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SPATIAL DISTRIBUTION OF HEAVY METALS IN SOILS IN THE REPUBLIC OF MACEDONIA

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A b s t r a c t: The distribution of various elements in soils in the Republic of Macedonia was analyzed in terms of air pollution with heavy metals carried out for more than 10 years within the European moss biomonitoring programme of air pollution in Europe. In 2010 in parallel to moss sampling, on the same locations, soil samples were also collected using a network of 72 locations all over the country. In total of 144 samples (top and bottom soil) were collected and 18 elements (Al, Ba, Ca, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) were analyzed using inductively coupled plasma – atomic emission spectrometry (ICP-AES). Both, top and bottom soil samples were analyzed to identify possible anthropogenic influences and to assess whether the metal content is associated with anthropogenic sources or it is a result of lithology. The obtained data were statistically processed and distribution maps for all analyzed elements were prepared. The results are compared with international standards for soil and with the locations of the industry. The analysis generally indicates a connection with the lithological appearances, but also shows a possible association with certain industrial activities.

Key words: heavy metals; soil; pollution; spatial distribution; ICP-AES; Republic of Macedonia

INTRODUCTION

Soil is a very sensitive medium and an important natural and economic resource. Also, it has a number of environmental functions that are essential for the protection of the environment, as well as for the economy and the progress of society as well. Impacts on the soil caused by the human activities are constantly evolving and leading to a degradation and desertification causing serious socio-economic consequences. Main threats to the healthy condition of soil are erosion, local and diffuse contamination, salinization, impoverishment etc. Contamination is usually caused by industrial and mining activities, pesticides, fuel combustion or irregular waste disposal. Subject of this research is soil contamination with heavy metals as one of the most complex and long-term issue (Kabata-Pendias & Pendias, 2001; Artiola et al., 2004; Kabata-Pendias & Mukherjee, 2007; Sherameti & Varma, 2010).

The pollution of soil with metals has begun long ago with the first human activities of mining and smelter activities. Contamination of soil lasts longer than other environmental media or parts of the biosphere due to the processes of accumulation of metals in soil. Heavy metals and their compounds get dissolved in soil and then accumulated by plants or removed by erosion and evaporation. Their half-life can be very long and it may last from decades to thousands of years. The accumulation of heavy metals in soil can be very harmful to humans as well as to animals and plants. Metal intoxication is usually chronic. Accumulated heavy metals in soil are transferred to plants that are used as food by humans and animals (Sherameti & Varma, 2010).

Anthropogenic activities for utilization of natural resources and further technological processing as well waste management are a global environmental pollution problem. The Republic of Macedonia was involved in the UNECE ICP Vegetation – Heavy Metals in European Mosses, for the first time in 2002 (survey 2000/2001) and again in 2005 and 2010 when atmospheric deposition of trace elements was studied over the entire territory of the country using samples of terrestrial mosses *Hypnum cupressiforme* and *Homalothecium lutescens*. The results of these studies of air pollution in Macedonia give an indication of impaired air and soil quality in terms of presence of heavy metals and possible pollution (Barandovski et al., 2012, 2013, 2015). The main emission sources appear to be metallurgic activities, power plants and mining activities. Therefore, special studies were performed in the area with the highest pollution with heavy metals, including air (moss biomonitoring or attic dust) or soil pollution, such those with Pb-Zn (Stafilov et. al., 2008a, 2010), ferronickel metallurgical activities (Stafilov et al., 2008b, 2010a, Bačeva et al., 2011, 2012), copper ore (Stafilov et al. 2010c; Balabanova et al., 2010, 2011, 2013, 2014) and Pb-Zn mines environs (Stafilov et al., 2014).

The aim of this study is to analyze the presence of various elements in top-soil (0–5 cm) and bottom-soil (20–30 cm) samples, collected from all over the territory of the Republic of Macedonia on 72 locations. The results were used to identify possible anthropogenic influences and to assess whether the presence of some heavy metals is associated with anthropogenic sources or is it due to the lithological composition. The obtained data were statistically processed and the distribution maps were prepared for the analyzed elements. The obtained results were compared with those obtained from the moss biomonitoring study and with the international standards for soil and the relationship with the locations of the industry in Macedonia was also analyzed.

STUDY AREA

The Republic of Macedonia is continental country, occupying the central part of the Balkan Peninsula, between latitudes 40°50’ and 42°20’ N and between longitudes 20°27’ and 23°05’ E with a total area of 25.713 km^2. The territory of Macedonia is under the influence of two climates types Mediterranean (along the valleys of the Vardar and Strumica rivers) and mildly continental (in the northern parts of the country), as well as mountain climate dominant in the mountainous regions. The biggest airline distance north to south is about 150 km, and east-west about 210 km.

Republic of Macedonia has complex geology and extensive configuration which causes large variations of soil types (Figure 1). There are many geologic formations with different age, different geographic and granular composition. Influence of different climates whose elements vary to large extent leads to appearance of many different floral associations. Due to the long term influence of pedogenetic factors soils in time were changing and attained different degree of evolution. The long term human influence had also its own contribution which had changed the direction of the natural pedogenetic processes of the soils.

As shown on Figure 1 there are four major geotectonic units present on the territory of the Republic of Macedonia: West-Macedonian Zone (WMZ), Pelagonian Massif (PM), Vardar Zone (VZ) and Serbo-Macedonian Massif (SMM) (Jovanovski et al., 2012). West-Macedonian Zone geologically is a very complex zone. The most abounded are the Paleozoic and Triasstic schists as well as the Paleozoic and Mezozoic carbonates (Arsovski, 1962). Less present are the Quaternery and Tertiary sediments and Paleozoic sandstones. This zone is also characteristic by the presence of magmatic and volcanic rocks mostly in the southern part (Dumurdžanov, 1987). Pelagonian Massif is mostly built by Precambrian formations (gneisses, gneiss-granites, micashists, marbles) as well as Paleozoic and Mezozoic carbonates with a series of marbles (Arsovski and Dumurdžanov, 1984). Quaternary sediments are mostly present along the river of Crna Reka. Vardar Zone (VZ) is characterized by the processes of sedimentation (Tertiary sediments) as well as by the intensive imprinting of magmatism expressed by the presence of Magmatic and volcanic rocks (Figure 2) (Arsovski and Dumurdžanov, 1995). The Serbo-Macedonian Massif (SMM) situated in the eastern part of the country and spread to Serbia to the north, to Greece to the south and to Bulgaria to the east. It is built up mostly of Precambrian gneisses and schists and Paleozoic schists. This zone also contains magmatic and sedimentary rocks (Tompson et al., 1998).

