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Chapter 5

HEAVY METALS AIR POLLUTION STUDY IN MINES ENVIRONMENTS. CASE STUDY BREGALNICA RIVER BASIN, REPUBLIC OF MACEDONIA

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ABSTRACT

Application of several moss species and attic dust for monitoring of anthropogenic impact on heavy metals air pollution in Bregalnica River Basin, Republic of Macedonia, was studied. Moss samples were reviewed for their potential to reflect heavy metals air pollution. The attention was focused on their quantification ability, underlying the metal accumulation within moss plant tissue and attic dust "historical archiving." Potential "hot spots" were selected in areas of copper mine (Bučim mine) and lead and zinc mines (Zletovo mine and Sasa mine) as main metal pollution sources in the Eastern part of the Republic of Macedonia. Continuously,

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dust distribution from ore and flotation tailings occurs. This results with air-introduction and deposition of higher contents of certain metals. Several moss species (*Hypnum cupressiforme*, *Homalothecium lutescens* and *Scleropodium purum*) were used as plant sampling media. Determination of chemical elements was conducted by using both instrumental techniques: atomic emission spectrometry with inductively coupled plasma (ICP-AES) and mass spectrometry with inductively coupled plasma (ICP-MS). Combination of multivariate techniques (PCA, FA and CA) was applied for data processing and identification of elements association with lithogenic or anthropogenic origin. Spatial distribution maps were constructed for determination and localizing of narrower areas with higher contents of certain anthropogenic elements. In this way influences of selected human activities in local (small scale) air pollution can be determined. Summarized data reveal real quantification of the elements distribution not only in order determination of hazardously elements distribution, but also present complete characterization for elements deposition in mines environs.

Keywords: chemical elements, toxic metals, monitoring, moss, attic dust, air pollution, Bregalnica River Basin, Republic of Macedonia

1. INTRODUCTION

The environmental pollution at hazardously levels for living presents a global problem and a macro-case for monitoring. Some sub-disciplines were occurred with time in order to consider the realistic environmental conditions. Arguably, the understanding of atmospheric pollution is one of the most emergent areas of the environmental science (Fernández, 2015). Atmospheric pollution represents solutions or suspensions of minute amounts of harmful compounds in the air (Wang et al., 2009). The degree and the extent of environmental changes over the last decades has given a new urgency and relevance for detection and understanding of environmental changes, due to human activities, which have altered global biogeochemical cycling of heavy metals and other pollutants (Athar and Vohora, 1995; VanLoon and Duffy, 2000; Akimoto, 2003). Monitoring toxic air pollutants is needed for understanding their spatial and temporal distribution and ultimately to minimize their harmful effects. In addition, to direct physical and chemical methods of air pollution monitoring, *bioindication* has also been used to evaluate air pollution risk (Rühling and Tyler, 1971, 1973; Kanaroglou et al., 2005; Valero, 2008; Aboal et al., 2010).

Mosses have been frequently used to monitor time-integrated bulk deposition of metals as a combination of wet, cloud, and dry deposition, thus eliminating some of the complications of precipitation analysis due to the heterogeneity of precipitation (Coşkun et al., 2005; Tyler, 2008). Ectohydric mosses in particular draw negligible amounts of water and minerals from the soil, and almost entirely depend on the atmospheric inputs of nutrients (Ruhling and Tyler, 1971). Because mosses have a high cation exchange capacity (CEC), they act as hyper-accumulators of metals and metal complexes. The metals are bound to the tissue with minimal translocation within the plant due to a lack of vascular tissue (Aceto et al., 2003). This results in biological tissue that can be analyzed to reveal time-integrated deposition (Van het Bolcher et al., 2006). Additional advantages of using mosses as heavy metal biomonitors include their stationary nature, widespread geographical distribution, and low genetic variability between populations. It has been shown that there is some experimental error due to heterogeneity in morphological characteristics and microenvironments among different populations (Sokhi, 2011; Manara, 2012). There is also an incomplete understanding of the degree of mineral uptake by ectohydric mosses in direct contact with substrate (Marschner, 1995, Market, 2007). Despite the accuracy and precision of precipitation analysis techniques, however, mosses offer an efficient, low-cost complement for determining metal concentrations at a large number of locations and offer analyses of biologically relevant fluxes at multiple scales.

Harmens and his European colleagues have found that mosses are reliable indicators of air pollution risks to ecosystems; because they get most of their nutrients direct from the air and rain, rather than the soil. Since 2000, the European moss survey has been conducted by a special international program (ICP Vegetation). Moss data provides a better geographical coverage than measured deposition data and reveals more about actual atmospheric pollution at a local level (http://icpvegetation.ceh.ac.uk/). Latest data reported from Harmens et al., (2015) and Barandovski et al., (2013) indicates on the significant enrichments of some toxic elements.

An alternative approach is to use exposed attic dust, because over long periods of time atmospheric particles can accumulate, providing a record of historical local deposition (Alijagič and Šajn, 2001, 2006; Cizdziel et al., 2000; Ilacqua et al., 2003, Jeffrey et al., 2005; Gosar et al., 2006; Jemec Auflič and Šajn, 2007; Žibret, 2012; Žibret and Šajn, 2008a, 2008b, 2010; Šajn, 1999, 2000, 2001, 2002, 2003, 2005, 2006; Šajn et al., 2012). The determination of historical emissions is based on the data of heavy metals concentration in the

attic dust from different measurement sites of the weight of total monthly air deposit. The main idea behind determining past emissions is that heavy metals characterization of deposited dust on a small area is multiplied by the concentration of the elements in that area, the mass of the polluter which has been transported to the place of interest by air can be determinate. Undisturbed attic dusts are potential archive for atmospherically deposited particles and have been shown to be effective across urban areas and in the vicinity of smelters, mines and other potentially emission sources. These have the additional benefit that they are protected from wash and aqueous alteration that may affect other tips of samples (monitors) over long periods of time. Atmospheric emissions attributed to the extraction stage of mining come mainly from the action of wind on disturbed land and stockpiles of ore and waste material. As a result of these processes in the atmosphere permanently introduces dust (Sengupta 1993, Ilacqua et al., 2003). Continuous monitoring of the content of heavy metals and other toxic components contained in dust is possible thought implementation of monitoring by using samples of dust from attic beams (Ilacqua et al., 2003, Atriola et al., 2004). Attic dust is derived primary from external sources through aerosol deposition and as a result of soil dusting, and less than household activities (Žibret, 2012; Žibret and Šajn, 2008a, 2008b, 2010; Šajn, 1999, 2000, 2001, 2002, 2003, 2005, 2006; Šajn et al., 2012). Usefulness of attic dust as a suitable long-term monitor for determination the status and content in air is proven by numerous studies (Alijagič and Šajn, 2001, 2006; Cizdziel et al., 2000; Ilacqua et al., 2003, Jeffrey et al., 2005; Gosar et al., 2006; Jemec Auflič and Šajn, 2007; Žibret, 2012; Žibret and Šajn, 2008a, 2008b, 2010; Šajn, 1999, 2000, 2001, 2002, 2003, 2005, 2006; Šajn et al., 2012).

Attic dust is commonly used as monitor for this process. These kind of monitoring programs have been performed as part of a large number of analytical studies for a longtime, but their application in recent decades has taken as wing. This is due to the fact that monitoring does not require the use of expensive technical equipment. Analytical results reflect the situation for a long period of time. The monitoring allows analysis of large areas and the types of monitors are chosen according to the analyst and the type of analysis.

Monitoring of air pollution has proved as a most useful technique for determining deposition of heavy metals and atmospheric pollution with it's in different geographical areas. The Republic of Macedonia does not deviate from the global framework of air pollution with heavy metals. The results obtained from previous studies on air pollution, suggest that the situation in the Republic of Macedonia is not favorable in terms of air pollution with

heavy metals. The main emission sources appear to be power plants, mines, as well as flotation for lead, zinc and copper and metallurgical plants for the production of nickel, steel, lead, zinc and different ferroalloys (Barandovski et al., 2008; 2010, 2015; Stafilov et al., 2003, 2008a, 2008b, 2010, 2011, 2014).

Regarding the dominance of volcanic geological units and Pb-Zn mineral deposits, the region of Bregalnica river basin in the Republic of Macedonia, is a specific region to monitor the atmospheric distribution of various chemical elements (Stafilov et al., 2014; Balabanova et al., 2010, 2011, 2012; Bačeva et al., 2012; Barandovski et al., 2013, 2015). This region is characterized with several significant pollution sources of potentially toxic metals and other chemical elements in the environment: the copper mine and flotation "Bučim" near the town of Radoviš, the lead and zinc mines "Sasa" near the town of Makedonska Kamenica and "Zletovo" near the town of Probištip (Stafilov et al., 2014). The excavation of the copper minerals is carried out from an open ore pit, while in the lead-zinc mines the exploitation is underground, and the ore tailings are stored outdoors. The ore produced in the mines is processed in the flotation plants, and in the process of flotation of the relevant minerals, flotation tailings are separated and disposed on a dump site in the open.

Multivariate assessment and spatial hunting of dominant elements associations was conducted in the Bregalnica river basin and presents first attempt in this very lithologicaly unique area. The appearance of dominant Oligocene volcanism in the area of "Sasa" mine (Pb-Zn hydrothermal exploitation), Kratovo-Zletovo district and "Bučim" mine area (Cu-Au hydrothermal exploitation), it creates specific environmental conditions leading to natural and anthropogenic poly-metallic enrichments. Therefore, the main objective of this study was to assess the lithologenic and anthropogenic distribution of total of 69 elements along the Bregalnica river basin. Multivariate statistical approach was used for hunting the dominant geochemical associations. Moss species and attic dust samples were used for recording the lithological and anthropological impact on atmospheric deposition of potentially toxic and nontoxic elements. The dominant lithogenic and anthropogenic markers were extracted. The spatial distribution patterns of each geochemical marker were also generated.

2. INVESTIGATING AREA

2.1. Geographic Characterization of the Investigated Area

The investigated area includes the basin of the Bregalnica river which is found in the area of the east planning region of the Republic of Macedonia. The investigated area covers ~200 km (W-E) x 200 km (S-N), that is, a total of ~4000 km^2, within the following geographic coordinates N: 41°27'-42°09' and E: 22°55'-23°01' (Figure 1). The region of the investigated area is geographically composed of several sub-regions. The area is characterized by two valleys – Maleshevska and Kočani valley. The Maleshevska valley represents the upper course of the Bregalnica river where the river source is also located, with average altitude of 700-1140 m. The valley is enclosed by the Maleshevski mountains on the east, by the Ograzhden mountain on south-southeast, and Plachkovica and Obozna on the west. The Malesevska valley is a specific geographical area, characterized by mountain, hilly, sloping and plain parts. The Kochanska valley includes the middle course of the Bregalnica river, between the mountains Plachkovica to the south and Osogovo to the north. The Maleshevski mountains are found to the east in relation to the valley, which is divided from them by the medium high mountains, Golak and Obozna. Morphologically, the valley is diverse, covering plain, hilly and mountain areas. The Kočani valley spreads on both sides of the Bregalnica river. The valley bottom that is, its plainest part occupies an area of 115 km^2 and represents an important agricultural cultivated fertile area. The lowest point above sea level in the area is located at the spot where the Zletovska river flows into the Bregalnica river (290 m).

The Bregalnica river is the central hydrographic factor in the eastern region of the R. Macedonia. The river's total length is 225 km, and the area of its basin amounts to 742 km^2. The more important tributaries are: from the right side – Zletovska, Kochanska and Orizarska river, and from the left side – Osojnica and Zrnovska river.

The source of the Bregalnica river is located in the forest area of the Maleshevski mountains near the Bulgarian border, east of Berovo, under the Chengino Kale peak, at altitude of about 1690 m. In its upper part it is characterized by a narrow canyon, the sides of which reach up to 360 m height above the river bed. The first erosive enlargement in this direction is the Ablanica area, at about 2 km from the town of Berovo, which is actually a spacious terrace positioned at about 2 m height from the water. The length of this enlargement is about 2 km, and the width 500-700 m. This whole area is

intensively cultivated with cultures for the irrigation of which the water from the Bregalnica river is used. With the exception of this erosive enlargement, the narrow rocky part continues up to Berovo, with the river banks being stable and forested. Up to the village of Budinarci, the Bregalnica flows through the Berovo field. Because of the mild slope of the river bank, at this point the river flows rather slowly, enabling accumulation of gravel and sand, deposited in the river bed and around it. Here is also present the terrace of two to three meters, in which the river bed is positioned. From Budinarci all the way up to the point before the Delchevo field, the river bed is characterized with three rocky parts, among which there are two erosive enlargements. Starting right after Budinarci, and all the way to the village of Mitrashinci, the course of the Bregalnica river becomes curved, as a result of which at certain points real meanders and narrow rocky ravines are formed, the sides of which at certain points are vertical and with relative height of 60 to 80 m.

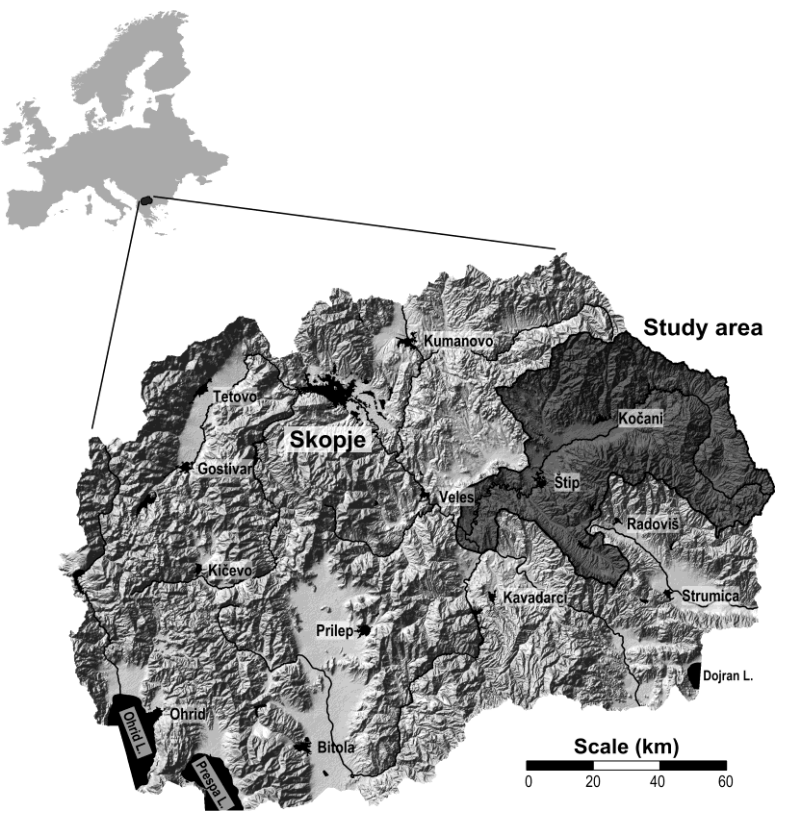

Figure 1. The investigated area on the territory of the Republic of Macedonia.

The second rocky part follows in the course of the river and spreads up to the village of Razlovci. It is also characterized by a narrow river bed, 10-20 m with curved watercourse and precipitous sides. The erosive enlargement at Razlovci, through which the Bregalnica flows, is about 5 km long and about 500 m with before the village, and after it about 800 m. The river does not have a single bed here, but the water is spread on the whole width, forming pools at certain points. Taking into account that along the river course a small and rather interesting canyon is formed, there are morphological and geological conditions for building of a dam that would enable accumulation in the Razlovci field. Entering into the Delchevo field, before the village of Trabotivishte, the Bregalnica river deposits huge quantities of material along the whole field, up to the mouth of the Ochepalska river, that is, to the entrance into the canyon along the river course. This deposit is mainly composed of bulky and fine gravel. At this point the course of the Bregalnica river is still small and does not have a single river bed, but instead several inlets are formed. In the Delchevo field the river waters are also extensively used for irrigation based on primitive dams and ditches, as for example, the ones near Trabotivishte and Delchevo. The water is almost completely used for irrigation of the cultivated low terrace (2 to 3 m) on the right river side (Mitrev et al., 2010).

