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Multivariate factor assessment for lithogenic and anthropogenic distribution of macro and trace elements in water from Pčinja River Basin, North Macedonia

Мултиваријантна факторна проценка на литогената и антропогената дистрибуција на макроелементи и елементи во траги во водите од сливот на реката Пчиња, Северна Македонија

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Abstract

In this work the distribution of chemical elements in surface water from the Pčinja River Basin, North Macedonia, was assessed. For this purpose, along the course of the Pčinja River, in accordance with a previously specified sampling network with 10 locations from the rivers and 4 locations from the Glažnja and Lipkovsko Lakes, the samples of surface water were collected in the period from June to July 2017. Apart from six locations on the river Pčinja, two samples were collected from the Tabanovska River and one sample each from the tributaries of Kumanovska River, Konjarska River and Kriva River. In all of the collected samples 22 macro and trace elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, P, Ni, Pb, Sr, V and Zn) were analyzed by inductively coupled plasma - atomic emission spectrometry (ICP-AES). A multivariate factor analysis was applied to analyze relations between the number of variables. The method includes the processing of information from a large number of original variables and their processing into a smaller set (factor) with minimal loss of information from the original variables. From the gathered results spatial distribution maps of factors for the separate groups were prepared as well as distribution maps for the analyzed elements. It was found that the distribution of most elements follows the lithology of the study area, except for some elements (Cu, P) whose increased concentrations are as a result of urban and agricultural and industrial activities.

Key words: River Pčinja, Water, Macroelements, Microelements, North Macedonia

Апстракт

Во овој труд извршена е проценка на дистрибуцијата на хемиски елементи во површинските води од сливот на реката Пчиња, Северна Македонија. За таа цел, по текот на реката Пчиња, во согласност

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со претходно одредена мрежа за земање примероци со 10 локации на реките и четири локации од езерата Глажња и Липково, примероци од површинските води се земени во периодот од јуни до јули 2017. Освен шест локации на реката Пчиња, беа земени два примерока од Табановска Река и по еден примерок од притоките Кумановска, Коњарска и Крива Река. Во сите примероци анализирани се 22 макроелементи и елементи во траги (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, P, Ni, Pb, Sr, V и Zn) со примена на индуктивно спрегната плазма – атомска емисиона спектрометрија (ICP-AES). Применета е мултиваријатна факторна анализа за да се анализираат односите помеѓу бројните променливи. Методот вклучува обработка на информации од голем број оригинални променливи и нивна обработка во помал сет (фактор) со минимална загуба на информации од оригиналните променливи. Од собраните резултати изработени се карти на просторна дистрибуција на факторите на одделните групи, како и карти на дистрибуција за анализираните елементи. Утврдено е дека дистрибуцијата на повеќето елементи ја следи литологијата на испитуваната област, освен некои елементи (Cu, P) чии зголемени концентрации се резултат на урбаните, земјоделските и индустриските активности.

Клучни зборови: река Пчиња, води, макроелементи, микроелементи, Северна Македонија

Introduction

Due to its unusual physical and chemical properties, constant circulation in nature and the presence of microorganisms, water has great power for self-purification. However, most of the human population lives on the banks of rivers, lakes and seas, so the water in some parts is so polluted that it is almost unusable. Water with its circular motion in nature comes in contact with substances of organic and inorganic origin, which dissolve in water. Some of these substances are necessary for the living organisms in the waters to certain concentrations, so that by exceeding those concentrations, the balance of the flora and fauna in the water is disturbed. The chemical composition depends on the type and origin of water, the elemental composition of the soil with which water is in direct contact and the processes that take place, then the biological activity in water and soil, dry and wet deposition of the atmosphere, precipitation, population of the area etc. (Naiman & Bilby 1998; Bhardwaj et al. 2008).

Surface waters such as rivers, lakes, swamps, streams, seas and oceans have higher amounts of mineral substances that come mainly from soils. As a result of the decomposition of biological material as well as the metabolic processes that take place in water, it also contains organic substances. The composition of these waters varies widely depending on the type of water. For example, freshwater is dominated by calcium and hydrocarbonate ions, while salt water is dominated by sodium and chloride ions. In fresh water there are about 30, and in salt about 70 elements but in insignificant quantity. The composition mainly depends on the geological composition of the terrain, the depth at which they are located and the time of its retention. The physical properties most commonly determined to assess water quality are temperature, odor, taste, color, density, turbidity, radioactivity, and conductivity (Gaillardet et al. 2003; Bhardwaj et al. 2008).

Natural water pollution can occur through the processes of soil erosion, then through precipitation that washes the soil, especially if it has been previously treated with pesticides or fertilizers or waste material is left on it, then by drainage of liquid landfills waste in agricultural holdings as well as through the dry and wet deposition of pollutants from the air. However, the most intense and dangerous sources are wastewater. Wastewater can come from communal needs or from the needs of various industries (textile industry, leather industry, food industry, paper and cellulose industry, metal industry, oil industry, chemical industry).

