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Original scientific paper

DISTRIBUTION OF CHEMICAL ELEMENTS IN SEDIMENTS AND ALLUVIUM SOILS FROM THE PČINJA RIVER BASIN, NORTH MACEDONIA

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A b s t r a c t: In this work, the distribution of chemical elements in sediment and alluvial soil samples from the Pčinja river basin was investigated. For this purpose, samples of sediments and natural and anthropogenic alluvium soils from the river and lake plains were collected along the course of the Pčinja river in the period from June to July 2017, according to a previously established sampling network with 10 sites on the rivers and 4 sites on the Glažnja and Lipkovo lakes. In addition to five sites on the Pčinja river, two samples were collected from the river of Tabanovska and one sample from each of the tributaries of Pčinja: Kumanovska, Konjarska and Kriva rivers. At each site, the following samples were collected: river sediment, lake sediment and natural alluvium (topsoil sample, 0–5 cm, and subsoil sample, 20–30 cm). In all samples collected, 22 macro- and trace elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, P, Ni, Pb, Sr, V and Zn) were analyzed by inductively coupled plasma – atomic emission spectrometry (ICP-AES). The contents of almost all the analyzed elements are within the expected values and are consistent with the lithology of the area studied. A multivariate factor analysis was applied to analyze the relationships between the number of variables. The method includes processing information from a large number of original variables and processing them into a smaller set (factor) with minimal loss of information from the original variables. From the obtained results, spatial distribution maps of the factors for each group and distribution maps the analyzed elements were created. It was found that the distribution of most elements follows the lithology of the study area, with the exception of some elements (As, Cu, P) whose increased contents are to urban, industrial and agricultural activities.

Key words: Pčinja river basin; North Macedonia; sediment; alluvial soil; heavy metals; distribution

INTRODUCTION

River sediments is a mixture of inorganic and organic matters suspended by the river. Sediment yield is the total amount of sediment transported to the shore by the river in a given period of time. Erosion is the process by which soil, rocks, or other type of material are broken down into smaller fractions by natural causes (Davis & Reynolds, 2009). Every river carries fine sedimentary material with its flow. When the river's capacity to hold sediment is exceeded, the river accumulates sediment deposits. Such deposits occur on the riverbed and on both sites of the river (Bogen et al., 2003). The most common sediment deposits are river channel deposits, alluvial deposits, delta deposits, and river bank deposits. Sediment is known to have tendency to accumulate heavy metals and anthropogenic compounds. It is an excellent indicator of the presence of anthropogenic elements and is considered the best indicator for determining river pollution. Sediments that accumulate on river banks contribute to the formation of alluvial soils from fluvial deposits (Slatt & Zavala, 2006).

Alluvium is the material carried and transported by rivers and deposited in considerable thickness on river banks to promote plant growth. River floods also contribute to the formation of alluvial soils near rivers. When the river receded in the river channel, all the sedimentary materials remain in the floodplains and provides a suitable base for soil formation (Bridge, 2003; Owens & Collins, 2006).

Data on river quality in Northern Macedonia show that many of the rivers are polluted, mainly because of the lack of treatment of municipal and industrial water (Dimitrovska et al., 2012, 2020; Levkov & Krstic, 2002; Stafilov & Levkov, 2007;

Stafilov, 2014, 2016). River basins surveys show that water pollution by various potentially toxic elements (PTEs) as a result of past and present industrial activities is significant. This also affects the pollution of river sediments and longer-term pollution of water and sediments and alluvial soils. For example, the largest river in the country, the Vardar river, is affected by industry and urban activities almost throughout its course (Dimitrovska et al., 2012, 2020; Levkov & Krstic, 2002; Stafilov & Levkov, 2007; Serafimovska et al., 2011; Stafilov et al., 2010; Stafilov, 2014; Ilić Popov et al., 2014, 2016). The impact of river pollution from the Bregalnica river basin effluents and flotation tailings from lead, zinc and copper mines is also particularly evident (Alderton et al., 2005; Dolenec et al., 2005; Vrhovnik et al., 2013; Ramani et al., 2014; Stafilov, 2014; Stafilov et al., 2014, 2015; Balabanova et al., 2016). Some cases of urban and industrial pollution of water bodies and river sediments are also noted on the Crn Drim river basin (Vasilevska et al., 2018, 2019). The impact of pollution of rivers in the catchment area of the Crna Reka river from the operation of the ferronickel mine and smelter, and the abandoned arsenic and antimony mine „Allchar" was also noted (Stafilov et al., 2013; Bačeva et al., 2014; Tomovski et al., 2019).

The main objectives of this work are to determine the content of various chemical elements in river and lake sediments collected at various sites of the Pčinja river basin on the territory of North Macedonia including some of its main tributaries and several sited of the artificial lakes of Glažnja and Lipkovo Lake. The content of 22 chemical elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, P, Ni, Pb, Sr, V and Zn) was analyzed by inductively coupled plasma – atomic emission spectrometry (ICP-AES). The obtained results were subjected to basic descriptive statistics. Comparative tests were performed to identify possible differences in the distribution of the elements. A matrix of correlation factors was also prepared, and the degree of correlation of the values of content of chemical elements in water samples is represented by correlation coefficients in the matrix. Factor analysis and statistical processing through histograms to represent the elements through by means divided by regions are also applied to the results obtained.

MATERIALS AND METHODS

Study area

The studied area is the water catchment area of the Pčinja river including the artificial lakes Glažnja and Lipkovsko Lake (Figure 1). This area is located in the northern part of North Macedonia including the city of Kumanovo. Figure 2 shows the satellite images of this area in the infrared (Figure a) and visible spectral range (Figure b), showing the mountainous part and valleys.

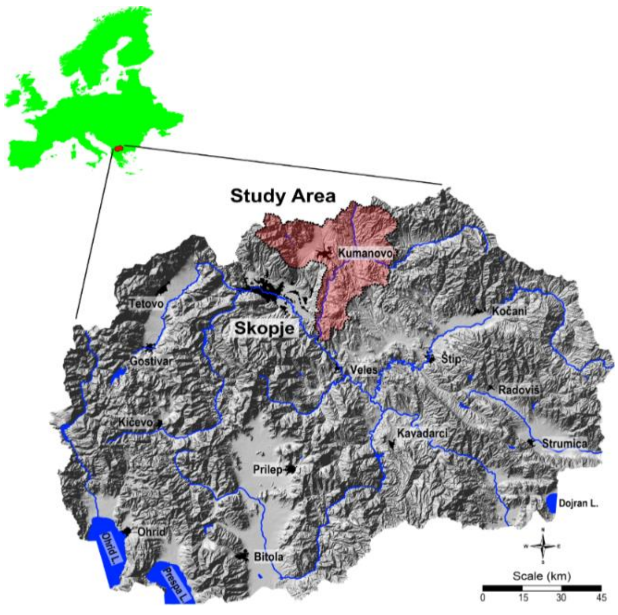
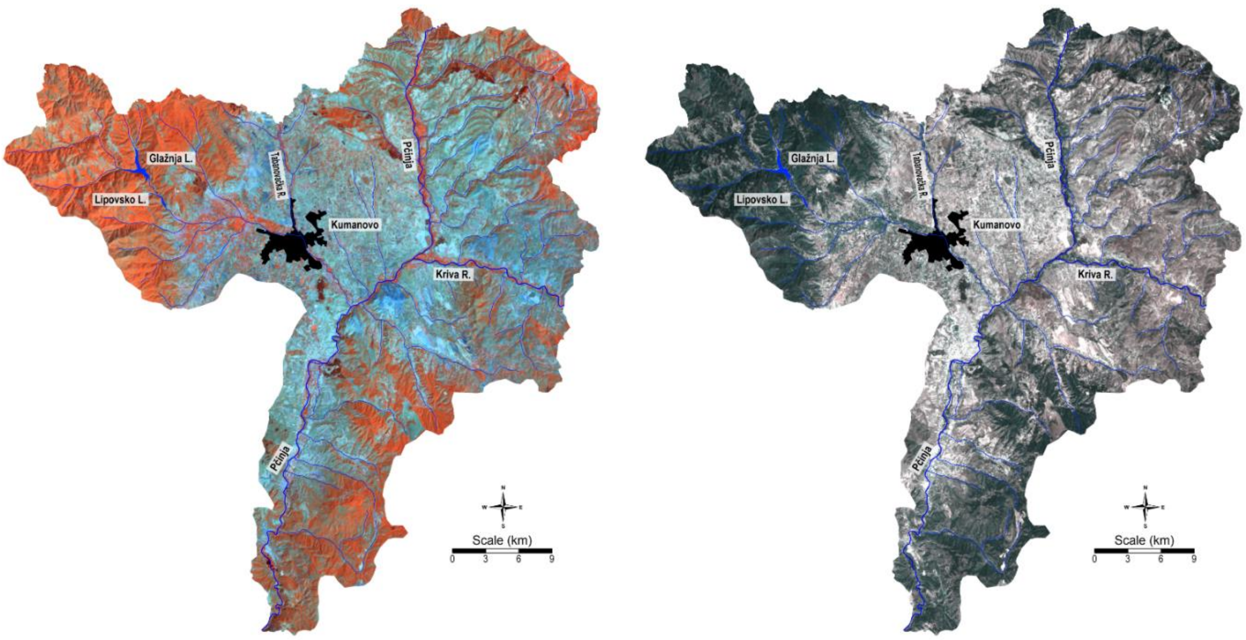