From the mouth of the Ochipalska river, and all the way along the river course, there is a long and picturesque canyon that spreads up to the village of Istibanja, that is, to the entrance into the Kočani valley, about 35 km long. The canyon is poorly forested and hardly passable (today it is cut by a modern asphalt road), as its sides and banks are very steep, almost canyonlike, so that the valley is completely narrowed. Erosive enlargements are found only at the mouths of the larger rivers.

The Bregalnica flows into the Vardar river at Gradsko, at altitude of 137 m. Along the river course of the Bregalnica river two hydro accumulations were built: Ratevo (near Berovo) and Kalimanci (near Makedonska Kamenica), 80 m deep, 14 km long, 0,3 km wide, which accumulates 127 million m^3 water.

Taking into consideration the diverse morphological-geographical structure of the investigated area, the climate conditions also vary in the different sub-regions. Generally, the region is characterized with moderate continental climate. The altitude varies between 290 m in the plain of the Kočani valley up to 1932 m (Kadaica) on the Maleshevski mountains. The average annual temperature also varies in the different sub-regions. In the Kočani valley the average annual temperature is about 13°C, the warmest

months in the year are July and August with average temperature of 25°C, and the coldest month is January with average temperature of about 1.2°C (Mitrev et al., 2010). In the region of Shtip, the average annual temperature is about 12.9°C, with high frequency of winds (out of 365 days in the year, there are air movements on 270 days). The Berovo valley can be singled out as the coldest region, which is under direct influence of the local mountain climate with an average annual temperature of 10°C (Environment statistics, 2013). Most common are the winds from western direction with frequency of 199‰ and speed of 2.7 m s^{-1} and the winds from eastern direction with frequency of 124 ‰ and speed 2.0 m s^{-1}.

The average annual precipitation amounts to about 500 mm with significant variations from year to year, as well as in the different sub-regions (Lazerevski, 1993). The precipitation is mostly related to and conditioned by the Mediterranean cyclones (Lazarevski, 1993). During the summer period, the region is most often found in the centre of the subtropical anticyclone, which causes warm and dry summers. From the central area of the region, as the driest area, the average annual precipitation increases in all directions, because of the increase either in the influence of the Mediterranean climate or the increase in altitude (Environment statistics, 2013).

The precipitation information refers to the annual average precipitation as measured by the meteorology stations in mm, information taken from the Hydrometeorological Administration. As regards the annual total number of sunny hours, there are about 6.0 hours annually in this area. In the region are distinguished about ten climatic-vegetation soil areas with considerably heterogeneous climate, soil and vegetation characteristics (Lazarevski, 1993).

Regarding the demographic structure in the region of the Bregalnica basin, only 4% of the populated areas belong to the category of urban areas, while 96% of the total populated areas are categorized as rural areas. In accordance with the data processed by the State Statistical Office (2013), the population density in the eastern region of R. Macedonia is <51 inhabitant on km^2. In accordance with the processed data, provided by Mitrev et al., (2010), in this region there is unequal distribution of urban and rural population. Considering land use, the region is considerably diverse. Along the whole course of the Bregalnica river dominate agricultural cultivated lands. Pastures are also considered as agricultural lands, and are represented in Figure 2, as open areas. About 30% belong to the forest regions, localized around the Maleshevska valley, represented by the Maleshevski Mountains, then around the Kočani valley, represented on one side by the Osogovo Mountains, and by Plackovica on the other side.

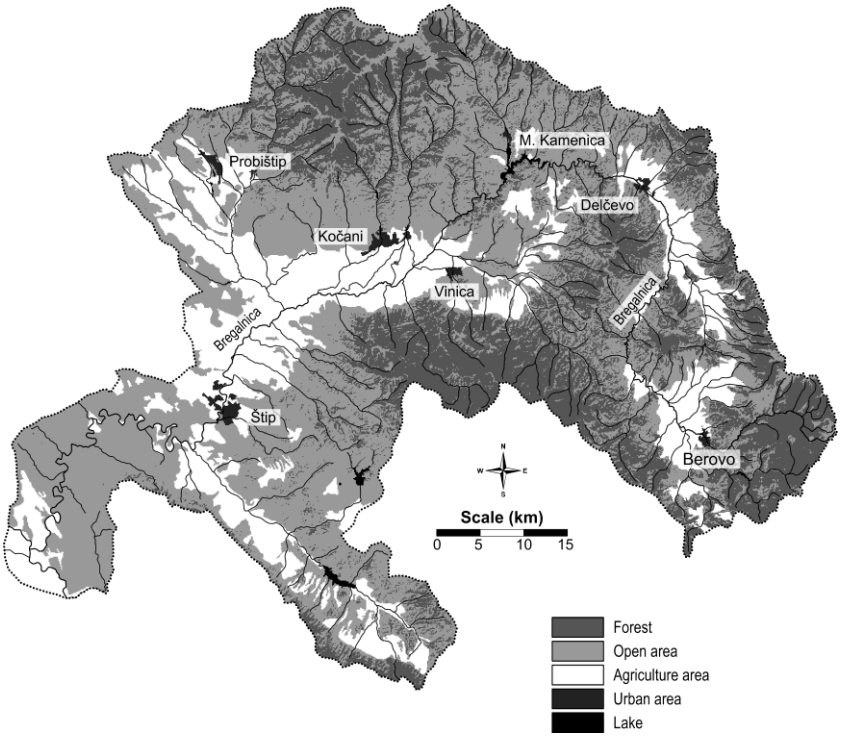

Figure 2. The region of the investigated area including the type of land use.

The hydrographic conditions show influence on the formation, characteristics and geography of soils through: surface flows, floods and irrigation. As a consequence of industrialization, urbanization and lack of treatment of wastewaters from the industry, mines and the city sewerage, the waters of this important hydrographic factor are exposed to a high level of pollution, from the aspect of introduction of higher contents of certain toxic metals. The pollution is most frequently particularly high at low river flows, as in the case of the Bregalnica river in its course through the Kočani valley.

2.2. Generalized Geology of the Investigated Area

The investigated area that covers the basin of the Bregalnica river lies on the two main tectonic units - the Serbian-Macedonian massive and the Vardar zone (Dumurdzanov et al., 2004). The polyphasal Neogene deformations through the insignificant movements associated with the volcanic activities

had direct influence on the gradual formation of the reefs and the formation of deposits in the existing basins. From the middle Miocene to the end of the Pleistocene there were alternating periods of fast and slow landslide accompanied with variable sedimentation (deposition).

The Cenozoic volcanism represents a more recent extension in the Serbian-Macedonian massive and the Vardar zone. The oldest volcanic rocks occur in the areas of Bučim, Damjan, the Borov Dol district and in the zone of Toranica, Sasa, Delchevo and Pehchevo (Dumurdzanov et al., 2004). These older volcanic rocks were formed in the mid Miocene from sedimentary rocks that represent the upper age limit of the rocks. The origin of these oldest volcanic rocks is related to the Oligocene – the early Miocene period.

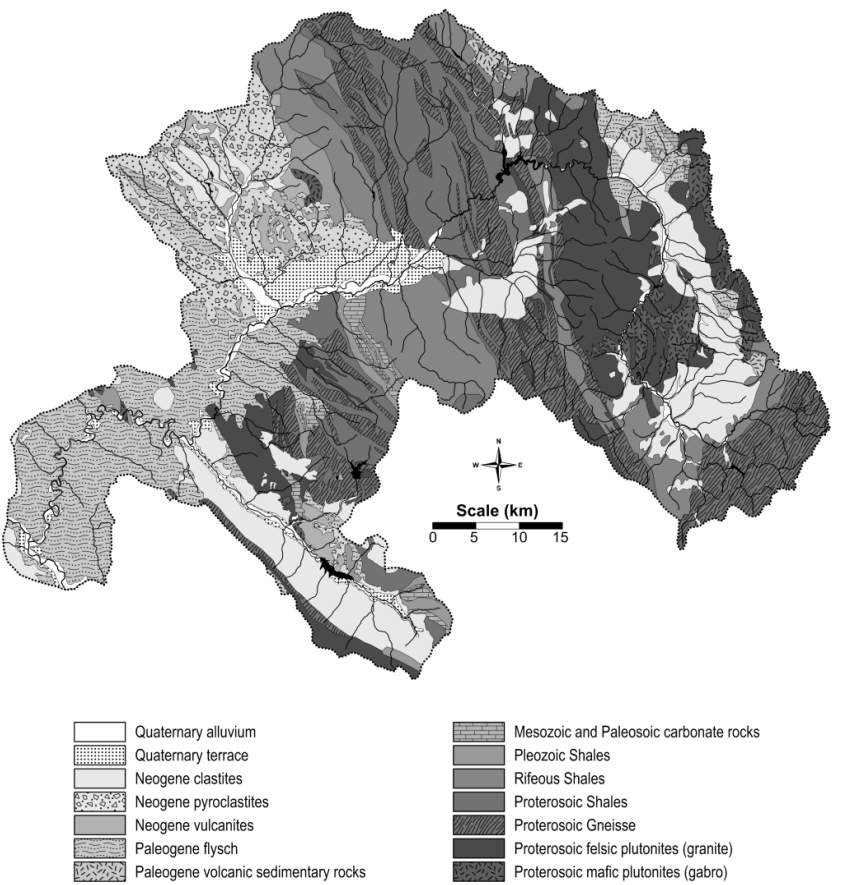

Figure 3. Generalized geology of the investigated area.

As volcanic rocks are categorized the following: andesite, latite, quartz-latite, dacite. Volcanism appears sequentially and in several phases forming sub-volcanic areas. On the other hand, the pyroclastites are most frequently found in the Kratovo-Zletovo volcanic area, where the dacites and andesites are the oldest formations. Generalized geology of the area is produced based on the data provided by Rakićević et al., (1968) and presented in Figure 3.

3. MATERIALS AND METHODS

3.1. Dataset Building Sampling Strategy and Analytical Methods

The monitoring activities implemented included determining of the contents of a total of 69 elements: Ag, As, Al, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Ti, Th, Tl, Tm, V, W, Y, Yb, Zn и Zr. The content of these elements was determined in moss samples and attic dust samples.

For each location where from samples were taken the location characteristics were recorded (geographic coordinates and altitude) using a global positioning system. This positioning, that is, specifying the position of the locations where from samples for investigation were taken, is required for the construction of maps for the distribution and deposition of the analyzed elements in the investigated area.

3.1.1. Moss Samples

The carpet-forming moss species *Pleurozium schreberi* and *Hylocomium splendens* are usually preferred for moss trace elements deposition monitoring (Fernández et al., 2015). But these species are commonly found only in some parts of the country at an elevation above 1000 m (Cekova, 2005). However, the altitude of the investigated area varies between 290 to 1932 m. Therefore, the samples of the pleurocarpous moss species *Homalotecium lutescens* and *Hypnum cupressiforme* were also collected in the investigated area in the period of August-September 2012. Researchers setting up large-scale survey often face the problem that the location of the predicted sampling spot becomes subordinate to the presence/absence of the selected species (Fernández et al., 2015). This problem can be overcome by using more than one moss species within the same survey; however, it is clear that the

concentrations of elements may vary considerably between species thus precluding comparison of the results obtained (Market, 2007). Carballeira et al., (2008) suggested that when the regression line slope and elevation do not differ significantly from the line of slope 1 (covariance analysis), the species could be combined. Considering this four species were used for conducting the monitoring for smaller range scale deposition.

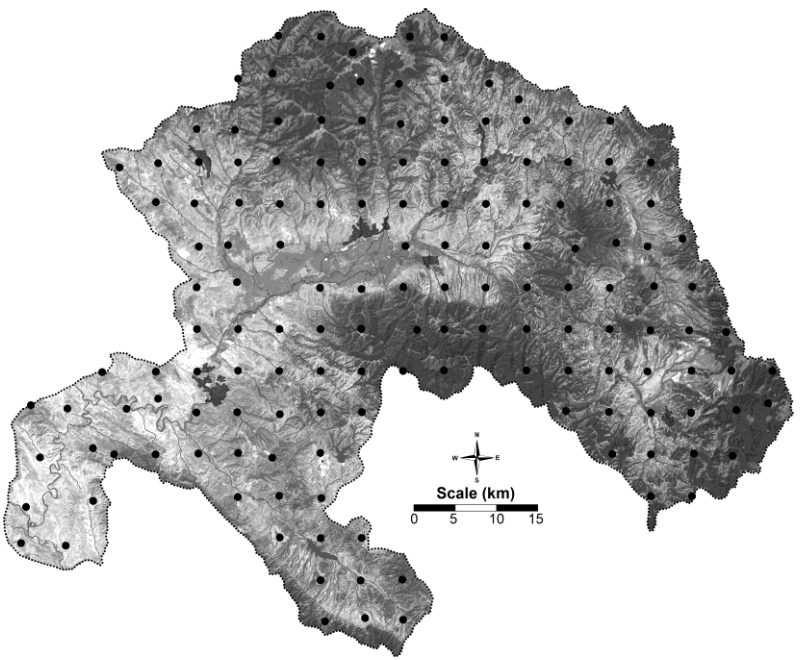

Figure 4. Digital elevation model and location of sampling points for moss samples.

Depending on the conditions and the accessibility of the locations the specie that is available and typical for the region was collected. Random samples (in the very close vicinity of the pollution source) and samples according to sampling network (5 x 5 km) were collected from total 149 sample location, as presented in Figure 4. Detailed description of the collection of samples (according officially accepted techniques) is given by Fernández et al., (2015).

3.1.2. Attic Dust Samples

Attic dust samples were collected from the attic of total 84 houses built between 1920 and 1970. The collection of attic dust samples was performed

according to the adopted protocol form Šajn (2005). Dust samples were collected with plastic brush in polyethylene bags. At each location for sampling attic dust, topsoil (0-5 cm) samples from the house yards were collected (Figure 5).

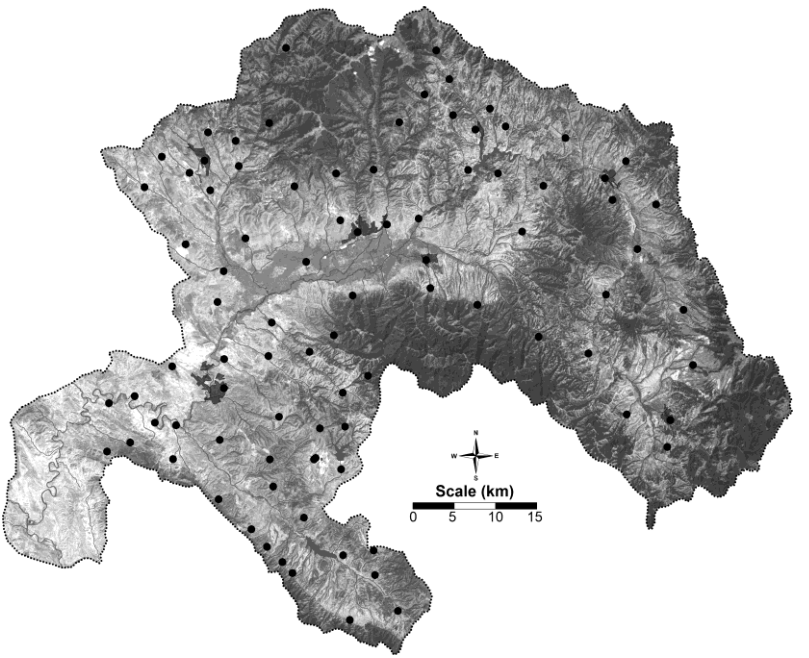

Figure 5. Digital elevation model and location of sampling points for attic dust and top soil samples.

