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GEOME 2
Manuscript received: August 9, 2019
Accepted: October 22, 2019

Geologica Macedonica, Vol. **33**, No. 2, pp. 125–145 (2019)
IISSN 0352 – 1206
e-ISSN 1857 – 8586
UDC: 550.42:551.311.2(497.784/.785)

Original scientific paper

DISTRIBUTION OF CHEMICAL ELEMENTS IN SEDIMENTS AND ALLUVIAL SOILS FROM THE CRNA REKA RIVER BASIN

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A b s t r a c t: The distribution of 23 chemical elements (Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V and Zn) in sediments and alluvial soils from the entire basin of the river of Crna Reka, Republic of North Macedonia, is presented. In total 31 sediments and 31 soil samples were collected, from which 9 locations are from the river of Crna Reka and 4 from four main tributaries of Crna Reka in the Pelagonia Valley (Blato, Prilepska Reka, Dragor and Jelaška Reka). Also, sediments and soil samples were collected from 3 locations at the shore of the Tikveš Lake, 8 locations from the rivers of Majdanska Reka and Blašnica before its inflow into Tikveš Lake, and from 7 locations of the lower course of the Crna Reka river after the dam of Tikveš Lake until its inflow into the river of Vardar. Determination of the contents of the investigated elements was performed by atomic emission spectrometry with inductively coupled plasma (ICP-AES). All data obtained for the analyzed samples were statistically processed using software Stat Soft 11.0. The maps of spatial distribution of the contents for each element and a histogram with the mean values of the contents for each element by regions were also prepared. In the matrix of the load factors for the elements in the sediment and soil samples there are five factors. Factor 1 includes the chemical elements Mg, Ba, Li, Sr, Al and Ca. Factor 2 includes the chemical elements V, Fe and Cu, while factor 3 includes Ni, Cr and As. Factor 4 includes Pb and Zn, while factor 5 includes Na, P and K. The correlation coefficients matrix for sediments and soil samples from whole investigated area showed that there is a strong correlation between the contents of the elements: Sr-Mg (0.85), Ba-Al (0.83), Mg-Ba (0.83), Ni-As (0.81), Sr-Ba (0.81), Sr-Ca (0.81), V-Fe (0.80), Mn-Al (0.80), Sr-Al (0.79), Mg-Al (0.74), Mn-Fe (0.74) and Mg-Ca (0.70). The obtained results show that the main sources of anthropogenic pollution in whole area of the Crna Reka river basin originate from the rivers of Blašnica and Majdanska Reka as a result of anthropogenic mining activities in that region.

Key words: Crna Reka; Republic of North Macedonia; river basin; sediment; soil; heavy metals; distribution

INTRODUCTION

Water is one of the most important and most prevalent components on the Earth as well as a source of the life on the planet. Its quality and integrity are of equal and essential importance to all living systems. The required daily quantities of drinking water are increasing every day, even though the aquatic reserves on the Earth are still high. Human activities are broad and complex and lead to irreversible processes and permanent pollution of waters. Heavy metals, in addition to being natural constituents of the Earth's crust, regardless of their origin from natural or anthropogenic sources, are environmental pollutants (Kabata-Pendias & Mukherjee, 2007). Water resources have a direct influence on the quality of life of the people, their health and overall productivity (Naiman & Bilby, 2008). Sediments are parts of the environment that provide essential environmental information and are increasingly recognized as carriers and as a potential source of contamination of aqua systems. Metals dissolved in soil solution, surface waters and those adsorbed in the sediments with the cation exchange process are usually available for aquatic and benthic organisms, as well as for plants. The anthropogenic elements accumulated in alluvial soils pose a danger because they accumulate in all agricultural products that are grown on that soil. Water used for irrigation from the rivers also contaminates by anthropogenic elements, contributes to the production and distribution of agricultural products that are potentially dangerous to human health (Agarwal, 2009).

The water pollution in the Republic of North Macedonia is connected with the developing industry, agriculture activities, illegal landfills, uncontrolled discharge of sewage waters into rivers contributed to creating contaminated water ecosystems (Dimitrovska et al., 2012; Stafilov, 2014). As a central water ecosystem, the river of Vardar's basin which represents the most important and humanly influenced water resource in N. Macedonia, was previously investigated (Stafilov & Levkov, 2007; Serafimovska et al., 2011; Ilić Popov et al., 2014), as well as its tributaries: the river of Bregalnica (Balabanova et al., 2016; Krstić et al., 2016), the river of Crn Drim (Vasilevska et al., 2018, 2019) and the quality of the river water from the river of Crna Reka (Tomovski et al., 2018).

The aim of this work is to shown the status of the river of Crna Reka which is the largest tributary of the river of Vardar and the primary objective of this investigation is to present data about the spatial distribution of 23 chemical elements (Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V and Zn) in sediments and alluvial soil samples collected at different locations in the Crna Reka river basin and to interpret and correlate their contents with the lithogenic occurrence and possible anthropogenic impact.

EXPERIMENTAL

Investigated area

The spring of the river of Crna Reka is located in the district of the town of Demir Hisar, and it consists of two rivers: Ilinska and Cerska. Before village of Železnec they merge and continue to flow under the common name Crna Reka. In its lower stream, Crna Reka flows into the artificial Tikveš Lake, and after it flows into the river of Vardar, near the village of Gradsko (Figure 1).

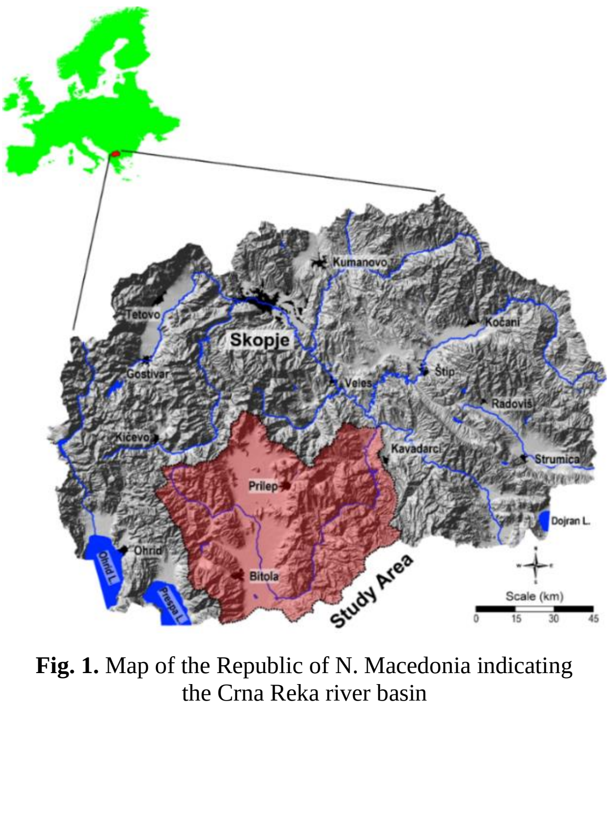

Fig. 1. Map of the Republic of N. Macedonia indicating the Crna Reka river basin

The area of the Crna Reka basin is an area that extends into two states: in the south-western part of the Republic of N. Macedonia and the northern part of the Republic of Greece. Its total length is 207 km with the total area of the catchment area in both countries of 5775 km^2, of which to the Republic of North Macedonia belongs the largest part of 4870 km^2, while the catchment area in the Republic of Greece is 905 km^2 (Koteski, 2009).

The Crna Reka river basin belongs to three geotectonic structural units: the upper western part lies in the area of the West-Macedonian zone, the middle part is on the Pelagonian zone and the lower part belongs to the Vardar zone (Stafilov & Šajn, 2016). The upper western part which lies in the area of the West-Macedonian zone is built mainly from Paleozoic and Triassic formations, primarily from crystalline schists and limestones (marbles and dolomites), as well as from granites (Figure 2). The middle part which belongs to the Pelagonian geotectonic zone is dominated by Precambrian rocks, such as micas and marbles, as well as Neogene deluvial and alluvial formations. In the lower part of the flow of Crna Reka, which belongs to the Vardar zone covering the areas of the eastern part of Mariovo and a part of the Tikveš Valley, the most present are the crystalline schists, granites and granodiorites, flysch sediments, volcanic breccias, limestones, marble dolomites etc. (Koteski, 2009; Stafilov & Šajn, 2016).

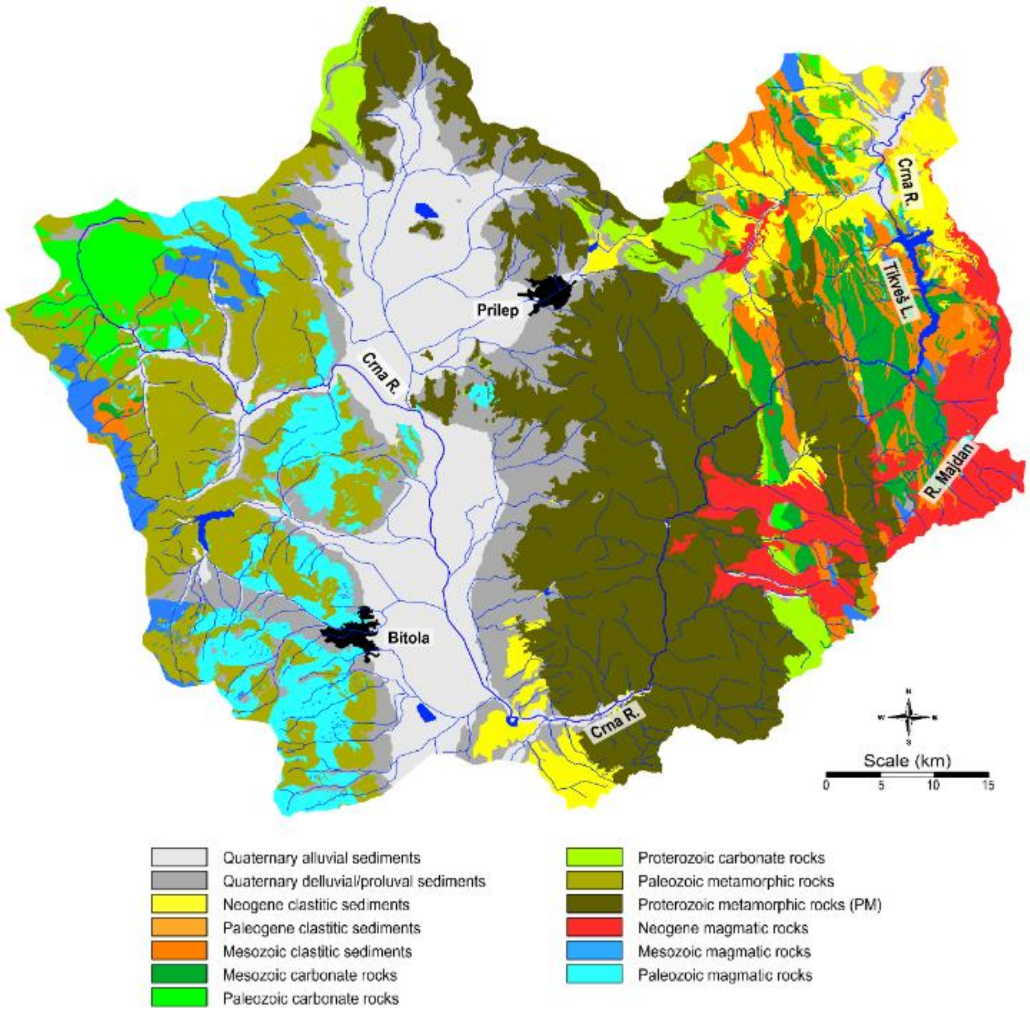

Fig. 2. Geological map of the Crna Reka river basin

Sampling and analysis

In the period from June to September 2016, 31 samples of sediment and 31 alluvial soil samples were collected, from which 13 samples are collected from the source of the Crna Rela river to the estuary in Tikveš Lake, including 9 from the Crna Reka river and 4 from four main tributaries of Crna Reka in the Pelagonia Valley (Blato, Prilepska Reka, Dragor and Jelaška Reka). Also, samples were collected from 3 locations at the shore of Tikveš Lake, from 8 locations at the rivers of Blašnica and its tributary and Majdanska Reka before its inflow into Tikveš Lake, and from 7 locations of the lower course of Crna Reka after the dam of Tikveš Lake (Figure 3).

