FACULTY OF NATURAL AND TECHNICAL SCIENCES, GEOLOGY DEPARTMENT, UNIVERSITY OF LJUBLJANA, SLOVENIA AND SLOVENIAN UNESCO-IGCP COMMITTEE WITH A SPONSORSHIP FROM THE UNESCO ORGANIZE

3rd INTERNATIONAL WORKSHOP ON THE PROJECT

ANTHROPOGENIC EFFECTS ON THE HUMAN ENVIRONMENT IN THE NEOGENE BASINS IN THE SE EUROPE

PROCEEDINGS

Edited by:
T. Dolenec & T. Serafimovski
Ljubljana, 1-3 December 2011

HEAVY METALS DISTRIBUTION IN SOIL FROM KIČEVO BASIN, REPUBLIC OF MACEDONIA

Trajče Stafilov[1], Robert Šajn[2], Florije Sulejmani[1], Katerina Bačeva[1]

[1]Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Skopje, Republic of Macedonia, POB 162, 1000 Skopje, Republic of Macedonia; e-mail: trajcest@pmf.ukim.mk
[2]Geological Survey of Slovenia, Dimičeva ulica 14, 1000 Ljubljana, Slovenia

Abstract

Data from the study of spatial distribution of various elements in surface soil over of the Kičevi basin, Republic of Macedonia, known for its coal mine and thermoelectical power plant activities are reported. The investigated region is covered by a sampling grid of 2×2 km^2; with the denser grid in the urban zone and around the thermoelectric power plant (1×1 km^2). In total 52 top soil samples (0–5 cm) were collected. The samples were analysed by inductively coupled plasma - atomic emission spectrometry (ICP-AES) Data analysis and construction of maps were performed using the Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) and Surfer (ver. 8.09) software. Three natural geochemical associations has been defined (Cr-Ni-Li-Co-Fe-As; Al-Ca-Mg-Sr and Ba-K-Cu).

Introduction

The abundance of heavy 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. Urban and regional contamination of soil occurs mainly in mining and industrial regions and within centres of large settlements (Kabata-Pendias and Pendias, 2001). Because of heterogeneity and ceaseless changing of urban areas, 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 (Kabata-Pendias and Pendias, 2001), which is the case with some regions in the Republic of Macedonia (Barandovski et al., 2008; Stafilov et al., 2010a, 2010b; Balabanova et al., 2011).

The aim of this study is to present the results of a first systematic investigation of spatial distribution of different chemical elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn) in surface soil over of the Kičevo region known for its coal mine and thermoelectrical power plant "Oslomej" and to assess the size of the area eventually affected by the thermoelectrical power plant situated near the town.

Geographic description

Kičevo is settled in the valley of Kičevo in the south-eastern foothills of Bistra Mountain (Fig. 1) in the western part of Macedonia. Kičevo is surrounded by mountains and forests, and is a town that is attractive not only of its natural beauties, but also its anthropogeneous and cultural values. According to the 2002 census, Kičevo had a population of 30,138 inhabitants.

The whole region with the community of Kičevo, Oslomej and Zajas has about 52,000 people and contains an extraordinary diversity of social and economic patterns. Kičevo is an important industrial center in this part of Macedonia, due to the iron mine in Tajmište (closed at the moment), the coal mine and the thermoelectric power plant Oslomej. Kičevo is a mining town that started to develop very intensively after the 2nd World War. Main feature of the economy in the region is the mining and thermoelectric power plant REK "Oslomej". It is the first facility of its kind built in the country. REK "Oslomej" has the installation capacity is 125 MW with net annual production of around 700 GWh. REK Oslomej began its production in 1980 and has had excellent production results. It provides for about 9% of the total electrical energy production in the Republic of Macedonia.

The study area is located in the western part of the Republic of Macedonia with surface of *ca.* 12 km (W–E) × 16 km (S–N), in total of 148 km^2, limited with coordinates N: 41°29'57"–41°38'43" and E: 20°54'35"–21°03'22" (Figs. 1 and 2). The altitude varies between 570 and 1260 m. The area of the different land uses is: 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 thermoelectric power plant 6.1 km^2 (4.3 %).

