

Geochemical properties of topsoil around the coal mine and thermoelectric power plant

Trajče Stafilov, Robert Šajn, Mila Arapčeska, Ivan Kungulovski & Jasminka Alijagić

To cite this article: Trajče Stafilov, Robert Šajn, Mila Arapčeska, Ivan Kungulovski & Jasminka Alijagić (2018): Geochemical properties of topsoil around the coal mine and thermoelectric power plant, Journal of Environmental Science and Health, Part A, DOI: [10.1080/10934529.2018.1445076](https://doi.org/10.1080/10934529.2018.1445076)

To link to this article: <https://doi.org/10.1080/10934529.2018.1445076>



Published online: 19 Mar 2018.



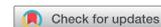
Submit your article to this journal [↗](#)



View related articles [↗](#)



View Crossmark data [↗](#)



Geochemical properties of topsoil around the coal mine and thermoelectric power plant

Trajče Stafilov^a, Robert Šajin^b, Mila Arapčeska^c, Ivan Kungulovski^d, and Jasminka Alijagić^b

^aInstitute of Chemistry, Faculty of Science, Ss. Cyril and Methodius University, Skopje, Republic of Macedonia; ^bGeological Survey of Slovenia, Ljubljana, Slovenia; ^cFaculty of Biotechnical Sciences, St. Kliment Ohridski University, Bitola, Republic of Macedonia; ^dBio Inženering DOO, Skopje, Republic of Macedonia

ABSTRACT

The results of the systematic study of the spatial distribution of trace metals in surface soil over the Bitola region, Republic of Macedonia, known for its coal mine and thermo-electrical power plant activities are reported. The investigated region (3200 km²) is covered by a sparse sampling grid of 5 × 5 km, but in the urban zone and around the thermoelectric power plant the sampling grid is denser (1 × 1 km). In total, 229 soil samples from 149 locations were collected including top-soil (0–5 cm) and bottom-soil samples (20–30 cm and 0–30 cm). Inductively coupled plasma – atomic emission spectrometry (ICP-AES) was applied for the determinations of 21 elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn). Based on the results of factor analyses, three geogenic associations of elements have been defined: F1 (Fe, Ni, V, Co, Cr, Mn and Li), F2 (Zn, B, Cu, Cd, Na and K) and F3 (Ca, Sr, Mg, Ba and Al). Even typical trace metals such as As, Cd, Cu, Ni, P, Pb and Zn are not isolated into anthropogenic geochemical associations by multivariate statistical methods still show some trends of local anthropogenic enrichment. The distribution maps for each analyzed element is showing the higher content of these elements in soil samples collected around the thermoelectric power plants than their average content for the soil samples collected from the whole Bitola Region. It was found that this enrichment is a result of the pollution by fly ash from coal burning which deposited near the plant having a high content of these elements.

ARTICLE HISTORY

Received 29 November 2017
Accepted 15 February 2018

KEYWORDS

Soil; trace metals; pollution; thermoelectric power plant; Bitola; Republic of Macedonia

Introduction

Anthropogenic environmental changes, associated mainly with chemical pollution, lead to a degradation of the natural environment. Among all chemical pollutants, trace elements are of a special ecological, biological and health significance. The production of energy and the consumption of natural resources are the main source of trace elements as contaminants. However, agricultural activities, especially the application of fertilizers and pesticides, also contribute significantly to trace metal pollution in the environment. Many elements are potentially hazardous trace metals to the biosphere.^[1] Although some elements such as Cr, Cu, Mn and Zn are essential for plants and humans, they can be hazardous for the environment if released in excessive amounts.^[2,3]

The soil, as a part of the ecosystem, is vital for the survival of mankind which is closely connected to its productivity. Soil functions as a filtering, buffering, storage and transformation system protect against the effects of trace element pollution. The soil is the main source of trace elements for plants, both in terms as micronutrients and as pollutants.^[4] The soil is dynamic, open habitats that provide plants with physical support, water, nutrients and air for growth. They also sustain an enormous population of microorganisms, such as bacteria and

fungi that recycle chemical elements, notably carbon and nitrogen, as well as toxic substances. The presence of man-made substances in the soil is of great public concern. Many of these chemicals are carcinogens or may accumulate in the environment with toxic effects on ecosystems. Although human exposure to these substances is primarily through food, inhalation or drinking water, soils play an important role because they affect the mobility and biological impact of these toxins.

The abundance of trace metals in the soil has been increased dramatically by the accelerated rate of mineral and fossil fuel extraction and by industrial processes. The problem of ecosystem degradation due to pollution became increasingly acute during the latter decades of the 20th century. Most of the metals were typically found in low concentrations in pristine waters, therefore referred to as trace metals. Rapid increases of trace metal concentrations in the environment are commonly coupled to the development of exploitative technologies.

The soil contains trace elements of various origins: lithogenic elements which are directly inherited from the lithosphere, geogenic elements which are of lithogenic origin, but their concentration and distribution in soil layers and soil particles are changed due to pedogenic processes or anthropogenic elements resulting from direct or indirect anthropogenic

activities. The behavior of trace elements in the soil and, consequently, their bioavailability differs in regards to their origin and depend on soil conditions and chemical and physical properties.

However, regardless of the chemical forms of the anthropogenic trace metals in the soil, their phytoavailability is significantly higher than those of geogenic origin. Soils of several regions of the world (and especially of Europe) have been and will be in the future subject to increased mineral fertilization, pesticide application, waste disposal and industrial pollution. All these human activities affect both chemical and physical soil properties and lead to changes in the behavior of trace elements in soils. The impacts of soil acidification, alkalinisation, salinity and losses of organic matter on the uptake of trace elements by vegetation, particularly by crop plants, have already become serious environmental and human health issues.^[5]

Urban soil pollution with trace metals has recently become a subject of many studies, some of which are concerned about large polluted areas.^[6–10] Regional contamination of soil occurs mainly in industrial regions and within centers of large settlements where factories, traffic and municipal wastes are the most important sources of trace metals.^[11] Because of heterogeneity and ceaseless changing of urban areas, it is necessary to understand the natural distribution of trace metals and the methods for distinguishing man-made anomalies in nature. However, in cases where industrial enterprises, especially mining and metallurgical plants, are situated near cities, pollution can be increased. Recently published papers state that mining and metallurgical activities lead to enormous soil contamination.^[11–17] In this direction very interesting are the results from the study on the soil pollution due to the coal-fired power plants.^[16,18]

The first results on trace metals environmental pollution in the Republic of Macedonia were obtained from the study on moss biomonitoring of air pollution with trace metals started in 2002. The results of these studies of air pollution in Macedonia indicate decreased air and soil quality in terms of trace metal pollution.^[19–22] The main emission sources are most likely metallurgic activities, power plants and mining activities. Therefore, special studies were performed in the areas with the highest trace metal pollution, including air (moss biomonitoring or attic dust) or soil pollution.

A detailed study was performed to environmental impacts of the Pb-Zn-Cd smelter plant in the city of Veles and detected soil pollution with possibly harmful elements (As, Cd, Cu, Hg, In, Pb, Sb Zn) exceeding the intervention values.^[13,23] The study also detected pollution of water and sediment of the river Vardar.^[24–26] Similar effects were detected in an area with ferronickel metallurgical activities near the city of Kavadarci regarding the contamination of soil.^[27–29] A detailed study of the impact of the copper mining and flotation plant “Bučim” near the town of Radoviš was also performed, showing the input to soil^[30,31] or air pollution.^[29,30] There are three active Pb-Zn mines and flotation plants situated in the eastern part of the country, and their activities pollute the environment with Pb, Zn, Cd and some other trace metals, which can be found in the soil,^[32,33] air,^[34] the river water and in sediments.^[24,25,29,35]

The arsenic-antimony abounded mine “Allchar” near the city of Kavadarci also affects the environment, with the main pollutants As, Sb and Tl in the soil,^[36] or in river waters and sediments.^[24,25,37] It was concluded that this pollution is a result of both lithological and anthropogenic sources.

Preliminary studies also found an influence of the thermoelectric power plants near the city of Bitola and Kičevo, producing about one million tons of fly ash per year, deposited on the surface close to the plant. This plant pollutes soils with Pb and Zn^[29,38,39] as well and air with radioactive fly ash containing U and Th,^[19] as well as As, Pb and Zn.^[40]

Therefore, in the frame of this work, a more detailed study on the pollution with the potentially toxic metals in the wide region of Bitola was performed. For that goal in total 229 soil samples were collected and analyzed for the assessment of the distribution of 21 elements in soil from the region of Bitola with specific attention of the effects from the thermoelectric power plant activities.

Study area

Study area is located in southwest part of the country, in Pelagonia valley (Figs. 1 and 2) with an area of 3200 km². Thermoelectric power plant “REK Bitola” is a facility of strategic importance and primary installation for electricity generation in the country. It satisfies over 70% of the demand for electricity in the country, as well as major part of the needs for coal (lignite) of industrial boiler plants and general consumption. REK Bitola has been built on the basis of the finds of coal-lignite, at around 12 km eastwards from the city of Bitola. This power plant is major polluter of the environment in the region and it constantly creates large amounts of waste in the form of fly ash and slag.^[41]

The biggest settlement in the study area is the city of Bitola, which is the administrative, cultural, economic, industrial, educational, scientific and diplomatic centre. Bitola is set in the foothills of Mount Baba in middle part of Pelagonia Valley. Through Bitola flows the river Dragor. Bitola is located 14 km north of Greek border at the altitude of 576 meters. Bitola covers the area of 795 m².

The Pelagonia region has agricultural land with an area of 276,777 ha, from which 117,770 ha are arable agricultural land, and the remaining 159,007 ha are pastures (Fig. 2). The structure of arable land – ploughed fields and gardens participate with 83%. As an industry, the agriculture accounts for 4% of production and 5% of total employment in the region. The total forest area in 2014 was 143,545 ha or 14.6% of total forest land. Of ore deposits in the region, most economically important are the coal bearings (lignite) in Pelagonia and Mariovo which today are used in the three blocks of REK Bitola and non-metallic bearings diatomaceous earth in Bitola-Mariovo and white marble in Prilep. The special mineral resource are the cold mineral springs in the village Medjitlija, Bitola. On the territory of Pelagonia region, there are two national parks, Pelister National Park and a part of the National Park Galičica. The basic water resource for watering of agricultural areas in Pelagonia is Strezevo Lake. It is also a source of technological water for the needs of REK Bitola. Moreover, there is artificial accumulation Suvodol near REK Bitola.