The data on the quality of the rivers in Northern Macedonia indicate that many of the rivers are polluted mostly due to the lack of treatment of communal waters from urban and rural areas (Dimitrovska et al. 2012, 2020; Levkov & Krstic 2002; Stafilov & Levkov 2007). However, detailed studies of certain river basins show a significant impact on water pollution with various potentially toxic elements (PTEs) as a result of past and present industrial activities. Thus, the river Vardar, which is the dominant river in Northern Macedonia, is influenced by industry and urban activities almost throughout its course, especially in larger cities such as Tetovo, Skopje and Veles (Dimitrovska et al. 2012, 2020; Levkov & Krstic 2002; Stafilov & Levkov 2007; Serafimovska et al. 2011; Stafilov 2014; Ilić Popov et al. 2014). Also, the impact of the pollution of the rivers from Bregalnica River Basin from the wastewater and flotation tailings from the mines for lead, zinc and copper is especially noticeable (Alderton et al. 2005; Dolenec et al. 2005; Vrhovnik et al. 2013; Ramani et al., 2014; Stafilov 2014; Balabanova et al. 2016). The impact of the pollution of the rivers from the Crna Reka watershed by the operation of the mine and the nickel smelter (Tomovski et al. 2018), as well as the abandoned mine for arsenic and antimony (Stafilov et al. 2013; Bačeva et al. 2014) has also been noticed.

The main goal of this work is to determine the concentration of various chemical elements in surface water samples collected from different locations of the Pčinja River Basin on the territory of the Republic of North Macedonia including some of its main tributaries and several locations of artificial lakes Glažnja and

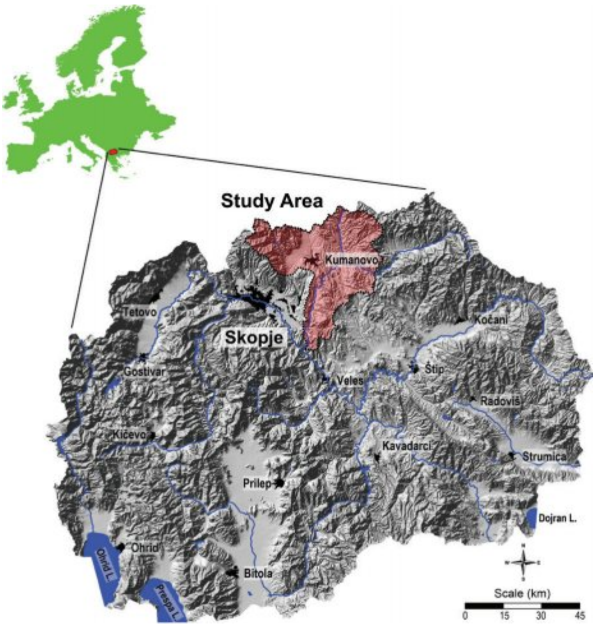

Figure 1. Location of the investigated area in the map of North Macedonia

Lipkovsko Lakes. The concentration of 22 chemical elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, P, Ni, Pb, Sr, V and Zn) was analyzed using inductively coupled plasma - atomic emission spectrometry (ICP-AES). Basic descriptive statistics were made on the obtained results. Comparative tests have been performed to determine the possible difference in the distribution of elements. A matrix of correlation factors was also created and the degree of correlation of the values of the concentration of chemical elements in water samples is shown by correlation coefficients in the matrix. Also, factor analysis as well as statistical processing through histograms for the representation of the elements through mean values divided by regions are applied to the obtained results.

Materials and methods

Study area

The investigated area is the watershed of the river Pčinja including the artificial accumulations of Glažnja and Lipkovsko Lake (Figure 1). This area is located in the northern part of North Macedonia including the major town of Kumanovo. Vegetation in the region can be classified into shrubs and grass vegetation, natural pastures, heterogeneous agricultural areas, hilly meadows and forests (Figure 2a). The mountain Skopska Crna Gora is a predominantly of cambisol soil with small areas containing lithosol and regosol. The most common soil in the examined region is vertisol which is dominant in the central and eastern part of the region. In the southern part along the Pčinja river basin before the inflow into the Vardar river, the most common soil is the cambisol, as well as the fluvial soil after the basin. Fluvial soil is observed along all rivers in this region (Filipovski et al., 2015). The least represented in this region are the colluvial and lithosol soil (Figure 2b).

