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Geochemical properties of topsoil around the open coal mine and Oslomej thermoelectric power plant, R. Macedonia

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ABSTRACT

The results of the first systematic study of the spatial distribution of trace metals in surface soil over the Kičevo region, Republic of Macedonia, known for its coal mine and thermal power plant activity are reported. The investigated region (148 km^2) is covered by a sparse sampling grid of 2×2 km; but in the urban zone and around the thermal power plant the sampling grid is denser (1×1 km). In total, 52 topsoil samples (0–5 cm) were collected. Inductively coupled plasma – atomic emission spectrometry (ICP-AES) was applied for the determinations of 18 elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn). Based on the results of factor analyses, three natural geogenic associations of elements have been defined: F1: Cr-Ni-Li-Co-Fe-As; F2: Al-Ca-Mg-Sr; and F3: Ba-K-Cu.

Even the distributions of typical heavy metals such as Pb and Zn which are not isolated into anthropogenic geochemical association by multivariate statistical methods still show some trends of local anthropogenic enrichment. First of all, the distribution of Pb is not only influenced by the open coal pit and“„Oslomej” thermal power plant, but also by river transportation processes from the“„Tajmište” iron mine into alluvial sediments of the river Zajaska. The distribution of Zn is influenced by the“„Metal industry Kičevo” operation and atmospheric transport.

Keywords: multivariate statistics, potentially toxic elements, geochemical mapping, soil, Kičevo

1. INTRODUCTION

The abundance of trace metals in soil has been increased dramatically by the accelerated rate of extraction of minerals and fossil fuels and by highly technological industrial processes. Rapid increases of trace metal concentrations in the environment are commonly coupled to the development of exploitative technologies. The presence of heavy metals in soil could be in trace amounts. Soils contain trace elements of various origins (KABATA-PENDIAS & PENDIAS, 2001). Lithogenic elements are directly inherited from the lithosphere. Pedogenic elements are types of elements with a lithogenic origin, but their concentration and distribution in soil layers, as well as in soil particles are changed due to pedogenic processes. Anthropogenic elements are all those deposited into soil as direct or indirect results of man's activities. The behaviour of trace metals in soil and consequently their bioavailability differs depending on their origin. However, regardless of the forms of the anthropogenic elements in soil, their phytoavailability is significantly higher than those of pedogenic origin.

Urban and regional contamination of soil occurs mainly in industrial regions and within centres of large settlements, where factories, motor vehicles and municipal wastes are the most important sources of trace metals (KABATA-PENDIAS & PENDIAS, 2001; ŠAJN, 2004; 2005; DAVIDSON et al., 2006). Given the heterogeneity and ceaseless change in urban areas (CHEN et al. 2005), it is necessary first to understand the natural distribution. However, there are cases when the industrial enterprises, especially mining and metallurgical plants, situated near cities can increase the pollution. It is obvious from the papers published recently that mining and metallurgical activities lead to enormous soil contamination

(WILSON et al., 2005; PRUVOT et al., 2006; ŠAJN et al., 2011), which is the case with some regions in the Republic of Macedonia (STAFILOV et al., 2008a, b; 2010a, b, c).

The purpose of this study is to present the results of the first systematic research of multi elemental soil characterisation over the Kičevo region, known for its coal mine and the"„Oslomej" thermal power plant. Studies on the atmospheric deposition of trace metals elements over the entire territory of the Republic of Macedonia identified the most polluted areas and characterized the different pollution sources (BARANDOVSKI et al., 2008; BALABANOVA et al., 2010, 2011; GJORGIEVA et al., 2010; 2011). It was found that the most important sources of trace metal deposition are ferrous and non-ferrous smelters including the emission from the thermal power plants using coal. For this reason, two specific purposes of the present study were (1) to determine the content of the following trace elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn) in the soil, and (2) to assess the size of the affected area by the thermal power plant situated very close to the town.

2. STUDY AREA

Kičevo is located in the western part of Macedonia, in the south-eastern foothills of Bistra Mountain (Fig. 1), at the mid point on the road between Ohrid (61 km) and Gostivar (46 km). It is 112 km from the capital Skopje Kičevo is surrounded by mountains and forests, and is a town that is attractive not only because of its natural beauty, but also because of its cultural values. According to the 2002 census, Kičevo had a population of about 30.000 inhabitants (Macedonians, Albanians, Turks, Serbs and Gypsies). The whole region, with the communities of Kičevo, Oslomej and Zajas has about 52.000 people and comprises extraordinary patterns of social and economic diversity.

Kičevo is an important industrial centre in this part of Macedonia, due to the iron mine in Tajmište (abandoned at the moment), the coal mine and the „Oslomej" thermal power plant. Kičevo is a mining town that started to develop very intensively after World War II. The main feature of the economy in the region is the mining and REK „Oslome" thermal

