Faculty of Natural and Technical Sciences, University “Goce Delčev”-Štip, R. Macedonia with a grant from the CEI-ES Know How Programme organize

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CENTRAL EUROPEAN INITIATIVE
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1st INTERNATIONAL WORKSHOP ON THE PROJECT

Environmental Impact assessment of the Kozuf metallogenic district in southern Macedonia in relation to groundwater resources, surface waters, soils and socio-economic consequences (ENIGMA)

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Edited by:
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GEOCHEMISTRY OF SOIL OF KAVADARCI AND THE ENVIRONS

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Abstract

The results of a first systematic study of spatial distribution of different elements in surface soil over of the Kavadarci region, Republic of Macedonia, known for its nickel industrial activity are reported. The investigated region (360 km^2) is covered by a sampling grid of 2×2 km^2; whereas the sampling grid of 1×1 km^2 was applied in the urban zone and around the ferronickel smelter plant (117 km^2). In total 344 soil samples from 172 locations were collected. At each sampling point soil samples were collected at two depths, topsoil (0–5 cm) and bottom soil (20–30 cm). Inductively coupled plasma-mass spectrometry (ICP-MS) was applied for the determinations of 36 elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mn, Na, Mg, Mo, Ni, P, Pb, S, Sb, Sc, Se, Sr, Th, Tl, Ti, U, V, W and Zn). 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. Four geogenic and three anthropogenic geochemical associations were established.

Introduction

Soils differ widely in their properties because of geologic and climatic variation over distance and time. In spite of this variability, soils have a unique structural characteristic that distinguishes them from mere earth materials and serves as a basis for their classification: a vertical sequence of layers produced by the combined actions of percolating waters and living organisms (Kabata-Pendias and Pendias, 2001). 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. This kind of sudden change exposes the biosphere to a risk of destabilization.

The subject of this study is to present the results of a first systematic study of spatial distribution of different elements in surface soil over of the Kavadarci region, Republic of Macedonia, known for its ferronickel industrial activity in the nearest past. There were several studies of soil, vegetables and fruits produced in this region but they were mainly concerned with contamination by nickel, iron, cobalt and chromium (Boev et al. 2005). Other elements were not determined though it is known that the minerals of many other heavy metals are present in iron-nickel ores used for the production of nickel in the smelter plants (Everhart et al. 2006; Stafilov et al. 2008; 2010). The study on the atmospheric deposition of trace metals over the entire territory of Macedonia identified the most polluted areas and characterize different pollution sources (Barandovski et al., 2008; 2012, 2013) and it was found that the most important sources of trace metal deposition are ferrous and non-ferrous smelters including the area of Kavadarci. For that reason, the goal of this work was to determine the content of 36 elements in the soil from the town of Kavadarci and its environ and to assess the size of the area eventually affected by the ferronickel smelter plant situated near the town.

Geological description of the studied area

The study area is large 18 (W-E) × 20 (S-N) km (Fig. 1 and 2) and is located in the south-central part of Macedonia, which is limited with coordinates (Gauss Krueger zone 7) 7574000 (W) – 7592000 (E) and 4582000 (S) – 4602000 (N). Of the total 360 km^2 of the study area, the water surface (rivers and lakes) covers 6 km^2 (2 %), cultivable land 221 km^2 (61 %), non-cultivable area (mainly forests) 120 km^2 (33 %) and urbanized area (settlements, industry zones, archaeological sites, quarries and tailings) 13 km^2 (4 %).

The geological description and the construction of geological map (Fig. 1) were performed on the base of data given by Rakićević et al. (1965) and Hristov et al. (1965). The oldest formations have direction NW-SE and belong to the inner parts of the Vardar zone. The Lower Paleozoic (Pz) metamorphic complex is present with two series: amphibole and amphibole-chlorite schists with marbles and quartz-sericite schists with marbles and phylite layers. Serpentinite is present in the form of the narrow belts along the ruptures inside the Vardar zone. The uttermost part in the SW of the study zone is covered with marbles and dolomites probably from Devonian ages. Over the Paleozoic are developed Mesozoic (Mz) formations, mainly from Late Cretaceous ages. The Turonian (K_2) sandstones, conglomerates and massive limestones are spread in the SW and W side of the study area. Diabase and spilite submarine flows are frequent in the lower parts of this sequence, where the minor masses of gabbros, occur as well. Paleozoic and Mesozoic rocks cover 39 km^2 in the SW and W part of the investigated area. Complexes of Tertiary and Quaternary sediments cover the most of the study area. The Upper Eocene ($^4E_3$) flysch sediments and yellow sandstones are developed along Vardar, Crna Reka and Luda Mara valleys and marginal part of the Tikveš basin. Those sediments cover 34 km^2 mainly in the N. The Pliocene (Pl) sediments fill the Tikveš basin, limited with the Vardar on the North, and Paleozoic-Mesozoic formations that have direction NW-SE represented mainly with sandy series. Pliocene (Pl) sediments cover the biggest part (about 182 km^2) in the central part of the investigated area. SE from the Kavadarci are found the Quaternary (Q) pyroclastic vulcanites represented with tuffs, breccias and agglomerates, which cover approximately 25 km^2. Quaternary ages, represented with the deluvium, river terraces and alluvium. Deluvial sediments (12 km^2) contain rugged material from surrounding rocks, mixed with clay-sandy material. Along the rivers Vardar, Crna Reka and Luda Mara terraces sediments are formed (23 km^2). Terraces contain gravels, sand and clay. Alluvial sediments (40 km^2) cover the flood planes of the Vardar, Crna and Luda Mara rivers and contain mainly sand and clay.

Material and methods

Sampling

Samples of natural surface soils were collected according to the guidelines for soil pollution studies (Šajn, 2003, 2005, 2006; Reimann, 2008). The complete investigated region (360 km^2) was covered by a sampling grid 2×2 km^2, but in urban zone of Kavadarci and around the ferronickel smelter plant (117 km^2), the sampling grid was denser, 1×1 km^2 (Fig. 2). Altogether 344 soil samples were collected from 172 locations. In each sampling point soil samples were collected at two depths, topsoil (0–5 cm) and subsoil (20–30 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.

