

Chapter 3

Environmental Pollution of Soil and Anthropogenic Impact of Polymetallic Hydrothermal Extractions: Case Study—Bregalnica River Basin, Republic of Macedonia



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3.1 Introduction

The distribution of certain chemical elements, which in higher contents represent hazard to the environment, causes certain unwanted consequences on human health (Brulle and Pellow 2006; Duruibe et al. 2007). Pollution of the environment with toxic metals has been topic of numerous studies which specify as their main subject matter the industrialized areas, the areas where exploitation and processing of natural resources (oil, ore, etc.) take place or highly populated areas where the traffic and communal waste represent the main sources of metals (Alloway and Ayres 1997; Siegel 2002; Järup 2003).

The exploitation of mineral resources by man leads to excavation, separation, transportation and dispersion of the metals contained in the fine dust (microparticles). In this way the metals are introduced into the environment in much greater contents than normally found in nature (Sengupta 1993; Salomons 1995). With the passage of time and the long-term activities of the human factor, the contents of certain metals have been completely and permanently changed in relation to their natural existence in the environment. These changes can have a significant influence

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on the physiology and ecology of the organisms adapted to survive in thus created conditions of higher metal contents or as VanLoon and Duffy (2000) term it, *specific environment*. The distribution of the different chemical elements, including the potentially toxic metals, creates characteristic conditions for the living organisms. Taking into account that their contents in the environment is variable, it is important to identify the regions with changed contents, differing from the natural distribution of the elements in the different segments of the biosphere (Athar and Vohora 1995; Siegel 2002; Artiola et al. 2004).

The anthropogenic activities for exploitation of natural resources and their processing through adequate technological processes and management of the waste produced by the same represent a global problem of pollution of the environment. Republic of Macedonia does not diverge from this global framework of pollution of the environment with certain toxic metals. The studies implemented so far show that certain areas on the territory of the Republic of Macedonia are stricken by the anthropogenic introduction of different chemical elements in high contents in the air and soil (Stafilov 2014; Stafilov et al. 2003, 2008a, b, 2010a, b, c, 2011; Balabanova et al. 2010, 2011, 2012, 2013, 2014a, b, 2016a, b, c, 2017; Angelovska et al. 2016; Barandovski et al. 2013).

In the region of the basin of the river Bregalnica in the eastern part of the Republic of Macedonia, there are several significant emission sources of potentially toxic metals and other chemical elements in the environment, which are the following: 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 Probishtip. 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 in the open air. 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. The exposure of mining and flotation tailings, as well as the exposure of the open ore pit to the air streams, leads to distribution of the finest dust (Sengupta 1993; Athar and Vohora 1995). On the other hand, rain waters wash the ore tailings and make water extraction of the available metals. In this way, metals and other potentially toxic chemical elements are introduced into the soil and waters (surface and underground). At the same time, the particles from flotation and mining tailings are continually distributed by the winds. These particles, depending on the weather conditions, can be distributed in the air for longer or shorter periods of time and, thus, deposited on smaller or greater distances from the emission source (Van het Bolcher et al. 2006).

The most suitable technique for this type of study is application of relevant monitoring that will enable more lasting and efficient determination of the environment quality in the relevant investigated area (Thothon 1996; Artiola et al. 2004). Monitoring programmes have been implemented as part of numerous analytical research activities since long time ago, but in the last decades their application has been highly promoted both on regional and global level (Koljonen 1992; Sengupta 1993; Hoenig 2001). This is due to the fact that monitoring programmes do not require usage of expensive technical equipment, while analytical results reflect the situation for a longer period of time.

The main goal of this study was to determine the lithogenic and anthropogenic distribution of 69 elements in alluvial, automorphic and paddy soil from the Bregalnica river basin.

3.2 Materials and Methods

3.2.1 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) \times 200 km (S–N), that is, a total of ~ 4000 km², within the following geographic coordinates N: 41°27'–42°09' and E: 22°55'–23°01' (Fig. 3.1). The region of the investigated area is geographically composed of several sub-regions. The area is characterized by two valleys—Maleševska and Kočani valley. The Maleševska 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 Maleševski mountains on the east, by the Ograzhden mountain on south-southeast and by Plačkovica and Obozna on the west. The Maleševska valley is a specific geographical area, characterized by mountain, hilly, sloping and plain parts. The Kočanska valley includes the middle course of the Bregalnica river, between the mountains Plačkovica to the south and Osogovo to the north. The Maleševski 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 river Bregalnica. The valley bottom, that is, its plainest part, occupies an area of 115 km² and represents an important agricultural cultivated fertile area. The paddy soil of Kočani Field was estimated to originate from the composite material of the sediment derived from igneous, metamorphic, and sedimentary rocks located in the Kočani region. The sediment material was transported by the Bregalnica river and its tributaries and was deposited in the Kočani depression (Dolenec et al. 2007; Serafimovski and Aleksandrov 1995; Šmuc et al. 2012). The lowest point above sea level in the area is located at the spot where the Zletovska river flows into the river Bregalnica (290 m).

The river Bregalnica 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 km². The more important tributaries are from the right side (Zletovska, Kočanska and Orizarska rivers) and from the left side (Osojnica and Zrnovska rivers).

The source of the river Bregalnica is located in the forest area of the Maleševski mountains near the Bulgarian border, east of town of Berovo, under the Čengino Kale peak, at an altitude of about 1690 m. Its upper part 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

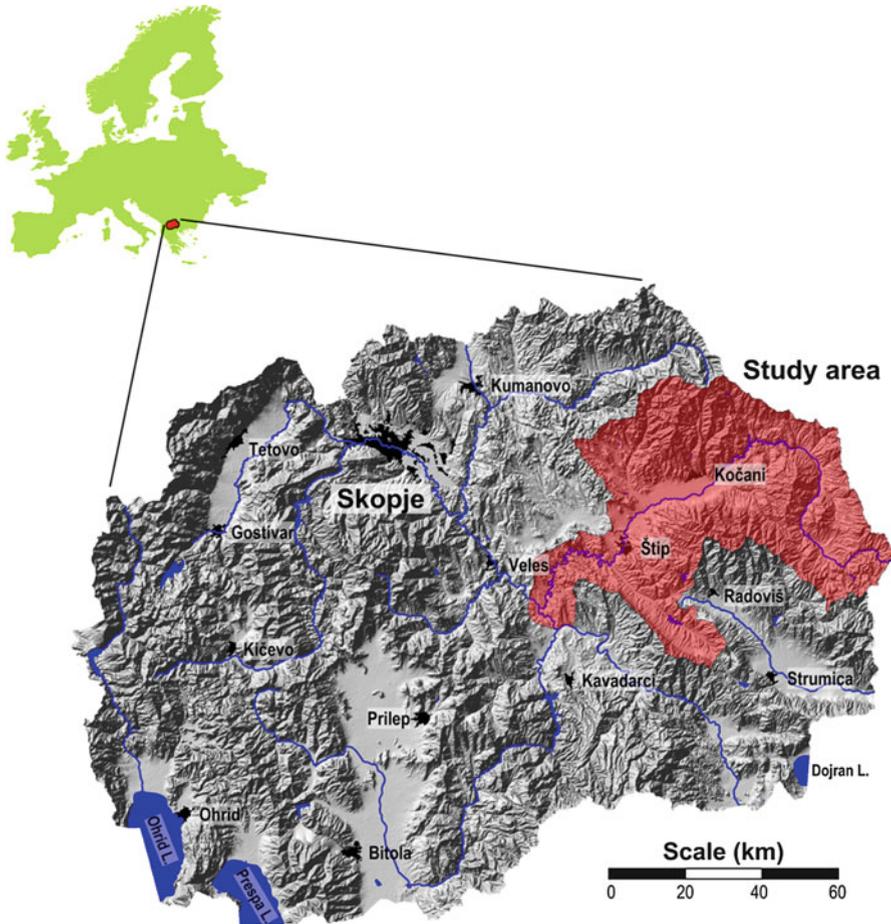


Fig. 3.1 The investigated area on the territory of the Republic of Macedonia

whole area is intensively cultivated with cultures for the irrigation of which the water from the river Bregalnica 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 2–3 m, in which the river bed is positioned. From Budinarci all the way up to the point before the Delčevo 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 Mitrašinci, the course of the river Bregalnica becomes curved, as a result of which at certain points real meanders and narrow rocky ravines are formed and the sides of which at certain points are vertical and with a relative height of 60–80 m.

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 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 Delčevo Field, before the village of Trabotivište, the river Bregalnica deposits huge quantities of material along the whole field, up to the mouth of the Očepalska 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 Delčevo Field, the river waters are also extensively used for irrigation based on primitive dams and ditches, for example, the ones near Trabotivište and Delčevo. The water is almost completely used for irrigation of the cultivated low terrace (2–3 m) on the right river side.

From the mouth of the Očepalska 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 the village of Gradsko, at an altitude of 137 m. Along the river course of the river Bregalnica, 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 m³ water.

Taking into consideration the diverse morphological–geographical structure of the investigated area, the climate conditions also vary in the different subregions. Generally, the region is characterized with moderate continental climate. The altitude varies from 290 m in the plain of the Kočani valley up to 1932 m (Kadaica) on the Maleševski mountains. The average annual temperature also varies in the different subregions. In the Kočani valley, the average annual temperature is about 13 °C, the warmest months in the year are July and August with an average temperature of 25 °C, and the coldest month is January with an average temperature of about 1.2 °C (Environmental Quality in Republic of Macedonia 2016). In the region of Štip, 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 (Environmental Quality in Republic of Macedonia 2016). 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 (Lazarevski 1993).

The average annual precipitation amounts to about 500 mm with significant variations from year to year, as well as in the different subregions (Lazarevski 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 (Lazarevski 1993). 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, 65% of the populated areas belong to the category of urban areas, while 35% of the total populated areas are categorized as rural areas. 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 Fig. 3.2, in yellow, as open areas. About 30% belong to the forest regions, localized around the Maleševska valley, represented by the Maleševski

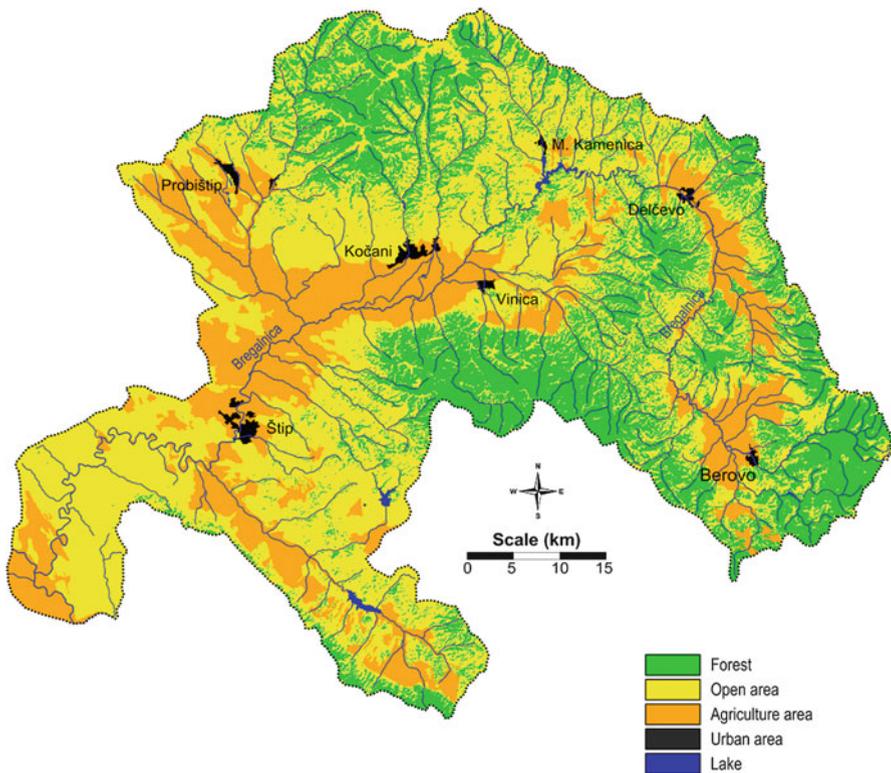


Fig. 3.2 The region of the investigated area including the type of land use

mountains, and then around the Kočani valley, represented on one side by the Osogovo mountains and by Plačkovica on the other side. Kočani valley is one of the most agriculture used lands along the Bregalnica river basin.

The most severely polluted tributaries of the Bregalnica river are the Kamenica river in the NE part of the Bregalnica river drainage basin and the Zletovska river on the western side of Kočani Field. Both tributaries are severely impacted by acid mine drainage. The Kamenica river drains mine waste, including tailings, mill sewages and mine effluents of the Pb–Zn polymetallic ore deposit Sasa, directly into the artificial Kalimanci Lake constructed for the purposes of irrigating the paddy fields during the dry season. Upon mixing with the lake water, the concentrations of the pollutants decline. For this reason the Bregalnica river, when it leaves the Kalimanci Lake, is less polluted than the Kamenica river. The Zletovska river originally drains the central part of the Kratovo–Zletovo volcanic complex; it also drains the abandoned old mine sites and bare tailings as well as the effluents from the Pb–Zn Zletovo mine and its ore-processing facilities including flotation tailings. Acid mine water and the effluents from tailings were discharged untreated into the riverine water that was used for the irrigation of the paddy fields of the western side of Kočani Field. The pollution of the Zletovska river by acid mine drainage is easily recognizable in the field. The bed sediments are coated with Fe and Mn oxides/hydroxides, which are the major sink for contamination with several trace elements. The Zletovska river, which is more polluted than the Bregalnica river, adds water to the Bregalnica river in the western edge of Kočani Field at Krupište. Two small tributaries, the Orizarska and Kočanska rivers, which drain the southern part of the Osogovo mountains as well as the more or less untreated municipal wastes and domestic sewage of the cities of Kočani and Orizari were also used for irrigation of the paddy fields located in the NE part of Kočani Field (Dolenec et al. 2007; Šmuc et al. 2012).

