ПРИЛОЗИ, Одделение за природно-математички и биотехнички науки, МАНУ, том **39**, бр. 1, стр. 31–49 (2018)
CONTRIBUTIONS, Section of Natural, Mathematical and Biotechnical Sciences, MASA, Vol. **39,** No. 1, pp. 31–49 (2018)

Received: September 12, 2017
Accepted: November 3, 2017

ISSN 1857–9027
e-ISSN 1857–9949
UDC: 556.551:504.5(497.775)
DOI: 10.20903/csnmbs.masa.2018.39.1.118

Original scientific paper

DISTRIBUTION OF CHEMICAL ELEMENTS IN SURFACE WATERS FROM THE CRNA RIVER BASIN, REPUBLIC OF MACEDONIA

Dimitri Tomovski[1], Trajče Stafilov[2,3*], Robert Šajn[4], Katerina Bačeva Andonovska[3]

[1]Alkaloid AD, Skopje, Republic of Macedonia
[2]Institute of Chemistry, Faculty of Natural Sciences and Mathematics,
Ss. Cyril and Methodius University, Skopje, Republic of Macedonia
[3]Research Center for Environment and Materials, Macedonian Academy of Sciences and Arts,
1000 Skopje, Republic of Macedonia
[4]Geological Survey of Slovenia, Ljubljana, Slovenia
e-mail: trajcest@pmf.ukim.mk

An investigation of 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 surface water samples from the entire basin of the Crna River, Republic of Macedonia, was carried out. In total 31 water samples were collected, from which 8 samples from the Crna River and 4 samples from four main tributaries of Crna River in the Pelagonia Valley (Blato, Prilepska Reka, Dragor and Jelaška Reka). Also, surface water samples were collected from 3 locations in the Tikveš Lake, 8 locations from the Majdanska River and river of Blašnica before its inflow into the Tikveš Lake and from 7 locations of the lower course of the Crna River after the dam of Tikveš Lake until its inflow into the river of Vardar. Determination of the concentration of the investigated elements was performed by using 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 where the descriptive statistical analysis of the value for the concentration of the elements was performed. The maps of spatial distribution of the concentration for each element and a histograms for the representation of elements with mean values of the concentrations by regions, were also prepared. The obtained results show that the concentration of investigated element are mainly followed the lithology of the region. However, higher concentrations of arsenic were found in the water samples from the river of Blašnica which is a result of anthropogenic influence from the abounded Allchar mine on the Kožuf Mountain. Also, the increased concentrations of nickel were found in the samples from the lower couse of the Crna River after the dam of Tikveš Lake due to the anthropogenic influence from the ferronickel smelter plant Feni Industry, which can influence the quality parameters of surface waters.

Key words: Crna River, Republic of Macedonia, river basin, water, 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 is 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 [1].

Rivers and streams can be defined as dynamic systems that constantly adjust to natural and human-caused changes. Generally, water resources have a direct influence on the quality of life of the people, their health and overall productivity [2, 3]. The increase of the world's population, the rapid development of the industry, the needs for increased crops in agriculture and food technology, as well as the urbanization require increasing quantities of water. In such conditions of increased anthropogenic activities and consumption, the degree of water pollution increases sharply. If the change in the quality and integrity of naturally occurring water, whether it comes from a natural source or from anthropogenic sources, contributes to the unsuitability or danger of use for humans, animals and plants, such water is considered contaminated [4].

About 2% of the territory of the Republic of Macedonia is under water. There are about 35 rivers and 53 natural and artificial lakes. According to the quantities of water resources, Macedonia is an area with satisfactory water resources, but with their uneven distribution. The water pollution in the Republic of Macedonia is connected with the developing industry, agriculture activities, creation of illegal landfills, uncontrolled discharge of sewage waters into rivers contributed to creating contaminated water ecosystems [5, 6]. As a central water ecosystem, river of Vardar's basin which represents the most important and humanly influenced water resource in R. Macedonia, was studied previously [7–11], as well as its tributary the river of Bregalnica [12, 13].

The aim of this work is to shown the status of Crna River which is the largest tributary of the river of Vardar, the main river in the Republic of Macedonia, 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 и Zn) in samples of surface water collected from different locations in the Crna River basin, Republic of Macedonia, and to interpret and correlate there concentrations 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 River (Crna Reka). However, the location of Crna Hole, close to village of Železnec with an altitude of 760 m, is considered as the true spring of Crna River. In its lower stream, the Crna River flows into the artificial Tikveš Lake, and after it flows into the river of Vardar, near the village of Gradsko at an altitude of 129 m (Figure 1). The total length of the river course is 207 km, with a mean slope of 3.1 ‰. The average flow at the stream is 37 m^3/s.

The area of the Crna River basin is an area that extends into two states in the south-western part of the Republic of Macedonia and the northern part of the Republic of Greece. On the territory of the Republic of Macedonia, the Crna River basin extends between 40°51'56" and 41°36'20" north latitude and 20°56'45" and 22°4'58" eastern longitude. 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 Macedonia belongs the largest part of 4870 km^2, while the catchment area in the Republic of Greece is 905 km^2.

In the river basin of Crna River the influences of the Mediterranean, Mediterranean-altered, temperate-continental and mountainous climate are present. The mean annual air temperature ranges from 8.4 ºC to 13.5 ºC over a period of 23 years. The average absolute maximum air temperatures in the Crna River are within the limits of 32 ºC. The absolute minimum air temperature for the same period is within the limits of –15ºC. The amplitudes of the extreme temperatures are quite large and they range from 51.5 ºC to 66.6 ºC [14]. The warmest months for all meteorological stations in the Crna River basin are July and August and the coldest month is January. According to the regions of this basin, in Tikveš Valley the influence of the sub-Mediterranean climate is generally present, in the central part of the basin (Pelagonia Valley) the continental climate is represented, while the influence of the moderate continental climate appears in the upper part of the basin [14, 15].

The Crna 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 to the Vardar zone [16]. 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. 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 River, which belongs to the Vardar zone, covering the areas of the eastern part of Mariovo and part of the Tikveš Valley, the most present are the crystalline schists, granites and granodiorites, flysch sediments, volcanic breccias, limestones, marble dolomites etc. [15, 16].

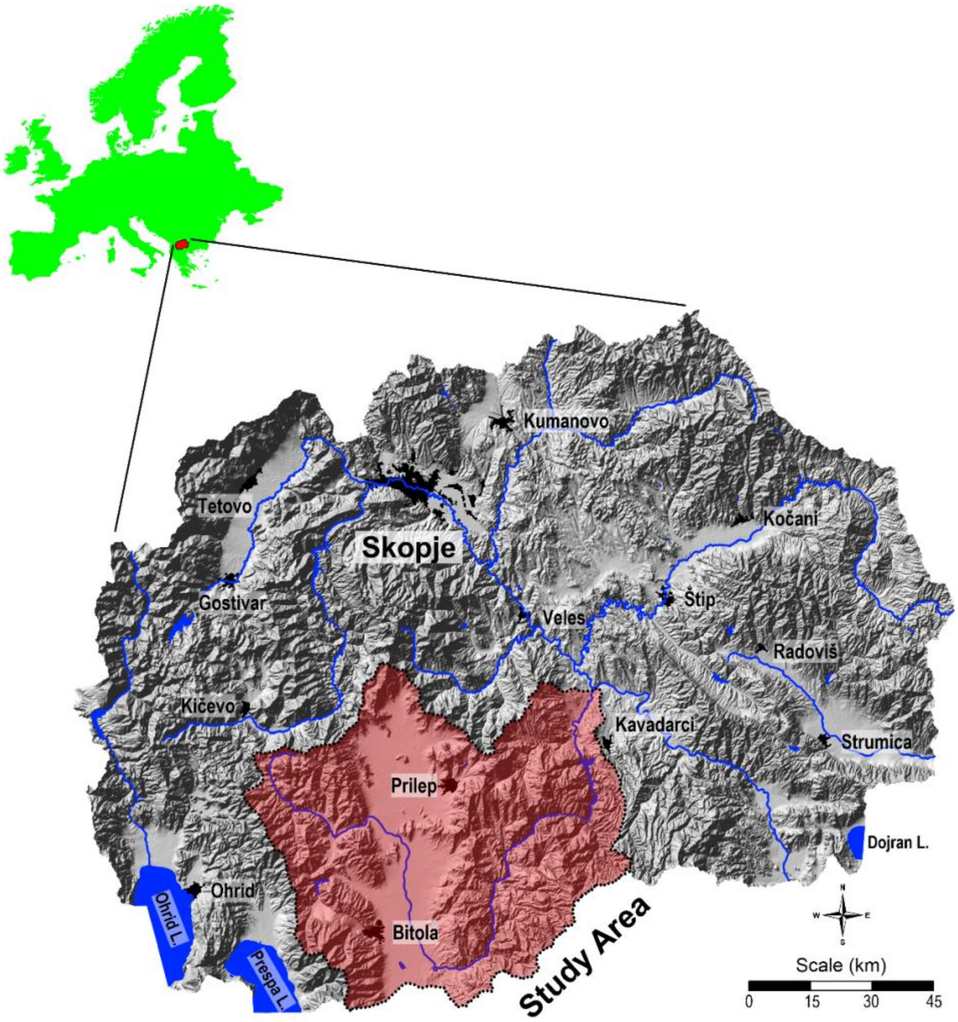

Figure 1. Map of the Republic of Macedonia indicating the Crna River Basin

Sampling

In the period from June to September 2016 year, 31 water samples were collected, from which 13 water samples are collected from the source of Crna River to the estuary in Tikveš Lake, including 8 from the Crna River and 4 from four main tributaries of Crna River in the Pelagonia Valley (Blato, Prilepska Reka, Dragor and Jelaška Reka). Also, surface water samples were collected from 4 locations in the Tikveš Lake, 8 locations of the river Blašnica and its tributary Majdanska River before its inflow into the Tikveš Lake and 7 locations of the lower course of the Crna River after the dam of Tikveš Lake (Figure 2).

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 and each sample was inscribed with the sample mark, sample type and date of sampling. From each location, one sample of water was taken in a purely sterile plastic bottle with a plastic closure. Surface water samples (1 liter each) are prepared immediately upon arrival in the laboratory, filtered through a Whatman membrane filter with a pore sizes < 0.45 μm using vacuum pump (Merck) and acidified with 1 ml of concentrated nitric acid (HNO_3, 69 %, ultra pure). The preserved samples were stored in the refrigerator until analysis. The reagent blank was prepared by filtering MilliQ water through the filter and acidified the sample.

