	10	5.3–970	17	<3.0–940	17	2.5–700	14	0.80–660
Sr	74	21–390	63	22–320	89	8.0–3100	95	6.0–2000	71	9.4–540	68	9.9–580
V	50	21–110	48	23–130	60	2.7–540	63	1.3–330	67	14–300	71	19–370
Zn	96	490210	84	50–190	52	<3–2900	47	<3–3100	39	3.1–440	38	4.4–490

Table 5

Correlation matrix of coefficients

Element	Ag	Al	B	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	Sr	V	Zn
Ag	1.00																		
Al	–0.02	1.00																	
B	0.36	–0.43	1.00																
Ba	0.39	–0.11	0.51	1.00															
Ca	0.15	0.71	–0.33	–0.03	1.00														
Cr	–0.03	0.53	–0.50	–0.14	0.46	1.00													
Cu	0.13	0.57	–0.32	0.04	0.47	0.71	1.00												
Fe	0.14	0.66	–0.39	–0.03	0.51	0.77	0.72	1.00											
K	–0.02	–0.30	0.24	0.22	–0.47	–0.48	–0.34	–0.37	1.00										
Li	0.11	0.40	–0.32	–0.08	0.16	0.51	0.61	0.73	–0.04	1.00									
Mg	0.21	0.59	–0.32	0.12	0.54	0.76	0.74	0.85	–0.39	0.65	1.00								
Mn	0.13	0.48	–0.34	0.00	0.48	0.70	0.68	0.65	–0.40	0.48	0.65	1.00							
Na	0.09	–0.51	0.50	0.34	–0.43	–0.77	–0.69	–0.69	0.61	–0.55	–0.61	–0.65	1.00						
Ni	0.11	0.59	–0.38	–0.01	0.52	0.89	0.79	0.83	–0.54	0.59	0.87	0.74	–0.81	1.00					
P	0.13	0.38	–0.17	0.14	0.52	0.37	0.46	0.52	–0.14	0.24	0.61	0.45	–0.22	0.40	1.00				
Pb	–0.08	0.32	–0.26	–0.13	0.32	0.38	0.37	0.31	–0.07	0.28	0.22	0.33	–0.30	0.26	0.36	1.00			
Sr	0.03	0.34	0.00	0.44	0.47	–0.01	0.04	0.07	–0.02	–0.26	0.23	0.01	0.18	0.06	0.51	0.08	1.00		
V	0.16	0.58	–0.33	0.07	0.44	0.75	0.73	0.95	–0.34	0.71	0.88	0.66	–0.64	0.83	0.56	0.27	0.10	1.00	
Zn	0.16	0.46	–0.29	0.04	0.55	0.62	0.65	0.72	–0.22	0.50	0.64	0.54	–0.50	0.61	0.62	0.59	0.15	0.67	1.00

Table 6

Matrix of overload of dominant rotating factors (F)

Element	F1	F2	F3	Communality
Cr	**0.75**	0.23	0.36	74.6
Cu	**0.74**	0.28	0.32	73.3
Fe	**0.86**	0.18	0.34	89.0
Li	**0.83**	0.22	-0.12	74.8
Mg	**0.85**	0.05	0.39	87.3
Mn	**0.65**	0.21	0.37	61.3
Ni	**0.84**	0.09	0.41	88.0
V	**0.90**	0.13	0.27	89.4
Pb	0.11	**0.95**	0.15	93.2
Zn	0.54	**0.63**	0.32	78.1
Al	0.39	0.14	**0.76**	74.5
Ca	0.18	0.21	**0.91**	90.1
Total variability	47.4	13.6	20.1	81.1
Eigen value	7.66	1.15	0.93	
Expllain variance	5.69	1.63	2.41	

Factor 1 (Cr, Cu, Fe, Li, Mg, Mn, Ni and V) represents a lithogenous association of elements with the highest load factor values (47%). The spatial distribution of factor scores of F1 is given in Figure 5. 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. 5) that the high contents of the elements from factor 1 occur in the areas of Tertiary sediments and volcanic and magmatic rocks. As it can be seen from the results given in Tables 1 and 2, and shown in Figure 6, the values of these elements in the top soils and subsoils are very similar suggesting their geological origin. 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. Only the content of manganese in the surface soil is slightly greater than in the subsurface soil especially in soils of Veles and its immediate surroundings, which may be due to contamination of soil from the work of the smelter for lead and zinc in the city (Stafilov et al., 2010).