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.

3.2.2 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 the Bučim, Damjan and Borov Dol districts and in the zone of Toranica, Sasa, Delčevo and Pehčevo (Boev and Yanev 2001; Dumurdzanov et al. 2004; Serafimovski et al. 2006). 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 (Boev et al. 1992). Volcanic rocks are categorized as the following: andesite, latite, quartz-latite and 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 Rakičević et al. (1968) and presented in Fig. 3.3.

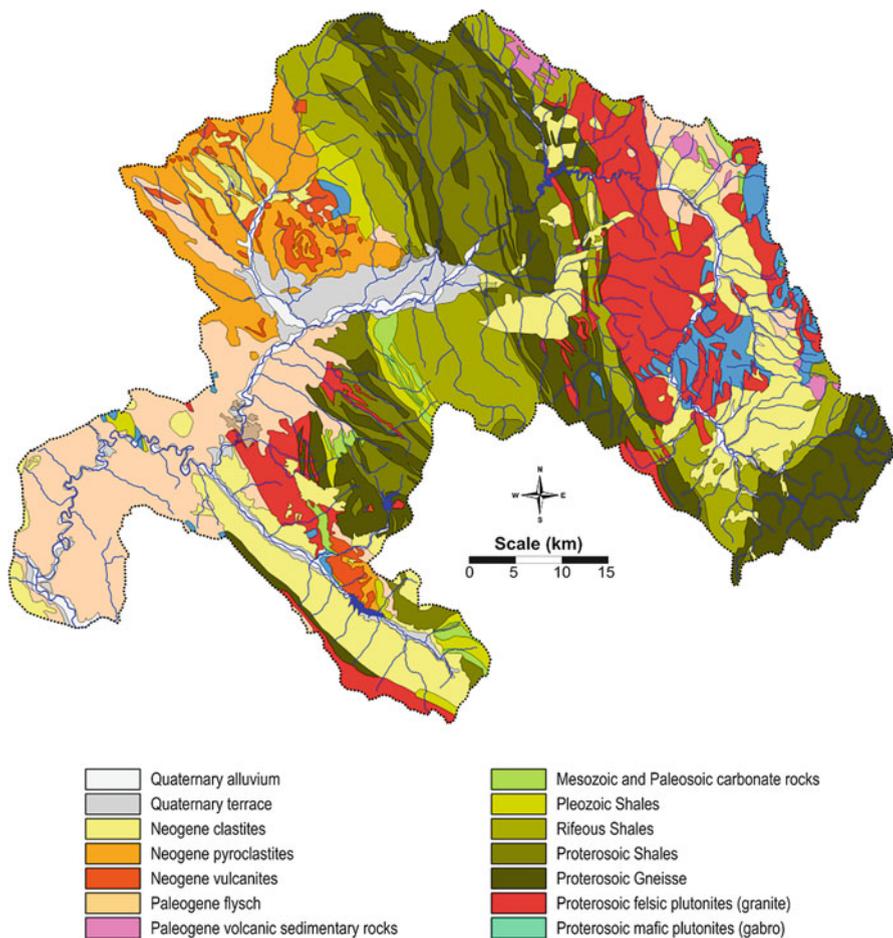


Fig. 3.3 Generalized geology of the whole investigated area

3.2.3 Samples Analysis

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 and Zr. The content of these elements was determined in surface soil 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 production of maps for the distribution and deposition of the analysed elements in the investigated area.

3.2.3.1 Soil Samples

In the period between March and November 2012, samples of topsoil and subsoil were collected in the investigated area. A total of 155 locations compose the network of locations for taking samples of soil from the surroundings and the basin of the river Bregalnica (Fig. 3.4). The location network is with a density of 5×5 km, in

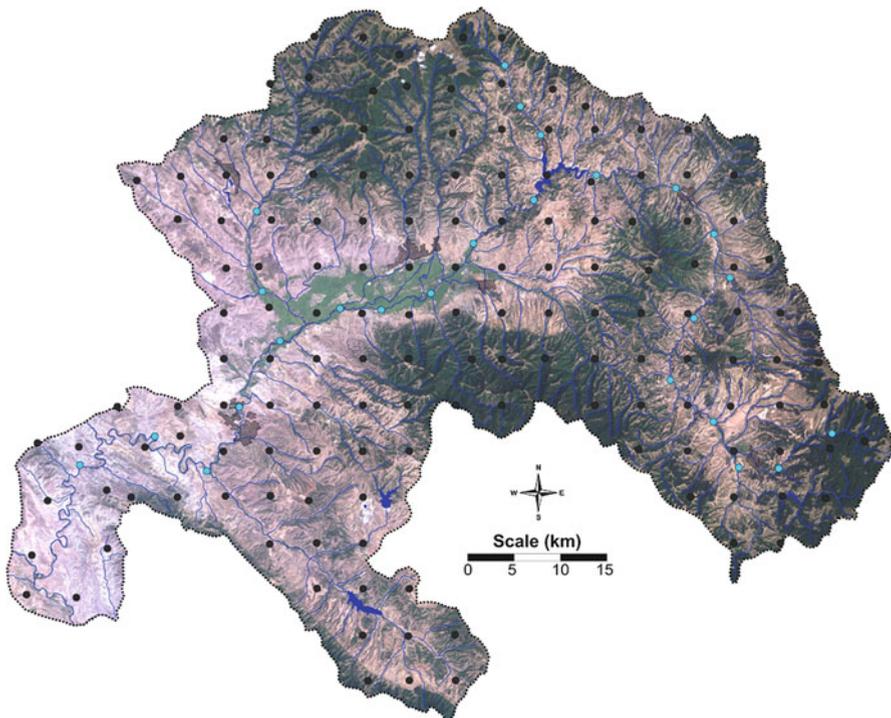


Fig. 3.4 Locations for collection of soil samples in the investigated area

order to enable mapping and specifying the distribution of the chemical elements examined. On each location (for automorphic soil) was taken a sample of topsoil, at depth of 0–5 cm, and a sample of subsoil, at depth of 20–30 cm. The collection of soil samples was undertaken in accordance with the relevant standards for collection of this type of samples from the environment (Reimann et al. 2012). Near-surface paddy soils (0–20 cm in depth) were sampled with a plastic spade to avoid heavy metal contamination. Near-surface soils were collected because in the agricultural soil it is not possible to distinguish the A, B and C horizon. The locations for collection of soil samples were previously determined by constructing a network for sample collection. Depending on the conditions on the site and the accessibility, that is, passability of the same, the samples were collected in the surroundings of the specified locations, recording the relevant coordinates. On every location, with each sample of topsoil and subsoil, five subsamples were collected. At the specified location, a square with area 10×10 m was formed. Four samples were collected from the angles of the square, while the fifth subsample was collected from the intersection of the square diagonals. In this way, a representative composite sample of topsoil (0–5 cm) was formed. From the same holes formed with the taking of the topsoil subsamples, the subsoil subsamples were also collected, for the formation of a representative sample of a subsoil sample.

3.2.3.2 Analytical Reagents

All used reagents and standards are with the following analytical purity level: nitric acid, HNO_3 , 69%, ultrapure (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 and $10 \mu\text{g L}^{-1}$) and *series 2* (10, 20, 30, 50 and $100 \mu\text{g L}^{-1}$) for elements in traces (determined using ICP-MS) and for the remaining elements *series 3* (0.1; 0.2; 0.3; 0.5; 1 mg L^{-1}), *series 4* (1, 2, 3, 5 and 10 mg L^{-1}) and *series 5* (10, 20, 30, 50 and 100 mg L^{-1}) for the elements in macro contents.

3.2.3.3 Sample Preparation

The preparation of the collected samples for the analysis of the 69 elements was implemented by their cleaning, drying, breaking and digestion. For digestion of soil samples, method of open digestion with mixture of mineral concentrated acids was applied. The samples brought in the laboratory were subjected to cleaning and homogenization and drying at room temperature, or in a drying room at 40°C , to

a constantly dry mass. Then the samples were passed through a 2 mm sieve and finally were homogenized by grinding in a porcelain mortar until reaching a final size of the particles of 25 μm . Following the physical preparation, the samples were chemically prepared by wet digestion, applying a mixture of acids in accordance with the international standards (ISO 14869–1: 2001). 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.

3.2.3.4 Instruments Used for Determining the Content of Elements

The analysis of the digested samples is conducted by applying atomic emission spectrometry with inductively coupled plasma (ICP-AES) and mass spectrometry with inductively coupled plasma (ICP-MS). For each element analysed, previous optimization of the instrumental conditions was performed. In all samples, the contents of a total of 23 elements were analysed: 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 ICP-AES. By applying ICP-MS, a total of 69 isotopes were analysed, 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 and Zr.

The instrumental and operating conditions for each of the above-mentioned techniques are given in Table 3.1.

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 3.2.

Both certified reference materials (NIST 1643c) and spiked intra-laboratory samples were analysed at a combined frequency of 20% of the samples. The recovery for all of the analysed 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).

3.2.4 Data Processing

All data on the content of the investigated elements were statistically processed using a statistical software (Stat Soft, 11.0), by applying parametric and non-parametric analysis. Basic descriptive statistical analysis was conducted on the values of the contents of the elements in all types of samples. At the same time, normalization tests were made, and based on the obtained results and the visual check of distribution histograms, the distribution of data on independent variables (elements' contents) was determined.

Table 3.1 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 (iso- tope)/s	/	300	
Repetitions measurement	3 per point		
Conditions for programme			
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,	
Ca	370.602	¹⁴⁰ Ce, ⁵⁹ Co, ⁵³ Cr, ¹³³ Cs, ⁶³ Cu, ¹⁶³ Dy, ¹⁶⁶ Er, ¹⁵³ Eu, ^{56/57} Fe,	
Fe	238.204	⁶⁹ Ga, ¹⁵⁷ Gd, ⁷² Ge, ¹⁷⁸ Hf, ^{201/202} Hg, ¹⁶⁵ Ho, ¹²⁷ I, ¹¹⁵ In, ¹⁹³ Ir,	
Mg	280.270	¹³⁹ La, ⁷ Li, ¹⁷⁵ Lu, ⁵⁵ Mn, ⁹⁵ Mo, ⁹³ Nb, ¹⁴⁶ Nd, ⁶⁰ Ni, ¹⁸⁹ Os,	
K	766.491	^{206/207/208} Pb, ¹⁰⁵ Pd, ¹⁴¹ Pr, ¹⁹⁵ Pt, ⁸⁵ Rb, ¹⁸⁵ Re, ¹⁰³ Rh, ¹⁰¹ Ru,	
Na	589.592	¹²¹ Sb, ⁴⁵ Sc, ⁷⁷ Se, ¹⁴⁷ Sm, ¹²⁰ Sn, ⁸⁸ Sr, ¹⁸¹ Ta, ¹⁵⁹ Tb, ¹²⁵ Te, ⁴⁷ Ti,	
P	213.618	²³² Th, ²⁰⁵ Tl, ¹⁶⁹ Tm, ⁵¹ V, ¹⁸² W, ⁸⁹ Y, ¹⁷² Yb, ⁶⁶ Zn, ⁹⁰ Zr	

Data transformation means performing the same mathematical operations on each component of the original data. If the original data are simply multiplied or divided by a specific quotient or they are continually subtracted or added, then we are talking about linear transformations. Yet, these linear transformations do not change the data form (i.e. their distribution) and, accordingly, do not help in the normalization of the data distribution. This is most often characteristic for the data on certain variables from the environment whose distributions are log-normal or positively curved. Therefore, it is required before processing, first to subject the data to transformation, that is, perform normalization of their distributions. Logarithmic transformation is widely applied in order to normalize the positively skewed data distributions. The aim of the application of data transformation is to actually decrease the difference between the extreme values. For data normalization, the method of *Box-Cox* transformation (Box and Cox 1964) was also applied.

The level of correlation of the values of the chemical elements' content in all types of samples was estimated using bivariate statistics (using linear correlation of

Table 3.2 Calculated instruments lower detection limits for the analysed elements

Element	Limit of detection, $\mu\text{g/L}$
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

coefficients, r), with significance level $p < 0.05$ and $p < 0.01$. For a clearer overview, the correlation coefficients are represented in a matrix of correlation coefficients. In the case of a large number of variables (e.g. $n > 20$), bivariate analysis is not useful. Therefore, the application of multivariate analysis enables reduction of the number of variables by creating new synthetic variables, again dependent on the correlation (r). For processing of certain data for comparative analysis, the F -test was applied.

For the reasons of this study, several methods of multivariate analysis were used: factor analysis (FA) and cluster analysis (CA).