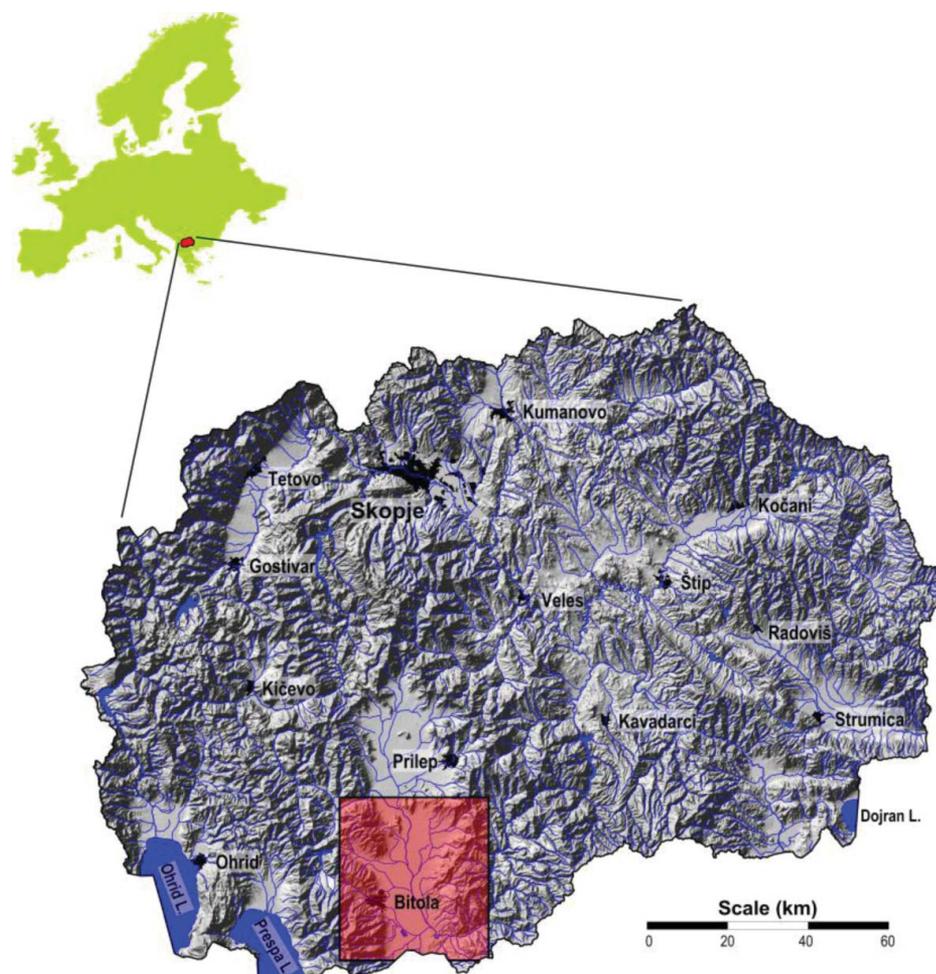


Figure 1. The study area on the territory of the Republic of Macedonia.

The Bitola region, as well as the whole Pelagonia Valley, is rather southern positioned and due to the latitude should have an altered Mediterranean climate. However, although Pelagonia Valley is at a distance of 155 km from the Adriatic Sea, and at about 130 km from the Aegean Sea, still the Mediterranean climate influence isn't much felt, because of the high mountainous surrounding of the valley, and its own height above the sea level (from 571 to 770 m). That's why the temperate-continental, continental and mountainous climate are mostly felt.^[42]

In this area the north wind prevails and is with the average annual constancy of 189%, the average speed is 2.2 m/s, the second for its constancy is the south wind with an average of 134% with the annual average speed of 3.7 m/s and the third is the northwest wind with an average of 83% and average speed of 2.4 m/s. The often drought and relatively high temperatures allow increasing of vapor conditions from free water and soil surface. The average rainfall is 640 mm per m².^[42] The hydrological potential in Pelagonia Valley consists of the river Crna Reka with its tributaries Blato, Šemnica, Dragor and Eleška River.

The study area includes parts of two large tectonic units: the Pelagonian massif and the West-Macedonian zone. The Pelagonian massif is separated from the West-Macedonian zone by a big revers Pelagonian fault, which is covered by young Quaternary deposits.^[43] Simplified geological map with the major lithological unit is provided in Figure 3. The Pelagonian massif is built of

Precambrian metamorphic and igneous rocks. The predominant rocks on the western Pelagonian massif are banded muscovite gneisses, but also other varieties such as the banded muscovite-biotite gneisses and Augen-amygdaloidal two-mica gneisses. Medium to coarse-grained granodiorites, garnet-staurolite and garnet-cyanite occur as intrusive bodies in the gneiss-mica-shist series. By the influence of granodioritic magmas, the surrounding rocks were feldspatized and Augen-amygdaloidal two-mica gneisses and banded two-mica gneisses originated, the feldspatisation processes of muscovite gneiss was weak. Some relicts of amphibolite and schistose amphibolite are present in the study area.

The oldest rocks in the Western Macedonian zone are Paleozoic age and consist of low metamorphic schists and granitic rocks. The most widespread granite is alkalic granite, extending in N-S direction. The oldest granitoid rocks are represented by biotite and amphibolitic granodiorites to which granosyenite and syenite are connected on the southern part of the Western Macedonian zone. Following the direction N-S, on the left side of the map, Silurian-Devonian formation occur composed of phyllite, slate, metasandstone and metaconglomerate which alter to some older Paleozoic rocks. Ordovician-Silurian greenschist and conglomerates with intrusions of quartz-sericite schist and schistose quartzite developed southern of Bitola. During Pliocene and Quaternary were first deposited the lacustrine

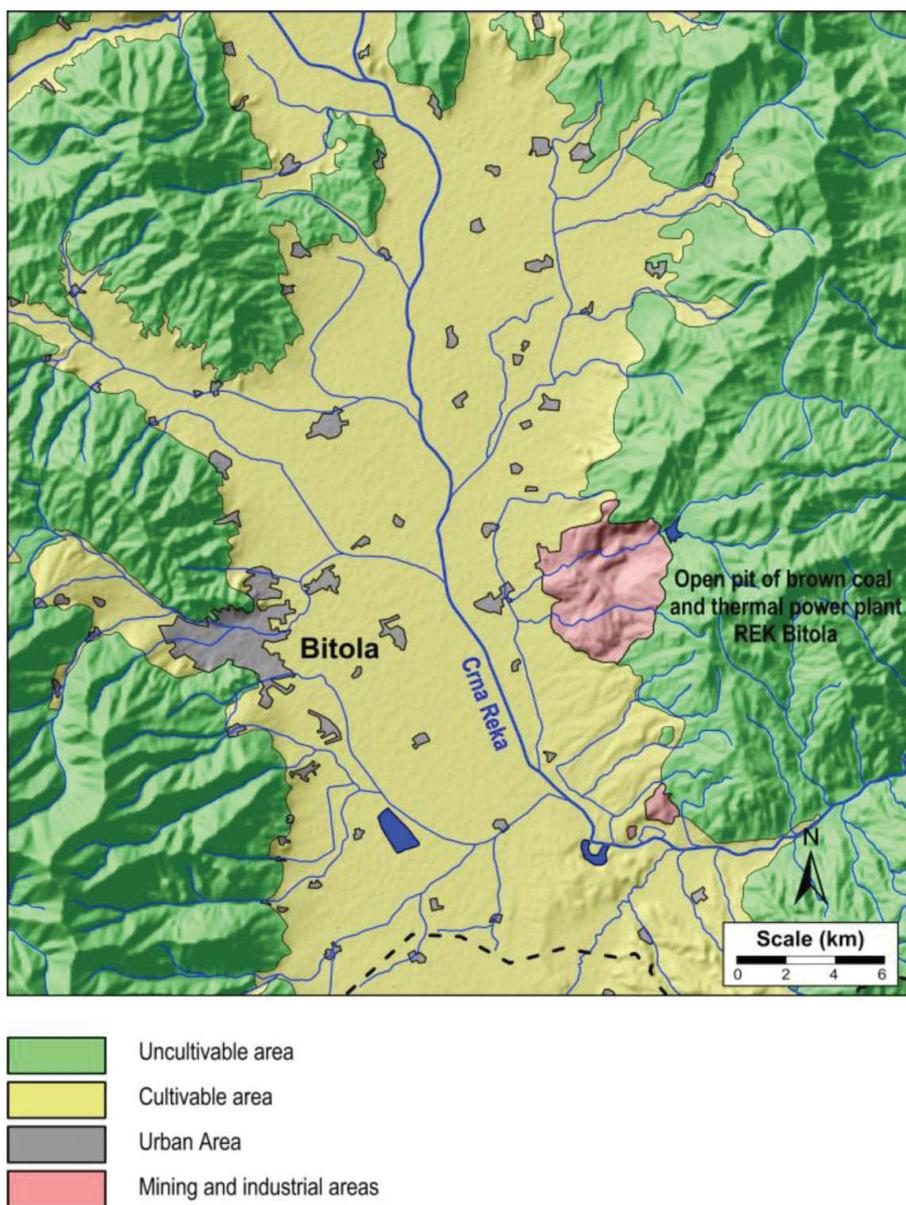


Figure 2. Land-use map of the studying area.

sediments in the Pelagonian depression. They begin with Middle Pliocene gravels, sands and clays with coal beds, while the upper part is composed of poorly sorted gravel, sand and silty clays. Holocene is represented by diluvial and alluvial deposits.

Material and methods

Soil sampling

For the assessment of soil quality in the Bitola Region, soil samples were collected from 149 locations. From 102 of these locations topsoil (0–5 cm) samples were collected, from 72 locations bottom soil samples from depth 20–30 cm were also collected, and from additional 45 locations samples were collected from the depth of 0–30 cm. Also, from 2 locations 10 samples from 5 vertical profiles were collected (0–20 cm, 20–40 cm, 40–60 cm, 60–80 cm 80–

100 cm) were collected. Thus, in total 229 soil samples were collected and analyzed. The soil sampling locations are presented in Figure 4. Sampling locations were determined by constructing a network. Depending on site conditions and accessibility, samples were collected in the surroundings of the specified locations, recording the relevant coordinates. To obtain representative composite samples,^[44] five subsamples from each location on a square plot of 10 × 10 m were collected: four samples at the corners of the plot and one sample at the intersection of the square diagonals.

