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Distribution of chemical elements in soil samples from the Pelagonia region, Republic of Macedonia

Ana Puteska[1], Bojana Dimovska[1], Robert Šajn[2*] and Trajče Stafilov[1]

[1] Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss Cyril and Methodius University in Skopje, POB 162, 1000 Skopje, Republic of Macedonia

[2] Geological Survey of Slovenia, Ljubljana, Slovenia; (Robert.Sajn@geo-zs.si)

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ABSTRACT

This study represents the first systematic investigation of the spatial distribution of different chemical elements in the soil cover of the Pelagonia region, Republic of Macedonia. For this purpose, 262 soil samples (from 131 locations) were analyzed to determine the content of 17 major and trace elements in the soil from this region and to assess the size of the area eventually affected by heavy metal pollution. All samples were analyzed by atomic emission spectroscopy with inductively coupled plasma (ICP-AES). Cluster and factor analysis (R-mode) were applied in order to show the associations of chemical elements. Three factors were obtained. Factor 1 (Al, Ba, Mg, Mn, Fe, Ni, P and V), Factor 2 (Cr, Cu, Pb and Zn) and Factor 3 (Ca and Sr). It was established that the distribution of these associations are mostly as a result of the complex geology and lithology of the region.

Keywords: soil, Pelagonia Region, Republic of Macedonia, multivariate statistics, geochemical mapping

1. INTRODUCTION

Urban pollution with heavy metals is a global problem initiated by the world's technological progress and human exploitation of natural resources, and as such has become the subject of many studies. The regional contamination of soil occurs mainly in industrial areas and within centres of large settlements, where factories, motor vehicles and municipal wastes are the most important sources of trace metals (KABATA-PENDIAS & PENDIAS, 2001). The level of environmental pollution will depend on the proper control of anthropogenic activities such as well extraction, the concentration and separation of waste (QIN et al., 2012).

The major causes of emissions are anthropogenic sources specifically mining operations (HUTTON and SYMON, 1986; BATTARBEE et al., 1988; NRIAGU, 1989). In some cases, even long after mining activities have ceased, the emitted metals continue to persist in the environment (PEPLOW, 1999). The potential for contamination is increased when mining exposes metal-bearing ores rather than the natural exposure of ore bodies through erosion (GARBARINO et al., 1995). Heavy metals occur as natural constituents of the earth's crust, and are persistent environmental contaminants since they cannot be degraded or destroyed. Some heavy metals have bio-importance as trace elements but, the biotoxic effects of many of them in human biochemistry are of great concern. Hence, there is the need for proper understanding of the conditions, such as the concentrations and oxidation states, which make them harmful, and how biotoxicity occurs (DURUIBE et al., 2007).

The Republic of Macedonia has the same problem with global pollution by heavy metals (STAFILOV et al., 2009; STAFILOV, 2014). Recent 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, in addition to 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). Degradation of soils in Macedonia began a long time ago (FILIPOVSKI, 2003). Some hotspots are enriched in soil pollution with heavy metals (STAFILOV et al., 2009; STAFILOV, 2014). Plants near the hotspots accumulate heavy metals directly from the soil or from the air, which are passed through them to man and animals (FILIPOVSKI, 2003). Disposal of fly ash and slag from thermoelectric power plants using coal also degrades the environment, especially soils.

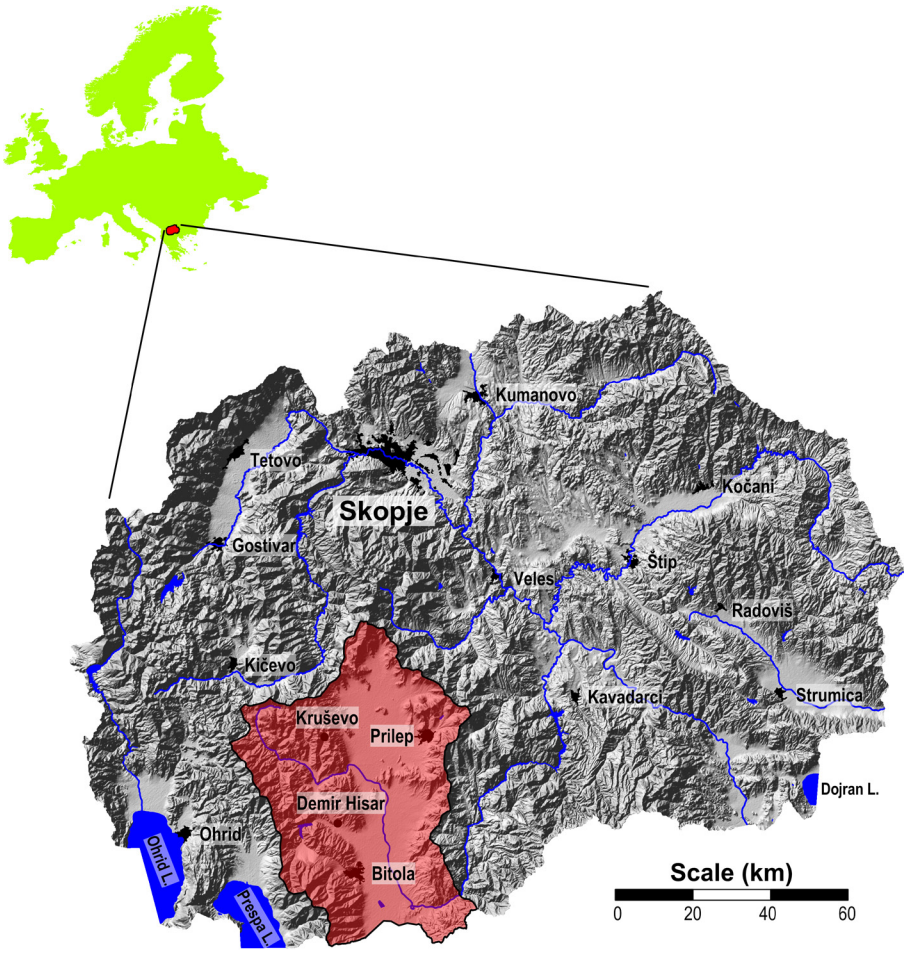
The purpose of this research was to determine the level of soil contamination with heavy metals in the Pelagonia Valley, Republic of Macedonia, mostly as a result of the impact of the thermoelectric power plant "Bitola" situated near the city of Bitola, as well as from traffic and industrial activities in the cities in the valley (Bitola, Prilep, Demir Hisar and Kruševo) and their environs.

2. STUDY AREA

The Pelagonia Valley is located in the south-southwest of the Republic of Macedonia, meeting the border with the Republic of Greece at its southern part. Geographically, Pelagonia lies between the following coordinates: north-south: 41° 30' – 40° 50'; east-west: 21° 50' – 20° 50' (Fig. 1). Pelagonia is the largest Macedonian valley, and includes the environs of Bitola, Prilep and Demi Hisar. The Pelagonia region lies between 550 and 900 m above sea level in the low areas, up to 2601 m a.s.l. at Pelister, on Mount Baba, the highest peak in the region. Kruševo and the area around the city are at an altitude of 1,200 m.