Geological description

The geological description (Fig. 3) was written according to Petkovski and Ivanovski (1973), and Dumurdjanov et al. (1972). The study area is a part of western Macedonian zone, which belongs to the Inner Dinnarids characterized by strong structural forms such as thrusts, syncline, anticline, etc. The structure has a direction NW-SE. Two types of orogeny strongly influenced a development of the zone. The Hercynian (Variscan) Orogeny has influence on Palaeozoic rocks which are regionally metamorphosed and fluted but on other side the Alpine Orogeny caused very strong metamorphism, intensive fluting and conversion of older structures. Subsequent radial tectonic has resulted in 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 consist phyllitoid with inclusion of metasandstone quartzite and carbonatic schist. The Lower Palaeozoic rocks are developed in the north of the study area. Devonian (D) rocks lies over 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 are developed the Mesozoic rocks. There are represented by the Jurassic diabase rocks (penetrations or inclusions of magmatic rocks), which outcrop on very limited part on 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. 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 grain material gravel, sand and sandy clay.

From 148 km^2 of the studied area, the Quaternary deposits are found on 41.4 km^2 (28 % of study area), Pliocene marl, clay, sand and gravel on 28.9 km^2 (20 %), Jurassic diabase on 1.1 km^2 (<1 %), Devonian marble on 8.3 km^2 (5.6 %), Devonian quartzite on 1.3 km^2 (<1 %), Devonian phyllitoides on 15.7 km^2 (11 %), Devonian sandstone and conglomerate on 16.4 km^2 (11 %) and Lower Palaeozoic shists on 34.9 km^2 (23%).