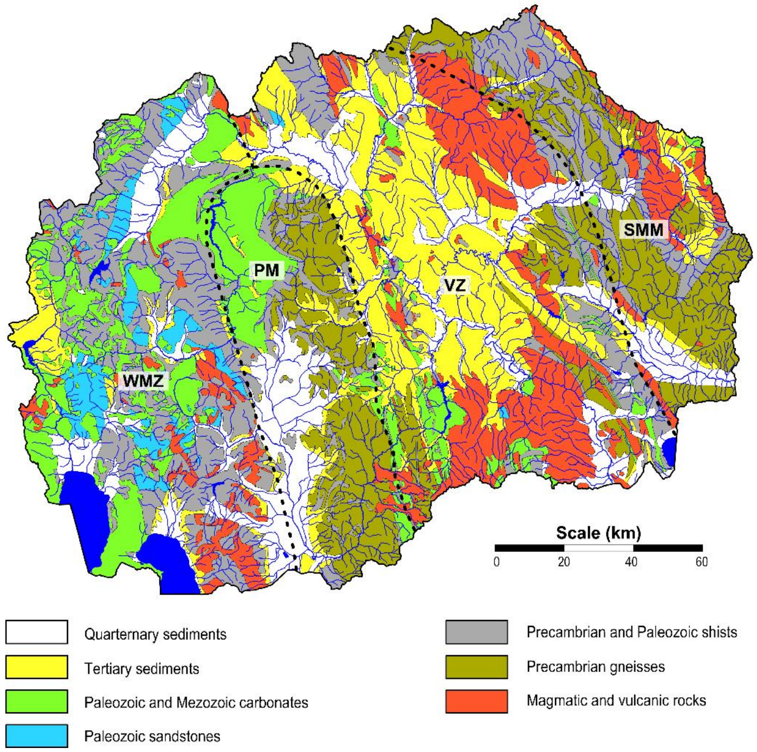

Fig. 1. Lithological map of Macedonia.
WMZ – West-Macedonian zone, PM – Pelagonian massif, VZ – Vardar zone, SMM – Serbo-Macedonian massif
(Institute for Geological and Mining Exploration and Investigation of Nuclear and Other Mineral Raw Materials, 1970)

MATERIALS AND METHODOLOGY

Soil sampling and pre-treatment

The total study area was covered with a network of 72 sampling locations, a network of 17 × 17 km, i.e. approximately 3 soils samples were collected per 1000 km^2 (Figure 2).

Two soil samples were taken at each location: a sample from the surface layer of soil – topsoil (0–5 cm) and a deep soil layer – subsoil (20–30 cm). The collection of samples was conducted in the period of June–September 2010. In total 144 soil samples (72 top and 72 bottom soil) were collected and analyzed. Soil samples were collected according to soil sampling standards (Salminen et al., 2005). Each sample was a composite of five subsamples collected in the area within a 10×10 m with an approximate mass of 1 kg.

Soil samples were dried at room temperature for about 2 weeks, then crushed and sieved through 2 mm screen and grinded bellow 0.125 mm. Digestion of the samples was performed by applying nitric, perchloric, hydrofluoric and hydrochloric acids for total digestion. Precisely measured mass of dust samples (0.5 g) with the accuracy of 0.0001 g was placed in teflon vessels. After this 5 ml concentrated nitric acid was added. For total digestion of inorganic components, 5–10 ml of HF was added. When the digest became a clear solution, 2 ml of $HClO_4$ were added. After cooling for 15 min, 2 ml of HCl were added for total dissolving of metal ions. Finally, the vessels were cooled and digests quantitatively transferred to 25 ml volumetric flasks.

Instrumentation and analysis of the elements contents

The analysis of soil samples was performed by using of inductively coupled plasma – atomic emission spectrometry (ICP-AES), model Varian 715-ES. Standard solutions were prepared by dilution of 1000 mg l^{-1} solution (11355-ICP multi Element Standard). The analyses of digested samples were performed with an atomic emission spectrometry with inductively coupled plasma (ICP-AES), Optimization of instrumental condition for each element was previously done (Balabanova et al., 2010). Total contents of 18 elements (Al, Ba, Ca, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) were determined. The quality control analysis was performed by using the method of standard additions, and obtained satisfactory analytical values for the analytical yield of analyzed elements. Also, certified referent material of soil (JSAC-041) and rock material (SARM-3) were applied and the obtained results were within the certified values of the analyzed elements.