Depending on location conditions and availability, samples were collected in the near vicinity of the previously specified locations. When collecting samples, the geographical coordinates were recorded using a global positioning system. From each sampling site two samples of sediment were collected, one from each side of the river of the sampling site. Soil samples were taken from two layers, topsoil (0–5 cm) and bottom soil (20–30 cm), and also from both sides of the river at each sampling site. From each soil layer, five separate soil samples were collected within a radius of 10×10 m. All five subsets were mixed and a representative sample was obtained (Salminen et al., 1998, 2005; Reimann et al., 2012; Stafilov & Šajn, 2016).

The preparation of river sediments and soil samples for the analysis was carried out by cleaning and drying for several days at room temperature and then crushed to smaller parts. After drying, the sediments were sifted through a 0.125 mm sieve, while the soil samples were sifted through a 2 mm sieve and then were ground below 100 μm. Such prepared samples were digested by applying mixtures of mineral concentrated acids according to international standard ISO 14869-1: 2001 (2001) by using concentrated HNO_3, HF, $HClO_4$ and HCl.

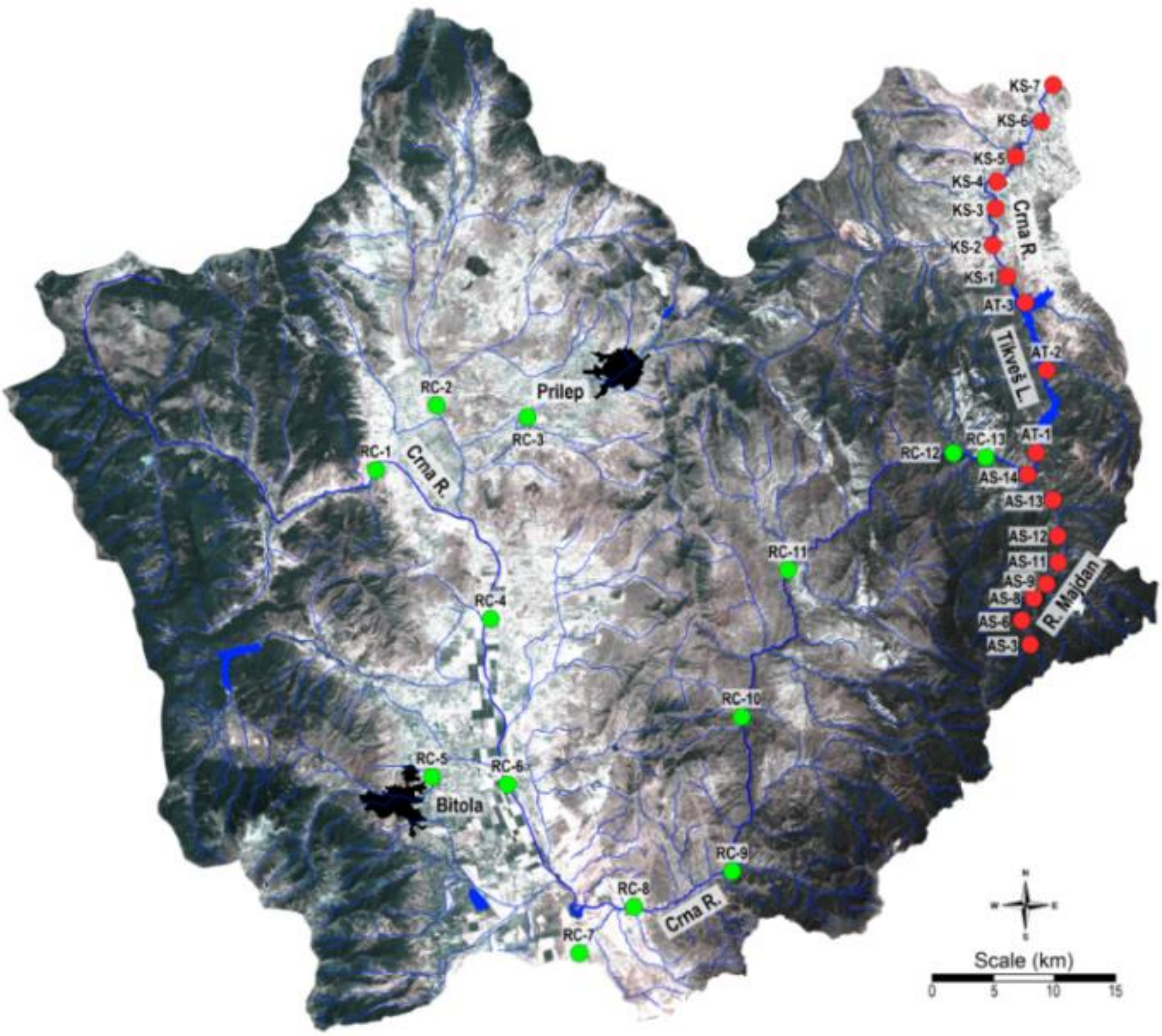

Fig. 3. Map of the investigated basin with the sampling locations

The analysis of sediment and soil samples was performed using an inductively coupled plasma – atomic emission spectrometry, ICP-AES (Varian, 715ES). In all samples, a total of 23 chemical elements were analyzed (Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V and Zn). Standard solutions of elements were prepared by dilution of 1000 mg/l solutions (11355-ICP multi-element standard solution). The optimal instrumental parameters for these techniques are given in our previously published paper (Balabanova et al., 2010). The quality control of the applied techniques was performed by standard addition method, and it was observed that the recovery for the analyzed elements ranges between 98.0% and 101.5%. Certified reference material (CRM) was also used for the quality control of the analytical method. Both certified reference materials (NIST-SRM 2711a, Montana II Soil, National Institute of Standards & Technologies, USA) and spiked intra-laboratory samples were analyzed at a combined frequency of 20% of the samples. The recovery for all of the analyzed elements ranges from 87.5% for Na to 112% for P.

All data for the contents of the tested elements were statistically processed using the software Stat Soft, 11.0. For all of the sediment samples as well as for the top- and bottom alluvial soil samples the basic descriptive statistical analysis of the values for the concentration of the elements was performed. By using bivariate statistics with a level of significance $p < 0.05$, $p > 0.01$ the degree of correlation of the values of the contents of the chemical elements in the samples is estimated, and the coefficients of correlation are presented in the correlation matrix.

RESULTS AND DISCUSSION

Tables 1 and 2 give data on the contents of 18 elements (Al, As, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) because the contents of the other elements in most of the samples are below the detection limit of 1 mg/kg for Ag, B and Cd and 10 mg/kg for Co and Mo.

Table 1

Descriptive statistics for elements content in sediment samples from the Crna Reka river basin (in mg/kg)

Element	Unit	X	Md	Min	Max	P_{10}	P_{90}	S	Sx	CV	A	E
Al	%	3.1	2.7	0.13	6.4	0.44	6.1	2.2	0.46	0	0.25	–1.54
As	mg/kg	21	10	10	73	10	43	19	3.9	90	1.75	2.34
Ba	mg/kg	290	340	31	580	78	530	190	40	65	0.07	–1.60
Ca	%	2.3	1.4	0.20	5.5	0.38	4.8	1.7	0.36	0	0.52	–1.21
Cr	mg/kg	83	71	35	200	50	120	36	7.6	44	1.60	3.64
Cu	mg/kg	44	35	16	290	18	57	54	11	122	4.33	19.86
Fe	%	2.3	2.5	0.90	3.4	1.2	3.2	0.67	0.14	0	–0.59	–0.27
K	%	1.5	1.5	0.44	2.1	1.3	2.0	0.39	0.082	0	–0.93	1.78
Li	mg/kg	18	19	4.6	35	7.8	27	8.6	1.8	49	0.29	–0.58
Mg	%	0.59	0.74	0.043	1.1	0.061	1.1	0.44	0.092	0	–0.19	–1.87
Mn	mg/kg	690	680	300	1300	360	1100	270	56	39	0.47	–0.49
Na	%	1.0	1.1	0.22	1.7	0.57	1.4	0.32	0.066	0	–0.53	1.35
Ni	mg/kg	80	38	19	310	22	220	85	18	107	1.69	1.67
P	%	0.10	0.10	0.033	0.20	0.045	0.15	0.041	0.009	41	0.27	0.30
Pb	mg/kg	28	24	5.6	110	9.0	42	21	4.5	76	2.94	11.46
Sr	mg/kg	210	110	21	560	48	470	30	38	87	0.82	–0.99
V	mg/kg	75	73	36	110	50	98	19	4.0	25	–0.25	–0.54
Zn	mg/kg	110	100	40	280	65	160	52	11	47	1.65	3.98

X – arithmetic mean, Md – median, Min – minimum, Max – maximum, P_{10} – 10 percentiles, P_{90} – 90 percentiles, S – standard deviation, Sx – standard deviation (standard error), CV – coefficient of variation, A – asymmetry, E – distribution

Table 2

Descriptive statistics for elements content in topsoil and bottom alluvial soil samples from the Crna Reka river basin (in mg/kg)