The primary aim of factor analysis is to explain the variation in a set of multidimensional data using as few factors as possible and to reveal the hidden data structure (Žibret and Šajin 2010). In other words, the factor analysis is performed on a great number of variables in order to create a small number of new, synthetic variables, called factors. The factors contain a great deal of information about the original variables, and they may have some significance. Factor analysis is performed on variables that are standardized to zero values of a standard deviation unit. Data can be transformed and/or standardized (Šajin 2006).

Cluster analysis (CA) was used with a similar aim as factor analysis, in case high values for the loadings of certain variables were not acquired. In such case is applied the data processing method based on a matrix of remoteness (distances) or nearness (similarities). How the dependence between the variables will be expressed will depend on the use of a single or several dimensions. To establish the dependence among a series of variables in a multidimensional system, the Euclidean distance matrix is most commonly used.

To construct the maps for the individual element's distribution, as well as for the factor associations, the universal *Kriging* method was applied. Kriging is an optimal prediction method, indented for geophysical variables with continuous data distribution. The obtained values of variables can sometimes be random, but their variance is not described with geometric function. This method performs projection of an object by using the values of certain parameters that describe its position (latitude, longitude and oval height), i.e. any object on Earth can be spatially defined (Kaymaz 2005). All data about variables are organized in several possible ways; most commonly used is raster. Generally, raster consists of a matrix of cells (pixels), arranged in rows and columns, where each cell contains values that provide information about variables. Digital air photography, satellite imagery, digital images and

scanned maps can be used as a raster. Kriging interpolation method performs the output of each raster cell by calculating the average load of nearby vectors. Kriging method analyses the statistical variation of the values of different distances and, at various positions, determines the shape and size of the specified point for examination as a set of load factors (Sakata et al. 2003).

In the making of the distribution maps, the Kriging method with linear variogram interpolation was applied. The following seven areas of percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100.

3.3 Results and Discussion

The total contents of 69 elements were quantified in a total of 310 samples of topsoil (TS) and subsoil (SS). The values for the elements' contents were statistically processed. At the start, the distribution of the elements as variables, individually, was monitored. For these reasons, comparative analysis was performed on normal and transformed values. Two statistical comparative methods were applied (*T*-test and *F*-test) to examine whether there were certain differences in the elements' distributions between the non-transformed and the transformed values. On the other hand, lithogenic distribution of different chemical elements should not significantly differ in the samples of topsoil (0–10 cm) and subsoil (20–30 cm). As it can be seen in Table 3.3, any significant difference cannot be observed. Box-Cox transformation was used for normalization of the values for the elements' contents in the soil samples. Because of the fact that no significant difference was detected in the contents, and consequently also in the distribution of the elements in the soil, the further statistical processing of the values for the elements' contents in the soil refers to the mean values of their contents (the content as a mean value of the TS and the SS).

In order to determine the dependence of the contents of the analysed elements between the topsoil and the subsoil, a matrix of correlation factors was produced (Table 3.4). The elements' distribution should not vary significantly between the topsoil (0–5 cm) and the subsoil (20–30 cm), except if certain destructive anthropogenic or natural processes do not contribute to the opposite (Dudka and Adriano 1997). Almost for all elements, significant correlations were received for their content in the topsoil vs. subsoil, $T/B > 0.30$, and only for Ag, Ge, Ni and Pt, lower values were received (Table 3.4). The elements Ca, P, Sr and Zr show characteristically significant stability in the distribution of their contents in a vertical direction ($T/B > 0.70$).

Out of all analysed elements, the contents of 8 elements (Au, Hg, Ir, Os, Re, Rh, Ru, Se) are below the detection limit for the analytical techniques applied. The basic descriptive statistics are provided in Table 3.5, in which are presented the average of non-transformed and Box-Cox transformed values, the values' range, percentile areas (10, 25, 75, 90), standard deviation and distribution of the values from the

Table 3.3 Comparative analysis of the elements' contents in topsoil and subsoil (*T*-test and *F*-test) for normal and Box-Cox transformed values

	ME	TS-(X)	SS-(X)	TS-(BC)	SS-(BC)	<i>F</i>	Sign
Ag	mg/kg	0.91	0.82	0.76	0.72	1.13	NS
Al ^a	%	5.3	5.5	5.4	5.6	1.03	NS
As	mg/kg	26	26	18	17	1.16	NS
B	mg/kg	200	250	22	22	1.17	NS
Ba	mg/kg	530	570	460	490	1.09	NS
Be	mg/kg	2.9	3.0	2.7	2.8	1.06	NS
Bi	mg/kg	0.22	0.21	0.13	0.13	1.04	NS
Br	mg/kg	3.6	3.6	2.5	2.6	1.02	NS
Ca ^a	%	2.0	2.1	1.2	1.2	1.11	NS
Cd	mg/kg	0.24	0.23	0.13	0.13	1.05	NS
Ce	mg/kg	29	31	26	28	1.10	NS
Co	mg/kg	13	13	11	11	1.03	NS
Cr	mg/kg	61	59	48	46	1.10	NS
Cs	mg/kg	3.0	3.2	2.3	2.3	1.33	NS
Cu	mg/kg	27	27	21	22	1.05	NS
Dy	mg/kg	3.1	3.2	2.8	2.9	1.03	NS
Er	mg/kg	1.7	1.7	1.5	1.6	1.02	NS
Eu	mg/kg	0.83	0.87	0.76	0.80	1.03	NS
Fe	%	3.0	3.0	2.7	2.7	1.00	NS
Ga	mg/kg	15	16	15	15	1.07	NS
Gd	mg/kg	3.9	4.1	3.6	3.8	1.06	NS
Ge	mg/kg	0.96	0.97	0.90	0.91	1.02	NS
Hf	mg/kg	1.1	1.1	0.94	0.95	1.14	NS
Ho	mg/kg	0.61	0.63	0.54	0.56	1.03	NS
I	mg/kg	0.21	0.21	0.17	0.18	1.02	NS
In	μg/kg	43	34	23	22	1.02	NS
K	%	1.9	2.0	1.4	1.5	1.17	NS
La	mg/kg	13	14	12	12	1.08	NS
Li	mg/kg	42	42	31	32	1.08	NS
Lu	mg/kg	0.27	0.27	0.25	0.25	1.00	NS
Mg	%	1.0	1.0	0.78	0.76	1.07	NS
Mn	mg/kg	900	890	650	660	1.11	NS
Mo	mg/kg	0.85	0.90	0.65	0.68	1.25	NS
Na	%	1.8	1.8	1.4	1.4	1.07	NS
Nb	mg/kg	7.7	7.9	7.1	7.3	1.11	NS
Nd	mg/kg	15	16	14	14	1.12	NS
Ni	mg/kg	33	34	22	22	1.08	NS
P*	mg/kg	500	490	440	420	1.04	NS
Pb	mg/kg	880	750	40	40	1.40	NS
Pd	mg/kg	0.63	0.66	0.48	0.50	1.07	NS
Pr	mg/kg	3.7	3.9	3.4	3.5	1.14	NS
Pt	mg/kg	0.22	0.21	0.21	0.20	1.02	NS

(continued)

Table 3.3 (continued)

	ME	TS-(X)	SS-(X)	TS-(BC)	SS-(BC)	F	Sign
Rb	mg/kg	58	59	53	54	1.19	NS
Sb	mg/kg	5.7	6.2	0.53	0.54	1.02	NS
Sc	mg/kg	16	17	12	13	1.13	NS
Sm	mg/kg	3.2	3.4	3.0	3.1	1.08	NS
Sn	mg/kg	2.8	2.9	2.0	2.0	6.67	NS
Sr	mg/kg	160	170	120	120	1.24	NS
Ta	mg/kg	0.75	0.73	0.66	0.65	1.05	NS
Tb	mg/kg	0.56	0.58	0.51	0.53	1.03	NS
Te	µg/kg	54	58	36	40	1.12	NS
Ti	%	0.39	0.41	0.31	0.32	1.18	NS
Tl	mg/kg	0.58	0.67	0.42	0.42	1.23	NS
Tm	mg/kg	0.25	0.25	0.22	0.23	1.02	NS
V	mg/kg	120	120	94	98	1.04	NS
W	mg/kg	1.3	1.3	1.1	1.1	1.29	NS
Y	mg/kg	12	13	11	11	1.06	NS
Yb	mg/kg	1.6	1.7	1.5	1.5	1.00	NS
Zn	mg/kg	87	84	72	71	1.35	NS
Zr	mg/kg	38	40	31	31	1.15	NS

ME measurement unit, TS topsoil (0–5 cm), SS subsoil (20–30 cm), X non-transformed values, BC Box-Cox transformed values, Sig. significance, NS non-significant difference

^aThe elements' contents were determined using AES-ICP

Table 3.4 Matrix of correlation coefficients for the elements' contents in TS vs. SS (the elements' contents were determined using ICP-MS)

Element	T/B	Element	T/B	Element	T/B	Element	T/B
Ag	0.23	Dy	0.39	Mg	0.59	Sm	0.34
Al ^a	0.54	Er	0.40	Mn	0.55	Sn	0.59
As	0.69	Eu	0.40	Mo	0.62	Sr	0.71
B	0.63	Fe	0.43	Na	0.52	Ta	0.44
Ba	0.52	Ga	0.10	Nb	0.42	Tb	0.36
Be	0.39	Gd	0.35	Nd	0.34	Te	0.53
Bi	0.65	Ge	0.16	Ni	0.09	Ti	0.57
Br	0.34	Hf	0.64	P ^a	0.95	Tl	0.69
Ca ^a	0.94	Ho	0.40	Pb	0.65	Tm	0.39
Cd	0.61	I	0.42	Pd	0.41	V	0.43
Ce	0.38	In	0.48	Pr	0.34	W	0.59
Co	0.54	K	0.48	Pt	0.29	Y	0.43
Cr	0.53	La	0.37	Rb	0.43	Yb	0.36
Cs	0.69	Li	0.50	Sb	0.80	Zn	0.54
Cu	0.56	Lu	0.35	Sc	0.40	Zr	0.70

^aThe elements' contents were determined using AES-ICP; TS topsoil (0–5 cm), SS subsoil (20–30 cm); T/B ratio of the content in topsoil and bottom soil

Table 3.5 Descriptive statistics of the values of elements' contents in samples of topsoil and subsoil

Element	Unit	X	X (BC)	Md	Min	Max	P _{2.5}	P _{7.5}	S	Sx	CV	A	E	A (BC)	E (BC)
Ag	mg/kg	0.86	0.74	0.74	0.16	4.9	0.57	0.97	0.54	0.043	62	3.78	22.2	0.22	6.05
Al	%	5.4	5.5	5.4	3.0	7.9	4.9	5.9	0.77	0.062	14	0.03	0.74	0.47	0.62
As	mg/kg	26	17	18	3.2	230	10	32	26	2.1	100	3.91	23.6	-0.00	0.27
B	mg/kg	220	22	19	0.23	9200	12	38	1000	83	460	6.75	49.8	0.14	6.23
Ba	mg/kg	550	480	500	63	2000	330	710	300	24	54	1.43	3.43	0.01	0.16
Be	mg/kg	3.0	2.7	2.8	0.30	9.0	2.0	3.7	1.3	0.11	45	1.17	2.54	0.03	0.54
Bi	mg/kg	0.21	0.13	0.13	0.005	3.6	0.094	0.20	0.34	0.027	160	7.26	68.8	0.07	2.08
Br	mg/kg	3.6	2.5	2.8	0.005	20	1.7	4.4	3.1	0.25	86	2.39	8.30	-0.14	0.50
Ca	%	2.0	1.2	1.3	0.15	24	0.62	2.4	2.6	0.21	130	4.71	33.0	0.06	-0.33
Cd	mg/kg	0.24	0.13	0.13	0.005	3.9	0.088	0.21	0.43	0.035	180	5.85	40.7	0.07	2.36
Ce	mg/kg	30	27	28	3.6	65	20	39	14	1.1	47	0.37	-0.64	0.02	0.11
Co	mg/kg	13	11	11	2.1	38	8.5	16	6.5	0.52	51	1.33	2.16	0.01	0.30
Cr	mg/kg	60.2	47	50	0.001	220	30	77	43	3.5	72	1.28	1.66	-0.48	0.65
Cs	mg/kg	3.11	2.3	2.4	0.17	26	1.5	3.5	3.0	0.24	98	4.05	23.8	0.06	1.39
Cu	mg/kg	27.2	22	22	5.3	140	17	31	20	1.6	73	2.98	11.7	-0.01	1.04
Dy	mg/kg	3.21	2.9	2.9	0.50	10	2.2	3.8	1.5	0.12	47	1.49	3.69	0.09	1.44
Er	mg/kg	1.70	1.5	1.6	0.29	5.9	1.2	2.0	0.84	0.068	49	1.64	4.12	0.08	1.55
Eu	mg/kg	0.85	0.78	0.84	0.12	2.3	0.58	1.0	0.37	0.030	44	0.83	1.43	0.06	0.81
Fe	%	3.0	2.7	2.7	0.96	9.2	2.1	3.6	1.3	0.11	44	1.53	3.61	0.0001	0.67
Ga	mg/kg	15.1	15	15	4.3	30	12	19	4.9	0.39	32	0.39	0.19	0.15	1.65
Gd	mg/kg	4.02	3.7	3.8	0.56	11	2.9	4.8	1.7	0.13	42	0.83	1.41	0.09	1.04
Ge	mg/kg	0.96	0.91	0.89	0.10	2.2	0.69	1.2	0.39	0.032	41	0.68	0.54	0.13	1.63
Hf	mg/kg	1.1	0.95	0.94	0.18	4.2	0.64	1.4	0.71	0.057	62	1.57	3.25	0.03	0.87
Ho	mg/kg	0.62	0.55	0.56	0.099	2.1	0.42	0.72	0.30	0.024	49	1.64	4.23	0.08	1.53
I	mg/kg	0.21	0.18	0.18	0.005	0.76	0.11	0.27	0.13	0.011	63	1.49	3.08	0.08	1.05