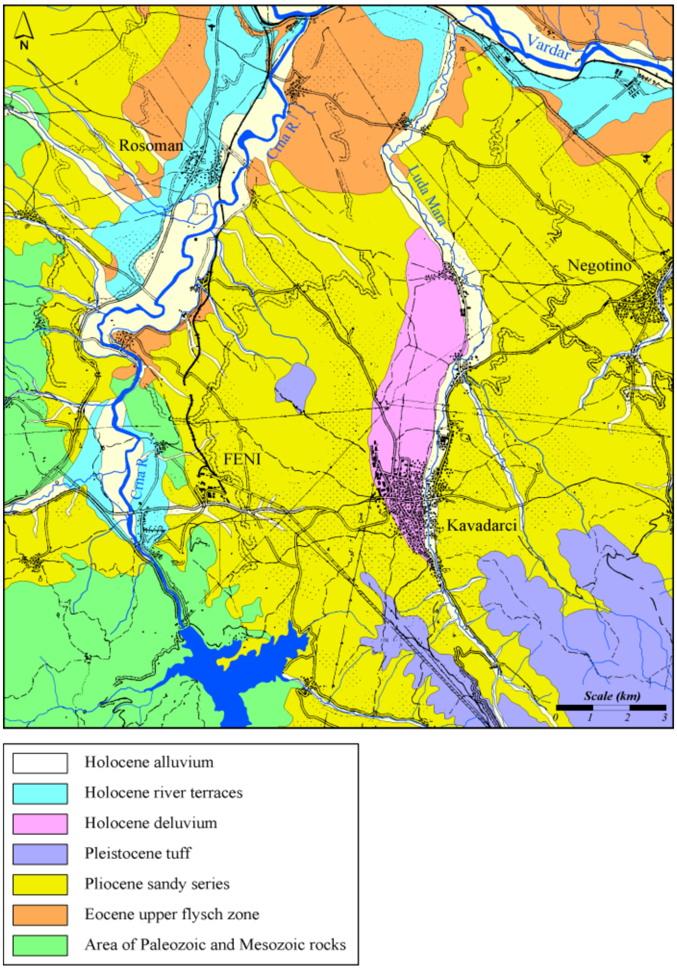

Fig. 1. Lithological map of the Kavadarci area

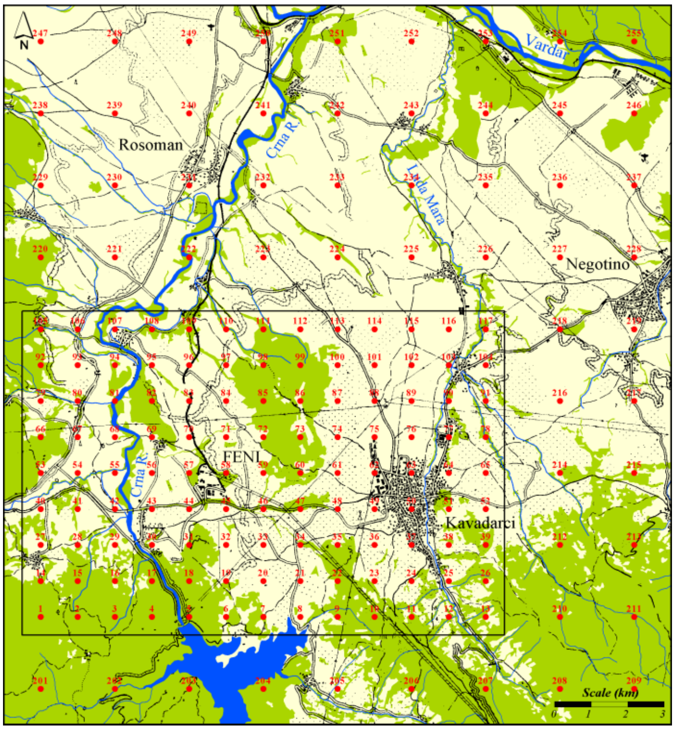

Fig. 2. Soil samples locations

Sample preparation and analyses

The soil samples were air dried indoors, then they were gently crushed, sifted through a plastic sieve with 2 mm (Salminen et al., 2005), quartered and milled below 0.125 mm. Mass spectrometry with inductively coupled plasma (ICP-MS) determination of 36 elements was performed after aqua regia digestion. The obtained results for the median (Md), geometric mean (X_g), minimal (Min) and maximal (Max) values are given in Table 1.

Table 1. Descriptive statistics of measurements (n = 344)
Values of Al, Ca, Fe, K, Mg, Na, P and Ti are in %, Au in µg/kg, remaining elements in mg/kg.

	Md	X_g	Min	Max
Al	1.5	1.5	1.1	2.1
Ca	3.6	3.1	0.76	8.2
Fe	2.3	2.3	1.7	3.3
K	0.26	0.25	0.16	0.36
Mg	0.92	0.93	0.54	1.6
Na	0.0080	0.0087	0.0050	0.016
P	0.049	0.051	0.031	0.085
Ti	0.015	0.017	0.008	0.049
As	8.8	8.5	5.1	13
Au	1.5	1.5	0.70	3.0
Ba	110	110	69	160
Cd	0.30	0.32	0.20	0.60
Co	15	15	11	24
Cr	50	55	31	110
Cu	30	30	18	52
Ga	4.0	4.3	3.0	6.0
Hg	0.020	0.019	0.010	0.040
La	15	14	10	20
Mn	780	780	520	1100
Mo	0.30	0.27	0.20	0.40
Ni	72	74	42	150
Pb	21	21	14	33
Sb	0.20	0.25	0.20	0.50
Sc	3.7	3.7	2.5	5.4
Sr	62	68	29	180
Th	4.7	4.7	3.0	7.1
Tl	0.20	0.17	0.10	0.30
U	0.50	0.55	0.30	1.0
V	37	37	28	51
W	0.10	0.12	0.050	0.30
Zn	57	56	40	78

Data processing and construction 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. The methods of parametric and nonparametric statistics were used for the data analysis (Snedecor and Cochran, 1967; Davis, 1986). On the basis of the results of the normality tests and visual inspection of the distribution histograms the logarithms from the content for the normal distribution was used for all elements. The basic statistics data for the 31 selected chemical elements (Al, As, Au, Ba, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mn, Na, Mg, Mo, Ni, P, Pb, Sb, Sc, Sr, Th, Tl, Ti, U, V, W and Zn) with regards to the basic lithological units in topsoil (0–5 cm) and subsoil (20–30 cm) are shown in Table 2.