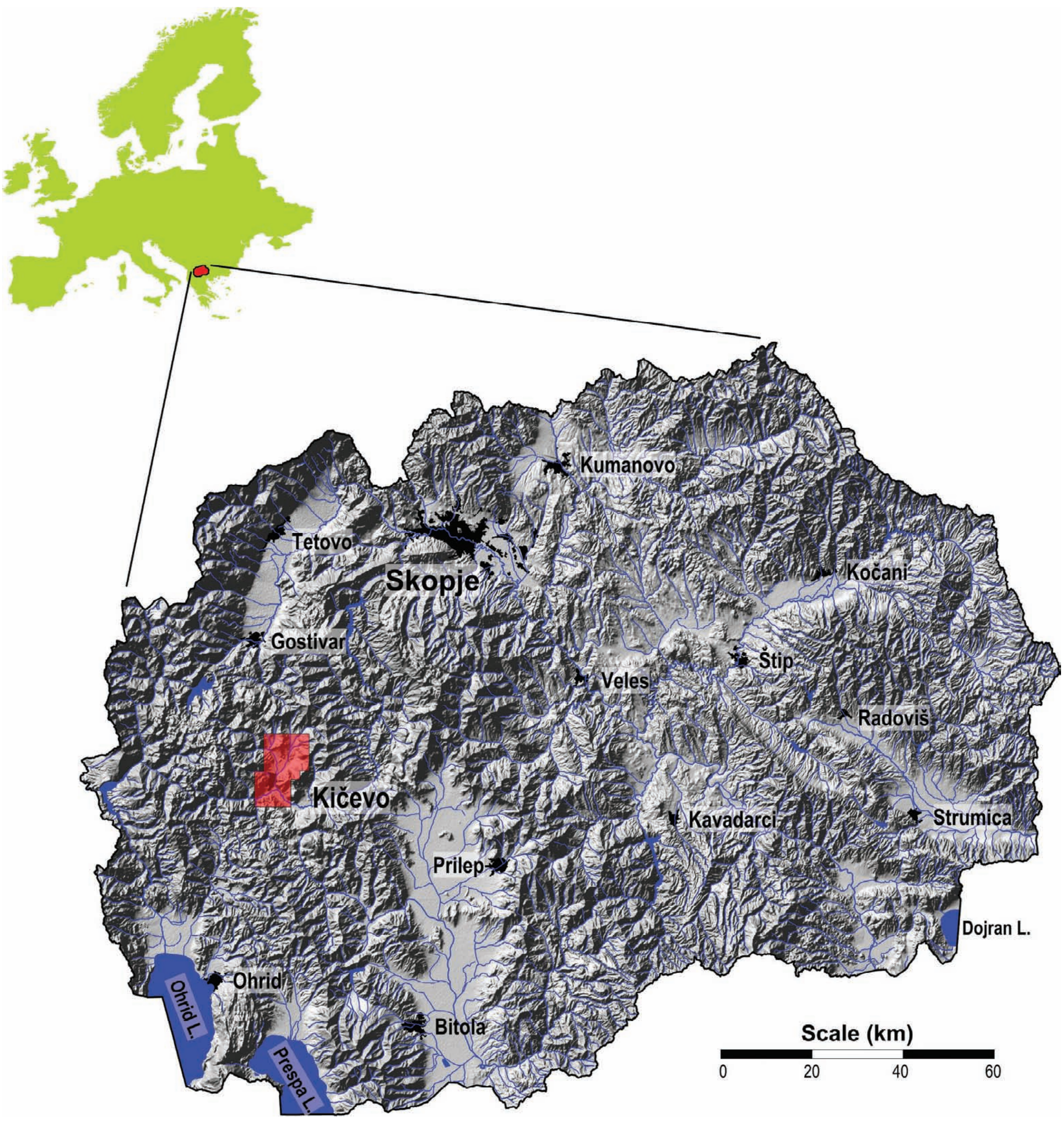

Figure 1: Location of the study area.

power plant. It is the first facility of its kind built in the country. REK"„Oslome"" has the installation capacity of 125 MW with a net annual production of around 700 GWh. REK Oslomej began production in 1980 and has had excellent production results. It provides about 9% of the total electrical energy production in the Republic of Macedonia.

Kičevo region is influenced by the warm continental and mountain climate. The zone of influence of the warm continental climate in Macedonia is from 600 to 900 m a.s.l., meaning this climate area in the Kičevo region includes the town of Kičevo and most of the settlements. Mountain areas are affected by the mountain climate.

The annual average temperature in the immediate area of the city is 10.7^{o}C with the absolute monthly maximum temperature of 40.5^{o}C, while the absolute monthly minimum was –23^{o}C. The mean annual maximum temperature is 17.1^{o}C and an average annual minimum temperature is 5^{o}C. The average annual rainfall is about 750 mm while the most frequent wind direction is N-S (LAZAREVSKI, 1993) The above climatic and other natural conditions in this region have a constraining influence on the cultivation of apples and pears, and favourable conditions for growing some of the stone fruit types (cherry, plum) but also for breeding walnut and chestnut.

The study area is located in the western part of the Republic of Macedonia with a surface of *ca.* 12 km (W–E) × 16 km (S–N), (148 km^2), between the coordinates N: 41°29'5""–41°38'4"" and E: 20°54'3""–21°03'2"" (Figs. 1 and 2). The altitude varies between 570 and 1260 m. Land use (Fig. 2a) is as follows: the cultivable area covers 64 km^2 (43 %), non-cultivable area (mainly forests) 68 km^2 (46 %), settlements 9.9 km^2 (6.7 %) and area of Oslomej open pit and thermal power plant 6.1 km^2 (4.3 %).

3. GEOLOGY

The geological description (Fig. 2b) is according to PETKOVSKI & IVANOVSKI (1973), and DUMURDJANOV et al. (1972). The study area is a part of the western Macedonian zone, which belongs to the Inner Dinarides. The structure strikes in a NW-SE direction. Two types of orogeny strongly influenced the development of the zone. The Hercynian (Variscan) Orogeny has influence on Palaeozoic rocks which are regionally metamorphosed and fluted bu the Alpine Orogeny caused very strong metamorphism, intensive fluting and the conversion of older structures. Subsequent radial tectonics have resulted in the formation of anticline structures and basins (The Kičevo basin), that were filled by younger Pliocene and Quaternary sediments.

The oldest rocks belong to the Lower Palaeozoic (Pz) metamorphic complex, mostly consisting of phyllitoides with inclusion of metasandstone quartzite and carbonatic schist. The Lower Palaeozoic rocks are developed in the north of the study area. Devonian (D) rocks overlie this complex. These are phyllitoides, sandstone and conglomerate, quartzite and marble. The Devonian rocks outcrop in the southern part of the study area. Over the Palaeozoic beds, Mesozoic rocks occur, represented by the Jurassic diabase rocks (penetrations or inclusions of magmatic rocks), which outcrop on very limited part to the south. Middle and Upper Pliocene sediments are developed in the central part of the study area (the Kičevo basin) and consist of marl, sand and clay with coal layers, not exceeding 250 m in thickness. Pliocene sediments were developed in the central part of the study area. Alluvial sediments cover the flood plains along the rivers Treska, Zajaska and Temnica that contain mainly coarse grained material such as gravel, sand and sandy clay.