(continued)

Table 3.5 (continued)

Element	Unit	X	X (BC)	Md	Min	Max	P _{2.5}	P _{7.5}	S	Sx	CV	A	E	A (BC)	E (BC)
In	µg/kg	39	22	29	5.0	940	17	39.3	80.2	6.41	210	9.67	105	-0.01	0.81
K	%	2.01	1.4	1.5	0.066	7.2	0.99	2.4	1.5	0.12	78	1.73	2.68	0.01	0.37
La	mg/kg	13	12	12	1.6	42.3	8.70	18	6.7	0.53	50	0.72	1.02	0.04	0.32
Li	mg/kg	42	32	31	5.4	360	22.4	51	39	3.10	92	4.48	30.74	0.01	1.57
Lu	mg/kg	0.27	0.25	0.25	0.046	0.74	0.18	0.33	0.12	0.009	43	1.13	1.84	0.12	1.60
Mg	%	1.02	0.77	0.77	0.15	5.70	0.51	1.2	0.85	0.068	83	2.48	8.45	0.03	0.61
Mn	mg/kg	900	660	700	180	12,000	500	1000	1000	80	110	8.13	84.56	-0.03	0.81
Mo	mg/kg	0.88	0.66	0.64	0.005	7.5	0.46	0.96	0.89	0.071	100	4.14	22.95	0.22	3.11
Na	%	1.8	1.4	1.5	0.19	5.9	1.0	2.0	1.2	0.097	67	1.55	1.97	-0.0001	0.34
Nb	mg/kg	7.8	7.2	7.4	1.7	21	5.6	9.3	3.0	0.24	38	1.11	2.15	0.02	1.05
Nd	mg/kg	15	14	15	1.9	34	10	20	6.7	0.54	43	0.40	-0.19	0.04	0.46
Ni	mg/kg	34	22	20	0.005	210	11	39	37	3.0	110	2.20	5.08	0.05	0.71
P*	mg/kg	490	430	440	89	2300	330	600	300	24	61	2.59	11.6	0.01	0.71
Pb	mg/kg	820	40	26	4.4	46,000	17	75	4120	330	510	9.21	96.79	-0.19	7.64
Pd	mg/kg	0.64	0.49	0.54	0.050	2.3	0.34	0.85	0.45	0.036	69	1.43	2.28	-0.04	-0.49
Pr	mg/kg	3.8	3.4	3.7	0.48	7.8	2.6	4.8	1.7	0.13	44	0.36	-0.45	0.04	0.33
Pt	mg/kg	0.22	0.21	0.21	0.039	0.52	0.16	0.27	0.078	0.006	36	0.47	0.69	0.10	0.91
Rb	mg/kg	59	53	57	8.3	150	43	74	26	2.1	44	0.64	0.67	0.02	0.39
Sb	mg/kg	5.9	0.53	0.46	0.074	290	0.33	0.95	27	2.1	450	8.89	91.82	-0.01	1.09
Sc	mg/kg	17	13	13	1.6	99	9.4	19	13	1.0	77	3.01	12.69	-0.01	0.64
Sm	mg/kg	3.3	3.1	3.2	0.43	8.2	2.3	4.3	1.4	0.11	42	0.58	0.50	0.06	0.70
Sn	mg/kg	2.9	2.0	2.0	0.47	45	1.6	2.7	4.1	0.33	140	7.78	72.99	-0.15	3.32
Sr	mg/kg	160	120	110	15	820	72	200	140	11	87	2.02	4.64	0.0001	0.20
Ta	mg/kg	0.74	0.65	0.68	0.14	2.1	0.52	0.88	0.35	0.028	47	1.41	2.85	0.05	1.83
Tb	mg/kg	0.57	0.52	0.54	0.088	1.7	0.40	0.67	0.25	0.020	44	1.20	2.76	0.09	1.24
Te	µg/kg	56	38	39	5.0	350	25	63	56	4.5	100	3.05	11.4	0.0001	0.30

Ti	%	0.40	0.32	0.33	0.084	1.9	0.22	0.51	0.27	0.021	67	2.42	8.70	0.0001	0.0001
Tl	mg/kg	0.63	0.42	0.40	0.050	14	0.30	0.61	1.2	0.096	190	10.2	116	-0.10	2.79
Tm	mg/kg	0.25	0.23	0.23	0.043	0.82	0.17	0.29	0.12	0.010	48	1.56	3.68	0.10	1.74
V	mg/kg	120	96	95	18	390	69	150	74	6.0	62	1.60	2.71	0.0001	0.65
W	mg/kg	1.3	1.1	1.1	0.15	4.7	0.84	1.5	0.77	0.062	59	1.83	4.40	0.03	1.18
Y	mg/kg	12	11	11	2.1	41	8.5	15	6.1	0.49	50	1.40	3.09	0.12	1.45
Yb	mg/kg	1.7	1.5	1.5	0.29	5.0	1.1	2.0	0.75	0.061	46	1.41	2.94	0.09	1.55
Zn	mg/kg	85	72	68	21	690	52	96	72	5.8	85	4.97	34.39	0.46	6.33
Zr	mg/kg	39	31	31	6.8	180	21	47	28	2.2	71	2.28	7.09	-0.0001	0.79

ME measurement unit, *X* mean, *X(BC)* mean of Box-Cox transformed values, *Med* median, *Min* minimum, *Max* maximum, *P₂₅* 25th percentile, *P₇₅* 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

range, by the skewness of distributions. In Table 3.6 are presented the values of the elements' contents in different geogenic formations within the examined area.

The values of macroelements Al, Ca, Fe, K, Mg, Na and Ti are in the following ranges: 3.0–7.9%, 0.15–24%, 0.96–9.2%, 0.066–7.2, 0.15–5.7%, 0.19–5.9% and 0.084–1.9%, respectively. The contents of macroelements are most frequently a result of the dominant geological formations of the area: Proterozoic schists and gneisses; Neogene clastites, pyroclastites and volcanites; and Paleogene flysch. Comparative analysis was conducted based on the data on the contents of different chemical elements in the soils in Europe, provided by Salminen et al. (2005). For the comparative analysis, the values of the medians were used (as a more stable parameter), while regarding the Box-Cox transformed values, the average and the median were identical almost for all elements. This confirms the importance of using the Box-Cox transformation in order to normalize the skewed distributions of the different chemical elements. The Al and Fe contents are lower in relation to the data published by Salminen et al. (2005), while for the other macroelements, including phosphorus and manganese, the values did not show any significant variations. The distribution of the remaining chemical elements is characteristic corresponding to the lithogenic origin of the rocks in the separate subregions of the area.

The arsenic distribution is specifically related to the old volcanism in the western region of the investigated area (Probištip–Kratovo). The values of arsenic contents in the topsoil and subsoil are in the range from 3.2 to 230 mg/kg. Characteristic and potentially toxic contents of As in the soil were found in the region of Probištip (>38 mg/kg). Compared with the results of the European studies, an enrichment factor of $ER = 2.6$ was obtained (Salminen et al. 2005). Compared with the Dutch standards, the median value for the total area (18 mg/kg) does not exceed the upper optimum value for As (29 mg/kg). Nevertheless, in the region of the Kamenička and Zletovska rivers (42 mg/kg), the As content is higher than the optimum value for the content of this element (<http://www.contaminatedland.co.uk/std-guid/dutch-1.htm>).

Boron distribution in the investigated area is related to the river terraces in the upper course of the Bregalnica river, as well as the river terraces of its most important tributaries, the Kamenička and the Zletovska rivers (Table 3.6). The values for boron contents in the investigated area show a high coefficient of variation (460) and are in the range from 0.23 to 9200 mg/kg (Table 3.5).

Barium distribution, similarly to the arsenic, is closely related to the volcanism in the investigated area. Specific for barium is the fact that its natural enrichment is related both to the old and the young volcanism in the investigated area. Paleogenic volcanic sedimentary rocks represent the young volcanism which is found distributed along the eastern border of the investigated area. This region is characterized with naturally distributed barium (530 mg/kg) as shown in Table 3.6. Neogene pyroclastites are the dominant geogenic formations that represent the old volcanism in the investigated area (690 mg/kg). These Ba contents exceed the optimum and action values in accordance with the Dutch standards (200 и 625 mg/kg, respectively). Barium distribution is specifically related also to the Quaternary river terraces in the lower course of the Bregalnica river (B-2). On the other side, the beryllium content is nonspecifically related to certain geologic formations in the

Table 3.6 Distribution of the elements in the soil in different geologic formations in the examined area

	Unit	B-1 (Q)	B-2 (Q)	K-Z (Q)	Terraces (Q)	River sediment (Ng)	Characteristic geological formation							F	Sign
							Pyr. (Ng)	Flysh (Pg)	Schist (Pz)	Schist (R)	Schist (Pt)	Gn. (Pt)	Gr. (Mz-Pt)		
Ag	mg/kg	0.60	0.71	1.6	1.2	0.77	0.82	0.82	0.72	0.64	0.56	0.65	0.76	4.22	*
Al ^a	%	6.2	6.3	6.5	5.8	5.4	5.8	5.4	4.9	5.4	5.8	5.5	5.3	8.28	*
As	mg/kg	12	9.7	42	30	13	31	25	35	17	14	14	12	9.53	*
B	mg/kg	0.11	0.12	0.45	69	24	7.7	14	18	17	20	32	34	48.9	*
Ba	mg/kg	430	480	900	690	540	690	530	340	310	370	490	480	5.78	*
Be	mg/kg	1.4	1.5	2.5	3.2	2.5	2.9	2.5	2.0	2.5	3.0	3.1	2.9	8.16	*
Bi	mg/kg	0.037	0.076	0.99	0.23	0.12	0.19	0.16	0.11	0.10	0.12	0.16	0.12	11.1	*
Br	mg/kg	0.76	0.92	0.72	5.4	2.2	3.8	3.0	5.1	2.8	2.3	1.8	1.5	9.19	*
Ca ^a	%	2.0	1.6	1.5	1.6	1.2	1.4	3.1	4.2	0.91	0.99	0.73	0.68	16.5	*
Cd	mg/kg	0.052	0.20	2.0	0.38	0.10	0.25	0.15	0.18	0.09	0.15	0.13	0.11	11.4	*
Ce	mg/kg	28	27	43	43	28	28	34	29	21	24	25	23	3.43	*
Co	mg/kg	9.2	7.3	11	15	9.7	11	14	12	14	9.4	10	8.9	5.62	*
Cr	mg/kg	41	35	37	56	40	22	83	65	53	47	46	32	4.22	*
Cs	mg/kg	1.4	2.0	4.4	3.3	1.9	4.7	2.9	1.3	1.8	2.4	1.8	2.1	5.50	*
Cu	mg/kg	19	18	75	37	18	23	24	21	25	20	24	16	6.47	*
Dy	mg/kg	3.3	2.7	3.4	4.2	2.7	2.9	3.0	2.8	3.0	2.9	2.8	2.5	1.39	NS
Er	mg/kg	1.7	1.4	1.7	2.3	1.5	1.6	1.6	1.5	1.7	1.6	1.5	1.3	1.32	NS
Eu	mg/kg	0.86	0.69	1.1	1.2	0.75	0.92	0.85	0.72	0.80	0.69	0.71	0.67	2.46	*
Fe	%	3.7	2.6	5.5	3.8	2.3	2.9	2.8	2.3	3.3	2.7	2.7	2.3	4.65	*
Ga	mg/kg	12	11	20	19	14	14	14	12	15	16	16	15	3.04	*
Gd	mg/kg	4.0	3.4	4.7	5.3	3.6	3.7	4.1	3.6	3.6	3.5	3.5	3.2	1.62	NS
Ge	mg/kg	0.44	0.48	0.99	1.3	0.86	0.84	0.87	0.79	0.99	0.86	0.94	0.89	6.17	*
Hf	mg/kg	0.58	0.54	0.72	1.7	0.86	1.5	1.1	0.64	0.87	0.77	0.74	0.95	8.32	*
Ho	mg/kg	0.65	0.55	0.64	0.81	0.53	0.55	0.57	0.54	0.59	0.56	0.53	0.47	1.39	NS

(continued)

Table 3.6 (continued)