Sample preparation and analysis

The soil samples brought in the laboratory were cleaned from plant material and stones and homogenized, dried at room temperature or in a drying oven at 40°C. Subsequently, they were passed through a 2 mm sieve and ground in a porcelain mortar until reaching a final particle size of 125 μm. Prior to

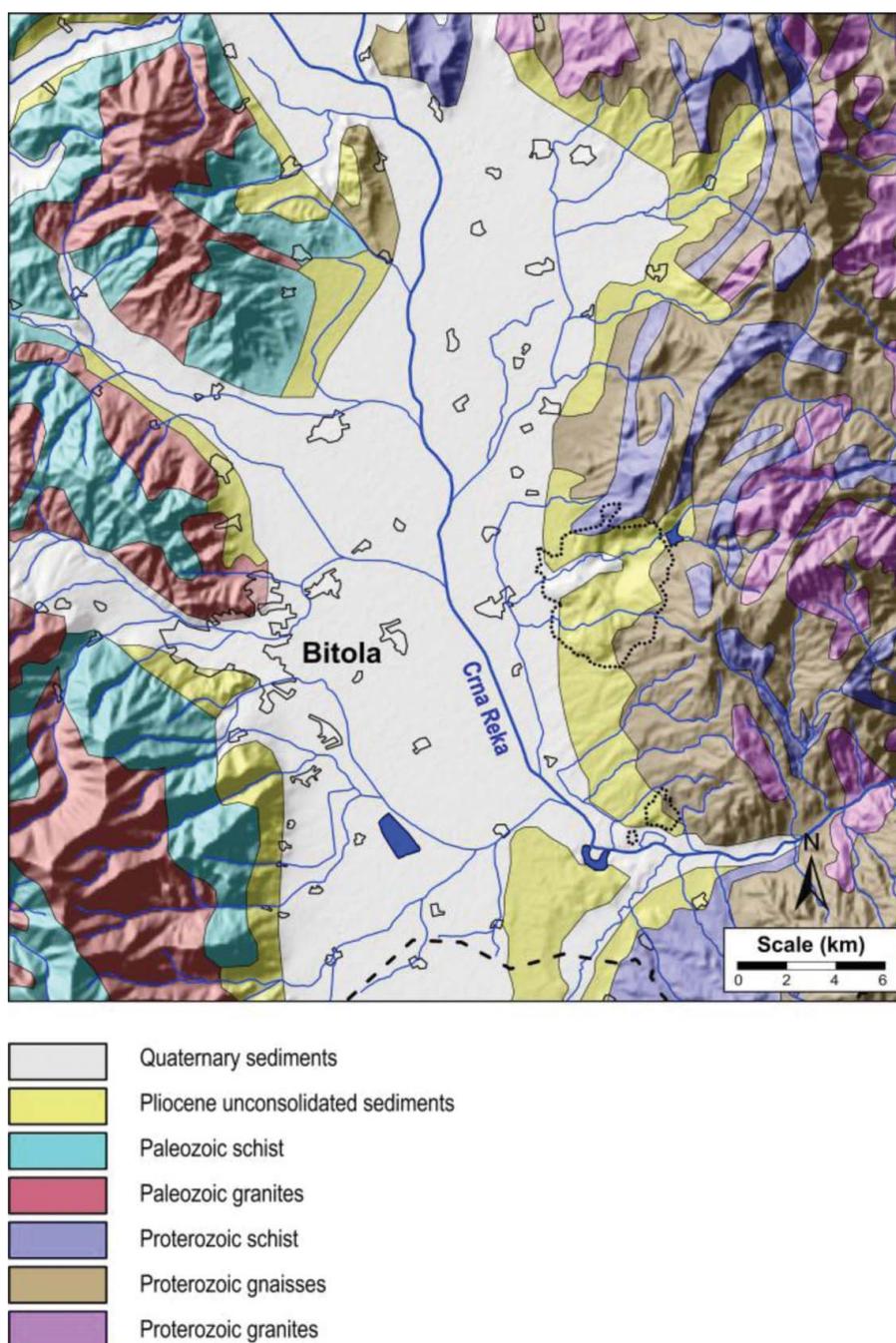


Figure 3. Geological map.

the determination of the elements by atomic emission with inductively coupled plasma (ICP-AES), the samples were digested, applying a mixture of acids (HNO_3 , HF, HClO_4 and HCl) in accordance with the international standards (ISO 14869–1:2001).

All used reagents and standards contained the required analytical purity levels. 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 a concentration of 1,000 mg/l (11355–ICP, Multi-Element Standard, Merck).

For each element analyzed, previous optimization of the instrumental conditions was performed. In all samples, the

content of a total of 21 elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) was determined. The quality control was performed by the analysis of certified reference soil and geological samples: soil sample JSAC 0401 (The Japan Society for Analytical Chemistry) and rock CRM samples undersaturated igneous rock SARM 3 NIM-L Lujaurite (SA Bureau of Standards, Pretoria, S. Africa), rock NCS DC71306 (GBW07114) (China National Analysis Centre).

Data processing of the obtained results

Statistical relationships between two variables can be measured by correlation. Correlations are useful because they can indicate

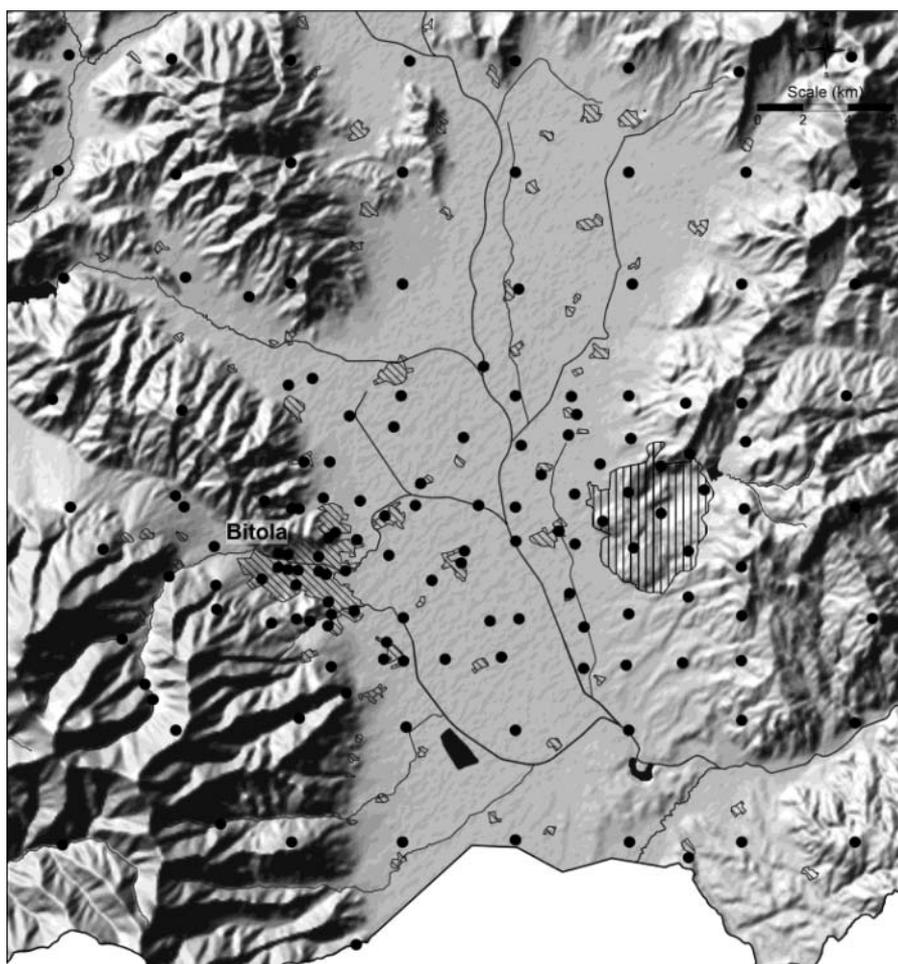


Figure 4. The locations in Bitola region for soil sampling.

a predictive relationship that can be exploited in practice. A measure of the correlation between two variables is expressed by the correlation coefficient, and the most common is the Pearson correlation coefficient (r), which is mainly sensitive to a linear relationship between two variables. Other correlation coefficients have been developed to be more robust than the Pearson correlation, or more sensitive to nonlinear relationships.

Correlation of the values was estimated using bivariate statistics (using the linear correlation of coefficients, r), with significance levels of $p < 0.05$ and $p < 0.01$. In the case of a large number of variables (for example $n > 20$), the bivariate analysis is not useful. Therefore, we applied multivariate analysis to enable a reduction of the number of variables by creating new synthetic variables, dependent on the correlation. For processing certain data for comparative analysis, the F-test was applied. We also applied 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 to reveal the hidden data structure.^[45] In other words, 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 large amounts 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. As a measure of similarity between variables, the product moment correlation coefficient (r) was applied. For orthogonal rotation, the varimax method was used.

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.

Results and discussion

Data from the descriptive statistics of the measurements of 21 elements determined by ICP-AES (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) in all of the topsoil samples (0–5 cm), collected from 102 sampling locations in Bitola Region are presented in Table 1. Data from the descriptive statistics for the content of the same elements in bottom soil samples (20–30 cm and 0–30 cm) collected from 117 sampling locations are

Table 1. Descriptive statistics for the content of the elements in surface soil.

Element	Unit	N	X	X(BC)	Md	Min	Max	P10	P90	P25	P75	S	Sx	CV	A	E	A(BC)	E(BC)
Al	%	102	2.2	2.1	2.1	0.67	6.2	1.2	3.5	1.6	2.7	0.95	0.075	42	1.06	1.88	0.10	0.03
As	mg/kg	69	21	18	18	2.1	150	6.2	38	13	25	16	1.4	77	4.08	27.84	0.04	1.56
B	mg/kg	84	17	11	18	0.10	97	1.1	33	2.4	27	16	1.3	91	1.58	5.61	-0.38	-1.01
Ba	mg/kg	160	330	280	320	19	1500	71	590	130	460	220	17	67	1.10	3.44	-0.16	-0.52
Ca	%	160	0.80	0.53	0.54	0.019	11	0.15	1.7	0.29	0.97	1.1	0.086	135	6.44	58.18	0.02	1.01
Cd	mg/kg	74	0.46	0.28	0.28	0.10	4.5	0.10	1.0	0.15	0.62	0.52	0.045	112	4.37	29.88	-0.05	-1.18
Co	mg/kg	78	9.4	8.0	8.6	1.2	31	3.3	16	4.9	12	6.0	0.52	64	1.55	3.03	-0.00	-0.17
Cr	mg/kg	102	71	56	56	9.3	650	28	120	42	77	64	5.1	91	5.55	43.69	-0.11	1.82
Cu	mg/kg	102	23	18	20	0.30	250	3.6	41	9.2	32	23	1.8	101	6.18	58.38	0.24	2.57
Fe	%	102	2.2	2.0	2.0	0.53	5.2	1.2	3.5	1.5	2.6	0.90	0.071	42	0.92	0.64	0.02	-0.13
K	%	102	1.8	1.8	1.8	0.19	3.1	1.2	2.5	1.5	2.1	0.49	0.039	27	0.20	0.50	-0.08	0.89
Li	mg/kg	102	17	13	13	1.5	93	4.0	34	6.5	23	13	1.1	80	1.97	6.71	-0.00	-0.62
Mg	%	102	0.43	0.34	0.41	0.0003	1.3	0.030	0.89	0.11	0.64	0.33	0.026	76	0.52	-0.49	-0.28	-0.97
Mn	mg/kg	102	600	540	540	170	2400	310	890	420	680	320	25	53	2.62	10.56	0.12	0.97
Na	%	102	1.2	1.1	1.1	0.067	3.7	0.44	2.0	0.74	1.5	0.62	0.049	53	1.04	1.67	0.01	0.35
Ni	mg/kg	102	26	24	24	1.8	76	9.2	44	16	35	14	1.1	55	0.94	1.18	-0.05	0.10
P	%	102	0.088	0.052	0.050	0.012	1.9	0.025	0.14	0.035	0.083	0.17	0.014	195	8.06	79.2	0.23	0.52
Pb	mg/kg	102	27	10	10	1.0	1500	4.5	34	5.0	20	120	9.7	456	11.87	146.2	-0.28	1.57
Sr	mg/kg	102	89	68	70	3.6	420	16	190	36	120	76	6.0	85	1.72	3.65	-0.01	-0.20
V	mg/kg	102	71	65	65	14	230	34	120	49	90	33	2.6	46	1.25	2.77	-0.13	0.20
Zn	mg/kg	102	96	51	59	1.4	3500	13	150	30	82	280	22	294	11.08	132.2	-0.19	3.08