The climate in the region is a modified continental or moderate continental one, with hot and dry summers, and cold and wet winters in some micro-regions and a Mediterranean climate elsewhere. The annual amount of precipitation ranges from 570 mm in the region of Prilep to 915 mm per year in the district of Kruševo. The temperature range is large and large temperature fluctuations are persistent throughout the year. Maximum summer temperature reach 40 °C, and the minimum winter temperatures drop to -30 °C, while the average annual temperature is slightly above +10 °C. These climatic conditions are typical for aridic and semi-aridic areas (LAZAREVSKI, 1993).

The region is the most important agricultural region in the country as it produces 50% of the total tobacco produc-



Figre 1: Study area.

tion in Macedonia and 30% of the wheat production. Other important agricultural products grown in this region include vegetables, corn, sugar beet, grapes and oilseed crops such as sunflower. In this context it should be emphasized that there is a relatively well developed livestock industry. Most of the industries are located in major cities such as Bitola and Prilep. This sector is in development, with a particular rise in industries centred around architectural building stone, food, alcoholic and non-alcoholic beverages, processing, and printing. In addition, the thermoelectric-power plant near Bitola produces about 70% of the total electricity production in Macedonia. This power plant constantly creates large amounts of waste in the form of ash and slag, explained by the fact that in one year the Mining and Energy Combine (CEM) "Bitola" consumes 6.5 million tons of lignite. Lignite is low quality: it contains relatively few calories and produces much ash: from 13.4 to 16.3% (TRAJKOVSKA & VRENCOVSKI, 2001). The fly ash and slag are present and include heavy metals: Mn, Cr, Ni and Pb (BILJANOVSKA et.al., 1996).

3. GEOLOGIC DESCRIPTION

The Pelagonia valley, according to the geology, belongs to two tectonic units: the Pelagonian Massif and the West Macedonian Zone, each of which is characterized by its tectonic history. Tectonic processes at different stages exhibited different intensities, which is the main feature of each tectonic unit. In the western part of Macedonia, the Dinarides (Helenites) were defined on these principles (ARSOVSKI, 1997). Within the Dinarides, the following separate tectonic zones are defined from W-E: the Vardar Zone, Pelagonian horst-anticlinorium, Western- Macedonian (Šara-Pelister) Zone and Cukali-Crasta Zone (see Fig. 2 for the geology).

Pelagonia massif or Pelagonian horst-anticline. The Pelagonia horst–anticline represents a relict of the Precambrian and Prebaikal earth's crust in this part of Helenite-Dinarides. Pelagonia as a horst, is characterized by separation from the neighboring tectonic units on all sides by regional faults and depth. The geological structure of the Pelagonian massif is divided into two parts: north and south. The ridge line Pletvar-Sivec-Debrešte is a natural border between the northern and southern parts of Pelagonia, well expressed at the contact between the marble and gneisses in the area of Pletvar and the marble and micashists in the area of Sivec. Towards the west it is covered with Neogene Quaternary sediments. In the southern part of Pelagonia, the Prilep granite massif includes highly metamorphic rocks, gneiss, micashists, marble etc. A large amount of magmatic rocks are represented with granites (ARSOVSKI, 1997). A series of marbles is very well preserved and expressed. The lower horizon is dominated by dolomite and dolomitic marble but the upper layer is represented by calcite marble (BOEV, 2006). The coal layers are well developed in the eastern part of the gravel, and thin in the west and north (ANDREEVSKI, 1990). The upper unit, consisting of diatomite, siltstone, and claystone, has been well studied in the southern part of the graben from outcrops and in the Suvodol coal mine. In the Bitola area, there is a 70 m continuous section (DUMURDZANOV, 1997). During the Neogene, Pliocene lake sediments accumulated, represented by sandy, marled and carbonized clays, marls and fine grained sandstone with the total thickness exceeding 100 m (STOJANOVIĆ, 1989). Granitoid rocks and their core differentials represent an important part of the Pelagonia horst-anticlinorium in the south (GAPKOVKI & JOVANOVSKI, 2007). Prilep granodiorite-adamelite is a massive, light gray, coarse, felsic rock (STOJANOV, 1974). Quaternary sediments are present over the entire Pelagonian graben. They consist of alluvial and proluvial sediments (DUMURDZANOV et al., 2004). The Pelagonian formation consists of ~600 m of terrigenous coal-bearing strata that can be divided into three superposed lithological units. The basal unit consists of gravel, sandstone and silty claystone. The middle coal-bearing unit consists of interbedded siltstone, silty claystone and a few coal-bearing layers. The coal layers are well developed in the eastern part but much less at the west and north (ANDREEVSKI, 1990). The upper unit consisting of diatomite, siltstone, and claystone (DUMURDZANOV, 1997).

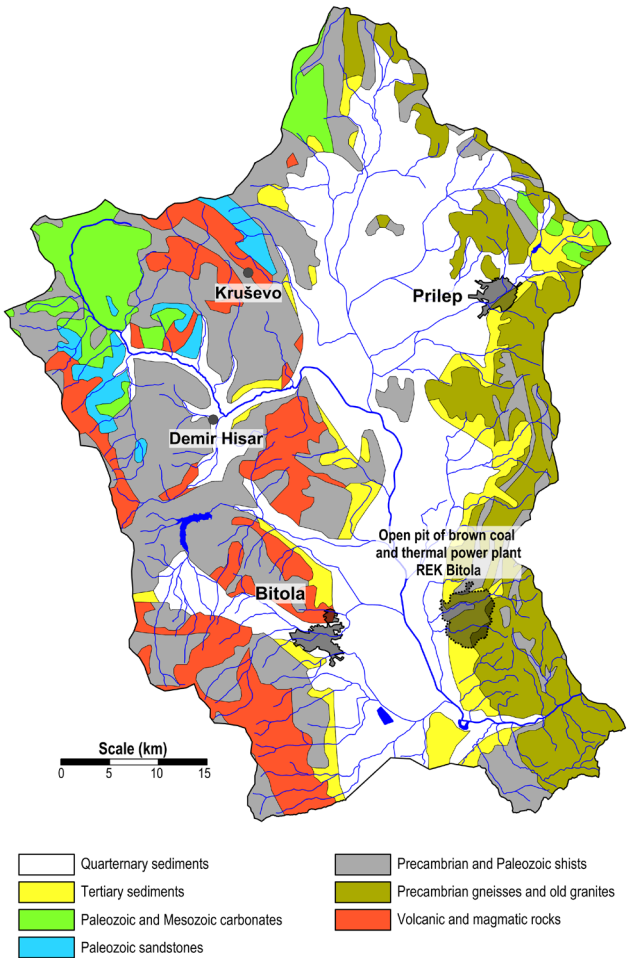


Figure 2: Geological map of Pelagonia Valley.