The study area covers 148 km^2, but the Quaternary deposits comprise 41.4 km^2 (representing 28 % of the study area), Pliocene marl, clay, sand and gravel account for 28.9 km^2 (20%), Jurassic diabase, 1.1 km^2 (<1%), Devonian marble represents 8.3 km^2 (5.6%), Devonian quartzite; 1.3 km^2 (<1%), Devonian phyllitoides; 15.7 km^2 (11%), Devonian sandstone and conglomerate cover 16.4 km^2 (11%) and Lower Palaeozoic schists 34.9 km^2 (23%).

4. MATERIALS AND METHODS

4.1. Sampling

Samples of natural surface soils in the town of Kičevo and the surrounding region were collected according to the European guidelines for soil pollution studies (REIMANN et al., 2008), and also according to our experience (STAFILOV et al., 2008 a, b; ŠAJN, 2003, 2005, 2006).

The study area (148 km^2) is covered by a sampling grid of 2×2 km but in the urban zone of Kičevo and around the Oslomej thermal power plant the sampling grid is denser, 1×1 km. Altogether 52 soil samples were collected (Fig. 2c). At each sampling point, soil samples were collected as topsoil (0–5 cm). The possible organic horizon was excluded. One sample represents the composite material collected at the central sample point itself and at least four points within a radius of 10 m around it towards N, E, S and W. The mass of such a composite sample was about 1 kg (DARNLEY et al., 1995). According to the basic lithological units, 10 sampling sites are located in the area of Quaternary alluvium of the Treska River, 14 in the Quaternary alluvium of the Zajaska and Temnica rivers, 10 on Pliocene marl, clay, sand and gravel, 3 from Devonian sandstone and conglomerate, 4 on Devonian marble, 6 on Devonian phyllitoids and 10 on the Lower Palaeozoic schists (Fig. 2c).

4.2. Sample preparation and analysis

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

For digestion of soil samples, open wet digestion with a mixture of acids was applied. The digestion was carried out in this order: a precisely measured mass of dust samples (0.5 g) with the accuracy of 0.0001 g was placed in a Teflon vessel. 5 ml of concentrated nitric acid (HNO_3) was added, until the brown vapours came out from the vessels. Nitric acid is a very suitable oxidant for the digestion of organic

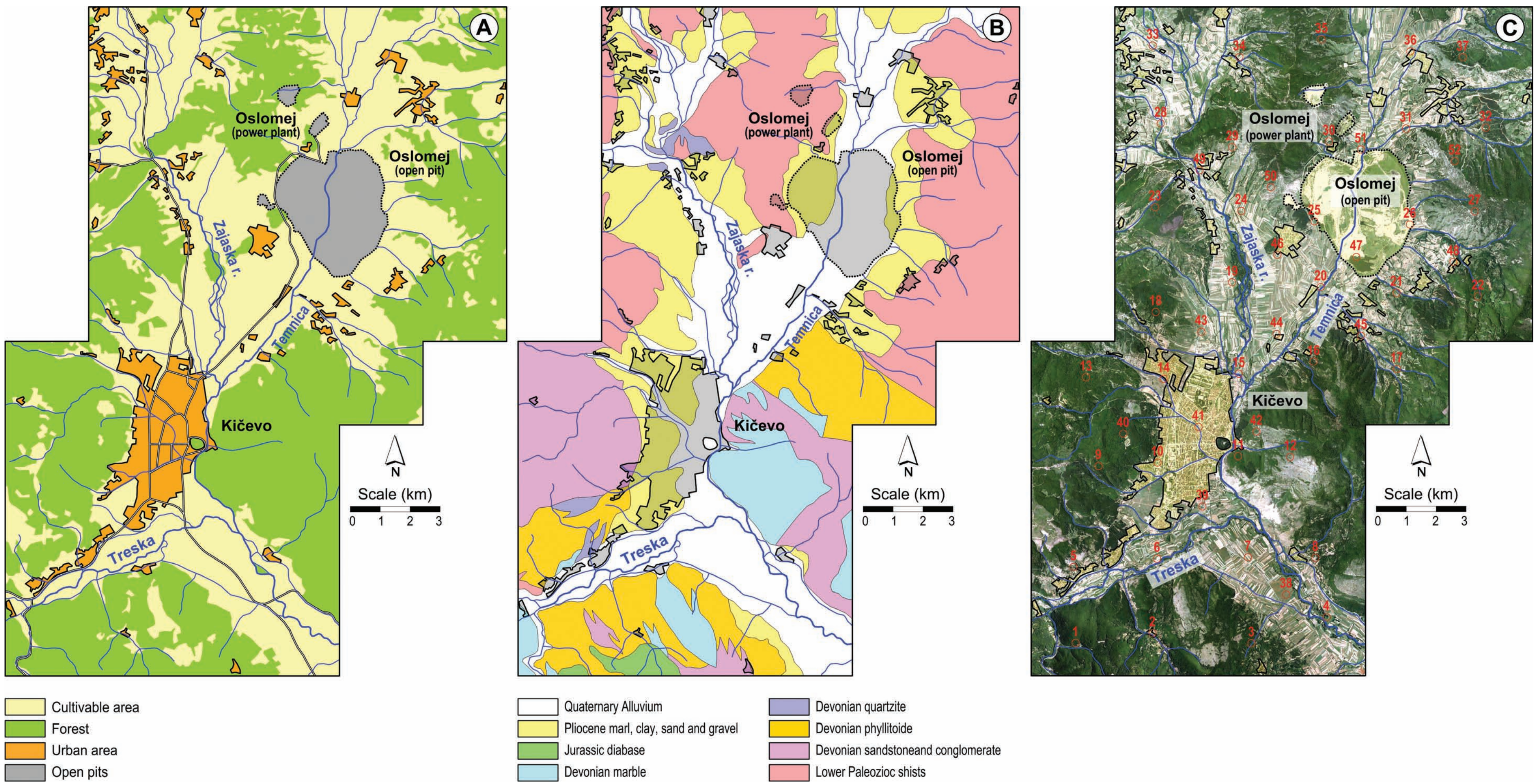

Figure 2: A – Land use map; B – Lithological map; C – Location of soil sampling sites