X = arithmetical average; X(BC) = arithmetical average after Box-Cox method; Md = median; min = minimum; max = maximum; P₁₀ = 10th percentile; P₉₀ = 90 percentile; P₂₅ = 25th percentile; P₇₅ = 75th percentile; S = standard deviation; Sx = standard error; CV = coefficient of variation; A = skewness; E = kurtosis; BC = Box-Cox transformed values.

given in Table 2. Descriptive statistics of the measurements of these elements in both, top and bottom soil samples (229 samples) are given in Table 3. In Tables 1–3 the following statistical parameters are given: N – number of samples; X – arithmetical average; X(BC) – arithmetical average after Box-Cox method; Md – median; Min – minimum; Max – maximum; P₁₀ – 10th percentile; P₉₀ – 90th percentile; P₂₅ – 25th percentile; P₇₅ – 75th percentile; S – standard deviation; Sx – standard error; CV – coefficient of variation; A – skewness; E – kurtosis; BC – Box-Cox transformed values.

All data were statistically processed using statistic software Stat Soft, 11.0; parametric and nonparametric analyses were applied. Data were subjected to normalization tests and basic

descriptive statistical analysis was conducted on the values of the metal contents in all samples. Distribution histograms were checked visually and the distribution of data on independent variables (elements' contents) was determined.

It could be seen that the median values and ranges of the content of macroelements (Al, Ca, Fe, K, Mg and Na) are in the following ranges: 2.2% and 0.64–6.2% for Al; 0.52% and 0.013–11% for Ca; 2.0% and 0.53–5.2% for Fe; 1.8% and 0.19–3.4% for K; 0.41% and 0.003–1.4% for Mg and 1.1% and 0.067–3.7% for Na. The contents of macroelements are most frequently a result of the dominant geological formations of the area: Quaternary Pliocene unconsolidated sediments, Paleozoic schists and granites and Proterozoic schists, gneisses and granites (Fig. 3).

Table 2. Descriptive statistics for the content of the elements in bottom soil.

Element	Unit	N	X	X(BC)	Md	Min	Max	P10	P90	P25	P75	S	S _x	CV	A	E	A(BC)	E(BC)
Al	%	117	2.3	2.2	2.2	0.64	4.6	1.2	3.7	1.6	2.9	0.91	0.084	39	0.59	-0.22	-0.05	-0.47
As	mg/kg	96	22	19	18	2.0	76	7.8	37	13	27	13	1.4	63	1.61	3.31	0.05	0.37
B	mg/kg	111	17	8.2	6.8	0.10	180	0.79	36	1.6	29	22	2.1	134	3.95	26.27	0.16	-0.99
Ba	mg/kg	117	350	290	330	14	1500	72	680	130	470	240	23	71	1.19	3.23	-0.13	-0.43
Ca	%	117	0.68	0.44	0.45	0.013	7.6	0.096	1.5	0.23	0.84	0.84	0.078	124	5.13	38.79	-0.11	0.40
Cd	mg/kg	101	0.48	0.24	0.21	0.10	4.3	0.10	1.0	0.10	0.61	0.71	0.071	147	3.67	16.18	0.38	-1.12
Co	mg/kg	106	10	9.2	8.9	1.8	32	4.3	19	6.4	13	5.8	0.56	55	1.23	2.00	-0.04	-0.22
Cr	mg/kg	117	75	61	61	16	540	34	120	45	88	60	5.6	81	4.69	31.96	-0.03	0.90
Cu	mg/kg	117	24	19	20	0.55	250	4.3	45	8.2	31	27	2.5	110	5.73	47.61	0.55	2.55
Fe	%	117	2.3	2.2	2.1	0.82	5.1	1.3	3.6	1.7	3.0	0.93	0.086	40	0.64	-0.06	-0.10	-0.50
K	%	117	1.8	1.8	1.7	0.66	3.4	1.2	2.5	1.4	2.1	0.52	0.048	29	0.37	0.01	0.20	-0.12
Li	mg/kg	117	19	16	17	2.0	94	5.9	34	10	24	14	1.3	72	2.09	7.30	-0.12	-0.03
Mg	%	117	0.43	0.35	0.42	0.0003	1.4	0.029	0.85	0.13	0.65	0.32	0.030	75	0.49	-0.43	-0.34	-0.92
Mn	mg/kg	117	630	560	560	150	2400	300	1000	430	720	330	31	53	2.30	8.28	-0.02	0.82
Na	%	117	1.1	1.0	1.1	0.13	3.3	0.37	2.1	0.68	1.5	0.62	0.058	55	0.73	0.48	-0.12	-0.26
Ni	mg/kg	117	30	27	27	1.0	93	10	52	17	38	17	1.6	58	1.06	1.56	-0.02	0.22
P	%	117	0.082	0.046	0.045	0.008	1.9	0.021	0.11	0.031	0.074	0.18	0.017	224	8.48	81.61	0.01	0.97
Pb	mg/kg	117	25	11	9.6	1.6	410	4.8	39	5.3	21	54	5.0	219	5.31	31.54	0.46	0.28
Sr	mg/kg	117	85	65	64	2.6	370	15	170	37	110	75	6.9	88	1.79	3.58	0.02	-0.04
V	mg/kg	117	79	72	72	20	250	41	130	54	95	39	3.6	49	1.76	5.02	0.09	0.44
Zn	mg/kg	117	110	47	55	0.87	3100	11	140	27	83	390	36	340	7.33	53.72	0.28	3.69

X = arithmetical average; X(BC) = arithmetical average after Box-Cox method; Md = median; min = minimum; max = maximum; P₁₀ = 10th percentile; P₉₀ = 90 percentile; P₂₅ = 25th percentile; P₇₅ = 75th percentile; S = standard deviation; S_x = standard error; CV = coefficient of variation; A = skewness; E = kurtosis; BC = Box-Cox transformed values

Table 3. Descriptive statistics for the content of the elements in surface and bottom soil.

Element	Unit	N	X	X(BC)	Md	Min	Max	P10	P90	P25	P75	S	SX	CV	A	E	A(BC)	E(BC)
Al	%	229	2.3	2.1	2.2	0.64	6.2	1.2	3.5	1.5	2.8	0.93	0.059	41	0.84	1.10	-0.01	-0.23
As	mg/kg	176	21	18	18	2.0	150	6.7	37	13	25	16	1.1	73	3.49	22.41	0.04	1.21
B	mg/kg	206	17	9.9	16	0.10	180	0.94	35	2.1	28	19	1.3	112	3.39	23.25	-0.14	-0.99
Ba	mg/kg	245	330	280	320	14	1500	71	600	130	460	230	15	70	1.29	3.89	-0.08	-0.38
Ca	%	245	0.76	0.49	0.52	0.013	11	0.12	1.6	0.24	0.94	1.0	0.066	136	6.09	53.12	0.02	0.70
Cd	mg/kg	186	0.49	0.27	0.26	0.10	4.5	0.10	1.0	0.12	0.64	0.64	0.045	130	3.87	19.54	0.11	-1.22
Co	mg/kg	194	9.9	8.4	8.7	1.2	32	3.6	18	5.5	13	6.2	0.43	63	1.37	2.14	-0.01	-0.30
Cr	mg/kg	229	74	58	57	9.3	650	31	120	42	82	66	4.2	89	4.96	34.90	-0.05	1.27
Cu	mg/kg	229	23	18	20	0.30	250	3.4	42	8.8	32	21	1.4	93	5.50	55.55	0.06	1.47
Fe	%	229	2.2	2.1	2.0	0.53	5.2	1.2	3.6	1.6	2.7	0.94	0.060	42	0.79	0.14	-0.01	-0.36
K	%	229	1.8	1.8	1.8	0.19	3.4	1.2	2.5	1.5	2.1	0.51	0.032	28	0.29	0.27	0.05	0.43
Li	mg/kg	229	17	14	14	1.5	94	4.7	33	7.2	23	14	0.88	79	2.16	7.54	-0.01	-0.41
Mg	%	229	0.43	0.34	0.41	0.0003	1.4	0.027	0.87	0.13	0.65	0.33	0.021	77	0.56	-0.39	-0.27	-0.95
Mn	mg/kg	229	610	550	550	150	2400	310	980	430	700	310	20	51	2.30	8.60	-0.01	0.76
Na	%	229	1.2	1.1	1.1	0.067	3.7	0.42	2.0	0.71	1.5	0.63	0.040	54	0.96	1.23	0.00	0.07
Ni	mg/kg	229	28	25	25	1.0	93	9.2	47	16	36	16	1.0	58	1.07	1.63	0.00	0.14
P	%	229	0.080	0.049	0.048	0.008	1.9	0.023	0.14	0.033	0.076	0.14	0.009	181	9.03	104.9	-0.05	0.72
Pb	mg/kg	229	28	11	10	1.0	1500	4.7	39	5.2	22	110	6.7	382	12.4	173.4	-0.07	1.19
Sr	mg/kg	229	86	66	68	2.6	420	15	180	36	120	73	4.7	85	1.75	3.81	-0.02	-0.14
V	mg/kg	229	74	67	67	14	250	35	120	49	92	37	2.4	50	1.58	4.20	0.00	0.27
Zn	mg/kg	229	110	51	59	0.87	3500	13	160	30	84	350	22	317	8.39	72.41	0.05	3.40

X = arithmetical average; X(BC) = arithmetical average after Box-Cox method; Md = median; min = minimum; max = maximum; P₁₀ = 10th percentile; P₉₀ = 90 percentile; P₂₅ = 25th percentile; P₇₅ = 75th percentile; S = standard deviation; Sx = standard error; CV = coefficient of variation; A = skewness; E = kurtosis; BC = Box-Cox transformed values.