Element	Unit	X	Md	Min	Max	P_{10}	P_{90}	S	Sx	CV	A	E
Al	%	1.8	1.1	0.34	4.6	0.48	3.9	1.4	0.27	0	0.78	–0.89
As	mg/kg	<10	<10	<10	<10							
Ba	mg/kg	250	270	68	480	88	390	120	24	49	0.02	–1.06
Ca	%	2.2	1.4	0.064	19	0.11	4.2	3.8	0.74	0	3.96	17.77
Cr	mg/kg	56	59	22	83	28	74	16	3.2	29	–0.55	–0.49
Cu	mg/kg	37	38	15	53	26	51	10	2.0	27	–0.43	–0.13
Fe	%	2.4	2.5	0.37	3.4	1.8	3.0	0.65	0.13	0	–1.60	3.69
K	%	1.5	1.6	0.54	1.8	1.4	1.7	0.30	0.058	0	–2.46	6.34
Li	mg/kg	18	17	6.1	34	8.0	29	7.4	1.4	42	0.49	–0.48
Mg	%	0.42	0.34	0.004	1.6	0.013	1.2	0.42	0.083	0	1.43	1.65
Mn	mg/kg	550	560	210	790	440	690	1	25	23	–0.93	1.98
Na	%	1.1	1.1	0.20	2.1	0.56	1.9	0.51	0.10	0	0.19	–0.48
Ni	mg/kg	26	27	17	40	17	35	6.7	1.3	25	0.12	–1.06
P	%	0.08	0.07	0.026	0.13	0.038	0.10	0.023	0.004	30	–0.08	0.56
Pb	mg/kg	20	17	5.0	92	5.0	37	18	3.5	90	2.74	9.62
Sr	mg/kg	97	80	7.2	260	9.4	200	77	15	80	0.52	–0.94
V	mg/kg	79	81	26	110	58	110	21	4.1	26	–0.81	0.96
Zn	mg/kg	100	91	43	240	66	140	40	7.9	40	1.89	5.19

X – arithmetic mean, Md – median, Min – minimum, Max – maximum, P_{10} – 10 percentiles, P_{90} – 90 percentiles, S – standard deviation, Sx – standard deviation (standard error), CV – coefficient of variation, A – asymmetry, E – distribution

In order to determine whether there is a significant difference in the distribution of elements in the topsoil and bottom soil, as well as whether there is a difference in the distribution of the elements between the topsoil and bottom soil, comparative statistics with a specific load coefficient and three methods have been made [t-test, F-ratio and R(T/B)] (Table 3). The F-ratio and t-test and R(T/B) show that there is no significant difference in the distribution of elements between the analyzed soil and surface soil samples. In addition, the same statistical analysis was performed to compare the results obtained from the sediment and surface soil samples (Table 4), where significant differences were observed only in the distribution of calcium from all the elements in the three tests due to its higher content in topsoil samples (average of 3%) compared with the lower content of Ca in sediments (1.2%) and in bottom soil (1.5 %). The ratio R(T/B) also indicates the difference between the distribution of some other chemical elements in the sediment and surface soil samples (Ni, P, Zn), but this difference is insignificant because it is below 1.

In order to determine the degree of correlation between the elements in the samples of river sediments and soils across the whole river basin, a bivariate statistic was used where the strong correlation between the investigated elements shows the absolute value of the correlation coefficient from 0.7 to 0.9, while good correlation is found if the correlation coefficient is between 0.5 and 0.7.

Table 5 gives the correlation coefficient matrices for all samples (sediment, topsoil and bottom soil). It was found that there is a strong correlation between the contents of the following elements: Sr-Mg (0.85), Ba-Al (0.83), Mg-Ba (0.83), Ni-As (0,81), Sr-Ba (0.81), Sr-Ca (0.81), V-Fe (0.80), Mn-Al (0.80), Sr-Al (0.79), Mg-Al (0.74), Mn-Fe (0.74) and Mg-Ca (0.70). A weaker correlation exists between the contents of the following elements: Cr-As (0.69), Li-Ba (0.68), Zn-Cu (0.67), V-Ca (–0.65), Sr-As (0.64), Mn-Cr (0.64), Mg-Li (0.63), Mg-As (0.60), Mn-As (0.60), As-Al (0.59), K-Ba (0.59), V-Cu (0.59), Mn-Ba (0.58), Mn-Mg (0.56), Zn-P (0.55), Sr-Mn (0,54), Li-Al (0.53), Ca-Ba (0.53), Fe-Cr (0.53), Ni-Mn (0.53), K-Al (0.52), Ba-As (0.52), Fe-Cu (0.52) and Mn-K (0.52). The contents of Na and Pb elements do not show or have very poor correlation with the contents of the other elements. All of these data are in agreement with the distribution of these elements in soil from the Crna Reka river basin (Stafilov & Šajn, 2016).

Table 3

Comparative statistics with a specified load coefficient and three methods [t-test, F-ratio and R (T/B)] for the results obtained from the samples of alluvial soil from the Crna Reka river basin

Element	Unit	Topsoil (T)	Bottom soil (B)	FO (T/B)	t-test	Sign	F test	Sign	R (T/B)	Sign
Al	%	1.9	1.6	1.2	0.58	NS	1.95	NS	0.76	NS
As	mg/kg	10	10	–	–	–	–	–	–	–
Ba	mg/kg	260	230	1.1	0.63	NS	1.22	NS	0.62	NS
Ca	%	3.0	1.5	2.0	1.02	NS	14.43	NS	0.79	NS
Cr	mg/kg	54	57	1.0	–0.42	NS	1.45	NS	0.88	NS
Cu	mg/kg	39	35	1.1	0.81	NS	1.10	NS	0.84	NS
Fe	%	2.3	2.4	1.0	–0.15	NS	1.76	NS	0.84	NS
K	%	1.4	1.5	1.0	–0.63	NS	1.03	NS	0.60	NS
Li	mg/kg	19	16	1.1	0.73	NS	1.21	NS	0.62	NS
Mg	%	0.46	0.37	1.2	0.53	NS	1.33	NS	0.59	NS
Mn	mg/kg	550	550	1.0	0.02	NS	1.30	NS	0.89	NS
Na	%	1.1	1.2	0.9	–0.49	NS	1.71	NS	0.84	NS
Ni	mg/kg	25	28	0.9	–1.32	NS	1.04	NS	0.73	NS
P	%	0.081	0.070	1.2	1.28	NS	1.26	NS	0.86	NS
Pb	mg/kg	23	17	1.4	0.90	NS	3.73	NS	0.53	NS
Sr	mg/kg	110	87	1.2	0.62	NS	1.30	NS	0.67	NS
V	mg/kg	76	83	0.9	–0.86	NS	1.35	NS	0.86	NS
Zn	mg/kg	110	91	1.2	1.24	NS	4.08	NS	0.44	NS

FO(T/B) – enrichment factor: ratio of the contents in topsoil and bottom soil; Sign – significant at $p < 0.01$; R(T/B) – ratio between the results for topsoil and bottom soil; NS – the difference is not significant

Table 4

Comparative statistics with load factor coefficient and three methods [t-test, F-ratio and R(T/B)] for the results obtained from the samples of river sediments from the Crna Reka river basin and topsoil

Element	Unit	Sediment	Topsoil (T)	FO(T/B)	t-test	Sign	F ratio	Sign	R(T/B)	Sign
Al	%	2.2	1.9	1.1	0.49	NS	1.48	NS	0.23	NS
As	mg/kg	10	10	1.0						
Ba	mg/kg	220	260	0.8	–0.84	NS	1.17	NS	–0.06	NS
Ca	%	1.2	3.0	0.4	–1.21	NS	29.02	NS	0.30	NS
Cr	mg/kg	62	54	1.1	1.28	NS	1.19	NS	0.43	*
Cu	mg/kg	42	39	1.1	0.83	NS	1.01	NS	0.51	NS
Fe	%	2.4	2.3	1.0	0.16	NS	1.37	NS	0.64	*
K	%	1.5	1.4	1.0	0.25	NS	3.32	NS	0.05	NS
Li	mg/kg	16	19	0.9	–0.60	NS	1.79	NS	–0.31	NS
Mg	%	0.41	0.46	0.9	–0.35	NS	1.13	NS	–0.38	NS
Mn	mg/kg	580	550	1.1	0.52	NS	1.38	NS	0.60	*
Na	%	1.1	1.1	1.0	0.19	NS	2.32	NS	0.59	NS
Ni	mg/kg	29	25	1.2	1.62	NS	1.02	NS	–0.09	NS
P	%	0.11	0.081	1.4	2.18	*	3.34	*	0.64	NS
Pb	mg/kg	27	23	1.1	0.34	NS	1.43	NS	0.27	NS
Sr	mg/kg	95	110	0.9	–0.38	NS	1.81	NS	–0.07	NS
V	mg/kg	80	76	1.1	0.56	NS	1.03	NS	0.40	*
Zn	mg/kg	130	110	1.2	0.80	NS	1.36	NS	0.71	NS

FO(T/B) – enrichment factor: ratio of the contents in topsoil and bottom soil; Sign – significant at $p < 0.01$, R(T/B) – ratio between the results for topsoil and bottom soil; NS – the difference is not significant; * – the difference is significant

Table 5

Matrix of correlation coefficients for the analyzed elements in the sediment and alluvial soil samples from the Crna Reka river basin

	Al	As	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	Sr	V	Zn
Al	1.00																	
As	0.59	1.00																
Ba	0.83	0.52	1.00															
Ca	0.45	0.42	0.53	1.00														
Cr	0.38	0.69	0.31	0.01	1.00													
Cu	0.02	–0.29	0.00	–0.49	0.05	1.00												
Fe	0.48	0.26	0.33	–0.32	0.53	0.52	1.00											
K	0.52	0.29	0.59	0.00	0.21	0.15	0.39	1.00										
Li	0.53	0.16	0.68	0.34	0.12	0.06	0.34	0.40	1.00									
Mg	0.74	0.60	0.83	0.70	0.44	–0.16	0.22	0.22	0.63	1.00								
Mn	0.80	0.60	0.58	0.14	0.64	0.14	0.74	0.52	0.41	0.56	1.00							
Na	0.48	–0.12	0.36	0.05	–0.09	0.24	0.25	0.37	0.16	0.20	0.38	1.00						
Ni	0.33	0.81	0.27	0.21	0.88	–0.21	0.29	0.16	0.07	0.44	0.53	–0.29	1.00					
P	0.26	0.01	0.11	–0.15	–0.07	0.33	0.18	0.44	–0.13	–0.11	0.23	0.35	–0.16	1.00				
Pb	0.09	0.40	0.15	0.00	0.31	0.12	0.15	0.23	–0.07	0.02	0.18	–0.05	0.36	0.30	1.00			
Sr	0.79	0.64	0.81	0.81	0.36	–0.32	0.04	0.36	0.46	0.85	0.54	0.30	0.44	0.07	0.13	1.00		
V	0.03	–0.09	–0.12	–0.65	0.30	0.59	0.80	0.19	0.09	–0.24	0.39	0.13	0.07	0.12	0.06	–0.40	1.00	
Zn	0.17	–0.28	0.21	–0.20	–0.16	0.67	0.35	0.27	0.16	0.00	0.14	0.39	–0.30	0.55	0.29	–0.07	0.28	1.00

From the multivariate factor analysis of the contents of chemical elements in all sediment and soil samples, load factor matrix was obtained (Table 6). The factor analysis separates five factors from which factor 1 (F1) has the highest load value (4.17) and variability of 24.5% of the total variability of 85.1%. This factor binds the following elements: Mg, Ba, Li, Sr, Al and Ca. The highest loading value in this geochemical association of the elements was obtained for Mg (0.89) and the lowest for Ca (0.69).