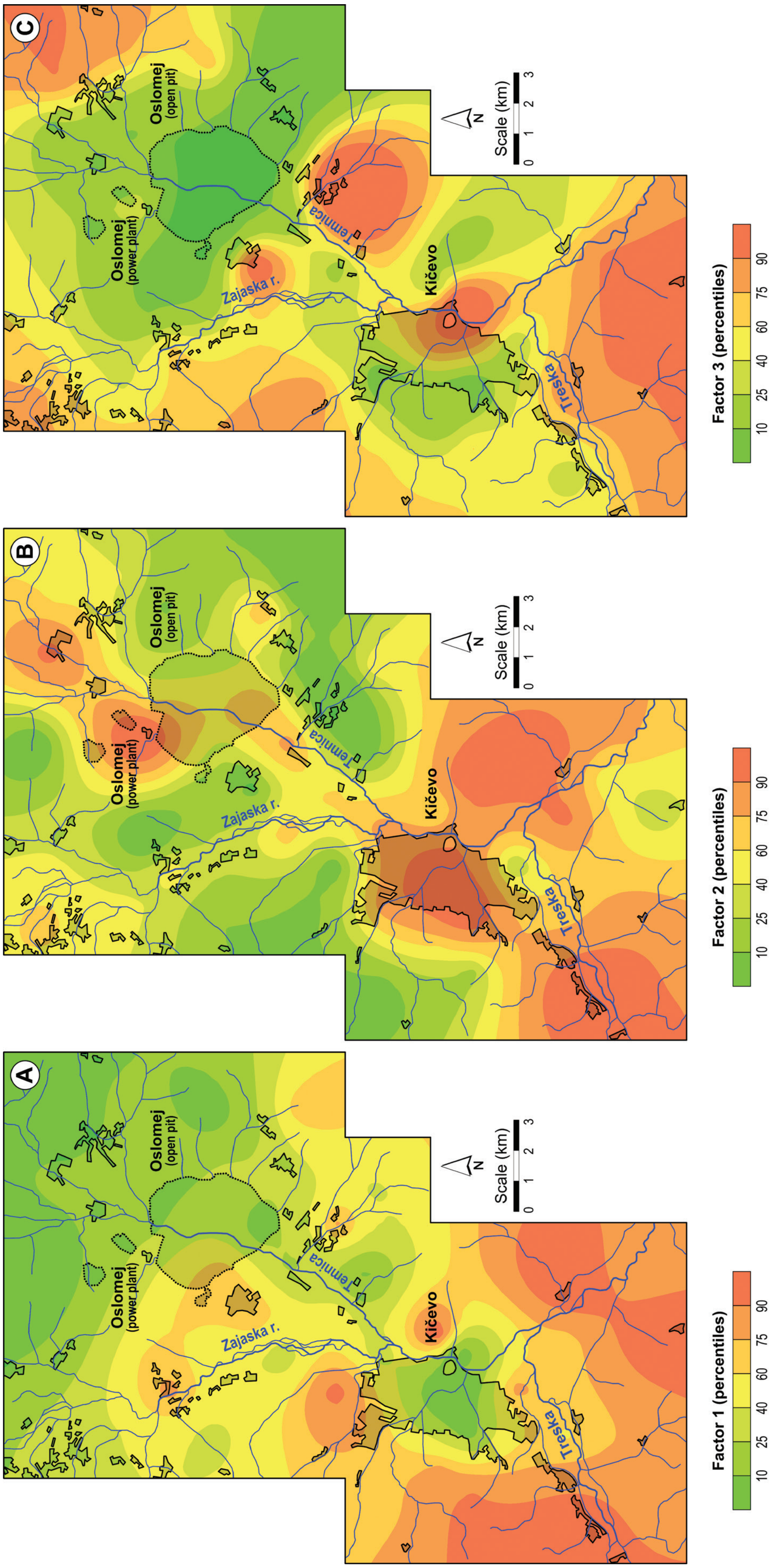

Figure 3: Spatial distribution of Factor scores: A – Factor 1 (Cr, Ni, Li, Co, Fe and As); B – Factor 2 (Ca, Sr, Mg and Al); C – Factor 3 (Ba, K and Cu)

matter in samples. For total digestion of the inorganic components 5–10 ml hydrofluoric acid (HF) was added. When the digest became a clear solution, 2 ml of $HClO_4$ was added. Perchloric acid was used for total digestion of organic matter. After cooling the vessels for 15 min, 2 ml of HCl and 5 ml of H_2O were added for total dissolution of the metal ions. Finally, the vessels were cooled and digests quantitatively transferred to 50 ml calibrated flasks (STAFILOV et al., 2008a; 2010c; BALABANOVA et al., 2011).

Then the soil samples were analysed by atomic absorption (electrothermal – ETAAS, and flame – FAAS) and atomic emission spectrometry with inductively coupled plasma (ICP-AES). Optimization of the instrumental conditions for each element had been done previously (STAFILOV et al., 2010c; BALABANOVA et al., 2011). Total contents of 18 elements were analysed in the collected samples: Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn.

The QC of the three applied techniques was performed by the standard addition method, and it was found that the recovery ranges for the investigated elements were: for FAAS 97.2% – 102.5%, for ETAAS 96.9% – 103.2%, for ICP-AES 98.2% – 100.8%.

5. RESULTS AND DISCUSSION

5.1. Data processing

All field observations, analytical data and measurements were introduced to the data matrix. For each observation there are 44 variables: sample identification number, sampling material type, geographic coordinates, type of analysis, land use, basic lithological units, level of soil pollution and determination of 18 analysed elements.