A comparative analysis was conducted based on the data of the contents of the analyzed elements in the soils from Bitola region and soil from Macedonia^[43] and Europe^[6] is given in Table 4. For the comparative analysis, the median values were used as a more stable parameter as well as the range of the content for each element. From data presented in Table 4 it can be seen that the content of Al (2.2%) is higher than the median for the soil from the whole territory of Macedonia, while the contents of the other macro-elements (Ca, Fe, K, Li, Mg and Na are lower in relation to the data for Macedonian soil. The median values for all of

the trace elements are lower in soil samples from Bitola region compared with those for Macedonian soil which show that their distribution corresponds to the lithogenic origin of the rocks. Namely, the geology of this region is very specific belonging to the Pelagonian Massif as separate tectonic units in Macedonia.^[43] Comparison of the median, minimal and maximal values for the macro-elements in soil for the Bitola Region and European soil^[6] show lower values for the content of Al, Ca, Mg and Na, and not significant higher value for Fe and K. The content of microelements in soil from Bitola Region is generally

Table 4. Comparison of the median, minimal and maximal values for the content of analyzed elements in soil from Bitola Region with those for the Republic of Macedonia and Europe.

Element	Unit	Bitola Region (this study)		Macedonia (Stafilov & Šajin, 2016)		Europe (Salminen et al., 2005)		Dutch standard*	
		Md	Min–Max	Md	Min–Max	Md	Min–Max	Target	Intervention
Al	%	2.2	0.64–6.2	1.3	0.05–35	5.8	0.70–14.1	—	—
As	mg/kg	18	2.0–150	10	1.0–720	12	0.32–562	29	55
B	mg/kg	16	0.10–180	—	—	—	—	—	—
Ba	mg/kg	320	14–1500	430	6–2900	375	30–1870	200	625
Ca	%	0.52	0.013–11	1.3	0.05–35	0.66	0.019–34.3	—	—
Cd	mg/kg	0.26	0.10–4.5	0.30	0.01–110	0.92	0.03–14	0.8	12
Co	mg/kg	8.7	1.20–32	17	0.5–150	7.78	<3–249	20	240
Cr	mg/kg	57	9.3–650	88	5.0–2700	60	<3–6230	100	380
Cu	mg/kg	20	0.30–250	28	1.6–270	13	0.81–256	36	190
Fe	%	2.0	0.53–5.2	3.5	0.03–12	1.34	0.049–10.6	—	—
K	%	1.8	0.19–3.4	1.9	0.02–5.3	1.59	0.022–5.1	—	—
Li	%	14	1.5–94	26	1.8–210	22	0.14–271	—	—
Mg	%	0.41	0.0003–1.4	0.94	0.12–13	0.47	<0.006–15	—	—
Mn	mg/kg	550	150–2400	900	17–10000	510	31–6070	—	—
Na	%	1.1	0.067–3.7	1.3	0.007–3.7	0.6	0.03–3.34	—	—
Ni	mg/kg	25	1.0–93	46	2.1–2500	18	<2–2690	35	210
P	mg/kg	0.048	0.008–1.9	0.062	0.011–0.39	0.96	0.0082–0.99	—	—
Pb	mg/kg	10	1.0–1500	32	1.2–10000	23	5.3–970	85	530
Sr	mg/kg	6.8	2.6–420	140	21–1400	89	8–3120	—	—
V	mg/kg	67	14–250	89	1.0–470	60	2.7–537	—	—
Zn	mg/kg	59	0.87–3500	83	8.0–10000	52	<3–2900	140	720

Md – median; Min – minimum; Max – maximum.

*https://www.esdat.net/Environmental%20Standards/Dutch/annexS_I2000Dutch%20Environmental%20Standards.pdf

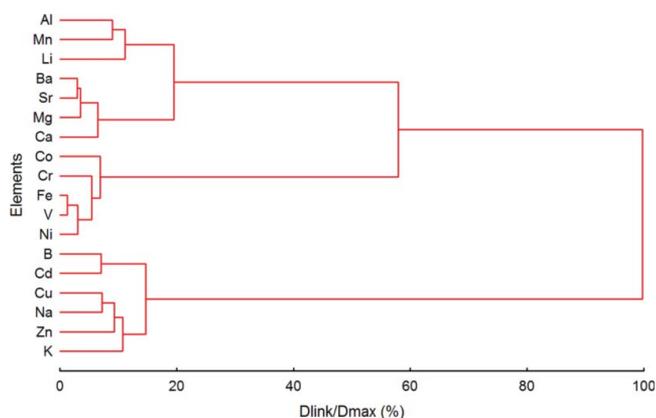


Figure 5. Dendrogram from the cluster analysis.

cadmium in the samples from 2 drillings down to 1 m from the fly ash deposit show a high content of cadmium ranging from 1.0 mg/kg in the soil layers from 80–100 cm to 4.5 mg/kg in the top layer of 0–20 cm. Similar results were obtained for the contents of Pb and Zn showing high

content in the top layers of fly ash deposit (3070 mg/kg for Zn and 204 mg/kg for Pb).

The matrix of correlation coefficients between all of the analyzed elements is given in Table 6. By applying bivariate statistics the degree of correlation between the analyzed elements in the soil samples was determined. It was usually assumed that the absolute value of the correlation coefficient between 0.3 and 0.7 indicates a good association and between 0.7 and 1.0 points to the existence of a strong connection between elements. The values for the content of each element were correlated with the values for the content of the other elements. All correlation coefficients between all elements are represented in the matrix of correlation coefficients (Table 6).

In the factor analysis, the distribution is reduced to three synthetic variables (F1 to F3). As it can be seen from the results obtained by factor analysis (Table 7) three factors (i.e., associations of elements) were obtained F1 (Fe, Ni, V, Co, Cr, Mn and Li), F2 (Zn, B, Cu, Cd, Na, K) and F3 (Ca, Sr, Mg, Ba and Al). The total communality of the factors amounts to 72.2%. A total of 21 elements were reduced by

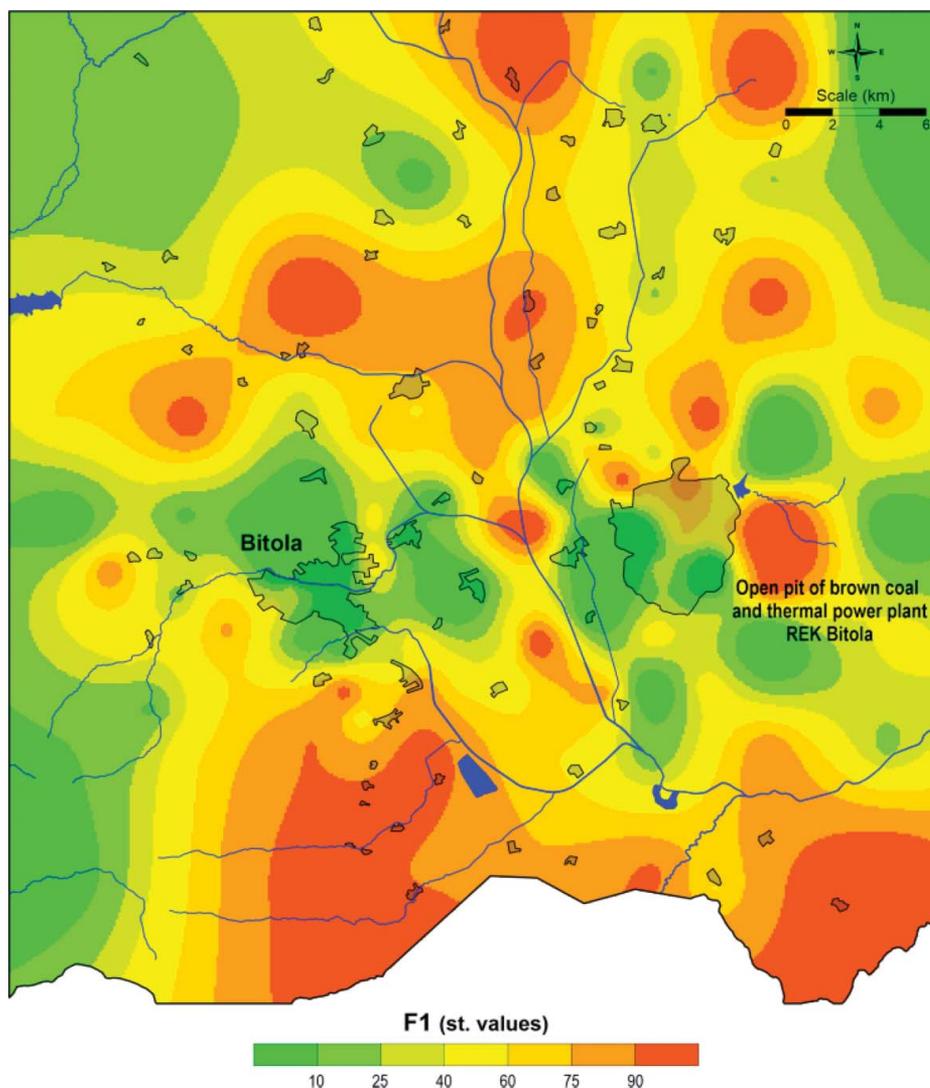


Figure 6. Spatial distribution of factor scores of F1 (Fe, Ni, V, Co, Cr, Mn and Li).

Table 8. The average content of the analyzed elements in soil and fly ash.

Element	Unit	Soil	Fly ash
Al	%	2.1	2.2
As	mg/kg	18	31
B	mg/kg	9.9	36
Ba	mg/kg	280	127
Ca	mg/kg	0.49	0.42
Cd	mg/kg	0.27	2.3
Co	mg/kg	8.4	5.8
Cr	mg/kg	58	47
Cu	mg/kg	18	42
Fe	%	2.1	2.1
K	%	1.8	0.87
Li	mg/kg	14	31
Mg	%	0.34	0.20
Mn	mg/kg	550	322
Na	%	1.1	0.14
Ni	mg/kg	25	32
P	%	0.049	0.11
Pb	mg/kg	11	102
Sr	mg/kg	66	22
V	mg/kg	67	61
Zn	mg/kg	51	1002

factor analysis to 18 elements, which had a total factor loading of 74.4% of the variability (Table 7). The rest of the elements (As, P and Pb) were eliminated from further analysis because they had a low share of communality or low tendency to form independent factors.