Geological characteristics

In the eastern part of the region around the rivers Pchinja and Kriva Reka the most present are Neogene igneous rocks as well as Proteozoic metamorphic rocks and Paleogene clastitic sediments. In the central and

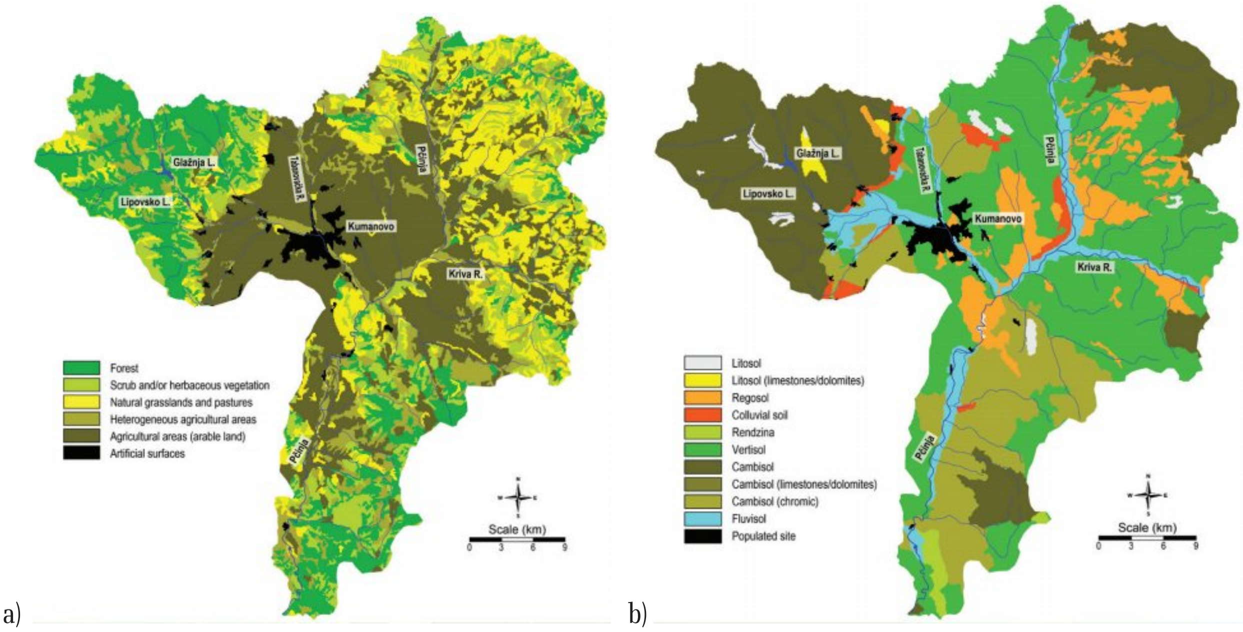

Figure 2. A land-use map (a) and the pedological map (b) of the investigated area (after www.maksoil.ukim/mk/masis/)

southern part, the most common are the Neogene clastic sediments, while the less common are the Quaternary deluvial and proluvial sediments and the Paleogene clastitic sediments. In the western part (the mountain Skopska Crna Gora) the most common are Paleozoic metamorphic rocks, Mesozoic clastitic sediments and Mesozoic igneous rocks (Figure 3).