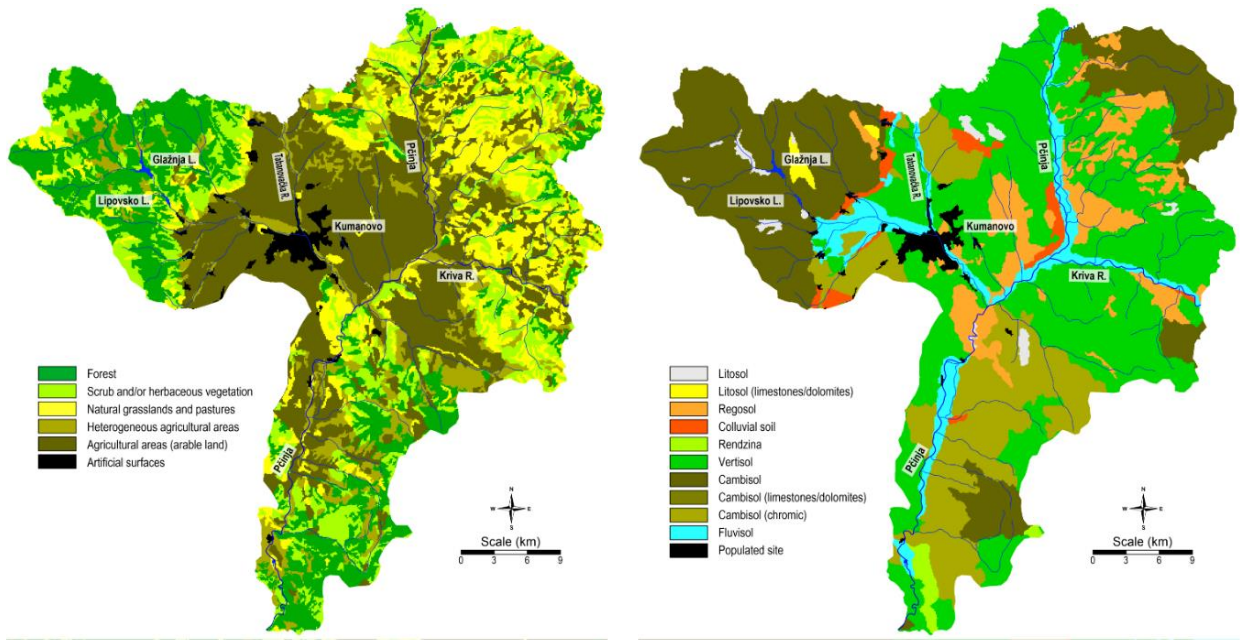
Fig. 1. Location of the studied area on the map of North Macedonia



a) b)

Fig. 2. Satellite image of the Pčinja river basin in the infrared (a) and visible spectral range

The vegetation of the region can be divided into shrubs and grass vegetation, natural pastures, heterogeneous agricultural lands, hilly meadows and forests (Figure 3a). The mountain of Skopska Crna Gora consist mainly of cambisol soils with small areas containing lithosol and regosol. The most common soil in the studied region is vertisol, which is predominant in the central and eastern part of the region. In the southern part along the Pčinja river before its inflow into the Vardar river, the most common soil is the cambisol, as well as fluvial soil. Fluvial soil is observed along all rivers in the studied area (Filipovski et al., 2015). Colluvial and lithosol soils are the least represented in this area (Figure 3b).



a) b)

Fig. 3. A land-use map (a) and the pedological map (b) of the studied area (after www.maksoil.ukim/mk/masis/)

Geological characteristics

In the eastern part of the region around the Pčinja and Kriva Reka rivers, there are mainly Neogene igneous rocks, as well as Proteozoic metamorphic rocks and Paleogene clastitic sediments. In the central and southern parts, Neogene clastic sediments are most abundant, while Quaternary deluvial and proluvial sediments and Paleogene clastitic sediments are less abundant. In the western part (the mountain of Skopska Crna Gora), Paleozoic metamorphic rocks, Mesozoic clastitic sediments and Mesozoic igneous rocks are most common (Figure 4).

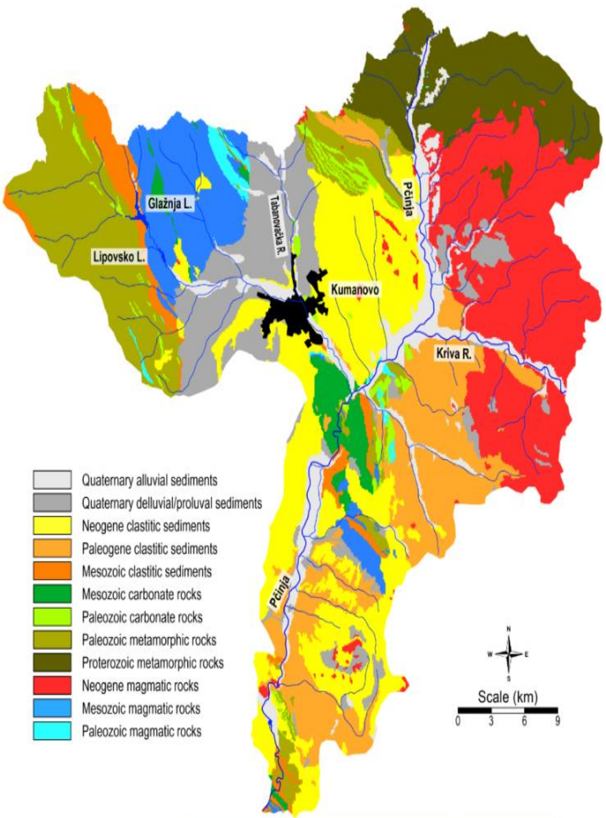


Fig. 4. Geological map of the investigated area

The western part of the area is characterized by a different geological composition and a very complex tectonic structure. There are different types of sedimentary, metamorphic and igneous rocks from the Paleozoic, Mesozoic and Tertiary-Quaternary. The rocks of this area consist of crystallized limestone, serpentine, granite and marble. The metamorphic complex of this series is quite complex and is characterized by lithological differences and various fractures of tectonic complexes. Marble occurs in this area in many zones and different forms, especially near the villages of Lojane and Nikuštak and other places. The serpentine masses appear in the vicinity of the village of Lojane as an elongated mass extending from the northwest. They date back to the Jurassic period. A number of granites, diabases and gabbrodiorts occur in the vicinity of the village of Slupčane. Quaternary sediments consists of sandstones, conglomerates, alluvial sediments and more. Most of these sediments occur in the zone of river outflows of the mountain complex. Such sediments are widely distributed in the bed of the rivers Lojanska, Suva and Slupčanska. Of the ores, the most important are the occurrence of animony and arsenic ores in the rhyolites and serpentines near the village of Lojane, and in the area of the village of Nikuštak with the occurrence of antimony and nickel ores. The main ore minerals are stibnite and realgar with 6.50% As and 4% Sb (Markoski, 2005; UNDP, 2007; Alderton et al., 2014; Stafilov and Šajn, 2016, 2019; Kolitsch et al., 2–18; Đorđević et al., 2019).

Climate characteristics

The area of the Kumanovo valley is open to the north, which allows unimpeded penetration of air masses from higher latitudes, which cause a decrease in air temperature during the winter months (Lazarevski, 1993; Zikov, 1995). For these reasons, the average annual temperature is 11.8°C. The warmest month is July with an average temperature of 22.3°C, and the coldest is January, with an average temperature of 0.4°C. The average annual minimum temperature is 8.0°C, and the average monthly temperatures are below 0°C only in January and February. In summer, the warm continental air in this area provides quite high air temperatures. The average annual rainfall is 549 mm, ranging from 320 to 913 mm. Relative humidity decreases from January to August, and increases from that month to December. The average annual relative humidity is 72% with a maximum in December (85%), and a minimum in August (60%).

Basic hydrological characteristics

The most important hydrographic object in this area is the river of Pčinja. It rises on the territory of Serbia, below the Bela Voda peak on the mountain of Dukat, at an altitude of 1664 metres. The river valley has a composite character. From the entrance to the Republic of Macedonia it passes through three gorges, between which there are shallow sections. It flows into Vardar in Taor gorge at an altitude of 191 m. The total length of the river is 135 km, with an average slope of 10.9‰. The average flow at the mouth is 16 m^3/s. The total area of the catchment is 2840 km^2, of which 2317 km^2 is in Macedonia. On the Macedonian territory, 8 tributaries flow to Pčinja, from which on the right site only the 44.5 km long Kumanovska River with a catchment area of 460 km^2, and on the left side the other 7 significant tributaries with a total length of 178.5 km and a catchment area of 1290 km^2. The Pčinja river basin also includes two artificial reservoirs of Lipkovo and Glažnja.

Sampling

In the period from June to September 2017, 10 samples of sediments and alluvial soils were collected in the Pčinja river basin. Depending on the location, conditions and availability, samples were collected near the indicated sites (Figure 5), with samples collected from 5 sites along the Pčinja river and 5 along its main tributaries (Tabanovska, Kumanovska, Konjarska and Kriva rivers). In addition, lake sediments and soil were collected from the artificial reservoirs of the Glažnja and Lipkovo lakes (Figure 5). Three water samples and lake sediments were collected from Lake Glažnja and from one site of Lipkovo Lake. When taking the samples, the geographical coordinates were recorded using a global positioning system and the sample name, sample type and date of sampling were noted for each sample (Stafilov & Šajn, 2016, 2019).

Soil samples were collected from two layers, topsoil (0–5 cm) and subsoil (20–30 cm), and from both sides of the river at each sampling point. Five separate soil samples were collected square, following the appropriate standards for collecting this type of sample. Four samples were taken at the corners of the surface quadrat, and the fifth sample was taken at the intersection of the diagonals of the quadrat. All five subsets were mixed to obtain a representative sample.