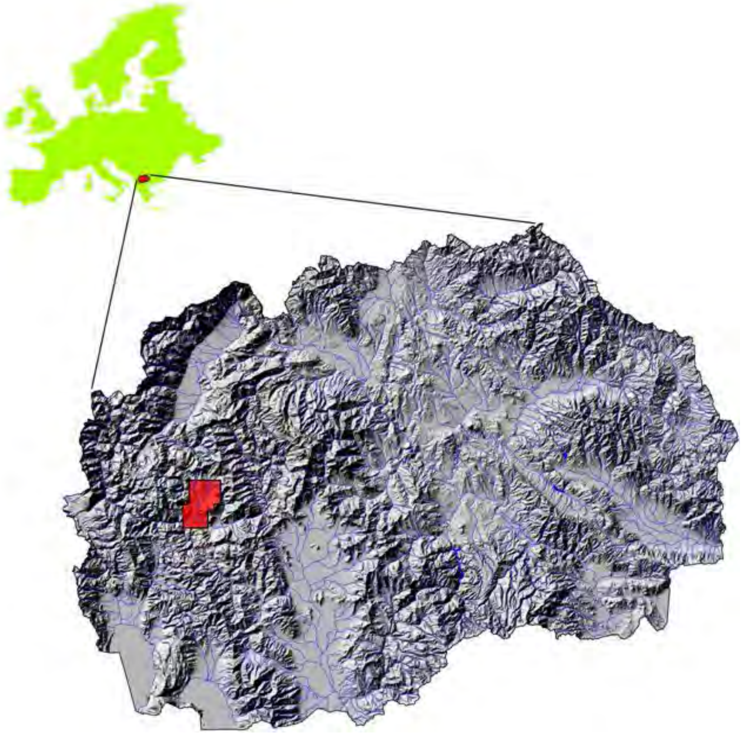

Fig. 1. Location of the study area

Fig. 2. Location of the study area and soil samples locations in the Kičevo area

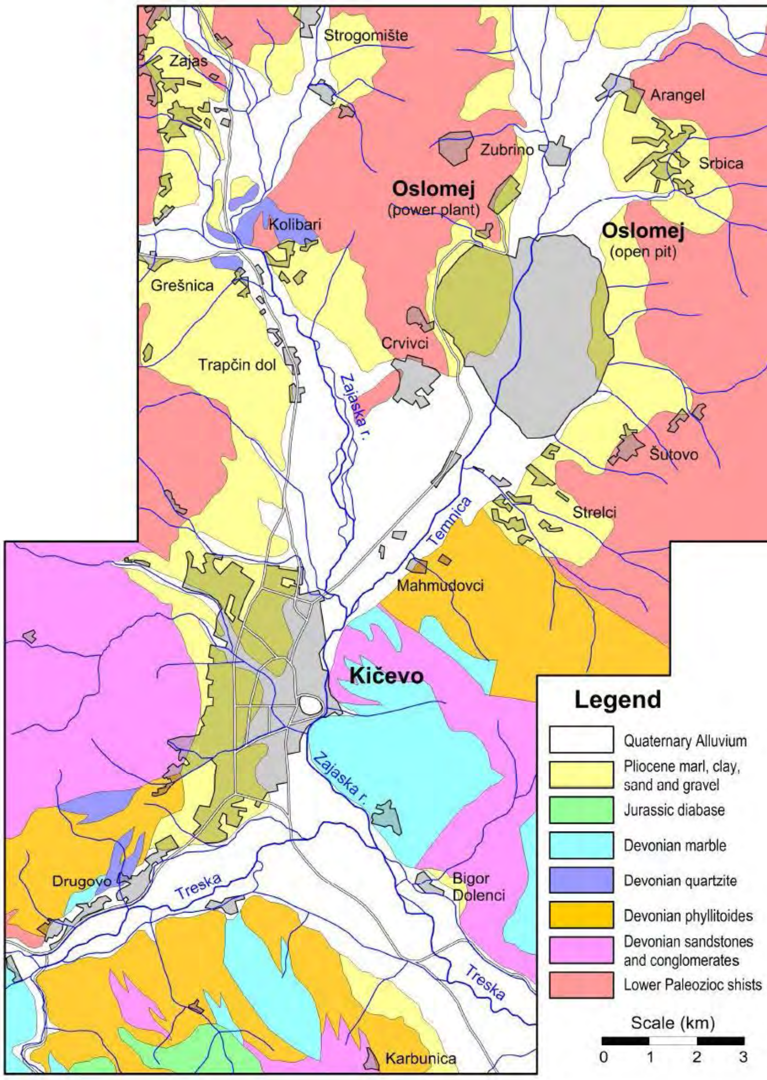

Fig. 3. Lithological map of the Kičevo area

Material and methods

Sampling

Samples of surface soils (0-5 cm) were collected according to the European guidelines for soil pollution studies (Salminen et al., 2005), and also according to our experience (Šajn, 2005, 2006; Stafilov et al., 2010a, 2010b). The study area (148 km^2) is covered by a sampling grid of 2×2 km^2 but in the urban zone of Kičevo and around the Oslomej thermoelectric power plant the sampling grid is denser, 1×1 km^2 (Fig. 2). Altogether 52 soil samples were collected. In 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 the radius of 10 m around it towards N, E, S and W. According to the basic lithological units, 10 sampling sites are located on the area of Quaternary alluvium of the Treska River, 14 on the Quaternary alluvium of the Zajaska and Temnica rivers, 10 on Pliocene marl, clay, sand and gravel, 3 on Devonian sandstone and conglomerate, 4 on Devonian marble, 6 on Devonian phyllitoides and 10 on Lower Palaeozoic shists.

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 (Davis, 1986). The shifted mass was quartered and milled in agate mill to an analytical grain size below 0.125 mm. For digestion of soil samples, open wet digestion with mixture of 4 acids (HNO_3, HF, $HClO_4$ and HCl) was applied (Balabanova et al., 2011). The obtained solutions of soil samples were analyzed with the application of atomic emision spectrometer with inductively coopled plasma Varian 715ES.