Table 2. Average content of the chemical elements according to basic lithological units
Values of Al, Ca, Fe, K, Mg, Na, P and Ti are in %, Au in µg/kg, remaining elements in mg/kg.

	Topsoil (0-5 cm)							Botomsoil (20-30 cm)						
	Mean (EU)	Rocks (Pz-Mz)	Flysch (E)	Sand (Pl)	Tuff (Q)	Terraces (Q)	Alluvium (Q)	Mean (EU)	Rocks (Pz-Mz)	Flysch (E)	Sand (Pl)	Tuff (Q)	Terraces (Q)	Alluvium (Q)
n		24	10	90	29	10	9		24	10	90	29	10	9
Al	5.8	1.9	1.9	1.4	1.5	1.6	1.1	6.2	2.0	2.0	1.5	1.6	1.7	1.1
Ca	0.66	2.3	5.4	5.2	2.6	2.5	2.4	0.81	2.5	5.5	5.6	2.5	2.5	2.5
Fe	2.5	3.2	2.9	2.2	2.1	2.3	1.9	2.6	3.4	2.9	2.2	2.2	2.4	2.0
K	1.6	0.26	0.34	0.23	0.33	0.35	0.32	1.7	0.24	0.30	0.23	0.30	0.31	0.31
Mg	0.46	1.4	1.5	0.98	0.77	0.92	0.97	0.59	1.5	1.5	1.0	0.79	0.92	0.98
Na	0.59	0.0060	0.011	0.0079	0.016	0.0080	0.015	0.64	0.0071	0.010	0.0087	0.018	0.0083	0.016
P	0.056	0.054	0.067	0.052	0.070	0.064	0.078	0.042	0.052	0.057	0.050	0.069	0.056	0.075
Ti	0.34	0.023	0.017	0.014	0.036	0.019	0.044	0.34	0.026	0.016	0.017	0.040	0.016	0.046
As	7.0	9.4	9.6	8.7	8.0	9.9	16	6.0	9.6	9.3	8.6	7.8	9.8	16
Au	–	1.6	1.7	1.3	1.6	2.1	2.0	–	2.3	1.8	2.1	1.9	2.2	1.8
Ba	380	97	100	100	160	120	100	390	99	100	100	160	120	100
Cd	0.15	0.66	0.40	0.37	0.38	0.39	0.50	0.090	0.29	0.34	0.28	0.29	0.34	0.44
Co	7.8	26	21	14	13	15	12	9.0	29	22	14	14	16	13
Cr	60	130	94	55	37	57	45	62	140	94	62	38	57	48
Cu	13	39	63	32	31	44	21	14	40	53	30	29	39	22
Ga	14	5.4	5.5	4.0	4.3	4.5	3.4	14	5.7	5.3	4.1	4.6	4.7	3.4
Hg	0.037	0.034	0.021	0.016	0.028	0.018	0.060	0.022	0.030	0.020	0.016	0.030	0.020	0.058
La	24	12	12	14	20	15	15	26	13	12	14	22	15	16
Mn	500	1100	960	740	740	970	650	0.047	1300	980	740	780	1000	570
Mo	0.62	0.38	0.33	0.24	0.32	0.34	0.42	0.52	0.35	0.31	0.23	0.30	0.36	0.37
Ni	18	180	160	75	50	81	53	22	190	160	80	51	83	57
Pb	23	33	21	20	29	23	22	17	25	20	19	25	25	22
Sb	0.60	0.45	0.23	0.23	0.30	0.31	1.9	0.47	0.33	0.18	0.20	0.25	0.24	1.7
Sc	8.2	4.8	5.4	3.6	3.5	3.6	2.8	9.2	5.2	5.3	3.7	3.7	3.7	2.9
Sr	89	35	150	100	71	52	51	95	40	150	100	71	53	50
Th	7.2	4.3	3.8	4.5	7.1	4.4	5.5	7.6	4.6	3.7	4.5	7.8	4.5	5.7
Tl	0.66	0.17	0.17	0.15	0.30	0.22	0.63	0.67	0.14	0.16	0.16	0.28	0.20	0.62
U	2.0	0.47	0.48	0.57	0.74	0.53	0.93	2.0	0.51	0.47	0.58	0.76	0.50	1.0
V	60	49	45	34	42	34	33	63	50	46	35	43	38	35
W	–	0.16	0.090	0.13	0.16	0.18	0.18	–	0.14	0.080	0.13	0.14	0.13	0.20
Zn	52	76	70	57	63	62	58	47	66	63	51	57	59	55

Mean (EU) – European topsoil average (Salminen et al., 2005); Rocks (Pz-Mz) – Area of Paleozoic and Mesozoic rocks (39 km^2); Flysch (E) – Eocene upper flysch zone (34 km^2); Sand (Pl) – Pliocene sandy series (182 km^2); Tuff (Q) – Pleistocene tuff, Holocene deluvium and Holocene alluvium of the river Luda Mara (46 km^2); Terraces (Q) – Holocene river terraces (23 km^2); Alluvium (Q) – Holocene alluvium of the rivers Crna and Vardar (21 km^2)

The multivariate R-mode factor analysis (Snedecor and Cochran, 1967; Davis, 1986) was used to reveal the associations of the elements. 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, 344 samples of the topsoil (0–5 cm) and subsoil (20–30 cm) and analysis of 24 elements were considered. With the factor analysis the distribution is decreased to seven synthetic variables (F1 to F7) (Table 3). The universal method kriging with linear variogram interpolation (Davis, 1986) was applied for construction of the areal distribution maps of the 31 particular elements and the factor scores (F1–F7) in topsoil (0–5 cm) and subsoil (20–30 cm). The basic grid cell size for interpolation was 20×20 m.

Table 3. Matrix of dominant rotated factor loadings (n = 344)

	F1	F2	F3	F4	F5	F6	F7	Com
Al	0.91							88
Ga	0.91							89
Rb	0.90							83
Sc	0.83							81
Fe	0.80							90
V	0.74							67
Ni		0.94						92
Cr		0.91						94
Mg		0.82						84
Co		0.78						90
Th			0.89					91
La			0.87					90
U			0.72					74
Ba			0.72					74
Sr				0.94				89
Ca				0.82				76
Cd					0.86			77
Pb					0.79			81
Hg					0.77			76
Zn					0.75			84
Sb						0.89		87
As						0.86		83
Tl						0.77		89
P							0.87	84
K							0.75	79
Var	19	15	13	8.5	12	9.8	7.4	84

F1 … F7 – Factor loadings; Com – Communality (%); Var – Variance (%)

Results and Discussion

Four geogenic and three anthropogenic geochemical asociation were established on the basis of: visually indicated similarity of geographic distribution of elemental patterns in topsoil and subsoil, comparisons of the averages of particular chemical elements according to basic lithological units (Table 2), the correlation coefficient matrix and the results of factor analyses (Table 3) and comparisons of the enrichment ratios. Following the results of factor analysis (Table 3) and the trends shown on the geochemical maps, four natural geochemical associations in soil were defined. For naturally distributed geochemical association the contents of the elements increase with soil depth.