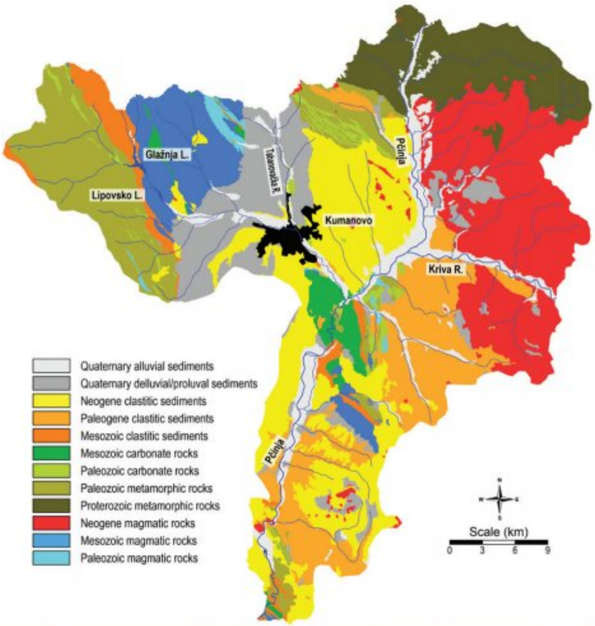

Figure 3. Geological map of the investigated area

The western part of the area is characterized by different geological composition and very complex tectonic structure. There are various types of sedimentary, metamorphic and igneous rocks that have Paleozoic, Mesozoic and Tertiary-Quaternary age. The rocks of this area are built of crystallized limestone, serpentine, granite and marble. The metamorphic complex of this series is quite complex and is characterized by lithological differences and different fractures of tectonic complexes. Marbles in this area appear in many zones and different shapes, especially in the vicinity of the villages of Lojane, Nikuštak and other locations. The serpentine mass appears around the village of Lojane as an elongated mass extending from the northwest. They originate from the Jurassic period. In the vicinity of the village of Slupcane, a series of granites, diabases and gabbrodiorts appear. Quaternary sediments are represented by sandstones, conglomerates, alluvial sediments and more. Most of these sediments occur in the zone of river outflows of the mountain complex. Such sediments have a wide spread in the bed of rivers Lojanska Reka, Suva Reka and Slupčanska Reka. Of the ores, the most important are the appearance of the ore of animony and arsenic in the rhyolites and serpentines near the village of Lojane, and in the area of the village of Nikuštak with the presence of antimony and nickel ores. The main ore minerals are stibnite and realgar with 6.50% As and 4% Sb (Markoski, 2005; UNDP, 2007; Stafilov and Šajn, 2016, 2019).

Climate characteristics

The area of the Kumanovo valley is open to the north, which enables unobstructed penetration of air masses from greater latitudes, which in the winter months affect the lowering of air temperature (Lazarevski, 1993; Zikov, 1995). Due to these reasons, the average annual temperature is 11.8°C. The warmest month is July with an average temperature of 22.3°C, and the coldest is January, with an average temperature of 0.4°C. The average annual minimum temperature is 8.0°C, and the average monthly temperatures are below 0°C only in January and February. In the summer part of the year in this area the warm continental air conditions quite high air temperatures. The average annual rainfall is 549 mm, with the range from 320 to 913 mm. The relative humidity decreases from January to August, and from this month to December it increases. The average annual relative humidity is 72% with a maximum in December (85%), and a minimum in August (60%).

Basic hydrological characteristics

The main hydrographic object in this area is the river Pčinja. It springs on the territory of Serbia, below the peak Bela Voda on the mountain Dukat, at an altitude of 1664 meters. The river valley has a composite character. From the entrance to the Republic of North Macedonia it passes through three gorges between which there are flat parts (Stojmilov 2011). It flows into Vardar in Taor gorge at an altitude of 191 m. The total length of the river is 135 km, with an average slope of 10.9‰. The average flow at the confluence is 16 m^3/s. The total area of the watershed is 2840 km^2 of which in North Macedonia 2317 km^2. On the territory of North Macedonia, river Pčinja receives 8 tributaries, of which on the right side only Kumanovska river 44.5 km long with a catchment area of 460 km^2, and on the left side the other 7 significant tributaries with a total length of 178.5 km and an area of basin of 1290 km^2.

One of the main features are the rather attractive artificial accumulation lakes Lipkovo and Glažnja. The first one is accumulated on the Lipkovska River, near the village of Lipkovo. It was built in 1958, on an area of 0.40 km^2, and 2,250,000 m^3 of accumulated water and its main purpose is water supply to the town of of Kumanovo. Downstream is a slightly larger lake called Glaznja. Located on the northeastern slopes of the mountain Skopska Crna Gora, built in 1973, it collects 22,000,000 m^3 of water. To use this water potential, the construction of the regional multipurpose hydrological system “Zletovica” for providing water for more than 200,000 inhabitants.

Materials and Methods

Sampling

In the period from June to September 2017, 10 samples of surface water were collected from the Pčinja River Basin. Depending on the location conditions and availability, samples were taken near the vicinity of the specified locations (Figure 4) whereby the samples were collected from five locations along the river Pčinja and five from its major tributaries (Tabanovska, Kumanovska, Konjarska and Kriva Reka rivers). Additionally, water samples were collected from the artificial accumulations Glažja and Lipkovo Lake (Figure 4). Three water samples and lake sediments were collected from Lake Glažnja and from one location of the one Lipkovo Lake. When collecting the samples, the geographical coordinates were recorded using a global positioning system and for each sample a sample designation, and date of sampling were written (Stafilov & Šajn, 2016, 2019).

From each location, one sample of water was taken in a sterile plastic bottle with a plastic closure. Surface water samples (11 each) were prepared immediately upon arrival in the laboratory, filtered through a Whatman membrane filter with a pore sizes <0.45 µm using a vacuum pump (Merck) and acidified.