The West-Macedonian Zone was defined by Arsovski (1960). According to the magmatic characteristics, the West-Macedonian zone can be divided into two subzones: an eastern dominated acidic granite magmatic province and a western zone dominated by alkaline and ultra-alkaline rocks (ARSOVSKI, 1997; DUMURDZANOV, 1997). The West–Macedonian zone represents an inner massif in the northeastern part of the Hellenides, mostly built of old Palaeozoic formations, which is intensively dislocated together with the formation of the early Alpine roof. The area of the West-Macedonian zone is divided into five segments (ARSOVSKI, 1990). The West Macedonian zone (ZM) is represented by several lithostratigraphic formations. The oldest vulcanogenic formation is represented by Palaeozoic spilites and keratophyres. Elsewhere there is a series of phyllites and marble. The lower Caledonian complex in the West-Macedonian zone is represented by green schists. On the eastern slopes of Mount Buševa, lower Caledonian formations at the base are represented by quartz-sericite schists, as well as above the green schist formation. Granites are also prevalent in the Caledonian complex (DUMURDZHANOV et. al., 2004).

4. MATERIAL AND METHODS

4.1. Sampling

Samples of natural surface soils in the Pelagonia Valley were collected according to the European guidelines for soil pollution studies (THEOCHAROPOULOS et. al. 2001), and also according to our experience (ŠAJN, 2003, 2005, 2006; STAFILOV et al., 2008a; 2008b). The study area (3100 km^2) is covered by a sampling grid of 5×5 km^2 (Fig. 3). At 131 sampling sites 262 soil samples were collected attwo soil horizons, topsoil (0-5) and subsoil (20-30 cm), respectively. Any possible organic horizon was excluded. One sample represents a composite sample collected at the central sample point itself, and with materials from at least four points within a 10 m radius towards the north, east, south and west. The mass of the composite sample was about 1 kg. At each location where soil samples were collected, location characteristics (geographic coordinates and altitude) were recorded using a global positioning system. Such positioning, i.e. determining of the position of sample locations is necessary in order to construct the distribution of each metal in the study area.

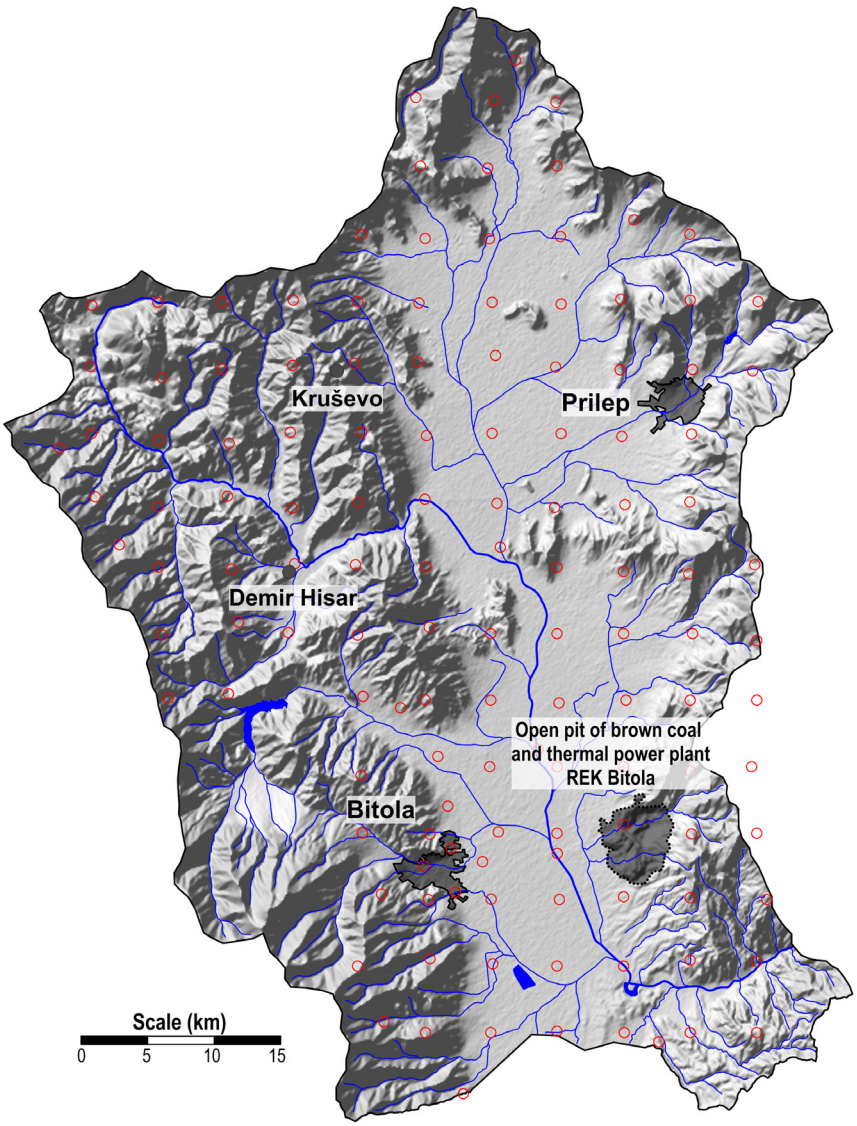


Figure 3: Soil samples locations in Pelagonia Valley.

4.2. Sample preparation

The soil samples were air dried indoors at room temperature for about two weeks. Then they were gently crushed, cleaned of extraneous material and passed through a plastic sieve with 2 mm mesh (SALMINEN et al., 2005). The sifted mass was quartered and milled in an agate mill for an analytical grain size below 0.125 mm.

For the digestion of soil samples, open wet digestion with a mixture of acids was applied. A 0.25 g (+/- 0,0001g) sample was placed in a teflon vessel. 5 ml of concentrated nitric acid (HNO_3) was added, until the brown vapours were released indicating oxidation of organic matter in the samples. For total digestion of the inorganic components, 5–10 ml hydrofluoric acid (HF) was added. When the digestion became a clear solution, 2 ml of $HClO_4$ was added. Perchloric acid was used for total digestion of organic matter. After cooling the vessels for 15 min, 2 ml of HCl and 5 ml of H_2O were added to aid the total dissolution of the metal ions. Finally, the vessels were cooled and the digestions quantitatively transferred to 50 ml calibrated flasks (STAFILOV et al., 2008a; 2010b; BALABANOVA et al., 2011).