Results and discussion

Data processing and drawing of maps

Data analysis and production of maps were performed on a PC using the Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) and Surfer (ver. 8.09) software. All field observations, analytical data and measurements were introduced to the data matrix. For each observation there are 45 variables: sample identification number, sampling material type, geographic coordinates (X, Y, Z), kind of analysis, land use, basic lithological units, level of soil pollution and determination of 19 analyzed elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn) with ICP-AES method (n = 52). The methods of parametric and nonparametric statistics were used for the data analysis (Davis, (1986). The basic statistics data for the 19 selected chemical elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn) and the average of elements are shown in Table 1.

Table 1. Descriptive statistics of measurements (n = 52) Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg/kg.

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

Dis. – distribution (N – normal, Log – lognormal); X – mean; X_g – geometrical mean; Md – median; min – minimum; max – maximum; s – standard deviation; CV – coefficient of variation (%); s_x – standard error of mean; A – skewness; E – kurtosis

The multivariate R-mode factor analysis (Davis, (1986) 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. The 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. With the factor analysis the distribution is decreased to three synthetic variables (F1 to F3), have connected in regard to geochemical similarities, which are include 74.3 % of the variability of the treated elements (Table 2).

The universal kriging method with linear variogram interpolation (Davis, 1986) was applied for construction of the areal distribution maps of the 19 particular elements and the factor scores (F1–F3) in topsoil (0–5 cm). The basic grid cell size for interpolation was 20×20 m. For class limits the percentile values of distribution of the interpolated values were chosen. Seven classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100 (Fig. 4-6).

Table 2. Matrix of dominant rotated factor loadings (n = 52, 13 selected elements). Bold letters represent anthropogenically distributed geochemical association

Element	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 (%)

Chemical elements in soils of the Kičevo area

The distributions of elements that reflect natural processes are indicated by elements that are rarely or never included industrial processes. Their contents usually change gradually across the landscape and depend on the geological background. Following the results of factor analysis (Table 2) and the trends shown on the geochemical maps (Figs. 4-6), three natural geochemical associations in soil has been defined.

Geochemical association Cr-Ni-Li-Co-Fe-As

The most characteristic association links As, Co, Cr, Fe, Li and Ni, which are assembled in the Factor 1 (Table 2, Fig. 4). The strongest Factor 1 contains high values of previously mentioned elements, explaining 29 % of the total variability within the data (the 13 selected chemical elements). 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 the lithology. Their highest contents were found in areas of the Devonian sandstone and Quaternary deposits of the Treska River and their lowest values in area of the Lower Palaeozoic shists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers. Those chemical elements are connected mostly to the sandy fraction in soil.