All data for the concentration of the tested elements were statistically processed using the software Stat Soft, 11.0. For 31 water 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 concentrations of the chemical elements in the samples is estimated, and the coefficients of correlation are presented in the correlation matrix.

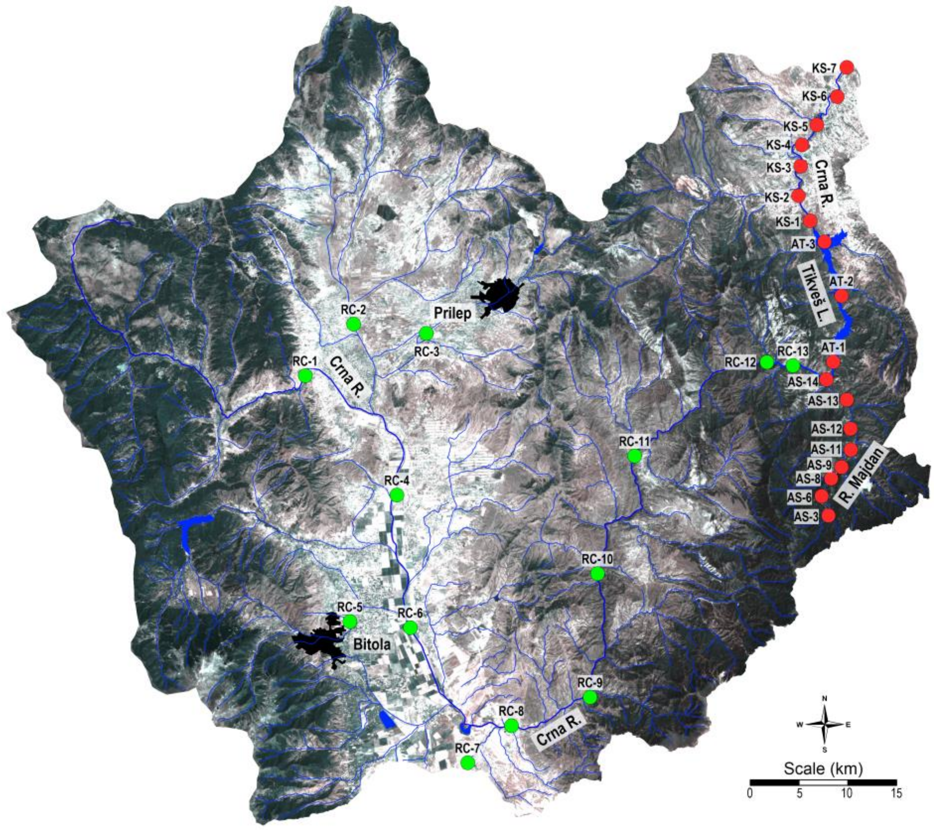

Figure 2. Map of the investigated basin with the locations of water samples

The analysis of water samples was performed using an atomic emission spectrometry with the inductively coupled plasma – atomic emission spectrometry, ICP-AES (Varian, 715ES). For better adjusting of the sensitivity for the most of the analyzed elements in the moss digests, an ultrasonic nebulizer CETAC (ICP/U-5000AT) was used. 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 и Zn. Standard solutions of elements were prepared by dilution of 1000 mg/l solutions (11355-ICP multi-element standard solution). The method of standard additions was applied, and it was found that the recovery of the investigated elements ranged between 98 and 101 % for ICP-AES. The optimal instrumental parameters for these techniques are given in our previously published paper [17].

RESULTS AND DISCUSSION

The obtained data for the concentration of the analyzed elements determined in surface water samples from 13 locations from the source of Crna River to the estuary in Tikveš Lake, including 8 from the Crna River, and 4 from four main tributaries of Crna River in the Pelagonia Valley (Blato, Prilepska Reka, Dragor and Jelaška Reka), as well as 7 locations of the lower course of the Crna River after the dam of Tikveš Lake. They were statistically processed. Their descriptive statistics are presented in Table 1. Due to the specificity of the lithology and mining activities in the Kožuf Mountain region, the descriptive statistics of the concentrations of the same elements in the surface water samples collected from 8 locations of the Majdanska and Blašnica rivers (the right tributary of Crna River) before its inflow into the Tikveš Lake, are given in a separate table (Table 2). The following statistical parameters are given in Tables 1 and 2: X – arithmetic mean, Md – median, Min – minimum, Max – maximum, P_{10} – 10 percentiles, P_{90} – 90 percentiles, S – standard deviation, S_x - standard deviation (standard error), CV – coefficient of variation, A – asymmetry and E – distribution.

Tables 1 and 2 give data on concentrations of only 14 elements because the concentration of the other elements are below the detection limit of 0.001 mg/l for Ag, B, Cd, Co, Cr and V, 0.005 mg/l for Mo and Ni and 0.01 mg/l for P and Pb.

Table 1. Descriptive statistics of the concentrations of the analyzed elements in surface water samples collected from the Pelagonia Valley, Mariovo region, Tikveš Lake and from the part of the Crna River after the dam of the Tikveš Lake (in mg/l)

Element	X	Md	Min	Max	P_{10}	P_{90}	S	S_x	CV	A	E
Al	0.076	0.052	0.021	0.45	0.027	0.12	0.09	0.018	115	3.86	16.50
As	< 0.010	< 0.010	< 0.010	< 0.010							
Ba	0.031	0.028	0.015	0.051	0.022	0.045	0.01	0.002	31	0.80	-0.19
Ca	42	39	10	74	32	59	14	2.9	34	0.11	0.84
Cu	0.017	0.015	0.002	0.063	0.003	0.027	0.01	0.003	77	1.97	6.00
Fe	0.16	0.11	0.021	0.85	0.032	0.28	0.18	0.037	114	2.88	10.39
K	4.8	4.8	2.4	10	3.0	6.7	1.6	0.33	33	1.50	4.11
Li	0.029	0.033	0.001	0.051	0.004	0.047	0.02	0.004	59	-0.59	-1.26
Mg	11	11	2.6	18	5.0	17	4.1	0.86	36	-0.42	-0.28
Mn	0.064	0.040	0.006	0.31	0.009	0.15	0.07	0.014	107	2.44	7.19
Na	11	13	0.005	37	0.005	19	9.3	1.9	85	0.65	1.01
Ni	0.033	0.019	0.005	0.11	0.007	0.071	0.03	0.006	84	1.17	0.92
Sr	0.19	0.19	0.050	0.28	0.11	0.28	0.06	0.012	31	-0.42	0.38
Zn	0.023	0.021	0.005	0.088	0.011	0.029	0.02	0.004	77	2.67	7.96

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

Table 2. Descriptive statistics of the concentrations of 8 surface water samples collected from the Majdanska and Blašnica rivers (in mg/l)

Element	X	Md	Min	Max	P_{10}	P_{90}	S	S_x	CV	A	E
Al	0.081	0.075	0.015	0.145	0.015	0.145	0.002	0.042	0.039	0.044	-0.357
As	0.082	0.052	0.010	0.199	0.010	0.199	0.005	0.071	0.066	0.938	-0.714
Ba	0.047	0.042	0.032	0.084	0.032	0.084	0.000	0.017	0.016	1.71	3.182
Ca	51	52	24	74	24	74	327	18.09	16.92	-0.17	-1.40
Cu	0.017	0.012	0.004	0.053	0.004	0.053	-	0.016	0.015	1.982	4.266
Fe	0.107	0.076	0.013	0.327	0.013	0.327	0.010	0.100	0.094	1.769	3.469
K	2.7	2.3	1.6	4.1	1.6	4.1	1.2	1.1	1.04	0.431	-2.121
Li	0.008	0.003	0.001	0.019	0.001	0.019	0.000	0.009	0.008	0.637	-2.206
Mg	15	13	5.3	22	5.26	22.4	42.2	6.50	6.1	0.021	-1.482
Mn	0.060	0.017	0.012	0.35	0.012	0.352	0.014	0.12	0.111	2.811	7.926
Na	3.99	2.77	2.48	6.50	2.48	6.50	3.62	1.90	1.78	0.642	-2.186
Ni	< 0.005	< 0.010	< 0.010	< 0.010							
Sr	0.24	0.21	0.14	0.35	0.14	0.35	0.007	0.083	0.077	0.426	-1.934
Zn	0.06	0.041	0.021	0.161	0.021	0.161	0.003	0.051	0.048	1.274	0.492

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

To determine the degree of correlation between the analyzed elements in the samples of surface water in the investigated area the bivariate statistics was used to obtain the correlation coefficients between the analyzed elements. If the absolute value of the correlation coefficient ranges between 0.50 and 0.72, it is considered that we have good correlation between the individual elements and a strong correlation between the analyzed elements exists if the correlation coefficient ranges from 0.72 and 1. Table 3 provides the correlation coefficient matrix for 31 surface water samples in all zones of the investigated area. It could be seen that a strong correlation was obtained between the concentrations of the earth-alkaline elements: Mg-Sr (0.98), Ca-Sr (0.88), Ca-Mg (0.88), Ba-Sr (0,80), Ba-Mg (0.77) and Ba-Ca (0.79) and between Fe-Al (0.87), while a good correlation exists between the concentrations of the following elements: Mn-Al (0.69), Mn-Ba (0.56), Zn-Cu (0.54), Na-K (0.54) and for the Blašnica river between As and Zn (0.50). All of these data are in agreement with the distribution of these elements in soil from the Crna River Basin [16].

Table 3. Matrix of correlation coefficients for the analyzed elements in the samples of surface and waters from the Crna River Basin

Element	Al	As	Ba	Ca	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Sr	Zn
Al	1.00													
As	0.12	1.00												
Ba	0.22	0.40	1.00											
Ca	-0.07	0.22	**0.79**	1.00										
Cu	0.35	0.20	-0.18	-0.17	1.00									
Fe	**0.87**	-0.01	0.14	-0.14	0.13	1.00								
K	-0.04	-0.42	0.08	0.30	-0.15	0.13	1.00							
Li	-0.25	-0.40	-0.16	0.03	-0.19	-0.10	0.47	1.00						
Mg	-0.03	0.21	**0.77**	**0.88**	-0.19	-0.13	0.29	0.30	1.00					
Mn	0.69	0.05	0.58	0.32	0.08	**0.73**	0.28	-0.09	0.28	1.00				
Na	0.11	-0.27	-0.20	-0.18	0.00	0.44	0.54	0.09	-0.25	0.25	1.00			
Ni	-0.01	-0.31	0.13	0.27	-0.02	-0.15	0.26	0.41	0.27	0.09	-0.42	1.00		
Sr	-0.01	0.15	**0.80**	**0.88**	-0.19	-0.09	0.29	0.29	**0.98**	0.33	-0.24	0.26	1.00	
Zn	0.16	0.50	0.21	0.16	0.54	-0.08	-0.30	-0.32	0.15	-0.04	-0.30	-0.13	0.16	1.00

According to the national Decree on the categorization of water courses, lakes, accumulations and ground water [18] the water quality of the Crna River and its tributaries are defined as follow:

– Second class: water from Crna River at sampling locations close to the spring (RC-1), all locations after the dam of Tikveš Lake (KS-1 to KS-7), water from the tributary Eleška River – RC-7 (which is the only tributary that covers the catchment area in Greece), sampling locations of Majdanska River (AS-3, AS-6 and AS-8) and water from Tikveš Lake (AT-1, AT-2 and AT-3).