	Unit	Characteristic geological formation										F	Sign		
		B-1 (Q)	B-2 (Q)	K-Z (Q)	Terraces (Q)	River sediment (Ng)	Pyr. (Ng)	Flysh (Pg)	Schist (Pz)	Schist (R)	Schist (Pt)			Gn. (Pt)	Gr. (Mz-Pt)
I	mg/kg	0.029	0.039	0.041	0.26	0.14	0.18	0.23	0.20	0.16	0.13	0.19	0.15	20.1	*
In	µg/kg	19	31	230	54	20	29	16	13	27	25	28	18	7.37	*
K	%	0.22	0.44	0.51	2.1	1.3	1.2	2.0	1.3	0.94	1.7	1.4	1.6	18.4	*
La	mg/kg	12	12	19	18	13	13	15	14	8.8	10	11	10	3.47	*
Li	mg/kg	15	16	29	34	30	27	50	24	31	29	26	31	8.52	*
Lu	mg/kg	0.26	0.23	0.29	0.36	0.23	0.27	0.25	0.23	0.26	0.26	0.24	0.22	1.26	NS
Mg	%	0.67	0.51	0.90	0.90	0.68	0.46	1.4	1.1	0.81	0.73	0.67	0.57	6.62	*
Mn	mg/kg	680	640	2000	1300	520	860	710	590	750	590	620	550	4.83	*
Mo	mg/kg	0.24	0.35	1.8	1.4	0.66	1.1	0.57	0.52	0.52	0.57	0.72	0.63	10.2	*
Na	%	2.2	1.3	2.7	1.6	1.4	0.94	1.1	1.1	1.6	1.3	1.6	1.6	2.99	*
Nb	mg/kg	6.0	5.7	6.6	9.1	6.4	7.7	6.9	4.9	7.7	7.4	7.6	6.5	3.03	*
Nd	mg/kg	14	13	20	21	14	15	17	14	12	13	13	12	2.39	*
Ni	mg/kg	11	14	12	31	21	8.7	54	41	19	15	22	12	9.87	*
P ^a	mg/kg	660	660	750	540	390	740	490	420	460	450	370	300	11.7	*
Pb	mg/kg	20	40	3100	100	28	95	24	54	51	38	58	30	6.07	*
Pd	mg/kg	0.21	0.41	0.60	0.864	0.46	1.0	0.76	0.46	0.35	0.35	0.36	0.39	7.82	*
Pr	mg/kg	3.5	3.3	5.2	5.1	3.4	3.6	4.1	3.6	2.9	3.1	3.3	3.0	2.59	*
Pt	mg/kg	0.072	0.015	0.015	0.29	0.17	0.25	0.22	0.18	0.21	0.22	0.20	0.20	48.7	*
Rb	mg/kg	46	50	94	75	52	59	65	40	37	55	52	53	4.43	*
Sb	mg/kg	0.32	0.39	1.5	0.64	0.55	0.61	0.41	0.86	0.50	0.51	0.56	0.62	2.55	*
Sc	mg/kg	5.4	6.9	8.2	15	11	14	13	12	14	10	16	11	8.67	*
Sm	mg/kg	3.1	2.6	4.0	4.5	3.0	3.2	3.4	3.0	2.9	2.8	2.9	2.7	2.03	*
Sn	mg/kg	1.4	1.4	2.2	2.4	1.8	2.3	2.0	1.8	1.7	2.5	2.5	1.9	4.09	*
Sr	mg/kg	120	120	190	190	110	260	220	170	84	86	78	70	13.2	*

Ta	mg/kg	0.55	0.51	0.59	0.87	0.58	0.78	0.64	0.43	0.64	0.71	0.69	0.61	2.65	*
Tb	mg/kg	0.57	0.49	0.64	0.75	0.50	0.52	0.56	0.51	0.53	0.51	0.50	0.45	1.41	NS
Te	µg/kg	18	18	170	76	29	67	39	29	42	48	36	27	10.7	*
Ti	%	0.22	0.21	0.22	0.42	0.28	0.40	0.31	0.28	0.41	0.33	0.30	0.24	5.64	*
Tl	mg/kg	0.18	0.33	0.85	0.60	0.36	0.93	0.42	0.27	0.31	0.41	0.42	0.44	10.2	*
Tm	mg/kg	0.26	0.23	0.27	0.33	0.21	0.23	0.23	0.21	0.24	0.23	0.22	0.19	1.30	NS
V	mg/kg	79	64	120	130	79	120	110	100	110	91	90	76	4.25	*
W	mg/kg	0.64	0.87	2.1	1.6	1.0	1.6	1.3	0.71	0.86	1.1	0.98	1.1	6.86	*
Y	mg/kg	14	12	14	16	11	11	12	11	11	11	11	9.1	1.60	NS
Yb	mg/kg	1.6	1.4	1.7	2.1	1.4	1.5	1.5	1.4	1.6	1.5	1.4	1.3	1.18	NS
Zn	mg/kg	35	76	480	150	58	120	69	54	72	72	77	54	16.5	*
Zr	mg/kg	16	17	21	62	30	50	38	20	27	23	24	30	10.9	*

ME measurement unit, NS non-significant difference, B-1 upper course of the Bregalnica river, B-2 lower course of the Bregalnica river, K-Z region of the Kamenichka and Zletovska rivers, P_{yr}: pyroclastite, Q Quaternary, Ng Neogene, Pg Paleogene, Pt Paleozoic, R Riphean, Pt Proterozoic

^{a3}Significant difference

investigated area (Table 3.6). Natural enrichment is found in the areas of the Quaternary river terraces of the Bregalnica river as well as of its major tributaries (3.2 mg/kg).

The values for the bismuth contents are in the range from 0.005 to 3.6 mg/kg (Table 3.5), with significant lithogenic enrichment in the Quaternary lithogenic units in the region of the Kamenička and the Zletovska rivers, from 0.99 mg/kg (Table 3.6). Halogen elements Br and I show a great similarity in their distribution in the investigated area. Both elements are specifically related to the Quaternary river terraces, with contents of 5.4 and 0.26 mg/kg, respectively, for Br and I (Table 3.6). On the other side, the maximum values for the distribution of these two elements are obtained in the region of the old volcanism within the investigated area.

The Cd contents in topsoil and subsoil are in the range from 0.005 to 3.9 mg/kg with median of 0.13 mg/kg, and compared with the data provided by Salminen et al. (2005), the medians do not show any significant variability (0.145 mg/kg, for European soils). The Cd distribution is related to the ore and flotation activities and the Pb–Zn and Cu mineralization in the region of Makedonska Kamenica, village of Zletovo, Propištip and village of Bučim. The values for the cobalt content do not show great variability in the different subregions of the investigated area (Table 3.5). The values range from 2.1 to 38 mg/kg with median of 11 mg/kg (Table 3.5). Compared with the Dutch standards, these Cd contents are higher (0.8 mg/kg).

The Co distribution is specifically related to the Quaternary sediments of the river terraces (15 mg/kg) in the upper course of the Bregalnica river and partially in the lower course. Certain influence of the Co distribution is found also in the areas of Paleozoic flysch and Riphean schists, 14 mg/kg (Table 3.6).

The area specifics are undoubtedly related to certain processes related to major destructive influence of the basic lithogenic formations. This was surely shown in the distribution of As, Ba, Bi, Cu and, in fact, Cs. The caesium distribution is specifically related to the Paleogenic volcanism of the Kratovo–Zletovo lithologic zone. The natural cesium distribution in the investigated area is represented in the content range from 0.17 to 26 mg/kg (Table 3.5). The comparative analysis with the European standards points to the fact that volcanism has influence on the occurrence of much higher Cs values in Europe, with median for topsoil of 3.71 mg/kg and maximum value of 69.1 mg/kg (Salminen et al. 2005).

Copper contents in the investigated area range from 5.3 to 140 mg/kg (Table 3.5). The Cu median of 22 mg/kg is higher than the respective value referring to the European soils (13 mg/kg), as specified by Salminen et al. (2005). Copper distribution is characteristic for the area of Borov Dol–Damjan block and the specific Cu mineralization in the vicinity of the “Bučim” mine. The statistical analysis of the copper contents, depending on their distribution in different lithogenic formations, shows specific natural enrichment with copper (median 75 mg/kg) in the area of the Kamenička river and the Zletovska river (K–Z, Table 3.6). These values exceed the optimum values for Cu contents in accordance with the Dutch standards (36 mg/kg) (<http://www.contaminatedland.co.uk/std-guid/dutch-1.htm>).

Gallium and germanium show similarities in their distribution in the whole investigated area, mainly related to the river terraces (Table 3.6). The medians for

both elements do not differ significantly from the corresponding values specified by Salminen et al. (2005). Along the whole course of the Bregalnica river, naturally enriched contents of these two elements (values >20 mg/kg and >1.3 mg/kg) are found in the areas of Quaternary alluvium, on river terraces, as well as in the areas of Neogene clastites and partially pyroclastites. Hafnium is one of the elements which is specifically related to the old volcanism (Neogene pyroclastites and volcanites) in the area. As it can be seen in Table 3.6, the highest contents of this element are found in areas of Riphean schists (>1.8 mg/kg). The range of values for Hf (0.18–4.2 mg/kg) points to nonspecific distribution of this element in the investigated area, compared with the distribution of this element in the soils all over Europe (<0.2 –21.2 mg/kg).

Indium in the investigated area is distributed in contents ranging from 0.005 to 0.94 mg/kg (Table 3.5). The ninetieth percentile of distribution values for this element is found in the areas of Pb–Zn mineralization (K–Z, Table 3.6), related to the old (Neogene) and the young (Paleogene) volcanism in the area.

In the lower course of the Bregalnica river (B-2) are obtained lithium contents >68 mg/kg, while the whole area of the Bregalnica river basin is characterized with Li contents ranging from 5.4 to 360 mg/kg. The correlation analysis showed a high presence of lithium on the river terraces, which is due to the long-term deposition of this element during the creation of the alluvium (Table 3.6). Similarly to the lithium also behaves the manganese, whose distribution is related to the Pb–Zn mineralization along the courses of the Zletovska and the Kamenička rivers, as well as on the river terraces in the upper course of the Bregalnica river (B-1, Table 3.6). The Mn contents in the area of the Bregalnica basin range from 0.018 to 1.2% (Table 3.5).

Molybdenum belongs to the group of elements that are related to the old and the new volcanism in the area. In the region of the Neogene volcanism, which represents a part of the Kratovo–Zletovo district (block), and in the region of the new volcanism (Paleogene) are found Mo contents ranging from 1.5 to 7.5 mg/kg. These values for the Mo contents are in line with the corresponding optimum values according to the Dutch standards (<http://www.contaminatedland.co.uk/std-guid/dutch-l.htm>).

Niobium (Nb) most often occurs in the environment in minerals that contain tantalum, which certainly proved true in the distribution of these elements in the region of the Bregalnica river basin. Their distribution is related dominantly to the river terraces (medians for Nb = 9.1 mg/kg and for Ta = 0.87 mg/kg, Table 3.5). The contents of these elements in topsoil and subsoil are in the range from 1.7 to 21 mg/kg for Nb and 0.14 to 2.1 mg/kg for Ta (Table 3.5).

The Ni content in the soils occurs in the range from 0.005 to 210 mg/kg. The comparative analysis of the median values for the Ni content (20 mg/kg) in the soils on the whole territory of Europe (18 mg/kg) shows insignificant variability. The nickel distribution is intensively distinguished in the lower course of the Bregalnica river basin, with median of 31 mg/kg on the river terraces, related to Paleogene flysch and Proterozoic schists (Table 3.6). These values for the Ni contents are in line with the corresponding optimum values according to the Dutch standards (<http://www.contaminatedland.co.uk/std-guid/dutch-l.htm>).

The examined area lies on parts of the Kratovo–Zletovo and Toranica-Sasa ore areas, on the both sides of the Osogovo massive. Both areas lie on metamorphic and

volcanic rocks originating from the Tertiary. The Pb–Zn mineralization in this area characteristically influences the distribution of these two elements in the wider area. The lead contents in the whole investigated area range from 4.4 to 46,000 mg/kg (Table 3.5). High variability is obtained in the distribution of the data on lead, which also confirms a great difference in the values for the average (820 mg/kg) and the median (40 mg/kg). Because of the high values for the standard deviation and the coefficient of variation, data normalization was performed using the Box-Cox transformation and standardizing the median to the value of 26 mg/kg (Table 3.5). Compared with the data provided by Salminen et al. (2005), the Pb median is 22.6 mg/kg, and there is no significant variation. For the isolated areas of the Kamenička river (Sasa mine surroundings) and the Zletovska river (Zletovo mine surroundings), a median for the lead contents of 3100 mg/kg was obtained (Table 3.6). Lead distribution is also related to the areas of Neogene pyroclastites, with a median of the isolated samples located on these geologic formations of 100 mg/kg (Table 3.6). The values obtained for zinc contents in the soils range from 21 to 690 mg/kg, with median of 68 mg/kg, which is 1.3 times higher than the European average (Salminen et al. 2005). Almost identical is the distribution of this element with lead distribution, which is most probably due to the two major areas with dominant Pb–Zn mineralization in the region of the Kamenička and the Zletovska rivers, with median of 480 mg/kg (K–Z, Table 3.6), and again the influence of the old volcanism, where a median of 120 mg/kg was obtained. The values of the medians for lead and zinc contents in the vicinity of the Kamenička and Zletovska rivers are 3100 mg/kg and 480 mg/kg, which, compared with the upper optimum values in accordance with the Dutch standards (85 and 140 mg/kg, respectively), points out to pollution. The lead contents also exceed the action value of 530 mg/kg (<http://www.contaminatedland.co.uk/std-guide/dutch-1.htm>).