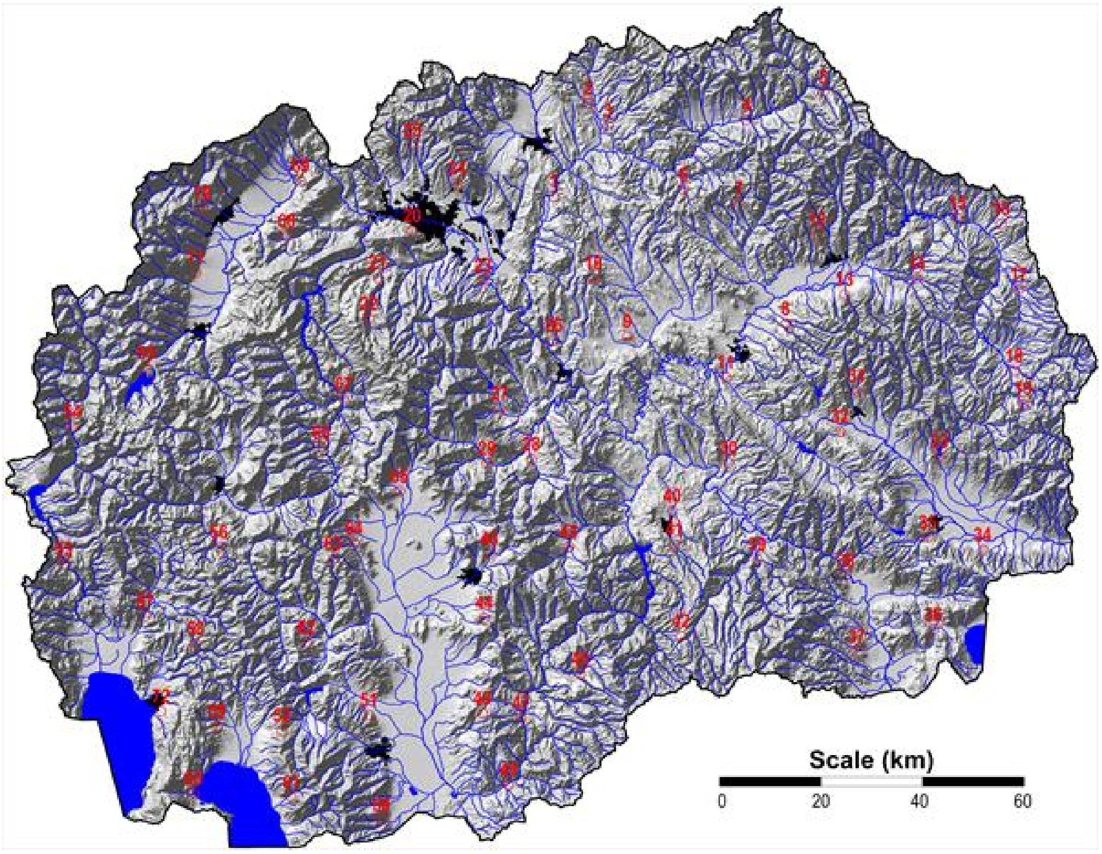

Fig. 2. Map of soil samples locations

Data processing

Parametric and nonparametric statistical methods were used (Zhang et al., 1998), and normality tests of data distributions were performed. The degree of association of chemical elements was assessed using the linear coefficient of correlation (Cohen, 1988). Multivariate R-mode factor analyses (FA) was used to reveal associations of chemical elements (Garson, 2000; Šajn, 2005; Šajn, 2006). The factor analysis (FA) was performed on variables standardized to zero mean and unit standard deviation (Davis, 1986). Universal kriging with linear variogram interpolation method was used for the construction of maps showing spatial distribution of factor scores, as well as the distribution maps displaying the distribution of analyzed elements (Davis, 1986). For class limits, seven classes of the percentile values of distribution of interpolated values were chosen (0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100).

RESULTS AND DISCUSSION

Elemental content and data processing

Data obtained from the analysis of soil samples were processed statistically by descriptive analysis. The following parameters for both, top- and bottom soil samples are calculated: mean, geometrical mean, median, minimum, maximum, 10, 25, 75 and 90 percentile, arithmetic standard deviation, geometric standard deviation coefficient of variance, skewness and kurtosis (Table 1). In Table 1 the average values for the content of the elements in top and subsoil samples in European top- and bottom soils (Salminen et al., 2005) are also given.

T a b l e 1

Descriptive statistics for elements content value in soil samples

Element	T/B	Dis	Unit	X_a (EU)	X_a	X_g	Md	Min	Max	P_{10}	P_{25}	P_{75}	P_{90}	S	S_x	CV	A	E
Al	T	Log	%	5.56	2.40	2.10	2.20	0.79	4.30	1.30	1.60	3.1	3.80	0.97	0.11	41	–0.33	–0.56
Al	B	Log	%	5.93	2.50	2.30	2.30	0.77	5.10	1.20	1.50	3.50	4.10	1.20	0.14	45	–0.25	–0.96
Ba	T	Log	mg/kg	400	450	370	420	41	1600	150	250	570	710	260	31	59	–0.97	1.26
Ba	B	Log	mg/kg	411	490	410	440	66	1700	180	280	590	840	320	38	65	–0.54	0.71
Ca	T	Log	%	2.53	1.80	0.85	0.79	0.092	21.0	0.18	0.34	2.00	4.40	3.00	0.35	165	0.26	–0.45
Ca	B	Log	%	3.17	2.00	0.84	0.78	0.10	21.0	0.16	0.26	2.40	4.30	3.20	0.38	163	0.27	–0.79
Cr	T	Log	mg/kg	95	71	52	54	11	600	19	32	93	110	75	8.8	106	–0.05	0.44
Cr	B	Log	mg/kg	87	77	57	63	11	600	17	36	100	120	77	9.1	100	–0.10	0.25
Cu	T	Log	mg/kg	17	20	17	16	1.7	73	9.1	11	25	44	14	1.7	69	–0.18	1.68
Cu	B	Log	mg/kg	17	22	17	16	3.2	78	9.1	12	27	46	17	2.0	76	0.14	0.20
Fe	T	Log	%	2.66	2.60	2.40	2.50	0.63	6.70	1.40	1.80	3.30	4.00	1.20	0.14	44	–0.62	0.76
Fe	B	Log	%	2.83	2.80	2.60	2.70	0.77	8.00	1.50	2.00	3.50	4.10	1.30	0.15	44	–0.32	0.74
Ga	T	N	mg/kg	13	12	12	12	2.0	23	7.5	9.8	16	17	4.4	0.52	35	–0.13	–0.10
Ga	B	N	mg/kg	14	13	12	13	4.1	26	7.1	9.4	16	20	5.1	0.60	38	0.30	–0.40
K	T	N	%	1.68	1.50	1.30	1.40	0.26	3.20	0.72	1.00	2.00	2.30	0.62	0.73	42	0.43	–0.18
K	B	N	%	1.77	1.60	1.40	1.50	0.52	3.30	0.78	1.10	2.00	2.30	0.62	0.73	39	0.42	–0.07
Li	T	Log	mg/kg	–	20	17	18	4.8	79	7.6	12	28	35	13	1.5	64	–0.10	–0.33
Li	B	Log	mg/kg	–	22	19	20	5.2	69	8.5	13	29	38	12	1.4	56	–0.12	–0.44
Mg	T	Log	%	0.89	0.80	0.66	0.66	0.11	2.90	0.32	0.46	1.00	1.40	0.52	0.061	64	–0.43	0.86
Mg	B	Log	%	1.06	0.84	0.71	0.73	0.15	3.10	0.34	0.52	1.10	1.50	0.52	0.061	62	–0.44	0.60
Mn	T	Log	mg/kg	630	760	630	620	160	3200	270	460	870	1300	560	66	74	0.08	0.90
Mn	B	Log	mg/kg	570	830	650	640	99	4300	310	490	890	1400	730	86	88	0.16	1.51
Na	T	N	%	0.85	0.99	0.72	0.85	0.033	2.30	0.23	0.46	1.50	1.90	0.64	0.075	65	0.34	–1.07
Na	B	N	%	0.93	1.10	0.80	0.94	0.078	2.40	0.23	0.53	1.60	2.00	0.65	0.077	62	0.29	–0.99
Ni	T	Log	mg/kg	37	49	33	35	2.5	530	10	19	60	88	65	7.7	134	0.00	1.07
Ni	B	Log	mg/kg	39	54	36	37	5.2	530	10	19	63	100	71	8.4	131	0.16	0.38
P	T	Log	mg/kg	510	470	420	450	120	1400	200	330	580	760	230	27	49	–0.47	0.16
P	B	Log	mg/kg	480	450	380	430	74	1300	150	270	600	740	250	29	55	–0.66	0.26
Pb	T	Log	mg/kg	33	27	13	17	2.5	700	2.5	5.9	26	33	81	9.6	298	0.22	1.17
Pb	B	Log	mg/kg	23	26	13	14	0.77	660	2.5	8.9	24	37	77	9.1	293	0.18	2.04
Sr	T	Log	mg/kg	130	93	65	71	9.4	540	21	32	120	180	86	10	93	–0.11	–0.46
Sr	B	Log	mg/kg	143	100	70	68	9.9	580	22	41	120	230	98	12	98	0.06	–0.32
V	T	Log	mg/kg	68	83	70	67	14	300	31	53	95	130	55	6.5	66	–0.16	0.91
V	B	Log	mg/kg	70	90	75	71	19	370	40	53	100	150	68	8.0	75	0.37	1.08
Zn	T	Log	mg/kg	68	57	37	39	3.1	440	11	24	67	88	69	8.2	122	–0.23	0.76
Zn	B	Log	mg/kg	61	57	35	38	4.4	490	11	19	65	89	82	9.6	144	0.20	0.74