The dendrogram obtained by the application of cluster analysis is given in Figure 5. In the dendrogram, the elements are divided into clusters according to the degree of correlation between them. The first cluster includes the elements Al, Mn, Li, Ba, Sr, Mg and Ca, which are included in Factor 3 of the matrix of loading of the dominant rotating factors (Table 7), except for Mn and Li which belong to the association of elements from Factor 1. The second cluster is composed of Co, Cr, Fe, V and Ni. These elements belong to Factor 1 of the factor analysis. The third cluster consists of B, Cd, Cu, Na, Zn and K, which belong to Factor 2).

To construct the maps for the distribution of the elements 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

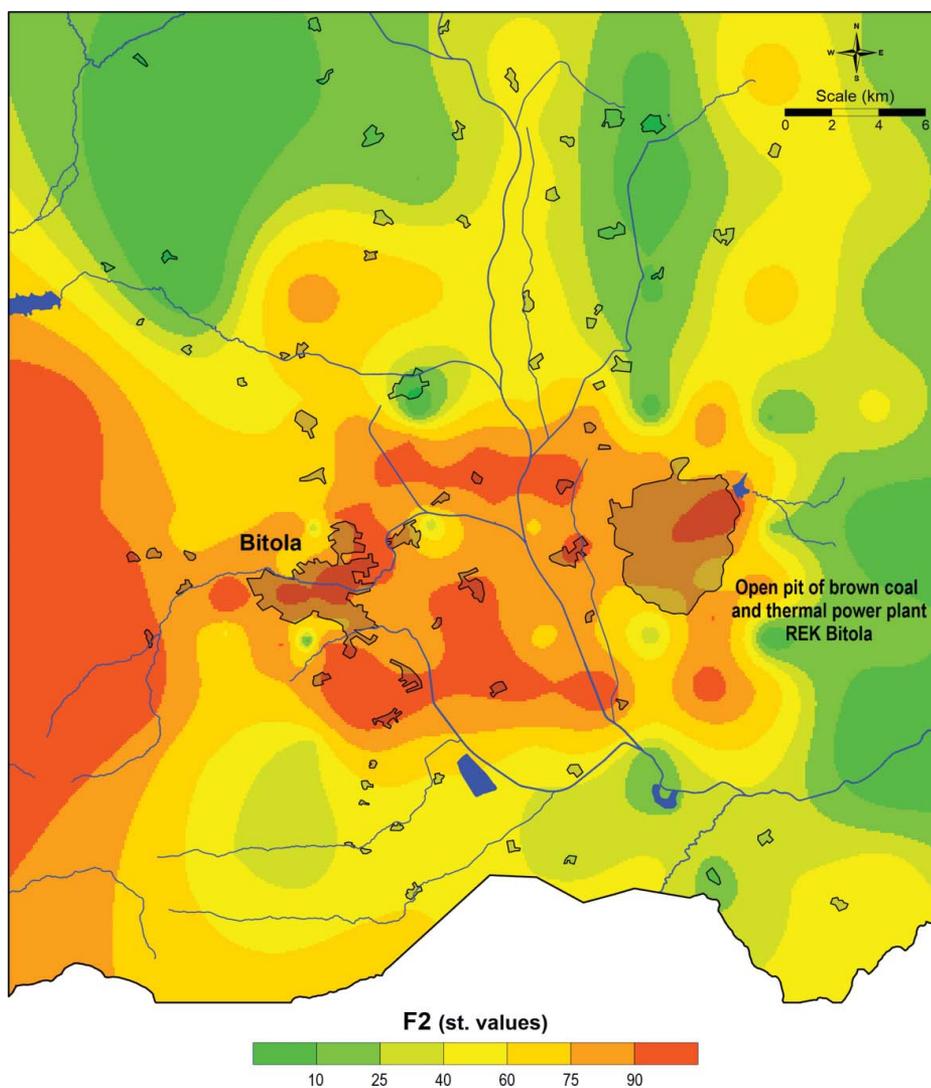


Figure 7. Spatial distribution of factor scores of F2 (Zn, B, Cu, Cd, Na, K).

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 can be spatially defined.^[47] All data about variables are organized in several possible ways; most common one 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 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.^[48]

For the development of the distribution maps, the kriging method with linear variogram interpolation was applied. As area limits, we considered the percentile values of the distribution of the interpolated values. The following seven areas of percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100. For a graphical display of spatial distribution, the maps with percentile distribution have been used, where different colors represent different concentration arrangements. The distribution maps for the individual elements are prepared in 7 concentration ranges for each element.

Factor 1 (Fe, Ni, V, Co, Cr, Mn and Li)

The spatial distribution map of the factor scores of factor F1 (Fig. 6) shows that these elements are present in varying concentrations throughout the studied area. Higher contents of these elements are found in the soil samples from the southern part (Mts. Baba and Nidže), in some part of the Selečka Mountain to the eastern part and in the central part of the studied the area. According to geological formations, higher content of these elements are present in the soil from the areas were Pliocene sediments and Paleozoic and Proterozoic schists are dominant (Figs. 3 and 6). The distribution maps for all of the elements included in F1 show that their distribution follows the distribution of factor values of F1. In general, it could be concluded that the distribution of the elements from Factor 1 is, their highest contents are found in soil over Mesozoic and Paleozoic magmatic rocks from Pelagonian massif, but they are characterized by their almost complete absence in the Pelagonian massif (Precambrian metamorphic and carbonate rocks).^[43] From the data presented in Table 8, it could be seen that the content of the elements in soil samples from the Bitola area included in Factor 1 are a bit higher or very close to their content in fly ash samples confirming their lithological origin.

Factor 2 (Zn, B, Cu, Cd, Na, K)

The spatial distribution map of the factor scores of factor F2 (Fig. 7) shows that these elements are also present in

varying concentrations throughout the studied area. Higher content of the elements associated with this factor was found in the soil samples from the mountain Baba as well as in the area of the valley between the city of Bitola and REK Bitola. According to geological formations, higher content of these elements are present in the soil from the areas were Paleozoic and Proterozoic schists and granites and Quaternary sediments. It could be seen that the distribution of each element from this association follows the distribution factor values F1. From data presented in Table 8 and from the distribution maps for the elements included in this association it could be concluded that Factor 2 represents a geogenic and anthropogenic association. Namely, the average contents of Cd, Cu and Zn are several times

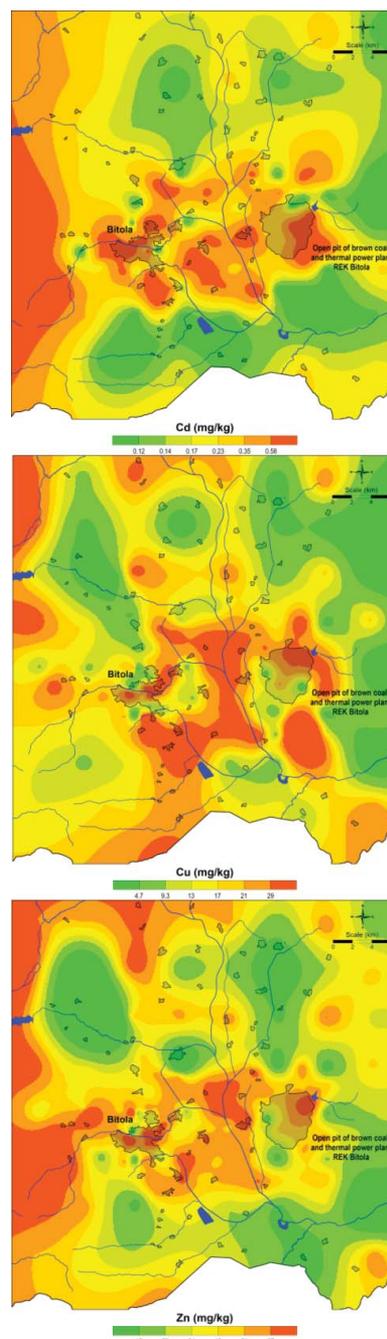


Figure 8. Spatial distribution maps of cadmium, copper and zinc.

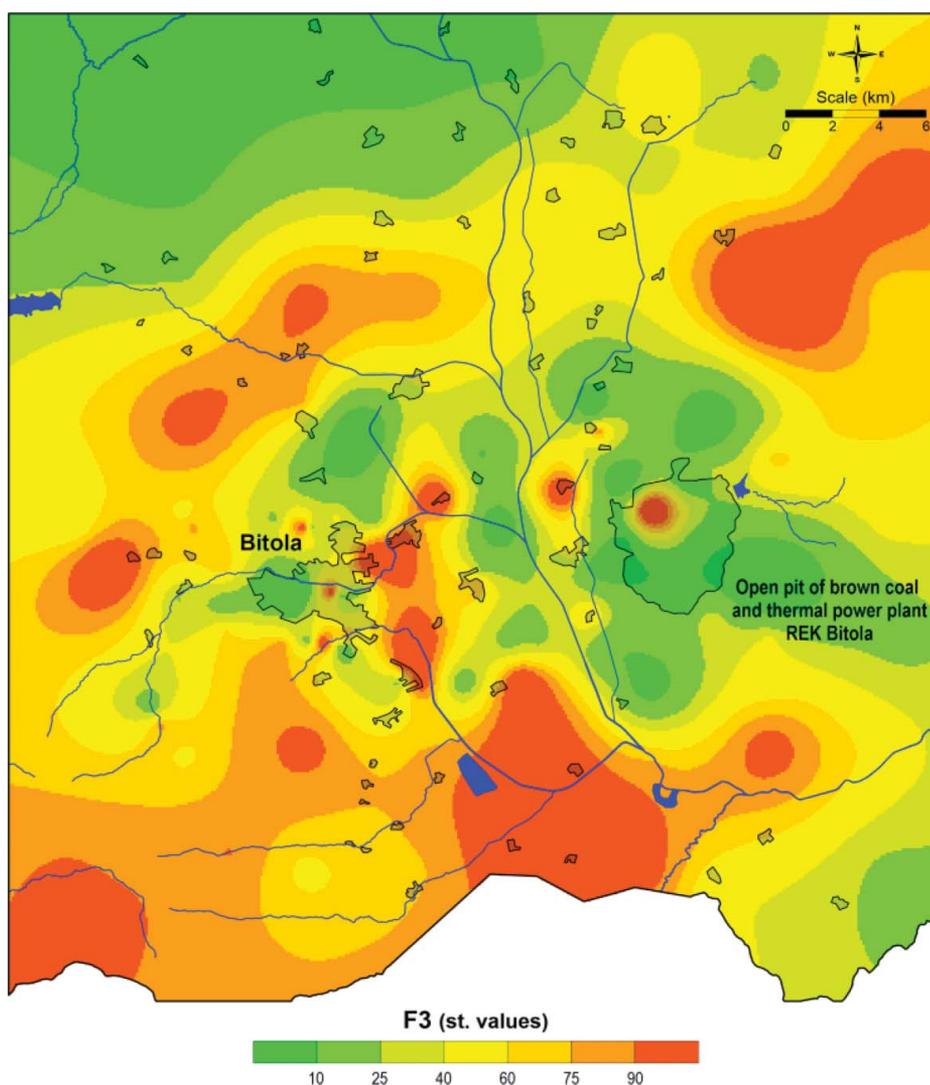


Figure 9. Spatial distribution of factor scores of F3 (Ca, Sr, Mg, Ba and Al).

higher in fly ash than their average content in soil from the whole region (Table 8). This influence from the fly ash pollution could be seen also from the distribution maps of these elements (Fig. 8) with increased content of these elements in the soil in the area around the thermoelectric power plant and the city of Bitola.