Factor 2 (F2) has a load value of 3.11 and a variability of 18.3%, and links the following elements: V, Fe, and Cu. The highest loading value in the second geochemical association was obtained for V (0.92) and the lowest for Cu (0.74).

The third factor (F3) represents 20.1% of the total variance of the matrix with a load value of 3.42 and links the elements Ni, Cr and As. The highest loading value in the third geochemical association is for Ni (0.94) and the lowest for As (0.86).

Table 6

Factor analysis

	F1	F2	F3	F4	F5	Comm
Mg	**0.89**	–0.14	0.32	–0.03	0.05	91.6
Ba	**0.85**	–0.02	0.21	0.10	0.35	90.4
Li	**0.85**	0.23	–0.07	–0.06	–0.03	78.6
Sr	**0.74**	–0.40	0.37	0.01	0.32	94.9
Al	**0.70**	0.06	0.32	–0.01	0.54	88.6
Ca	**0.69**	–0.57	0.11	0.00	–0.02	88.1
V	–0.16	**0.92**	0.12	–0.04	0.10	90.0
Fe	0.25	**0.83**	0.32	0.03	0.24	90.9
Cu	0.00	**0.74**	–0.26	0.41	0.09	78.8
Ni	0.16	0.02	**0.94**	0.05	–0.13	92.8
Cr	0.18	0.30	**0.87**	0.01	–0.01	87.6
As	0.33	–0.17	**0.86**	0.08	0.13	90.1
Pb	–0.06	–0.02	0.42	**0.80**	0.05	81.4
Zn	0.18	0.41	–0.41	**0.66**	0.28	88.3
Na	0.25	0.13	–0.28	–0.07	**0.75**	72.2
P	–0.16	0.05	–0.08	0.51	**0.71**	79.9
K	0.28	0.19	0.19	0.13	**0.67**	61.7
Prp.Totl (%)	24.5	18.3	20.1	9.1	13.0	85.1
Expl.Var	4.17	3.11	3.42	1.55	2.21	
EigenVal	5.78	3.71	2.56	1.52	0.89	

F – load factors values; F1, F2, F3, F4 and F5 – load factors values for each appropriate factor 1, 2, 3, 4 and 5; Comm – communality (%); Prp.Totl – total variance of the system; EigenVal – Eingene values; Expl.Var – variance of the special component

The fourth factor (F4) represents 9.1% of the total variance of the matrix with a load value of 1.55 and links the Pb and Zn. Higher load values in the fourth geochemical association has Pb (0.80) and lower Zn (0.66).

Due to the size of the river basin and in order to see any differences between the contents of the elements in the sediment samples in individual parts of the investigated area, the following sections have been divided: values for the samples taken from Pelagonia Valley (Pelagonija) with 8 samples, Mariovo with 5 samples, Tikveš Lake with 3 samples, lower flow of Crna Reka river (Lower flow) with 7 samples and samples taken from the Majdanska and Blašnica rivers (Majdan R.) with 8 samples.

From Figure 4a it can be seen that a high factor value of factor 1 (Mg, Ba, Li, Sr, Al and Ca) was observed for river sediments and soils in the Pelagonia Valley, higher in the lower part of the Crna Reka after the Tikveš Lake dam, and the highest in the catchment area of the Blašnica and Majdanska rivers. The lowest factor value for factor 1 was recorded in the Mariovo part of the study area.

The geochemical association F2 (V, Fe and Cu) is the most present in the Pelagonia part of the investigated area, while in the watershed of the Blašnica and Majdanska rivers and Mariovo region it has almost equal distribution (Figure 4a). The smallest presence of F2 geochemical association is found in the Tikveš Lake region and the lower course of Crna Reka after the dam of Tikveš Lake.

The third geochemical association F3 (Ni, Cr and As) has the highest factor values in the sediments of the Majdanska Reka and Blašnica rivers and in the lower course of Crna Reka (Figure 4a). It can be noticed that the presence of the content of these elements linearly increases starting from the Pelagonia region where it has the smallest presence along the Tikveš Lake dam.

The highest factor values of the F4 geochemical association (Pb and Zn) are found in the Pelagonia region, in the part of Prilep, while similar factor values are found in the Mariovo area and in the lower course of Crna Reka after the dam of Tikveš Lake. The lowest factor value is noticed in the part of Lake Tikveš (Fgure 4b).

The fifth and last geochemical association (Na, P and K) has the highest factor value with factor 5 in the Blašnica river area, but it is important to note that it is slightly smaller in the other parts of the Pelagonia region, Tikveš Lake and the lower part of Crna Reka, except in the Mariovo region where it has the smallest values (Figure 4b).

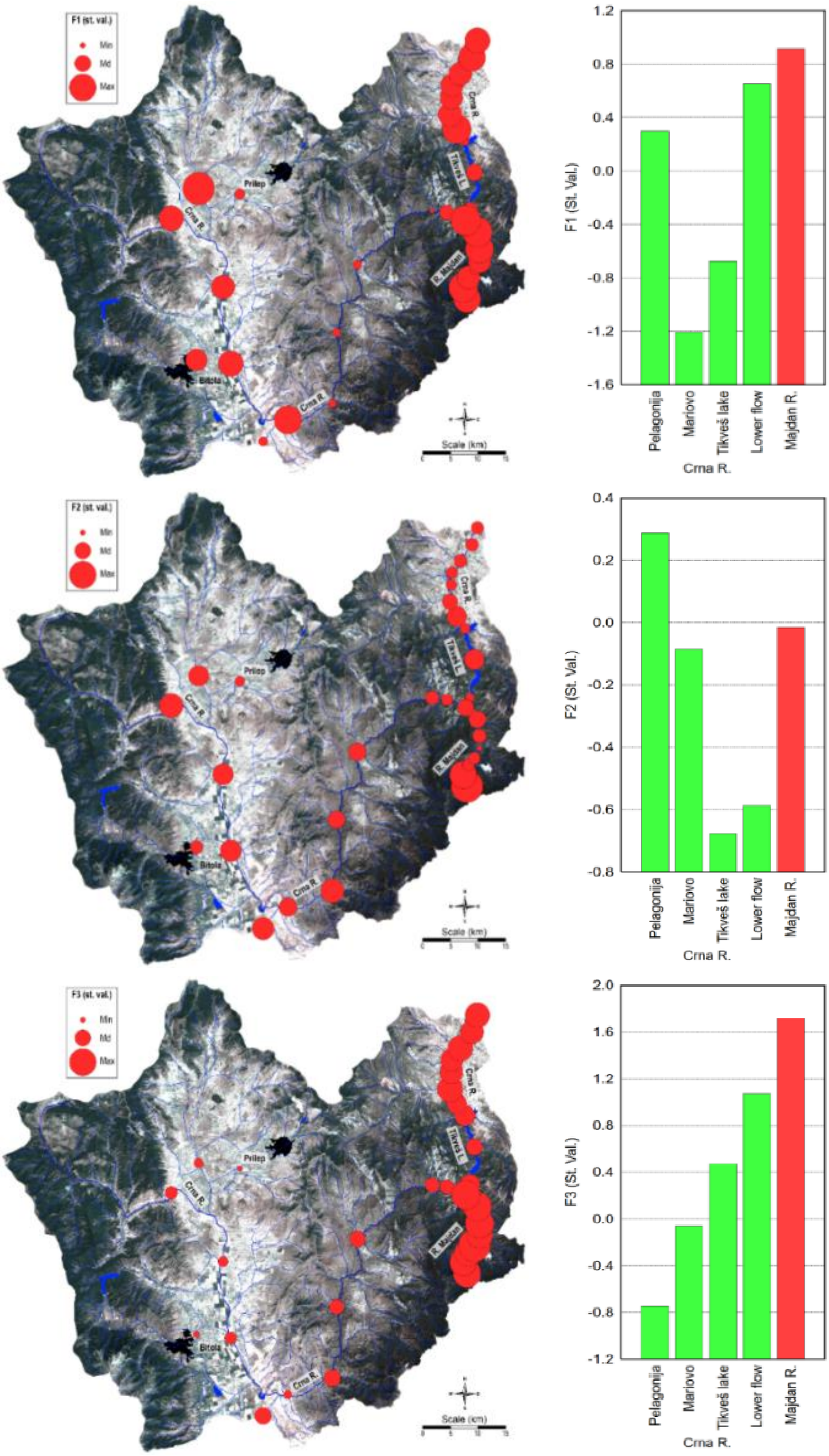

Fig. 4a. Spatial distribution of factor scores and factor standard values by region of factor 1 (Mg, Ba, Li, Sr, Al and Ca), factor 2 (V, Fe and Cu) and factor 3 (Ni, Cr and As),