T/B – Top soil/Bottom soil; Dis. – distribution (Log – lognormal; N – normal); X_a – arithmetical mean; X_g – geometrical mean ; Md – median; Min – minimum; Max – maximum;
P_{10} – 10 percentile; P_{25} – 25 percentile; P_{75} – 75 percentile; P_{90} – 90 percentile; S – standard deviation; S_x – standard error deviation; CV – coefficient of variation; A – skewness; E – kurtosis

As seen in the Table 1, the maximum values are almost 6 times higher than the average values for most of the elements, except for Ca, Ni and Pb where the maximum values are more than ten times higher than the average values. The comparison of the maximum and minimum values again points out to the same elements with an average of factor 100, whereas the highest values are related to Ca (230 times), Ni (215 times) and Pb (907 times).

There are two locations with very high values of Ca (No. 53 on Mt. Jablanica and No 64 near the village of Krivogaštani) in the lower and upper layer of soil as well, and one location with very high values of Ni (No. 68 on Mt. Žeden). The wide concentration range was found for Pb (maximal value higher than average for 22 times), whereupon very high values are identified on the location No. 14 near the village of Blatec (estern part of the Republic of Macedonia) (Figure 2).

Locations No. 64 and 53, according to the geological structure belong to the metamorphic rocks, location number 64 to chlorite and amphibole shale, location number 53 belongs to marbles, while 68 and 14 of the limestone tabular cherts, massive limestones and dolomites. The highest contents of lead and zinc content are found in the soil samples collected in Zletovo region mainly due to their natural present, but mining activities in this region are also source of anthropogenetic influence. Chromium, copper, manganese, nickel and lead are naturally occurring in the soils of the Kratovo region as a result of the mineralization processes. The high values of nickel and chromium also occur in the Šara massif and in other places where the geological structure of the soil is represented with Palaeozoic rocks (Jablanica and Šara on the west and the lowlands from north to south in the central part). Copper is more naturally present in the eastern regions (Osogovo, German, Kožuf) and manganese in the Kičevo region.

The ratio of the content of the elements in the top and bottom layers does not indicate significant differences among all elements. However, some elements distinguish on some locations where more than twice bigger differences in the ratio have been identified. Such example is barium wherein the gap ranges from two to three times the value of the upper layer on 5 locations, zinc with gap range from two to seven times higher differences on 10 locations and also lead with differences of 2 to 4 times higher on 13 locations.

Multivariate factor analysis with R-method was applied in order to show associations of geochemical elements. Factor analysis (FA) was performed in order to lower the number of the variables to a small number of new, synthetic variables called factors. Factor analysis was performed on the variables standardized to zero and unit standard deviation. The analysis reviewed total of 144 samples of surface and bottom soil and analysis of 18 elements. The matrix of rotated factor loadings is given in Table 2.

Further analysis of the results includes analysis of enrichment factor and comparison with EU averages, analysis of the connection with the industrial facilities locations in the country, and comparison with Dutch standards for soil quality. Specific distribution maps of the elements in the soil samples, for the topsoil and subsoil were prepared separately.

Four geogenic geochemical associations (Table 2) have been defined based on the obtained results from the factor analysis: F1: Cu-Fe-Ga-P-V-Zn; F2: Cr-Ni; F3: Al-Ca-Mg, and F4: Ba-K-Na-Sr.

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Matrix of dominant rotated factor loadings (f > 0.50)

Element	F1	F2	F3	F4
Al	0.34	0.26	0.66	–0.13
Ba	0.22	–0.11	–0.10	–0.70
Ca	–0.22	–0.04	0.64	0.20
Cr	0.11	0.95	0.11	0.04
Cu	0.53	0.41	–0.08	0.21
Fe	0.87	0.22	0.11	0.02
Ga	0.73	–0.02	–0.15	–0.40
K	0.07	–0.12	–0.47	–0.56
Li	0.30	0.33	–0.11	0.16
Mg	0.15	0.28	0.69	0.12
Mn	0.42	0.36	–0.10	0.39
Na	–0.05	–0.30	–0.13	–0.58
Ni	0.05	0.96	0.09	0.11
P	0.56	0.06	0.25	–0.01
Pb	0.29	0.01	–0.22	0.26
Sr	0.01	–0.11	0.30	–0.53
V	0.83	0.04	0.07	–0.07
Zn	0.59	0.03	0.08	0.13
Var. (%)	19.6	14.2	10.3	11.0

F1, F2, F3, F4 – factor loading; Var – variance (%); Comm – communality (%)

Geochemical association of Cu, Fe, Ga, P, V and Zn interpreted as Factor 1 is directly related to the lithological formations. Its origin is directly related to the natural processes of flysch sediment and flysch formations. This is confirmed by the similar content of these elements in both, the topsoil and subsoil. Therefore, the distribution maps only for topsoil are presented in Figure 3.