– Third class: water from the tributaries Blato (RC-12), Prilepska River (RC-3), Dragor (RC-5) and water from the Crna River from the town of Bitola to the inflow into Tikveš Lake (RC-8 to RC-13).

Such a classification of waters, in fact, defines the quality of surface waters in the Republic of Macedonia, since for each class there are maximum permissible concentrations of individual parameters and pollutants given in the national Decree on classification of waters [19]. The maximum permitted concentrations of the analyzed elements are given in Table 4. According to this Decree there are no limits for the concentrations of Ca, K, Li, Mg, Na and Sr.

Table 4. Maximum permissible concentration of the analyzed elements according to the Decree on Classification of Waters [19]

Element	Maximum permissible concentration, mg/l	
	Class II	Class III
Al	1.5	1.5
As	0.03	0.05
Ba	1.0	4.0
Cu	0.01	0.05
Fe	0.3	1.0
Mn	0.05	1.0
Ni	0.05	0.1
Zn	0.1	0.2

Table 5. Mean, median, minimal and maximal concentration of the analyzed elements for the whole river basin and for the zones (in mg/l)

Element/region		Al	As	Ba	Ca	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Sr	Zn
Whole area	Mean	0.078	0.029	0.035	44.0	0.017	0.144	4.30	0.024	12.2	0.053	12.5	0.025	0.200	0.034
	Median	0.054	0.010	0.031	39.3	0.015	0.099	4.21	0.030	11.8	0.034	13.2	0.013	0.190	0.022
	Min	0.015	0.010	0.015	10.4	0.002	0.013	1.63	0.001	2.6	0.006	2.5	0.003	0.050	0.005
	Max	0.451	0.199	0.084	74.2	0.063	0.855	10.0	0.051	22.4	0.310	36.8	0.115	0.346	0.161
Pelagonia	Mean	0.121	0.010	0.030	37.0	0.020	0.268	4.71	0.010	7.8	0.101	15.2	0.020	0.144	0.021
	Median	0.083	0.010	0.028	37.0	0.020	0.185	4.42	0.006	6.9	0.089	14.5	0.019	0.144	0.021
	Min	0.036	0.010	0.015	10.4	0.006	0.074	2.42	0.001	2.6	0.022	5.1	0.007	0.050	0.014
	Max	0.451	0.010	0.049	74.2	0.035	0.855	10.0	0.047	14.4	0.310	36.8	0.038	0.231	0.028
Mariovo	Mean	0.054	0.010	0.026	35.4	0.016	0.209	4.95	0.045	11.2	0.053	17.6	0.019	0.188	0.019
	Median	0.054	0.010	0.025	34.7	0.015	0.190	4.21	0.047	10.9	0.043	18.0	0.013	0.190	0.023
	Min	0.031	0.010	0.023	31.9	0.009	0.146	3.63	0.037	10.2	0.023	15.5	0.003	0.167	0.005
	Max	0.069	0.010	0.028	39.2	0.027	0.284	7.27	0.051	12.1	0.098	18.9	0.050	0.202	0.029
Tikveš Lake	Mean	0.045	0.010	0.026	34.8	0.019	0.046	4.28	0.032	10.5	0.008	13.8	0.012	0.162	0.018
	Median	0.053	0.010	0.025	35.0	0.017	0.146	4.52	0.041	10.8	0.030	16.5	0.015	0.177	0.020
	Min	0.041	0.010	0.024	34.2	0.015	0.032	3.79	0.030	10.5	0.006	13.2	0.007	0.159	0.015
	Max	0.052	0.010	0.028	35.0	0.025	0.068	4.81	0.033	10.7	0.009	14.2	0.015	0.167	0.022
Lower flow of Crna River	Mean	0.055	0.010	0.038	54.0	0.014	0.041	5.18	0.038	15.8	0.053	14.7	0.007	0.246	0.032
	Median	0.051	0.010	0.041	50.7	0.004	0.034	5.26	0.040	15.2	0.034	15.9	0.007	0.225	0.016
	Min	0.021	0.010	0.025	49.7	0.002	0.021	4.94	0.031	14.4	0.015	12.3	0.005	0.221	0.008
	Max	0.118	0.010	0.051	60.8	0.063	0.099	5.36	0.042	17.7	0.152	17.2	0.011	0.279	0.088
Majdanska and Blašnica rivers	Mean	0.081	0.082	0.047	51.3	0.017	0.107	2.74	0.008	14.8	0.020	4.0	0.063	0.235	0.063
	Median	0.075	0.052	0.042	51.6	0.012	0.075	2.34	0.003	13.1	0.017	2.80	0.050	0.207	0.041
	Min	0.015	0.010	0.032	24.4	0.004	0.013	1.63	0.001	5.3	0.012	2.50	0.047	0.141	0.021
	Max	0.145	0.199	0.084	73.9	0.053	0.327	4.16	0.019	22.4	0.035	6.50	0.115	0.346	0.161

In order to easily notice the differences that would arise between the concentrations of the analyzed elements, the investigated region is divided into five zones, as follows:

– Crna River and its tributaries in the Pelagonia Valley (8 samples),

– the part of Crna River in Mariovo (3 samples),

–Tikveš Lake (3 samples),

– lower flow of Crna River after the dam of Tikveš Lake (8 samples), and

– rivers Majdanska and Blašnica in the Kožuf Mt. area (8 samples).

The mean, median, minimal and maximal concentrations of the analyzed elements for the whole river basin and for the zones are presented in Table 5. The results for each individual element together with the maps for their spatial distribution and histograms with the mean values for each river basin zone are given and interpreted in the text below.

Aluminum is the third most abundant largest element in the Earth's crust just after oxygen and silicon with the content of 8%. Aluminum is a light, non-ferrous, odorless, silver-white metal. Aluminum is a highly reactive metal and is not present in a free form in nature. Aluminium is commonly present in silicates in clay, soil, various minerals, rocks and precious stones. Higher concentrations of aluminum can have a negative impact on plants and animals in different ways. Spatial distribution of Al in surface water samples from the investigated river basin is shown in Figure 3.

The concentration of Al in water samples from the whole Crna River basin ranges from 0.015 to 0.451 mg/l with the mean concentration of 0.078 mg/l and median value of 0.054 mg/l (Tables 1, 2 and 5, Figure 4). The determined concentrations of Al in all water samples are below the maximum allowable concentration of Al for the second and third class of water (1.5 mg/l) according to the Decree for Classification of Waters of the Republic of Macedonia [19] in which the waters from the investigated region are classified [18].

The highest concentration of Al was found in the sample of surface water from the river Blato, a tributary of Crna River near the village of Vrbjani, municipality of Krivogaštani (0.45 mg/l) in the Pelagonia Valley. Probably the reason for such high concentration is the water treatment plant in the near vicinity of the sampling location (about 1 km upstream) using usually aluminum salts for the water purification. Considering the values obtained for Al concentrations by the zones in the river basin the highest concentration are found in the water samples from the Pelagonia Valley (mean concentration of 0.121 mg/l) and the courses of Majdanska and Blašnica rivers with a mean value of 0.081 mg/l (Table 5, Figures. 3 and 4) which is in agreement with the lithology of the river basin with the highest content of Al in these two zones [16].

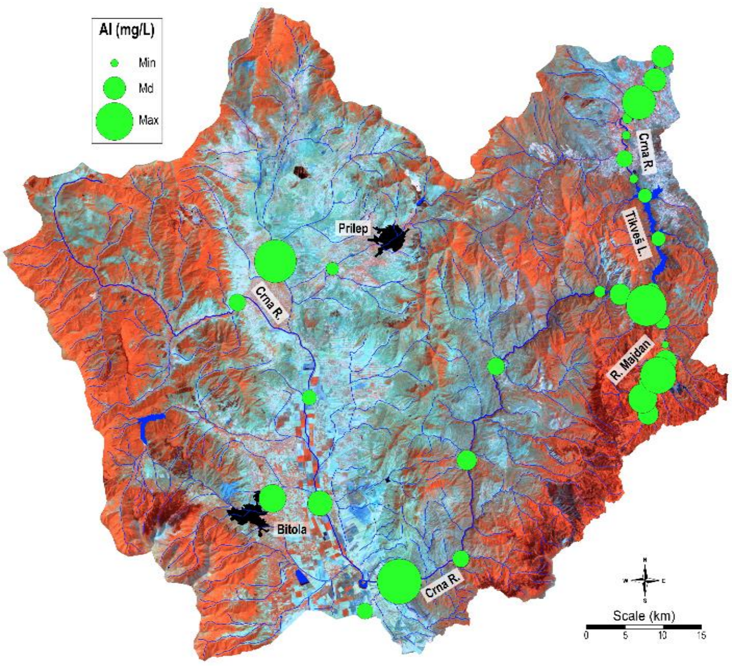

Figure 3. Spatial distribution of the concentrations of Al

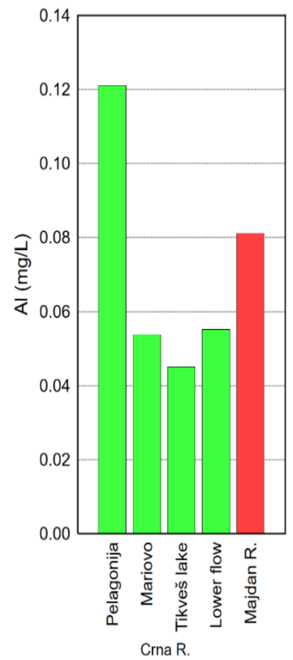

Figure 4. Mean concentrations of Al by zones

Arsenic is metalloid metal and it is usually present in the nature in the form of sulfides. By the content it is 40th element in the Earth's crust. The average presence of arsenic in soils in the world is 5 mg/kg [20]. This element is found in various allotropic modifications but only the gray form is significant from an industrial point of view. Arsenic and its compounds, especially trioxide, are widely used in the production of pesticides, herbicides and insecticides. The toxicity of arsenic is associated with its solubility, which is directly affected by the pH of the environment.