Parametric and nonparametric statistical tests were used for the data analysis (SNEDECOR & COCHRAN, 1967; DAVIS, 1986). On the basis of the results, the normality tests and a visual inspection of the distribution histograms, the logarithms of the content were used for all elements, except As and K. Differences between the defined groups of samples as well as their significance have been tested by t-test and f-test, respectively. The basic statistics for the 18 selected chemical elements and the averages of elements with regards to the basic lithological units in topsoil are shown in Tables 1 and 2.

The degree of association of chemical element content in the soil samples was assessed with the linear Pearson's *r* correlation coefficient (LE MAITRE, 1982). It was qualitatively assumed that the absolute values of *r* between 0.5–0.7 reveal a good association, and between 0.7–1.0 a strong association between elements (Table 3). Arsenic and potassium show a normal distribution, but all other elements follow a logarithmic distribution.

Multivariate R-mode factor analysis (DAVIS, 1986; BORŮVKA, 2005) was used to reveal the associations of the chemical elements. Factor analysis (FA or PCA) derives from numerous variables a smaller number of new, synthetic variables called factors. The factors contain significant information about the original variables, and they may have certain meanings. Factor analysis was performed on variables standardized to zero mean and unit of standard deviation (REIMANN, et al., 2002). As a measure of similarity between variables, the product-moment correlation coefficient (*r*) was applied. For orthogonal rotation, the varimax method was used.

In the factor analysis, 52 samples of the topsoil (0–5 cm) and analysis of 13 chemical elements were considered. From the multivariate R-mode factor analysis, 5 chemical elements (Cd, Mn, Na, Pb and Zn) were eliminated from further analysis because they have low share of communality or low tendency to form independent factors. Using factor analysis, the distribution was reduced to three synthetic variables (F1 to F3), which showed linkage in terms of geochemical similarities. They include c. 74% of the total variability for all treated elements (Table 4).

The universal kriging with linear variogram interpolation method (DAVIS, 1986) was applied for the construction of maps showing the spatial distribution of factor scores, as well as maps displaying the distribution of trace elements in topsoil. The basic grid cell size for interpolation is 20×20 m. For a graphical display of spatial distribution, the maps with percentile distribution have been used, where different colours represent different concentration arrangements. The seven classes of following percentile values were applied: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100 (Fig. 3 and 5).

5.2. Natural associations of chemical elements in soils

Elements whose distributions reflect natural background levels have been released during weathering processes. Their contents usually change gradually across the landscape and depend on the geological background. Following the results of factor analysis (Table 4) and the trends shown on the factor scores geochemical maps (Fig. 3), three natural geochemical associations in soil have been identified.

The most characteristic association comprises As, Co, Cr, Fe, Li and Ni, which are assembled in the Factor 1 (Table 4, Fig. 3a). The strongest factor explains 29 % of the total variability within the data of 13 selected chemical elements. All selected elements have a high correlation coefficient (Table 3), as well as significant statistical differences among the determined groups of samples from the various lithological units (Table 2).

Their sources are mainly natural phenomena, such as rock weathering and chemical processes in soil. In addition, the distribution of Factor 1 scores (As, Co, Cr, Fe, Li and Ni) in the topsoil is closely dependent on lithology (Figs. 2c and 4a). Their highest contents were found in areas of Devonian sandstone and Quaternary deposits of the Treska River and their lowest values in the areas of the Lower Palaeozoic schists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers. Those chemical elements are mostly connected to the sandy fraction in soil.

The association illustrated by Factor 2 associates Al, Ca, Mg and Sr. The second strongest Factor 2 contains high val-

Table 1: Descriptive statistics of measurements (n = 52).

	Dis.	X	X_G	Md	min	max	s	CV	s_X	A	E
Al	Log	1.7	1.5	1.4	0.53	4.7	0.92	54	0.13	0.22	–0.55
As	N	9.3	6.3	7.8	0.13	34	7.2	77	1.0	1.25	1.60
Ba	Log	390	380	380	160	890	120	31	17	-0.07	1.45
Ca	Log	0.54	0.30	0.24	0.042	3.1	0.66	122	0.091	0.32	–0.67
Cd	Log	0.47	0.42	0.42	0.17	0.99	0.21	44	0.029	–0.04	–0.74
Co	Log	15	11	11	0.59	60	11	78	1.6	–0.71	2.14
Cr	Log	44	41	43	13	110	17	38	2.4	–0.46	1.84
Cu	Log	17	15	14	5.4	53	8.6	51	1.2	0.08	–0.04
Fe	Log	2.9	2.8	2.8	1.5	5.4	0.66	23	0.092	0.11	0.94
K	N	1.4	1.4	1.4	0.63	2.2	0.34	23	0.047	–0.09	0.27
Li	Log	14	12	11	2.5	33	7.6	56	1.1	–0.29	–0.31
Mg	Log	0.64	0.57	0.59	0.20	1.6	0.31	49	0.043	–0.01	–0.34
Mn	Log	760	700	690	210	2600	370	48	51	0.11	1.74
Na	Log	0.55	0.44	0.50	0.064	1.6	0.36	65	0.050	–0.48	–0.30
Ni	Log	21	19	18	5.5	56	10	49	1.4	–0.17	0.40
Pb	Log	96	64	71	1.7	430	80	84	11	–1.14	2.37
Sr	Log	17	15	15	5.8	45	9.1	55	1.3	0.39	–0.11
Zn	Log	150	110	97	11	1700	230	154	31	0.71	6.60

Dis. – distribution (N – normal, Log – lognormal); X – mean; X_G – geometric mean; Md – median; min – minimum; max – maximum; s – standard deviation; CV – coefficient of variation (%); s_X – standard error of mean; A – skewness; E – kurtosis; Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg/kg; Values rounded at two digits

Table 2: Averages of the chemical elements according to basic lithological units.