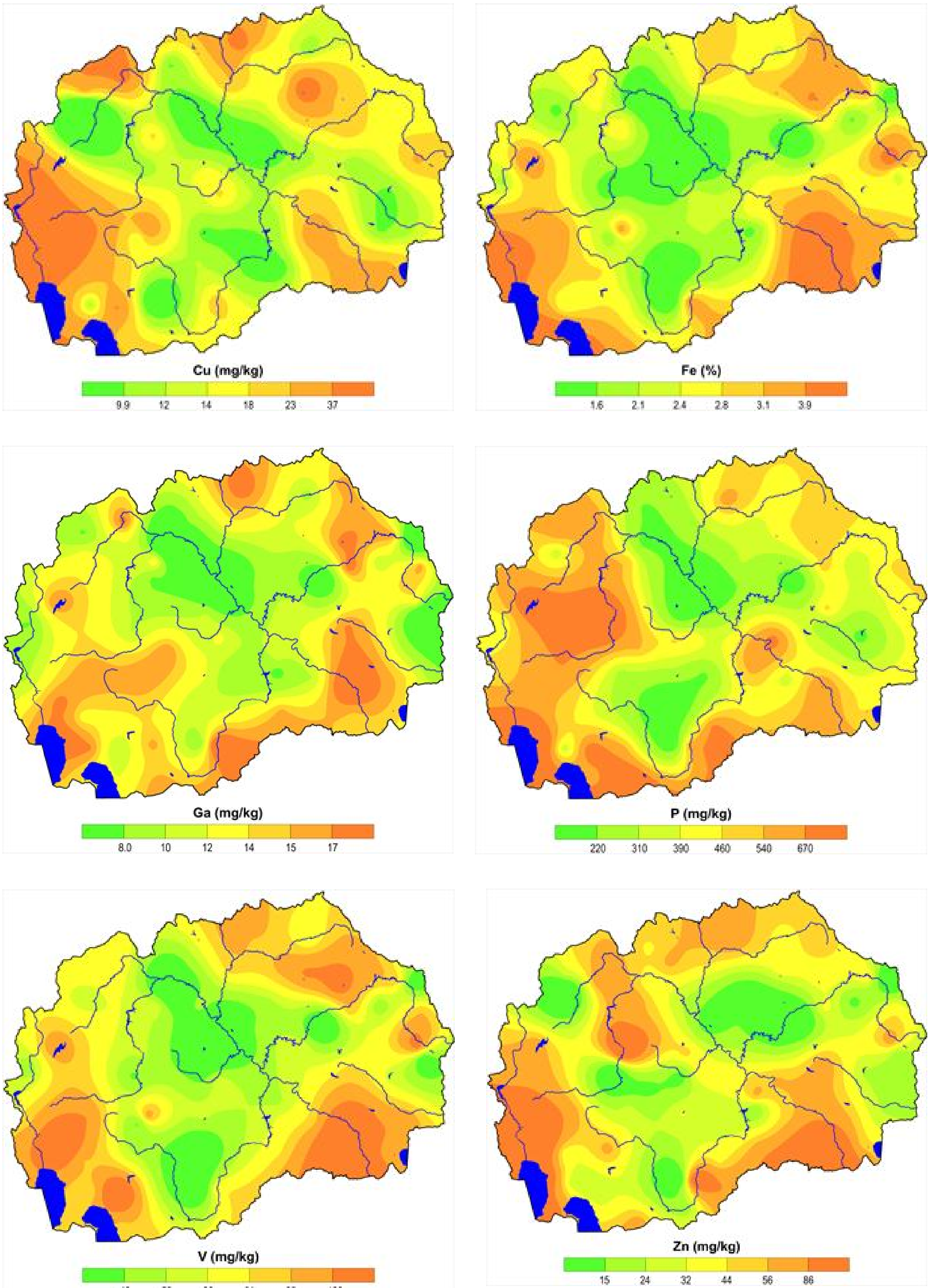

Fig. 3. Spatial distribution of Cu, Fe, Ga, P, V and Zn

The highest contents of copper are found in the area of Debar, Kičevo and Šara Mountain in western Macedonia, and Kratovo and Kožuf massifs in eastern and south Macedonia. The content of copper in the samples taken forms these areas is above 50 mg·kg^{-1}, while the contents of copper in the samples collected in other parts of the country are much lower. The content of zinc is naturally high in the Debar-Struga-Ohrid region, Kožuf massif in the south and in the Skopje region in northern part of the country (Figure 3).

Geochemical association of Cr and Ni (Factor 2) is related to Tertiary sediments (Paleogene and Neogene flysch). The highest values of chromium (>110 mg kg^{-1}) were found in the region of Debar and Struga, where limestones and dolomites are dominant, then in the Šara Mountain region in western Macedonia where meta-sands and conglomerates are present, in the area of Skopska Crna Gora mountain with the domination of quartz-sericite and albatic-biotic shales, in the region of Negotino with sandstone, limestone and marls, and in the Belasica massif on the east with double mica-gneiss granites (Figure 4). High values of the content of nickel (>90 mg·kg^{-1}) were found in the Debar-Struga region, north side of the Šara Mountain massif, Gradištanska Mt. above Veles and Negotino region (Figure 4).

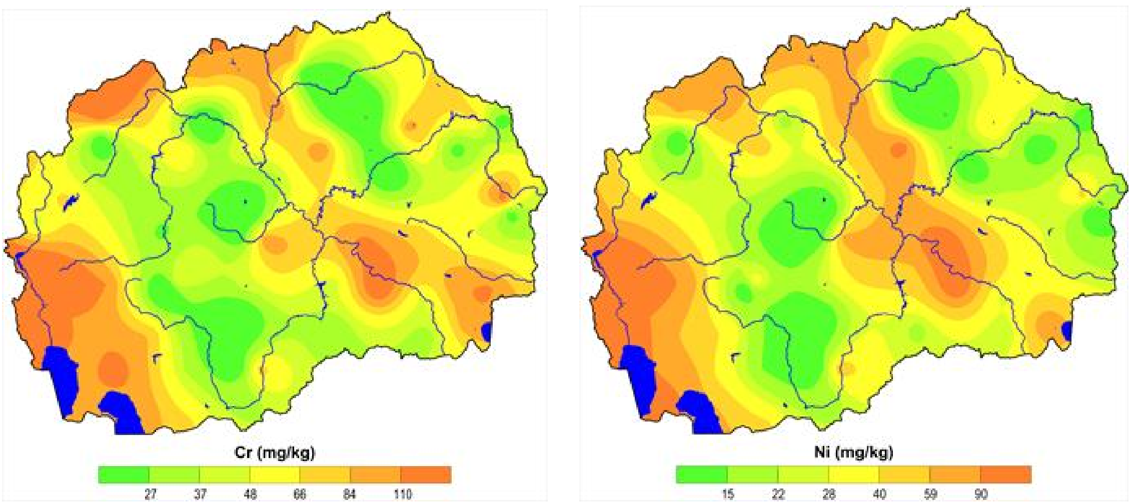

Fig. 4. Spatial distribution of Cr and Ni

Factor 3 (Al, Ca and Mg) and Factor 4 (Ba, K, Na and Sr) represent less expressed natural factors. Their presence is primarily associated with Paleozoic and Mesozoic carbonates in the soil (Al-Ca-Mg), i.e. their association with the volcanism phenomena's (Ba-K-Na-Sr). High presence of these associations of elements was found in areas enriched with volcanic rocks (andesite) and their pyroclastic rocks. Their geogenic natural anomaly on the presence of high content in soil is isolated in the north-eastern part of the country, where the Neogene volcanisms are dominant, and in the southern part of the country where Quaternary volcanisms are dominant. These formations are present in the lower Vardar and Belasica regions, then in the Polog region and the valley of the river of Treska in the west of the country and in the Osogovo massif in the east (Figures 5 and 6).

The contents of Mn, Li and Pb in the samples are not explained by any of the identified factors. As seen on distributional map of Mn (Figure 7) and the geological map (Figure 2), higher content of Mn are mostly present in the soils on the Tertiary sediments and Paleozoic and Mezozoic carbonates found in the western part of the country, as well as in the north-east parts where Precambrian and Palezoic schists are present. Lithium is mostly present on the northern and in the western part of the country. Lead (Figure 7) mostly is connected to the geological formations. Its higher content is mostly present in Kožuv Mt. region on south, Žeden Mt. on north and Karadžica-Bistra mountains region in the central and western part, Maleševo Mountains and Radoviš region on the east of the country. Lead is related also with magmatic and volcanic rocks and Paleozoic and Mezozoic carbonates. However, due to the anthropogenetic influence of the former Pb-Zn smelter plant in the city of Veles in the central part of Macedonia, as well as the Pb-Zn mines and flotation plants in the north-eastern part of the country higher content of Pb was found in topsoil samples than in the subsoil (Figure 7) (Stafilov et al., 2008, 2010a, 2014). This is confirmed by the higher median value of lead (for 1.21 times) in topsoil than in bottom soil (Table 1, Figure 7).