The most characteristic association is that of high contents of Al, Fe, Ga, Sc and V as assembled in Factor 1 (Table 2, Fig. 3). Their sources are mainly natural phenomena, such as rock weathering and chemical processes in soil. In addition, the distribution of Factor 1 scores (Al, Fe, Ga, Sc and V) in the topsoil and subsoil (Fig. 3) is closely dependent on the lithogenesis. Their highest contents were found in areas of the Paleozoic and Mesozoic rocks (inner parts of the Vardar zone) and Eocene upper flysch zone and their lowest values in area of the Holocene alluvial sediments of the river Crna Reka.

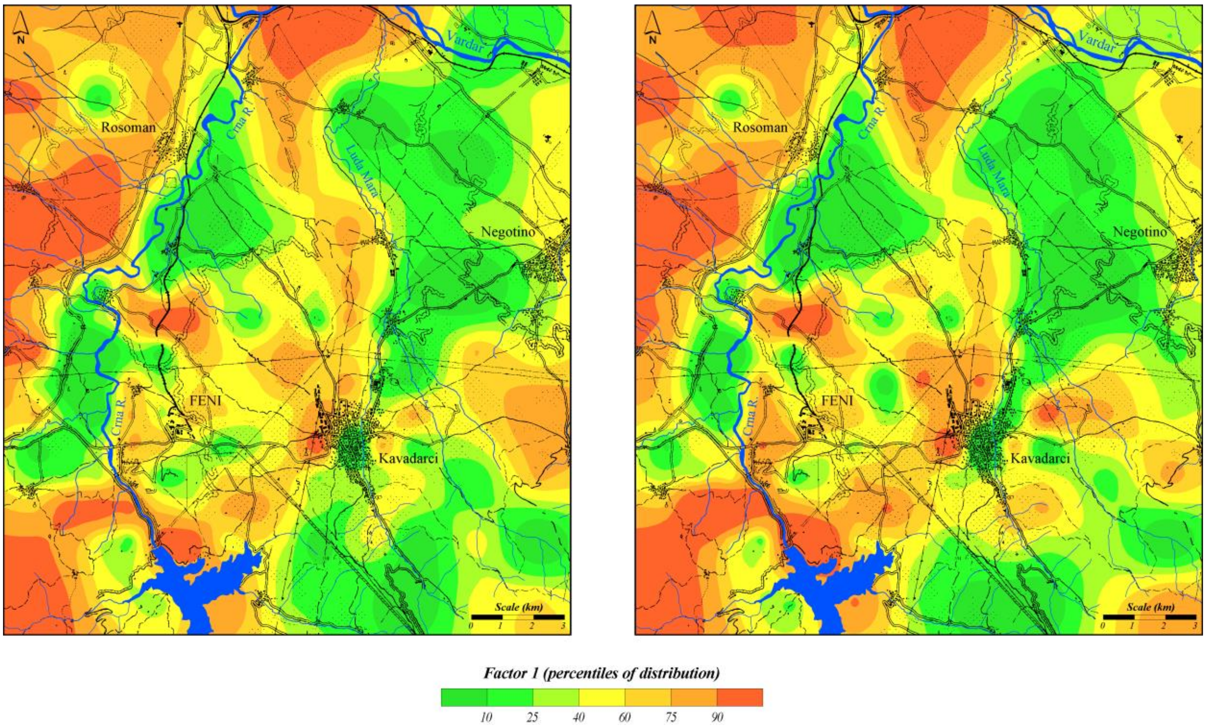

Fig. 3. Distribution of Factor 1 scores (Al, Fe, Ga, Sc and V) in topsoil (left) and subsoil (right)

The association illustrated by Factor 2 (Table 3, Fig. 4) consists of contributions of Co, Cr, Mg and Ni. Similarly to the example of distribution of the Factor 1 scores, the spatial distribution of Factor 2 scores in both soil layers (Fig. 4) is closely dependent on the lithogenesis. Their highest contents were found in areas of Paleozoic and Mesozoic rocks and Eocene upper flysch zone and their lowest values in area of the Pleistocene tuff, Holocene deluvium (W from the town of Kavadarci) and Holocene alluvium of the rivers Luda Mara, Crna Reka and Vardar. These findings are also confirmed by the average enrichment ratios of Co, Cr, Mg and Ni (Fig. 5). In the area of Paleozoic and Mesozoic rocks, their average contents exceed the average of the investigated area by more than twice. Taking into account the fact that the contents of these elements are higher in subsoil than in topsoil, it can be concluded that the occurrence is natural. High, sometimes critically content of Cr and Ni in the zone of Eocene flysch is already proven in numerous studies other Balkan countries (Šajn, 1999; 2003, 2013; Alijagić, 2008; Šajn et al., 2006). The ferronickel smelter plant "FENI", in spite of the obvious environmental pollution has not contributed significantly to the measured amount of these elements, which occurs in high contents in the background.