Certain regions in the Republic of Macedonia are rich in arsenic, among which is the Kožuf Mountain. Arsenic has a significant impact on the environment, especially in the region around the abandoned mine of arsenic, antimony and thallium "Allchar" [21–24]. As it can be seen from data presented in Tables 1, 2 and 5, and Figures 5 and 6, the concentration of arsenic is bellow the detection limit (< 10 mg/l) in all of the samples except for the samples from the Majdanska and Blašnica rivers after Allchar locality, where its concentration ranges from 0.010 to 0.199 mg/l, with a mean concentration of 0.082 mg/l and median of 0.052 mg/l, which is higher than the maximum permissible concentration (Table 4) for the second (0.03 mg/l) and the third class (0.05 mg/l). This very high concentration of As in waters from Majdanska and Blašnica rivers originated from the former mining activities at the former As-Sb-Tl mine "Allchar" [25–27], as well as high content of As in the soil from this locality [16, 23].

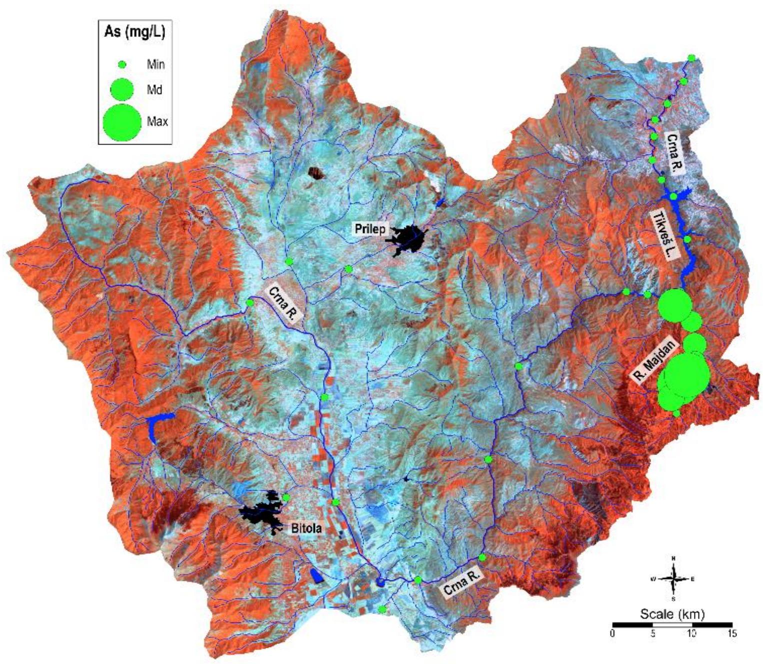

Figure 5. Spatial distribution of the concentrations of As

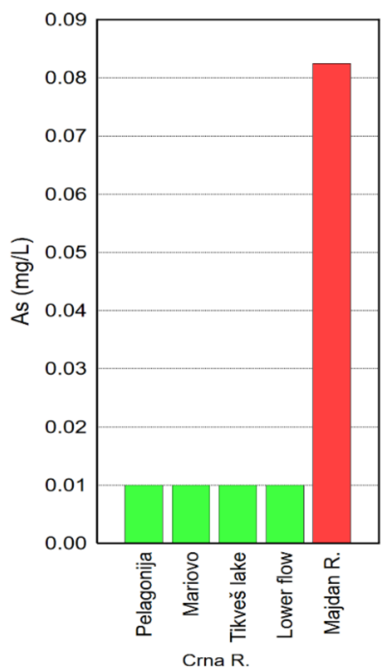

Figure 6. Mean concentrations of As by zones

Barium is found to be 14th most abounded element in the Earth's crust. Its compounds whether they are water soluble or acidic, are toxic. The most present Ba mineral is barite, but Ba is present in various silicate minerals. The spatial distribution of the concentrations of Ba in all water samples in the river basin is presented in Figure 7 while the histogram with the mean values for the zones in the basin is presented on Figure 8. The concentration of Ba ranges from 0.015 to 0.084 mg/l with the mean value of 0.035 mg/l and median of 0.031 mg/l, which is a much lower than the maximum permissible concentration for the second (1.0 mg/l) and third class (4.0 mg/l) of waters. The lowest Ba concentration was obtained in the water sample from the Crna River and the tributaries in the middle and lower flow of the Crna River in the Pelagonia Valley as well as in the Mariovo area, while the highest concentration of Ba was found in the waters from Majdanska and Blašnica rivers with the mean concentration of 0.081 mg/l. These differences are in agreement with a very high content of barium in soil and rocks from the Kožuf Mt. (over 800 mg/kg) [16].

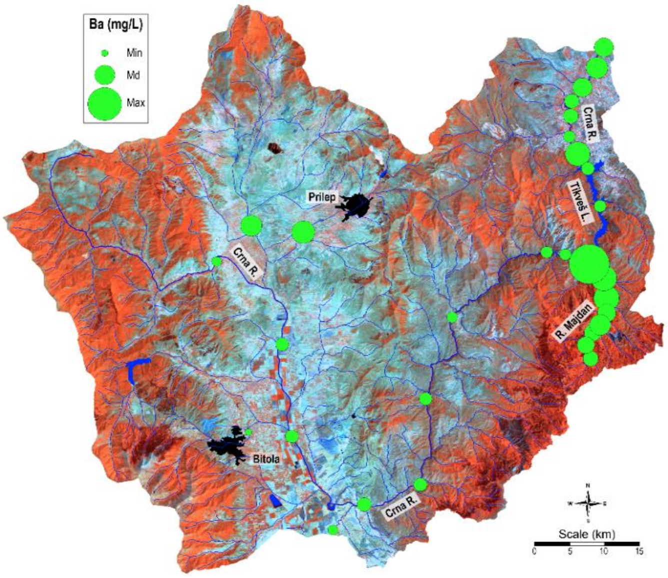

Figure 7. Spatial distribution of the concentrations of Ba

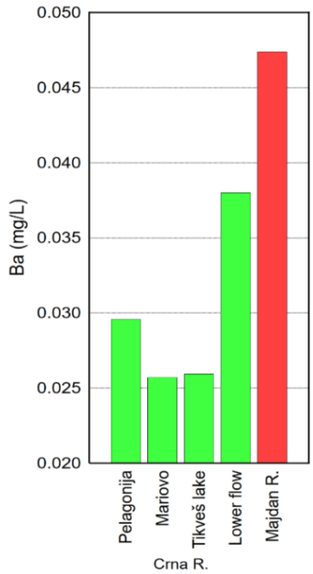

Figure 8. Mean concentrations of Ba by zones

Calcium is the fifth most abounded element in the Earth's crust. It is reactive, weak-yellow metal that exposes the air to form a dark oxide or nitride layer. It belongs to the group of alkaline earth metals. Calcium carbonate is the calcium compound that is most common on Earth. Calcium is an essential element for plants, animals and humans. Due to the high solubility of calcium compound in water its concentration in surface waters is usually high. The concentration of Ca in the waters from the Crna River basin is similar almost in the whole area (Figures 9 and 10) ranges from 10.4 to 74.2 mg/l with a mean value of 44.0 mg/l and median of 39.3 mg/l (Tables 1, 2 and 5). The highest Ca concentration of 74 mg/l is determined in the samples from the river Prilepska Reka (village of Kadino, Prilep) coming from the area rich in calcite and dolomite mineralization [16], while the lowest concentration (10 mg/l) was found in the sample from the Dragor river, a tributary of Crna River passing through the city of Bitola collecting all waste waters from the urban area. The increased concentrations of Ca in the waters of the Kožuf massif (mean concentration of 51.3 mg/l) and those from the lower flows of Crna River (mean concentration of 54 mg/l) are due to the increased contents of Ca in the rocks and soils in the tectonic Vardar zone to which this areas belongs [16].

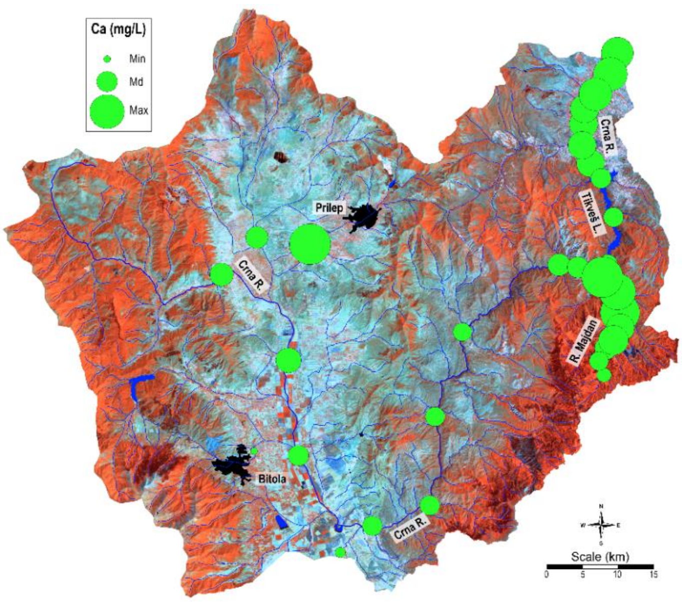

Figure 9. Spatial distribution of the concentrations of Ca

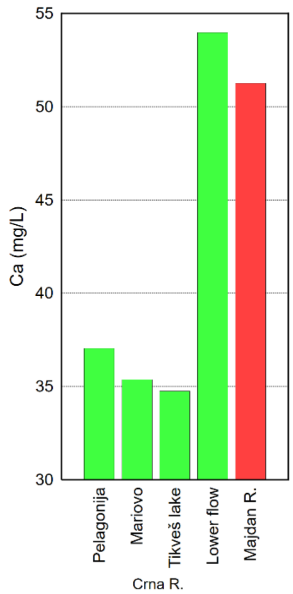

Figure 10. Mean concentrations of Ca by zones

Copper is known for its high thermal and electrical conductivity and therefore it is the most commonly used metal as a heat and electricity conductor in the industry. The spatial distribution of the concentrations of copper in water samples from the Crna River basin and the mean concentration of the waters from the zones are shown in Figures 11 and 12. The concentrations of Cu for the whole area range from 0.002 to 0.063 mg/l with a mean value of 0.017 mg/l and median value of 0.015 mg/l (Table 5). The highest value for the concentration of Cu (0.063 mg/l) was obtained from a sample of water of the lower flow of Crna River (Table 5), and the lowest value was obtained in the sample collected from Crna River after the dam of Tikveš Lake (0.002 mg/l). Sources of copper in surface waters are wastewater from industry, agricultural drainage waters that are partially or not completely purified and as such flow into the rivers. From the Figures 11 and 12 it could be seen that higher concentration of Cu was found in water from the river Dragor (0.035 mg/l) as a result of urban pollution from the city of Bitola. In general most of the obtained concentrations for Cu are bellow the maximal permitted concentrations for surface waters of II and III class.