Palladium is a representative of the platinum group metals. In the investigated area, it is contained in the soils in the range from 0.005 to 2.3 mg/kg (Table 3.5). The distribution of this element is dominantly related to the Neogene pyroclastites, with the highest median of all samples in these areas (1 mg/kg, Table 3.6). This element is most often found in a free form or associated with metals from the platinum group (Pt, Ru, Ir), and very often it is found in a linked form in mineral deposits of Cu and Ni (Qi et al. 2003). Platinum, similarly to palladium, is related to the Neogene pyroclastites, yet not as much emphasized as palladium. The platinum contents in the investigated area range from 0.039 to 0.52 mg/kg (Table 3.5). The ninetieth percentile part of the distribution of the platinum content (>0.30 mg/kg), in a wider area, is distributed in the Kočani valley, that is, on the river terraces in the middle course of the Bregalnica river.

Rubidium is a chemical element which is very frequently found in the environment, and in the basin of the Bregalnica river, the Rb content in soils ranges from 8.3 to 150 mg/kg. In the investigated area, the Rb distribution is related to the Quaternary sediments in the region of the Zletovska river (median of samples of this subregion is 94 mg/kg), while less pronounced is the distribution related to the river terraces along the whole Bregalnica basin.

Antimony can be found in the environment in a free form, but it is most frequently linked in a form of sulphide. Very frequently this element is found in association with heavy metals. In the investigated area, the Sb contents in soil range from 0.074

to 290 mg/kg and have a median of 0.46 mg/kg. Compared with the Sb distribution in the European soils (0.60 mg/kg), the median for the investigated area is lower. As regards the values' range, natural enrichment occurs in the areas of Paleozoic schists (median value 0.86 mg/kg), with significant difference in relation to the other geological formations: *F*-value 2.55 (Table 3.6). Higher values (P_{90} from 7.2 to 290 mg/kg) are obtained in the region of the Kamenička and Zletovska rivers, related to the Pb–Zn mineralization, as well as in the region of the Bučim mine, related to the Cu mineralization.

Scandium is most frequently found in areas with presence of rare earth elements, although scandium itself cannot be considered as a rare earth element, as its distribution is in the range from 16 to 54 mg/kg in Europe, and in the world it is in the range from 18 to 25 mg/kg (Bowen 1979; Salminen et al. 2005). The Sc distribution in the Bregalnica river basin is dominantly related to the river terraces in the upper river course (B-1, Table 3.6). The geological formations to which the scandium distribution is most probably related are the Proterozoic gneisses and Paleogene schists (with medians 16 and 14 mg/kg).

Tin is most often found in the environment in association with Bi, Ge, Pb and Zn, as specified by Alloway and Ayres (1997). In a similar way, it behaves in the investigated area (from 0.47 to 45 mg/kg), dominantly related to the areas of ore activities with significant medians of 2.2 mg/kg and 2.4 mg/kg, for the river terraces in the course of the Bregalnica river, that is, along the course of the Zletovska and Kamenička rivers (Table 3.6). Higher contents of Sn in the soil (>3.3 mg/kg) are found in the vicinity of the Bučim mine. Strontium distribution (from 15 to 820 mg/kg) is related to the river terraces of the Zletovska river, that is, it is significantly related to the Neogene pyroclastites (median 260 mg/kg) and the Paleogene flysch, with median of the samples of 220 mg/kg (in the lower course of the Bregalnica river, B-2), that is, to the old volcanism in the whole area.

Tantalum occurs in nature most often in association with niobium (VanLoon and Duffy 2000). In the investigated area, tantalum contents were found ranging from 0.14 to 2.1 mg/kg. Similarly to niobium, the distribution of this element is dominantly related to the river terraces (as it is the case with Ga and Ge), where their concentration on the river alluvium occurs in the course of time (median 0.87 mg/kg). On the other hand, tellurium joins the group of elements (Ba, Bi, Cd, Cs, In, Li, Mo) that are significantly related to the Neogene pyroclastites (67 µg/kg) and the Paleogene volcanic sedimentary rocks (39 µg/kg).

Thallium is contained in soils in the range from 0.050 to 14 mg/kg, with median of 0.40 mg/kg, similarly to the data obtained by Salminen et al. (2005). Thallium distribution in the Bregalnica river basin is significantly related to the old (median 0.93 mg/kg) and the new volcanism (Neogene pyroclastites, volcanites, Paleogene flysch and volcanic sedimentary rocks).

Vanadium contents in the Bregalnica river basin range from 18 to 390 mg/kg (Table 3.5). Its natural concentration in the investigated area occurs on the river terraces (the median is 130 mg/kg).

Tungsten is most frequently found in the environment associated with iron, manganese and calcium minerals (Dudka and Adriano 1997). Very similarly to the

iron distribution, the tungsten distribution is partially related to the Neogene pyroclastites and the Paleogene flysch (medians 1.6 and 1.3 mg/kg) and partially to the Proterozoic schists and granites (median 1.1 mg/kg). The tungsten contents in the whole area are in the range from 0.15 to 4.7 mg/kg (Table 3.5). Yttrium (Y) is very frequently found in the minerals of rare earth elements, as a result of which it was often considered as a rare element. In the investigated area, the Y contents in the soil range from 2.1 to 41 mg/kg with median of 11 mg/kg (Table 3.5). In the soils on the whole territory of Europe, yttrium is found even in contents >200 mg/kg (Salminen et al. 2005). The Y distribution is not specifically related to certain geological formations, because no significant difference was established in the distribution of this element in its occurrence in various geological units ($F = 1.60$, Table 3.6). Natural concentration of this element in the Bregalnica river basin occurs based on its deposition, i.e. retention on the river terraces, with higher median (2.1 mg/kg) than the corresponding values obtained in the remaining areas within the investigated area. Zirconium distribution is dominantly related to the Neogene pyroclastites (62 mg/kg) both on the river terraces (50 mg/kg) and in the lower course of the Bregalnica river (B-2, Table 3.6). Zirconium contents vary from 6.8 to 180 mg/kg (Table 3.5).

The group of rare earth elements (REE) (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb) is separately monitored because of their specific distribution. These elements are most frequently distributed together in the environment, due to their very similar geochemical affinities. In order to examine their distribution and the correlations among the contents of these rare elements, bivariate analysis was performed using the r -correlation factor. For better overview, a matrix of the correlation factors of these elements was generated (Table 3.7). Strongly distinguished correlation factors are obtained for all analysed rare elements ($r > 0.70$). The medians for these elements are as follows: 28, 2.9, 1.6, 0.84, 3.8, 0.56, 12, 0.25, 15, 3.7, 3.2, 0.54, 0.23 and 1.5 mg/kg, respectively (Table 3.5).

The monitoring of the distribution of these elements isolates two groups of lanthanides, which are the following: La–Gd (La, Ce, Pr, Nd, Sm, Gd) and Eu–Lu (Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu). The distribution of both groups of lanthanides (La–Gd) is specifically related to the river terraces, where their long-term concentration can actually be expected, with the deposition of sediment in the course of time. High loading values are obtained in the distribution of the La–Gd group of rare earth elements, particularly distinguished in the alluvial soils in the courses of the Kamenička and Zletovska rivers (standardized loading value 0.8), as well as significant distribution in the areas of Paleogene flysch. For the heavier lanthanides from the isolated group Eu–Lu, there is no significant difference in the distribution of these rare earth elements in relation to the different dominant geological formations in the Bregalnica river basin. The distribution of Eu, Tb, Dy, Ho, Er, Tm, Yb and Lu is specifically distinguished only on the river terraces.

Because of the great number of variables, that is, different chemical elements whose distribution in the area of the Bregalnica basin is monitored, data reduction was performed based on the application of a multivariate factor analysis. A matrix of correlation coefficients was produced based on previously standardized and Box-Cox transformed values for the elements' contents in the samples of topsoil and subsoil.

Only the elements presented in Table 3.8 are included in the factor analysis, while for the rest it was determined that they did not have significant loading values and possibility to form a new synthetic variable, and therefore they do not have significance

Table 3.8 Matrix of factor loadings: factor analysis (FA) of the elements' contents in samples of topsoil

Element	F1	F2	F3	F4	F5	F6	Comm.
Ti	0.90	0.01	-0.01	0.14	0.20	0.00	86.4
Eu-Lu	0.81	0.04	0.33	0.15	0.15	0.05	81.6
Y	0.78	0.01	0.29	0.12	0.28	-0.08	79.2
Fe	0.78	0.27	0.04	0.29	0.31	0.09	86.6
Sc	0.75	0.01	-0.15	0.05	0.20	0.15	64.5
V	0.74	0.18	0.11	0.22	0.30	-0.05	73.6
Nb	0.68	0.02	0.49	0.19	-0.08	0.25	80.8
Co	0.66	0.21	-0.04	0.25	0.59	-0.01	89.4
La-Gd	0.65	0.14	0.52	0.20	0.22	-0.12	81.3
Ga	0.63	0.33	0.37	0.10	-0.01	0.43	84.6
Ge	0.61	0.10	0.23	0.17	0.04	0.46	67.3
Cu	0.57	0.55	0.06	0.17	0.37	0.00	79.9
Pb	-0.01	0.85	0.15	0.01	-0.10	0.01	76.2
Sb	0.03	0.80	0.21	-0.09	0.02	-0.11	71.2
Cd	0.05	0.78	0.13	0.28	0.20	0.07	75.1
Sn	0.17	0.69	0.52	-0.14	0.06	0.13	81.4
Zn	0.44	0.66	0.12	0.33	0.02	-0.11	76.6
Te	0.12	0.57	0.08	0.52	-0.01	0.16	64.0
Rb	0.10	0.18	0.87	0.21	0.00	0.03	84.1
K	0.02	0.20	0.78	-0.05	0.26	0.14	73.8
W	0.17	0.26	0.66	0.29	-0.10	-0.10	63.7
Ba	0.21	0.29	0.62	0.33	-0.19	-0.01	65.7
Ta	0.58	0.00	0.61	0.14	-0.16	0.19	78.7
Tl	0.01	0.44	0.57	0.37	-0.26	-0.04	72.4
Zr	0.19	-0.08	0.36	0.76	-0.02	0.22	80.0
Hf	0.24	-0.08	0.40	0.72	-0.09	0.26	81.6
Br	0.13	0.18	-0.19	0.71	0.06	0.33	71.0
Pd	0.19	0.11	0.25	0.69	0.09	-0.20	63.6
Sr	0.23	0.09	0.24	0.67	0.23	-0.40	78.6
As	0.30	0.35	0.09	0.59	0.22	-0.24	67.9
Ni	0.21	-0.01	0.05	0.02	0.89	-0.06	85.2
Mg	0.27	0.06	-0.02	0.11	0.82	0.08	75.9
Cr	0.41	-0.02	-0.11	-0.03	0.80	0.07	82.3
B	-0.05	-0.02	0.02	0.13	0.06	0.82	69.9
Na	0.35	0.00	0.09	-0.10	0.01	0.67	58.9
Variability (%)	21.7	12.6	13.3	12.0	9.7	6.5	75.8
<i>Eigenvalue</i>	12.9	4.71	2.99	2.47	1.43	1.97	

F1 Factor 1 loadings, *F2* Factor 2 loadings, *F3* Factor 3 loadings, *F4* Factor 4 loadings, *F5* Factor 5 loadings, *F6* Factor 6 loadings, *Comm* communality, *E* eigenvalue

in the multivariate analysis. Out of 60 original variables (elements), by application of factor analysis, six new synthetic variables were isolated, that is, the reduction process resulted in six geochemical associations of elements. The geochemical associations of variables were processed based on the basic matrix of correlation coefficients. In Table 3.8 are shown the loading values for each individual element, for each geochemical association. The total communality of the factors amounts to 75.8% (Table 3.8). In the factor extraction, as significantly pronounced associations of elements were taken into consideration only those that had E-value (*eigenvalue*) higher than 1. The E-value, correspondingly for each factor, is presented in Table 3.8. The factor associations for elements' contents in topsoil and subsoil are the following: F1 (Ti, Eu–Lu, Y, Fe, Sc, V, Nb, Co, La–Gd, Ga, Ge, Cu), F2 (Cu, Pb, Sb, Cd, Sn, Zn, Te), F3 (Rb, K, W, Ba, Ta, Tl), F4 (Zr, Hf, Br, Pd, Sr, As), F5 (Ni, Mg, Cr) and F6 (B, Na). In order to determine the stability of these geochemical associations, the method of cluster analysis was also applied, by expressing the distance, that is, the remoteness of the dependencies of each individual variable (element). For these reasons the Ward's method for measuring the dependence was applied, while the 1-Pearson-r factor was used for measuring the distance of the variables. Identical results were achieved as in the case of application of multivariate factor analysis, and the graphical representation is shown in Fig. 3.5. By

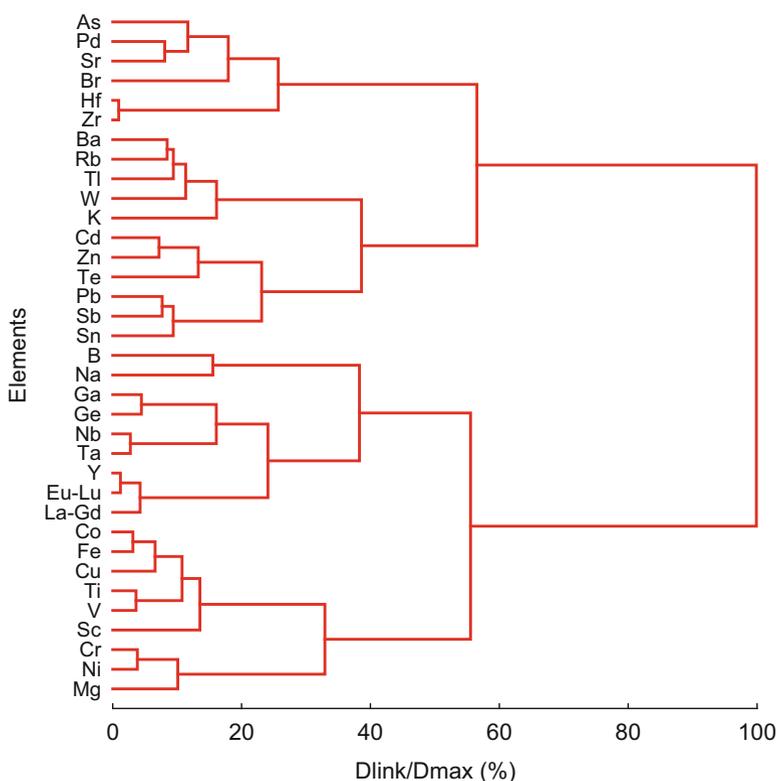


Fig. 3.5 Cluster analysis of the geochemical associations of elements in soil samples

visualization of nearness, that is, remoteness of the individual elements, the dependence of variables on the level of a single association of elements can also be observed. This is particularly emphasized in relation to Factor 1 (Ti, Eu–Lu, Y, Fe, Sc, V, Nb, Co, La–Gd, Ga, Ge, Cu), where the nearness, that is, the significant correlation of the two groups of rare earth elements (Eu–Lu and La–Gd), can be observed.