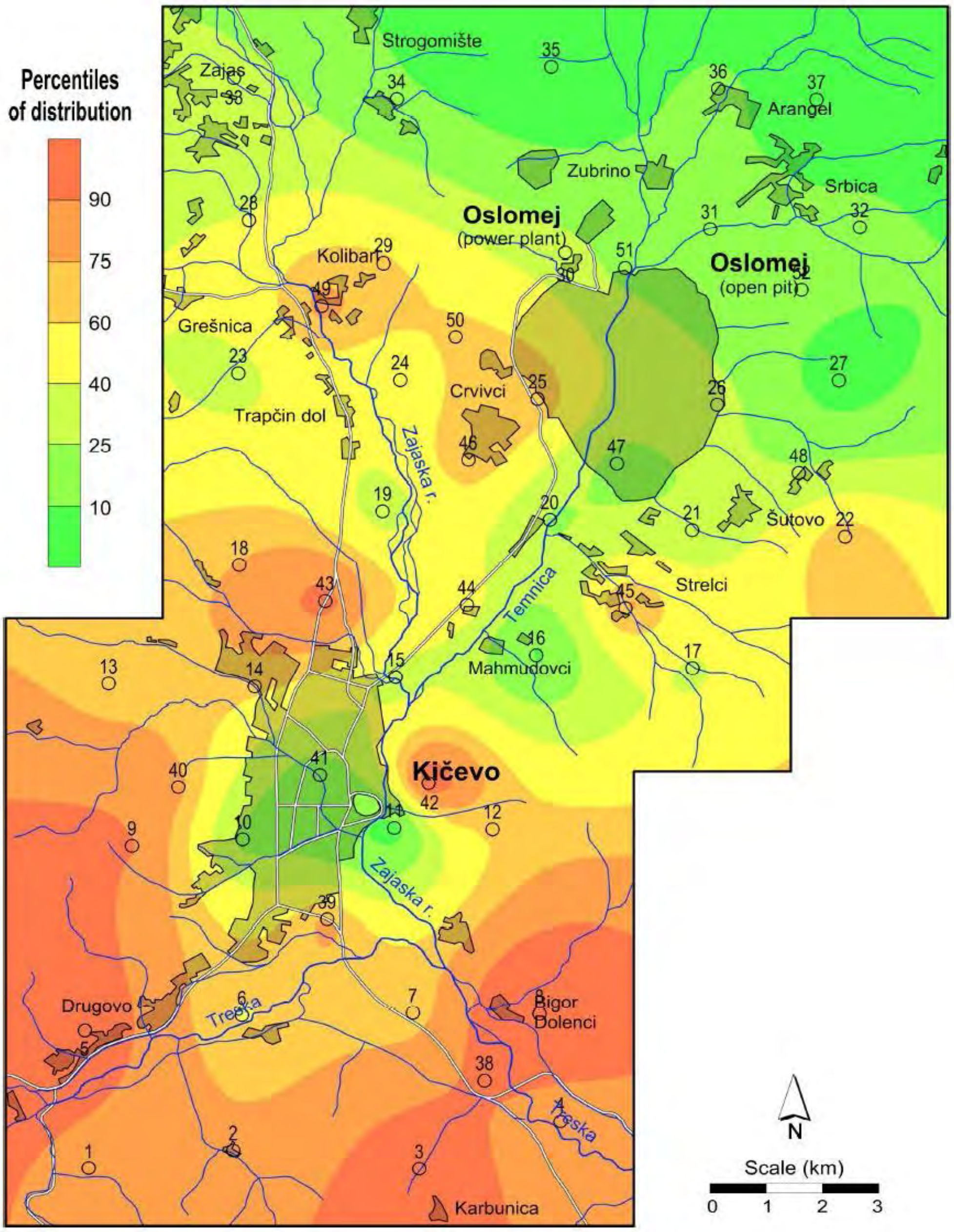

Fig. 4. Spatial distribution of factor 1 scores (Cr, Ni, Li, Co, Fe and As) in topsoil

Geochemical association Ca-Sr-Mg-Al

The association illustrated by Factor 2 associates Al, Ca, Mg and Sr. The second strongest Factor 2 contains high values of aforementioned elements, explaining 26 % of the total variability (Table 2). Areal distribution of the Factor 2 scores in topsoil is provided in Fig. 5. Similarly to the distribution of the Factor 1 scores, the spatial distribution of Factor 2 scores (Al, Ca, Mg and Sr) in topsoil closely depends on the lithology. Their highest contents were found in areas of the Devonian marble and Quaternary deposits of the Treska River and their lowest values, same as in the Factor 1, in area of the Lower Palaeozoic shists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers (Fig. 5). The elements from this factor are connected to the carbonitic minerals in soil, representing a product of marbles weathering processes.