Factor 3 (Ca, Sr, Mg, Ba and Al)

The spatial distribution map of the factor scores of factor F3 (Fig. 9) shows that these elements are also present in varying concentrations throughout the studied area. Higher content of the elements associated with this factor was found in the soil samples from the mountain Baba and southern part of the Pelagonia Valley. According to geological formations, higher content of these elements are present in the soil from the areas were Quaternary and Pliocene unconsolidated sediments, as well as Paleozoic schists and granites, are dominant geological formations (Fig. 3). The maps of spatial distribution of all elements included in Factor 1 are very similar following the geological formations.

Arsenic, phosphorous and lead are not included in the factors due to the absence of correlation with the other elements. The maps of spatial distribution of these elements are presented in Figure 10. From Figure 10 it could be seen that the content of arsenic in soils from the investigated area is relatively low (average value of 18 mg/kg) while the average content of arsenic in fly ash is 31 mg/kg. However, the content of arsenic in several soil samples collected in the area of REK Bitola and near surroundings are higher than target value according to the Dutch value (29 mg/kg) or even higher than the intervention value of 55 mg/kg. This is the results of the pollution with fly ash in the near surrounding of the REK Bitola plant (Table 8).

Spatial distribution of phosphorous presented in Figure 10 shows that higher content of P (average value of 0.049%) are found in soil samples collected from the agricultural land of Pelagonia Valley. It was also found that the content of P is higher in soil collected in the vicinity of REK Bitola (average of 0.11%). In some samples, the content of phosphorous is higher than 1%. Such high values are the most probably due to phosphate fertilizers used in the agricultural practice in this region.

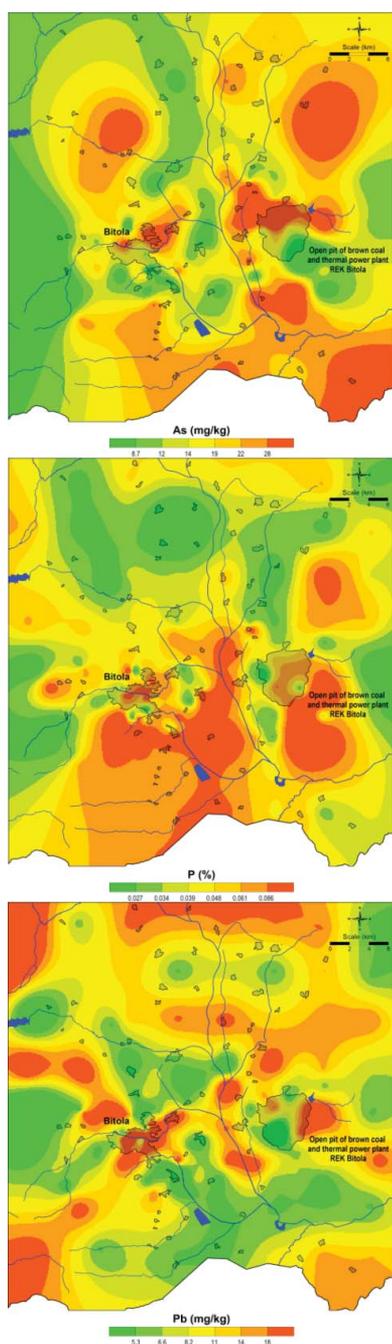


Figure 10. Spatial distribution of arsenic, phosphorous and lead.

The content of lead in the whole investigated area is relatively low ranging from 1 to 1500 mg/kg with an average value of 28 mg/kg and the median value of 10 mg/kg (Table 3). The higher content was found in the soil samples collected in the city of Bitola and in its near vicinity as well as in the area of REK Bitola (Fig. 10). The reason for higher content in these areas is probably the urban activities in the city of Bitola and the pollution in the area of REK Bitola due to higher content of lead in fly ash (from 20 to 258 mg/kg with an average of 102 mg/kg) (Table 8).

Conclusion

From the obtained results it could be concluded that the content of soil in the investigated area corresponds to the lithological

characteristics of the Bitola Region in the Southern Pelagonia. The factor analysis gives four associations of elements: F1 (Fe, Ni, V, Co, Cr, Mn and Li), F2 (Zn, B, Cu, Cd, Na, K) and F3 (Ca, Sr, Mg, Ba and Al). The higher content of the elements included in Factor 1 (Fe, Ni, V, Co, Cr, Mn and Li) are found in the soil samples over the Mesozoic and Paleozoic magmatic rocks from Pelagonian massif following the lithology of the area. The spatial distribution map of the factor scores of factor F2 (Zn, B, Cu, Cd, Na, K) shows that these elements are also present in varying concentrations throughout the studied area. Higher content of the elements associated with this factor was found in the soil samples over the Paleozoic and Proterozoic schists and granites and Quaternary sediments. The exception is the distribution of cadmium, copper and zinc because their higher contents are found in the around the fly ash deposit due to the dispersion of fly ash reach with these elements. The spatial distribution of the factor scores of factor F3 (Ca, Sr, Mg, Ba and Al) shows that these elements are following the lithology of the area with higher content in soil over the Quaternary and Pliocene unconsolidated sediments, as well as Paleozoic schists and granites. The distribution maps of arsenic and lead show that their content in soils from the investigated area is relatively low. However, their content in soil samples collected in the area of thermo-electrical power and it in its surroundings is higher than target values confirming the pollution with these elements from fly ash deposit because of much higher content of As and Pb in fly ash that in the soil from the area.

Acknowledgement

This study was realized as part of the project “Soil Degradation Assessment and Rehabilitation Strategies for Sustainable Land use planning” – TERRA MED – IPA/2010/DN023658/CN362856, founded by the Europe Union and by Ministry of Local Self-Government of the Republic of Macedonia under the IPA Cross Border Programme with Greece and part of the research was financially supported by the Slovenian Research Agency (research core funding No. P1-0020 – Groundwaters and geochemistry).

References

- [1] Bowen, H. T. M. *Environmental Chemistry of the Elements*; Academic Press: London, 1979.
- [2] Mustafa, G.; Komatsu, S. Toxicity of Heavy Metals and Metal-Containing Nanoparticles on Plants. *Biochim. Biophys. Acta (BBA) – Proteins Proteomics* 2016, 1864(8), 932–944. DOI: 10.1016/j.bbapap.2016.02.020.
- [3] Shahid, M.; Dumat, C.; Khalid, S.; Schreck, E.; Xiong, T.; Niazi, N. K. Foliar Heavy Metal Uptake, Toxicity and Detoxification in Plants: A Comparison of Foliar and Root Metal Uptake. *J. Hazard. Mater.* 2017, 325, 36–58. DOI: 10.1016/j.jhazmat.2016.11.063.
- [4] Kabata-Pendias, A.; Mukherjee, A. B. *Trace Elements from Soil to Human*; Springer: Heidelberg, 2007.
- [5] Mirsal, I. A. *Soil Pollution: Origin, Monitoring & Remediation*; Springer Verlag: Berlin, Heidelberg, 2008.
- [6] Salminen, R.; Batista, M. J.; Bidovec, M.; Demetriades, A.; De Vivo, B.; De Vos, W.; Duris, M.; Gilucis, A.; Gregorauskiene, V.; Halamic, J.; et al. *Geochemical Atlas of Europe, Part 1, Background Information, Methodology and Maps*; Geological Survey of Finland: Espoo, 2005.
- [7] Davidson, C. M.; Urquhart, G. J.; Ajmone-Marsan, F.; Biasioli, M.; Duarte, A. D.; Diaz-Barrientos, E.; Grman, H.; Hossack, L.; Hursthouse, A. S.; Madrid, L.; et al. Fractionation of Potentially Toxic Elements in Urban Soils from Five European Cities by Means of a Harmonised Sequential Extraction Procedure. *Anal. Chim. Acta.* 2006, 565, 63–72. DOI: 10.1016/j.aca.2006.02.014.