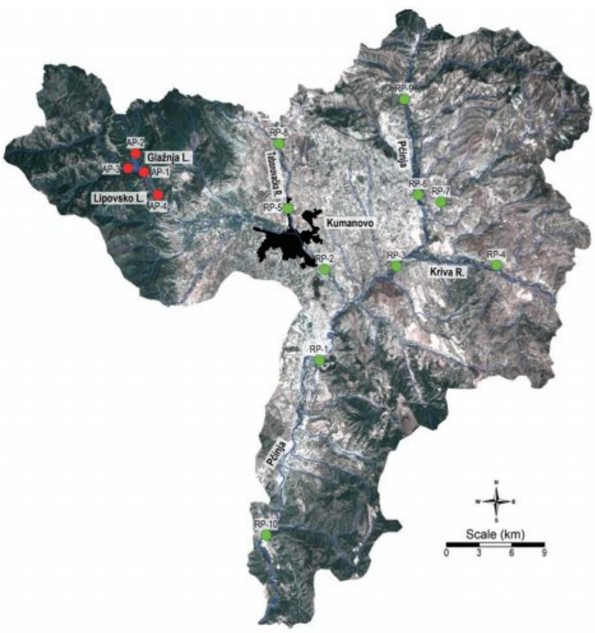

Figure 4. Sampling locations

Sample preparation and analysis

The water samples prepared immediately after their collection, filtered at the site on filter paper with a porosity of 2-3 µm and acidified with 1 ml of concentrated nitric acid (HNO_3, 69%, ultra pure) per 100 ml sample. Then the samples were stored in the refrigerator until the analysis. The reagent blank was prepared by filtering MilliQ water through the filter and acidified the sample.

The analysis of water samples was performed using inductively coupled plasma - atomic emission spectrometry (ICP-AES) model Varian 715 ES, according to the optimal parameters given by Balabanova et al. (2010). In all samples the concentrations of a total of 22 chemical elements are analyzed: Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, P, Ni, Pb, Sr, V and Zn.

The obtained data for elements concentrations were above the detection limit were statistically processed using StatSoft 11.0 software. For each type of sample, a basic descriptive statistical analysis of the values for the contents and concentrations of the elements was prepared. To assess the degree of correlation between the values of the concentration of the elements in the sediment samples and the concentrations in the water samples, bivariant statistics with a significance level $p <0.05$ was used; $p> 0.01$, and the correlation coefficients are represented in a correlation matrix.

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

Results and discussion

Table 1 shows the concentration of 12 elements (Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P, Sr and Zn) which are analyzed defined in the water samples, while Table 2 gives a descriptive statistical values of the concentrations of the elements in all 14 samples of water from rivers and lakes. Concentrations of the remaining elements are below the ICP-AES detection limit: <0.001 mg/l for Ag, Cd and Cr, <0.01 mg/l for Co and Li, and <0.1 mg/l for As, Ni, Pb, Mo and V. Table 2 shows the values for arithmetic mean, median, minimum and maximum, arithmetic standard deviation, coefficient of variation, asymmetry and kurtosis for the elements in water samples from all 14 locations.

To determine the degree of correlation between the concentrations of the elements in the water samples from the whole basin of the river Pčinja bivariant statistics was used according to which there is a strong correlation between the analysed elements if the absolute value of the correlation coefficient is from 0.7 to 0.9 and good correlation between the examined elements exists if the correlation coefficient is between 0.5 and 0.7. Table 3 shows the matrix of correlation coefficients for all elements applying Pearson parametric correlation test. It can be seen that there is a strong correlation between the concentrations of the following elements: Al-Fe (0.99), Al-Mn (0.96), Fe-Mn (0.94), Ba-Sr (0.92), K-Sr (0.85), K-Na (0.84), Mg-Mn (0.79), Ba-K (0.78) and Al -Mg (0.71), while there is a good correlation between the concentrations of the following elements: Fe-Mg (0.66), Mg-Sr (0.63), Na-Sr (0.62), Na-P (0.59), Ba-Na (0.57), Fe-Zn (0.53), Mn-Zn (0.52)

Table 1. Average concentration of the analysed elements in surface water samples (in mg/l). Bold typeface denotes exceeding the maximum permissible concentrations.