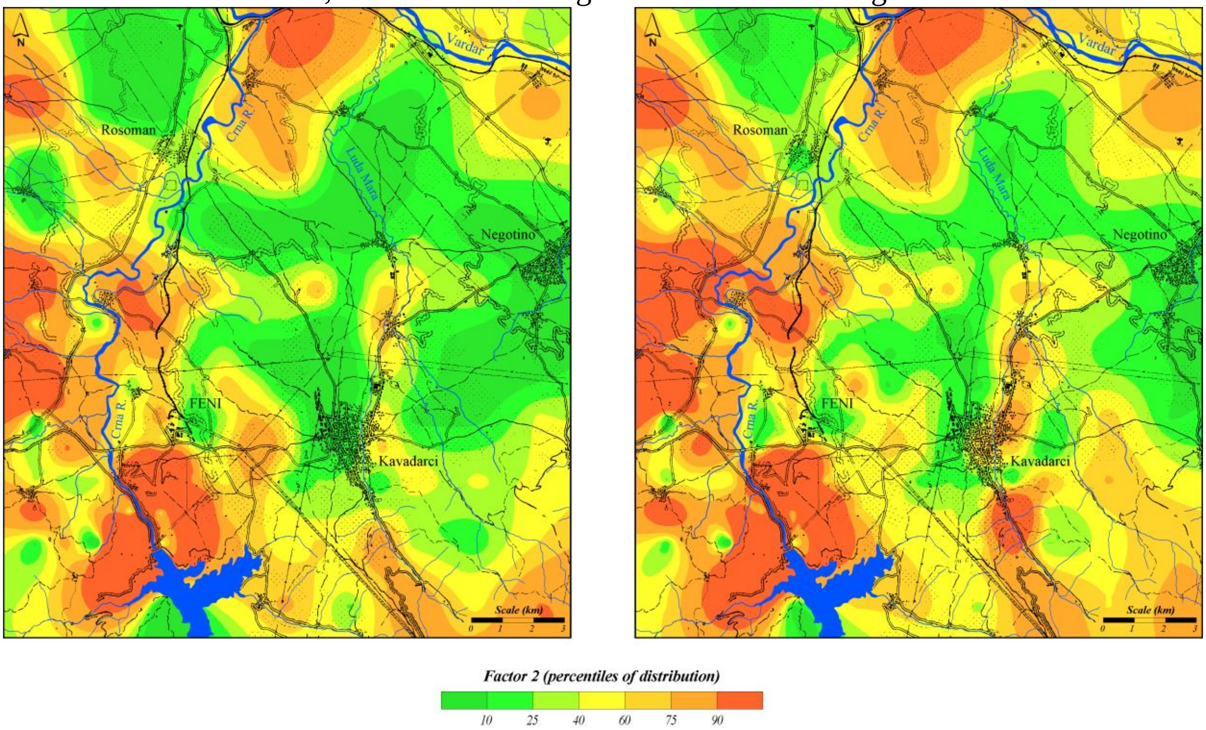

Fig. 4. Distribution of Factor 2 scores (Co, Cr, Mg and Ni) in topsoil (left) and subsoil (right)

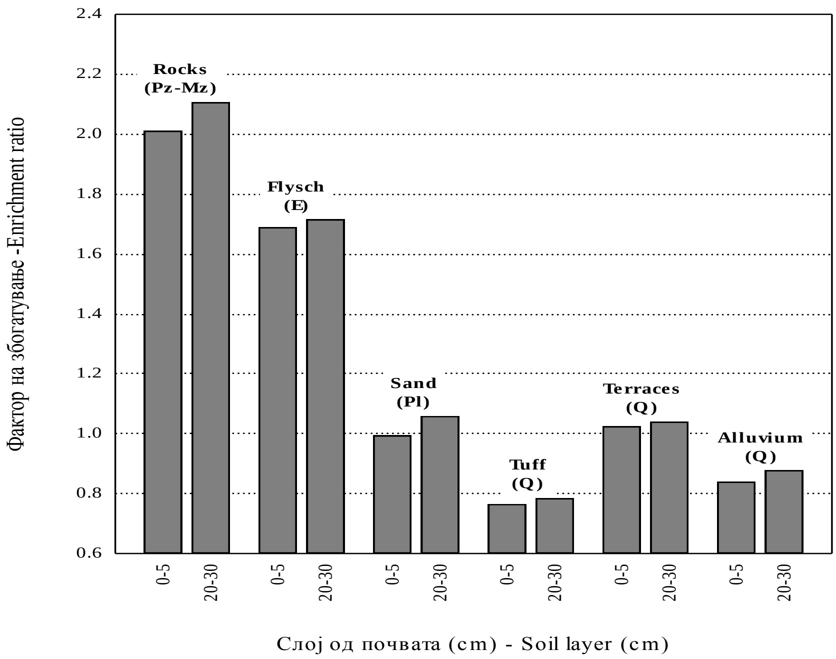

Fig. 5. Average enrichment ratios of Co, Cr, Mg and Ni in topsoil (depth 0–5 cm) and subsoil (20–30 cm) versus soil average of Kavadarci regarding to basic lithological units

The third naturally distributed geochemical association consists elements (Ba, La, Th and U) that are also little affected by anthropogenic activities. The Factor 3 (Table 3, Fig. 6) contains high values of the mentioned elements, explaining 13 % of the total variability within the data. Distribution of Factor 3 scores (Ba, La, Th and U) in the topsoil and subsoil

(Fig. 6) is closely dependent on the lithogenesis. Their highest contents were found in areas of the Pleistocene tuff, Holocene deluvium (W from the town of Kavadarci) and Holocene alluvium of the river Luda Mara, and their lowest values in areas of the Eocene upper flysch zone and Paleozoic and Mesozoic rocks.