- [8] Mico, C.; Reatala, L.; Peris, M.; Sanchez, J. Assessing Heavy Metal Sources in Agricultural Soils of an European Mediterranean area by Multivariate Analysis. *Chemosphere* **2006**, *65*, 863–872. DOI: 10.1016/j.chemosphere.2006.03.016.
- [9] Reimann, C.; Birke, M.; Demetriades, A.; Filzmoser, P.; O'Connor, P. (Eds.). *Chemistry of Europe's Agricultural Soils – Part A: Methodology and Interpretation of the GEMAS Data Set*. Geologisches Jahrbuch (Reihe B), Heft 102; Schweizerbarth: Hannover, **2014a**; pp 528.
- [10] Reimann, C.; Birke, M.; Demetriades, A.; Filzmoser, P.; O'Connor, P. (Eds.). *Chemistry of Europe's Agricultural Soils – Part B: General Background Information and Further Analysis of the GEMAS Data Set*. Geologisches Jahrbuch (Reihe B), Heft 103; Schweizerbarth: Hannover, **2014b**; pp 352.
- [11] Kabata-Pendias, A.; Pendias, H. *Trace Elements in Soil and Plants*, 3rd ed.; CRC Press: Boca Raton, **2001**.
- [12] Stafilov, T.; Aliu, M.; Šajin, R. Arsenic in Surface Soils Affected by Mining and Metallurgical Processing in K. Mitrovica Region, Kosovo. *Int. J. Environ. Res. Public Health* **2010a**, *7*, 4050–4061. DOI: 10.3390/ijerph7114050.
- [13] Stafilov, T.; Šajin, R.; Pančevski, Z.; Boev, B.; Frontasyeva, M. V.; Strelkova, L. P. Heavy Metal Contamination of Surface Soils Around a Lead and Zinc Smelter in the Republic of Macedonia. *J. Hazard. Mater.* **2010b**, *175*, 896–914. DOI: 10.1016/j.jhazmat.2009.10.094.
- [14] D'Emilio, M.; Caggiano, R.; Macchiato, M.; Ragosta, M.; Sabia, S. Soil Heavy Metal Contamination in an Industrial Area: Analysis of the Data Collected During a Decade. *Environ. Monit. Assess.* **2013**, *185* (7), 5951–5964. DOI: 10.1007/s10661-012-2997-y.
- [15] Li, Z.; Ma, Z.; Van der Kuijp, T. J.; Yuan, Z.; Huang, L. A Review of Soil Heavy Metal Pollution from Mines in China: Pollution and Health Risk Assessment. *Sci. Total Environ.* **2014**, *468–469*, 843–853. DOI: 10.1016/j.scitotenv.2013.08.090.
- [16] Modis, K.; Vatalis, K. I. Assessing the Risk of Soil Pollution Around an Industrialized Mining Region Using a Geostatistical Approach. *Soil Sediment Contam.: An Int. J.* **2014**, *23*(1), 63–75. DOI: 10.1080/15320383.2013.777393.
- [17] Šajin, R.; Aliu, M.; Stafilov, T.; Alijagić, J. Heavy metal Contamination of Topsoil Around a Lead and Zinc Smelter in Kosovska Mitrovica/Mitrovicë, Kosovo/Kosovë. *J. Geochem. Explor.* **2013**, *134*, 1–16. DOI: 10.1016/j.gexplo.2013.06.018.
- [18] Okedeyi, O. O.; Dube, S.; Awofolu, O. R.; Nindi, M. M. Assessing the Enrichment of Heavy Metals in Surface Soil and Plant (*Digitaria Eriantha*) Around Coal-Fired Power Plants in South Africa. *Environ. Sci. Pollut. Res.* **2014**, *21*(6), 4686–4696. DOI: 10.1007/s11356-013-2432-0.
- [19] Barandovski, L.; Cekova, M.; Frontasyeva, M. V.; Pavlov, S. S.; Stafilov, T.; Steinnes, E.; Urumov, V. Atmospheric Deposition of Trace Element Pollutants in Macedonia Studied by the Moss Biomonitoring Technique. *Environ. Monit. Assess.* **2008**, *138*, 107–118. DOI: 10.1007/s10661-007-9747-6.
- [20] Barandovski, L.; Frontasyeva, M. V.; Stafilov, T.; Šajin, R.; Pavlov, S.; Enimiteva, V. Trends of Atmospheric Deposition of Trace Elements in Macedonia Studied by the Moss Biomonitoring Technique. *J. Environ. Sci. Health, Part A* **2012**, *47*(13), 2000–2015. DOI: 10.1080/10934529.2012.695267.
- [21] Barandovski, L.; Stafilov, T.; Šajin, R.; Frontasyeva, M. V.; Bačeva, K. Air Pollution Study in Macedonia by Using Moss Biomonitoring Technique. ICP-AES and AAS. *Macedonian J. Chem. Chem. Eng.* **2013**, *32*(1), 89–107.
- [22] Barandovski, L.; Frontasyeva, M. V.; Stafilov, T.; Šajin, R.; Ostrovna, T. Atmospheric Deposition of Trace Elements in Macedonia Studied by the Moss Biomonitoring Technique. *Environ. Sci. Pollut. Res.* **2015**, *20*(22), 16077–16097. DOI: 10.1007/s11356-015-4787-x.
- [23] Stafilov, T.; Šajin, R.; Pančevski, Z.; Boev, B.; Frontasyeva, M. V.; Strelkova, L. P. *Geochemical Atlas of Veles and the Environs*; Faculty of Natural Sciences and Mathematics: Skopje, **2008a**.
- [24] Ilić Popov, S.; Stafilov, T.; Šajin, R.; Tănăselia, C.; Bačeva, K. Applying of Factor Analyses for Determination of Trace Elements Distribution in Water from River Vardar and its Tributaries, Macedonia/Greece. *Sci. World J.* **2014**, (2014), Article ID 809253, 1–11. DOI: 10.1155/2014/809253.
- [25] Ilić Popov, S.; Stafilov, T.; Šajin, R. Distribution of Trace Elements in Sediment and Soil from River Vardar basin, Macedonia/Greece. *J. Environ. Sci. Health, Part A* **2015**, *51*(1), 1–14. DOI: 10.1080/10934529.2015.1079097.
- [26] Serafimovska, J. M.; Arpadjan, S.; Stafilov, T.; Tsekova, K. Study of the Antimony Species Distribution in Industrially Contaminated Soils. *J. Soils Sediments* **2013**, *13*, 294–303. DOI: 10.1007/s11368-012-0623-9.
- [27] Stafilov, T.; Šajin, R.; Boev, B.; Cvetković, J.; Mukaetov, D.; Andreevski, M. *Geochemical Atlas of Kavadarci and the Environs*; Faculty of Natural Sciences and Mathematics: Skopje, **2008b**.
- [28] Stafilov, T.; Šajin, R.; Boev, B.; Cvetković, J.; Mukaetov, D.; Andreevski, M.; Lepitkova, S. Distribution of Some Elements in Surface Soil Over the Kavadarci Region. Republic of Macedonia. *Environ. Earth Sci.* **2010c**, *61*(7), 1515–1530. DOI: 10.1007/s12665-010-0467-9.
- [29] Stafilov, T. Environmental Pollution with Heavy Metals in the Republic of Macedonia. *Contrib. Sect. Nat. Math. Biotechnical Sci. MASA* **2014**, *35*(2), 81–119.
- [30] Stafilov, T.; Balabanova, B.; Šajin, R.; Bačeva, K.; Boev, B. *Geochemical Atlas of Radoviš and the Environs and the Distribution of Heavy Metals in the Air*; Faculty of Natural Sciences and Mathematics: Skopje, **2010d**.
- [31] Balabanova, B.; Stafilov, T.; Šajin, R.; Bačeva, K. Spatial Distribution and Characterization of Some Toxic Metals and Lithogenic Elements in Topsoil and Subsoil from Copper Mine Environs. *Int. J. Environ. Prot.* **2013**, *3*(9), 1–9.
- [32] Balabanova, B.; Stafilov, T.; Šajin, R. Litogenic Distribution of Rare Earth Elements in Automorphic and Alluvial Soils from Bregalnica River Basin. *Macedonian J. Chem. Chem. Eng.* **2015**, *34*(1), 201–212. DOI: 10.20450/mjce.2015.574.
- [33] Balabanova, B.; Stafilov, T.; Šajin, R.; Tănăselia, C. Geochemical Hunting of Lithogenic and Anthropogenic Impacts on Polymetallic Distribution (Bregalnica River Basin, Republic of Macedonia). *J. Environ. Sci. Health, Part A* **2016**, *51*(13), 1180–1194. (2016). DOI: 10.1080/10934529.2016.1206389.
- [34] Balabanova, B.; Stafilov, T.; Šajin, R.; Bačeva, K. Comparison of Response of Moss, Lichens and Attic Dust to Geology and Atmospheric Pollution from Copper Mine. *Int. J. Environ. Sci. Technol.* **2014**, *11*, 517–528. DOI: 10.1007/s13762-013-0262-8.
- [35] Stafilov, T.; Balabanova, B.; Šajin, R.; Rokavec, D. Variability Assessment for Lithogenic and Anthropogenic Distribution of Trace and Macroelements in Water, Sediment and Soil Samples. Case Study: Bregalnica River Basin, Republic of Macedonia. In *Advances in Environmental Research*; J. A., Daniels, Ed.; Nova Science Publishers Inc.: Hauppauge, NY, **2015**.
- [36] Bačeva, K.; Stafilov, T.; Šajin, R.; Tănăselia, C.; Makreski, P. Distribution of Chemical Elements in Soils and Stream Sediments in the Area of Abandoned Sb-As-Tl Allchar Mine. Republic of Macedonia. *Environ. Res.* **2014a**, *133*, 77–89. DOI: 10.1016/j.envres.2014.03.045.
- [37] Stafilov, T.; Šajin, R.; Alijagić, J. Distribution of Arsenic, Antimony and Thallium in Soil in Kavadarci and Its Environs, Republic of Macedonia. *Soil Sediment Contam.: An Int. J.* **2013**, *22*(1), 105–118. DOI: 10.1080/15320383.2012.714425.
- [38] Stafilov, T.; Šajin, R.; Sulejmani, F.; Bačeva, K. *Geochemical Atlas of Kičevo and the Environs*; Faculty of Natural Sciences and Mathematics: Skopje, **2011**.
- [39] Stafilov, T.; Šajin, R.; Sulejmani, F.; Bačeva, K. Geochemical Properties of Topsoil Around the Open Coal Mine and Oslomej Thermoelectric Power Plant, R. Macedonia. *Geologia Croat.* **2014a**, *67*(1), 33–44. DOI: 10.4154/GC.2014.03.
- [40] Dimovska, B.; Šajin, R.; Stafilov, T.; Bačeva, K.; Tănăselia, C. Determination of Atmospheric Pollution Around the Thermoelectric Power Plant Using a Moss Biomonitoring. *Air Qual., Atmosphere Health* **2014**, *7*, 541–557. DOI: 10.1007/s11869-014-0257-8.
- [41] ELEM. *An Application for Obtaining a Permit with Adjustment Plan*; Elektrani na Makedonija, Podružnica Bitola: Bitola, **2007**.

- [42] Lazarevski, A. *Climate in Macedonia*; Kultura: Skopje. (In Macedonian), **1993**.
- [43] Stafilov, T.; Šajn, R. *Geochemical Atlas of the Republic of Macedonia*; Faculty of Natural Sciences and Mathematics: Skopje, **2016**.
- [44] Darnley, A. G.; Björklund, A.; Bolviken, B.; Gustavsson, N.; Koval, P. V.; Plant, J. A.; Steenfelt, A.; Tauchid, M.; Xuejing, X.; Garrett, R. G.; et al. *A Global Geochemical Database for Environmental and Resource Management. Recommendations for International Geochemical Mapping*; Final report of IGCP project 259, UNESCO Publishing: Paris, **1995**; pp 122.
- [45] Žibret, G.; Šajn, R. Hunting for Geochemical Associations of Elements: Factor Analysis and Self-Organizing Maps. *Math. Geosciences* **2010**, *42*, 681–703. DOI: 10.1007/s11004-010-9288-3.
- [46] Esdat. **2000**. http://www.esdat.net/Environmental%20Standards/Dutch/annexS_I2000Dutch%20Environmental%20Standards.pdf
- [47] Kaymaz, I. Application of Kriging Method to Structural Reliability Problems. *Struct. Saf.* **2005**; *27*, 133–151. DOI: 10.1016/j.strusafe.2004.09.001.
- [48] Sakata, S.; Ashida, F.; Zako, M. Structural Optimization Using Kriging Approximation. *Comput. Methods Appl. Mech. Eng.* **2003**, *192*, 923–939. DOI: 10.1016/S0045-7825(02)00617-5.