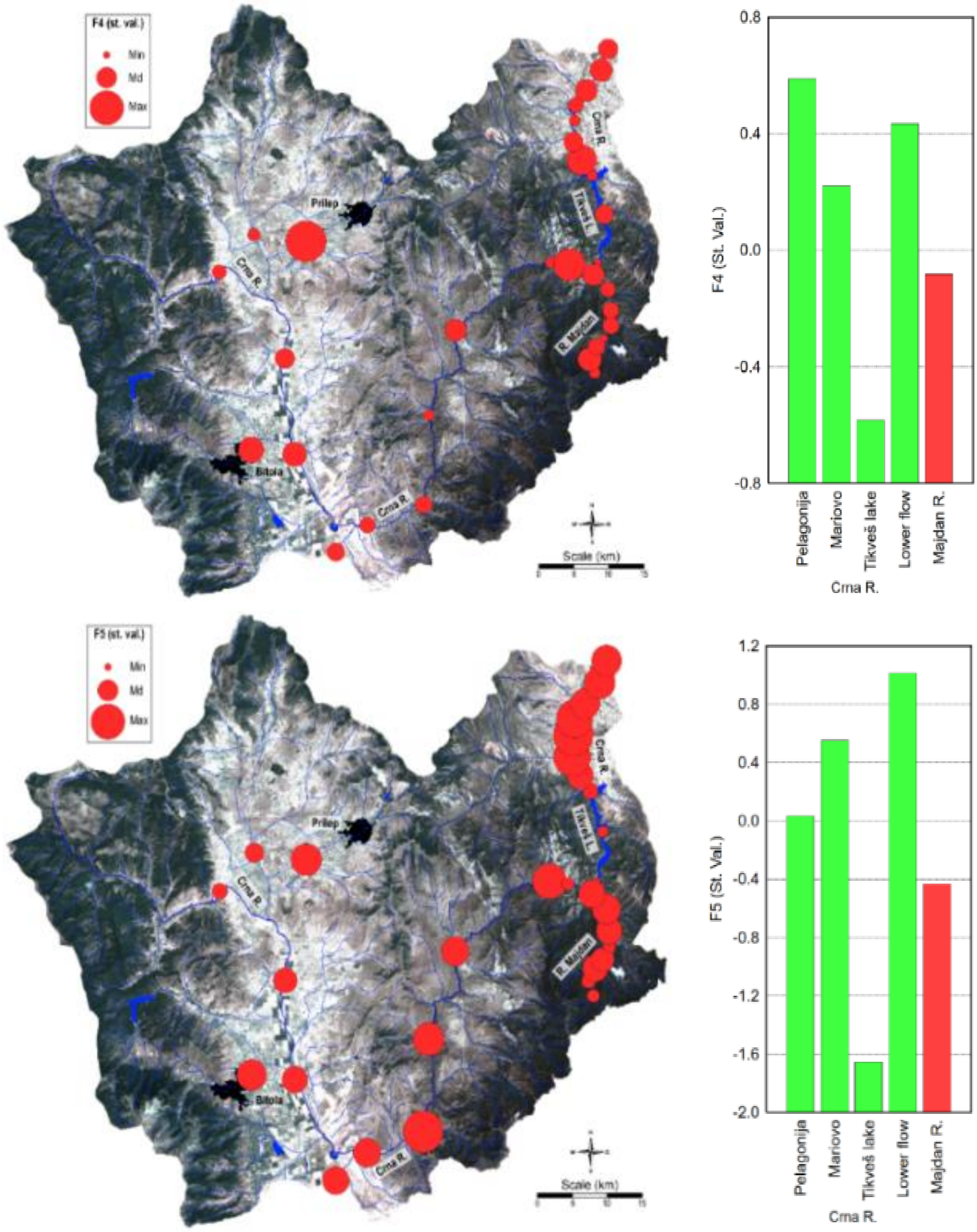

Fig. 4b. Spatial distribution of factor scores and factor standard values by region of factor 4 (Pb and Zn) and factor 5 (Na, P and K)

Due to the minimal and insignificant difference in the distribution of elements in the sediments and surface soils, as well as between the topsoils and bottom soils, in the preparation of spatial distribution maps and histograms with mean values divided by regions, only the values determined for the elements in sediments samples are considered. Since the Republic of North Macedonia does not have regulation on the restrictions on the presence of potentially tox elements in sediments and soil, the obtained results in this study are compared with the limits given in Dutch standards (http://www.contaminatedland.co.uk/std-guid/dutch-l.htm).

The spatial distribution maps and the histograms with the average contents by regions of the elements from the F1 association are given in Figure 5. This association includes Mg, Ba, Li, Sr, Al and Ca. The content of Mg in the sediments of the Crna Reka river basin (with the exception Majdanska Reka and Blašnica rivers) ranges from 0.043% to 1.1% (Table 1, Figure 5a). Magnesium has relatively high environmental mobility.

The highest Mg content was obtained in the Blašnica watershed of 2.1% due to the natural presence of Mg on the Kožuf Mountain, as well as the presence of magnesium in the ore from the Ržanovo mine (Janković et al., 1997; Boev et al., 2009; Serafimovski et al., 2012, 2013; Stafilov & Šajn, 2016).

Barium content in sediment samples in the Crna Reka river basin ranges from 31 to 580 mg/kg. Figure 5a shows the spatial distribution of Ba in sediment samples and the average values per regions, respectively. In all samples of sediments of the lower river course of Crna Reka, the contents of Ba are about 500 mg/kg. The highest value for Ba content in sediments throughout the catchment area of Crna Reka, including the rivers of Majdanska Reka and Blašnica, was found in a sample from the Blašnica river (775 mg/kg), which exceeds the action value of 625 mg/kg according to Dutch standards. The increased concentration in these two areas of the Crna Reka river basin is due to high content of Ba in the Neogene magmatic rocks that are highly represented in the Kožuf Mountain and in the lower part of the Vardar zone (Stafilov & Šajn, 2016). The lower Ba content in the sediment samples was determined in the sediments from Mariovo and Tikveš Lake.

The content of Li in the sediments ranges from 4.6 mg/kg to 35 mg/kg (Table 1, Figure 5a). The highest Li content was found in the Kožuf Mountain region, in the lower course of Crna Reka, as well as in the Pelagonia and Mariovo areas, which is a result of lithogenic origin of Li in these regions (Stafilov & Šajn, 2016).

The content of strontium in the sediment samples of the Crna Reka river basin (excluding sediments from the Majdanska Reka and Blašnica rivers) ranges from 21 mg/kg to 560 mg/kg (Figure 5b). The highest content of Sr is found in the river sediments from the Blašnica river (729 mg/kg), and the lowest content is in the sample from the Jelaška river tributary from the Pelagonia region (21 mg/kg). The presence of Sr in the sediment samples corresponds to its presence in the soils (Stafilov & Šajn, 2016).

The spatial distribution of Al content in soil samples from the investigated area ranges from 0.34% to 4.63%. In the samples of river sediment from the river of Crna Reka without the rivers of Blašnica and Majdanska Reka, the Al content ranges from 0.13 to 6.4%. The highest Al content (6.4%) was obtained in the sample of river sediment from Crna Reka after the dam of Tikveš Lake. From Figure 5b it can be noted that the sediments of the watershed of the rivers of Majdanska Reka and Blašnica are rich in Al which is a result of the natural presence of Al in Mesozoic carbonate rocks in that area, but also as a result of mining activities of the ferronickelous mine "Ržanovo" (Janković et al., 1997; Boev et al., 2009; Serafimovski et al., 2012, 2013). Aluminium content in sediments declines in samples from Lake Tikveš, again being significantly higher in the Crna Reka river basin after the lake dam. The high Al content in this part is due to the depositions of the Crna Reka originating from the river of Blašnica in the period before the dam construction of Lake Tikveš and this confirms very low content of Al in the sediment samples of Lake Tikveš.

The Ca content in the sediments of the Crna Reka river basin, excluding the samples from the rivers of Majdanska Reka and Blašnica, ranges from 0.20% to 5.5% (Table 1, Figure 5b). However, the highest Ca content of 12% was determined in the samples of the Blašnica watershed, as well as in the samples from the Crna Reka river at the lower course after the dam of the lake. The lowest Ca content was determined in a sample taken near the village of Skočivir. This distribution of Ca content in the sediments is according to its distribution in the soil from this river basin (Stafilov & Šajn, 2016).

The second geochemical association includes V, Fe and Cu and their spatial distributions and average contents by regions are given in Figure 6. The content of V ranges from 36 mg/kg to 110 mg/kg. The highest determined vanadium content in a river sediment sample is 147 mg/kg in a sample of the river of Majdanska in its upper course as a result of former mining activities in the Allchar mine region (Figure 6). By region the mean value for vanadium is the highest in the Mariovo region (86 mg/kg).

Iron along with copper and vanadium belong to the third geochemical association. Iron content in the samples of the Crna Reka river without the Blašnica watershed is in the range of 0.90% to 3.4%. The highest content is 4.6% in the sediment sample from the Blašnica watershed in its upper flow around the mines. The generally higher values of Fe content in the sediments of the Blašnica river and lower course of Crna Reka are the result of anthropogenic activities in the vicinity of the Kožuf mines as well as the enrichment of the lower course of the river by the waste waters from the ferronickel smelter plant near the village of Vozarci. The spatial distribution map for the Fe content in the river sediments (Figure 6) shows that the Fe content is within the average values for the basin (2.5%).

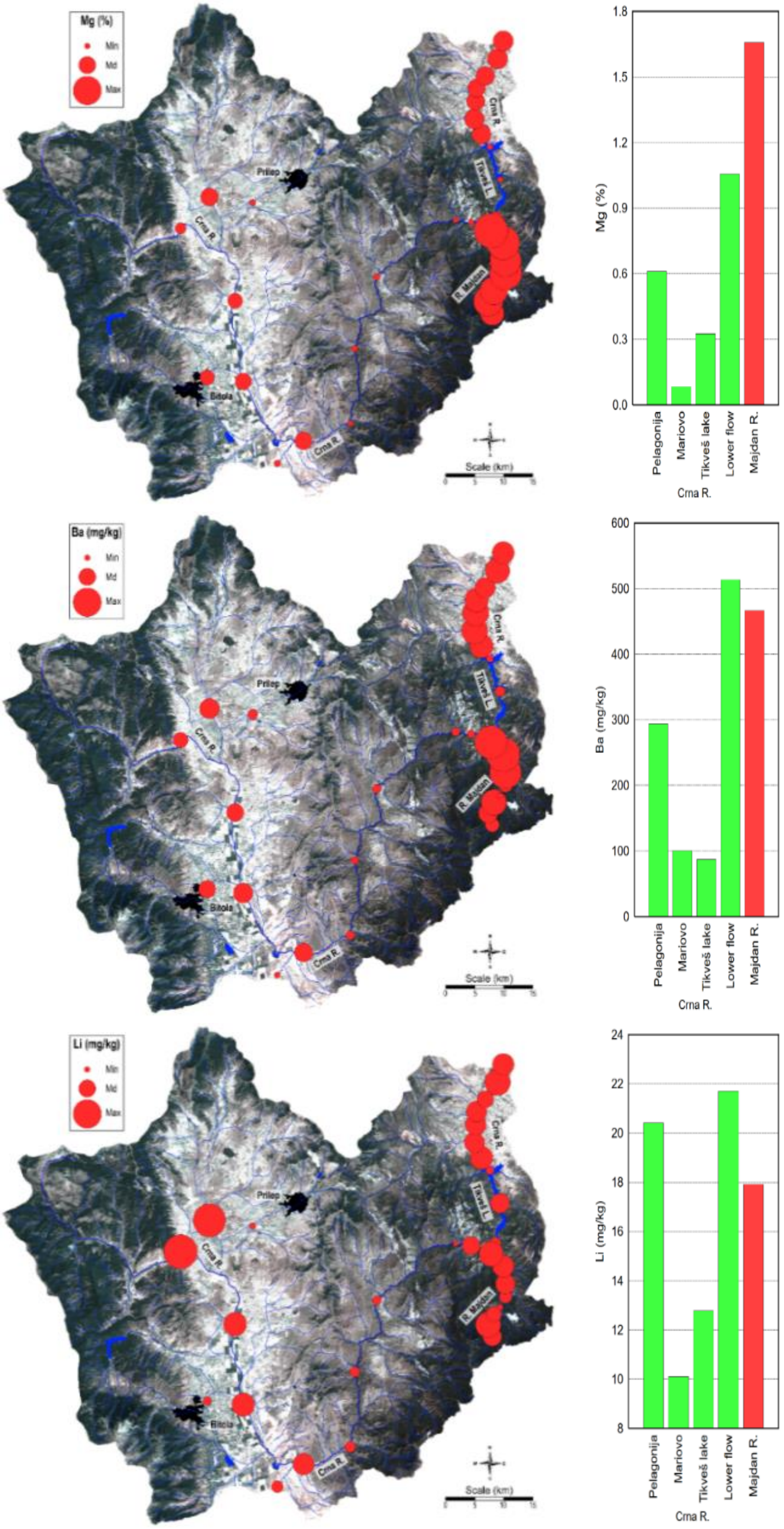

Fig. 5a. Spatial distribution and average contents by regions of the elements from F1 association (Mg, Ba and Li)