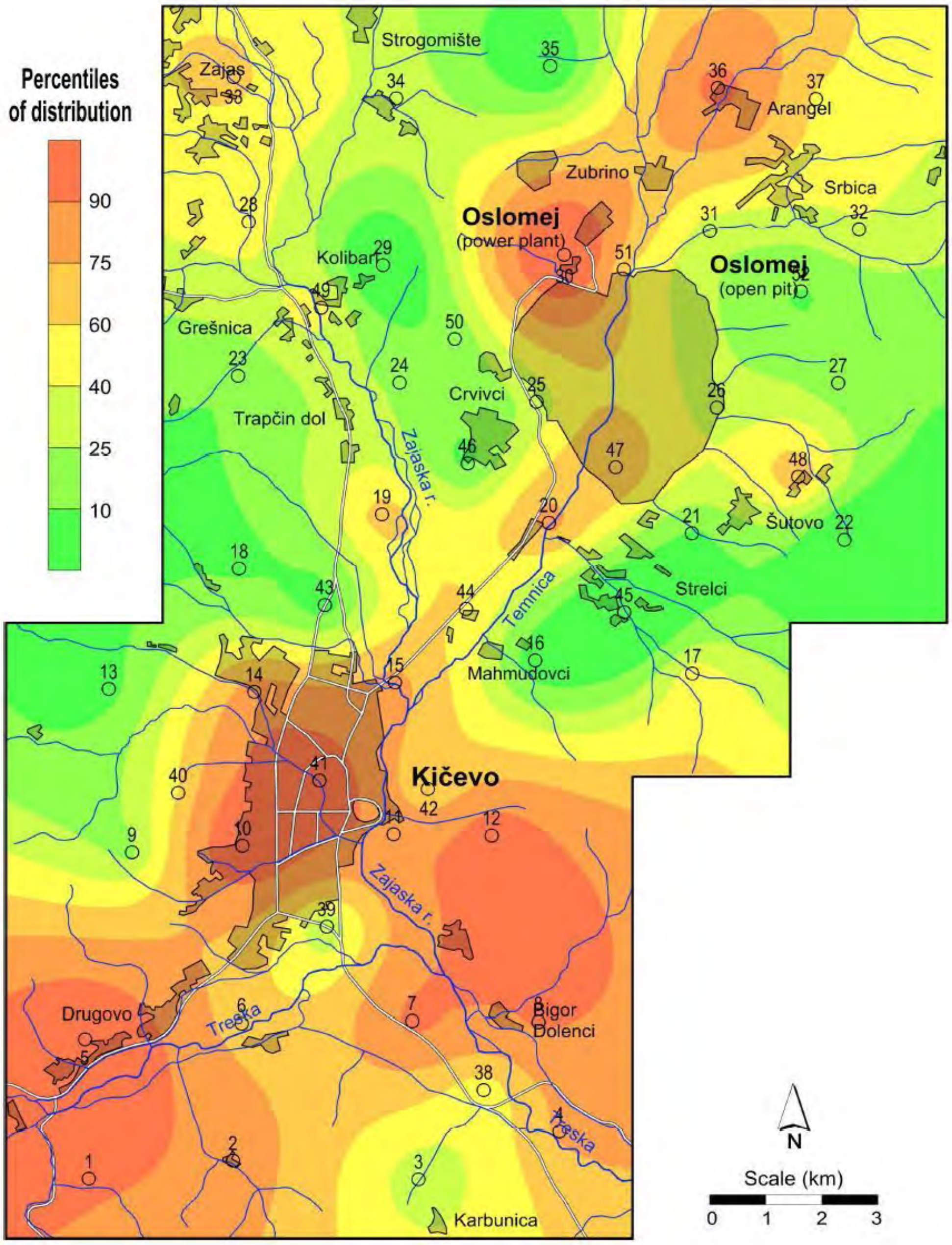

Fig. 5. Spatial distribution of factor 2 scores (Ca, Sr, Mg and Al) in topsoil

Geochemical association Ba-K-Cu

The third naturally distributed geochemical association consists Ba, Cu and K, chemical elements that are also little affected by anthropogenic activities. The Factor 3 contains high values of the mentioned elements, explaining 20 % of the total variability within the data (Table 2). Areal distribution of the Factor 3 scores in topsoil is shown in Fig. 6. Distribution of the Factor 3 scores (Ba, Cu and K) in topsoil also depends on the lithology (Fig. 6). Their highest contents were found in areas of the Devonian phyllitoides and their lowest values in area of the Lower Paleozoic shists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers, same as in F1 and F2. Those elements are connected to the clayey fractions.