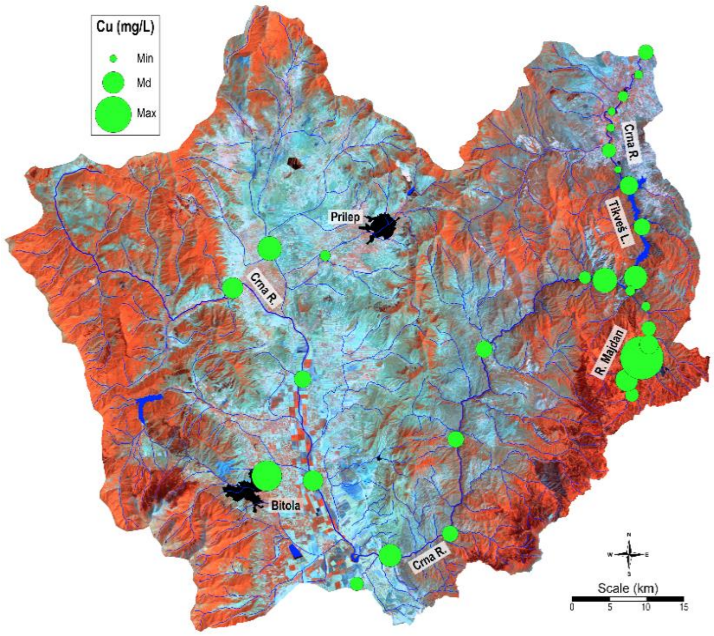

Figure 11. Spatial distribution of the concentrations of Cu

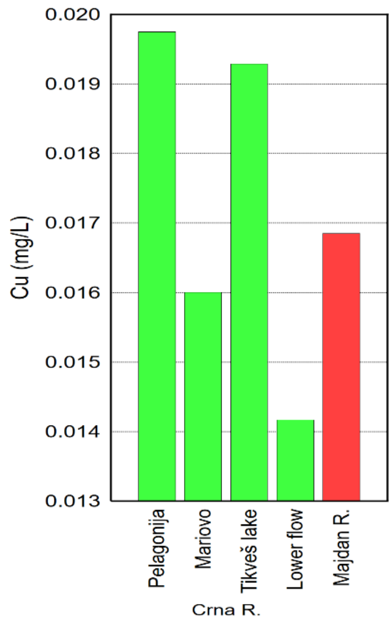

Figure 12. Mean concentrations of Cu by zones

The concentration of **iron** in the water samples from the investigated area ranges from 0.013 to 0.855 mg/l with a mean value of 0.144 mg/l and median of 0.099 mg/l (Table 5). Higher concentration of Fe was found in waters from the upper stream of Crna River, Pelagonia Valley and Mariovo ranges of 0.021 mg/l to 0.85 mg/l (Table 1 and 5) and mean value of 0.16 mg/l and median value of 0.11 mg/l. According to the zones (Figures 13 and 14) the highest average concentration of Fe was determined in water samples from the Pelagonia Valley (0.268 mg/l) and Mariovo zone (0.209 mg/l). This is probably as a result of the increased content of Fe in south-western part of the Pelagonia Valley [16], usage of iron salts as a fertilizer in agriculture, as well as a results of the pollution from industrial wastewater from the coal mines located in the Pelagonia Valley with high content of Fe_2O_3 (from 4.65% to 7.60%) [28].

The spatial distribution of **potassium** in the samples of water in the Crna River basin, as well as the histogram for the mean values of the obtained potassium concentrations in the surface water samples by zones are given in Figures 15 and 16, respectively. The concentration of potassium in the water from the Crna River basin ranges from 1.63 to 10.0 mg/l with a mean value of 4.30 g/l and median value of 4.21 mg/l (Tables 1, 2 and 5, Figures. 15 and 16). The lowest concentrations of K were found in the water samples from the Majdanska and Blašnica rivers (mean value of 2.74 mg/l) which is in accordance with the low content of K in the rocks and soils of the Kožuf Mountain region [16]. The mean concentrations of K in waters from the other zones are similar and range from 4.28 mg/l for waters from Tikveš Lake to 5.18 mg/l for waters from the lower flow of the Crna River (Tables 1, 2 and 5).

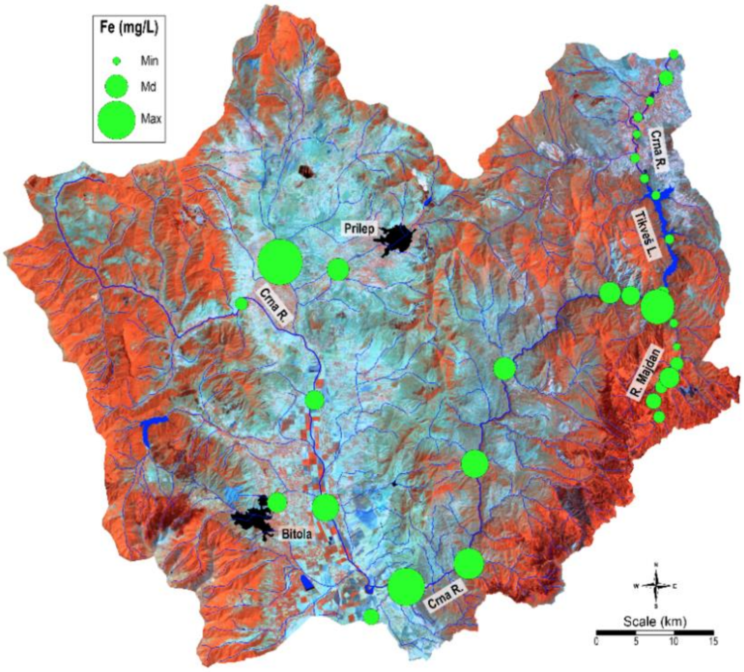

Figure 13. Spatial distribution of the concentrations of Fe

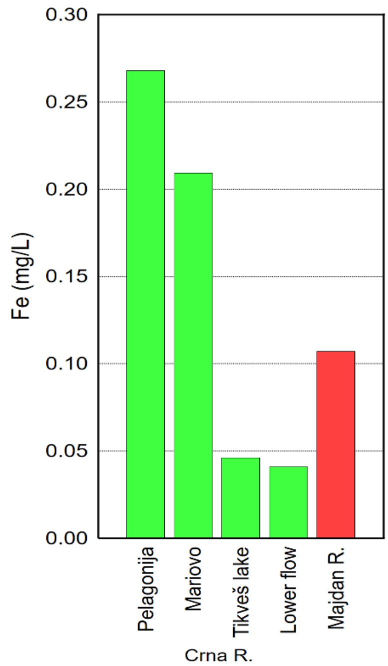

Figure 14. Mean concentrations of Fe by zones

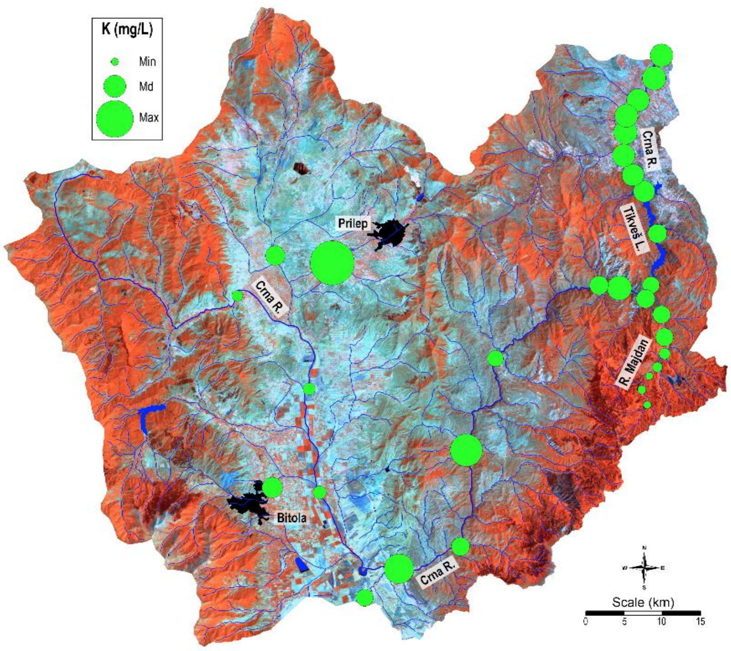

Figure 15. Spatial distribution of the concentrations of K

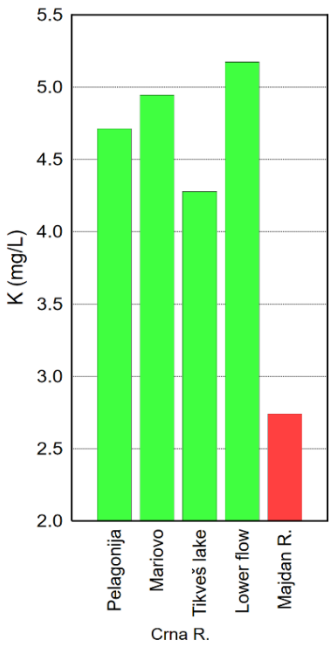

Figure 16. Mean concentrations of K by zones

The concentrations of **lithium** in the water samples from the Crna River basin are very low range from 0.001 mg/l to 0.051 mg/l with a mean concentration of 0.24 mg/l and median of 0.030 mg/l (Table 5). A maximal concentration was found in water sample collected from the river Crna River near the village of Skočivir (Figure 17). In general, according to zones, the concentration of Li is the highest in the samples from the Crna River in the Mariovo region with a mean value of 0.045 mg/l (Figure 18), which is in accordance with the high Li content in rocks and soils in this region, in particular the area of the Nidže Mountain located south of Mariovo [16]. This influence on the increase in the concentration of Li continues (with a certain decrease) in the water from the lower course of the Crna River (mean value of 0.038 mg/l), as well as in the water of Tikveš Lake (mean value 0.032 mg/l) (Figure 18).