Enrichment factors

In order to evaluate the content of heavy metals in soil and eventual anthropogenetic influence, an enrichment factor (EF) was used. The enrichment factor is a tool for a quantitative analysis of the degree of pollution of soil and is an important indicator of the presence of possible pollution. Enrichment factor was calculated as a ratio between the average values of each element in top- and bottom soil samples. The obtained data are presented in Figure 8. The enrichment factor showed general compatibility of the quality of the soil in surface and the lower parts, with a ration within 0.86–1.02 (Figure 8). The most significant deviation is obtained for lead (EF = 1.21) indicating possible contamination which could be expected in the area of Veles in the central part due to the pollution due to the Pb-Zn smelter plant activities (Stafilov et al., 2010a) and in the eastern part of the country with Pb-Zn mining and ore processing activities (Stafilov et al., 2014; Angelovska et al., 2014; Balabanova et al., 2014, 2016).

Additionally, in order to assess the natural enrichment and possible pollution, an enrichment factor has been calculated comparing the average content of European (Salminen et al., 2005) and Macedonian soils, ratio between surface and the bottom layer of soil (Figures 9 and 10). It is obvious that the enrichment factor for the ratio of the average content of the Macedonia's and Europe's soils showed deviation for Ba, Cu, Fe, Mg, Mn, Na and V. The deviation was characteristic for the topsoil and as well for the subsoil. The most significant deviation was recorded for enrichment factor of 1.7 for subsoil and 1.9 for topsoil showing specificity of high natural presence of these elements in the soil from Macedonia.