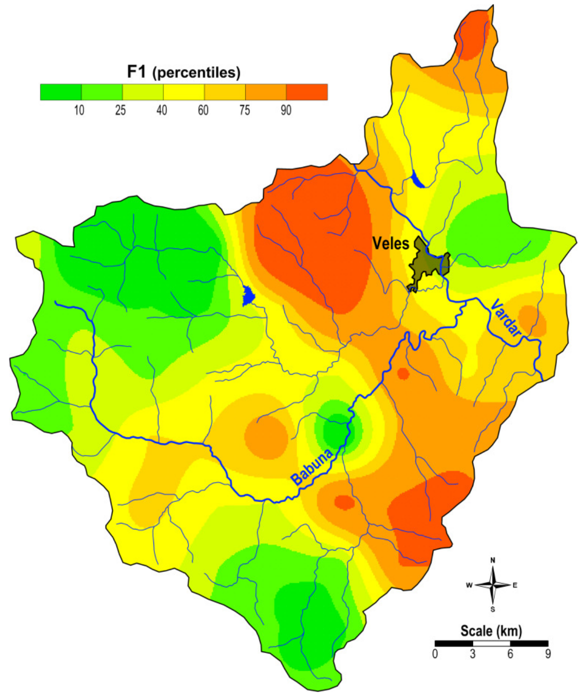

Fig. 5. Spatial distribution of factor values of Factor 1 (Cr, Cu, Fe, Li, Mg, Mn, Ni and V)

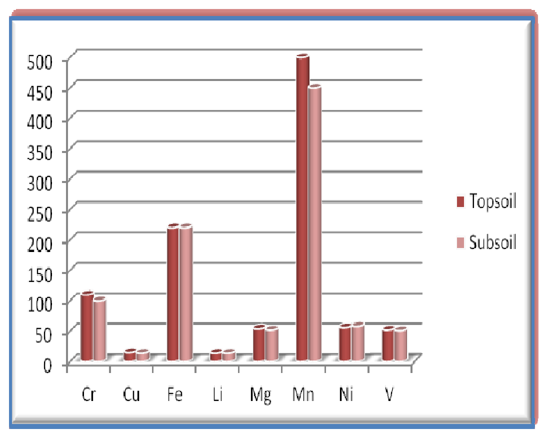

Fig. 6. Average contents of the elements of Factor 1 in surface and subsurface soil

According to the spatial distribution of the factor scores of **Factor 2** (Pb and Zn) given in Figure 7, represents mixed lithogenous and anthropogenic association with the highest content in the areas around the city of Veles providing confirmation of the impact on the work of former Pb-Zn smelter "Zletovo". It could be also seen from Figure 8 that the average content in the surface soil samples for both elements are higher than in the subsoil samples. From the distribution maps of lead and zinc (Figs. 9 and 10) can be seen that the highest specific values of the contents of these two elements were determined in soils from locations around the metropolitan area and along the Vardar river due to pollution from the smelter and in accordance with the wind-rose in this area (Stafilov et al., 2008, 2010). It should be mentioned the appearance of some increased content of these elements could be found in the areas of Tertiary sediments.

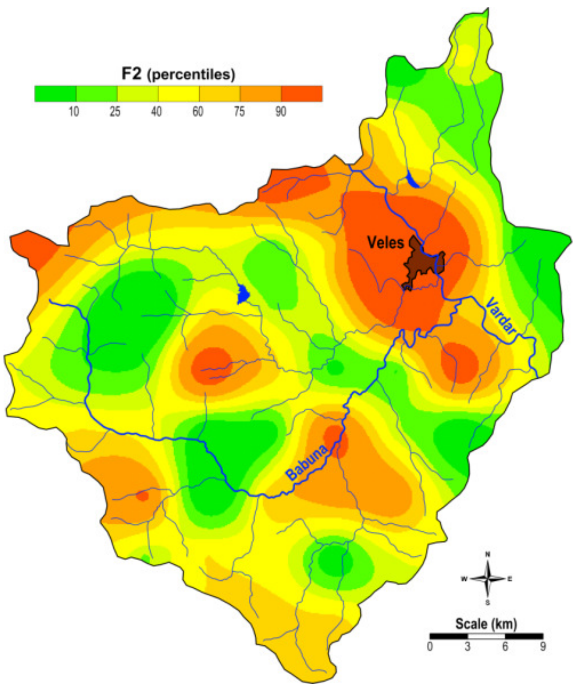

Fig. 7. Spatial distribution of factor values of Factor 2 (Pb, Zn)