3.2. Analytical Reagents

All used reagents and standards are with the following analytical purity level: nitric acid, HNO_3, 69%, ultra pure (Merck, Germany), hydrogen peroxide, H_2O_2, 30 % p.a. (Merck, Germany), concentrated hydrochloric acid, HCl 37%, p.a. (Merck, Germany), concentrated hydrofluoric acid, HF, p.a. (Merck, Germany) and concentrated perchloric acid, $HClO_4$, p.a. (Alkaloid Skopje). Redistilled water was used for the preparation of all solutions. The standard solutions for the elements examined were prepared by dissolution of the basic multi element standard solution with concentration of 1000 mg L^{-1} (11355-ICP, Multi Element Standard). A series of standard solutions were

prepared in a linear range in several concentration areas as, *series 1*: 1, 2, 3, 5, 10 µg L^{-1} and *series 2*: 10, 20, 30, 50, 100 µg L^{-1} for elements in traces (determined using MS-ICP), for the remaining elements; *series 3*: 0.1; 0.2; 0.3; 0.5; 1 mg L^{-1}; *series 4*: 1, 2, 3, 5, 10 mg L^{-1} and *series 5*: 10, 20, 30, 50, 100 mg L^{-1} for the elements in macro contents.

3.3. Sample Preparation

For digestion of moss samples, the microwave digestion system (CEM, model Mars) was applied. Precisely measured mass (0.5000 g) of moss samples, than 5 mL concentrated HNO_3 (trace pure), and 2 mL H_2O_2 (30%, m/V) were added. The Teflon vessels were carefully closed and the microwave digestion method was applied. Digestion method was performed in to two steps for total dissolving of moss tissue as previously given by Balabanova et al., (2010) and Bačeva et al., (2012). After the digestion method was finished, digests were quantitatively transferred into 25 ml volumetric flaks. Thus way prepared digests from moss tissue were analysed for the total elements contents.

For digestion of attic dust and soil samples, open wet digestion with mixture of acids was applied (ISO 14869-1:2001). Precisely measured mass of dust samples (0.5 g) was placed in teflon vessels and 5 mL concentrated nitric acid, HNO_3 was adding, until the brown vapours came out from the vessels. Nitric acid is very suitable oxidant for digestion of environmental samples. For total digestion of inorganic components was added 5-10 mL hydrofluoric acid. When the digest became clear solution, 2 mL of $HClO_4$ was added. Perchloric acid was used for total digestion of organic matter. After 15 min. cooling the vessels, 2 mL of HCl and 5 mL of H_2O were added for total dissolve of metal ions. Finally the vessels were cooled and digests quantitatively transferred to 50 mL calibrated flasks. In this way the digested soil and sediment samples were prepared for determining the contents of the different elements using atomic emission and mass spectrometry.

3.4. Instruments Used for Determining the Content of Elements in Various Samples

The analysis of elements content in digested samples was conducted with application of atomic emission spectrometry with inductively coupled plasma

(AES-ICP) and mass spectrometry with inductively coupled plasma (MS-ICP). For each element analyzed, previous optimization of the instrumental conditions was performed. In all samples, the contents of a total of 23 elements were analyzed: Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Ga, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, V and Zn by applying AES-ICP. By applying mass spectrometry with inductively coupled plasma a total of 69 isotopes were analyzed, which are the following: Ag, As, Al, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Ti, Th, Tl, Tm, V, W, Y, Yb, Zn, Zr.

The instrumental and operating conditions for each of the above mentioned techniques are given in Table 1.

The limits of detection (LOD) were based on the usual definition as the concentration of the analytic yielding a signal equivalent to three times the standard deviation of the blank signal, using 10 measurements of the blank for this calculation. The calculated values for the detection limits are given in Table 2.

SCIEX Perkin Elmer Elan DRC II (Canada) inductively coupled plasma mass spectrometer (ICP-MS, with quadrupole as single detector) was used for measurement of the concentration trace elements, while for the major elements content determination atomic emission with inductively coupled plasma (ICP-AES, Varian 715ES) was applied.

Certified reference materials NIST 2709 (for attic dust samples), M2 and M3 (for moss samples) were used to check method accuracy. For all considered elements, the difference between measured and certified values was within 15%. The theoretical limit for ICP-MS methods are in ppt (ng/L) range for the majority of the elements. Matrix effects above 1 ppb (μg/L) threshold while using Total Quant were not observed during our study. For some elements, values between these two levels were further investigated using more complex quantitative methods. Spiked intra-laboratory samples were analyzed at a combined frequency of 20% of the samples. The recovery for all of the analyzed elements ranges from 76.8% for Tl to 119% for Sb (for ICP-MS measurements) and from 87.5% for Na to 112% for P (for ICP-AES measurements).

Table 1. Instrumental conditions for ICP-AES and ICP-MS

RF Generator		ICP-AES	ICP-MS
Power output of RF generator		1500 W	
Power output stability		Better than 0.1%	
ICP Ar flow gas rate		15 L min^{-1}	
Plasma parameters			
Nebulizer		V- groove	Micromist
Spray Chamber		Double-pass cyclone	
Peristaltic pump		0-50 rpm	
Cones		/	Platinum
Plasma configuration		Radially viewed	Axially viewed
Spectrometer		Echelle optical design	Quadrupole
Polychromator		400 mm focal length	/
Polychromator purge		0.5 L min^{-1}	/
Total voltage /V		/	0.1
Integration measurement time /ms		/	0.1
Measurement at one point (isotope)/s		/	300
Repetitions measurement		3 per point	
Conditions for program			
ICP-AES measurements		ICP-MS measurements	
Element	Wavelength, nm	Isotopes	
Al	396.152	^{107}Ag, ^{75}As, ^{27}Al, ^{197}Au, ^{11}B, ^{137}Ba, ^{9}Be, ^{209}Bi, ^{79}Br, ^{114}Cd, ^{140}Ce, ^{59}Co, ^{53}Cr, ^{133}Cs, ^{63}Cu, ^{163}Dy, ^{166}Er, ^{153}Eu, $^{56/57}$Fe, ^{69}Ga, ^{157}Gd, ^{72}Ge, ^{178}Hf, $^{201/202}$Hg, ^{165}Ho, ^{127}I, ^{115}In, ^{193}Ir, ^{139}La, ^{7}Li, ^{175}Lu, ^{55}Mn, ^{95}Mo, ^{93}Nb, ^{146}Nd, ^{60}Ni, ^{189}Os, $^{206/207/208}$Pb, ^{105}Pd, ^{141}Pr, ^{195}Pt, ^{85}Rb, ^{185}Re, ^{103}Rh, ^{101}Ru, ^{121}Sb, ^{45}Sc, ^{77}Se, ^{147}Sm, ^{120}Sn, ^{88}Sr, ^{181}Ta, ^{159}Tb, ^{125}Te, ^{47}Ti, ^{232}Th, ^{205}Tl, ^{169}Tm, ^{51}V, ^{182}W, ^{89}Y, ^{172}Yb, ^{66}Zn, ^{90}Zr
Ca	370.602		
Fe	238.204		
Mg	280.270		
K	766.491		
Na	589.592		
P	213.618		

Table 2. Calculated instruments lower detection limits for the analyzed elements

Element	Limit of detection, μg L^{-1}
Ag, Au, Cs, Dy, Eu, Hf, Ho, In, Ir, Li, Lu, Os, Pd, Pt, Re, Ru, Ta, Tb, Te, Ti, Tl, Tm, W	0.001
Rh	0.002
As, Al, B, Ba, Be, Bi, Br, Cd, Co, Cr, Cu, Eu, Fe, Ga, Hg, I, K, La, Mg. Mn, Mo, Na, Nb, Nd, Ni, P, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Th, V, Y, Yb, Zn, Zr	0.010
Ce	0.050
Pb	0.100

3.5. Data Processing

The obtained values for the contents of the investigated elements were statistically processed using basic descriptive statistics. The application of bivariate statistic was used for data check of elements contents correlations. For that issue the linear coefficient of correlation was used. Two-dimensional scatter-plots were used to visualize relations between two data sets. Individual data points were represented by point markers in two-dimensional space, where axes represent the variables. Multivariate statistic method (cluster and R-mode factor analyses) was used to reveal the associations of the chemical elements. The factor analysis was performed on variables standardized to zero mean and unit standard deviation (Šajn, 1999, 2000, 2001, 2002, 2003, 2005, 2006). As a measure of similarity between variables, the product-moment correlation coefficient (*r*) was applied. There are various rotational strategies that have been proposed (Žibret and Šajn 2010; Šajn, 1999, 2000, 2001, 2002, 2003, 2005, 2006). The goal of all of these strategies is to obtain a clear pattern of loadings, factors that are somehow clearly marked by high loadings for some variables and low loadings for others. The elements with low communalities were excluded because of their lack of significant associations. In this study, the *varimax* method was used for orthogonal rotation (Sakata et al., 2003; Kaymaz, 2005). As before, we want to find a rotation that maximizes the variance on the new axes; put another way, we want to obtain a pattern of loadings on each factor that is as diverse as possible, lending itself

to easier interpretation Statistical softer *Statistica 11.0*, was used for data processing of obtained values for elements contents.

4. RESULTS AND DISSCUSION

4.1. Monitoring Distribution of Elements in Moss Samples

4.1.1. Summary Results of the Data Set

The assessments for the elements content distribution in the investigated area was characterized using values obtained from basic descriptive statistics (Table 3). The distribution of macroelements Al, Ca, Fe, K, Mg and P was in the range of worthwhile-ness typical of this kind of samples. High matrix content originated from plant tissues can sometimes enriches the actual values from atmospheric distribution of these elements. The determined median values for Al, Ca, Fe, K, Mg and P are: 0.27%; 0.94%; 0.26%; 0.22%; 0.17% and 0.14%, respectively (Table 3). Compared to data published from Barandovski et al., (2015) and Harmens et al., (2015) for the whole of R. Macedonia and the territory of Europe no significant variation of these elements occurs. The distribution of the rest of the elements was due to certain natural phenomena (geology of the area, winds, rain, anthropogenic activities, etc.). Silver content was determined in the range of 0.005-1.1 mg kg^{-1}, with a median of 0.038 mg kg^{-1} (Table 2). Native silver is sometimes associated with sulfide ores as a result of their chemical reduction. In the area of the copper sulfides hydrothermal exploitation occur in area of Proterosoic shales, the obtained median value for Ag was 0.051 mg kg^{-1}. Maximum median for Ag, accordingly to dominant geological units was obtained in moss samples from Quaternary terraces (Table 3). Very similar to Ag, distributes Cu in the investigated area, also enriched in the Quaternary terraces (median value of 6.7 mg kg^{-1} (Table 3). These metals, collectively known as the "coinage metals," have very similar geochemistry associated with their organometallic chemistry (Greenwood and Earnshaw, 2005).

For As, Sb and Bi no significant enrichments were obtained for the atmospheric deposition in moss. None of these three elements do not participate significantly in the composition of the Earth's crust, although several minerals containing as its major constituents. Median value for arsenic content (0.47 mg kg^{-1}) compared to data from the European report published from Harmens et al., (2015) was lower than the median value obtained for whole of R. Macedonia. Arsenic content compared to other European

countries, such as Norway (0.13 mg kg^{-1}), France (0.18 mg kg^{-1}) or Finland (0.11 mg kg^{-1}) was significantly enriched. Dumurdzanov et al., (2004) explained that natural enrichment of arsenic may occur in areas where the Neogene vulcanite's are dominant geological units. Bismuth content ranges from 0.005-1.9 mg kg^{-1}, with predominant distribution in areas with Neogene volcanism (median value 0.054 mg kg^{-1}). For antimony was obtained median value of 0.019 mg kg^{-1}. Investigation conducted on the whole territory of the Republic of Macedonia by Barandovski et al., (2015) showed that Sb enrichments are with anthropogenic origin, occurring in areas with Pb-Zn mineral hydrothermal exploitation.

Boron is the element with very specific chemistry in the environment. The content of B in the moss samples ranges from 1.8-59 mg kg^{-1} and a median of 13 mg kg^{-1}. The atmospheric distribution of boron in the investigated area was intensive on Paleogene flisch (median 20 mg kg^{-1}). Very similar to boron distributes the alkaline earth metals, such as Be, Ba and Sr. Barium in moss samples ranges from 14-350 mg kg^{-1}. Beryllium was dominantly enriched on the Quaternary terraces and in the areas with dominant Ng-volcanism (0.13 mg kg^{-1}), while the whole investigated area was characterized with Be deposition in range of 30-350 µg kg^{-1}, with median value of 96 µg kg^{-1} (Table 3). To this group of elements can be incorporated also lithium, cesium and rubidium. These elements showed very low variation in the deposition accordingly to the different geologic units. These alkaline metals have very good stability in marking the lithogenic distribution. The investigated area was characterized with medians for Li, Cs and Rb as follow: 2.6, 0.27 and 5.4 mg kg^{-1}, respectively (Table 3).

Gallium and thallium usually are correlated with the occurrence of vulcanite's; it has also been demonstrated in present investigation. Depositions of these elements relays dominantly in area of Neogene pyroclastites and vulcanite (Kratovo-Zletovo district). Characterization of the study area accordingly to dominant geological units, extracted Tl with 61 mg kg^{-1} in area of Neogene pyroclastites. River terraces were also enriched with Ga and Tl (1.3 mg kg^{-1} and 59 µg kg^{-1}, respectively). The halogens, bromine and iodine deposited with median values of 1.1 mg kg^{-1} and 91 µg kg^{-1}, respectively. These elements shows very high reactivity in environment and usually their deposition is correlated to geochemical occurrence as potassium and sodium salts. River terraces are mostly enriched with their contents, as in the present case. However, no significantly variation occurs in accordingly dominant geological units.