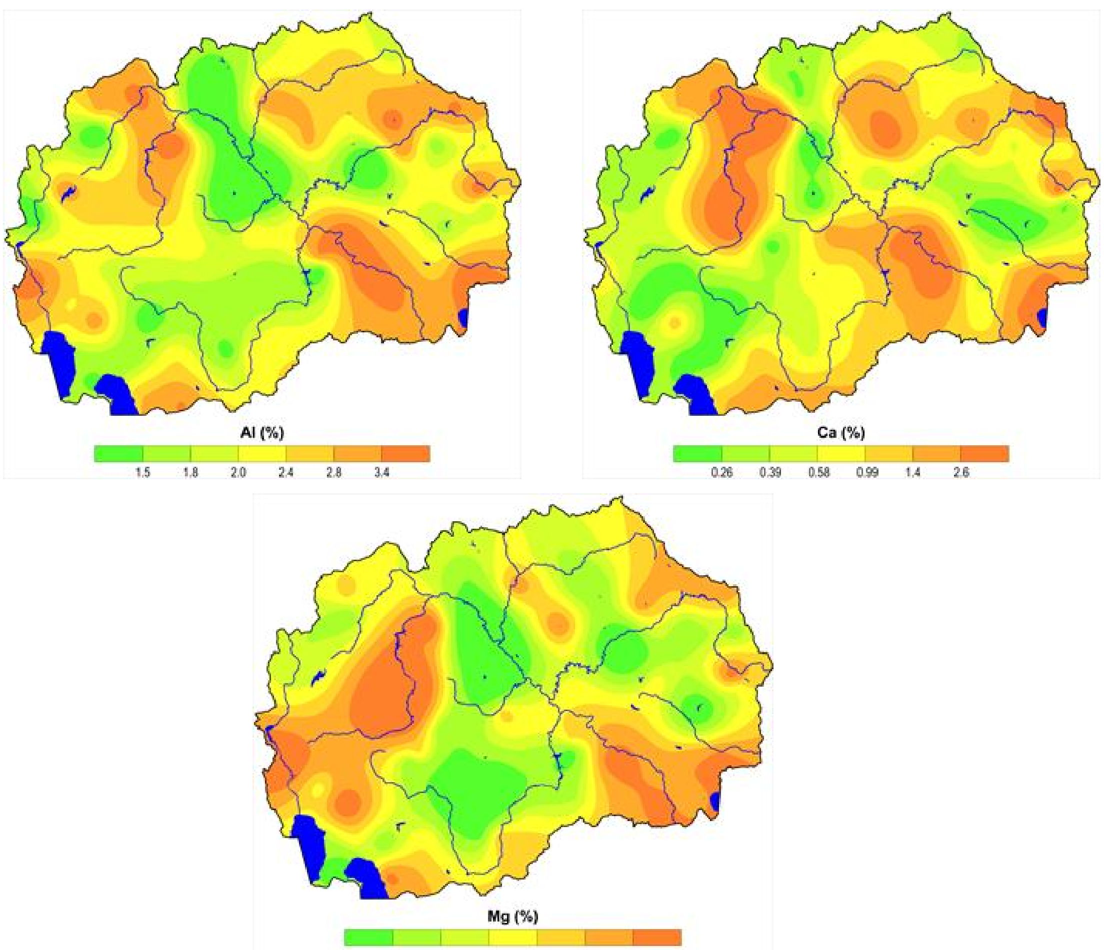

Fig. 5. Spatial distribution of Al, Ca and Mg

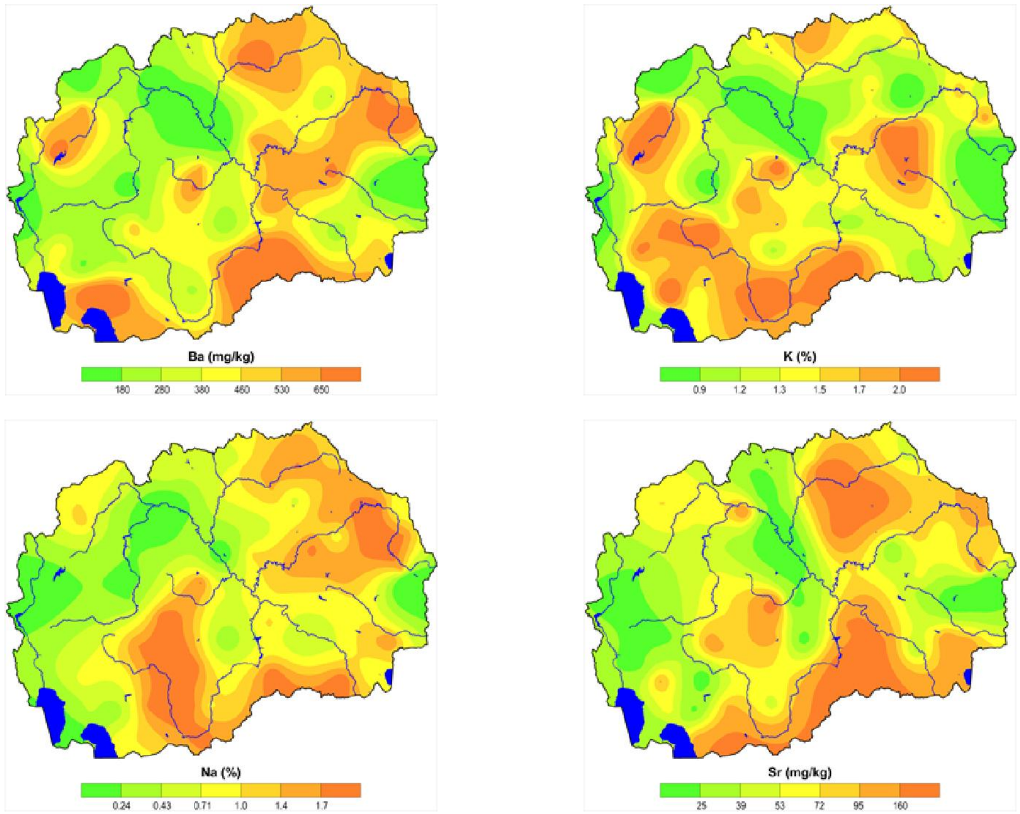

Fig. 6. Spatial distribution of Ba, K, Na and Sr

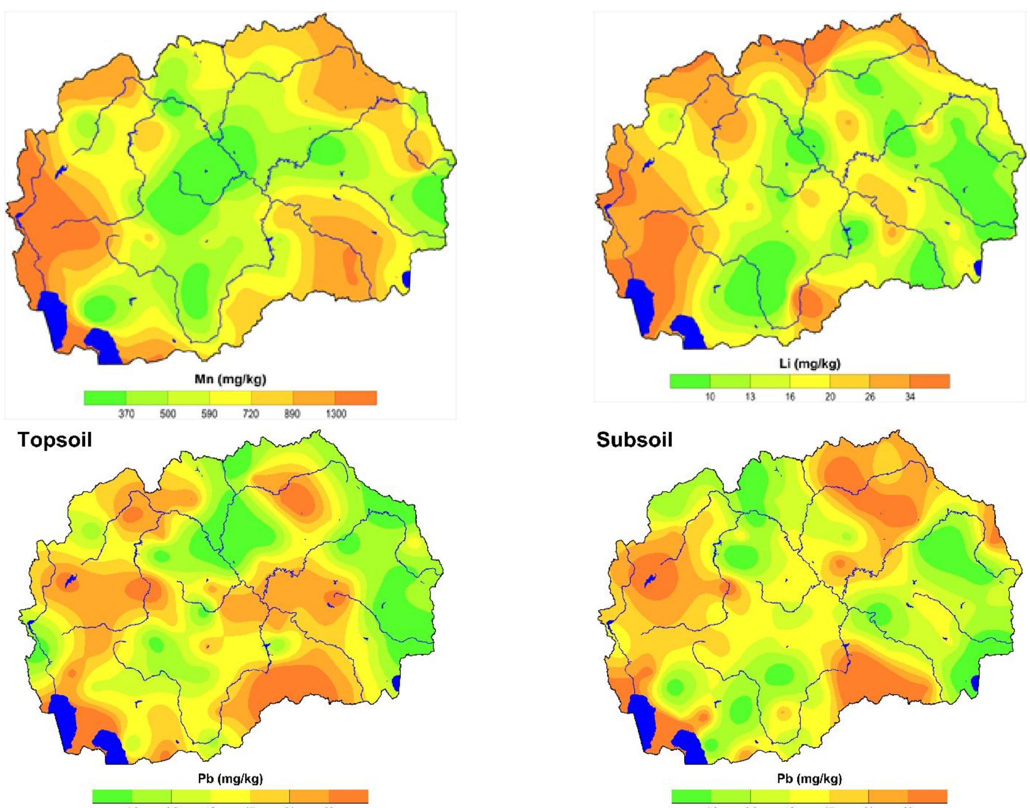

Fig. 7. Spatial distribution of Mn, Li and Pb

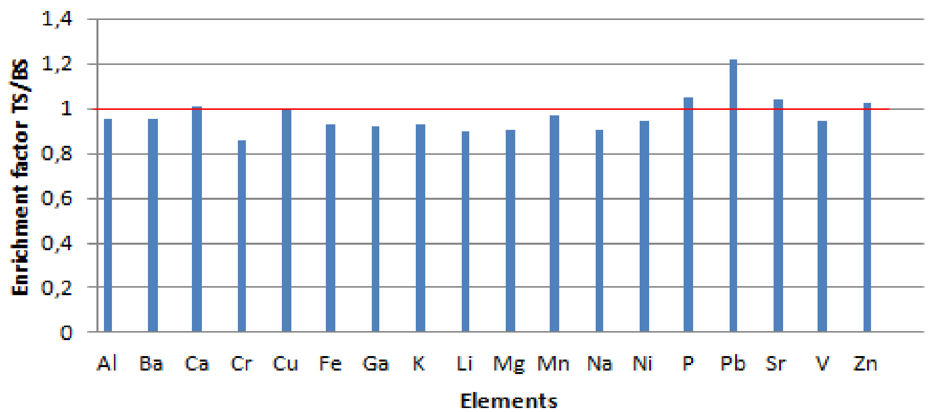

Fig. 8. Enrichment factor for the analyzed elements (topsoil/bottom soil)