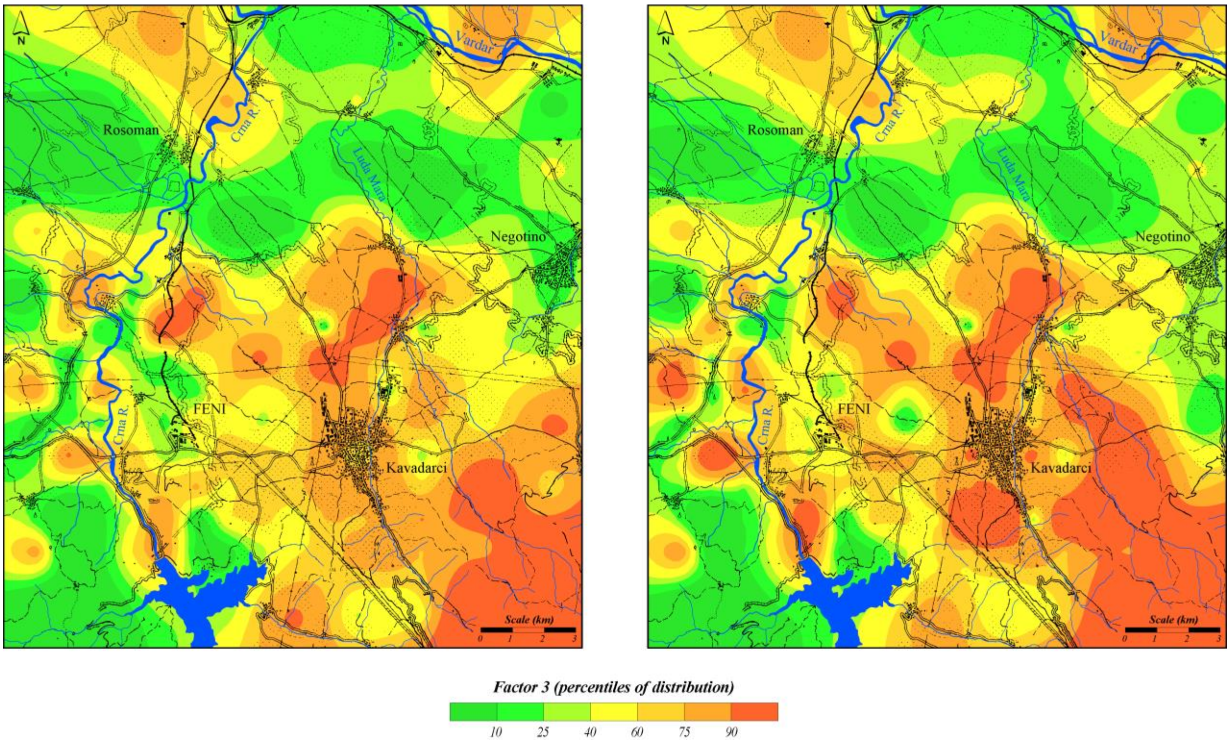

Fig. 6. Distribution of Factor 3 scores (Ba, La, Th and U) in topsoil (left) and subsoil (right)

The natural association of Ca and Sr is illustrated by Factor F4 (Table 3). The highest values of Factor 4 scores and also the highest contents of Ca and Sr (Table 2) occur in the areas of the Eocene upper flysch zone and Pliocene sandy series, while their lowest values in area of Paleozoic and Mesozoic rocks. Factor 4 exemplifies the distribution of carbonates on the study area (Fig. 7).

The group comprises of Cd, Hg, Pb and Zn (Factor 5), chemical elements that were introduced into the environment through anthropogenic activities. Typical for this elemental assemblage is the enrichment of the elements in topsoil versus subsoil (Fig. 8). High contents and the enrichments of these elements in topsoil are noticeable in the area of Paleozoic and Mesozoic rocks which is a clear anomaly in the top soil in the area of Paleozoic and Mesozoic rocks, in wider urban area of the town of Kavadarci and in the Holocene alluvium of the river Vardar. High contents of Cd, Hg, Pb and Zn found on the SW and W due to their high content in organic material of topsoil or the long distance transportations, already shown in Croatia and Slovenia (Šajn et al., 2006). High contents in the alluvium of the river Vardar occur from the Pb-Zn smelter plant in Veles (Stafilov et al., 2008). High contents of Hg and Zn were also found as a result of urban activities in the city of Kavadarci.

The association illustrated by Factor 6 (Fig. 9) consists of contributions of As, Sb and Tl. The Factor 6 contains high values of these elements, explaining 9.8 % of total variability. Samples collected on Holocene alluvium of the Crna Reka show high contents of these elements (Fig. 9). Their average enrichment ratios exceed the average of the total investigated area by 4 to 4.5 times (Fig. 10). The spatial distribution patterns of individual elements in both soil layers do not show a visible difference. In the topsoil there is a clear anomaly in the area of Holocene alluvium of the rivers Crna and Vardar which is consequence of natural erosion from the mine deposits (As and Sb) of Alšar on Kožuf Mountain, but also from mine activities in the past (Stafilov et al., 2013).

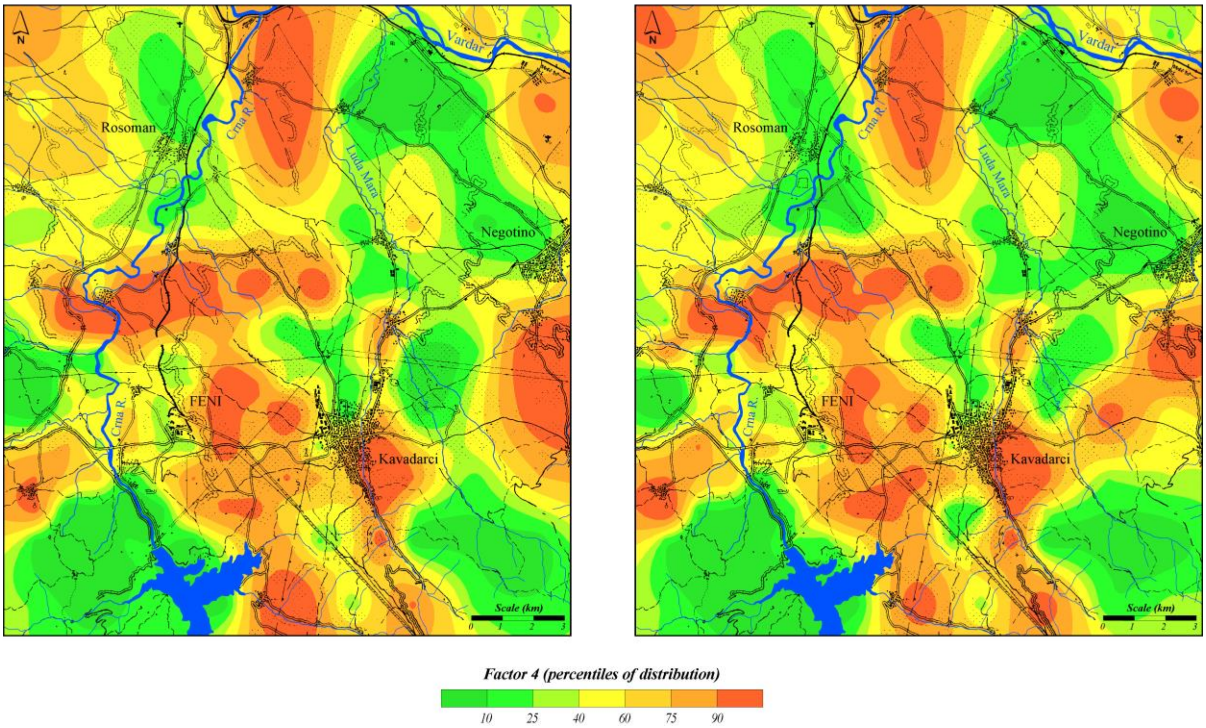

Fig. 7. Distribution of Factor 4 scores (Ca and Sr) in topsoil (left) and subsoil (right)