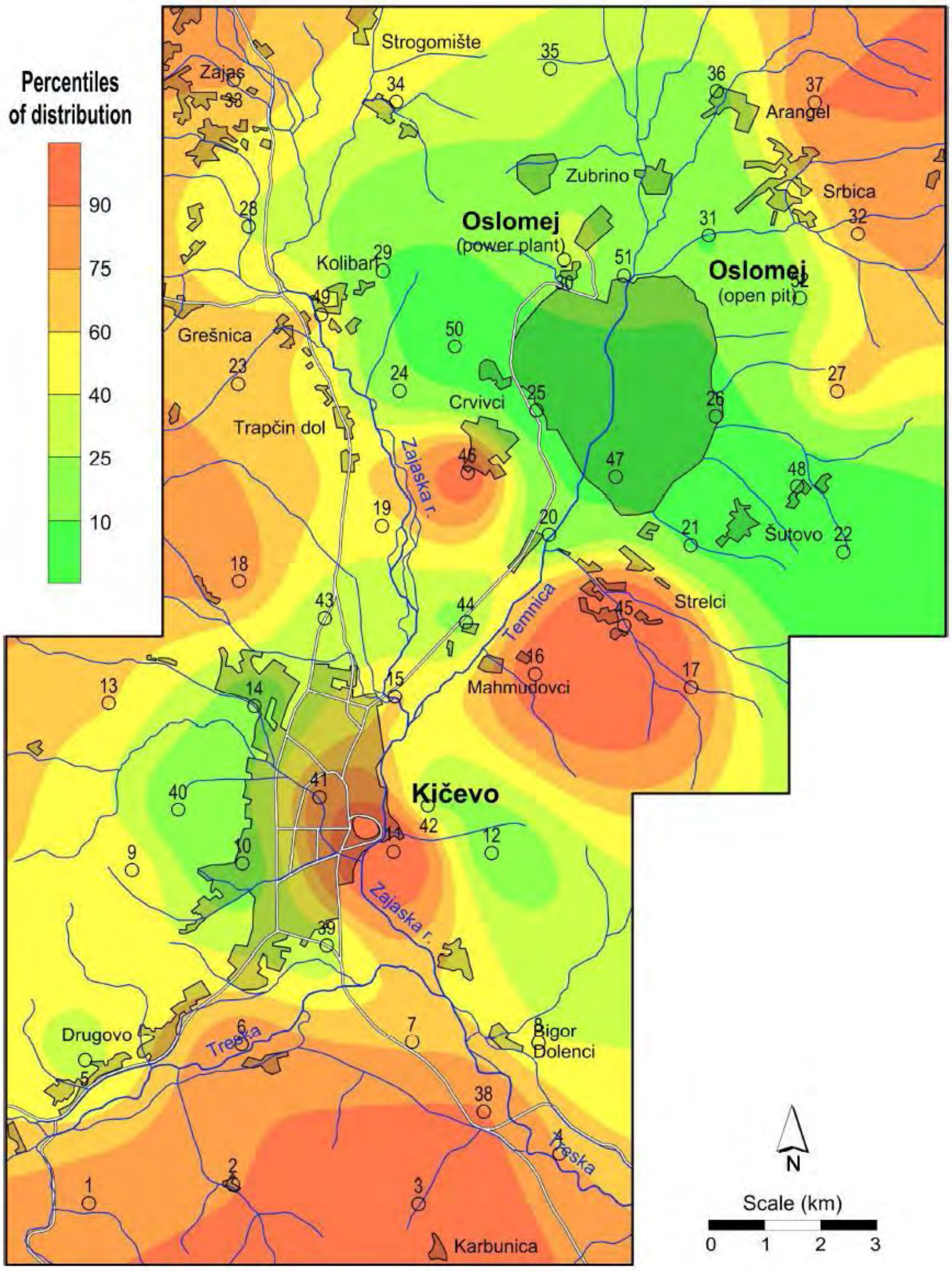

Fig. 6. Spatial distribution of factor 3 scores (Ba, K and Cu) in topsoil

Conclusion

Following the results of factor analysis and the trends shown on the geochemical maps, three natural geochemical associations in soil has been defined. The strongest Factor 1 contains high values of As, Co, Cr, Fe, Li and Ni. Their sources are mainly natural phenomena and closely dependent on the lithology. Their highest contents were found in areas of Devonian sandstone and Quaternary deposits of the river Treska and their lowest values in area of the Lower Palaeozoic shists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers. The association illustrated by Factor 2 (Al, Ca, Mg, Sr) has the highest and lowest values in the similar areas as it was found for the Factor 1. The elements from this factor are connected to the carbonitic minerals. The distribution of the Factor 3 (Ba, Cu, K) also depends on the lithology. Their highest values are in areas of the Devonian phyllitoides and the lowest in area of the Lower Paleozoic shists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers. These elements are connected to the clayey fractions.

References

Balabanova, B., Stafilov, T., Šajn, R., Bačeva, K. (2011). Distribution of chemical elements in attic dust as reflection of lithology and anthropogenic influence in the vicinity of copper mine and flotation, *Archives of Environmental Contamination Toxicology*, **61**, 173–184.

Barandovski, L., Cekova, M., Frontasyeva, M.V., Pavlov, S.S., Stafilov, T., Steinnes, E., Urumov, V. (2008). Atmospheric deposition of trace element pollutants in Macedonia studied by the moss biomonitoring technique, *Environmental Monitoring and Assessment*, **138**, 107–111.