Table 3. Descriptive statistic parameters for elements content in moss samples

	Unit	Mean	Med	Min	Max	P_{25}	P_{75}	*S*	*CV*	*A*	*E*
Al	%	0.27	0.27	0.080	1.5	0.18	0.42	0.018	67	0.19	-0.35
Ag	µg/kg	37	38	5.0	1100	24	55	12	200	-0.14	1.51
As	mg/kg	0.48	0.47	0.05	4.4	0.29	0.86	0.058	100	-0.02	0.46
B	mg/kg	13	13	1.8	59	8.1	19	0.82	67	0.03	-0.20
Ba	mg/kg	48	46	14	350	37	66	3.4	71	0.07	1.16
Be	µg/kg	95	96	30	530	64	150	6.2	65	-0.04	-0.43
Bi	µg/kg	32	35	5.0	1900	20	51	14	270	-0.16	1.68
Br	mg/kg	1.3	1.1	0.14	15	0.72	2.4	0.20	110	0.02	-0.38
Ca	%	0.95	0.94	0.29	2.1	0.77	1.1	0.026	33	0.41	0.74
Cd	µg/kg	82	80	32	2200	60	120	25	190	0.09	-0.14
Ce	mg/kg	3.6	3.6	0.93	24	2.3	5.9	0.29	75	0.05	-0.49
Co	mg/kg	1.0	1.1	0.31	4.0	0.65	1.6	0.067	64	0.03	-0.70
Cr	mg/kg	4.2	4.3	0.85	32	2.5	6.4	0.44	91	0.04	-0.08
Cs	mg/kg	0.27	0.27	0.057	5.1	0.16	0.49	0.052	130	0.03	-0.49
Cu	mg/kg	4.5	4.4	2.2	240	3.7	5.8	1.8	270	0.13	0.21
Dy	mg/kg	0.37	0.38	0.079	1.7	0.23	0.60	0.027	70	-0.02	-0.38
Er	mg/kg	0.18	0.19	0.041	0.87	0.12	0.30	0.013	70	-0.03	-0.31
Eu	µg/kg	84	85	22	390	50	130	5.9	68	-0.04	-0.60
Fe	%	0.25	0.26	0.077	1.2	0.15	0.39	0.016	65	0.18	-0.56
Ga	mg/kg	0.90	0.93	0.28	5.0	0.62	1.3	0.060	66	0.01	-0.36
Gd	mg/kg	0.48	0.50	0.11	2.6	0.29	0.76	0.036	72	-0.01	-0.47
Ge	µg/kg	25	25	11	91	18	34	1.1	49	-0.09	-0.40
Hf	µg/kg	37	36	5.0	340	27	49	3.5	90	-0.14	2.70
Ho	µg/kg	73	74	16	340	47	120	5.2	69	-0.05	-0.32
I	µg/kg	92	91	38	260	75	130	3.1	37	-0.08	-0.38
K	%	0.22	0.22	0.067	0.66	0.18	0.25	0.006	34	0.45	3.45
La	mg/kg	1.7	1.7	0.42	14	1.0	2.8	0.16	87	0.03	-0.42

Table 3. (Continued)

	Unit	Mean	Med	Min	Max	P_{25}	P_{75}	*S*	*CV*	*A*	*E*
Li	mg/kg	2.5	2.6	0.70	20	1.7	3.8	0.20	75	0.03	-0.22
Lu	µg/kg	25	26	5.0	120	16	41	1.7	70	-0.08	-0.14
Mg	%	0.16	0.17	0.058	0.42	0.13	0.20	0.005	37	0.30	0.41
Mn	mg/kg	150	150	32	810	100	220	9.4	64	0.12	0.14
Mo	mg/kg	0.22	0.22	0.063	4.2	0.16	0.34	0.038	140	-0.07	0.53
Na	mg/kg	58	59	28	2300	47	76	15	230	0.10	0.60
Nd	mg/kg	1.8	1.8	0.44	10	1.0	2.9	0.14	72	0.03	-0.61
Ni	mg/kg	4.0	4.1	1.6	45	3.0	5.6	0.51	110	0.06	0.05
P	%	0.14	0.14	0.041	0.29	0.11	0.17	0.004	34	0.29	0.25
Pb	mg/kg	5.4	4.9	2.0	1400	3.6	8.5	17	360	0.43	-0.35
Rb	mg/kg	5.5	5.4	1.9	47	3.7	8.3	0.40	73	0.06	-0.25
Sb	µg/kg	18	19	5.0	96	13	27	1.3	69	-0.08	0.12
Sc	mg/kg	1.2	1.2	0.55	6.5	0.93	1.7	0.066	56	0.03	-0.22
Sm	mg/kg	0.37	0.37	0.050	2.0	0.21	0.60	0.027	71	-0.02	-0.12
Sn	mg/kg	0.20	0.19	0.025	1.8	0.16	0.25	0.018	85	-0.11	3.82
Sr	mg/kg	27	26	9.4	110	20	41	1.6	59	0.10	-0.29
Tb	µg/kg	66	68	15	310	40	100	4.8	70	-0.05	-0.45
Ti	mg/kg	120	130	32	570	74	190	8.2	67	0.10	-0.42
Tl	µg/kg	39	36	5.0	280	25	65	4.0	90	-0.07	0.33
Tm	µg/kg	28	28	5.0	130	18	44	2.0	70	-0.07	0.06
V	mg/kg	5.9	6.0	1.8	32	3.6	8.8	0.43	71	0.06	-0.52
W	µg/kg	62	63	5.0	1300	24	140	17	150	-0.03	-0.26
Y	mg/kg	1.5	1.5	0.35	7.6	0.97	2.5	0.11	71	0.01	-0.38
Yb	mg/kg	0.16	0.17	0.033	0.77	0.10	0.26	0.01	69	-0.04	-0.29
Zn	mg/kg	16	16	6.6	240	13	20	2.6	140	0.08	0.99
Zr	mg/kg	1.1	1.0	0.037	13	0.80	1.5	0.11	99	0.05	5.36

Med – median; Min – minimum; Max – maximum; S – standard deviation; CV – coefficient of variation; A – skewness; E – kurtosis.

Chromium and nickel shows a great similarity in distribution in the range of 0.85 to 32 and 1.6-45 mg kg^{-1}, respectively (Table 3). Their distribution is dominant on Quaternary terraces, probably due to the accumulation of soil dust from soil formed in Paleogene flysch.

The distribution of the LREEs (La-Ce-Pr-Nd-Sm-Gd) is predominantly related to the Quaternary terraces and the Paleogene flysch. The anthropogenic activities that occur in the Pb-Zn surroundings and the Cu mineralization in the investigated area significantly influence the lithological distribution of this geochemical association of elements. On the other hand, the long-term deposition of the HREEs (Eu-Tb-Dy-Ho-Er-Tm-Yb-Lu) presents a typical geochemical marker of the area of the Bregalnica river basin (Balabanova et al., 2015).

The latest results reported from the UNECE ICP Vegetation – Heavy Metals in European Mosses (Barandovski et al., 2015; Harmens et al., 2015) indicate on one of the most health risk area with higher values of Cd, Pb and Zn. That area has been found in the eastern parts of Macedonia, due to the operation conducted in mines for Pb-Zn hydrothermal exploitation (Sasa mine and Zletovo mine). Lead and Zn are specifically distributed around Kamenička and Zletovska River, areas with dominant occurrence of Neogene and Paleogene volcanism. The intensive deposition of these elements includes maximum content in moss of 1400 mg kg^{-1} for Pb and 240 mg kg^{-1} for Zn (Table 3). Cadmium content vary in range of 0.032-2.2 mg kg^{-1}, compared to the whole territory of the Republic Macedonia (median 0.22 mg kg^{-1}), this element has a reduced content distribution (Barandovski et al., 2013; Harmens et al., 2015).

4.1.2. Multivariate Assessing for Dominant Geochemical Markers

Multivariate statistical *hunting* was applied for reducing the numerous elements distribution and identifying the dominant geochemical association. Extraction was simplified to 7 factor association, marked as: F1: Al-Be-Co-Fe-Ga-Ge-Li-Mg-Sc-Ti-V-Y-(La-Gd)-(Eu-Lu); F2: Ba-Bi-Cd-Pb-Sb-Zn; F3: As-Cs-Rb-Tl; F4: Ca-Sr-B; F5: Hf-Zr; F6: Cr-Cu-Ni; F7: Br-I, with a total variability for dominant loadings of 84%. Table 4 summaries factor loadings for dominant elements associations. Cluster analysis was also applied, in order to determine the functional dependence of internal associations (Figure 6).

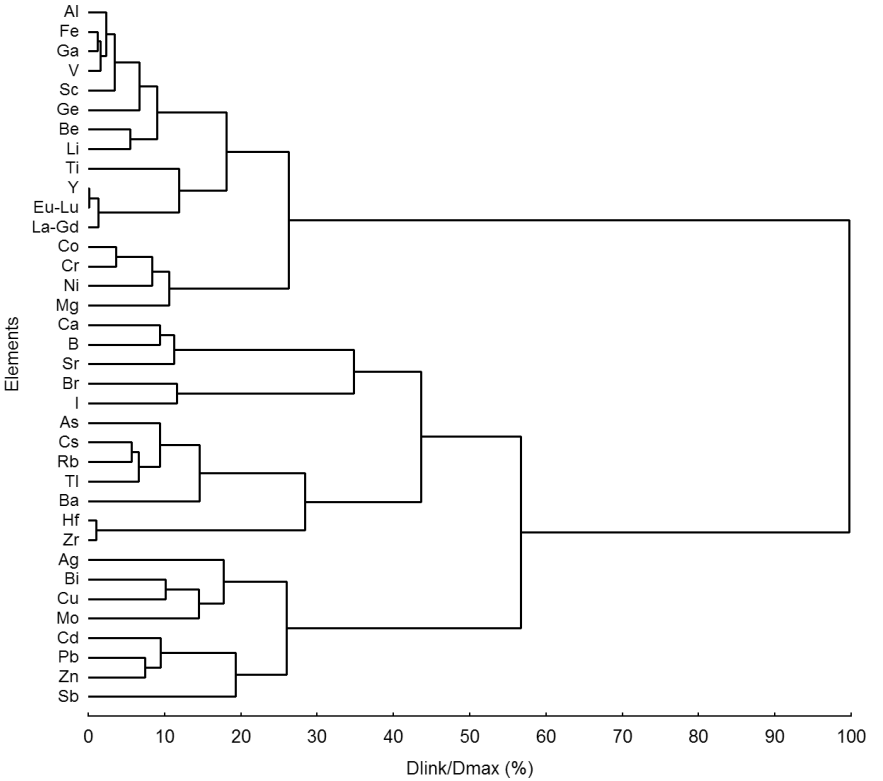

Figure 6. Dendogram for dominant clusters.

4.1.3. Areal Distribution Mapping of the Factors

For the spatial distribution of the factor scores, universal kriging with the linear variogram interpolation method was applied for the construction of maps showing the spatial distribution of factor scores (F1-F7).

Factor 1: [Al-Be-Co-Fe-Ga-Ge-Li-Mg-Sc-Ti-V-Y-(La-Gd)-(Eu-Lu)] can possibly be explained by elements associated with mineral particles, mainly windblown dust, and contributes to 30 % of the variance. The highest values of the factor loading were obtained for rare earth elements, (0.95 and 0.90). The distribution of these elements represents a specific lithological phenomenon, due to the strong dominance rare earth elements (Balabanova et al., 2015).

Table 4. Matrix of dominant factor loading

Element	F1	F2	F3	F4	F5	F6	F7	Communality
Al	0.76	0.14	0.38	0.19	0.24	0.23	0.07	89.0
Be	0.68	0.12	0.50	0.23	0.27	0.06	0.11	87.0
Co	0.73	0.10	0.19	0.20	0.11	0.50	0.19	92.0
Fe	0.82	0.11	0.30	0.14	0.17	0.34	0.13	95.9
Ga	0.81	0.10	0.37	0.14	0.27	0.22	0.15	96.9
Ge	0.70	0.05	0.14	0.28	0.43	0.23	0.13	84.6
Li	0.52	0.01	0.48	0.40	0.19	0.34	0.11	82.0
Mg	0.49	0.11	0.23	0.57	0.07	0.36	0.11	78.4
Sc	0.79	0.10	0.22	0.15	0.25	0.30	0.05	85.5
Ti	0.78	0.21	0.03	0.01	0.14	0.25	0.07	75.2
V	0.74	0.12	0.31	0.20	0.28	0.35	0.15	92.9
Y	0.95	0.07	0.14	0.10	0.02	0.04	0.07	94.5
La-Gd	0.90	0.10	0.22	0.13	0.09	0.01	0.12	91.0
Eu-Lu	0.95	0.09	0.15	0.08	0.05	0.03	0.06	95.4
Ba	0.35	0.52	0.23	0.22	0.37	0.26	0.19	73.5
Bi	0.37	0.55	0.31	0.01	0.07	0.31	0.25	70.1
Cd	0.04	0.88	0.10	0.06	0.06	0.09	0.08	81.2
Pb	0.08	0.81	0.32	0.06	0.16	0.10	0.10	80.9
Sb	0.51	0.63	0.09	0.10	0.15	0.17	0.09	73.7
Zn	0.25	0.82	0.15	0.05	0.08	0.22	0.00	81.8
As	0.40	0.34	0.55	0.24	0.09	0.25	0.21	75.3
Cs	0.33	0.21	0.77	0.27	0.14	0.03	0.14	86.4
Rb	0.47	0.24	0.66	0.07	0.30	0.07	0.10	82.2
Tl	0.41	0.31	0.60	0.12	0.35	0.03	0.26	82.8
Ca	0.21	0.06	0.01	0.85	0.01	0.18	0.13	81.7
B	0.16	0.02	0.22	0.81	0.01	0.09	0.04	73.7
Sr	0.02	0.18	0.13	0.78	0.38	0.07	0.09	82.0
Hf	0.34	0.09	0.19	0.13	0.87	0.11	0.03	94.9
Zr	0.25	0.15	0.21	0.11	0.88	0.15	0.02	94.7
Cr	0.55	0.07	0.17	0.29	0.16	0.65	0.22	91.4
Cu	0.24	0.54	0.22	0.16	0.09	0.55	0.09	74.0
Ni	0.27	0.08	0.02	0.35	0.16	0.72	0.16	77.8
Br	0.16	0.05	0.15	0.19	0.08	0.11	0.84	80.8
I	0.15	0.24	0.12	0.06	0.05	0.13	0.81	77.7
Total variability (%)	30.3	11.7	10.2	9.8	8.3	8.0	5.7	84.0
Eingen value	17.4	3.62	2.88	2.46	1.76	1.34	1.10	

As dominant lithogenic marker for atmospheric distribution for the whole territory of the Macedonia was identified the following association: Al-As-Ba-Ce-Co-Cs-Dy-Fe-Hf-La-Li-Mg-Na-Nd-Sc-Sm-Ta-Tb-Th-Ti-U-V-W-Yb-Zr (Barandovski et al., 2015). Content of these elements in mosses is significantly influenced by secondary sources-mineral particles released into the atmosphere by wind erosion of local sources or particles attached to the moss in the periods when the soil surface is covered by water. The highest contents of the aforementioned group of elements have been found in moss samples that were collected on the Precambrian and Paleozoic schists or close to them (Figure 7). As a result of the actions of natural conditions, weathering of shales, very fast and consequently releases these elements into the environment occur.

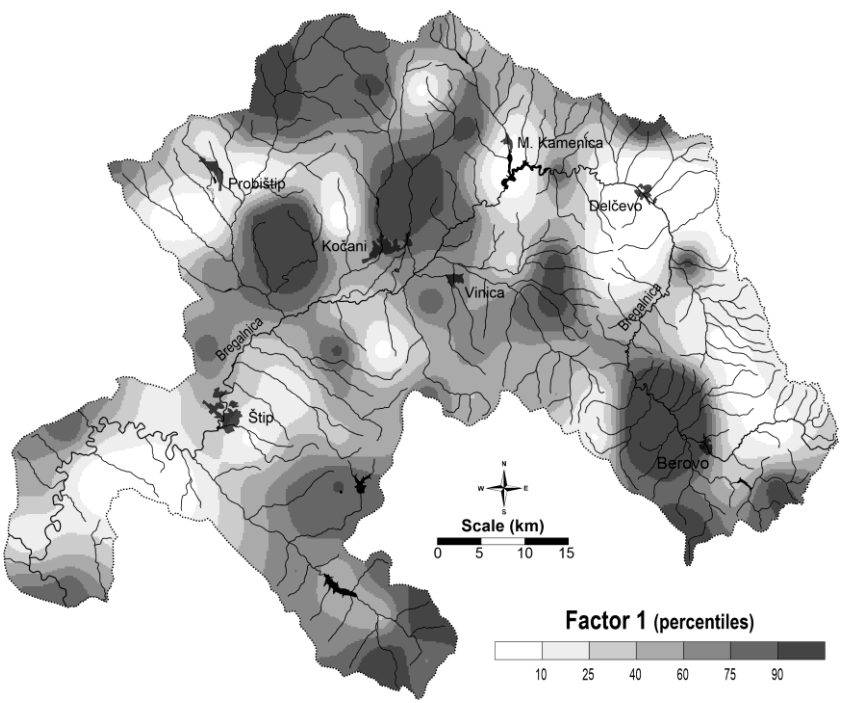

Figure 7. Areal distribution of Factor 1: Al-Be-Co-Fe-Ga-Ge-Li-Mg-Sc-Ti-V-Y-(La-Gd)-(Eu-Lu) in moss.