4.3. Instrumentation

Analysis of the digested samples was performed using atomic emission spectrometry with inductively coupled plasma (ICP-AES). Optimization of the instrumental conditions for each element was published in BALABANOVA et al., (2010). In total, 17 elements were analyzed from the collected samples: Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn. The Quality Control/Quality Assurance (QA/QC) of the three applied techniques was performed by standard addition method, and it was found that the recovery for the investigated elements ranges from 98.2 % – 100.8 %.

4.4. Data processing

Data analysis and the production of maps were performed on a PC using the Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk. (ver. 2008) and Surfer (ver. 8.09) software. All field observations, analytical data and measurements were introduced into the data matrix. For each observation there are 45 variables: sample identification number, sampling material type, geographic coordinates (X, Y, Z), type of analysis, land use, basic lithological units, level of soil pollution and the determination of the 17 analyzed elements (Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) with the ICP-AES method (n = 262).

Parametric and nonparametric statistical tests were performed on the data (SNEDECOR, 1976; DAVIS, 1986). On the basis of the results of the normality tests and visual inspection of the distribution histograms, logarithms of the element content were used for all elements. The basic statistical data for the 17 selected chemical elements (Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) and the average of elements with regards to the basic lithological units in the topsoil are shown in Tables 1 and 2.

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 factors contain significant information about the original variables, and they may have particular meaning. Factor analysis was performed on variables standardized to zero mean and unit of standard deviation (REIMANN et al., 2002). As a measure of the 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 17 selected elements and the factor scores (F1–F3) in topsoil (0–5 cm) and subsoil (20-30 cm) samples. The basic grid cell size for interpolation was 20×20 m. For class limits the percentile values of the 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.

5. RESULTS AND DISCUSSION

The distributions of elements that reflect natural processes are indicated by elements that are rarely or never included in industrial processes. Their contents usually change gradually across the landscape and depend on the geological background.

Data from the descriptive statistics of measurements for topsoil and subsoil samples from 131 locations (in total 262 soil samples) are presented in Tables 3 and 4. 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 17 elements (Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, Zn). In Tables 1 and 2 the following statistical parameters are given: X – arithmetic average X(BC) – arithmetic average after Box-Cox method, Md - median, min – minimum, max - maximum, P_{10} - 10 percentile, P_{90} - 90 percentile, P_{25} - 25 percentile, P_{75} - 75 percentil, S – standard deviation, Sx – standard error, CV – coefficient of variation, A –skewness; E – kurtosis, BC – Box-Cox transformed values. The Box-Cox transformation has proved their superiority compared to normal values (untransformed data) or logarithmic transformation because the skewness and kurtosis are significantly improved. The criteria of normal distribution that might be used later in multivariate statistical methods are better satisfied by using Boc-Cox transformations.

In order to determine the dependence of the average contents (Box Cox) of the analyzed elements between the topsoil and the subsoil, the ratio of the contents was calculated (Table 3). 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 contribute to the variation of the concentration (DUDKA & ADRIANO, 1997). For almost all elements, non-significant differences were received for their content

Table 1: Descriptive statistics of measurements for topsoil samples (n = 131). Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg/kg.

Element	Material	Unit	X	X (BC)	Md	Min	Max	P_{10}	P_{90}	P_{25}	P_{75}	S	CV	A	E	A (BC)	E (BC)
Al	Topsoil	%	2.1	2.0	1.9	0.46	6.2	0.96	3.3	1.3	2.8	1.1	50.3	1.06	1.46	0.22	–0.25
Ba	Topsoil	mg/kg	560	510	470	72	1700	280	1000	350	680	290	52.8	1.31	1.79	0.31	0.24
Ca	Topsoil	%	1.6	0.76	0.78	0.091	32	0.26	2.0	0.44	1.3	3.6	230.7	6.33	45.05	0.08	0.99
Cr	Topsoil	mg/kg	100	74	74	16	650	33	200	49	120	98	94.7	2.92	10.75	0.01	–0.06
Cu	Topsoil	mg/kg	20	16	17	0.30	120	3.4	37	9.0	29	17	82.8	2.45	10.15	–0.04	0.62
Fe	Topsoil	%	2.7	2.4	2.4	0.79	16	1.3	4.2	1.6	3.4	1.7	61.7	4.33	32.73	0.28	1.07
K	Topsoil	%	1.7	1.7	1.8	0.22	3.1	1.0	2.4	1.3	2.1	0.57	32.8	–0.04	–0.08	–0.06	–0.07
Li	Topsoil	mg/kg	18	16	15	3.7	93	6.8	33	10	23	13	69.1	2.51	10.02	0.35	0.26
Mg	Topsoil	%	0.53	0.50	0.50	0.074	1.6	0.23	0.89	0.32	0.69	0.27	50.8	0.86	0.92	0.10	–0.17
Mn	Topsoil	mg/kg	640	590	580	170	2200	320	1000	440	790	310	48.4	1.80	5.60	0.28	0.73
Na	Topsoil	%	1.3	1.2	1.2	0.056	3.7	0.39	2.1	0.69	1.8	0.71	55.5	0.50	0.18	–0.05	–0.44
Ni	Topsoil	mg/kg	30	27	27	3.2	76	9.1	53	16	42	17	56.8	0.65	–0.10	0.04	–0.62
P	Topsoil	mg/kg	530	430	440	59	3500	190	870	250	670	430	81.1	3.86	22.09	0.06	0.79
Pb	Topsoil	mg/kg	60	19	22	2.5	2300	5.0	55	10	31	240	396.8	7.92	66.16	0.34	0.97
Sr	Topsoil	mg/kg	110	91	95	14	420	38	190	56	140	75	67.9	1.95	4.87	–0.03	0.06
V	Topsoil	mg/kg	80	74	73	17	260	34	130	51	100	42	51.8	1.27	2.88	0.22	0.16
Zn	Topsoil	mg/kg	160	56	53	1.4	4700	13	230	25	120	530	320.9	7.18	55.52	0.33	1.68

n – Number of samples; X – mean; X(BC) – mean of Box-Cox transformed values; Med – median; Min – minimum; Max – maximum; P_{25} – 25th percentile; P_{75} – 75th percentile; S – standard deviation; S_x – standard deviation of transformed values; CV – coefficient of variation, A – skewness; E – kurtosis; BC – Box-Cox transformed values

Table 2: Descriptive statistics of measurements for subsoil samples (n = 131). Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg/kg.