Factor 1 (F1) represents the geochemical association of the elements Ti, Eu–Lu, Y, Fe, Sc, V, Nb, Co, La–Gd, Ga, Ge and Cu, with a total internal variability of 21.7% and E-value for factor significance of 12.9 (dominant geochemical association). The distribution of this geochemical association is dominantly related to the river terraces (Figs. 3.6 and 3.7). As it can be seen from Fig. 3.7, any significant difference among the distributions of these elements in the areas of deferring geological formations is almost not present. This points to the fact that the distribution of these elements, which also includes the rare earth elements, is due to their long-term deposition and carrying with river sediments along the basin of the Bregalnica river. Characteristic deposition of these elements is observed in the upper course of the Bregalnica river as well as in the Kočani valley (Fig. 3.6).

Factor 2 (F2) represents geochemical association of the elements Cu, Pb, Sb, Cd, Sn, Zn and Te, with a total internal variability of 12.6% and E-value for factor

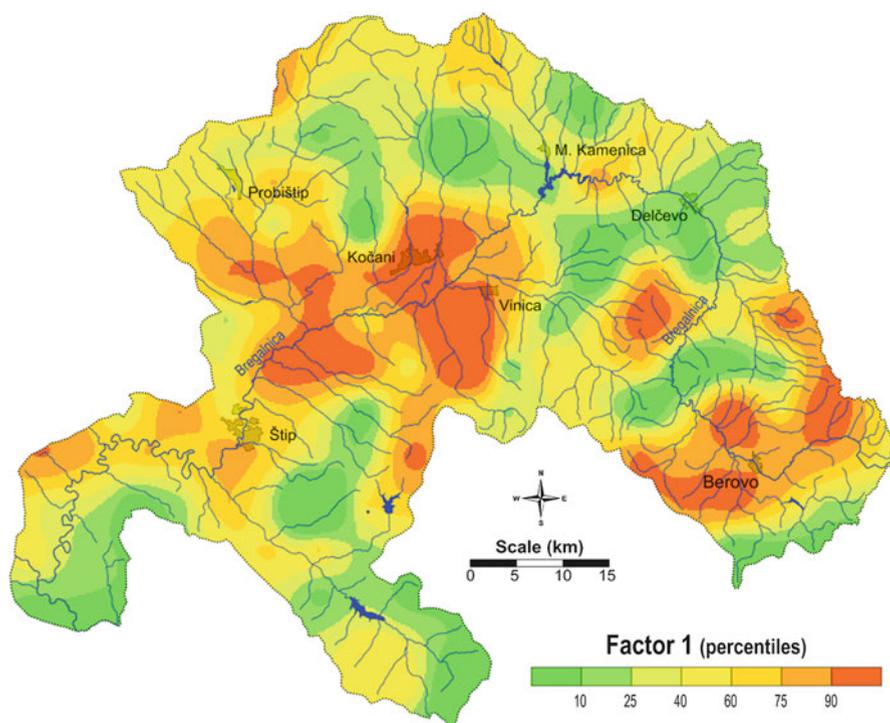
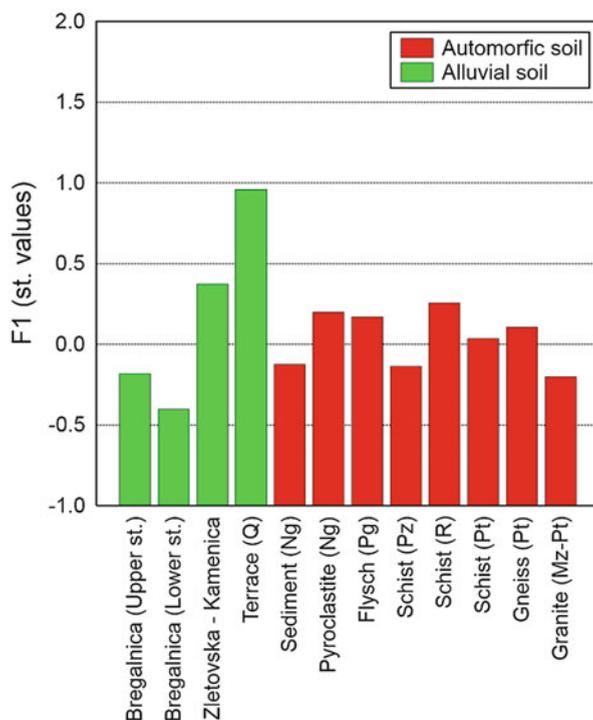


Fig. 3.6 Spatial distribution of F1 (Ti, Eu–Lu, Y, Fe, Sc, V, Nb, Co, La–Gd, Ga, Ge, Cu) in soil samples

Fig. 3.7 Distribution of F1 in soil samples depending on the different geological formations



significance of 4.71. This geochemical association is dominantly distributed on the river terraces of the Kamenička and Zletovska rivers, where the Pb–Zn mineralization is exploited by mining activities (the Zletovo and Sasa mines). The Neogene pyroclastites that represent the old volcanism in the investigated area have influence on the distribution of the elements in this geochemical association. The alluvium that deposits on the river terraces as time goes by represents a true archive of the elements carried by the river waters. Both rivers, the Zletovska and Kamenička, are exposed to the effect of the flotation tailings of the two mines Zletovo and Sasa, as a result of which the Pb and Zn contents continually increase and concentrate on river terraces. Cadmium, antimony and tin are elements whose occurrence in nature is related to lead, zinc and copper minerals. The natural enrichment of these elements is distributed in the surroundings of the Bučim mine, where dominant geological formations are the Proterozoic schists and gneisses, with participation of Proterozoic gneisses (Figs. 3.8 and 3.9). The distribution of this factor is partially influenced also by Proterozoic gneisses and granites, but not specifically. Although the distribution of this factor is specifically present in the regions of the three main mining activities (the Sasa, Zletovo and Bučim mines), their introduction in the environment is primarily due to natural enrichment (dominant mineralization). The open ore pit activities only contribute to the introduction of new contents of these elements in the vicinity of the mining activities.

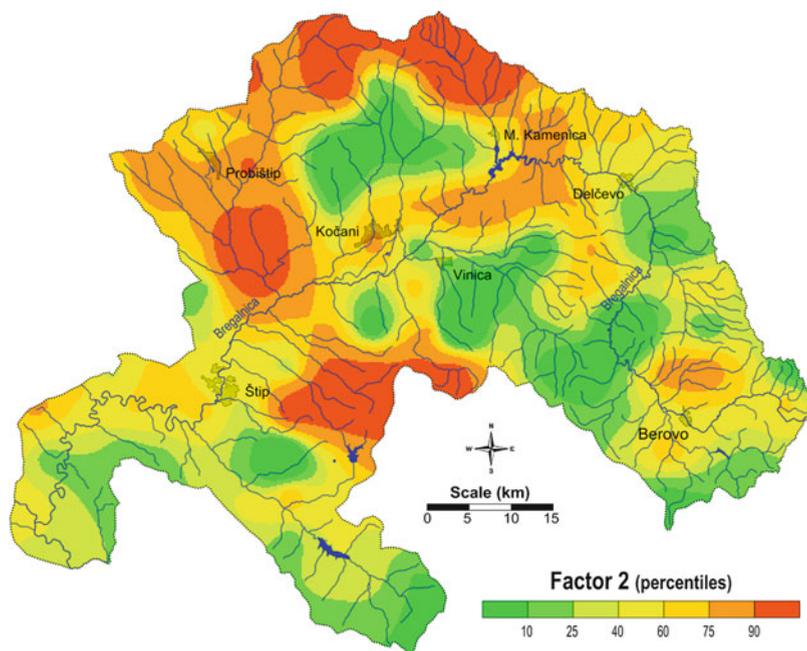


Fig. 3.8 Spatial distribution of F2 (Cu, Pb, Sb, Cd, Sn, Zn, Te) in soil samples

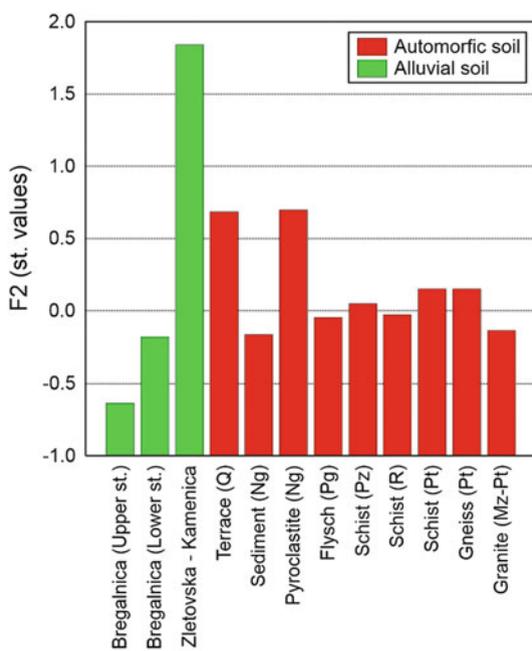


Fig. 3.9 Distribution of F2 in soil samples depending on the different geological formations

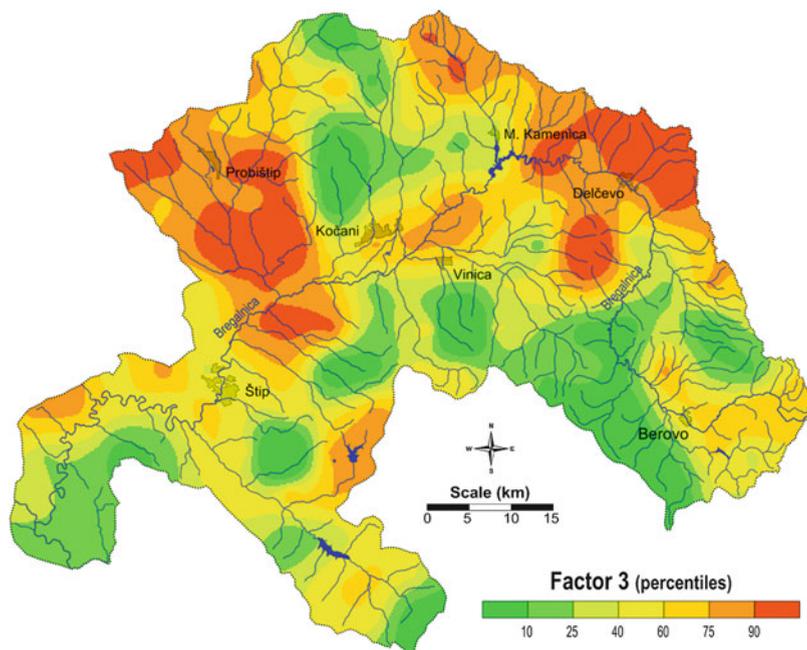


Fig. 3.10 Spatial distribution of F3 (Rb, K, W, Ba, Ta, Tl) in soil samples

Factor 3 (F3: Rb, K, W, Ba, Ta, Tl) associates the elements whose deposition is primarily related to the old and the new volcanism in the area (Fig. 3.10). For all elements, the values of the contents of the ninetieth percentile receive high loadings in the areas of Neogene pyroclastites and Paleogene flysch and sedimentary rocks. In this way is explained the characteristic deposition along the Kamenička and Zletovska river and partially in the upper course of the Bregalnica river (Fig. 3.11). In the lower course of the Bregalnica river are found P_{75} to P_{90} from the distribution of the contents of these elements. The highest loadings for this geochemical association were obtained for the elements Rh (0.87) and K (0.78), as typical markers of the old and the new volcanism in the area.