Location	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	P	Sr	Zn
RP-1[a]	0.12	0.043	49.2	0.041	0.23	4.59	13.8	0.027	21.2	**0.087**	0.223	0.001
RP-2	0.16	0.034	30.8	0.048	0.26	3.45	23.3	0.025	13.7	**0.068**	0.208	0.001
RP-3	0.02	0.063	30.7	0.001	0.07	4.09	12.2	0.017	14.3	**0.056**	0.242	0.001
RP-4	0.02	0.067	64.1	0.036	0.08	3.10	11.8	0.016	9.28	**0.056**	0.221	0.001
RP-5	1.08	0.093	42.0	0.021	**1.53**	4.04	55.5	0.42	15.1	**0.066**	0.330	0.002
RP-6	0.03	0.100	23.7	0.012	0.05	5.79	18.6	0.006	12.8	**0.061**	0.490	0.001
RP-7	0.09	0.036	59.8	0.034	0.19	2.91	8.13	0.017	7.62	**0.050**	0.161	0.002
RP-8	0.13	0.057	100	0.025	0.22	3.67	40.2	0.033	14.7	0.048	0.328	0.001
RP-9	0.06	0.047	35.9	0.030	0.17	4.76	10.6	0.021	15.3	**0.074**	0.235	0.001
RP-10	0.17	0.062	19.3	0.015	**0.36**	4.98	16.9	0.089	20.4	**0.074**	0.240	0.001
AP-1[b]	0.12	0.014	21.5	**0.028**	0.26	2.42	5.29	0.009	6.21	**0.062**	0.083	0.002
AP-2	0.34	0.024	22.1	**0.018**	**0.61**	2.06	5.27	0.027	3.86	**0.062**	0.085	0.001
AP-3	0.18	0.019	29.4	**0.022**	**0.33**	2.01	5.46	0.016	5.14	**0.061**	0.083	0.001
AP-4	0.09	0.010	31.8	0.001	0.16	2.01	4.43	0.009	3.27	**0.057**	0.066	0.001
MPC[c]	**1.5**	**4.0**		**0.05**	**1.0**			**1.0**		**0.05**		**0.2**
MPC[d]	**1.5**	**1.0**		**0.01**	**0.3**			**0.05**		**0.05**		**0.1**

aRP – River samples, bAP – Lake samples; cMPC – Maximal permitted concentrations in surface water;

dMPC – Maximal permitted concentrations in surface water in lakes (Regulation on the classification of waters, Official gazette of Republic of Macedonia, No. 18, 1999)

Table 2. Descriptive statistics of the concentrations of the elements in 23 surface water samples of the river Pčinja and the Glažnja and Lipkovo Lakes (in mg/l)

Element	X	Md	Min	Max	S	Sx	CV	A	E
Al	0.19	0.12	0.022	1.1	0.27	0.072	145	3.18	10.89
Ba	0.048	0.045	0.010	0.10	0.028	0.0074	58	0.49	-0.46
Ca	40	31	19	100	22	5.9	55	1.72	3.22
Cu	0.024	0.024	0.001	0.048	0.014	0.0037	58	-0.13	-0.37
Fe	0.32	0.22	0.046	1.5	0.38	0.10	117	2.92	9.41
K	3.6	3.6	2.0	5.8	1.2	0.32	34	0.21	-0.95
Mg	17	12	4.4	56	15	3.9	89	1.86	3.26
Mn	0.053	0.019	0.006	0.42	0.11	0.029	207	3.53	12.78
Na	12	13	3.3	21	5.8	1.6	50	0.06	-1.03
P	0.063	0.061	0.048	0.087	0.010	0.0028	17	0.81	0.93
Sr	0.21	0.22	0.066	0.49	0.12	0.032	55	0.78	0.94
Zn	0.0012	0.0011	0.0006	0.0019	0.0003	0.0001	33	0.53	-0.58

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

Table 3. Correlation matrix for the analyzed elements in samples from surface water from the investigated area. Red and bold typeface denotes very high correaltion; red typeface denotes high correlation.

	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	P	Sr	Zn
Al	1.00											
Ba	0.31	1.00										
Ca	-0.05	0.17	1.00									
Cu	-0.02	-0.12	0.32	1.00								
Fe	**0.99**	0.26	-0.08	-0.01	1.00							
K	-0.03	**0.78**	-0.01	0.00	-0.05	1.00						
Mg	**0.71**	0.64	0.42	0.09	0.66	0.38	1.00					
Mn	**0.96**	0.49	0.02	-0.05	**0.94**	0.17	**0.79**	1.00				
Na	0.09	0.57	0.16	0.22	0.07	**0.84**	0.48	0.27	1.00			
P	0.14	0.02	-0.41	0.30	0.16	0.44	-0.02	0.15	0.59	1.00		
Sr	0.13	**0.92**	0.24	-0.04	0.07	**0.85**	0.63	0.29	0.62	0.04	1.00	
Zn	0.52	-0.04	0.22	0.39	0.53	-0.28	0.33	0.52	-0.05	-0.08	-0.19	1.00

and Al-Zn (0.52). Ca and Cu do not show or have a very weak correlation with the concentrations of the other elements.

From the multivariate factor analysis of the obtained data for the concentrations of the elements in all samples, a matrix of load factors is obtained given in Table 4. The factor analysis distinguishes two factors of which Factor 1 (F1) has a higher value of load of 3.56 and variability of 44.6% of the total variability which is 88.9%. The first factor connects the alkaline and earth-alkaline elements (K, Sr, Ba and Na). The second factor (F2) represents 44.4% of the total variability of the matrix with a load value of 3.55 and connects the elements Al, Fe Mn and Mg.

Table 4. Matrix of factor loads – factor analysis of the concentrations of investigated elements in surface water samples from the investigated area. Boldface type denotes high factor scores.