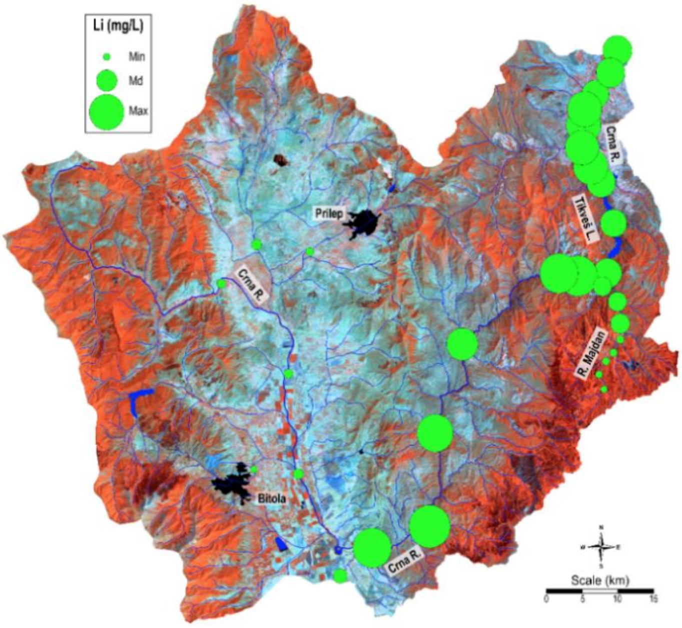

Figure 17. Spatial distribution of the concentrations of Li

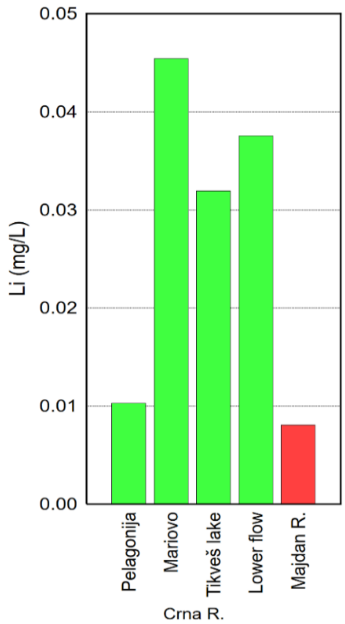

Figure 18. Mean concentrations of Li by zones

Magnesium is an alkaline earth metal found in dolomite, magnesite, epsomite, and other minerals. The spatial distribution of the concentrations of magnesium in water samples from the Crna River basin is given in Figure 19. Its concentration for the whole basin ranges from 2.6 mg/l to 22.4 mg/l, with a mean concentration of 12.2 mg/L and medina of 11.8 mg/l (Tables 1, 2 and 5). The highest concentrations of Mg are determined in the water from the lower course of the river Blašnica (mean concentration of 14.8 mg/l and its basin in Tikveš Lake, and the waters from the lower course of the Crna River (mean value of 15.8 mg/l) (Figure 20). This increased concentration of Mg in waters from these areas is due to its increased content in rocks and soils in the region of Kožuf Mountain and Tikveš Field, where the Neogene magmatic rocks and Neogene clastitic sediments are predominant [16]. On the other hand, the lowest concentrations of Mg are recorded in the waters from the region of Pelagonia (mean value of 7.8 mg/l), a region where the poorest rocks and soils with magnesium in Macedonia are present. Namely, the average content of Mg in soils in Macedonia is 0.92%, while in the region of Pelagonia its content is 0.67% [16].

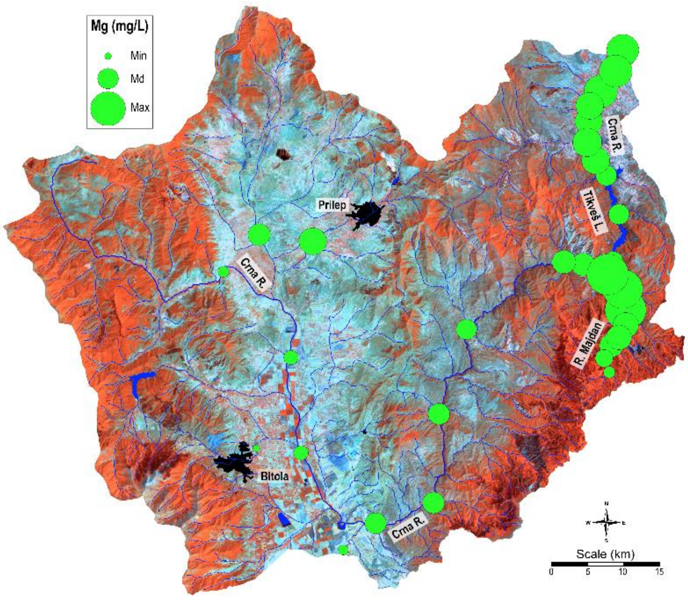

Figure 19. Spatial distribution of the concentrations of Mg

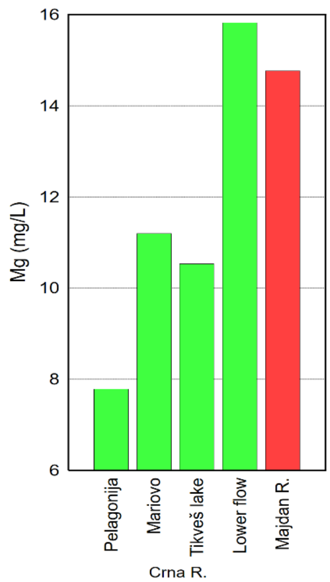

Figure 20. Mean concentrations of Mg by zones

Manganese is the 25th most abounded element in the Earth's crust, with an average content of 774 mg/kg, while its content in the Macedonian soils is 880 mg/kg [16]. Manganese is widely distributed in wildlife, and is a microelement of exceptional and essential importance. The spatial distribution of manganese in surface water samples is shown in Figure 21. The highest Mn concentration of 0.31 mg/l is determined in the water sample from the rivers Blato and Prilepska Reka, a tributaries of Crna River in the upper flow of Crna River and exceeds the maximum allowable concentration for water from the II class probably due to some anthropogenic influence (Figures 21 and 22) The concentration of Mn in almost all other samples does not exceed the maximum permissible concentration of Mn for the corresponding II class (0.05 mg/l) or III class (1.0 mg/l).

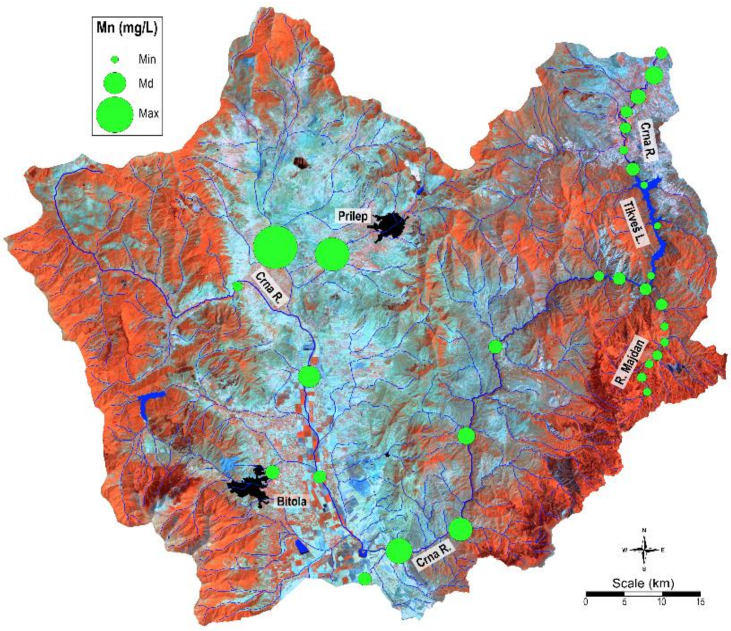

Figure 21. Spatial distribution of the concentrations of Mn

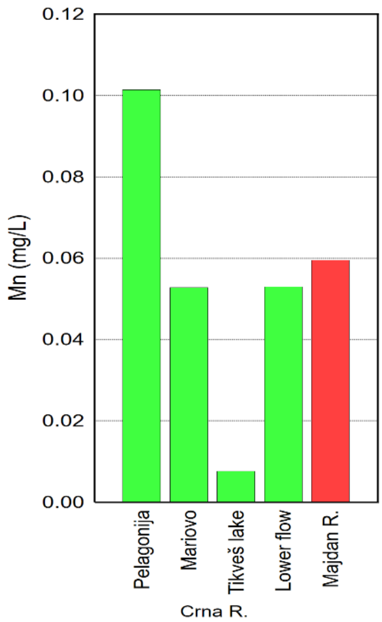

Figure 22. Mean concentrations of Mn by zones

Sodium is an alkali metal which is the sixth most abounded element in the Earth's crust. The spatial distribution of sodium in the water samples from the investigated area is shown in Figure 23. Its concentration ranges from 2.5 mg/l to 36.8 mg/l with a mean concentration of 12.5 mg/l and median of 13.2 mg/l (Table 5). The highest concentration of sodium is found in the sample of water from the tributary of Prilepska River (37 mg/l), which can be interpreted as a result of the increased content of Na in soils from the region of the city of Prilep (over 2.3% versus 1.2% content of Na in Macedonian soils) [16]. When comparing the Na concentrations by zones (Table 5, Figure 24), higher mean concentrations were found in the waters of the Mariovo region (17.6 mg/l) and Pelagonia (15.2 mg/l), while the lowest concentrations were found in the waters from lower flow (1.23 mg/l).

Nickel with atomic number 28 and chemical symbol Ni is placed as 28th the most abounded element in the Earth's crust with an average content of 34 mg/kg. It is a shiny, strong and elastic metal with a silvery tint. It is used in many industries. Similar to copper, it is used for preparing special alloys. Its main use is in the production of stainless steels and stainless steel cast iron. The spatial distribution of nickel concentrations in surface water samples and the histogram with mean values for nickel concentrations divided by regions are shown in Figures 25 and 26, respectively. It is obvious that the concentrations of Ni in the water samples from all of the region (beside lower flow of the Crna River) are very low, bellow 0.020 mg/L (Table 5, Figure 26), which is much lower than the maximal allowed concentration for the waters of II and III class of 0.05 mg/l and 0.1 mg/l, respectively. Higher concentration of Ni in waters from the lower flow of Crna River can be explained as being the result of waste water contamination from the ferro-nickel smelter plant "Feni industry" located near the Crna River close to the village of Vozarci [29–33].