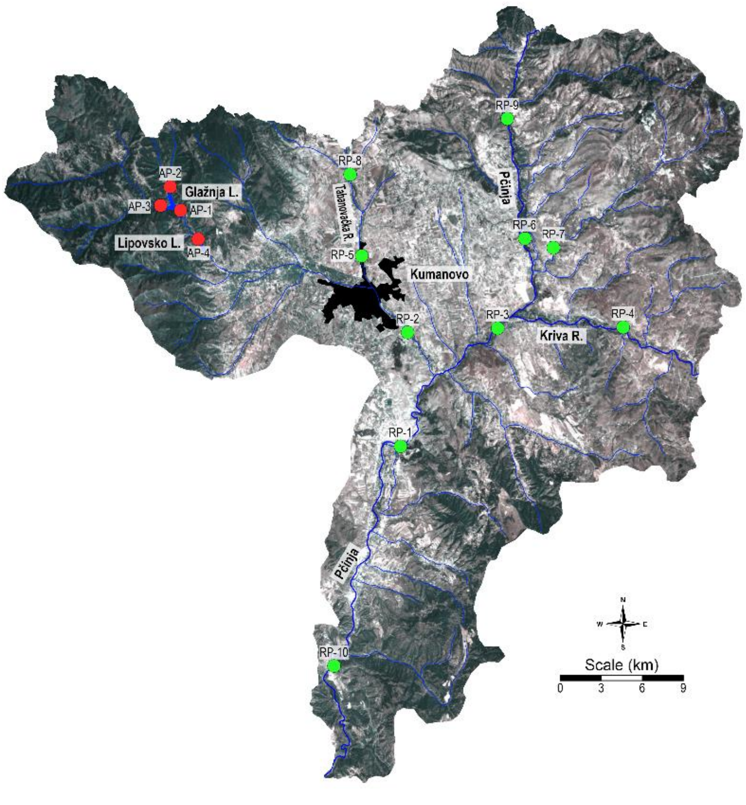


Fig. 5. Sampling locations

The river and lake sediments and soil were prepared for laboratory analysis by cleaning and drying for several days at room temperature. During drying, the samples were crushed and homogenized, lumps in the sediment were crushed to with a rubber hammer. After drying, river and lake sediments were sieved through a 0.125 mm sieve. Surface and bottom soil samples were sieved through a 2 mm sieve and then ground to fine material (below 100 μm) (Salminen et al., 1998; 2005; Reimann et al., 2012; Stafilov & Šajn, 2016, 2019).

Sample preparation and analysis

Soil and river sediment samples are first cleaned and dried indoors at room temperature for several days. During drying, they are finely crushed and homogenized. After drying, the river sediments were sieved through a sieve with an opening diameter of 125 μm. The soil samples were sieved through a 2 mm sieve and then ground in an agate mill. Digestion of these samples was carried out using a mixture of four acids (HNO_3, $HClO_4$, HF and HCl) for total digestion according to the international standard ISO 14869-1:2001. Subsequently, each solution obtained from the teflon vessels was filtered and collected in a 25 ml plastic flask.

Analysis of dissolved sediments and soils was performed using atomic emission spectrometer with inductively coupled plasma (AES-ICP), Varian, model 715 ES, according to the optimal parameters given by Balabanova et al. (2010). The content of a total of 22 chemical elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, P, Ni, Pb, Sr, V, Zn) was determined in all samples.

The obtained data for elements whose content was above the detection limit were statistically processed using StatSoft 11.0 software. A basic descriptive statistical analysis of the values for the contents of the elements was performed for each type of sample. To evaluate the degree of correlation between the contents of the elements in the sediment samples and the contents in the soil samples, a bivariant statistics was used with a significance level of $p < 0.05$ and $p > 0.01$, respectively, and the correlation coefficients were represented in a correlation matrix.

Bivariate analysis is one of the simplest forms of quantitative (statistical) analysis in which two variables are analyzed to determine the empirical relationship between them (Barbie, 2009). The following methods of multivariate analysis were also used: Factor analysis and spatial distribution of the mean content of the elements. To check whether there is a certain difference in the distribution of the elements in the surface and bottom soil, as well as whether there is a difference in the distribution between sediment and surface soil samples, comparative statistics were performed using a certain loading coefficient and three methods [*t*-test, *F*-ratio and R(T/B)]. The *F*-ratio, *t*-test and R(T/B) show that there is no significant difference in the distribution of elements between the topsoil and bottom soil samples.

RESULTS AND DISCUSSION

At the basin of Pčinja river, river sediments and alluvial soil (topsoil, 0–5 cm and bottom soil, 20–30 cm) were collected from 10 sites, and 4 sites of the Glažnja and Lipkovo lakes. In addition to five sites of Pčinja river, two samples were collected from the river of Tabanovska and one sample from each of the tributaries of Pčinja: Kumanovska, Konjarska and Kriva rivers. The sediment and soil samples were analyzed for 20 chemical elements (Ag, Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, P, Ni, Pb, Sr, V и Zn). Basic descriptive statistical analysis of the contents of the analyzed elements in the sediments and soils was carried out and the results are presented in Table 1.

A comparative analysis of the contents of the analyzed elements in sediments and alluvial soil samples from the Pčinja river basin with the whole territory of North Macedonia and Europe (Stafilov & Šajn, 2016; Salminen et al., 2005) is presented in Table 2. It was found that for many elements there are differences in the content in the soil of the basin of the Pčinja river compared to that of the Macedonian soils as well as the European soils (Table 2), which shows the dependence on the specific lithogenic origin of the rocks in the subregions of the area. It is important to note that, with the except of As, the median values for all elements included in the New Dutchlist (As, Cd, Co, Cr, Cu, Pb, Mo, Ni, and Zn) (http://www.contaminated land.co.uk), are below the target values, while in some parts of the region some of the elements exceed the target values (Cr, Cu, Ni, Pb, and Zn) or even the action values (As), which is due to the anthropogenic activities in the area of the village of Lojane.

To determine whether there is a significant difference in the distribution of elements in the surface and bottom soil samples. Comparative statistics with a certain loading coefficient were performed by three methods [*t*-test, *F*-ratio and R (T/B)] (Table 3). The *F*-ratio, *t*-test and R(T/B) show that there is no significant difference in the distribution of elements between the topsoil and bottom soil samples. Thus, the ratio of the content of the elements in the topsoil (T) and bottom soil (B) [R(T/B)] indicates that the difference between the distribution of the elements in the sediment and topsoil samples is insignificant (mostly close to 1).

T a b l e 1

Descriptive statistics for the content of analyzed elements in sediments, topsoil and bottom soil samples in the Pčinja river basin

Element	Unit	X	Md	Min	Max	S	Sx	CV	A	E
Ag	mg/kg	0.62	0.54	0.097	1.6	0.46	0.10	74	0.54	–0.75
Al	%	2.2	2.3	0.77	3.2	0.68	0.15	31	–0.55	–0.12
As	mg/kg	33	32	13	59	13	2.9	39	0.54	–0.44
Ba	mg/kg	210	190	110	460	93	21	43	1.65	2.43
Ca	%	0.81	0.73	0.42	1.3	0.29	0.065	36	0.44	–1.36
Co	mg/kg	12	11	6.8	19	3.8	0.84	31	0.65	–0.79
Cr	mg/kg	85	59	36	170	51	11	59	0.85	–1.12
Cu	mg/kg	41	42	25	51	7.8	1.7	19	–0.56	–0.60
Fe	%	2.3	2.3	1.2	3.0	0.49	0.11	21	–0.76	0.75
K	%	1.3	1.22	0.94	1.8	0.24	0.054	19	0.57	–0.49
Li	mg/kg	19	20	10	29	5.3	1.2	28	0.11	–1.15
Mg	%	0.14	0.12	0.069	0.31	0.061	0.014	44	1.54	2.28
Mn	mg/kg	660	660	450	850	100	23	16	0.08	0.03
Na	%	0.88	0.96	0.25	1.3	0.31	0.070	36	–0.90	–0.28
Ni	mg/kg	70	27	9.4	260	84	19	120	1.48	0.74
P	%	0.11	0.11	0.064	0.16	0.019	0.0042	16	–0.25	3.09
Pb	mg/kg	42	30	5.3	170	44	9.9	107	1.94	3.04
Sr	mg/kg	77	76	36	160	30	6.7	39	0.95	1.17
V	mg/kg	110	110	62	140	22	4.9	20	–0.96	0.17
Zn	mg/kg	110	100	74	180	33	7.4	29	0.85	–0.45

X = arithmetical average; Md = median; Min = minimum; Max = maximum; S = standard deviation; Sx = standard error; CV = coefficient of variation; A = skewness; E = kurtosis

T a b l e 2

Comparison of median, minimum and maximum values of the content of analyzed elements in topsoil from Pčinja River Basin with soils from North Macedonia and Europe