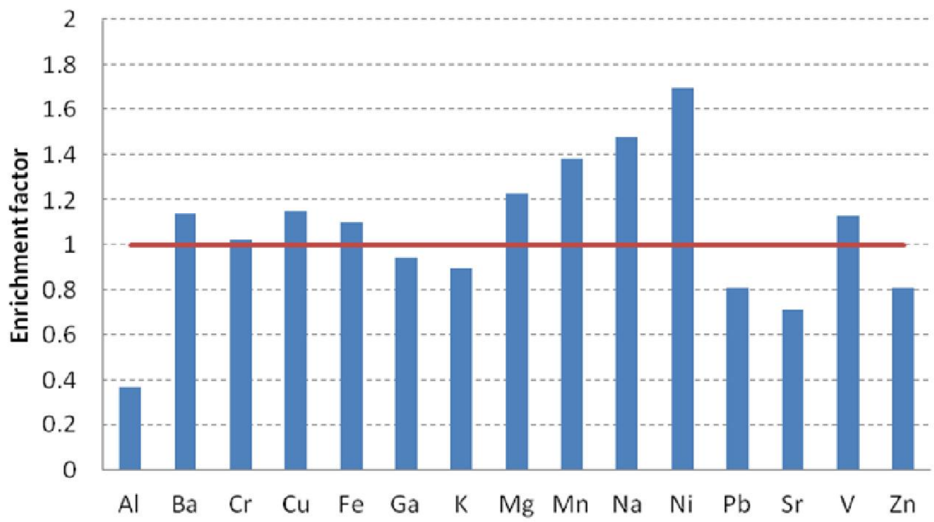

Fig. 9. Enrichment factor for Macedonia/EU topsoil

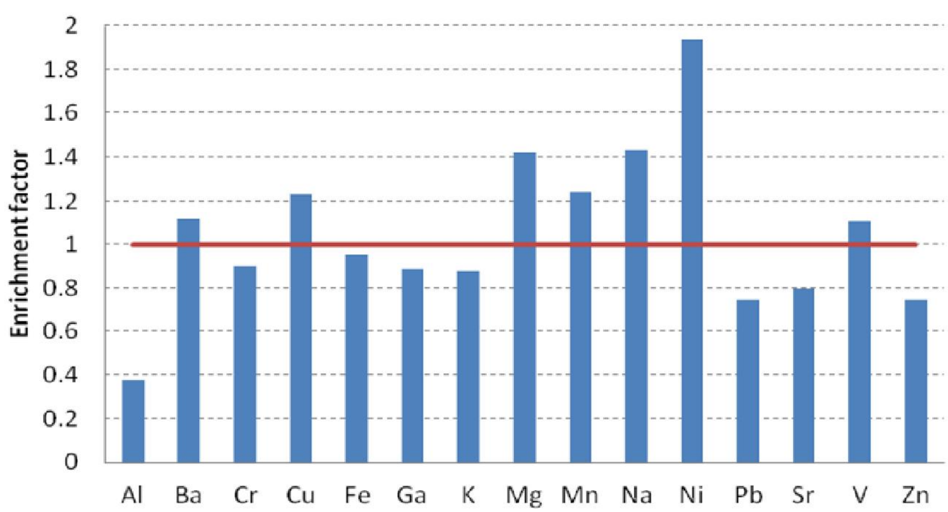

Fig. 10. Enrichment factor for Macedonia/EU subsoil

Soil quality standards

In the absence of national standards for the quality of the soil, the obtained results for Ba, Cr, Cu, Ni, Pb and Zn were compared with the Dutch standards (http://esdat.net/Environmental%20Standards/Dutch/annexS_I2000Dutch%20Environmental%20Standards.pdf). The number of top- and bottom soil samples with higher values than target (TV) and intervention values (IV) given in the Dutch standards is given in Table 3. It is obvious than the results of the analyses of the soil samples and the Dutch standards show that most of the samples are within the intervention values, while big number of the samples have a content which is higher than the target values. However, the most characteristic is the case with the content of lead and zinc where almost all samples have a value above the target value. The cases where values above intervention values were identified indicate the need for additional study in order to clarify whether the values are as result of anthropogenic or natural influences.

Table 3

Comparison of the obtained results by Dutch standards (in mg kg^{-1})

Element	Target value (TV)	Intervention value (IV)	Topsoil			Subsoil		
			<TV	TV–IV	>IV	<TV	TV–IV	>IV
Ba	200	625	11	47	14	10	47	15
Cr	100	380	57	13	1	53	18	1
Cu	36	190	63	9	–	61	11	–
Ni	35	210	37	34	1	35	35	2
Pb	85	530	71	1	1	70	1	1
Zn	140	720	68	4	–	67	5	–

Explanatory note: (TV) – value target, below which no known or expected impacts of the natural characteristics of the soil; (IV) – intervention value, the maximum allowed value above which required remediation of soil. (<TV) – number of samples with values under TV; (TV–IV) – number of samples with values between TV and IV; (>IV) – number of samples with values beyond IV.

CONCLUSIONS

Multivariate factor analysis with R-method was applied in order to show associations of geochemical elements and four geogenic geochemical associations were identified. It was concluded that the association of Cu, Fe, Ga, Pb and Zn (Factor 1) is directly related to the natural processes of flysch sediments and flysch formations. The second association of Cr and Ni is associated with geological formations of Tertiary sediments. In the remaining two associations (Al, Ca and Mg and Ba, K, Na and Sr), the appearance of elements is primarily associated with Paleozoic and Mesozoic carbonates in soil (Al, Ca and Mg), i.e. with vulcanization processes (Ba, K, Na and Sr). These two associations were specially isolated in the northeastern part of the country. The analysis also showed that Cr, Cu, Mn, Ni and Pb are naturally present with higher contents in soils of Kratovo massif as a result of the mineralization processes. Nickel and chromium are present in higher content in the Šara massif and in the areas where the geological structure of the soil involve Paleozoic rocks, copper is more present in the eastern regions, while manganese in Kičevo region.

Analysis of the content in the topsoil and subsoil does not indicate significant differences in the elements. Some differences were recorded for the content of Zn and Pb, whose content in the topsoil was higher than in the subsoil on 10 locations and 13 locations, respectively. The comparison of the average values for European and Macedonian soils shows higher content for some of the elements in Macedonian soils due to the specific geological characteristics of the country, especially for nickel (enrichment factor of 1.7 for subsoil and 1.9 for topsoil). The results of this study suggest a general correlation of the content of the analyzed elements with the lithology, but also may suggest a possible association with certain industrial activities (Pb and Zn).

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Р е з и м е

ПРОСТОРНА ДИСТРИБУЦИЈА НА ТЕШКИ МЕТАЛИ ВО ПОЧВИТЕ ОД РЕПУБЛИКА МАКЕДОНИЈА

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Анализирана е дистрибуцијата на различни елементи во почвите од Република Македонија во однос на загадувањето на воздухот со тешки метали, кое се следи повеќе од 10 години во рамките на програмата за следење на загадувањето на воздухот во Европа со помош на биомониторинг на мовови. Во текот на 2010 година паралелно со земањето на примероци од мов, на истите 72 локации на целата територија на Република Македонија беа земени и примероци од почви. Вкупно се земени 144 примероци почва (површинска и потповршинска) во кои е определена содржината на 18 елементи со примена на атомската емисиона спектрометрија со индуктивно спрегната плазма. Определувањето на содржината на овие елементи е извршено во двата примерока (површинска и потповршинска почва) за да се идентификува евентуално антропогено влијание и да се процени дали содржината на некои елементи во почвите е поврзана со антропогени извори или е резултат на литогени појави. Добиените резултати се обработени статистички, а подготвени се и карти на просторна дистрибуција за сите анализирани елементи. Резултатите се споредени со меѓународни стандарди за почви и со распоредот на индустриските објекти. Испитувањата генерално укажуваат на поврзаност на застапеноста на овие елементи со геолошките формации, но исто така укажуваат и на одредена поврзаност со некои индустриски активности.