	F1	F2	Comm
K	**0.96**	-0.06	92.6
Sr	**0.94**	0.13	89.3
Ba	**0.87**	0.31	84.8
Na	**0.83**	0.07	69.3
Al	0.01	**0.99**	98.7
Fe	-0.03	**0.98**	97.1
Mn	0.22	**0.96**	96.8
Mg	0.52	**0.74**	82.6
Prp.Totl	44.6	44.4	88.9
Expl.Var	3.56	3.55	
EigenVal	4.52	2.59	

F1 and F2 - Factor loadings of Factors 1 and 2; Comm-Communality (%), Prp. Totl - Total amount of the explained system variance; Expl. Var - particular component variance; Eigen Val – Eigen value

The standard factor values of F1 and F2 for the distribution of the elements in all zones of the examined area are shown on the maps of spatial distribution (Fig. 5). From Fig. 5 it can be seen that the distribution of alkaline-earth elements is evenly distributed in the waters of the river Pčinja and its tributaries except in the waters of the Lipkovska River and the lakes Glažnja and Lipkovo Lake. On the other hand, the distribution of the elements from the second geochemical association is higher only in the waters of Kumanovska Reka while in the waters from all other locations this correlation is very small.

The first association (F1) includes two alkaline (K and Na) and two earth-alkaline (Ba and Sr) elements. The distribution maps of these elements are presented in Fig. 6. From data given in Table 1 and Figs. 5 and 6 it can be seen that the concentration of these elements in water samples has the highest value in the sample from the Pčinja river collected near the village of Staro Nagoričane, while the lowest value was determined in water from both lakes. The increase of the concentration of these elements in the water samples from the river Pchinja in its upper course is probably due to the increased content of these elements in the soils of that area (Stafilov & Šajn, 2016) and is a result of their increased lithological presence in this area which from geological aspect attributed to the Neogene magmatic roks. Of these four elements, only the barium concentration is limited in the surface waters in North Macedonia according to the Regulation on the classification of waters (Official gazette of Republic of Macedonia, 1999) of 4.0 mg/l for river waters and 1.0 mg/l for lake's waters and it was determined that its concentration in all water samples is significantly lower than these limit concentrations.

The second association (F1) includes Al, Fe, Mn and Mg. The distribution maps of these elements are presented in Figure 7. From data given in Table 1 and Figures 5 and 7 it can be seen that the concentration of these elements in water samples has the highest value in the sample from the Tabanovska and Kumanovska Rivers (northwestern part of the study area) and the

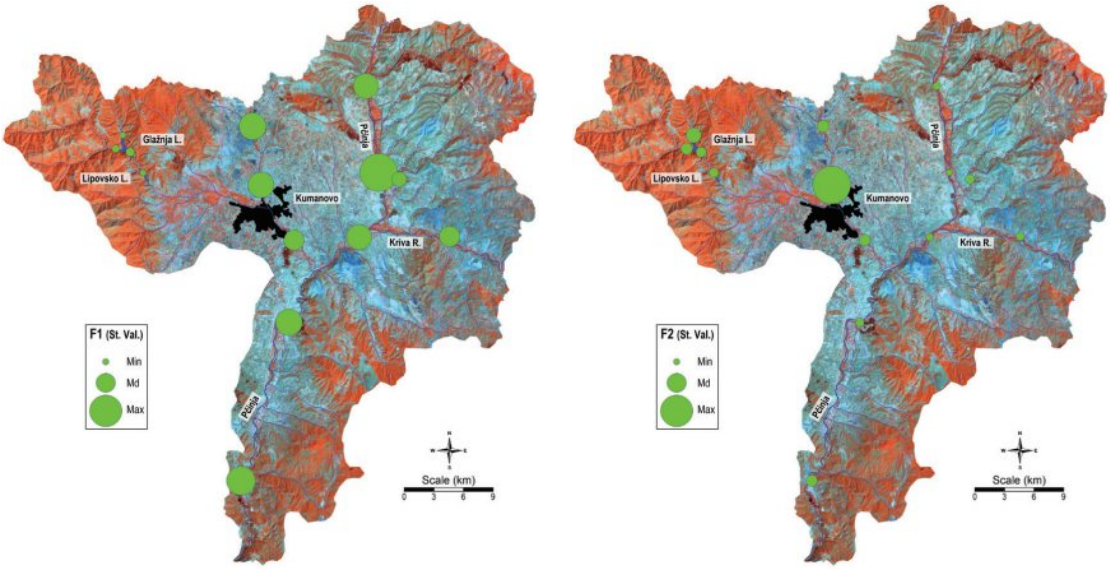

Figure 5. Spatial distribution of the factor scores of Factor 1 (F1) and Factor 2 (F2) in water samples