Element	Material	Unit	X	X (BC)	Md	Min	Max	P_{10}	P_{90}	P_{25}	P_{75}	S	CV	A	E	A (BC)	E (BC)
Al	Subsoil	%	2.1	2.0	2.1	0.14	4.9	0.99	3.4	1.3	2.7	0.96	45.8	0.58	–0.03	–0.25	0.13
Ba	Subsoil	mg/kg	570	520	470	15	1500	290	1000	360	740	310	53.2	1.05	0.65	–0.14	1.34
Ca	Subsoil	%	1.3	0.71	0.76	0.067	22	0.26	1.9	0.44	1.2	2.6	200.2	6.31	44.09	–0.22	1.33
Cr	Subsoil	mg/kg	98	73	74	16	540	33	180	49	110	87	89.1	2.96	10.45	–0.03	0.38
Cu	Subsoil	mg/kg	20	16	16	1.3	110	4.6	35	9.0	28	15	76.8	2.33	10.81	0.09	0.26
Fe	Subsoil	%	2.7	2.4	2.5	0.32	15	1.3	4.0	1.8	3.3	1.5	55.2	3.99	30.11	–0.26	2.25
K	Subsoil	%	1.8	1.8	1.8	0.041	3.4	1.1	2.5	1.4	2.1	0.56	31.5	0.07	0.18	0.04	0.20
Li	Subsoil	mg/kg	19	16	16	0.66	94	8.2	33	11	23	13	68.0	2.57	10.39	–0.26	2.54
Mg	Subsoil	%	0.53	0.49	0.49	0.049	1.4	0.22	0.84	0.33	0.67	0.26	50.1	0.84	1.10	–0.10	0.26
Mn	Subsoil	mg/kg	630	580	570	54	2000	340	1000	460	740	290	45.6	1.52	3.88	–0.19	2.23
Na	Subsoil	%	1.3	1.2	1.3	0.007	3.7	0.37	2.2	0.73	1.7	0.70	54.6	0.44	0.24	–0.16	–0.28
Ni	Subsoil	mg/kg	31	28	29	0.094	93	10	54	17	43	18	57.9	0.76	0.66	–0.12	–0.03
P	Subsoil	mg/kg	500	400	430	46	3500	170	870	250	630	420	82.9	3.90	23.53	–0.03	0.78
Pb	Subsoil	mg/kg	29	19	24	2.5	210	5.0	49	12	34	28	99.3	3.48	17.16	–0.54	–0.30
Sr	Subsoil	mg/kg	110	90	93	15	370	43	170	62	130	71	65.6	1.87	3.91	0.03	0.26
V	Subsoil	mg/kg	81	75	75	3.4	260	41	130	54	99	38	47.0	1.26	3.72	–0.15	1.42
Zn	Subsoil	mg/kg	92	51	55	0.87	780	12	200	26	110	120	134.4	3.66	16.55	–0.46	0.89

n – Number of samples; X – mean; X(BC) – mean of Box-Cox transformed values; Med – median; Min – minimum; Max – maximum; P_{25} – 25th percentile; P_{75} – 75th percentile; S – standard deviation; S_x – standard deviation of transformed values; CV – coefficient of variation, A – skewness; E – kurtosis; BC – Box-Cox transformed values

in the topsoil versus subsoil. Thus, this relationship varies from 0.97 for Ni to 1.10 for Zn which shows the absence of the significant influence of possible soil pollution from anthropogenic activities. This is also confirmed by great similarity in the spatial distribution of the investigated elements in the topsoil and subsoil samples.

Table 3: Average of the elements contents in topsoil and subsoil and their ratio. Box-Cox transformed values used.

Element	Unit	Topsoil	Subsoil	Topsoil/Subsoil
Al	%	2.0	2.0	1.00
Ba	mg/kg	510	520	0.98
Ca	%	0.76	0.71	1.07
Cr	mg/kg	74	73	1.01
Cu	mg/kg	16	16	1.01
Fe	%	2.4	2.4	0.98
K	%	1.7	1.8	0.98
Li	mg/kg	16	16	0.98
Mg	%	0.50	0.49	1.01
Mn	mg/kg	590	580	1.01
Na	%	1.2	1.2	1.00
Ni	mg/kg	27	28	0.97
P	mg/kg	430	400	1.07
Pb	mg/kg	19	19	1.00
Sr	mg/kg	91	90	1.01
V	mg/kg	74	75	0.98
Zn	mg/kg	56	51	1.10

The order of the distribution of the concentration data of major elements Al, Ca, Fe, K, Mg, Na, Ti are in the following ranges: 0.14–6.2% Al; 0.07–32% Ca; 0.32–16% Fe; 0.04–3.4 K; 0.05–1.6% Mg and 0.01–3.7% Na. The contents of major elements are most frequently a result of the dominant geological formations of the area: Quaternary sediments, Precambrian and Palaeozoic schists and gneisses, volcanic rocks and Palaeozoic and Mesozoic carbonates. A comparative analysis (Table 4) 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 they are a more stable parameter. The Al and Na contents are 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 any significant variations. The distribution of the remaining chemical elements characteristically corresponds 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 lead, which is two times greater in the topsoil and 1.5 times larger in subsoil samples than the European values. The values of the medians of the investigated elements in soil from the Pelagonia region were found to be similar to those of soil samples collected from the whole of the territory of Macedonia (MIHAJLOV et al., 2013; MIHAJLOV, 2014), Table 4. There are slightly higher contents of Cr, K, Na and Sr in the Pelagonian soils than those for Macedonian soil and lower content for Mg, Mn and Ni which is a result of the variation in the geology in some parts of Macedonia (JOVANOVSKI et al., 2012).

Table 4: Comparison of the median values for top- and subsoil samples in Pelagonia Valley, Macedonian and European values (in mg/kg).

Element	Pelagonia, 2014 (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	19000	4600-62000	21000	1400- 49000	5800	2000-14000	6200	1100-14000	22000	7900-43000	23000	7700-51000
Ba	470	72-1700	470	15-1500	380	30-1900	390	13-2100	420	41-1600	440	66-1700
Ca	7800	910-320000	7600	670-22000	6600	190-340000	8100	170-370000	7900	920-210000	7800	1000-210000
Cr	74	16-650	74	16-540	60	<3.0-6200	62	<3.0-2100	54	11-600	63	11-600
Cu	17	0.30-120	16	1.3-110	13	0.81-260	14	0.86-130	16	1.7-73	16	3.2-78
Fe	24000	7900-160000	25000	3200-150000	25000	1100–150000	26000	770-110000	25000	6300-67000	27000	7700-80000
K	18000	2200-31000	18000	410-34000	16000	220–51000	17000	<83-50000	14000	2600-32000	15000	5200-33000
Mg	5000	740-16000	4900	490-14000	4700	<61–150000	6000	<61-110000	6600	1100-29000	7300	1500-31000
Mn	580	170-2200	570	54-2000	510	31-61000	470	23-4700	620	160-3200	640	99-4300
Na	12000	560-37000	13000	70-37000	6000	300-33000	6500	230-36000	8500	330-23000	9400	780-24000
Ni	27	3.2-76	29	0.094-93	18	<2.0-2700	22	<2.0-2400	35	2.5-530	37	5.2-530
P	440	59-3500	430	46-3500	960	83-9900	720	53-12000	450	120-1400	430	74-1300
Pb	22	2.5-2300	24	2.5-210	10	5.3-970	17	<3.0-940	17	2.5-700	14	0.80-660
Sr	95	14-420	93	15-370	89	8.0-3100	95	6.0-2000	71	9.4-540	68	9.9-580
V	73	17-260	75	3.4-260	60	2.7-540	63	1.3-330	67	14-300	71	19-370
Zn	53	1.4-4700	55	0.87-780	52	<3-2900	47	<3-3100	39	3.1-440	38	4.4-490

Table 5: Matrix of correlation coefficients (n = 262, 17 elements).