	EU	Study area	Sed T (Q)	Sed Z (Q)	Sed (Pl)	Sand (D)	Marblele (D)D)	Phyll (D)	Schist (Pz)	Anova (F-test)	
N	–	52	5	14	10	3	4	6	10		
Al	11	1.5	1.9	1.3	1.5	1.3	2.5	2.0	1.1	1.95	NS
Ca	0.92	0.30	0.52	0.32	0.27	0.14	1.2	0.26	0.18	2.42	*
Fe	3.5	2.8	3.4	2.7	2.9	3.5	2.9	3.5	2.3	4.62	*
K	1.9	1.4	1.7	1.4	1.2	1.5	1.7	1.9	1.3	1.98	NS
Mg	0.77	0.57	1.0	0.57	0.50	0.46	0.75	0.59	0.48	0.71	NS
Na	0.8	0.44	0.64	0.74	0.35	0.25	0.35	0.17	0.49	3.49	*
As	7	9.3	12	5.5	7.3	10	16	15	8.9	3.58	*
Ba	380	380	510	370	350	340	390	520	310	5.86	*
Cd	0.15	0.42	0.54	0.46	0.44	0.42	0.45	0.40	0.33	5.08	*
Co	7.8	11	21	8.9	7.8	19	13	9.6	13	4.98	*
Cr	60	41	61	38	40	49	47	55	31	8.11	*
Cu	13	15	21	14	12	15	26	23	10	1.86	NS
Li	–	12	22	10	9.8	22	18	18	6.5	2.57	*
Mn	650	700	880	690	620	860	760	1000	510	3.50	*
Ni	18	19	34	18	17	21	27	26	12	6.46	*
Pb	23	64	50	57	110	56	91	46	60	0.72	NS
Sr	89	15	19	17	13	12	29	12	11	1.85	NS
Zn	52	110	160	120	87	120	200	120	65	0.56	NS

(EU) – European topsoil average (Salminen, 2005); Sed T (Q) – Quaternary alluvium of the Treska Piver (11.7 km^2); Sed Z (Q) – Quaternary alluvium of the Zajaska and Temnica rivers (29.7 km^2); Sed (Pl) – Pliocene marl, clay, sand and gravel (28.9 km^2); Sand (D) – Devonian sandstone and conglomerate (16.4 km^2); Marble (D) – Devonian marble (8.3 km^2); Phyll (D) – Devonian phyllitoids (15.7 km^2); Schist (Pz) – Lower Palaeozoic schists (34.9 km^2). Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg/kg. Values rounded at two digits.

Table 3: Matrix of correlation coefficients (n = 52).

Al	1.00																	
As	0.04	1.00																
Ba	0.33	0.38	1.00															
Ca	0.71	0.04	0.17	1.00														
Cd	0.17	–0.05	0.17	0.14	1.00													
Co	–0.05	0.59	0.16	–0.05	0.19	1.00												
Cr	0.14	0.42	0.29	0.03	0.30	0.43	1.00											
Cu	0.38	0.30	0.66	0.32	0.28	0.15	0.50	1.00										
Fe	0.38	0.44	0.56	0.09	0.36	0.34	0.71	0.62	1.00									
K	0.35	0.27	0.64	0.24	–0.07	0.12	0.16	0.65	0.39	1.00								
Li	0.23	0.47	0.45	0.25	0.25	0.43	0.72	0.63	0.63	0.39	1.00							
Mg	0.70	0.03	0.29	0.75	0.16	0.10	0.16	0.41	0.26	0.46	0.31	1.00						
Mn	0.22	0.30	0.50	0.05	0.36	0.30	0.52	0.61	0.71	0.30	0.50	0.14	1.00					
Na	0.07	–0.36	–0.02	0.17	0.02	–0.09	–0.40	–0.13	–0.26	0.09	–0.27	0.44	–0.09	1.00				
Ni	0.31	0.44	0.44	0.28	0.28	0.44	0.88	0.68	0.74	0.40	0.81	0.44	0.65	–0.17	1.00			
Pb	–0.03	–0.14	–0.01	–0.14	0.14	–0.07	0.24	0.04	0.05	–0.20	–0.09	–0.19	0.02	–0.22	0.12	1.00		
Sr	0.71	0.03	0.36	0.75	0.30	0.06	0.14	0.45	0.27	0.25	0.29	0.69	0.28	0.40	0.39	–0.02	1.00	
Zn	0.22	0.31	0.32	0.42	0.29	0.25	0.25	0.45	0.26	0.30	0.44	0.35	0.11	–0.05	0.35	–0.13	0.31	1.00
	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sr	Zn

r ≥ 0.5 and <0.7 – underlined; r ≥0.7 and <1.0 - bolded

ues of the aforementioned elements, explaining 26 % of the total variability (Table 4, Fig. 3b). There is a significant, high correlation coefficient (Table 3) for this group of elements, but no significant statistical difference between the groups of samples from various lithological units (Table 2). Despite these, similarities to the distribution of the Factor 1 scores, the spatial distribution of Factor 2 scores (Al, Ca, Mg and Sr) in topsoil depends on the lithology. Their highest contents were observed in areas of the Devonian marble and Quaternary deposits of the Treska River and their lowest values, (as in Factor 1), in the areas of the Lower Palaeozoic schists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers (Figs. 2c and 4b). The elements from this factor are connected to the carbonate minerals in soil, representing a product of marble weathering processes.

The third naturally distributed geochemical association consists of Ba, Cu and K, chemical elements that are also little affected by anthropogenic activities. The Factor 3 contains high values of the aforementioned elements, explaining 20% of the total variability within the data (Table 4, Fig. 3c). The elements from this group are showing lower correlation coefficients than the previous two, but still statistically significant (Table 3). Significant statistical differences between the defined groups of samples from isolated lithological units (Table 2) are present. Distribution of Ba, Cu and K in the topsoil also depends on the lithology (Figs. 2c and 4c). Their highest contents were discovered in areas of the Devonian phyllitoides and their lowest values in the areas of the Lower Palaeozoic schists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers, as for F1 and F2. These elements are connected to the clayey fractions.