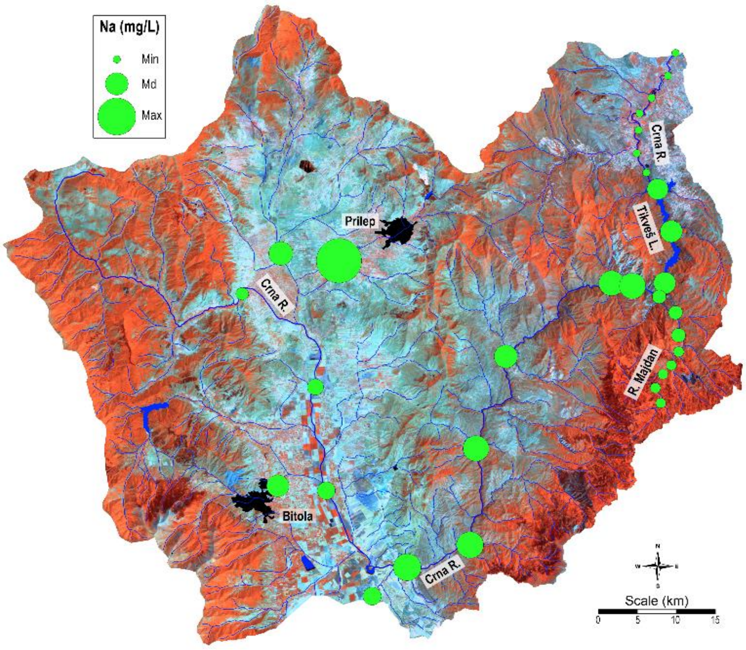

Figure 23. Spatial distribution of the concentrations of Na

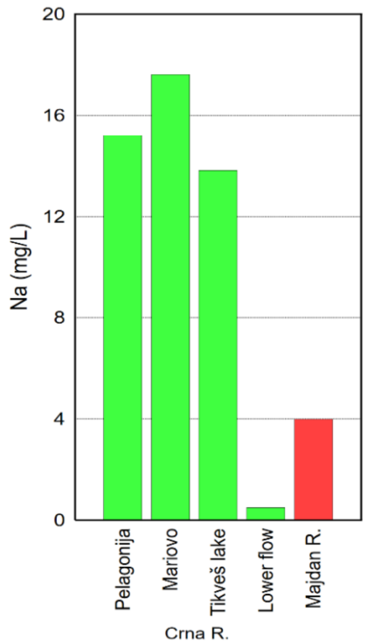

Figure 24. Mean concentrations of Na by zones

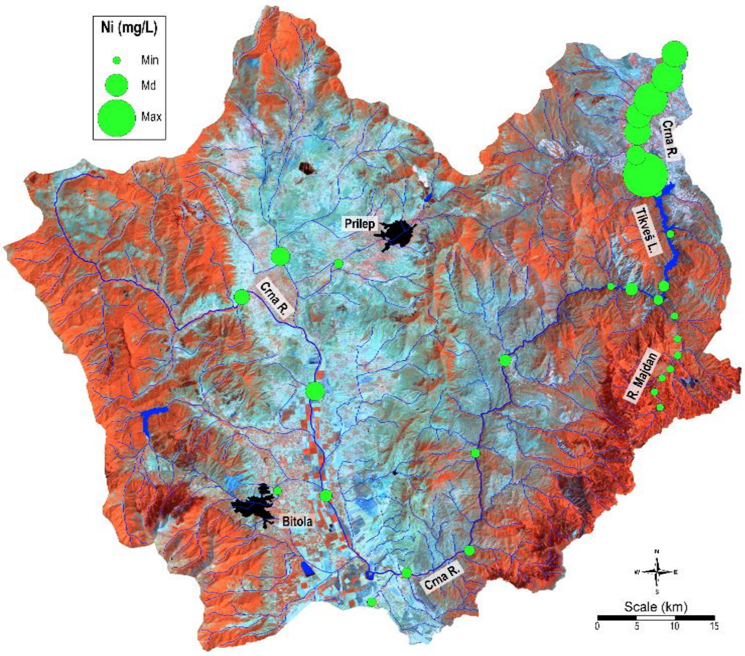

Figure 25. Spatial distribution of the concentrations of Ni

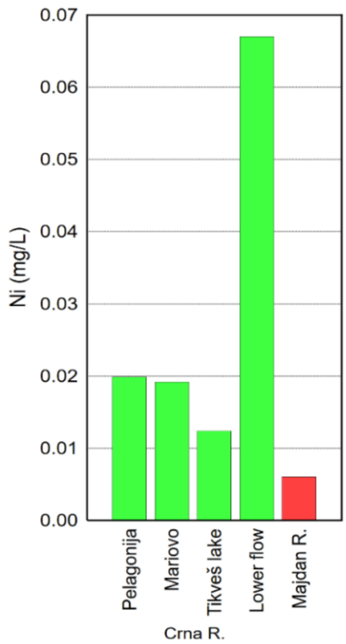

Figure 26. Mean concentrations of Ni by zones

Spatial distribution of **strontium** concentrations in surface water samples is shown in Figure 27. The highest concentration of Sr is found in samples from the lower flow of the Blašnica River of 0.35 mg/l as well as in the samples from the water from the lower stream of Crna River after the dam of the Tikveš Lake (Table 5, Figures 27 and 28). The higher concentration of Sr in the samples in these areas is due to the high content of Sr in rocks and soils in the region of Kožuf Mountain and Tikveš Field, where the Neogene magmatic rocks and Neogene clastitic sediments are dominant with the contents of Sr over 300 mg/kg compared to its average content in the Macedonian soils of 140 mg/kg [16].

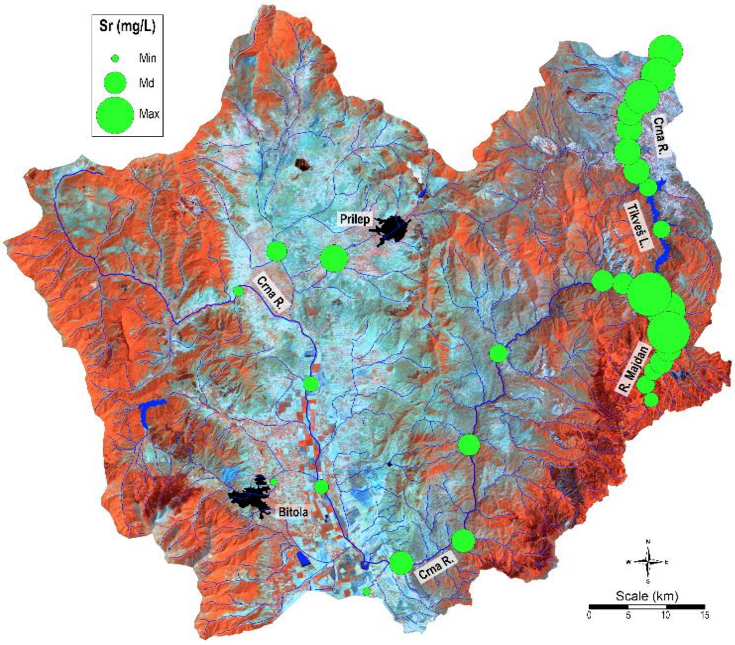

Figure 27. Spatial distribution of the concentrations of Sr

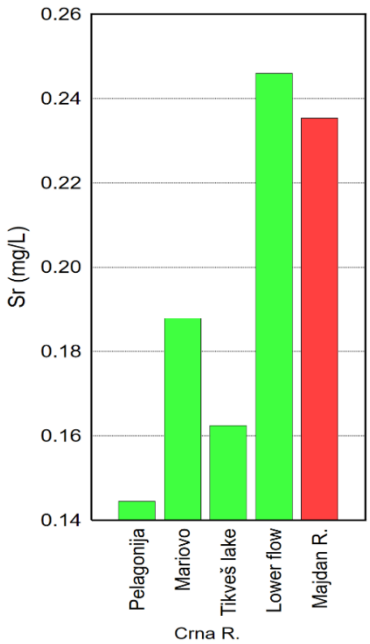

Figure 28. Mean concentrations of Sr by zones

Spatial distribution of **zinc** concentrations in water samples from the whole basin is shown in Figure 29 and the histogram with a mean concentration of Zn by region is shown in Figure 30. The concentrations of Zn in all of the samples from the regions of Pelagonia, Mariovo, Tikveš Lake and lower flow of Crna River are about 10 times lower (mean concentration ranges from 0.018 to 0.034 mg/l) from the maximal allowed concentration for the waters from II and III class (0.1 mg/l and 0.2 mg/l, respectively). The exception is only the water from the Majdanska and Blašnica rivers where the concentration of Zn is increased (0.063 mg/l), although it is still lower than the maximum permissible concentration, which is probably due to the anthropogenic influence of the activities of the nickel mine "Ržanovo" [23].

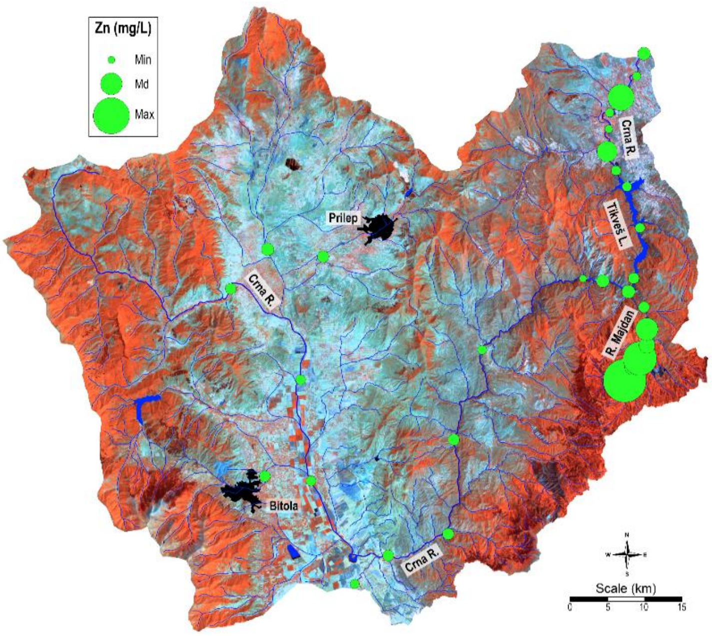

Figure 29. Spatial distribution of the concentrations of Zn

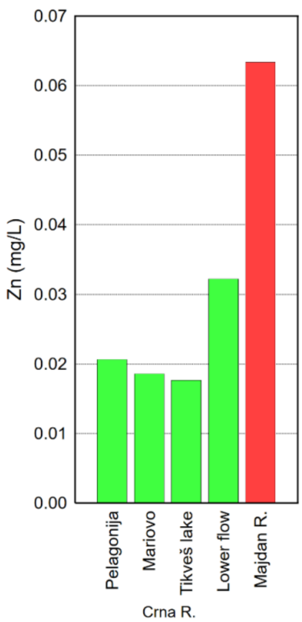

Figure 30. Mean concentrations of Zn by zones

CONCLUSION

In this study the results of the concentration 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 samples of surface water from the Crna River basin are presented. All data obtained were statistically processed using software Stat Soft, 11.0 and a descriptive statistical analysis of the value for the concentration 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 concentration of investigated elements follow the lithology of the region. However, higher concentration of As were found in the water samples from the river Blašnica which is a result of anthropogenic former mining activities at the abounded Allchar mine. Increased concentrations of Ni were found in the samples from the lower couse of the river Crna River after the dam of Tikveš Lake due to the anthropogenic influence from the ferronickel smelter plant Feni Industry.