Kabata-Pendias, A., Pendias, H. (2001). *Trace Elements in Soil and Plants*, Third Edition, CRC Press, Boca Raton.

Davis, J.C. (1986). *Statistic and Data Analysis in Geology*, Willey in Sons, New York.

Dumurdjanov, N., Stojanov, R., Petrovski, K. (1972). *Basic geological map of SFRJ, sheet Kruševo*, M 1:100,000 (map & interpreter), Federal Geological Survey, Beograd.

Petkovski, P., Ivanovski, T. (1973). *Basic geological map of SFRJ, sheet Kičevo*, M 1:100,000 (map & interpreter), Federal Geological Survey, Beograd.

Reimann, C., Filzmoser, P., Garrett, R.G. (2002). Factor analysis applied to regional geochemical data: problems and possibilities, *Applied Geochemistry*, **17**, 185–206.

Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Å., Ottesen, R.T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T. (2005). *Geochemical Atlas of Europe,* Part 1, *Background Information, Methodology and Maps*, Geological Survey of Finland, Espoo.

Šajn, R. (2005). Using attic dust and soil for the separation of anthropogenic and geogenic elemental distributions in an old metallurgic area (Celje, Slovenia), *Geochemistry: Exploration, Environment, Analysis*, **5**, 59–67.

Šajn, R. (2006). Factor analysis of soil and attic-dust to separate mining and metallurgy influence, Meza Valley, Slovenia, *Mathematical Geology*, **38**, 735–747.

Stafilov, T., Šajn, R., Pančevski, Z., Boev, B., Frontasyeva, M.V., Strelkova, L.P. (2010a). Heavy metal contamination of surface soils around a lead and zinc smelter in the Republic of Macedonia. *Journal of Hazardous Materials,* **175**, 896–914.

Stafilov, T., Šajn, R., Boev, B., Cvetković, J., Mukaetov, D., Andreevski, M., Lepitkova, S. (2010b). Distribution of some elements in surface soil over the Kavadarci Region, Republic of Macedonia, *Environmental Earth Sciences*, **61**, 1515–1530.