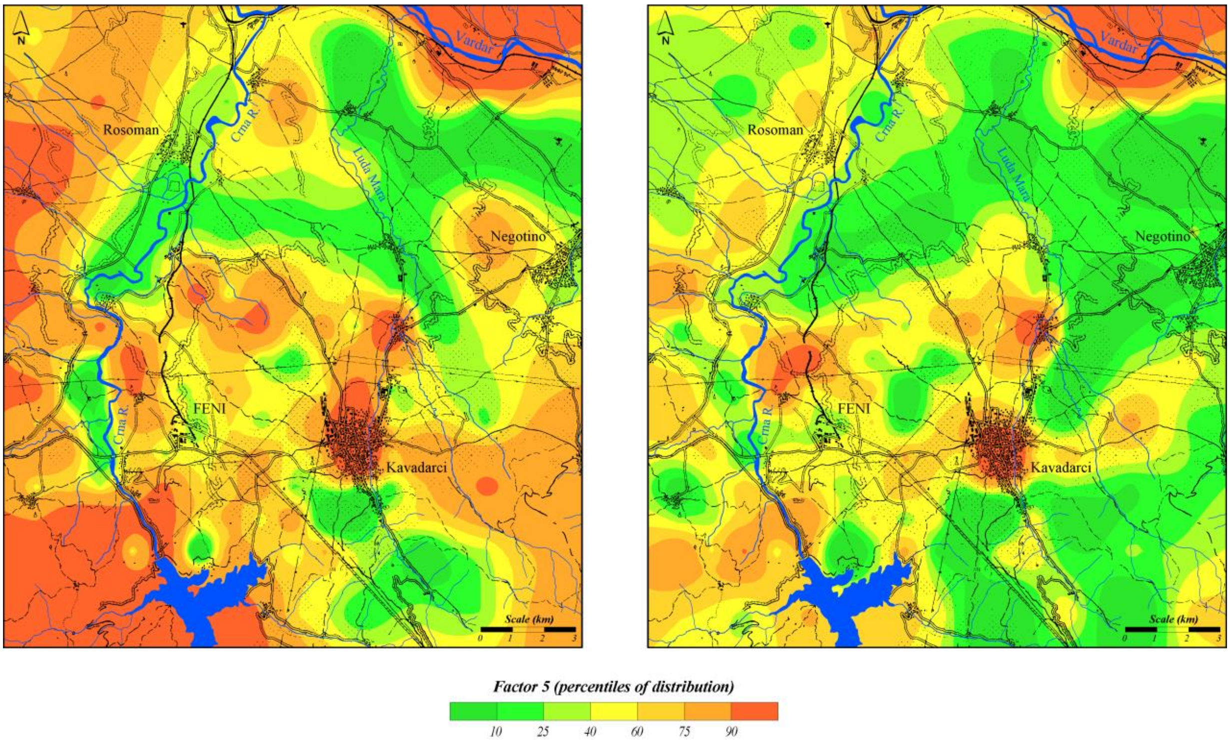

Fig. 8. Distribution of Factor 5 scores (Cd, Hg, Pb and Zn) in topsoil (left) and subsoil (right)

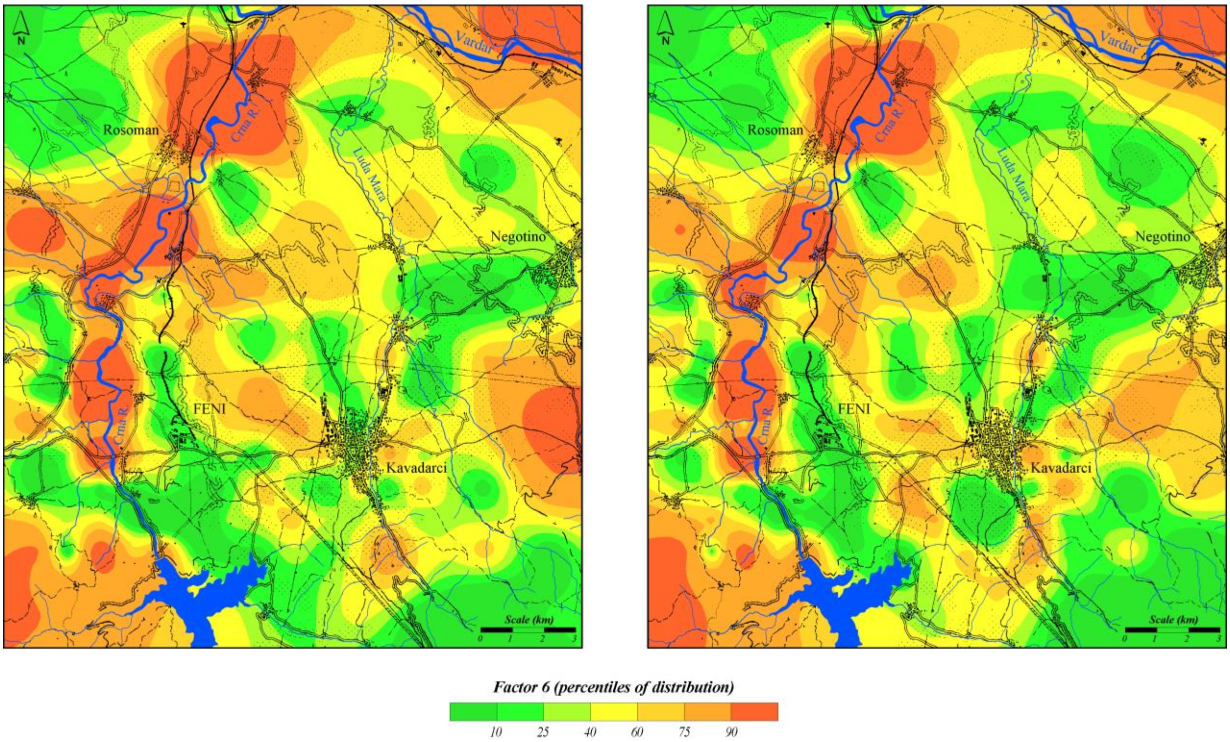

Fig. 9. Distribution of Factor 6 scores (As, Sb and Tl) in topsoil (left) and subsoil (right)