Factor 2 (Ba-Bi-Cd-Pb-Sb-Zn) is probably associated with long-range transport of air pollution and contributes to 11.7% of the variance. The highest loading values were obtained for Cd (0.88), Zn (0.82) and Pb (0.81). The

elements Cd, Pb, Zn and Sb were also identified as anthropogenic marker for the whole territory of the R. Macedonia (Barandovski et al., 2015). The atmospheric deposition of these elements has been intensified in the areas of Neogene pyroclastite and Proterozoic and Paleozoic schists (Figure 8). There are two dominant sub-areas that mostly affect on the anthropogenic enrichment of these elements. The first one is an area with dominant occurrence of the Neogene pyroclastites and vulcanite's, where the Pb-Zn hydrothermal exploitation is operated ("Zletovo" mine). The second one is in the area of very old volcanic minerals (Paleogene volcanic sedimentary rocks, and Paleogene flysh) where the Pb-Zn hydrothermal exploitation is operated also ("Sasa" mine). This area of very old volcanic rocks continuous in NW direction where also occur a Pb-Zn mineral exploitation ("Toranica" mine).

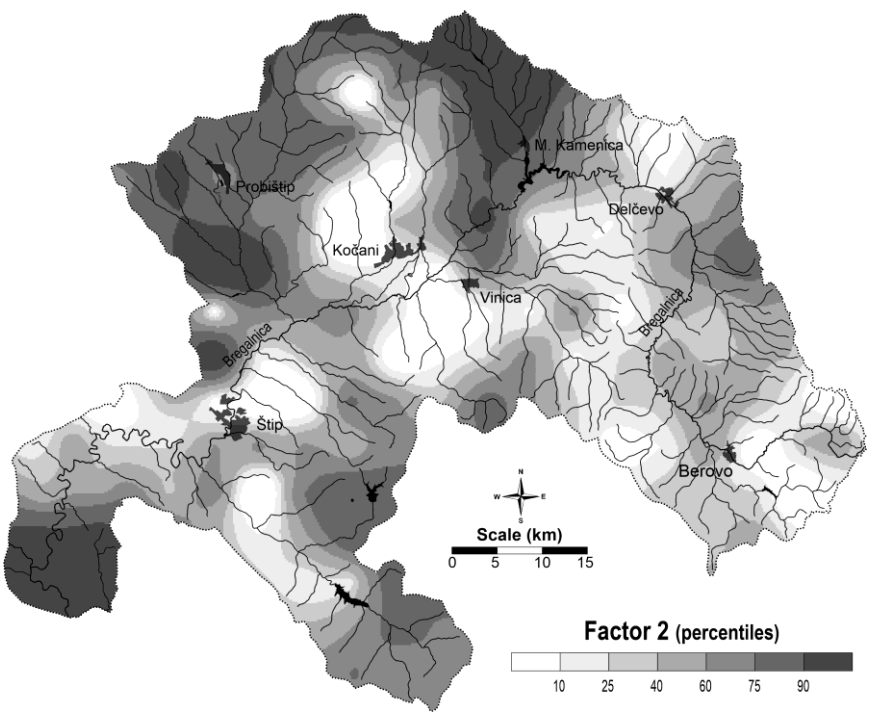

Figure 8. Areal distribution of factor 2: Ba-Bi-Cd-Pb-Sb-Zn in moss.

These mentioned sub-areas are predominantly affected with the dispersion of particles from flotation tailings dam sites near the "Zletovo" and "Sasa" mines. It should be pointed out that dust particles are significantly enriched with Pb and Zn contents. Soil surface wind-blowing dust is also affecting on

the Pb-Zn enrichments, due to the significant soil contamination that occurs in these areas (Stafilov et al., 2014). Similar anomaly was recorded in northern France, exhibiting similar pattern for environmental distribution of Pb *vs.* Zn (Buorennane et al., 2010). This anomaly was extended with the Cd enrichments, due to the existence of the urbanized areas (Buorennane et al., 2010). Present data pointing to pollution source ("Zletovo" and "Sasa" mines). Lead and zinc distribution patterns were separately given, pointing on diagnosis of industrial pollution (Figure 8). The affected areas with significantly enriched Pb/Zn deposition predominantly were detected in the area of Neogene and Paleogene volcanism. The geochemistry of the igneous rock is known to correlate with extended poly-metallic enrichments (Keller et al., 2015). Furthermore, this association can be used as a very intensive probabilistic model of anthropogenic poly-metallic enrichments.

Factor 3 (As-Cs-Rb-Tl) indicates on characteristic deposition of these elements linked to old volcanism in the test area (Figure 9).

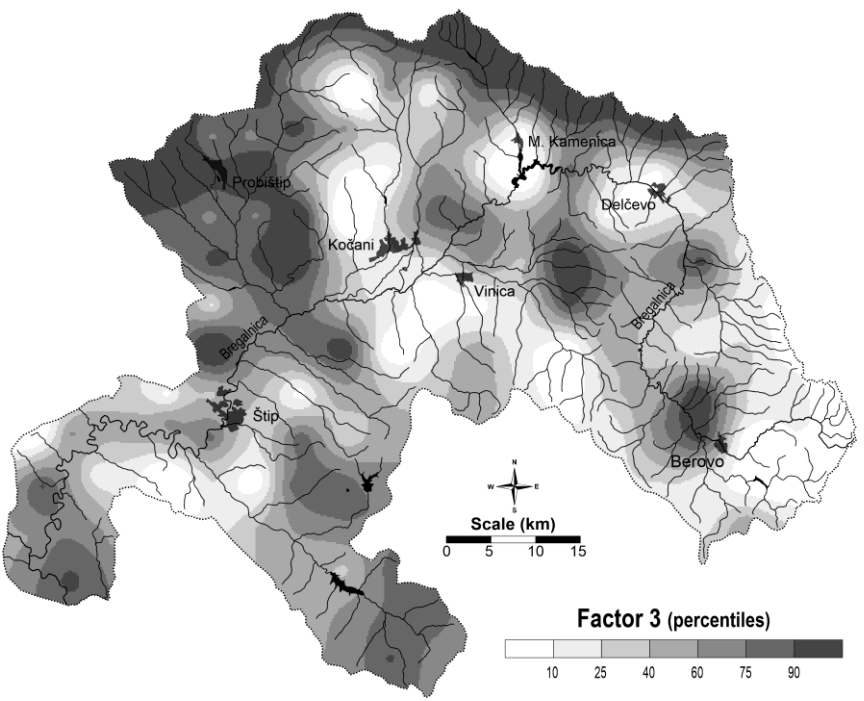

Figure 9. Areal distribution of factor 3: As-Cs-Rb-Tl in moss.

Spatial distribution of these elements follows the areal distribution of Factor 2. This geogenic marker probably occurs as secondary poly-metallic enrichments in area where the vulcanite dominates (Figure 9). Predominantly this occurrence marked the areas with Neogene vulcanite's vs. Paleogene vulcanite's.

The specific distribution of As, Cs, Rb and Tl was extended in the SE direction in the Berovo town vicinity. There are data that suggest a poly-metallic enrichment in this area (Serafimovski and Aleksandrov, 1995). This association can be used for the identification of the anthropogenic hydrothermal mineral exploitation, due to the areal distribution patterns (Figure 9). Higher paterns for these elements were obtained in Pb-Zn Sasa mine area, Pb-Zn Zletovo mine environ and copper mine Bučim area.

Factor 4 (Ca-Sr-B) was extracted with total variability of 9.8%. Distribution of Ca and Sr appear in the rocks of the Earth's crust, mainly as insoluble carbonates and sulfates and silicates (Greenwood and Earnshaw 2005). The processes of its total representation depend on the geochemical model they use, particularly the relative weights given to different types of volcanic and sedimentary rocks. According to the distribution in different geological units, this association dominates in Paleogene flysh (Figure 10).

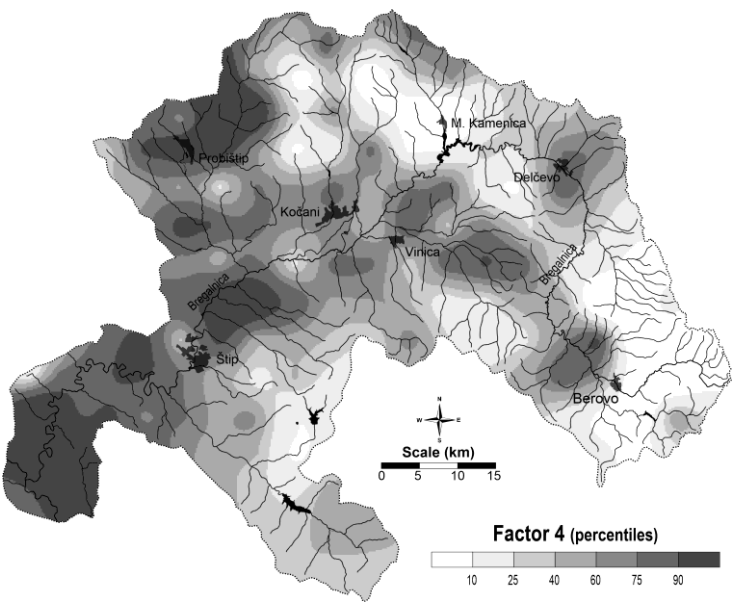

Figure 10. Areal distribution of factor 4: Ca-Sr-B in moss.

These old sedimentary rocks are natural archive for these elements. Along the whole couce of the Bregalnica river was determined dominance of this factor, with emphasis on the area where the Bregalnica river flows into Vardar river (intensive occurrence of Paleogene flysh, Figure 10). This lithogenic marker can be used for identification of natural enrichments due to the wind dusting in area of very old sedimentary rock in river basins.

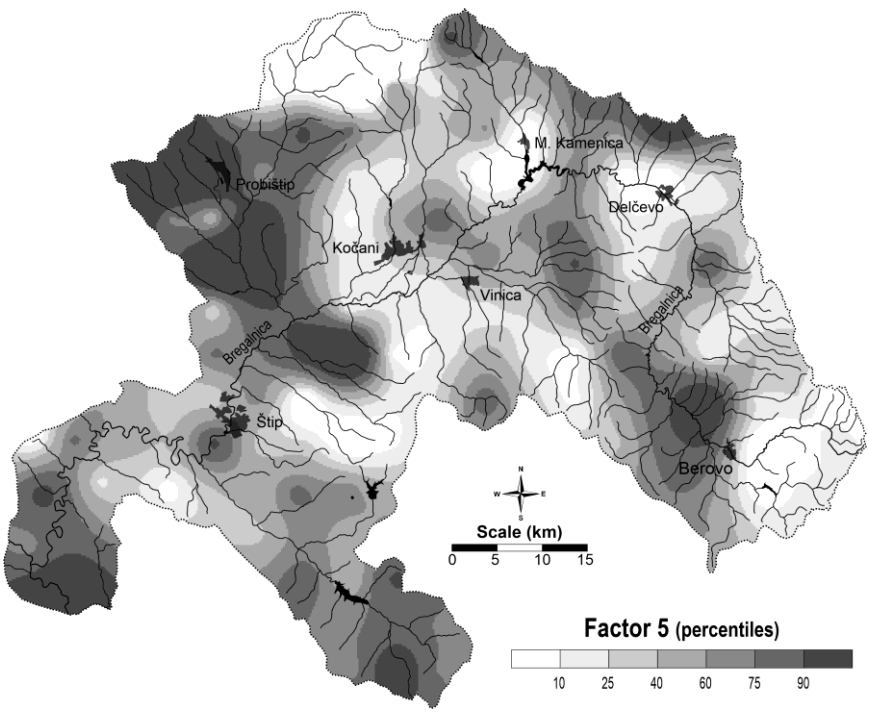

Figure 11. Areal distribution of factor 5: Hf-Zr in moss.

Factor 5 (Hf-Zr) presents a natural phenomenon in the investigated area, due to the specific geochemistry of these elements in environment (Figure 11). Their very similar chemical background correlated these elements. Zr and Hf behavior is similar to the HREEs (Prudêncio 2006). No significant variation occurs accordingly to dominant lithological units, but some intensive deposition can be singled out in area of Neogene volcanism. This area was characterized with poly-metalic enrichments (with special emphasis on Pb, Zn, Sb and Cd). Lower enrichments of Hf and Zr in this kind of area were also identified in Portugal, in correlation with significant Zn enrichments Prudêncio (2006). Barandovski et al., (2015) reports for decreasing trend in Hf-Zr

distribution pattern from 2005 to 2010 on the whole territory of the Republic of Macedonia. Data obtained in this work compared to values from the investigation in 2010 (Barandovski et al., 2015) shows lower medians. Despite the decreasing trend in Hf-Zr deposition, still this geogenic association can be correlated to some poly-metallic anomalies (Figure 11).

Factor 6 (Cr-Cu-Ni) associate elements primarily affected by natural factors such as lithological background. Paleogene flysch sediments and Neogene sediments which occur along Vardar zone repeatedly demonstrated in Macedonia (Stafilov et al., 2010). These elements can be connected to air pollution as well. Most emissions of these elements to the environment originate from local sources, mainly from mines. Copper mine Bučim, contributes in the anthropogenic copper emission, in the South-East part of the study area. But, significant enrichment of this geochemical association occurs in the area of Paleogene flysch, intercepting a part from the Vardar river basin. Barandovski et al., (2015) identify a strong anomaly in Cr-Co-Ni distribution along the Vardar river basin. This anomaly affects a part from the Bregalnica river basin that was demonstrated also within this study (Figure 12).

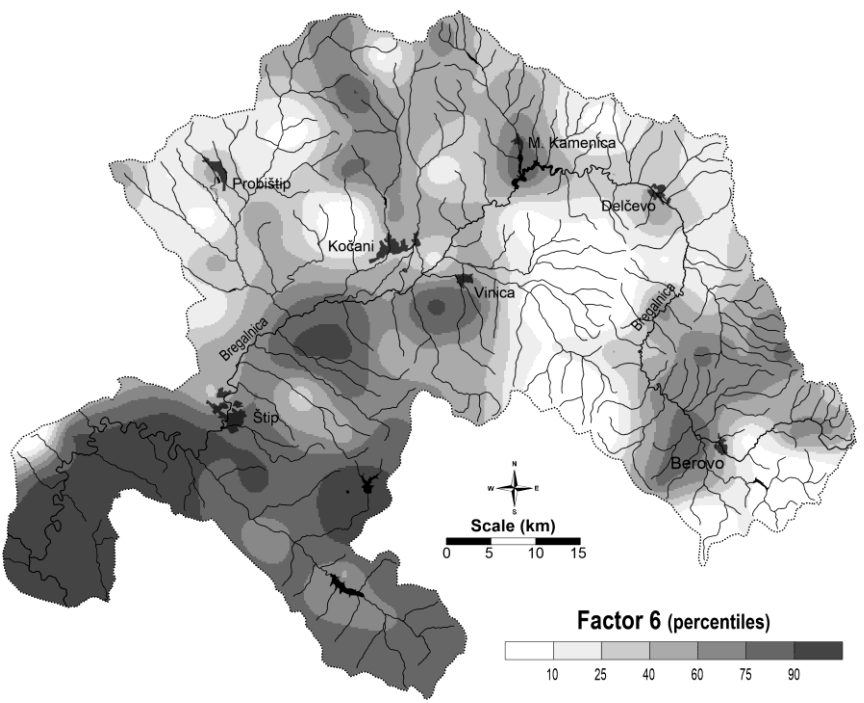

Figure 12. Areal distribution of factor 6: Cr-Cu-Ni in moss.