	Al	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	Sr	V	Zn
Al	1.00																
Ba	–0.24	1.00															
Ca	0.22	–0.10	1.00														
Cr	0.29	–0.14	–0.02	1.00													
Cu	0.26	0.07	0.00	0.43	1.00												
Fe	0.35	0.19	–0.02	0.32	0.57	1.00											
K	0.13	–0.20	–0.33	–0.03	–0.13	–0.22	1.00										
Li	0.21	–0.08	–0.12	–0.07	0.20	0.19	0.19	1.00									
Mg	0.66	–0.04	0.09	0.14	0.48	0.43	0.11	0.24	1.00								
Mn	0.47	–0.08	–0.05	0.18	0.51	0.51	0.09	0.28	0.50	1.00							
Na	–0.15	–0.13	–0.21	–0.31	–0.58	–0.53	0.29	–0.25	–0.30	–0.35	1.00						
Ni	0.42	0.15	–0.01	0.34	0.65	0.65	–0.05	0.38	0.61	0.61	–0.64	1.00					
P	0.39	0.18	0.15	0.15	0.40	0.69	0.00	0.16	0.43	0.41	–0.34	0.44	1.00				
Pb	0.01	0.01	–0.01	0.36	0.41	0.08	–0.01	–0.05	–0.03	0.07	–0.09	0.05	0.04	1.00			
Sr	0.44	0.09	0.10	–0.05	–0.18	–0.05	0.04	–0.09	0.39	0.04	0.34	–0.03	0.18	0.02	1.00		
V	0.41	0.18	–0.08	0.33	0.57	0.84	–0.15	0.24	0.58	0.56	–0.52	0.74	0.55	0.07	0.08	1.00	
Zn	0.06	–0.03	0.02	0.45	0.48	0.12	–0.02	–0.06	0.00	0.10	–0.17	0.11	0.06	0.98	–0.02	0.10	1.00

Because of the great number of variables, that is, different chemical elements whose distribution in the area of the Pelagonia Region is monitored, data reduction was performed based on the application of a factor analysis. A matrix of correlation coefficients was produced based on previously standardized and Box-Cox transformed values for the element contents in the samples of topsoil and subsoil (Table 5). In the factor analysis, 131 samples of the topsoil (0–5 cm), 131 samples of the subsoil (20–30 cm) and the analysis of 17 chemical elements were considered. From the R-mode factor analysis, 5 chemical elements (Ba, K, Li and Na) were eliminated from further analysis because they have low proportions of communality or a tendency to form independent factors. The geochemical associations of variables were processed based on the basic matrix of correlation coefficients. Table 6 shows the loadings of values for each individual element on each factor, showing three geochemical associations. The total communality of the factors amounts to 78.3% (Table 6). In the factor extraction, significantly pronounced associations of elements were taken into consideration - only those having an E-value (*Eingene value*) higher than 1 (Kaiser's rule). The E-value, correspondingly for each factor, is presented in Table 6.

Following the results of factor analysis (Table 6) and the trends shown on the geochemical maps, three natural geochemical associations in soil have been defined: **Factor 1** (Al, Fe, Mg, Mn, Ni, P and V), **Factor 2** (Cr, Cu, Pb and Zn) and **Factor 3** (Ca and Sr).

Identical results were achieved as in the case of application of cluster analysis (the graphical representation is shown in Fig. 4). Namely, **Factor 1** (Al, Fe, Mg, Mn, Ni, P and V) correspond to Cluster 1 and Cluster 2. The similarity of only 47% between Cluster 1 and Cluster 2 support the dual origin of the elements of Cluster 2 (Cr, Fe, V and Ni), geogenic and lithogenic origin; the classification of Cluster 3 (Cu, Pb and Zn) is the same of the results of **Factor 2** (Cr, Cu, Pb and Zn), and Cluster 4 is the same as **Factor 3** (Ca and Sr).

Table 6: Matrix of dominant rotated factor loadings (n = 262, 13 selected elements).

Element	F1	F2	F3	Com
Al	0.74	–0.14	0.40	72.5
Fe	0.72	0.56	–0.07	83.4
Mg	0.86	0.01	0.24	79.2
Mn	0.84	–0.03	–0.03	70.3
Ni	0.81	0.39	–0.09	81.5
P	0.83	0.17	0.24	77.5
V	0.82	0.37	–0.10	81.9
Cr	0.50	0.60	–0.07	62.2
Cu	0.43	0.79	–0.08	80.8
Pb	–0.11	0.90	–0.02	82.5
Zn	0.12	0.93	0.00	87.1
Ca	0.00	0.13	0.92	86.5
Sr	0.22	–0.45	0.69	73.0
Eigen Val	6.05	2.87	1.26	
Expl. Var	5.02	3.52	1.64	
Prp. Totl	38.6	27.1	12.6	78.3

F1 … F3 – Factor loadings; Com – Communality (%); Var – Variance (%)

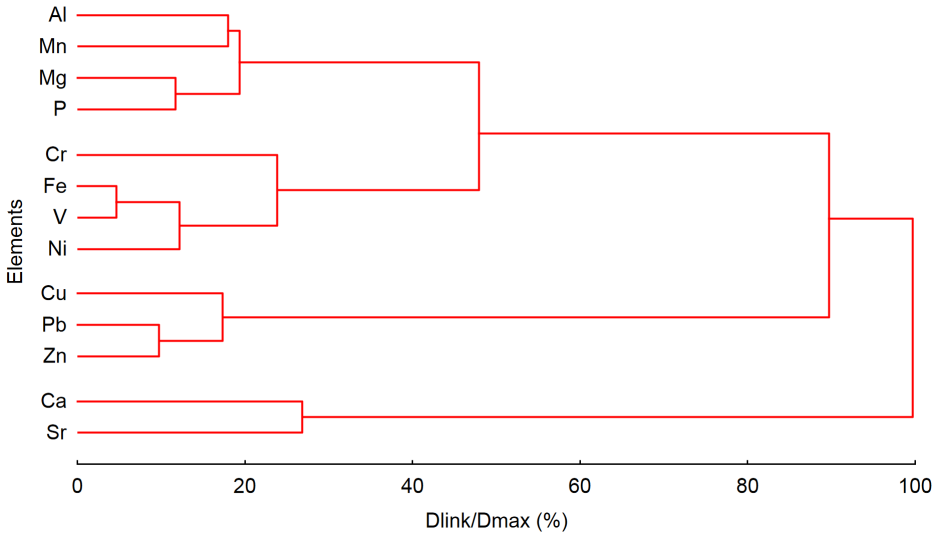


Figure 4: Dendrogram of cluster analysis.