Element	Unit	Dutch list		Pčinja river bBasin (this work)		North Macedonia (Stafilov & Šajn, 2019)		Europe (Salminen et al., 2005)	
		Target	Action	Md	Min–Max	Md	Min–Max	Md	Min–Max
Ag	mg/kg			0.54	0.01–1.6	–	–	0.27	0.01–3.15
Al	%			2.3	0.77–3.2	1.3	0.05–35	5.8	0.70–14.1
As	mg/kg	29	55	32	13–59	10	1.0–720	12	0.32–562
Ba	mg/kg	200	625	190	110–460	430	6–2900	375	30–1870
Ca	%			0.73	0.42–1.3	1.3	0.05–35	0.66	0.019–34.3
Co	mg/kg	20	240	11	6.8–19	17	0.50–150	8.0	<1.0–191
Cr	mg/kg	100	380	59	36–170	88	5.0–2700	60	<3–6230
Cu	mg/kg	36	190	42	2551	28	1.6–270	13	0.81–256
Fe	%			2.3	1.2–3.0	3.5	0.03–12	1.34	0.049–10.6
K	%			1.22	0.94–1.8	1.9	0.02–5.3	1.59	0.022–5.1
Li	mg/kg			20	10–29	26	1.8–210	–	–
Mg	%			0.12	0.064–0.31	0.94	0.12–13	0.47	<0.006–15
Mn	mg/kg			660	450–850	900	17–10000	510	31–6070
Na	%			0.96	0.25–1.3	1.3	0.007–3.7	0.6	0.03–3.34
Ni	mg/kg	35	210	27	9.4–260	46	2.1–2500	18	<2–2690
P	%			0.11	0.064–0.16	0.62	0.011–0.39	0.096	0.008–0.99
Pb	mg/kg	85	530	30	5.3–170	32	1.2–10000	23	5.3–970
Sr	mg/kg			76	36–160	140	21–1400	89	8–3120
V	mg/kg			110	62–140	89	1.0–470	60	2.7–537
Zn	mg/kg	140	720	100	74–180	83	8.0–10000	52	<3–2900

Md – median; Min – minimum; Max – maximum

Table 3

Comparative statistics with the determined load coefficient and three methods [t-test, F-ratio and R(T/B)] of the results of topsoil and bottom soil samples

El.	Unit	Topsoil (T)	Subsoil (B)	FO (T/B)	T-test	Sign	F (ratio)	Sign	R (T/B)	Sign
Ag	mg/kg	0.47	0.77	0.6	–1.55	NS	1.77	NS	–0.19	*
Al	%	2.2	2.2	1.0	0.11	NS	1.54	NS	0.79	NS
As	mg/kg	37	30	1.2	1.14	NS	1.66	NS	0.17	*
Ba	mg/kg	220	210	1.0	0.11	NS	1.61	NS	0.92	NS
Ca	%	0.80	0.83	1.0	–0.24	NS	1.32	NS	0.57	*
Co	mg/kg	13	11	1.1	0.59	NS	1.28	NS	0.90	NS
Cr	mg/kg	83	88	0.9	–0.25	NS	1.31	NS	0.98	NS
Cu	mg/kg	41	40	1.0	0.01	NS	1.10	NS	0.69	NS
Fe	%	2.3	2.4	1.0	–0.36	NS	1.16	NS	0.82	NS
K	%	1.3	1.2	1.1	0.69	NS	1.72	NS	0.85	NS
Li	mg/kg	18	19	1.0	–0.23	NS	1.03	NS	0.82	NS
Mg	%	0.14	0.14	1.0	0.11	NS	1.56	NS	0.84	NS
Mn	mg/kg	670	650	1.0	0.35	NS	1.79	NS	0.73	NS
Na	%	0.89	0.86	1.0	0.23	NS	1.12	NS	0.88	NS
Ni	mg/kg	70	70	1.0	0.01	NS	1.03	NS	1.00	NS
P	%	0.12	0.11	1.1	0.84	NS	2.25	NS	0.72	NS
Pb	mg/kg	49	34	1.4	0.71	NS	2.89	NS	0.62	NS
Sr	mg/kg	82	72	1.1	0.76	NS	2.03	NS	0.89	NS
V	mg/kg	110	110	1.0	–0.17	NS	1.16	NS	0.82	NS
Zn	mg/kg	120	110	1.0	0.07	NS	1.16	NS	0.60	NS

FO (T/B – Enrichment factor, ratio of the content in topsoil and subsoil; Sign – significance, NS – nonsignificant difference; * – significant difference

Furthermore, the same statistical analysis was performed to compare the results obtained from the sediment and topsoil samples (Table 4), and significant differences were only found in the distribution of phosphorus of all elements in the three tests. This difference is mainly due to the use of phosphorus in different mineral fertilizers in the area. Due to the minimal and insignificant differences in the distribution of elements in the sediments and topsoil and between topsoil and bottom soil, only the values obtained for the elements in the sediment samples in the whole catchment area are considered in the preparation of the distribution maps.

To determine the degree of correlation between the elements in the samples of river sediments and soils along the entire catchment of the Pčinja river, the bivariate statistic is used, according to which there is a strong correlation between the elements when the absolute value of the correlation coefficient is between 0.7 and 0.9, while there is a good correlation when the correlation coefficient is between 0.5 and 0.7.

Table 5 shows the matrix of correlation coefficients for all sediment, topsoil and bottom soil samples from the study area. There is a strong correlation between the content of the following elements: K-Ba (0.83), Sr-Ba (0.83), Ca-Mg (0.81), Fe-V (0.72) and Cr-Co (0.88) and a good correlation between the contents of Fe-Al (0.54), Li-Al (0.60), Sr-Al (0.56), Cu-Co (0.53), Mg-Cr (0.54), K-Sr (0.62), Mg-Li (0.61), Mg-Ni (0.54), Na-V (0.52) and Pb-Zn (0.68). The elements Ag, As and Cu show no or very weak correlation with the other elements.

T a b l e 4

Comparative statistics with the determined load coefficient and three methods [t-test, F-ratio and R(S/T)] of the results of the sediment and topsoil and bottom soil samples

El.	Unit	Sediment (S)	Topsoil (T)	FO (S/T)	*t*-test	Sign	F (ratio)	Sign	R (T/B)	Sign
Ag	mg/kg	1.2	0.47	2.5	3.40	*	1.97	*	0.22	*
Al	%	2.1	2.2	1.0	–0.29	NS	1.57	NS	–0.58	*
As	mg/kg	22	37	0.6	–3.08	*	1.29	*	0.19	*
Ba	mg/kg	200	220	0.9	–0.36	NS	1.09	NS	0.66	NS
Ca	%	2.0	0.80	2.5	2.42	*	30.88	*	0.67	NS
Co	mg/kg	9.5	13	0.8	–1.69	NS	1.43	NS	0.73	NS
Cr	mg/kg	76	83	0.9	–0.27	NS	1.26	NS	0.91	NS
Cu	mg/kg	38	41	0.9	–0.55	NS	1.95	NS	0.10	*
Fe	%	2.3	2.3	1.0	0.08	NS	1.16	NS	–0.00	*
K	%	1.1	1.3	0.8	–1.52	NS	1.53	NS	0.66	NS
Li	mg/kg	17	18	0.9	–0.42	NS	3.76	NS	–0.18	*
Mg	%	0.44	0.14	3.2	1.54	NS	126.02	NS	0.88	NS
Mn	mg/kg	700	670	1.1	0.35	NS	4.96	NS	–0.72	NS
Na	%	0.96	0.89	1.1	0.50	NS	1.43	NS	0.66	NS
Ni	mg/kg	59	70	0.8	–0.31	NS	1.34	NS	0.99	NS
P	%	0.13	0.12	1.1	0.64	NS	10.89	NS	0.28	*
Pb	mg/kg	37	49	0.8	–0.58	NS	2.26	NS	0.64	NS
Sr	mg/kg	84	82	1.0	0.14	NS	1.23	NS	0.49	*
V	mg/kg	100	110	1.0	–0.37	NS	1.59	NS	0.37	*
Zn	mg/kg	110	120	0.9	–0.56	NS	1.67	NS	0.61	NS

FO (T/B) – ratio of the content in topsoil (T) and sediment (S); Sign – significance, NS – nonsignificant difference; * - significant difference

T a b l e 5

Correlation matrix for the analyzed elements in sediment and soil samples

	Ag	Al	As	Ba	Ca	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	Sr	V	Zn
Ag	1.00																			
Al	–0.12	1.00																		
As	0.11	–0.07	1.00																	
Ba	–0.05	0.41	0.15	1.00																
Ca	0.26	0.15	0.10	0.12	1.00															
Co	–0.38	–0.12	0.31	–0.01	0.17	1.00														
Cr	–0.24	–0.26	0.30	–0.18	0.41	**0.88**	1.00													
Cu	0.00	0.27	0.09	–0.01	0.28	0.53	0.46	1.00												
Fe	0.10	0.54	–0.20	–0.12	–0.25	–0.28	–0.37	0.19	1.00											
K	–0.17	0.43	0.21	**0.83**	–0.07	0.03	–0.21	0.03	–0.14	1.00										
Li	–0.21	0.60	0.33	0.30	0.43	0.23	0.25	0.31	0.15	0.37	1.00									
Mg	–0.10	0.27	0.09	0.21	**0.81**	0.40	0.54	0.15	–0.19	0.06	0.61	1.00								
Mn	–0.02	0.17	0.13	0.34	0.09	0.04	0.03	0.29	0.24	0.34	0.41	0.17	1.00							
Na	–0.01	0.30	–0.52	–0.11	–0.25	–0.53	–0.60	–0.37	0.35	–0.09	–0.18	–0.25	–0.33	1.00						
Ni	–0.20	–0.34	0.42	0.01	0.41	0.79	0.89	0.26	–0.55	0.02	0.29	0.54	0.07	–0.72	1.00					
P	0.20	–0.11	–0.29	0.19	–0.33	–0.51	–0.55	–0.28	0.07	0.27	–0.35	–0.44	0.35	0.32	–0.43	1.00				
Pb	0.09	0.24	0.15	0.34	–0.13	–0.19	–0.39	0.16	0.22	0.54	0.15	–0.17	0.44	–0.13	–0.29	0.22	1.00			
Sr	0.05	0.56	–0.03	**0.83**	0.10	–0.37	–0.50	–0.19	0.17	0.62	0.19	0.10	0.25	0.28	–0.38	0.31	0.31	1.00		
V	0.03	0.21	–0.40	–0.43	–0.33	–0.12	–0.23	0.24	**0.72**	–0.45	–0.32	–0.38	–0.25	0.52	–0.54	–0.02	–0.04	–0.12	1.00	
Zn	0.17	0.18	0.22	0.07	0.06	0.07	–0.03	0.41	0.11	0.33	0.24	–0.11	0.35	–0.28	–0.03	0.11	0.68	–0.06	–0.05	1.00

From the multivariate factor analysis of the content of the elements studied, a matrix of five loading factors is obtained (Table 6).