Table 4: Matrix of dominant rotated factor loadings (n = 52, 13 selected elements).

	F1	F2	F3	Com
Cr	0.88	0.07	0.13	79.5
Ni	0.83	0.31	0.31	87.6
Li	0.77	0.22	0.33	75.0
Co	0.73	-0.06	-0.09	55.1
Fe	0.68	0.15	0.46	70.1
As	0.66	-0.10	0.22	49.5
Ca	0.00	0.92	0.04	84.1
Sr	0.11	0.87	0.16	78.6
Mg	0.11	0.85	0.21	78.3
Al	0.04	0.83	0.24	75.2
Ba	0.23	0.13	0.84	78.3
K	0.09	0.21	0.84	76.5
Cu	0.40	0.31	0.73	78.0
Var	28.8	25.8	19.7	74.3

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

5.3. Distribution pattern of Cd, Pb, and Zn

The multivariate statistical methods have not isolated one anthropogenic group with typical heavy metals such as Pb, Zn, and Cd. This was expected since the appearance of such an association is more characteristic around the ironworks and smelters, in areas where long lasting anthropogenic impact is evident. Their absolutely anthropogenic tendency is present however comparing their average values with Euro-

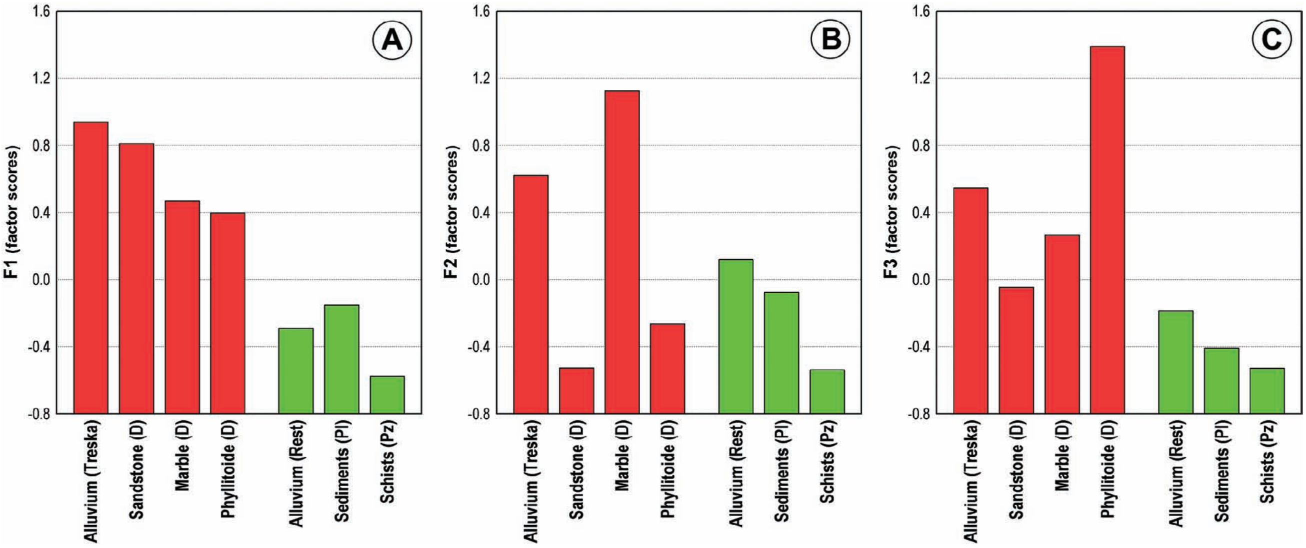

Figure 4: Distribution of Factor scores regarding the basic lithological units: A – Factor 1 (Cr, Ni, Li, Co, Fe and As); B – Factor 2 (Ca, Sr, Mg and Al); C – Factor 3 (Ba, K and Cu).

pean averages, as they exceed these by x3 or x4 (Tables 1 and 2). It is significant that these elements do not show significant statistical differences between samples collected at isolated lithological units (Table 2), meaning that their distributions are influenced by anthropogenic factors. When considering their spatial distributions (Fig. 5) it is necessary to observe more factors: (1) Impact of the coal open pit and the „Oslomej" thermal power plant, (2) Leaching from the „Tajmište" abandoned mine and a subsequent deposition of heavy metals in the alluvial sediments of the river Zajaska, and (3) Impact of „Metal industry Kičevo". For this purpose, several groups of samples that cover the aforementioned areas have been determined. For the Cd, Zn, and Pb distribution pattern, 39 sampling sites were selected to determine their background values, 8 samples East of the „Oslomej" open pit, and 5 samples around the River Zajaska. For example, the group of 12 samples collected in East Kičevo were selected to represent the distribution of Zn.

Based on the result of spatial distribution and average values of Cd (Fig. 5a) in the aforementioned groups, we cannot talk about the anthropogenic impact because the calculated averages are borderline in terms of a statistically significant difference. The average concentrations of Cd along the river Zajaska and Oslomej are up to 50% higher than the background values, but much lower than the target values of the New Dutch List. Some weak anthropogenic trends are noticed, but they are hidden by some background fluctuations because the surrounding Paleozoic rocks are enriched with these element (Fig. 5b).

It is a completely different case for the distribution of Pb (Fig. 5b). Statistical analysis shows highly significant differences between the average background values (64 mg/kg Pb in range 1.7 - 220 mg/kg), along the River Zajaska (170 mg/kg Pb, in range 120-220 mg/kg), and the area east of the „Oslomej" open pit (200 mg/kg Pb, in range 110 to 430 mg/kg). The aforementioned values exceed the target values but are still lower than intervention values (New Dutch List). A halo dispersion pattern with high values of Pb occurs east of the open pit in accordance with the dominant wind direction and wind intensity and can be attributed exclusively to atmospheric transport and deposition (Fig. 5b).