Factor 1 (Al, Fe, Mg, Mn, Ni, P and V) is a lithogenic and geogenic association. The spatial distribution of the elements of this factor is given in Fig. 5, both for top- and subsoil samples. In the Pelagonia Valley the maximum content of these elements are in areas with pertinent bedrock geology (Fig. 3), occupied by the Precambrian and Palaeozoic schists and volcanic and magmatic rocks. In Demir Hisar, these elements are found in a nearby iron mine at the Plakenska Mountain and continue south to Mount Baba (Fig. 5).

The highest iron content occurs in the Demir Hisar area, where there are abundant iron mines (Sopotnica, Žvan). A similar behaviour is shown for nickel where the maximum content is observed in the areas of Precambrian and Palaeozoic schists in the Demir Hisar area. Magnesium is found in the soil on Mount Baba, and originates from the granite formation where dolomite and amphibole minerals prevail. Manganese is mostly distributed in the Precambrian and Palaeozoic schists of the eastern slopes of the Plakenska Mountain, around Cer where it is assumed that there are deposits of manganese. Vanadium is an integral part of the volcanic and magmatic rocks, south of Kruševo to Demir Hisar.

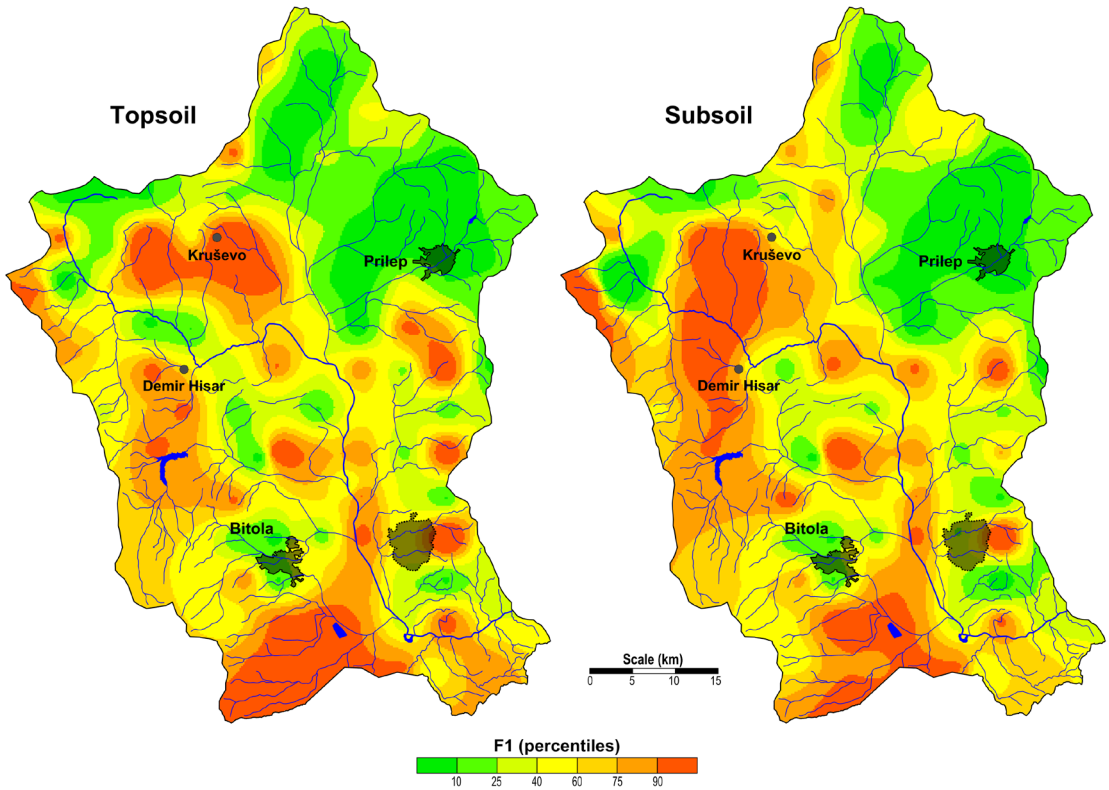


Figure 5: Spatial distribution of factor 1 scores: Al, Fe, Mg, Mn, Ni, P, V in topsoil (left) and subsoil (right).