Table 6

Matrix of factor loads – factor analysis of the contents of investigated elements in sediments and soil samples

Елемент	F1	F2	F3	F4	F5	Comm
Co	0.96	–0.01	–0.03	0.08	–0.09	94.5
Cr	0.86	–0.25	–0.14	0.31	–0.21	96.6
Ni	0.76	–0.08	–0.10	0.30	–0.50	92.9
Cu	0.65	–0.03	0.39	0.20	0.42	79.2
Ba	–0.01	0.95	0.06	0.12	–0.14	94.0
K	0.04	0.86	0.37	–0.03	–0.21	92.9
Sr	–0.39	0.85	–0.07	0.16	0.13	91.9
Zn	0.08	–0.01	0.95	0.04	0.02	90.7
Pb	–0.19	0.33	0.82	–0.08	0.07	83.9
Ca	0.09	–0.07	–0.01	0.90	–0.17	85.7
Mg	0.27	0.11	–0.17	0.88	–0.15	90.8
Li	0.21	0.31	0.24	0.70	0.09	69.5
Fe	–0.20	0.02	0.11	0.00	0.91	87.5
V	–0.06	–0.30	–0.07	–0.28	0.86	92.1
Prp.Totl	21.7	19.6	14.4	17.4	15.6	88.7
Expl.Var	3.04	2.74	2.01	2.44	2.19	
EigenVal	4.34	3.38	2.14	1.55	1.01	

F1, F2, F3, F4 and F5 – Factor loadings of Factors 1, 2, 3, 4 and 5; Comm – Communality (%).
Prp. Totl – Total amount of the explained system variance.
Expl. Var – Particular component variance.
Eigen Val - Eingene value.

Factor 1 (F1) connects Co, Cr, Ni and Cu and it has the highest loading value of 3.04 and a variability of 21.1% of the total variability of 88.7%. The highest load value in this geochemical association is obtained for Co (0.96) and the lowest for Cu (0.65). Factor 2 (F2) has a load value of 2.74 and a variability of 19.6%, and connects Ba, K and Sr. The highest load value in the second geochemical association of elements is obtained for Ba (0.95) and the lowest for Sr (0.85). The third factor (F3) represents 14.4% of the total variability of the matrix with a load value of 2.01 and associates Zn and Pb. Zn (0.95) has a higher load value than Pb (0.82). The fourth factor (F4) represents 17.4% of the total variability of the matrices with a load value of 2.44 and connects Ca, Mg and Li. The highest load value in the fourth geochemical association is Ca (0.90), and the lowest is Mg (0.88). The fifth factor (F5) represents 15.6% of the total variability of the matrix with a load value of 2.19% and connects Fe and V. The highest load value in the fifth geochemical association has Fe (0.91), and the lower has V (0.86). The standard factor values of F1, F2, F3, F4 and F5 for the distribution of elements in all zones of the studied area are shown with spatial distribution maps.

Figure. 6 shows that a high factor value for Factor 1 is observed for sediments from the lakes of Glažnja and Lipkovo and from the Konjarska Reka river near the villages of Tabanovce and Dolno Konjare. The spatial distributions of the elements of F1 are shown in Figure 7. For cobalt, only the sediment of the Konjarska river exceeds the optimal value according to the Dutch list (20 mg/kg), while the intervention value of 240 mg/kg (Table 2) is not exceeded (https://www.esdat.net/environmental%20standards/dutch/annexsi2000dutch%20environmental%20standards.pdf). High values are also found in the sediments and soil of Lipkovo Lake with a value of 20 mg/kg and 19.7 mg/kg, respectively (Figure 7). This region is rich in chromium and has values exceeding the target value of 100 mg/kg. The highest value was found in the samples taken near the village of Tabanovce (Konjarska Reka) with a value of 170 mg/kg, which is far below the intervention value (380 mg/kg). The region is also rich in copper with values above the target value (36 mg/kg) (Figure 7). The highest value was detected in the samples from the Lipkovo Lake with a value of 51 mg/kg, while the lowest value was observed in the Koince village. Pčinja river, with 25 mg/kg. The highest detected Ni content is 226 mg/kg in the sample from the Konjarska river near the village of Tabanovce and exceeds the intervention value (210 mg/kg). In the other regions, the Ni content follows the natural occurrence of nickel in the surrounding soils of the same regions (Stafilov & Šajn, 2016). A high content is found in the sample from the Pčinja river near the village of Koince (Figure 7).

The geochemical association of F2 is most widespread in the northwestern part of the area (Figure 6) and along the Konjarska river, while the lowest factor value for Factor 2 is recorded at the lakes of Glažnja and Lipkovo. Barium content in sediment and soil samples ranges from 37.7 mg/kg (Lake Glažnja) to 404 mg/kg (Konjarska Reka river near the village of Makreš). The increased Ba content in the samples from this area is due to the presence of Neogene igneous rocks (Figure 4). The highest potassium content of 1.8% was also found in the samples from the village of Makreš (Konjarska River). In general (Figure 8), it can be concluded that the K content in sediment samples is approximately the same in all regions. The spatial distribution of Sr in the sediments and soils is shown in Figure 8. The highest content is also found in a sample from the Konjarska river near the village of Makreš (160 mg/kg).

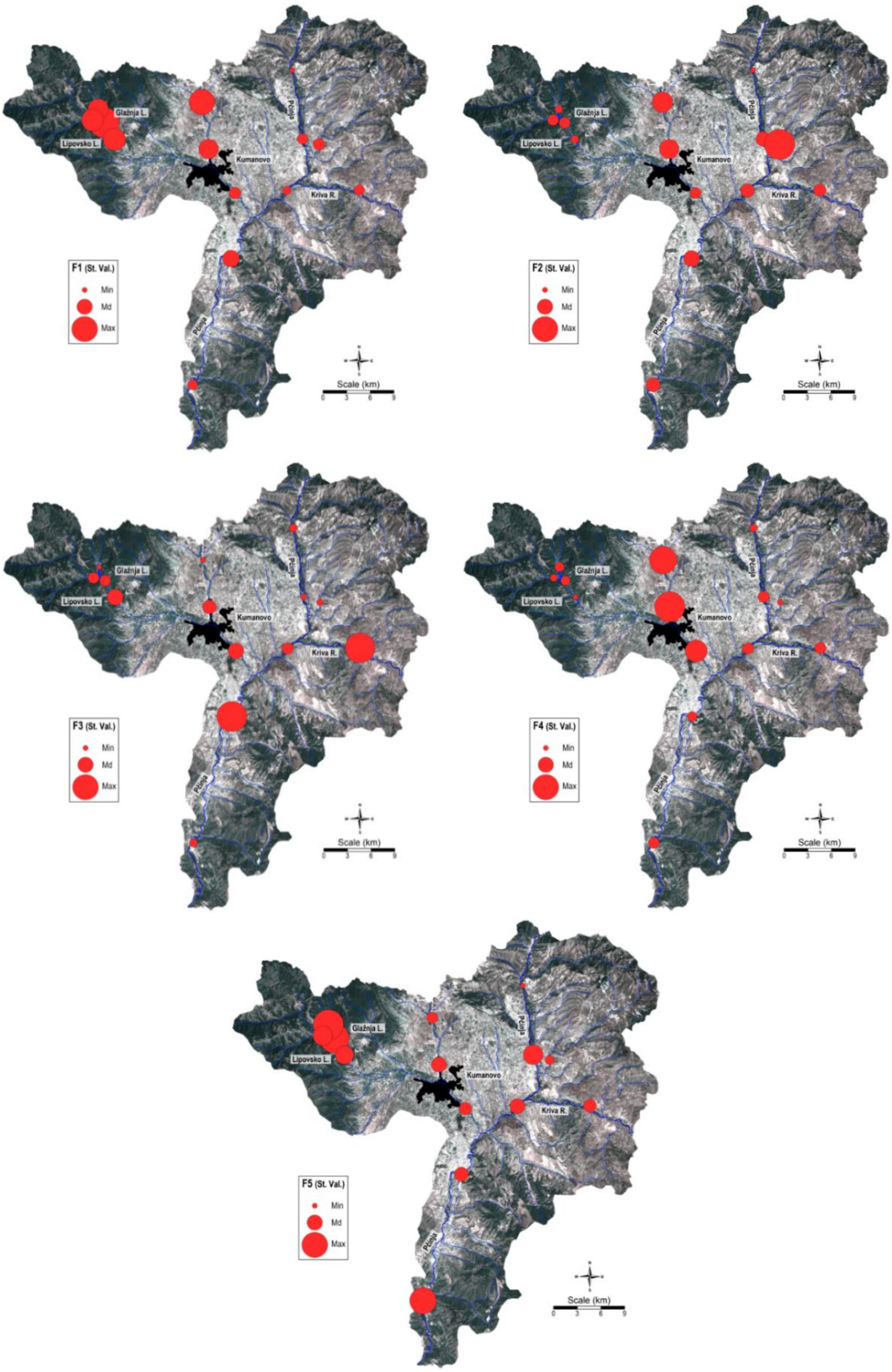


Fig. 6. Spatial distribution of factor scores of F1 (Co-Cr-Ni-Cu); F2 (Ba-K-Sr), F3 (Zn-Pb); F4 (Ca-Mg-Li), and F5 (Fe-V)