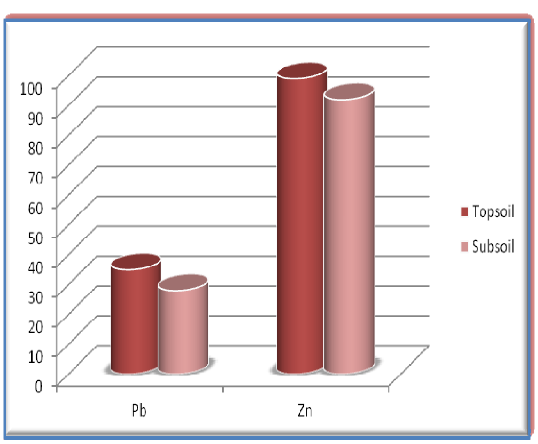

Fig. 8. Average values of the elements of Factor 2 in surface and subsurface soil

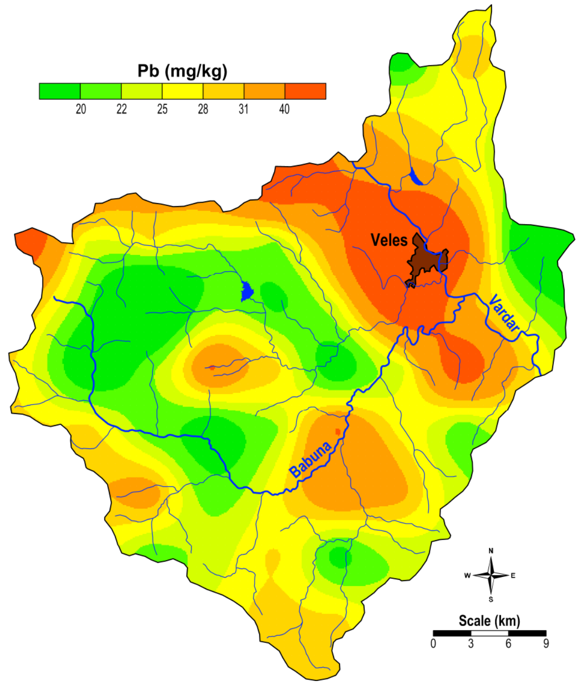

Fig. 9. Spatial distribution map of Pb

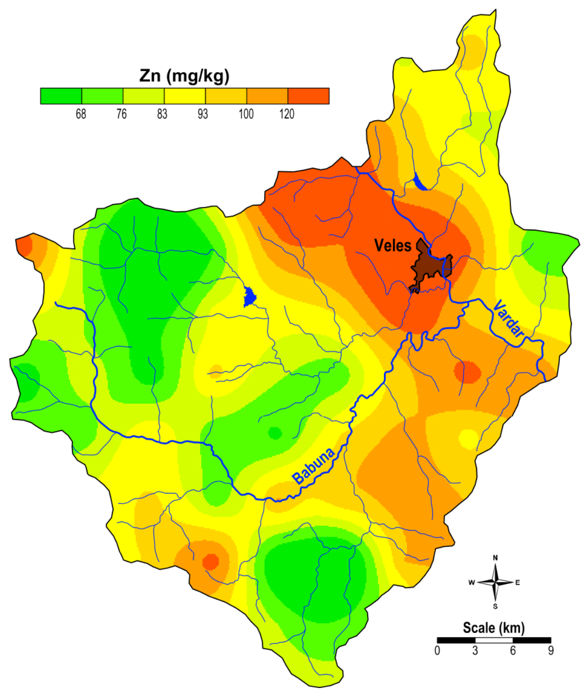

Fig. 10. Spatial distribution map of Zn

Factor 3 (Al and Ca) represents the second lithogenic association of elements. The increased content of aluminium and calcium is typical for the Tertiary sediments, Paleozoic and Mesozoic carbonates and volcanic and magmatic rocks (Fig.