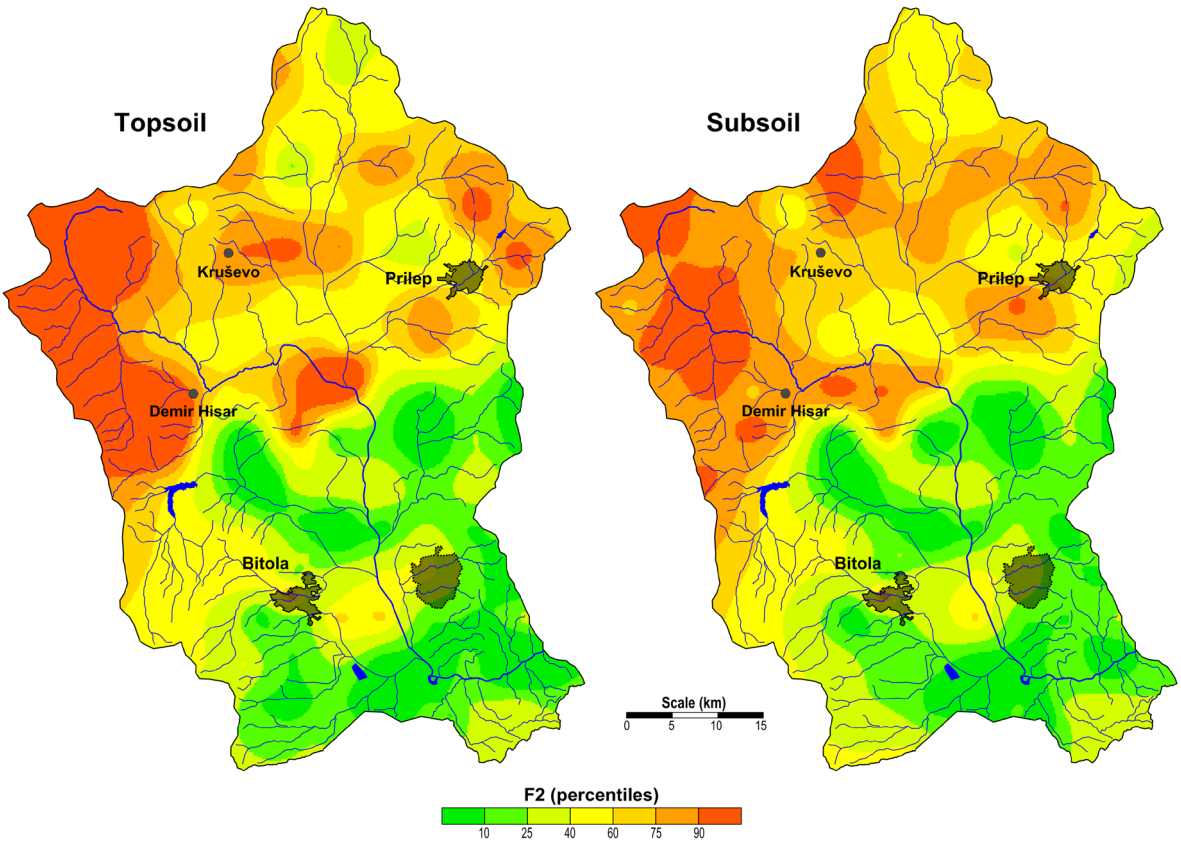


Figure 6: Spatial distribution of factor 2 scores: Cr, Cu, Pb, Zn in topsoil (left) and subsoil (right).

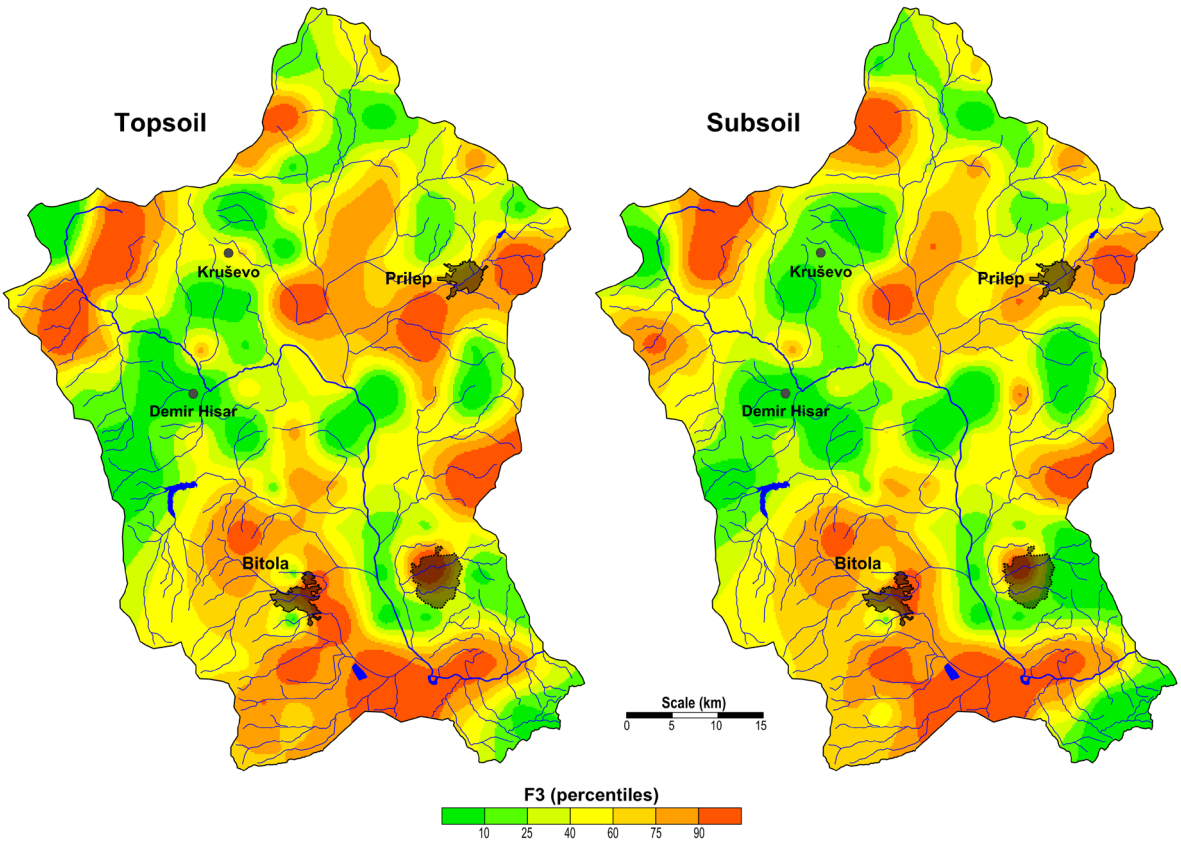


Figure 7: Spatial distribution of factor 3 scores: Ca, Sr in topsoil (left) and subsoil (right).

Factor 2 (Cr, Cu, Pb and Zn) represents the geogenic association and spatial distribution of the factor scores of this factor for top- and subsoil as shown in Fig. 6. The origin of these elements belongs to the Palaeozoic and Mesozoic carbonates and the Precambrian and Palaeozoic schists. The Demir Hisar area, where the highest concentrations of lead are present, is geologically composed of acidic volcanic rocks and Palaeozoic and Precambrian rocks, near the village of Strugovo, and in the Cer Field, which is the only karst field in the study area. The content of zinc is the highest in the area of Palaeozoic granitoids and is always in good correlation with the distribution of lead. Granite associated zinc deposits are found in limestone rocks known as skarn deposits (DAWSON, 1996). Chromium has lithological nature and is associated with alkaline and ultraalkaline rocks. It was found in the karst field of the village of Cer.

Factor 3 (Ca and Sr) is a natural factor that depends on the underlying lithology and the spatial distribution of the factor scores of top- and subsoil are almost identical (Fig. 7). Sources of these elements are mainly natural phenomena such as the erosion of rocks, and soil chemical processes. Higher contents of these elements are located in areas of Quaternary and Tertiary sediments and volcanic and magmatic rocks in Bitola and Demir Hisar, and in the Prilep region in areas of Precambrian gneisses and old granites.

6. CONCLUSION

The aim of this study is the systematic investigation of the spatial distribution of various chemical elements in surface soil over the Pelagonia region, Republic of Macedonia. In total 262 soil samples (from 131 locations) were collected and analyzed for 17 major and trace elements. Factor analysis with multivariance R-method was applied in order to show the associations of chemical elements and three factors were obtained: Factor 1 (Al, Ba, Mg, Mn, Fe, Ni, P and V), Factor 2 (Cr, Cu, Pb and Zn) and Factor 3 (Ca and Sr). 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 factor has not confirmed the correlation to anthropogenic influence, especially with REK Bitola. This also happened with soil sampling around REK Oslomej – Kičevo (STAFILOV, et al., 2014). It seems that the lignite from this area is clean, with only a very small amount of trace elements which are consequently not recorded in the soil. Alternatively, the pollution halos have been determined in moss samples (DIMOVSKA, et al, 2014). It seems that the moss is much better sampling material in determination this type of pollution.

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