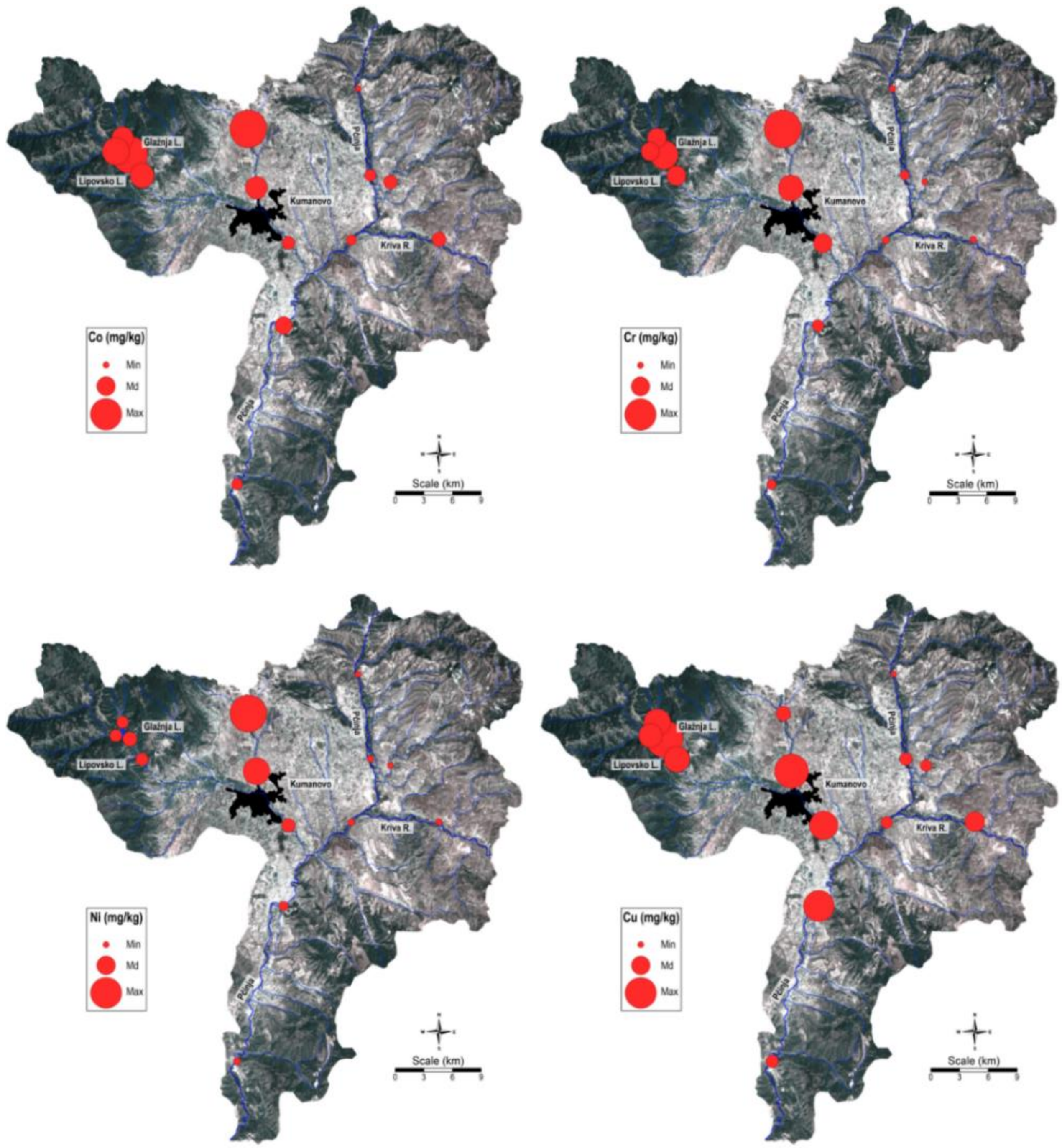


Fig. 7. Spatial distribution of elements included in Factor 1 (Co, Cr, N,i and Cu)

The geochemical association of F2 is most widespread in the northwestern part of the area (Figure 6) and along the Konjarska river, while the lowest factor value for Factor 2 is recorded at lakes of Glažnja and Lipkovo. Barium content in sediment and soil samples ranges from 37.7 mg/kg (Lake Glažnja) to 404 mg/kg (Konjarska river near the village of Makreš). The increased Ba content in the samples from this area is due to the presence of Neogene igneous rocks (Figure 4).

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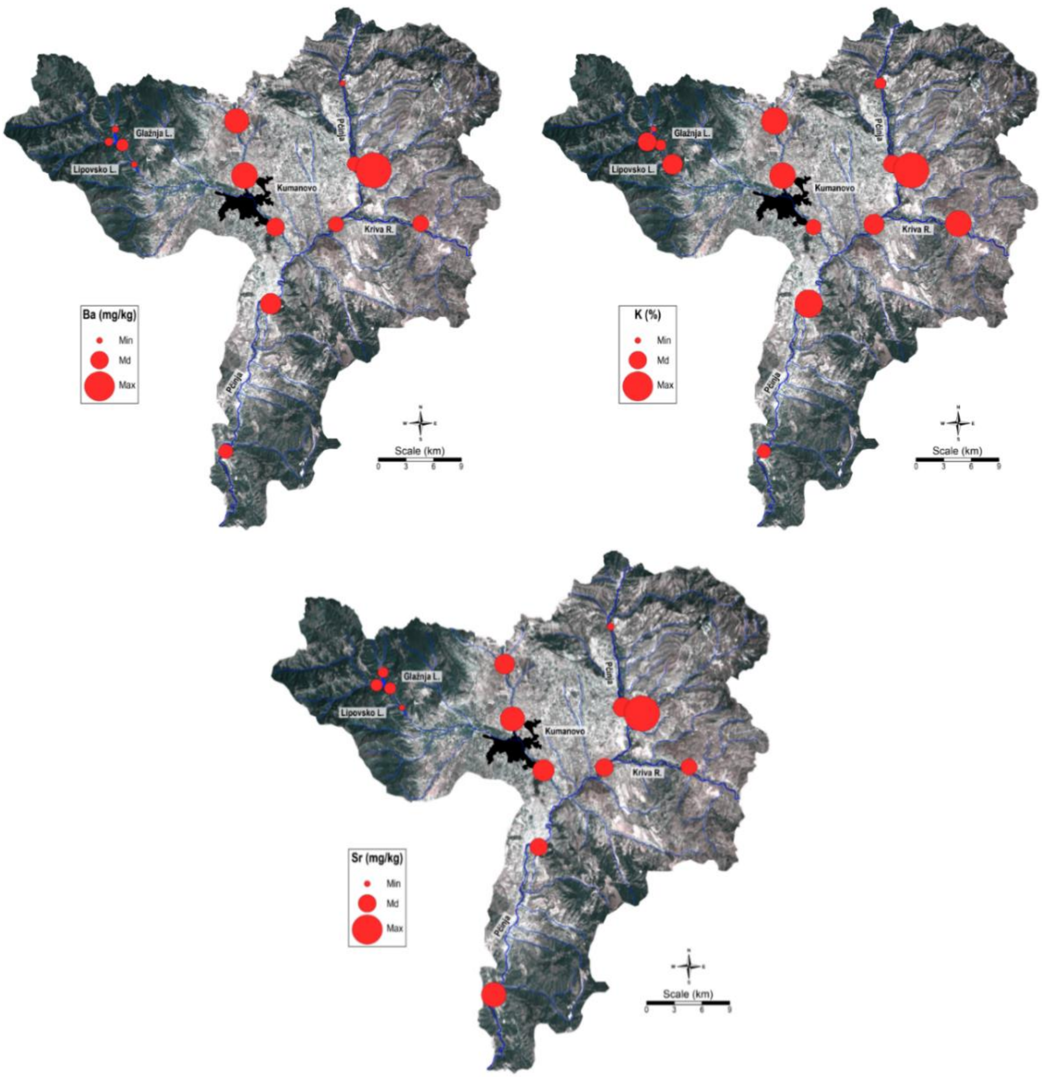

Fig. 8. Spatial distribution of the elements included in Factor 2 (Ba, K and Sr)

The highest value of geochemical association of Factor 3 is located at the river of Kriva Reka and in the village of Pčinja along the Pčinja river (Figure 6), pointing to the anthropogenic uptake of sediments enriched in Pb and Zn from the flotation landfill of the „Toranica" Pb-Zn mine (Stafilov et al., 2018). The region is rich in zinc exceed the target value (140 mg/kg) in samples from two sites (Figure 9). The highest value is found in the samples from the Pčinja river (near the village of Pčinja) with a value of 180 mg/kg, while the lowest value is found in the tributaries of Pčinja near the village of Koince (74 mg/kg). The region is rich in lead with values exceeding the optimal value according to Dutch standards (85 mg/kg) in two sites (Figure 9). The highest value is found in the samples from the Kriva Reka river near the village of Beljakovce (170 mg/kg), which is due to the pollution of Kriva Reka from the Toranica Pb-Zn mine, while the lowest value is found in the sample from Lake Glažnja (5.3 mg/kg).