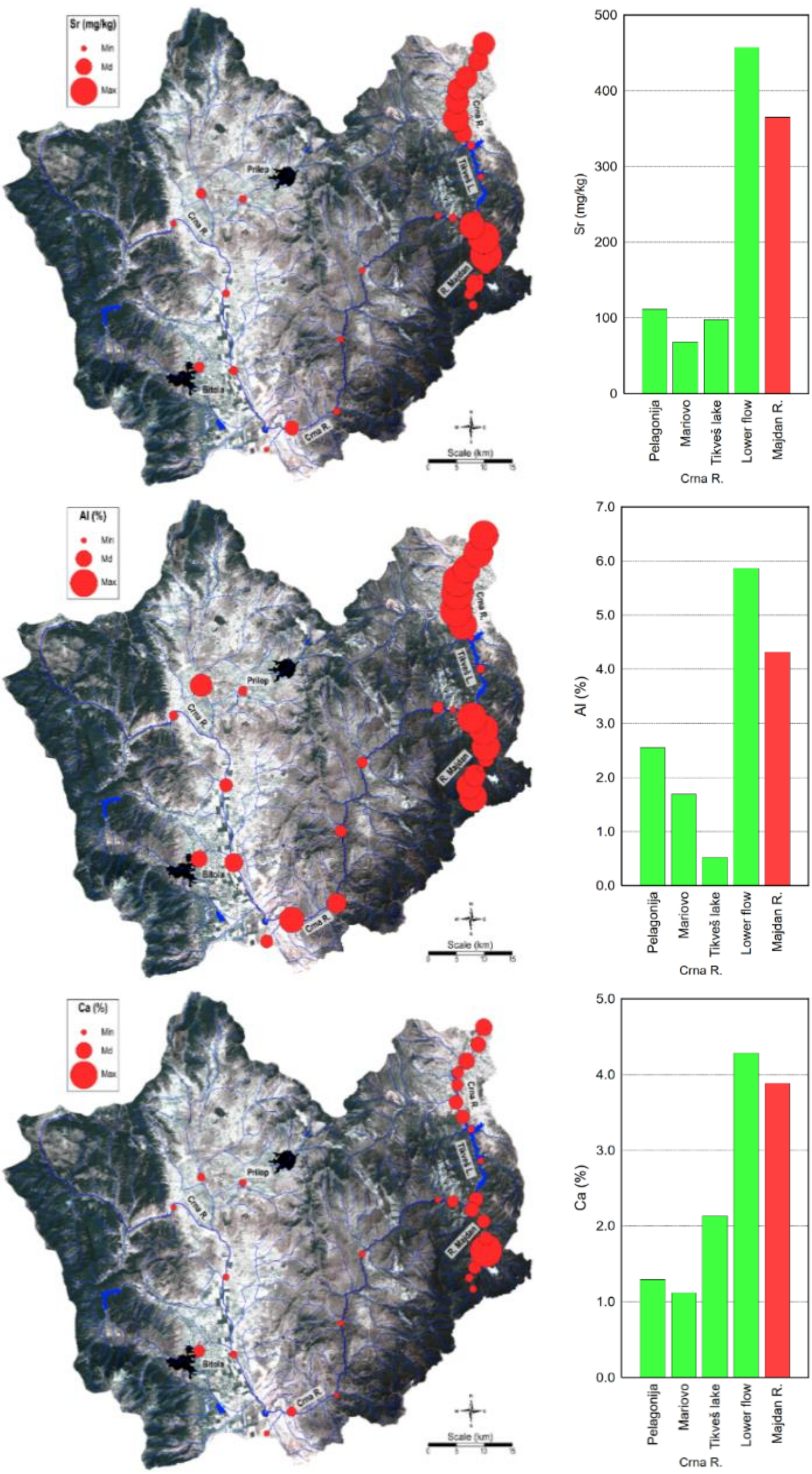

Fig. 5b. Spatial distribution and average contents by regions of the elements from F1 association (Sr, Al and Ca)

The Cu content in the sediments of the Crna Reka river basin (without the Blašnica river) ranges from 16 mg/kg to 290 mg/kg (Table 1). The lowest values are determined in the sediments from the lower course of Crna Reka (average of 24 mg/kg). From the spatial distribution map of Cu content (Figure 6) it can be seen that generally higher values for Cu are present sediments from the Pelagonia region, especially those samples collected from the rivers in the urban areas, i.e. in the vicinity of Bitola and Prilep, which is due to the anthropogenic sources of Cu from the municipal and industrial waste, dust, various copper chemicals, agricultural drainage waters and others.

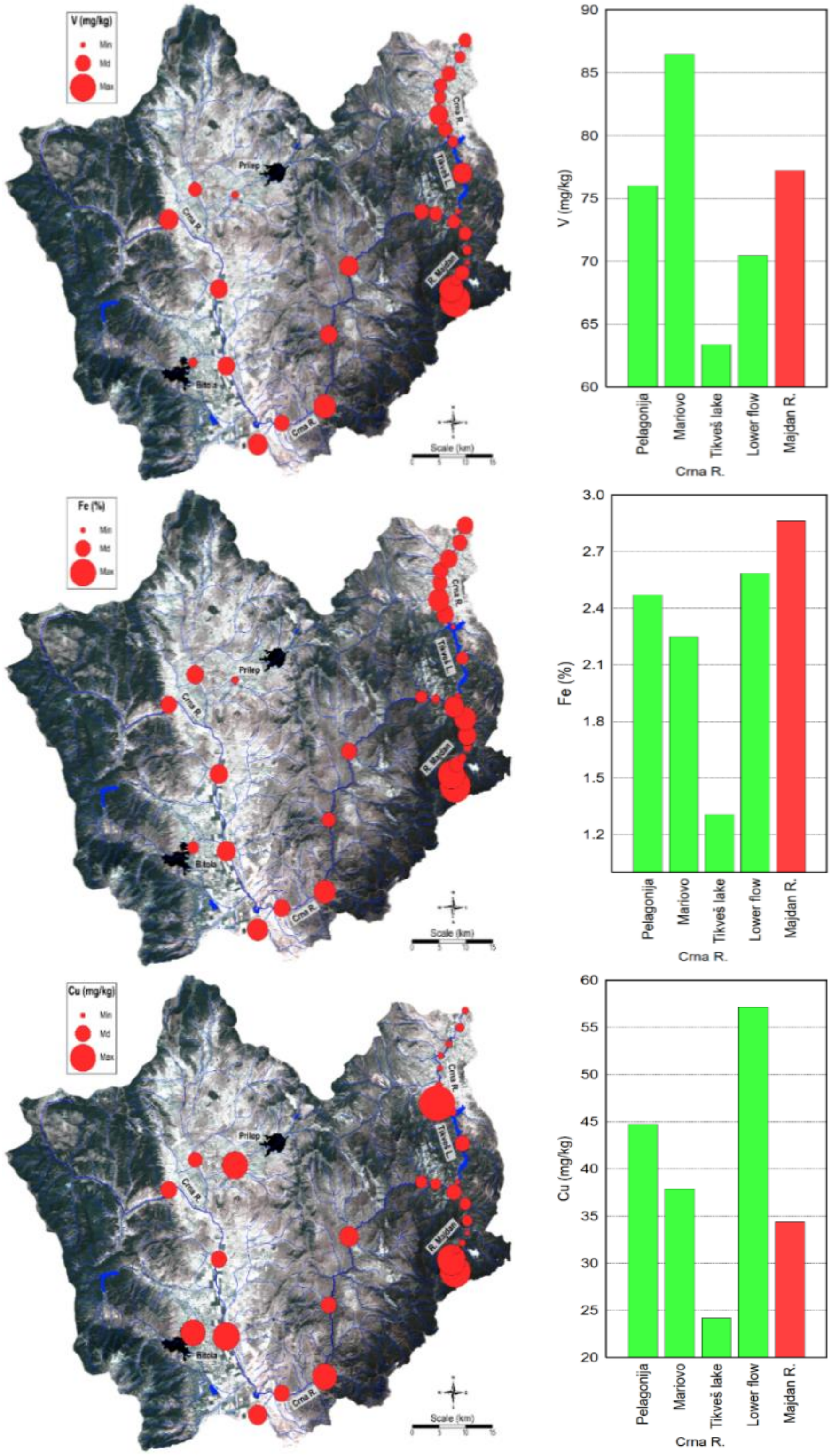

Fig. 6. Spatial distribution and average contents by regions of the elements from F2 association (V, Fe and Cu)

The third geochemical association (F3) includes Ni, Cr and As and their spatial distributions and average contents by regions are given in Figure 7. The spatial distribution of Ni in the river sediments shows very low Ni content in the river sediments along the Crna Reka river basin in the regions of Pelagonia and Mariovo and those from the coast of Tikveš Lake (Figure 7).