Factor 7 (Br-I) associates elements primarily affected by marine influence (Frontasyeva and Steinnes, 2004). Coast line of the Aegean Sea is less then 60 km from the south state border. Barandovski et al., (2015) reported for the influence of the wind blows along the Vardar river valley from the northern parts of Africa across the Mediterranean and the Aegean Sea. Elevated values of these elements in the mosses collected in area connected with the presence of Neogenic sediments along the river Begalnica (Figure 13). Lower enrichments of these elements were found in area of Rifeous schist.

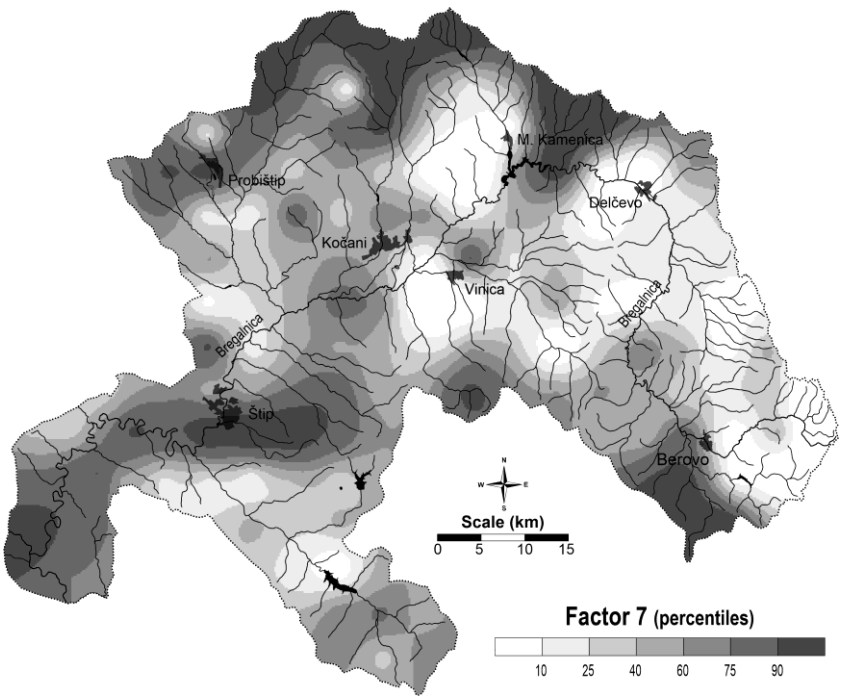

Figure 13. Areal distribution of factor 7: Br-I in moss.

4.2. Monitoring Distribution of Elements in Attic Dust Samples

4.2.1. Summary Results of the Data Set

From total 69 analyzed elements, for 60 elements were obtained values above the determined instrumental detection limits. Table 5 reports the descriptive statistic parameters (median and ranges values) corresponding to sixty elements contents in attic dust and topsoil samples from the house yards.

Data filtering was conducted to upgrade this investigation. The contents of the major elements in attic dust samples varied in thefollowing ranges: Al (4-7.4%), Ca (0.58-8.6%), Fe (0.07-16%), K (0.017-4.1%), Mg (0.08-2.6%), Na (0.01-2.6%), P (0.04-0.40%), Ti (0.002-0.79%). Almost identical results were obtained for the elements contents in topsoil samples, only for Ca and Fe were obtained extended distribution (max. value 17 % and 47%, respectively). Enrichments of these elements in Paleogene flysch areas suggest the typically depositions during an early stage of the orogenesis. The natural abundance of the major elements is strongly correlated to the sedimentary rocks in the investigated area. Keller et al., (2015) explain about similar anomaly composition rarity, during the volcanic-plutonic parity investigations. Enrichments in volcanic Ti and K may also suggest the influence of peralkaline volcanics onto the geochemistry of these elements. Predominantly, for the major elements distribution is the affect of the soil surface wind-blow dusting. The investigated area present a unique area of interweaves of the widely distributed type of rocks formed by high-grade regional metamorphic processes. More dynamic differences between lithogenic distributions in soil vs. elemental dust deposition occur for trace elements.

Trace elemental abundances consistently diverge in zones with occurrence of different lithological units. Rb, Cs, Sr, and Ba, are often collectively termed the large-ion-lithophile (LIL) elements. Because of their solubility, they are quite mobile during metamorphism and weathering. Thus the factors that most govern their behavior in igneous rocks are ionic radius and charge. Their enrichments in the investigated area were also correlated with intensive depositions in sub-areas with dominant occurrence of Neogene pyroclastite. In contrast to the heavy alkaline earths, Be and Li shows some different trends in chalcophile/lithophile deposition. River sediments areas dominates in Be and Li distribution where the maximum contents were deposited (3.4 and 44 mg/kg, respectively).

As the alkalis and alkaline earths, the rare earths and Y are strongly electropositive; thus have very similar geochemistry in the environment. Their abundance is usually correlated many continental rocks, as well as mostsediment. Many sedimentary rocks, andseawater, have rare earth patternsthat are similar to eachother, and to that of the continentalcrust. To accentuate the difference in rare earth patterns between sediments, low temperature geochemists often normalizer are earth abundances to the concentrations in average shale. Because the rare earths are highly insoluble and immobile, rare earth patterns often remain unchanged during metamorphism. Hence rare earth patterns can provide information on the

premetamorphic history of a rock. Indeed, even during the production of sediment from crystalline rock, the rare earth patterns often remain little changed, and rare earth patterns have been used to identify the provenance, i.e., the source, of sedimentary rocks. Shale-normalized REE earth patterns of the Bregalnica river basin are as follow: La (18 mg/kg), Ce (39 mg/kg), Pr 4 mg/kg), Nd (14 mg/kg), Sm (2.8 mg/kg), Eu (0.68 mg/kg), Gd (3.6 mg/kg), Tb (0.46 mg/kg), Dy (2.6 mg/kg), Ho (0.5 mg/kg), Er (1.4 mg/kg), Tm (0.20 mg/kg), Yb (1.3 mg/kg), Lu (0.19 mg/kg). Characterization of REE distribution in authomorphic and alluvial soil, reveals that the sum for total light rare earth elements (ΣLREEs) in the Bregalnica river basin ranges of 8.6-225 mg/kg, while for the total sum of the heavy rare earth elements (ΣHREEs) ranges from 0.92-33.7 mg/kg (Balabanova et al., 2015).

Zr and Hf are nominally incompatible in all major rock-forming minerals. Keller et al., (2015) report about inflection decreasing trends of Zr and Hf with increasing silica reflects saturation of zircon ($ZrSiO_4$). Rubatto (2002) and Kabata-Pendias (2010) observed these elements tend to be very immobile during weathering andmetamorphism. They are therefore particularly valuable in the study of ancient igneous rock suites asthey can sometimes provide insights into the environment in which those rocks formed. These elements range from 0.08 to 3.0 mg/kg for Hf and from 4.9 to 96 mg/kg. They are therefore particularly valuable in the study of igneous rock suites asthey can sometimes provide insights into the environment in which those rocks formed. Enriched median values were obtained in the Paleogene and Neogene volcanism. Zirconium was enriched to 27 mg/kg for both sub-areas, hafnium was enriched to 0.68 mg/kg.Ta and Nb are present in anomalously low concentration sin magmas associated with subduction zones; indeed, this is considered a diagnostic feature of subduction-related volcanism (Keller et al., 2015). Although this depletion is not well understood, it is probably at least in part a consequence of the low solubility of these elements and the consequent failure of aqueous fluids generated by dehydration of the subducting oceanic crust totransport these elements into the magma genesis zone Keller et al., 2015). Nb content in air deposited dust ranges from 0.28-17 mg/kg, while in top soil layer riches to 31 mg/kg. Similar distribution was obtained for Ta, from 0.05-1.3 mg/kg in attic dust and from 0.14-2.5 mg/kg in top soil (Table 5).

The geochemistry of the transition elements is considerably more complex than that of the elements we have discussed thus far. Their behavior in magmas is also variable. They range from moderately incompatible (e.g., Cu, Zn) to very compatible (e.g., Cr, Ni), but their exact behavior is generally a

stronger function of composition than that of the highly incompatible elements. Stafilov et al., (2012) reports about anthropogenic anomaly of Cu deposition Cd, Cr, Cu, Ni, Pb and Zn in mine environ (max values: 3.1, 110, 415, 59, 121 and 93 mg/kg, respectively). Balabanova et al., (2012) also explains that urban elements and those related to mine activities in dust were associated with fine particles, which are preferentially mobilized by wind and trapped in attics. Present investigation also demonstrates a very similar anomaly for abovementioned elements. Copper content in air-distributed dust ranges from 6.7 to 880 mg/kg; while in topsoil layer an extended distribution has occurred (max. value 1200 mg/kg). Enriched values were obtained from houses located very close to Cu mine Bučim. Cadmium contents also hsave an enrichments trend in air-distributed dust (0.054-25 mg/kg). Despite the Bučim area, enriched Cd (>10 mg/kg) contents were obtained in Pb-Zn Sasa mine. Content of Cd in topsoil layer does not indicate any significant enrichment (0.005-9 mg/kg). Therefore, the attic dust depositions indicate on the long time anthropogenic affected distribution in mine environs. Agarwal (2009) explain Cd enrichments of topsoil horizons is ascribed to agricultural activities such as the use of urban sludge, manure and phosphate-enriched fertilizers that are known to contain Cd in addition to atmospheric deposition in any case. Very similar to Cu and Cd, distribute Pb and Zn in the investigated area. Lead content ranges from 0.005 to 3900 mg/kg, while Zn contents shows lower enrichments from 26 to 3200 mg/kg. Lithogenic distribution in soil riches to 1200 mg/kg and 590 mg/kg, respectively for Pb and Zn. These significantly enriched contents for Pb and Zn are correlated with the lithogenic dominance of Rifeous shales, where the median values for Pb and Zn contents are 110 an 220 mg/kg, respectively. As most affected area with Pb/Zn enrichment separate Sasa mine environ, due to the continually long time wind dust dispersion from the flotation tailings.

From the platinum group, Pt and Pd were determined in traces above the instrumental limit detection. Their content distributes almost identically in attic dust and in surface soil. Platinum ranges from 0.005 to 0.78 mg/kg in soil, while in dust riches to 0.81 mg/kg. Palladium is more dominant platinum element, and distributes from 0.05 mg/kg to 1.4 mg/kg in attic dust and 1.7 mg/kg in soil. White (2013) clarify that chromites and sulfides are highly enriched in noble metals relative to the silicate magmatic rocks, consistent with their chalcophile nature and demonstrated affinity for oxide phases such as the spinels.

Table 5. Data summary for elements contents in attic dust samples (D) and topsoil samples (T); N = 168

Element	Unit	Median	Min	Max	Element	Unit	Median	Min	Max
Ag (D)	mg/kg	0.54	0.005	3.0	Mg (D)	%	0.59	0.08	2.6
Ag (T)	mg/kg	0.45	0.22	4.6	Mg (T)	%	0.47	0.06	7.2
Al (D)	%	5.7	4.0	7.4	Mn (D)	mg/kg	530	115	6900
Al (T)	%	6.0	3.0	8.9	Mn (T)	mg/kg	560	179	7000
As (D)	mg/kg	17	4.1	150	Mo (D)	mg/kg	0.67	0.005	17
As (T)	mg/kg	12	4.0	93	Mo (T)	mg/kg	0.48	0.005	8.3
B (D)	mg/kg	11	0.005	63	Na (D)	%	0.48	0.01	2.6
B (T)	mg/kg	0.56	0.005	42	Na (T)	%	0.78	0.08	3.3
Ba (D)	mg/kg	400	6.8	1400	Nb (D)	mg/kg	5.8	0.28	17
Ba (T)	mg/kg	420	76	2600	Nb (T)	mg/kg	5.8	2.4	31
Be (D)	mg/kg	0.93	0.13	3.4	Nd (D)	mg/kg	13	0.37	42
Be (T)	mg/kg	1.1	0.12	4.6	Nd (T)	mg/kg	12	3.1	69
Bi (D)	mg/kg	0.30	0.005	5.9	Ni (D)	mg/kg	21	4.4	250
Bi (T)	mg/kg	0.19	0.046	1.6	Ni (T)	mg/kg	14	4.6	260
Br (D)	mg/kg	2.4	0.005	20	P (D)	%	0.21	0.04	0.40
Br (T)	mg/kg	1.6	0.005	15	P (T)	%	0.07	0.01	0.31
Ca (D)	%	3.9	0.58	8.6	Pb (D)	mg/kg	51	0.005	3900
Ca (T)	%	2.3	0.26	17	Pb (T)	mg/kg	22	0.005	1200
Cd (D)	mg/kg	0.43	0.054	25	Pd (D)	mg/kg	0.35	0.05	1.4
Cd (T)	mg/kg	0.13	0.005	9.0	Pd (T)	mg/kg	0.31	0.05	1.7
Ce (D)	mg/kg	39	0.80	130	Pr (D)	mg/kg	3.6	0.08	11
Ce (T)	mg/kg	36	8.2	160	Pr (T)	mg/kg	3.5	0.82	18
Co (D)	mg/kg	6.6	0.94	20	Pt (D)	mg/kg	0.21	0.005	0.81
Co (T)	mg/kg	6.7	2.5	47	Pt (T)	mg/kg	0.16	0.005	0.78
Cr (D)	mg/kg	48	11	270	Rb (D)	mg/kg	48	3.5	120
Cr (T)	mg/kg	38	3.8	330	Rb (T)	mg/kg	54	9.2	250
Cs (D)	mg/kg	2.3	0.005	12	Sb (D)	mg/kg	0.63	0.060	3.2
Cs (T)	mg/kg	2.6	0.35	27	Sb (T)	mg/kg	0.42	0.10	3.9
Cu (D)	mg/kg	30	6.7	880	Sc (D)	mg/kg	6.9	0.54	92
Cu (T)	mg/kg	17	4.1	1200	Sc (T)	mg/kg	6.2	1.1	26
Dy (D)	mg/kg	2.5	0.08	7.8	Sm (D)	mg/kg	2.8	0.05	8.0
Dy (T)	mg/kg	2.3	0.66	15	Sm (T)	mg/kg	2.5	0.65	14
Er (D)	mg/kg	1.3	0.03	4.0	Sn (D)	mg/kg	3.2	0.005	23
Er (T)	mg/kg	1.2	0.35	7.6	Sn (T)	mg/kg	1.5	0.005	14
Eu (D)	mg/kg	0.72	0.02	2.3	Sr (D)	mg/kg	140	6.0	720
Eu (T)	mg/kg	0.68	0.16	4.7	Sr (T)	mg/kg	110	23	760
Fe (D)	%	1.5	0.07	16	Ta (D)	mg/kg	0.46	0.05	1.3
Fe (T)	%	1.5	0.18	47	Ta (T)	mg/kg	0.54	0.14	2.5
Ga (D)	mg/kg	9.1	2.1	20	Tb (D)	mg/kg	0.47	0.02	1.3
Ga (T)	mg/kg	9.2	5.3	56	Tb (T)	mg/kg	0.43	0.12	2.7
Gd (D)	mg/kg	3.6	0.13	10	Te (D)	µg/kg	31	5.0	1300