The fourth geochemical association F4 has the highest factor values in the sediments of the Konjarska and Kumanovska rivers, and the lowest factor values are found along the Pčinja watershed and in the lakes of Glažnja and Lipkovko Lake (Figure 6). Calcium content ranges from 0.58% (samples from Lake Glažnja) to 4.72% (sample from Tabanovska River near the Dolno Konjare village). The higher calcium content in sediments and soils in the Kumanovo valley is due to the higher calcium content in the soils in this region, as well as to the sewage, which is more present than in other areas (Stafilov & Šajn, 2016). A very similar distribution was also found for the content of magnesium (ranging from 0.069% to 0.31%), as well as for lithium (between 10 mg/kg and 29 mg/kg) in the same samples (Figure 10).

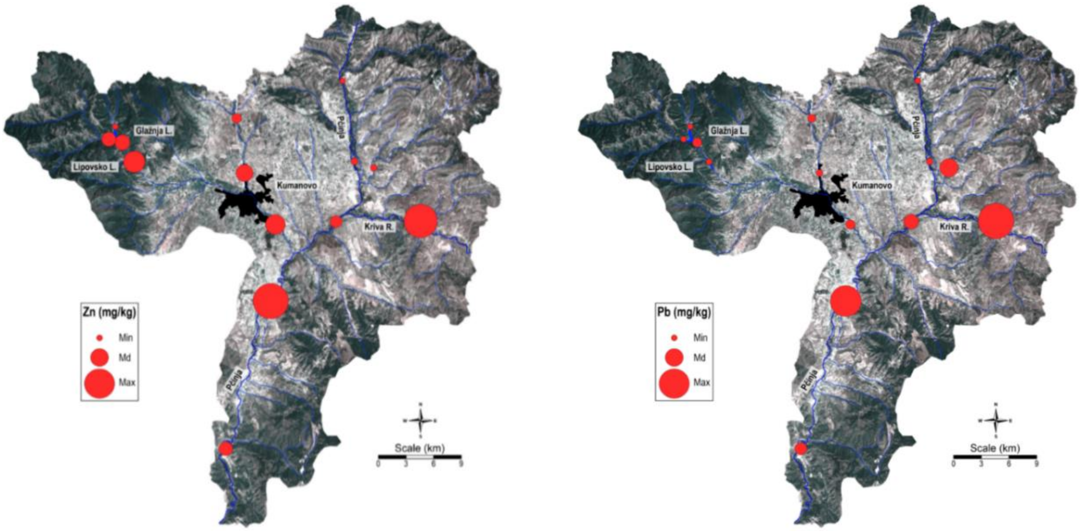

Fig. 9. Spatial distribution of the elements included in Factor 3 (Zn and Pb)

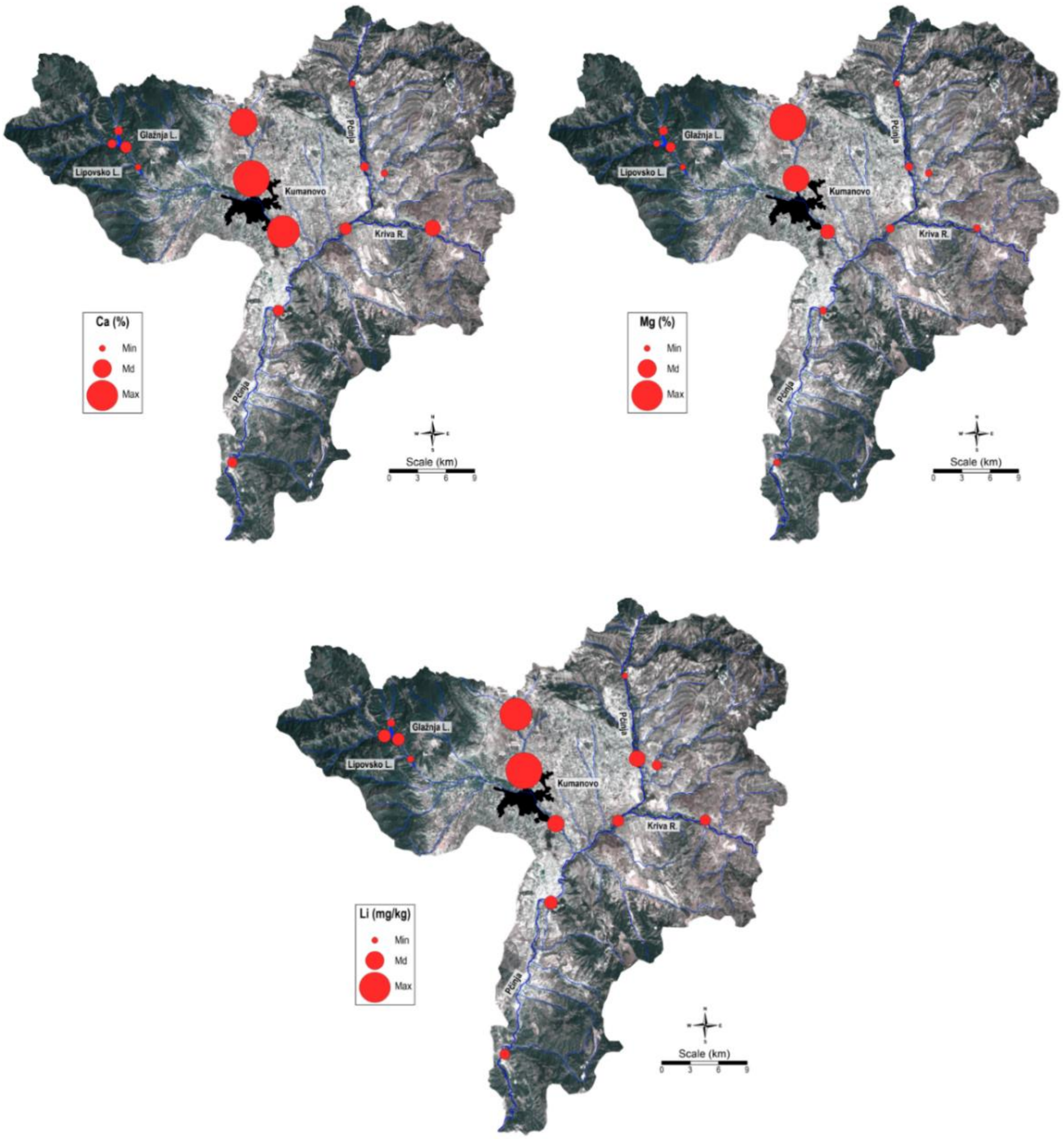

Fig. 10. Spatial distribution of the elements included in Factor 4 (Ca, Mg and Li)

The fifth geochemical association has the highest factor value in the lakes of Glažnja and Lipkovo and in the river of Pčinja before its confluence with the Vardar river (Figure 6). The highest Fe content of 3.3% was found in the samples from the Pčinja river near the village of Katlanovo (Figure 11), followed by its content in the samples from lakes of Glažnja and Lipkovo (2.7% to 3.2%). The spatial distribution of V in sediments and soils in the examined area is given in Figure 11. The highest determined V content is found in a sample from Lake Glažnja (140 mg/kg).

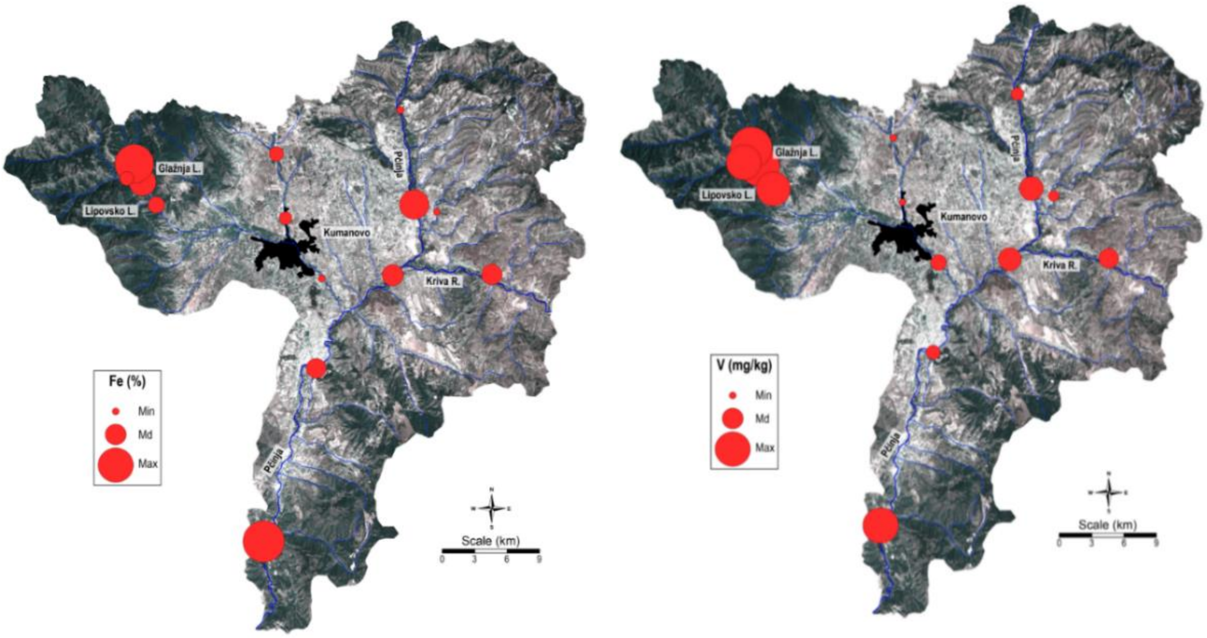

Fig. 11. Spatial distribution of the elements included in Factor 5 (Fe and V)

Some of the elements analyzed were not included in the factor associations (Ag, Al, As, Mn, Na and P) because they do not correlate with the other elements. Their spatial distribution is shown in Figure 12. The silver content ranges from 0.097 mg/kg (sample from Tabanovska River near the village of Tabanovce) to 1.6 mg/kg in the sample from Kriva River, which is also due to pollution from the flotation tailings from the Pb-Zn Toranica mine.