Factor 4 (Zr, Hf, Br, Pd, Sr, As) is a specific association of elements, which has isolated distribution in the areas of Neogene clastites, pyroclastites and volcanites. In this way the elements of this group are the main geogenic markers of the old volcanism, represented in the Kratovo–Zletovo district (block), as it can be seen in Figs. 3.12 and 3.13. Considering their natural enrichment in this region, the climate conditions (rains and winds) led to their distribution towards the lower part of the Bregalnica river basin (Fig. 3.12). This factor is characterized with a decreased variability in the loadings of the individual elements that make up the association. The loading values range from 0.59 for arsenic to 0.76 for zirconium. The total factor variability amounts to 12%.

Factor 5 (Ni, Mg, Cr) covers 9.7% of the total variability of factor groups. The loadings of these three elements are considerably high—Ni (0.89), Mg (0.82) and Cr

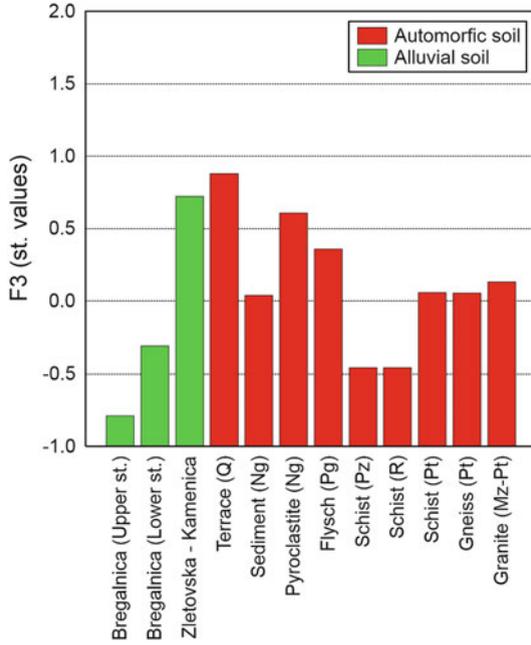


Fig. 3.11 Distribution of F3 in soil samples depending on the different geological formations

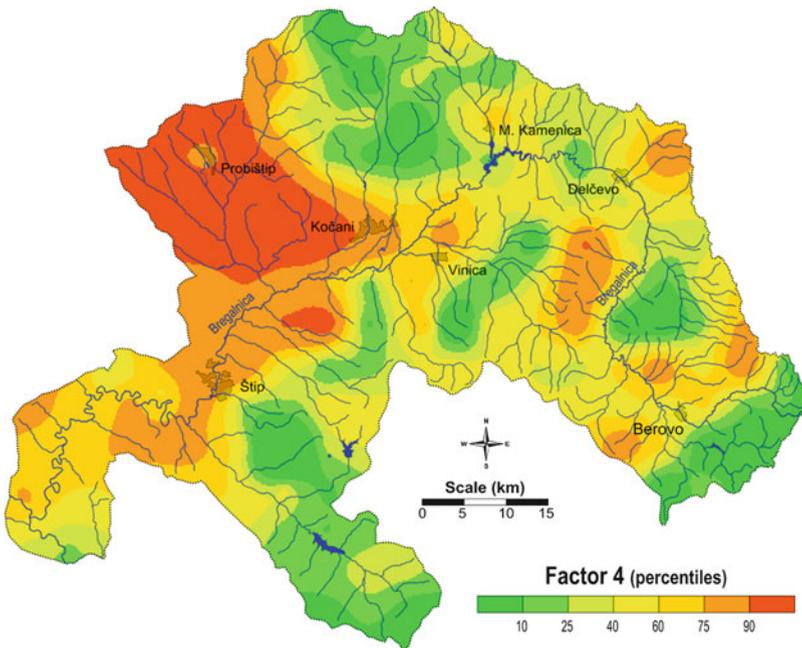
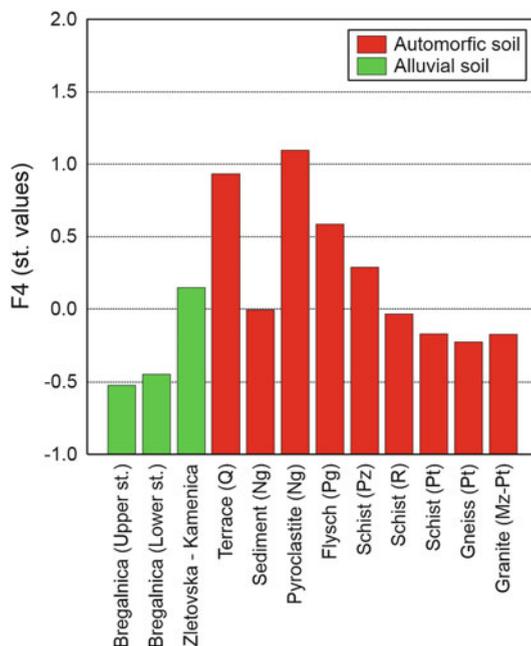


Fig. 3.12 Spatial distribution of F4 (Zr, Hf, Br, Pd, Sr, As) in soil samples

Fig. 3.13 Distribution of F4 in soil samples depending on the different geological formations



(0.80). The distribution of this geogenic association of elements is specifically related to the geology of the area with dominant correlation with the Paleogene flysch and Paleozoic schists that are part of the dominant geological formations in the area (Figs. 3.14 and 3.15). Their distribution, unlike the other geochemical associations, is not specifically pronounced on the river terraces (Fig. 3.15). In this way the Ni–Mg–Cr association represents a typical geogenic marker of the area with noticeably high manifestation, but with high stability of the elements' content related to the above-mentioned geologic formations.

Factor 6 (B, Na) represents a geochemical association of boron and sodium, with boron dominance in the association with loading of 0.82, compared with the sodium, with loading of 0.67. Although it is the least distinguished factor, nevertheless this geochemical association is related to the geological structure of the area. The dominant geological formations on which contents of these elements are found ($>P_{90}$) are in the areas of Proterozoic gneisses and Paleozoic granites (Figs. 3.16 and 3.17). This geochemical association, as well as F1, F2, F3 and F4, occurs on the Quaternary river terraces in the upper course of the Bregalnica river (Fig. 3.17).

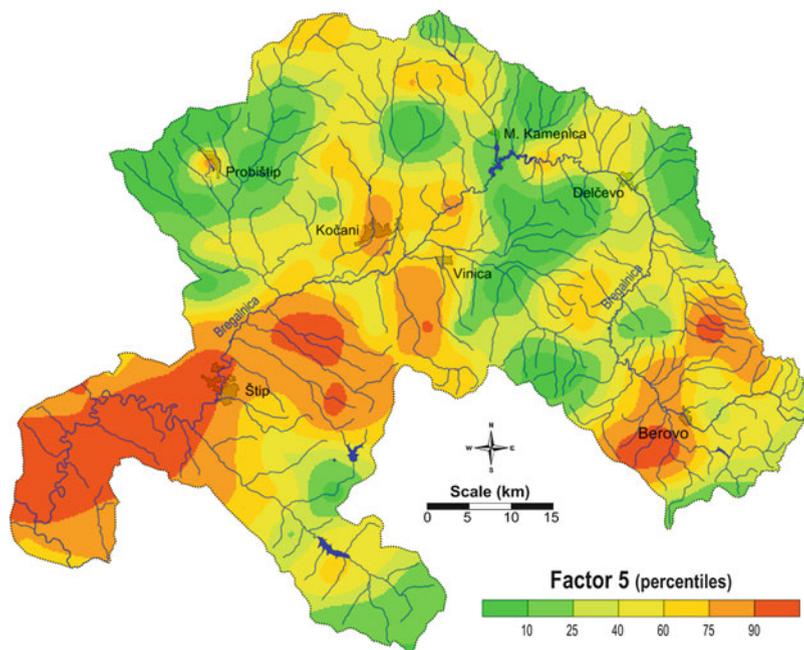


Fig. 3.14 Spatial distribution of F5 (Ni, Mg, Cr) in soil samples

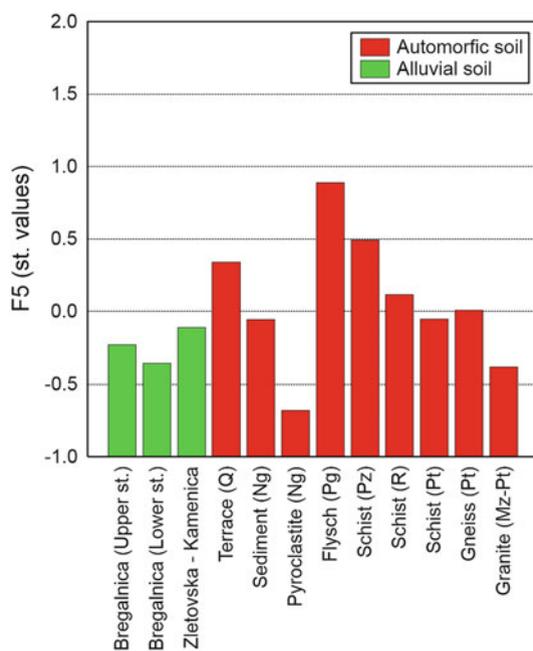


Fig. 3.15 Distribution of F5 in soil samples depending on the different geological formations

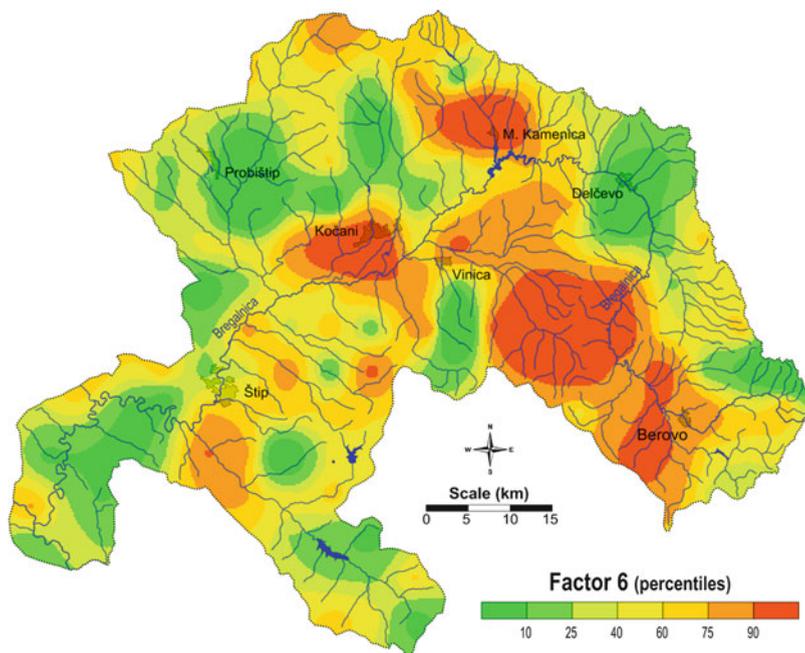


Fig. 3.16 Spatial distribution of F6 (B, Na) in soil samples

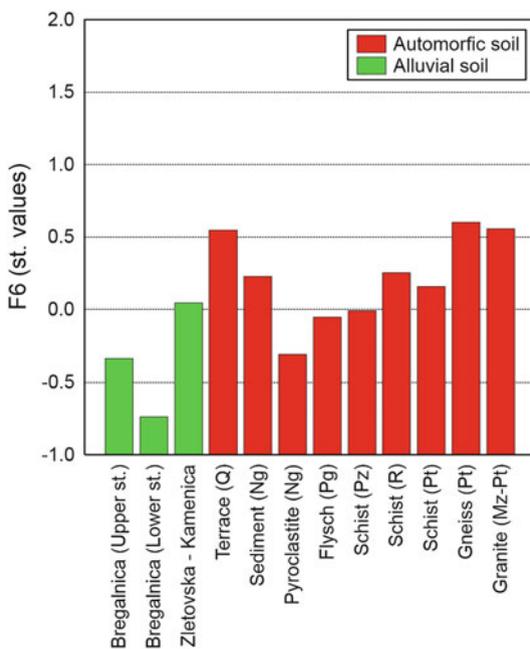


Fig. 3.17 Distribution of F6 in soil samples depending on the different geological formations

3.4 Conclusions

Automorphic soil samples were used as monitor for the distribution of various chemical elements in the upper separately in the vertical direction at two levels (0–5 cm) and (20–30 cm). Comparative analysis with the application of *T*-test and *F*-ratio showed that significant difference in the content of elements in the vertical direction is not found. This confirms that external (anthropogenic) impact: the environmental disasters do not disrupt lithogenic distribution. Dominant lithogenic markers are F1 (Ti, Eu–Lu, Y, Fe, Sc, V, Nb, Co, La–Gd, Ga, Ge, Cu), F2 (Cu, Pb, Sb, Cd, Sn, Zn, Te), F3 (Rb, K, W, Ba, Ta, Tl), F4 (Zr, Hf, Br, Pd, Sr, As), F5 (Ni, Mg, Cr) and F6 (B, Na). The second factor is characterized with increased contents of the given elements in the areas of Pb–Zn mineralization (related to “Sasa” and “Zletovo” mines presence) and Cu mineralization (related with “Bučim” mine presence). This element association also affects the Kočani Field in the middle part of the Bregalnica river basin. This area is also characterized with the dominant occurrence of F3 (Rb, K, W, Ba, Ta, Tl) and F4 (Zr, Hf, Br, Pd, Sr, As).

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