The average values of Zn among the background samples show quite significant differences (94 mg/kg of Zn, in range 110 to 230 mg/kg) from the group of samples from the urban area of Kičevo (320 mg/kg of Zn, in range 130 to 1700 mg/kg). The average values of Zn exceed the target values and even at some certain sampling sites, the intervention values determined by the New Dutch List. In this case there is a clear anthropogenic influence on the contamination halo, and high concentrations of Zn are consequences of the „Metal Industry Kičevo" (Fig.5c) operation. This assumption is proven by the position and shape of the contamination aureole, as well as the wind direction. Comparison with the distribution of Pb (Fig. 5b), indicates that this contamination halo solely depends on atmospheric transport.

6. CONCLUSION

The aim of this study was to present the results of an initial systematic investigation of the spatial distribution of various chemical elements in surface soil over of the Kičevo region known for its coal mine and „Oslomej" thermal power plant. Even the sparse soil measurements have been adequately sensitive for determination of the main geochemical associations and their connection to anthropogenic influence and lithological background.

Following the results of statistical analysis and the trends shown on the geochemical maps, three natural geochemical associations in soil have been defined (Cr-Ni-Li-Co-Fe-As; Al-Ca-Mg-Sr; and Ba-K-Cu). Their sources are mainly natural phenomena and closely dependent on the lithology.

Even the distributions of typical heavy metals such as Pb and Zn are not isolated into anthropogenic geochemical association by multivariate statistical methods, but they still

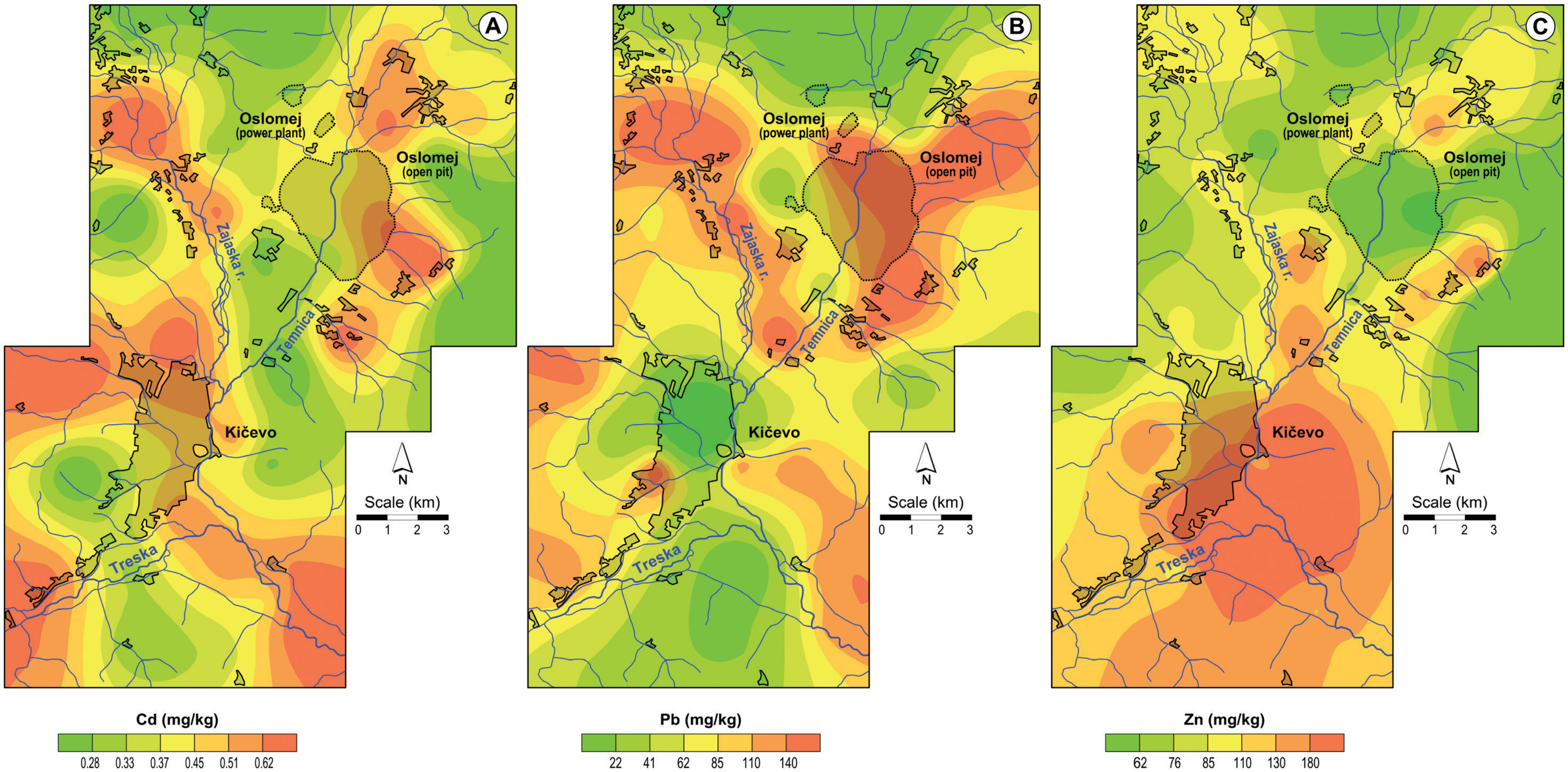

Figure 5: Spatial distribution of anthropogenically introduced elements: A – Cadmium; B – Lead; C – Zinc

show trends of local anthropogenic enrichment. Firstly, the distribution of Pb is not only influenced by the open coal pit and „Oslomej" thermal power plant but also by river transport. Eroded material from the iron mine „Tajmište" had been transported in alluvial sediments of the river Zajaska. The distribution of Zn is influenced by the „Metal industry Kičevo" operation. According to the distributions of heavy metals, especially Pb and Zn, it was possible to determine two main types of transportation, river transport and atmospheric transport respectively. Distribution of Pb is result of river transport, but distribution of Zn is solely result of atmospheric transport.

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