The aluminum content in sediments and soils is quite high, ranging from 0.77% to 3.24% (Figure 12). In sediments, it is most abundant in the sample from the Tabanovska and Konjarska rivers, and the lowest content is found in the sample from the Pčinja river near the village of Koince. The highest arsenic content was found in the sediment samples from Kumanovska river near the village of Dobrošane at 44 mg/kg (Figure 12) which is higher than the target value (29 mg/kg). A higher content than the target value was also detected in the sample from Tabanovska River near the village of Tabanovce (31.5 mg/kg). This elevated arsenic content in these samples is consequence of the pollution of the river of Tabanovska Reka (and then of Kumanovska Reka) by the abandoned mine for As, Sb and Cr near the village of Lojane (UNDP, 2007; Stafilov & Levkov, 2007; Stafilov, 2014; Alderton et al., 2014; Kolitsch et al., 2018; Đorđević et al., 2019). Sodium content in sediments and soils ranges from 0.25% to 1.3%. In sediments, it is most abundant in the Pčinja river near the village of Staro Nagoričane and in the samples from lakes (Figure 12). The spatial distribution of Mn in the sediments and soils in the study area is shown in Figure 12. The highest determined Mn content is found in a sample from the Pčinja river near the village of Pčinja (850 mg/kg) and in the samples from the Lipkovo and Glažnja lakes (Figure 12), while the Mn content in the other samples ranges from 450 mg/kg to 850 mg/kg. The average value of phosphorus content in the whole studied catchment is 0.064%. The highest determined P content in the samples is 0.16% in the sample from the lower course of the Pčinja river, taken near the village of Pčinja (Figure 12). The higher phosphorus content is due to municipal and industrial waste, as well as to the use of phosphate fertilizers in agriculture.

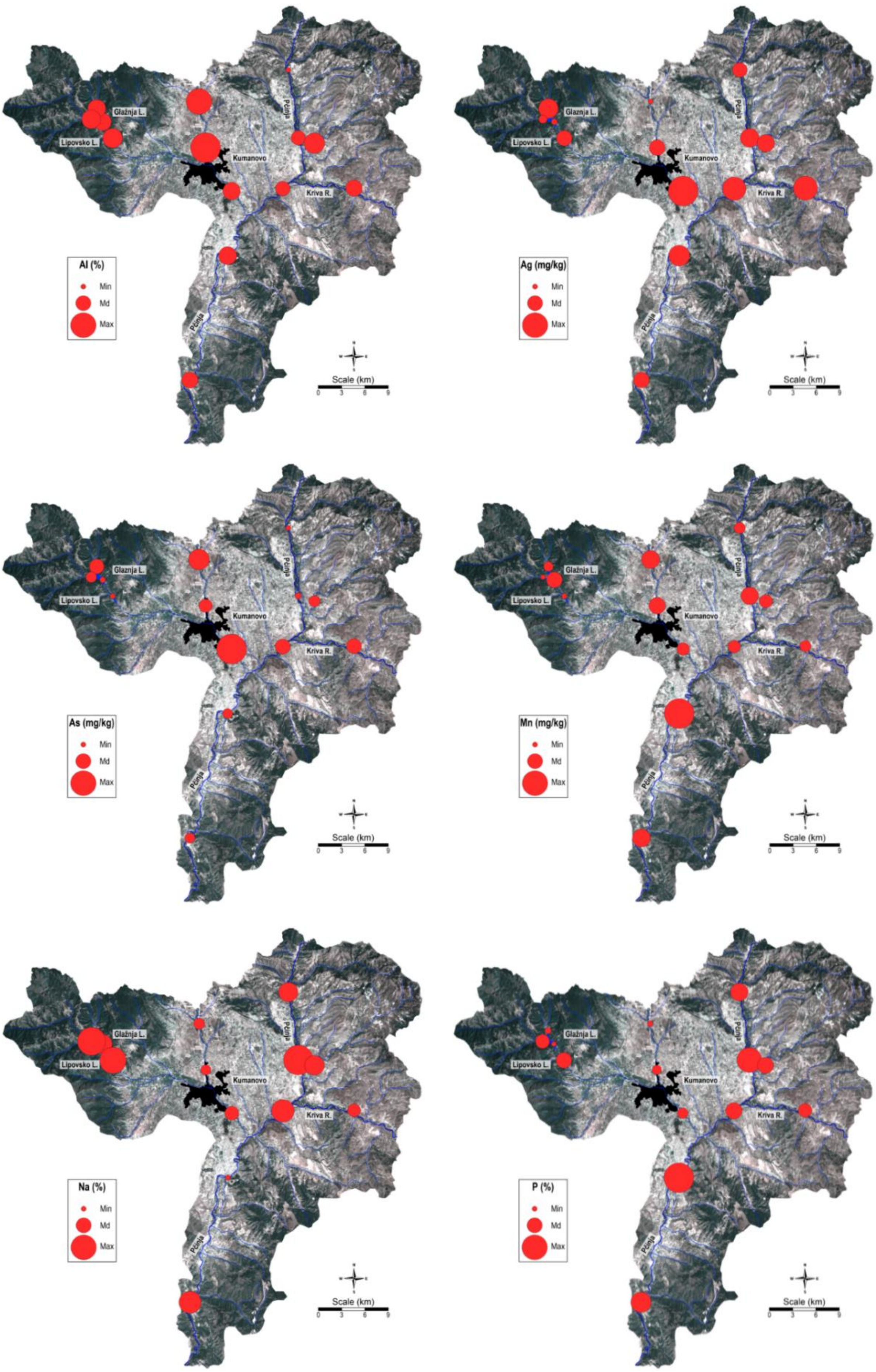

Fig. 12. Spatial distribution of the elements not included in the Factor associations (Ag, Al, As, Mn, Na and P)

CONCLUSION

In this work the contents of Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, P, Ni, Pb, Sr, V and Zn in sediment and alluvial soil samples in the basin of Pčinja river were analyzed. By applying multivariate factor analysis, five associations of elements in the sediment samples were identified: four lithogenic associations: Factor 1 (F1) which associates Co, Cr, Ni and Cu, Factor 2 (F2) which includes Ba, K and Sr, Factor 4 (F4), which includes Ca, Mg and Li; and Factor 5 (F5), which includes Fe and V; and one anthropogenic association, Factor 3 (F3), which includes Zn and Pb as a result of anthropogenic uptake of sediments enriched with Pb and Zn in the Kriva Reka river from the flotation landfill of the „Toranica" Pb-Zn mine near the town of Kriva Palanka. Elevated arsenic content in the samples from the Tabanovska and Kumanovska rivers was also detected, which is due to pollution from the abandoned mine for As, Sb and Cr near the village of Lojane.

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Р е з и м е

ДИСТРИБУЦИЈА НА ХЕМИСКИ ЕЛЕМЕНТИ ВО СЕДИМЕНТИТЕ И АЛУВИЈАЛНИТЕ ПОЧВИ ОД СЛИВОТ НА РЕКАТА ПЧИЊА, СЕВЕРНА МАКЕДОНИЈА

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Клучни зборови: Пчиња; Северна Македонија; речен слив; седименти; алувијални почви; тешки метали; дистрибуција

Извршено е истражување на дистрибуцијата на хемиски елементи во седименти и алувијални почви од сливот на реката Пчиња. За таа цел се земени примероци од речни и езерски седименти и од природни и антропогени алувијални почви по должината на текот на реката Пчиња во периодот од јуни до јули 2017. Според претходно утврдената мрежа за земање примероци, одбрани се 10 локации на реката Пчиња и нејзините притоки и 4 локации на вештачките езера Глажња и Липково. Освен од 5 локации на реката Пчиња, примероци се земени и од 2 локации на Табановска Река и од по еден примерок на притоките Кумановска, Коњарска и Крива Река. На секоја локација се земени следните примероци: речен/езерски седимент, алувијална почва (површинска почва, 0–-5 cm, и потповршинска почва, 20–-30 cm). Во сите примероци се анализирани 22 марко- и микроелементи (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, P, Ni, Pb, Sr, V и Zn) со примена на индуктивно спрегната плазма – атомска емисиона спектрометрија (ICP-AES). Содржината на речиси сите анализирани елементи е во границите на очекуваните вредности кои се во согласност со литологијата на испитуваното подрачје. Применета е мултиваријатната факторна анализа за да се утврдат односите меѓу бројот на променливите параметри. Методот вклучува обработка на податоците од голем број оригинални променливи и нивно процесирање во помали групи (фактори) со минимална загуба на информации за оригиналните променливи. Од добиените резултати се подготвени карти на дистрибуција на поединечните фактори и карти на дистрибуција за секој анализиран елемент. Утврдено е дека дистрибуцијата на повеќето елементи ја следи литологијата на испитуваната област, со исклучок на некои елементи (As, Cu, P) чијашто зголемена содржина во примероците од седиментот е резултат на урбаните, индустриските и земјоделските активности.