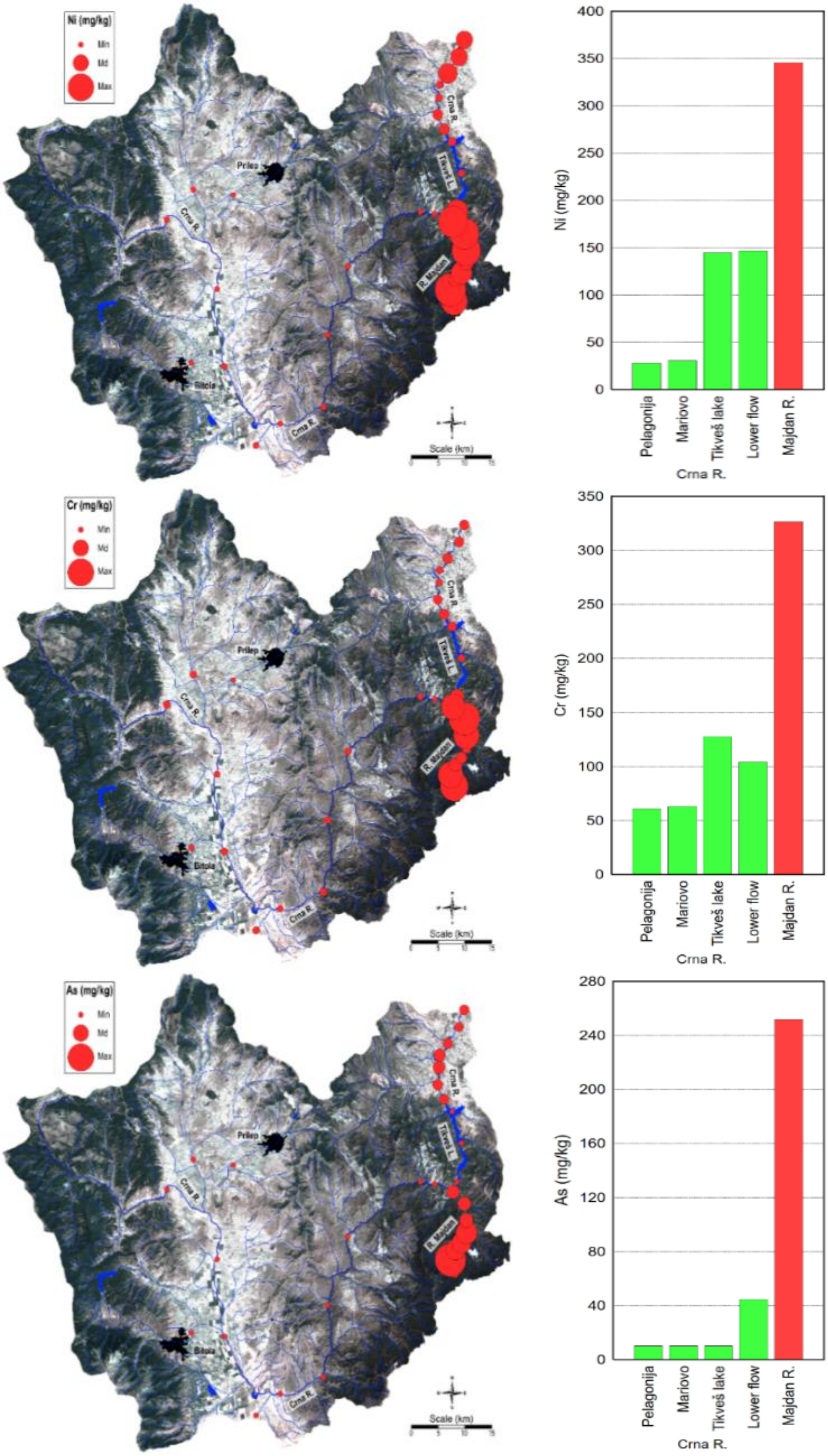

Fig. 7. Spatial distribution and average contents by regions of the elements from F3 association (Ni, Cr and As)

The content of Ni in the sediments of the rivers of Majdanska Reka and Blašnica is very high with an average of 340 mg/kg and maximal value of 459 mg/kg, which is over the action value according to the Dutch standards (210 mg/kg). The high Ni content in the river sediments from this part of the watershed is a result of the enriched soils of this element as well as of the mines in the Ržanovo mine during the excavation of ferro-nickel ore for the needs of the ferronickel smelter near Kavadarci (Janković et al., 1997; Boev et al., 2009; Serafimovski et al., 2012, 2013; Stafilov et al., 2010; Stafilov & Šajn, 2016) (Figure 7).

From the spatial distribution map of Cr content (Figure 7) it is seen that the highest presence of Cr is in the sediment samples from the Majdanska Reka and Blašnica rivers with the average content of 380 mg/kg, which is the same as the action value of the Dutch standards. The Cr content from the other regions in the Crna Reka river basin, the other catchment area of Crna Reka, is in the range of 35 to 200 mg/kg. The increased presence of Cr in the sediments of the Kožuf Mountain is result of lithogenic origin and anthropogenic mining activities in this area during the excavation of ore from the nickel mine 'Ržanovo' due to high Cr content in the ore (Boev & Janković, 1996; Janković et al., 1997; Boev et al., 2009; Serafimovski et al., 2012, 2013).

Arsenic is charterized with significant enrichment in the sediments from the Majdanska and Blašnica rivers, as well as in samples from the lower course of Crna Reka after the Tikveš Lake dam. In Figure 7 is clearly shown the difference in the contents of As in the sediment samples from the other regions of the river basin, where content is below the detection limit (10 mg/kg). The highest values of As content in the whole river basin without the Blašnica watershed were obtained in a sample of sediment from the lower stream of Crna Reka (73 mg/kg), while in some of the sediment samples from the Majdanska Reka river its content is extremely high (up to 839 mg/kg). The presence of As in sediment in this area is result of former anthropogenic mining activities at the Allchar mine (Janković et al., 1997; Boev; 2001–2002; Bačeva et al., 2014). The high As content in the lower Crna Reka is result of the same sedimentation activities from the preconstruction period of the Tikveš Lake dam (Stafilov et al., 2013; Bačeva et al., 2014). The As values obtained in these two areas significantly exceed the target (29 mg/kg) and action (55 mg/kg) values according to Dutch standards.

The fourth geochemical association (F4) includes Pb and Zn and their spatial distributions and average contents by regions are given in Figure 8. The content of Pb in the samples of river sediments in the study area is in the range of 5.6 mg/kg to 110 mg/kg and its spatial distribution is shown in Figures 8. In all the sediment samples from the Pelagonia region the Pb content is very low with the exception of the sediments from the river of Prilepska Reka where the content of Pb was the highest from the whole basin (110 mg/kg) due to pollution by the waste waters from the city of Prilep.

From the map of spatial distribution of zinc (Figure 8) it can be clearly observed that the highest values of zinc content in the sediment samples are determined in the samples from the urban areas, such as the Dragor river passing through the city of Bitola and Prilepska Reka collecting waste waters from the city of Prilep (280 mg/kg). The high zinc values in the samples from these two sites are result of urban anthropogenic activities – zinc and its compounds are widely used in the manufacture of noncorroded protective coatings, automotive batteries, alloys such as bronze, colors etc., as well as the waste waters from the industries present in these cities (Stafilov et al., 2018). Due to high zinc content in the sediments from the Pelagonia region (average of 155 mg/kg), Zn exceeds the optimal value according to Dutch standards of 140 mg/kg.

The fifth geochemical association (F5) includes Na, P and K and their spatial distributions and average contents by regions are given in Figure 9. The sodium content in the sediments of the investigated area ranges from 0.22% to 1.7%. The highest Na content in the basin (without Majdanska Reka and lower course of Crna Reka) was registered in Pelagonia of 1.7% (average value of 1.15%). In the sediments from the Mariovo region high Na values were also found (average of 0.9%), which corresponds to the natural presence of this element in these areas. High values of Na content are also found in the sediments from the lower course of Crna Reka (mean value of 1.12%).

The mean value of phosphorus content in the sediments from the whole river basin is 0.1%. The highest P content of 0.2% was found in a sample from the Prilepska river near village of Kadino. In general, high content of P was found in almost all sediment samples from the agricultural area of Pelagonia (average content of 0.12%), Mariovo (average of 0.125% and lower course of Crna Reka (0.13%) (Figure 9). This clearly indicates pollution of river sediments by the use of phosphate fertilizers in agriculture and the emission of phosphates by urban and industrial waste waters.

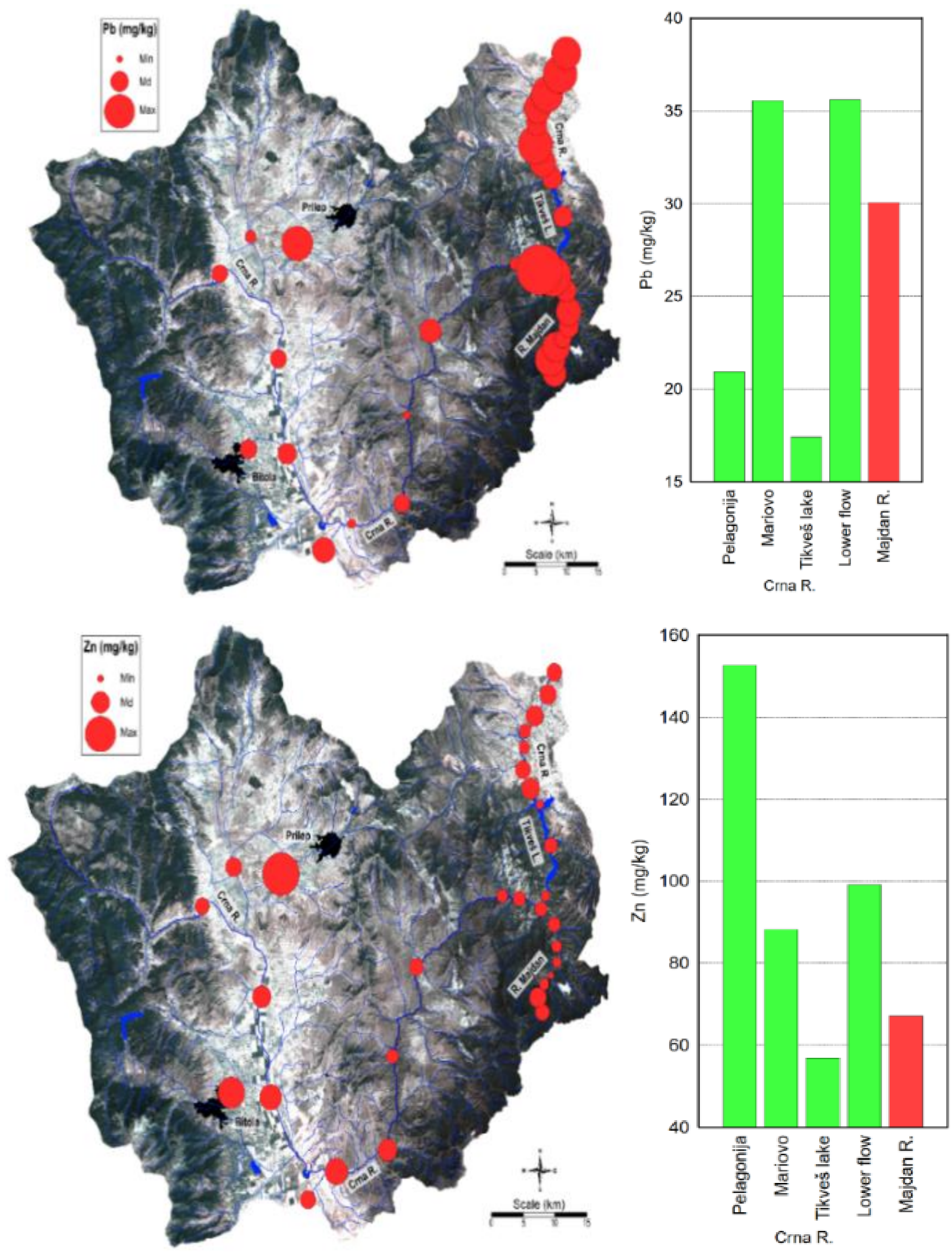

Fig. 8. Spatial distribution and average contents by regions of the elements from F4 association (Pb and Zn)

The spatial distribution of K content in the river sediments from the investigated area is almost uniform throughout the area, with values from 1% to 2%, with exception the sediments from the shore of Tikveš Lake where the lowest value of 0.44% is detected (Table 1, Figure 9). Potassium is naturally found in soils and sediment, but it is also widely used in agriculture as fertilizer and therefore the K content in sediments throughout the Crna Reka river basin is high.