REFERENCES

[1] A. Kabata-Pendias, A. B. Mukherjee, *Trace Elements Form Soil to Human*, Springer, Berlin, 2007.

[2] R. Naiman, R. E. Bilby, *River Ecology and Management*, Wayerhaevser Company, Tacoma, USA, 2008.

[3] R. M. Bhardwaj, J. Chilton, J. van der Gun, Y. Dieng, S. Diop, C. Gaye, A. Hansen, S. Mtetwe, O. Natale, H. Neikerk, K. Neilsen, W. Rast, B. Toguebaye, *Water Quality for Ecosystem and Human Helath*, GEMS Water Programme, Ontario, Canada, 2008.

[4] J. I. Drever, *Surface and Ground Water, Weathering and Soils*, Elsevier, Amsterdam, 2005.

[5] O. Dimitrovska, B. Markoski, B. Apostolovska Toshevska, I. Milevski, S. Gorin, Surface water pollution of major rivers in the Republic of Macedonia. *Procedia Environ. Sci*., **14** (2012), pp. 32–40.

[6] T. Stafilov, Environmental pollution with heavy metals in the Republic of Macedonia, *Contrib. Sect. Nat. Math. Biotech. Sci. MASA*, **35** (2014), pp. 81–119.

[7] S. Krstić, L. Melovski, Z. Levkov, P. Stojanovski, Complex investigations the river Vardar. II. The most polluted sites in the first three months, *Ecol. Protect. Environ.*, **2** (1994), pp. 13–29.

[8] Z. Levkov, S. Krstic, Use of algae for monitoring of heavy metals in the River Vardar, Macedonia, *Mediterr. Mar. Sci.*, **3** (2002), pp. 99–112.

[9] T. Stafilov, Z. Levkov, *Summary of Vardar River Basin Field Survey*, European Agency for Reconstruction and Ministry of Environment & Physical Planning of the Republic of Macedonia, Skopje, Macedonia, 2007.

[10] J. M. Serafimovska, S. Arpadjan, T. Stafilov, S. Ilik Popov, Dissolved inorganic antimony, selenium and tin species in water samples from various sampling sites of river Vardar (Macedonia/Greece), *Maced. J. Chem. Chem. Eng.*, **30** (2011), pp. 181–188.

[11] S. Ilić Popov, T. Stafilov, R. Šajn, C. Tánáselia, K. Bačeva, Applying of factor analyses for determination of trace elements distribution in water from river Vardar and its tributaries, Macedonia/Greece, *Sci. World J.*, **2014** (2014), Article ID 809253, pp. 1–11.

[12] B. Balabanova, T. Stafilov, R. Šajn, C. Tănăselia, Multivariate factor assessment for lithogenic and anthropogenic distribution of trace and macro elements in river water from Bregalnica River basin, R. Macedonia, *Maced. J. Chem. Chem. Eng*, **34** (2016), pp. 235–250.

[13] S. Krstić, T. Stafilov, Z. Zdravkovski, M. Kostadinovski, V. Slavevska-Stamenković, V. Kostov, Problems asocciated with not properly conducted wfd based monitoring during preparation of river basin management plans – Bregalnica river case study, *Water Resour. Manage.*, **6** (2016), pp. 35–43 .

[14] A. Lazarevski, *Climate in Macedonia*, Kultura, Skopje, 1993 (in Macedonian).

[15] C. P. Koteski, *Crna River Basin – Geographic-Cartographic Modeling, Differentiation and Functional Development of Selected Regional Parts*, PhD thesis, Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University, Skopje, 2009 (in Macedonian).

[16] T. Stafilov, R. Šajn, *Geochemical Atlas of the Republic of Macedonia*, Faculty of Natural Sciences and Mathematics, SS. Cyril and Methodius University, Skopje, 2016.

[17] B. Balabanova, T. Stafilov, K., Bačeva, R. Šajn, Biomonitoring of atmospheric pollution with heavy metals in the copper mine vicinity located near Radoviš, Republic of Macedonia. *J. Environ. Sci. Health A*, **45** (2010) 1504–1518.

[18] Decree on the categorization of watercourses, lakes, accumulations and groundwater, *Official Gazette of the Republic of Macedonia*, No. 18, March 31, p. 1173, 1999.

[19] Decree on classification of waters, *Official Gazette of the Republic of Macedonia*, No. 18, March 31, p. 1165, 1999.

[20] H. J. Rösler, H. Lange, *Geochemical Tables*, Elsevier, Amsterdam, 1972.

[21] K. Bačeva, T. Stafilov, R. Šajn, C. Tănăselia, Air dispersion of heavy metals in vicinity of the As-Sb-Tl abounded mine and responsiveness of moss as a biomonitoring media in small scale investigations, *Environ. Sci. Pollut. Res.*, **20** (2013), pp. 8763–8779.

[22] K. Bačeva, T. Stafilov, V. Matevski, Bioaccumulation of heavy metals by endemic *Viola* species from the soil in the vicinity of the As-Sb-Tl mine "Allchar", Republic of Macedonia, *Int. J. Phytoremediation,* **16** (2014), pp. 347–365.

[23] K. Bačeva, T. Stafilov, R. Šajn, C. Tănăselia, P. Makreski, Distribution of chemical elements in soils and stream sediments in the area of abandoned Sb–As–Tl Allchar mine, Republic of Macedonia, *Environ. Res.*, **133** (2014), pp. 77–89.

[24] K. Bačeva, T. Stafilov, V. Matevski, Distribution and mobility of toxic metals in *Thymus alsarensis* Ronniger in the Allchar As-Sb-Tl mine, Republic of Macedonia, *Plant Biosyst.*, **149** (2015), pp. 884–893.

[25] S. Janković, B. Boev, T. Serafimovski, *Magmatism and Tertiary Mineralization of the Kožuf Metalogenetic District, the Republic of Macedonia, with Particular Reference to the Allchar Deposit*, Faculty of Mining and Geology, Štip, Special Issue No. 5, pp. 1–262, 1997.

[26] B. Boev, V. Bermanec, T. Serafimovski, S. Lepitkova, S. Mikulcic, M. Soufek, G. Jovanovski, T. Stafilov, M. Najdoski, Allchar mineral assemblage, *Geol. Macedonica*, **15/16** (2001–2002) 1–23.

[27] B. Boev, S. Jelenković, Allchar deposit in Republic of Macedonia – Petrology and Age Determination, in: A. I. Juboury. (ed.), *Petrology - New Perspectives and Applications,* InTech, Rijeka, 131−168, 2012.

[28] M. Stojanovski, *Technology for selective exploitation of coal and interlayer tailings in a complex geotechnical conditions in PC "Brod Gneotino"*, MSc Thesis, University "Goce Delcev", Štip, 2012 (In Macedonian).

[29] K. Bačeva, T. Stafilov, R. Šajn, Biomonitoring of nickel air pollution near the city of Kavadarci, Republic of Macedonia, *Ecol. Protect. Environ.*, **12** (2009) 57–69.

[30] K. Bačeva, T. Stafilov, R. Šajn, C. Tănăselia, S. Ilić Popov, Distribution of chemical elements in attic dust in the vicinity of ferronickel smelter plant, *Fresenius Environ. Bull.*, **20** (2011) 2306–2314.

[31] K. Bačeva, T. Stafilov, R. Šajn, C. Tănăselia, Moss biomonitoring of air pollution with heavy metals in the vicinity of a ferronickel smelter plant, *J. Environ. Sci. Health A*, **47** (2012) 645–656.

[32] K. Bačeva, T. Stafilov, R. Šajn, Monitoring of air pollution with heavy metals in the vicinity of ferronickel smelter plant by deposited dust, *Maced. J. Ecol. Environ.*, **1** (2012) 47–57.

[33] B. Boev, T. Stafilov, K. Bačeva, A. Šorša, I. Boev, The nickel smelter plant influence on the mineralogical composition of attic dust in Tikveš Valley, Republic of Macedonia, *Environ. Sci. Pollut. Res.*, **20** (2013) 3781–3788.

ДИСТРИБУЦИЈА НА ХЕМИСКИ ЕЛЕМЕНТИ ВО ПОВРШИНСКИТЕ ВОДИ ОД СЛИВОТ НА ЦРНА РЕКА, РЕПУБЛИКА МАКЕДОНИЈА

Димитри Томовски[1], Трајче Стафилов[2,3], Robert Šajn[4], Катерина Бачева Андоновска[3]

[1]Алкалоид АД, Скопје, Република Македонија
[2]Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј“, Скопје, Република Македонија
[3]Истражувачки центар за животна средина и просторно планирање, Македонска академија на науките и уметностите, Скопје, Република Македонија
[4]Geological Survey of Slovenia, Ljubljana, Slovenia

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 површинските води од сливот на Црна Река, Република Македонија. Вкупно се земени 31 примерок од вода, од кои 13 примероци се земени во делот од изворот на Црна Река до нејзиниот влив во Тиквешкото Езеро, вклучувајќи 8 примероци од Црна Река и 4 примероци од нејзините главни притоки од Пелагониската Котлина (Блато, Прилепска Река, Драгор и Јелашка Река). Исто така, се земени примероци вода од 3 локации од Тиквешко Езеро, од 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 по браната на Тиквешкото Езеро до нејзиниот влив во реката Вардар. Определувањето на концентрацијата 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 концентрациите на сите испитувани елементи. Изработени се и карти на просторната дистрибуција на елементите, како и хистограми на застапеноста на елементи со средните концентрации по региони од сливот на Црна Река. Добиените резултати покажуваат дека концентрациите на испитуваните елементи главно ја следат литологијата на речниот слив. Меѓутоа, повисоките концентрации на арсен кои беа најдени во водите од реката Блашница покажуваат антропогено влијание од поранешните рударски активности на рудникот Алшар кој се наоѓа на планината Кожуф. Беа најдени зголемени концентрации на никел во водите од долниот тек на Црна Река, по браната на Тиквешкото Езеро, што исто така е резултат на антропогено загадување од отпадните води од топилницата за фероникел „Фени индустри“, коешто може да влијае на параметрите на квалитетот на површинските води.

Клучни зборови: Црна Река; Република Македонија; речен слив; води; тешки метали; дистрибуција