Element	Unit	Median	Min	Max	Element	Unit	Median	Min	Max
Gd (T)	mg/kg	3.3	0.95	21	Te (T)	µg/kg	17	5.0	280
Ge (D)	mg/kg	0.57	0.27	2.1	Ti (D)	%	0.23	0.002	0.79
Ge (T)	mg/kg	0.62	0.40	2.6	Ti (T)	%	0.22	0.03	0.96
Hf (D)	mg/kg	0.63	0.02	1.9	Tl (D)	mg/kg	0.34	0.05	1.7
Hf (T)	mg/kg	0.56	0.08	3.0	Tl (T)	mg/kg	0.38	0.05	2.5
Ho (D)	mg/kg	0.46	0.01	1.5	Tm (D)	mg/kg	0.18	0.01	0.52
Ho (T)	mg/kg	0.43	0.12	2.8	Tm (T)	mg/kg	0.17	0.05	1.1
I (D)	mg/kg	0.14	0.005	0.53	V (D)	mg/kg	72	29	370
I (T)	mg/kg	0.11	0.02	0.71	V (T)	mg/kg	62	28	600
In (D)	µg/kg	42	5.0	710	W (D)	mg/kg	1.0	0.045	8.9
In (T)	µg/kg	31	11	190	W (T)	mg/kg	0.99	0.24	5.9
K (D)	%	0.83	0.017	4.1	Y (D)	mg/kg	11	0.44	30
K (T)	%	0.89	0.16	6.1	Y (T)	mg/kg	8.9	2.4	58
La (D)	mg/kg	18	0.37	52	Yb (D)	mg/kg	1.1	0.050	3.4
La (T)	mg/kg	16	3.6	72	Yb (T)	mg/kg	1.1	0.33	7.1
Li (D)	mg/kg	13	3.4	44	Zn (D)	mg/kg	99	26	3200
Li (T)	mg/kg	13	2.8	65	Zn (T)	mg/kg	53	18	590
Lu (D)	mg/kg	0.17	0.005	0.56	Zr (D)	mg/kg	24	0.42	61
Lu (T)	mg/kg	0.17	0.05	1.1	Zr (T)	mg/kg	21	4.9	96

4.2.2. Multivariate Assessing for Dominant Geochemical Markers

Multivariate extraction was applied for reducing the numerous elements distribution and identifying the dominant geochemical association. On the basis of the matrix of correlation coefficients, multivariate cluster and R-mode factor analysis was used to reveal associations of chemical elements and to decrease the number of variables for the obtained data. Extraction was simplified to 6 factor association, marked as: F1: Ga-Nb-Ta-Y-(La-Gd)-(Eu-Lu), F2: Be-Cr-Li-Mg-Ni; F3: Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn, F4: Ba-Cs-Hf-Pd-Rb-Sr-Tl-Zr; F5: As-Co-Ge-V, F6: K-Na-Sc-Ti, with a total variability for dominant loadings of 81.5%. Table 6 summaries factor loadings for dominant elements associations. Variables with factor loading higher than 0.5 were assumed to contribute significantly to a given factor. The remaining elements were eliminated from the analysis, due to their tendency to form separate clusters, thus not showing a reasonable connection with other chemical elements and to satisfy the criteria of dimension variables based on number of observations. Elements with a low share of communality or tendency to form independent factors were also excluded. Factor analysis (FA) was performed on elements standardized to zero mean and unit standard deviation. The inter-elements similarity and distancing were revealing using the cluster dendrogram (Figure 14). Most distant clusters were Factor 1 [Ga-Nb-Ta-Y-(La-Gd)-(Eu-Lu)] and Factor 3 (Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn).

Table 6. Matrix of factor loadings-factor analysis (FA) of the elements' contents

Element	F1	F2	F3	F4	F5	F6	Communality
Ga	0.64	0.15	0.06	0.29	0.59	0.16	89.9
Nb	0.80	0.17	0.18	0.22	-0.02	0.27	82.8
Ta	0.77	0.07	0.16	0.42	-0.08	0.19	84.5
Y	0.87	0.17	0.14	0.11	0.00	0.21	86.4
La-Gd	0.81	-0.02	0.12	0.51	0.00	0.04	92.8
Eu-Lu	0.79	0.03	0.11	0.40	0.04	0.19	83.6
Be	0.11	0.53	0.41	0.10	0.25	0.42	71.1
Cr	0.24	0.83	-0.06	-0.10	0.23	0.20	85.4
Li	-0.06	0.76	0.22	0.33	0.10	0.18	77.8
Mg	0.10	0.84	0.17	-0.13	0.06	0.37	90.5
Ni	0.09	0.89	0.09	0.05	0.11	0.00	82.7
Ag	0.31	0.05	0.73	0.13	0.23	0.10	71.1
Bi	0.23	0.01	0.88	0.09	-0.09	0.03	84.7
Cd	-0.06	-0.01	0.82	0.36	0.08	0.08	81.6
Cu	0.26	0.32	0.64	-0.06	0.08	0.20	63.7
In	0.40	-0.18	0.70	0.31	0.21	0.08	82.8
Mn	0.27	0.20	0.68	0.31	0.35	0.21	83.3
Pb	-0.11	0.35	0.77	-0.05	-0.13	0.24	80.6
Sb	-0.13	0.16	0.77	0.38	0.00	0.14	79.9
Te	0.02	0.23	0.73	0.04	0.31	-0.13	70.2
W	0.38	0.08	0.85	0.20	-0.01	0.01	90.7
Zn	-0.11	-0.03	0.74	0.18	0.30	0.24	74.36
Ba	0.38	-0.26	0.05	0.79	0.00	0.10	84.2
Cs	0.20	0.21	0.31	0.76	-0.22	-0.17	83.9
Hf	0.34	0.00	0.12	0.86	0.01	0.14	87.9
Pd	0.05	-0.04	0.03	0.73	0.43	0.22	78.4
Rb	0.51	0.25	0.29	0.55	0.02	0.04	71.3
Sr	0.17	0.10	0.31	0.82	0.11	0.16	84.1
Tl	0.22	-0.03	0.51	0.72	-0.01	-0.08	83.9
Zr	0.30	0.12	0.15	0.84	0.07	0.16	86.9
As	-0.42	0.11	0.33	0.02	0.72	-0.15	83.5
Co	0.35	0.44	0.28	0.23	0.45	0.31	74.1
Ge	0.18	0.29	0.19	0.04	0.86	0.06	89.8
V	-0.23	0.30	0.10	-0.13	0.59	0.53	80.2
K	0.08	0.31	0.30	0.38	0.11	0.67	80.2
Na	0.28	0.18	0.11	0.10	0.15	0.84	85.9
Sc	0.29	0.14	0.11	0.19	-0.06	0.69	63.8
Ti	0.50	0.21	0.10	0.03	-0.03	0.76	88.7
Total variability (%)	15.6	11.3	20.1	16.8	8.03	9.61	81.5
Eingene value	15.2	5.36	4.36	2.46	1.91	1.71	

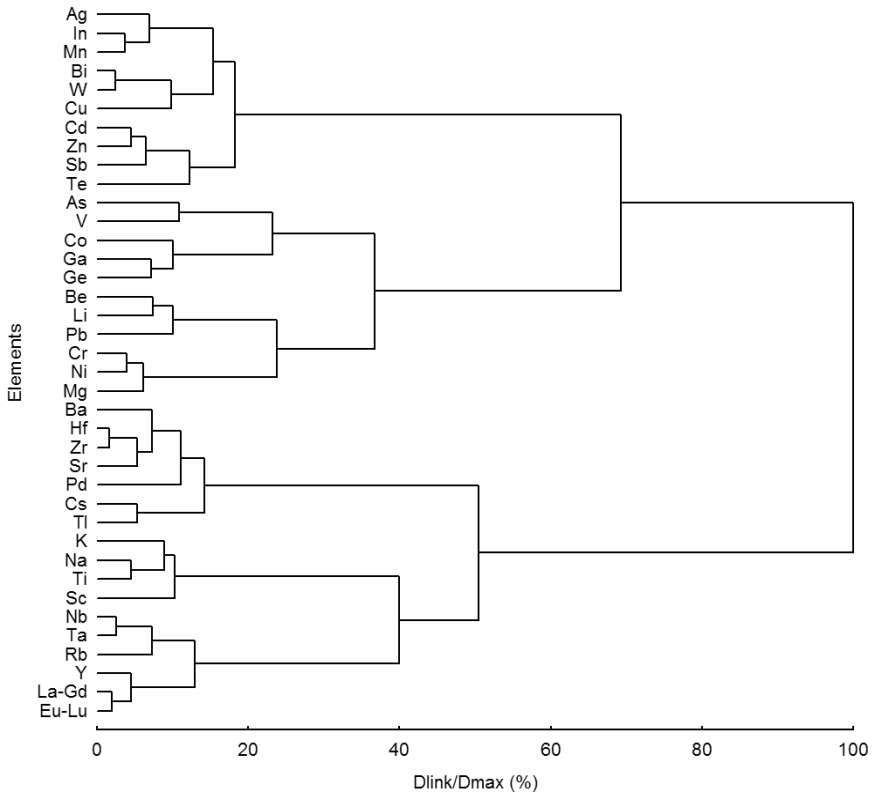

Figure 14. Dendrogram for dominant clusters.

4.2.3. Areal Distribution Mapping of the Factors

For the spatial distribution of the factor scores, universal kriging with the linear variogram interpolation method was applied for the construction of maps showing the spatial distribution of factor scores (F1-F6).

Distribution of Factor 1 [Ga-Nb-Ta-Y-(La-Gd)-(Eu-Lu)] clearly expresses the typical connection of some basic Earth forming process, due to the incorporation of the rare earth. Their sources are mainly natural phenomena such as rock weathering and chemical processes in soil. White (2013) explains that many sedimentary rocks have rare earth patterns that are similar to each other, and to that of the continental crust. However, the geochemistry of the rare earths in the investigate area doesn't dominate on the sedimentary rocks. Occurrence of this factor is typical for the Proterozoic formations (gneisses, granites and shale) (Figure 15). Because the rare earths are highly insoluble and immobile, rare earth patterns often remain unchanged during

metamorphism. Hence rare earth patterns can provide information on the premetamorphic history of a rock. Indeed, even during the production of sediment from crystalline rock, the rare earth patterns often remain little changed, and rare earth patterns have been used to identify the provenance, i.e., the source, of sedimentary rocks. A unique occurrence is correlation of these elements with Ta and Nb. Tantalum and niobium are present in anomalously low concentrations in magmas associated with subduction zones (indeed, this is considered a diagnostic feature of subduction-related volcanism). As the Figure 15 visualizes the maximum patterns for elements deposition, Proterosoic gneisses were most dominant areas with F1 enrichments.

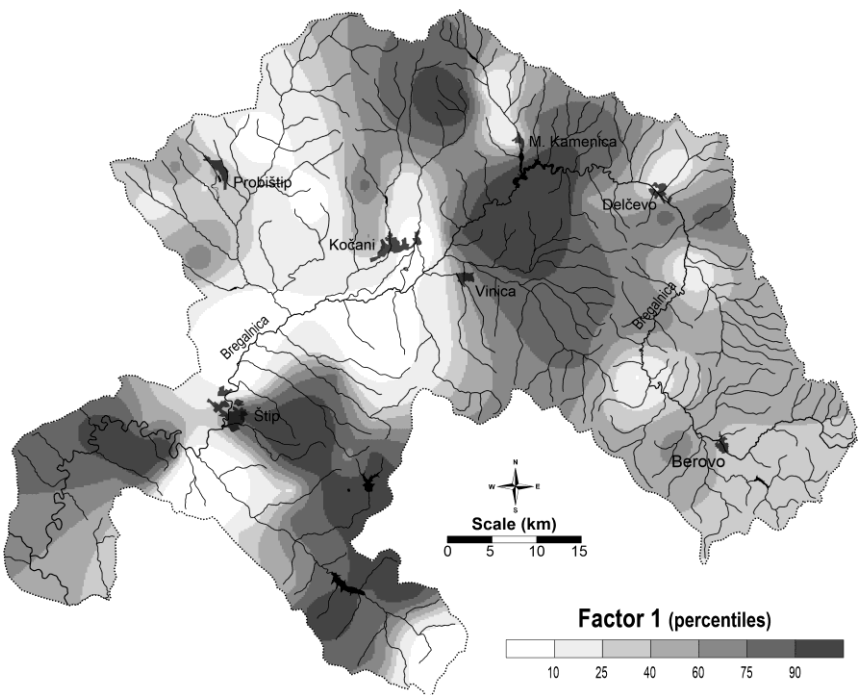

Figure 15. Distribution patterns for Factr 1: Ga-Nb-Ta-Y-(La-Gd)-(Eu-Lu).

The second geochemical association (Be-Cr-Li-Mg-Ni) relays also on the effect from the wind-blowing dust from the surface soil layers. These determined elements are considered “natural” because their origin is primarily crustal-soil particles suspended and transported by wind. High factor loadings are related to some old formation such as Paleogene flysch and Quaternary

unconsolidated sediments (Figure 16). The anomaly of the Cr-Ni distribution was severally times improved along the Vardar zone repeatedly demonstrated in Macedonia (Stafilov et al., 2010; Balabanova et al., 2010; 2011; et al., 2013, 2015), and in Balkan countries. Higher contents of aforementioned elements found in distributed dust along the valleys of rivers Vardar and Crna, where constant flow of air masses in both direction is present (Lazarevski, 1993), indicate an influence of lithological background (Bačeva et al., 2012). The specific distribution of Be-Cr-Li-Mg-Ni was extended in the SE direction in the Berovo town vicinity. There are data that suggest a poly-metallic enrichment in this area (Arsovski, 1997). These elements can be connected to air pollution as well. Most emissions of these elements to the environment originate from local sources, mainly from mines and smelters (Stafilov et al., 2014). Furthermore, this association can be used for the identification of the poly-metallic anomalies as secondary occurrence.

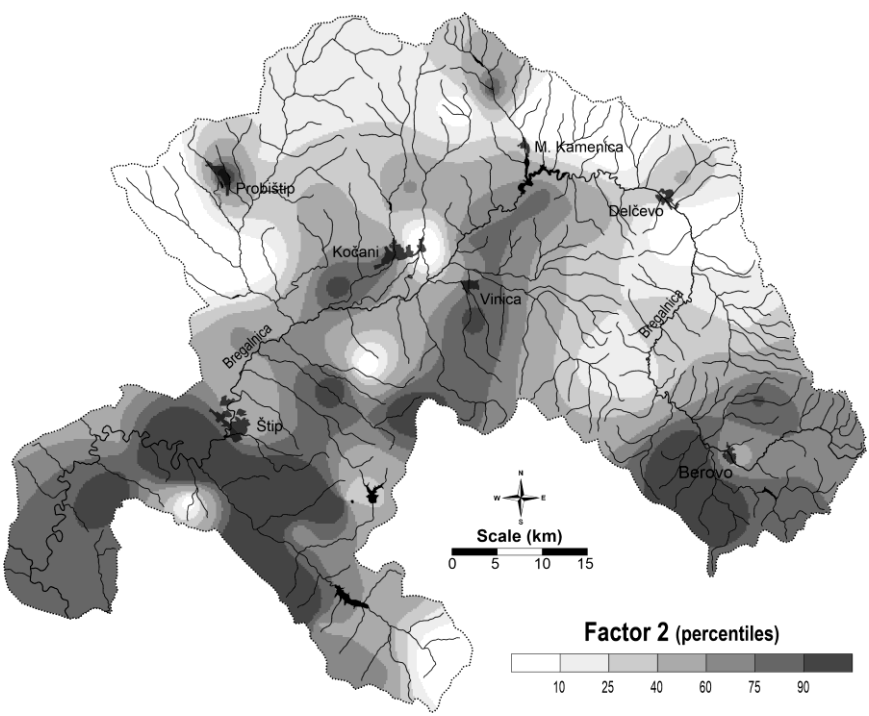

Figure 16. Distribution patterns for Factor 2: Be-Cr-Li-Mg-Ni.