Manganese doesn't correlate with the other elements and therefore it is not included into the factor associations. The spatial distribution of Mn in sediments in the investigated area is given in Figure 10. The highest content of Mn is determined in a sediment sample from the river of Blašnica (1300 mg/kg), while the highest average value was found in the sediments from the lower course of Crna Reka (1000 mg/kg). The determined Mn contents in the sediment samples throughout the catchment area followed the presence of this element in the soils of the corresponding regions (Stafilov & Šajn, 2016). Manganese in urban waters can precipitate depending on the conditions in the environment and pass into urban sediments.

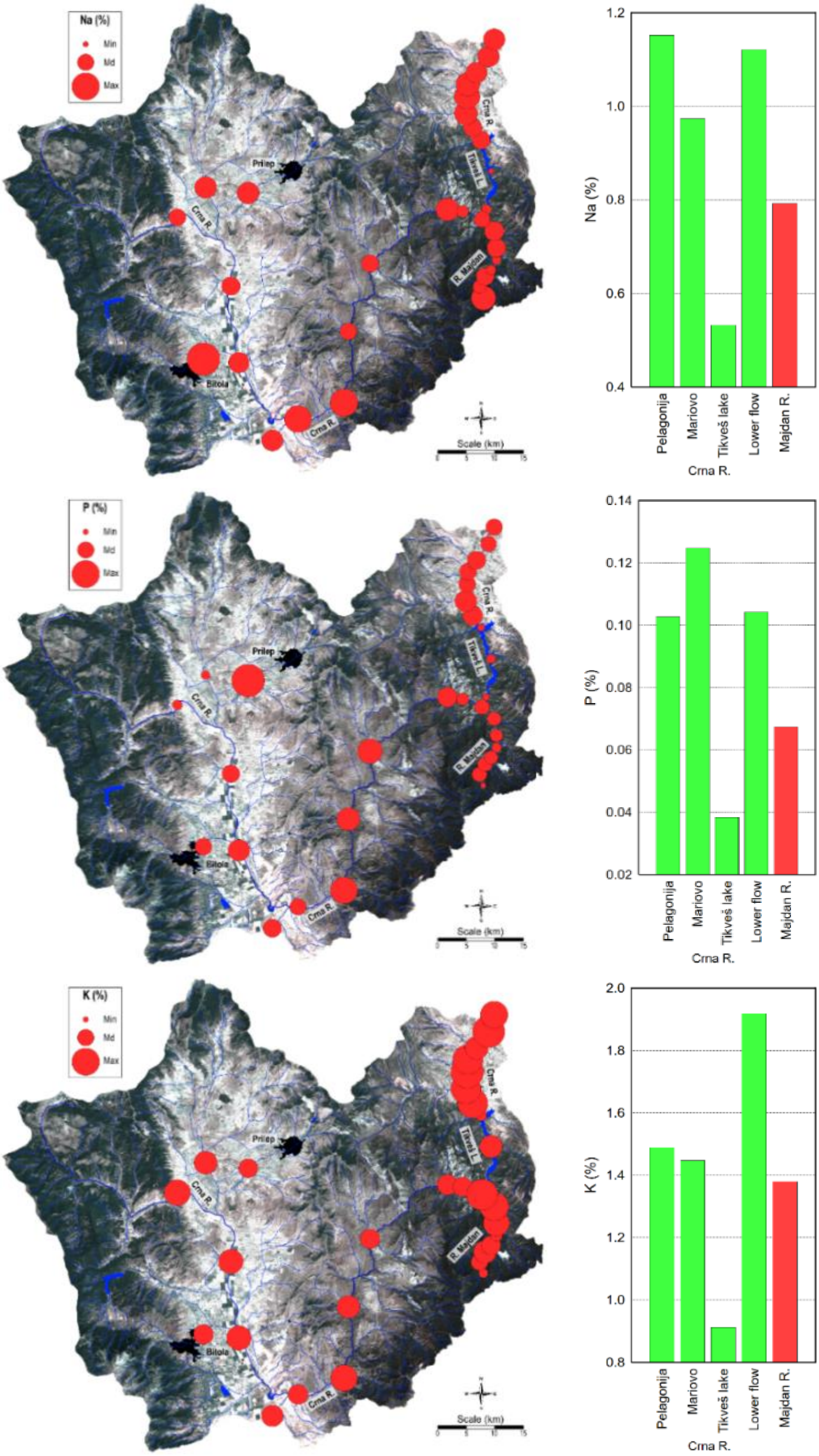

Fig. 9. Spatial distribution and average contents by regions of the elements from F5 association (Na, P and K)

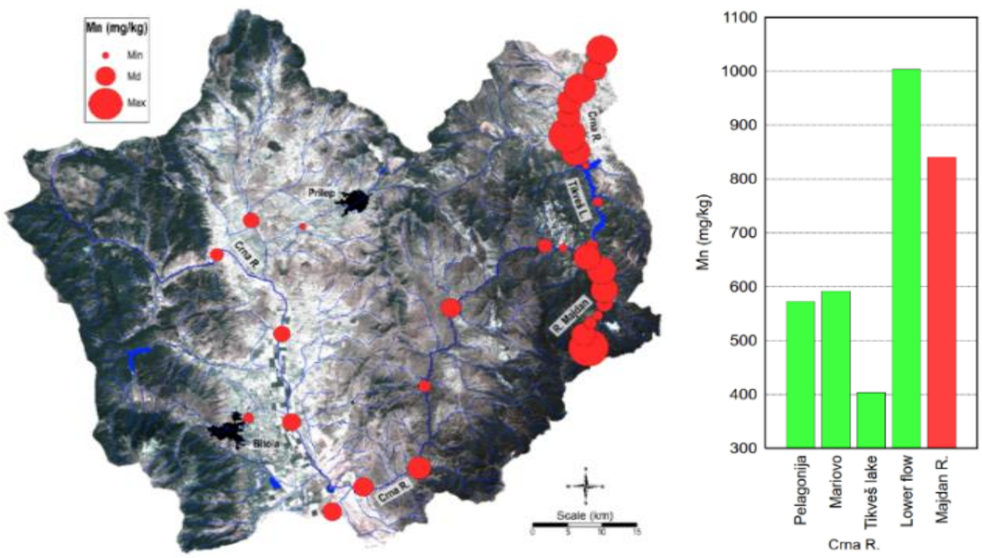

Fig. 10. Spatial distribution and average contents by regions of Mn

CONCLUSION

In this study the data summary for the contents of 23 elements (Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V, Zn) in sediment and soil samples from the Crna Reka river basin are presented. All data obtained were statistically processed and a descriptive statistical analysis of the values for the contents of the elements was performed. The maps of spatial distribution of elements and histograms with the mean concentrations of the elements analyzed by regions were also prepared. The obtained results show that the contents of investigated elements follow the lithology of the region. However, higher contents of some elements (As, Ni, Co and Cr) were found in the sediment samples from the rivers of Majdanska Reka and Blašnica (the Kožuf Mountain region), which is additionally a result of former anthropogenic mining activities at the abounded Allchar mine and continuous mining activities of nickel mine Ržanovo, as well as a result of the waste water pollution from the ferronickel smelter plant near the city of Kavadarci.

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Р е з и м е

ДИСТРИБУЦИЈА НА ХЕМИСКИ ЕЛЕМЕНТИ ВО СЕДИМЕНТИТЕ И АЛУВИЈАЛНИТЕ ПОЧВИ ОД СЛИВОТ НА ЦРНА РЕКА

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Клучни зборови: Црна Река; Република Северна Македонија; речен слив; седименти, почви; тешки метали; дистрибуција

Извршено е истражување на дистрибуцијата на 23 хемиски елементи (Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V и Zn) во примероци седименти и алувијални почви од сливот на Црна Река.

Вкупно се земени 31 примерок вода и 31 примероци почва, од кои 13 примероци се земени во делот од изворот на Црна Река до нејзиниот влив во Тиквешкото Езеро, од кои 9 примероци од Црна Река и 4 примероци од нејзините главни притоки во Пелагониската Котлина (Блато, Прилепска Река, Драгор и Јелашка Река). Исто така се земени примероци од 3 локации на Тиквешко Езеро, 8 локации од Мајданска Река и реката Блашница пред нејзиниот влив во Тиквешко Езеро, како и од 7 локации од долниот тек на Црна Река – од браната на Тиквешкото Езеро до вливот во реката Вардар. Определувањето на содржината на испитуваните елементи е извршено со примена на атомската емисиона спектрометрија со индуктивно спрегната плазма (АЕС-ИСП). Сите податоци од анализираните примероци статистички се обработени со примена на софтверот Stat Soft, 11.0, со што е извршена дескриптивна статистичка анализа на вредностите на содржината на сите испитувани елементи. За секој елемент е изработена карта на дистрибуција во испитуваното подрачје, како и хистограми со средните вредности за секој регион. Во матрицата на факторите на оптоварување за елементите во примероците од седиментите и почвата се добиени пет фактори. Во фактор 1 се групирани хемиските елементи Mg, Ba, Li, Sr, Al и Ca. Фактор 2 ги групира хемиските елементи V, Fe, Cu, додека фактор 3 ги групира Ni, Cr и As. Фактор 4 ги групира хемиските елементи Pb и Zn, а фактор 5 Na, P и K. Според матрицата на корелационите коефициенти во примероците на речни седименти и почви во испитуваното подрачје постои силна корелација помеѓу содржината на елементите: Sr-Mg (0,85), Ba-Al (0,83), Mg-Ba (0,83), Ni-As (0,81), Sr-Ba (0,81), Sr-Ca (0,81), V-Fe (0,80), Mn-Al (0,80), Sr-Al (0,79), Mg-Al (0,74), Mn-Fe (0,74) и Mg-Ca (0,70). Добиените резултати покажуваат дека главен извор на антропогено загадување во целото сливно подрачје на Црна Река се реките Блашница и Мајданска Река како резултат на антропогени рударски активности во тој регион.