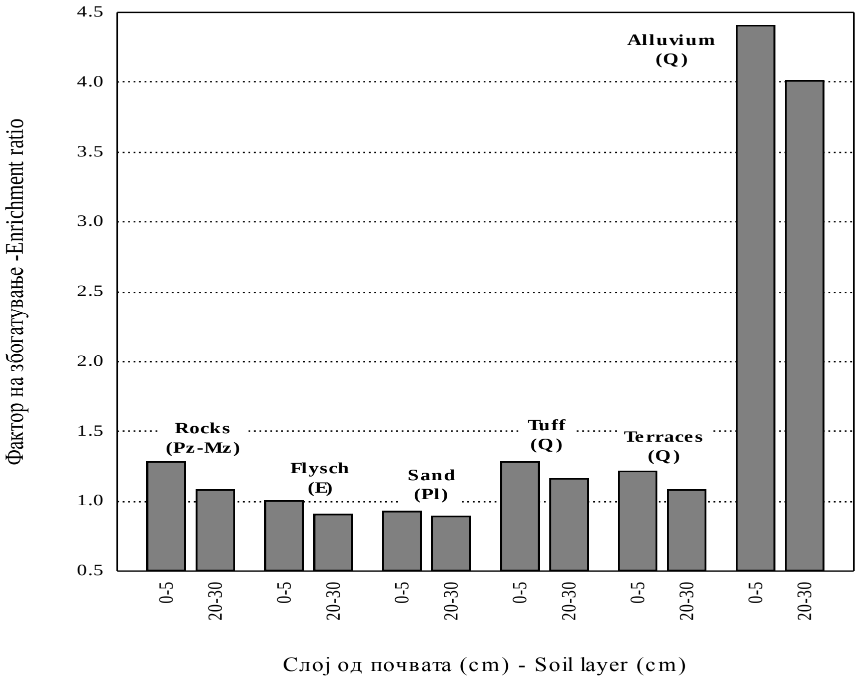

Fig. 10. Average enrichment ratios of As, Sb and Tl in topsoil (depth 0–5 cm) and subsoil (20–30 cm) versus soil average of Kavadarci regarding to basic lithological units

The anthropogenic association of K and P is illustrated by Factor F7 (Table 3). The highest values of Factor 7 scores and also the highest contents of K and P occur in topsoil of the Holocene alluvium and Holocene river terraces of the Crna Reka and wider urban area of town Kavadarci. Factor 7 represents distribution of elements that are introduced into the soil because of the use of fertilizers which contain K and P (Fig. 11).

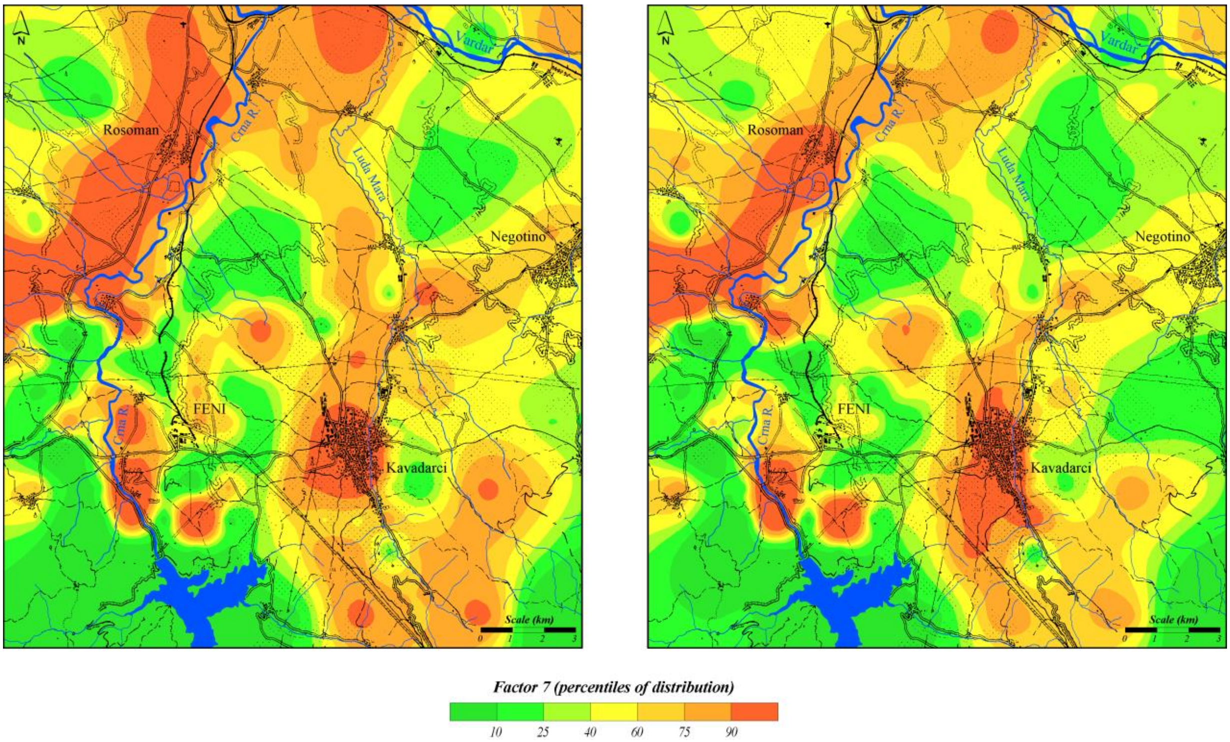

Fig. 11. Distribution of Factor 7 scores (K and P) in topsoil (left) and subsoil (right)

Conclusion

It was found that the critically high contents are related primarily to high contents of Ni and Cr in the western part of the investigated region. The contents of these elements are higher in subsoil than in topsoil, it can be concluded that the occurrence is natural. The high content of Cr and Ni are found in the zone of Eocene flysch indicating that the ferronickel smelter plant situated in this region, in spite of the obvious environmental pollution by dust, has not contributed significantly to the content of these elements in soil, due to the their high content in the background. Within the study, natural enrichment with heavy metals was determined. Principally, the natural enrichment is related especially to Ni. Pollution with As, Cd, Co, Cr, Cu, Hg, Mo, Pb and Zn is basically insignificant. Areas with critically high contents of Cr and Ni cover about 5.5 km^2 of the investigated area.

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