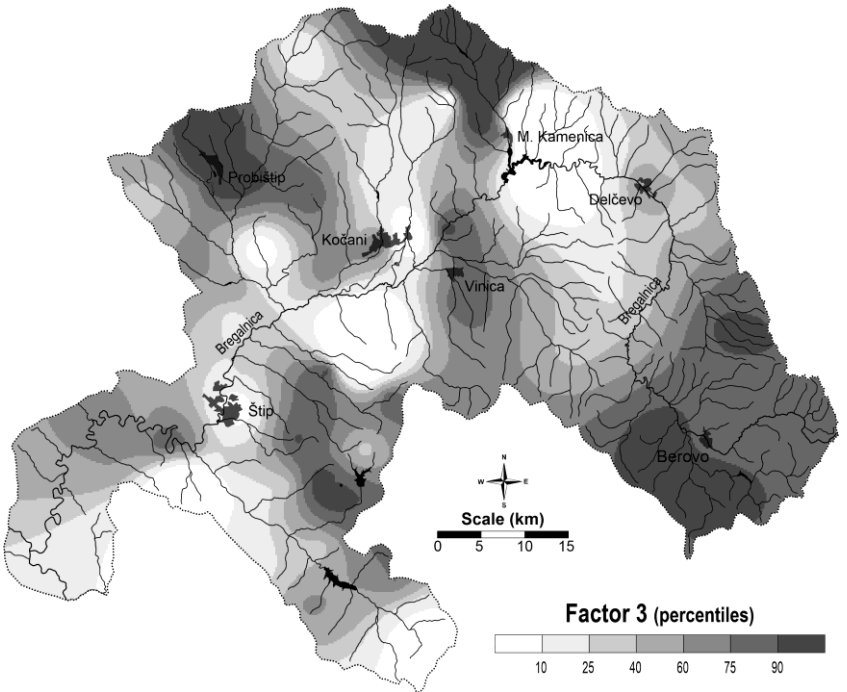

Figure 17. Distribution patterns for Factor 3: Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn.

Factor 3 (Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn) was the most heterogenic geochemical association. Enriched deposition occurred dominantly on Rifeous shale (Figure 17). These very old rocks occur as transition lithologic units between the Neogene and Paleogene volcanism in the investigated area. Pb-Zn mines "Sasa" and "Zletovo" are located in the areas with dominantly presence of the Oligocene and Neogene volcanism appears sequentially and in several phases forming sub-volcanic areas. On the other hand, the pyroclastites are most frequently found in the Kratovo-Zletovo volcanic area, where the dacites and andesites are the oldest formations. This geochemical association links typical elements which are normally associated with air pollution (Cd-Pb-Zn), and usually are not influenced by lithological background (Figure 17). Spatial patterns show intensive deposition in the area of poly-metallic hydrothermal exploitations, Sasa, Zletovo and Bučim (Figure 17). Thus, this factor can explain and mark the anthropogenic affects on air pollution. These anthropogenic anomalies have an historical record for decades continuously introduction of significant emission of dust particle with enriched contents of Cd, Pb and Zn. Also, this investigation fortifies an extended anthropogenic

association (Ag, Bi, In and Mn) that implement and some other anthropogenic activities such as agricultural activities (use of urban sludge, manure and phosphate fertilizers) or their occurrence can be a secondary affection from mine poly-metallic pollution. Affiliation of Te and W to this group, spread up a novel poly-metallic/metalloid anomaly in the Berovo region. For all elements that associate in this group, enriched values deposition occur in this mention area. Almost twenty years ago, Arsovski (1997) point on poly-metallic enrichment in this area so called Vladimirovo-Berovo, during the tectonic investigation. The present investigation also interpolates this area as metallic's/metalloids enriched zone, with emphasis on the anthropogenic elements.

The occurrence of Factor 4 (Ba-Cs-Sr-Rb-Pd-Tl-Zr-Hf), presents an interesting geochemical association, incorporating the incompatible/ hygromagmatophile elements. Elements enrichments occur in areas with predominance of Neogene pyroclastite and sediments (Figure 18).

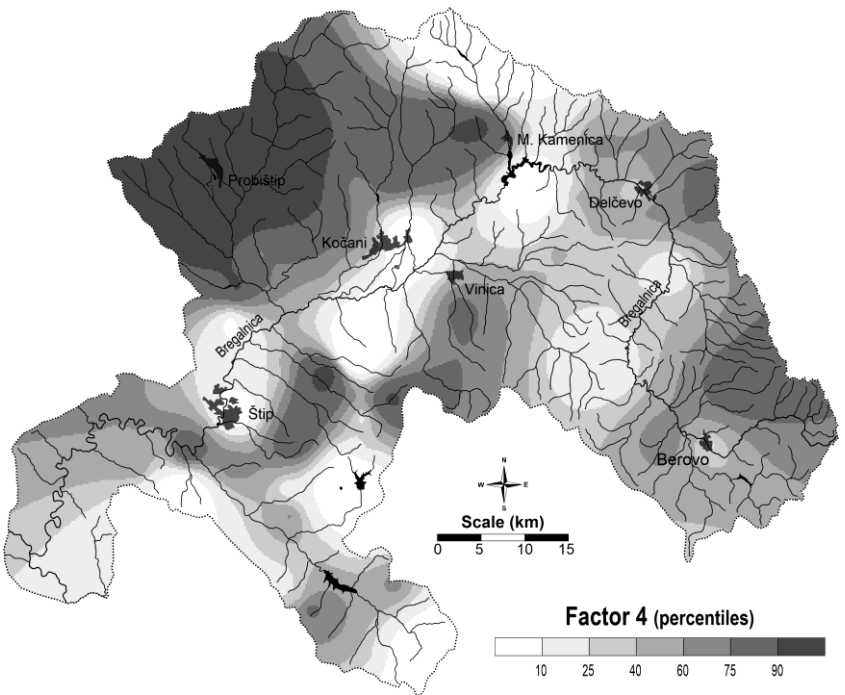

Figure 18. Distribution patterns for Factor 4: Ba-Cs-Hf-Pd-Rb-Sr-Tl-Zr.

According to generalized geology map (Figure 2), Kratovo-Zletovo region is the unique district in the region located along the continental margin and is closely related to the Tertiary volcanoes and hydrothermal activities in this area. According to Dumurdzanov et al., (2004) the pyroclastites are most frequently found in the Kratovo-Zletovo volcanic area, where the dacites and andesites are the oldest formations. These polyphasal Neogene deformations through the insignificant movements associated with the volcanic activities had direct influence on the gradual formation of the reefs and the formation of deposits in the Zletovo area. Spatial patterns are extended in eastern direction, due to the most common winds from western direction with frequency of 199‰ and speed of 2.7 m/s (Lazarevski, 1993). Barandovski et al., (2015) singled out lithogenic markers of Ba-Cs association enriched in areas of felsic volcanic rocks (andesite) and their pyroclastic rocks primarily occupies the Kriva Reka basin, bordered with the Kratovo-Zletovo region. The same geochemical anomaly occurs in smaller zones (Kožuf and Mariovo regions).

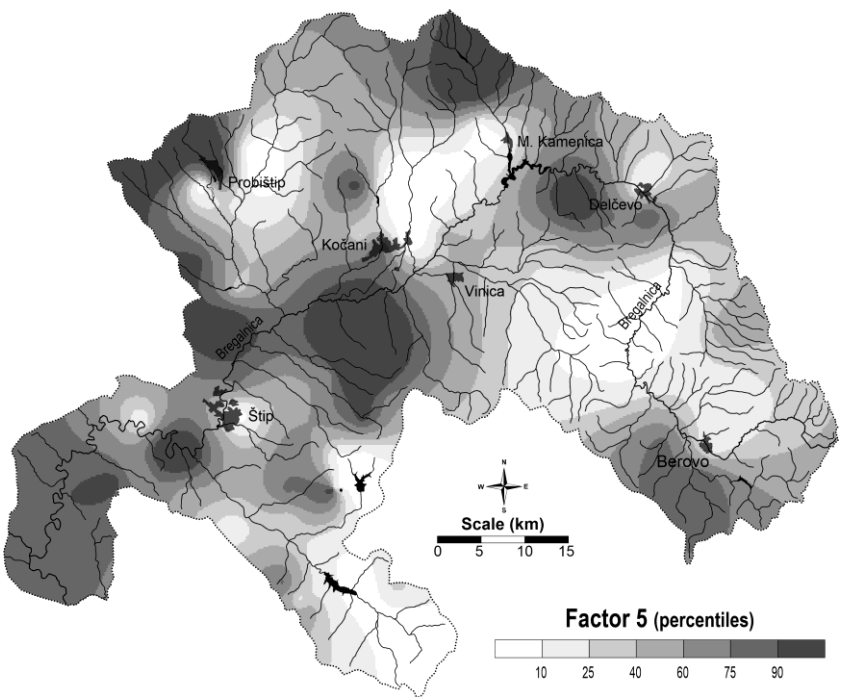

Figure 19. Distribution patterns for Factor 5: As-Co-Ge-V.

Factor 5 associates the following elements, As, Co, Ge and V, with predominant occurrence on Rifeous shales (Figure 19). This kind of geochemical *fingerprinting* occurs along the whole course of the Bregalnica river. Accordingly, the resulting areal distribution map used to support with high certainty the assessment for poly-metallic enrichments as ascribed to urbanization, including vehicular emissions and incinerators and industry. Comparative analysis for the areal patterns singled out a very similar behavior of the Factor 3 and Factor 5. Clustering method was very useful for determination of both geochemical associations. Dendrogram displays a very close interpolation of the mention elements from F3 and F5. Furthermore, there is a strong interconnection between the anthropogenic and lithogenic fingerprinting. Basically, the element geochemistry intermediate between atmospheric emissions and lithogenic wind-blow dusting. Therefore, the As-Co-Ge-V distribution can be used as proposed mechanism for possible tracking of anthropogenic poly-metallic enrichments.

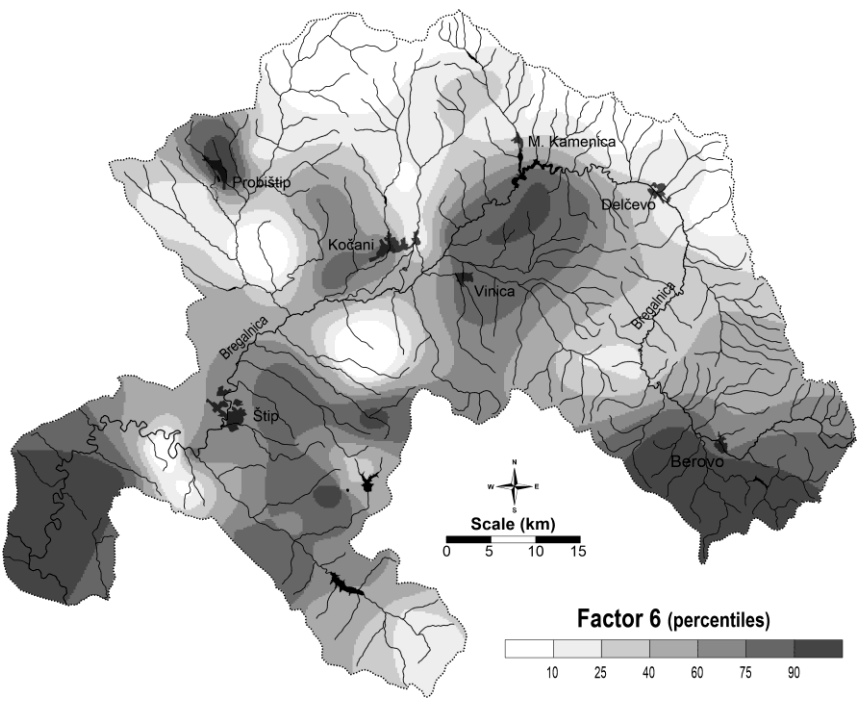

Figure 20. Distribution patterns for Factor 6: K-Na-Sc-Ti.

The sixth factor includes K-Na-Sc-Ti. Although it is the least distinguished factor; nevertheless this geochemical association is related with the lithogenic dominance of the Neogene sediments and Paleogene flysch as given in Figure 20. Their occurrence in the environment is usually correlated to the major minerals in basaltic and ultramafic rocks have two kinds of cationic lattice sites: small tetrahedral sites occupied by Si and Al (White et al., 2013). Because of their solubility, they are quite mobile during metamorphism and weathering. Basic hotspots were correlated with the sedimentary mineralization along the whole course of the Bregalnica river terraces. Quaternary terraces in Kočani valley are also marked with this lithogenic marker.

CONCLUSION

The focus of this investigation has been given on determinating and mapping of lithogenic and anthropogenic atmospheric distribution of 69 elements in the Bregalnica river basin, Republic of Macedonia, using moss and attic dust as sampling media. Using moss biomonitoring technique, several highlights could be point out:

- The specific poly-metallic enrichments occur in the areas of the very old Neogene volcanism and Paleogene volcanism. Strong relations occur between these dominant lithological units and the hydrothermal exploitation in the area of Pb-Zn Sasa mine, Pb-Zn Zletovo mine and Bučim copper mine.
- The multivariate approach and spatial distribution *hunting*, singled out seven dominant cluster for the atmospheric distribution of total of 69 analyzed elements: F1: Al-Be-Co-Fe-Ga-Ge-Li-Mg-Sc-Ti-V-Y- (La-Gd)-(Eu-Lu); F2: Ba-Bi-Cd-Pb-Sb-Zn; F3: As-Cs-Rb-Tl; F 4: Ca-Sr-B; F5: Hf-Zr; F6: Cr-Cu-Ni; F7: Br-I. Intensive effects are determined for the factor 1 distribution that is strongly correlated with dominant lithologic unit for whole territory of the Republic Macedonia (extracted as dominant lithogenic marker).
- The extracted geochemical association (including Cd-Pb-Zn-Sb) was defined as dominant anthropogenic marker for the atmospheric elements distributions. Significantly polluted sub-areas were determined, affected with significantly enrichments in Pb and Zn

atmospheric depositions and lower enrichments of Cd and Sb. "Zletovo" mine area and "Sasa" mine area were singled out as poly-metallic enriched areas; not only from the anthropogenic emission, but also the influence from the wind-blow dusting from soil surface was detected.

The historical records for elements deposition singled out the following conclusions:

- The activities carried out in the areas of poly-metallic hydro-thermal exploitation (*Sasa*, *Zletovo* and *Bučim* mines) lead to increased content of certain heavy metals in the atmosphere, which was determined through the monitoring of attic dust samples. The enforcement of statistical factor analysis singled out one dominant anthropogenic group of elements (Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn). The fine particles from the mining operations are spread in the atmosphere carried by wind. Microparticles penetrate the human body through inhalation via the respiratory system.
- The dominant lithogenic markers that characterized the investigated area were extracted as following: Ga-Nb-Ta-Y-(La-Gd)-(Eu-Lu), Ga-Nb-Ta-Y-(La-Gd)-(Eu-Lu), Ba-Cs-Hf-Pd-Rb-Sr-Tl-Zr and K-Na-Sc-Ti. The geochemistry of the As-Co-Ge-V was also assumed as secondary affection from the anthropogenic emissions, also correlated with the dominance lithogenic occurrence of the Oligocene and Neogene volcanism.

Future work will allow refinement and more precise "fingerprinting" of geochemical processes, including the role of dust emissions and trace element-enriched accessory minerals in metasomatic events. Also, experiments are needed to extend the partition coefficient determinations to much greater assurance, to resolve controversies over the geochemical evolution.

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