11). In certain locations these elements are with increased content in areas of Precambrian and Paleozoic schists. From the histogram (Fig. 12) it can be seen that the average value for the content of aluminium in surface soil is slightly higher compared to the average of subsurface soils, while the content of calcium is little but higher in subsurface soil. These differences are not due to anthropogenic pollution but because of the geology of land in this region.

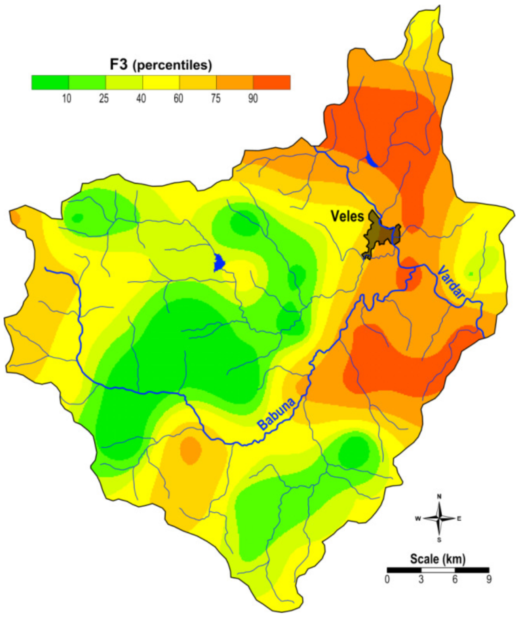

Fig. 11. Spatial distribution of factor values of Factor 3 (Al, Ca)

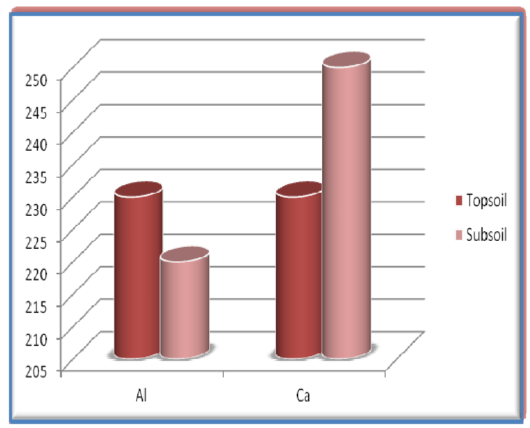

Fig. 12. Average values of the elements of Factor 3 in surface and subsurface soil

CONCLUSION

The aim of this study is the systematic investtigation of the spatial distribution of various chemical elements in surface soil over the Veles region, Republic of Macedonia. In total 106 soil samples (from 53 locations) were collected and analyzed for 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 three associations of the analyzed elements: Factor 1 (Cr, Cu, Fe, Li, Mg, Mn, Ni, V), Factor 2 (Pb, Zn) and Factor 3 (Al, Ca). It was established that the distribution of the first and second associations is mostly as a result of the complex geology and lithology of the region. However, the higher content of the elements included in Factor 2 (Pb and Zn) in the area in the city of Veles and its environ is due to anthropogenic pollution impact from the former work of the Pb-Zn smelter plant "Zletovo" located very close to the city.

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Р е з и м е

ПРОСТОРНА ДИСТРИБУЦИЈА НА ХЕМИСКИ ЕЛЕМЕНТИ ВО ПОЧВИТЕ ОД РЕГИОНОТ НА ВЕЛЕС, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: почви: тешки метали: факторна анализа: регион на Велес; ICP-AES

Презентирани се податоци за содржината и просторната дистрибуција на различни елементи во почвите во регионот на Велес, Република Македонија. За таа цел се земени примероци почва од два слоја (0–5 cm и 20–30 cm) на 53 локации со мрежа од 5 × 5 km. Пробите се анализирани со примена на атомска емисиона спектрометрија со индуктивно спрегната плазма (AES-ICP) и во пробите од почва е определена содржината на 19 елементи (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V и Zn). Од анализираните елементи се утврдени 3 хемиски асоцијации, од кои два фактора се карактеризирани како литогени асоцијации: F1 (Cr, Cu, Fe, Li, Mg, Mn, Ni и V) и F3 (Al и Ca), а F2 (Pb и Zn) како антропогена асоцијација. Од добиените резултати и од картите на дистрибуцијата на сите анализирани елементи може да се заклучи дека најголем извор на загадувањето на почвите со Pb и Zn во регионот на Велес е поранешната топилница за олово и цинк лоцирана во близина на градот Велес.