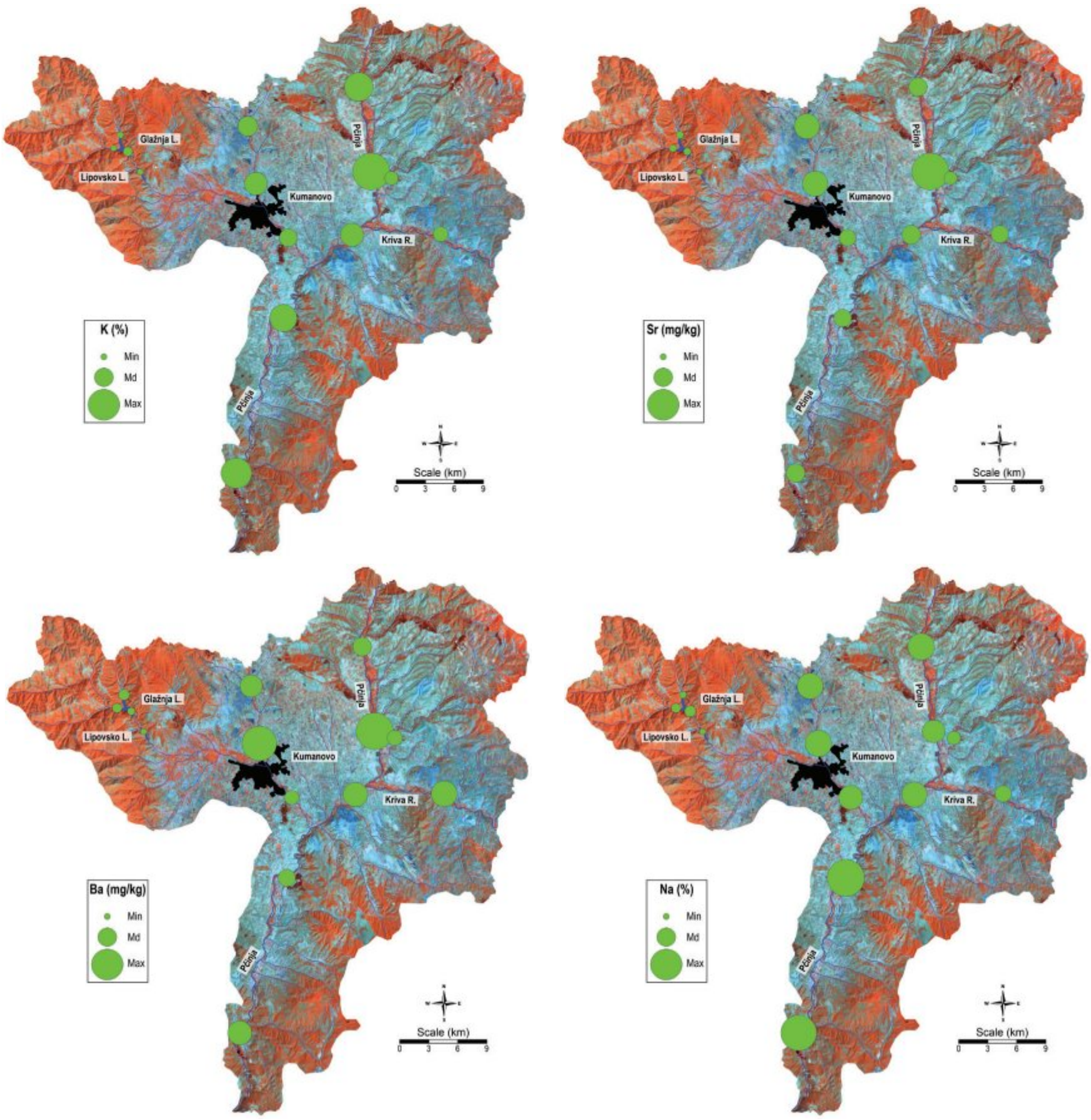

Figure 6. Spatial distribution of the elements from F1 (K, Sr, Ba and Na) in water samples

lowest value was determined in water from both lakes. The increase of the concentration of these elements in the water samples from these tributaries is probably due to the increased content of these elements in the soils of that area (Stafilov & Šajn 2016) as a result of their increased lithological presence in this area which from geological aspect attributed to the Mesozoic magmatic rocks Paleozoic metamorphic rocks. The concentrations of Al, Fe and Mn are limited according to the Regulation for surface waters in Macedonia (Official gazette of Republic of Macedonia, 1999) but from the data presented in Tables 1and 2 it can be seen that in no case do the concentrations of these elements exceed the maximum permitted concentration.

The elements that are not included in the factor associations due to the absence of a satisfactory association with other elements are Ca, Cu, P and Zn. Their distribution maps are presented in Fig. 8. The average concentration of Ca in the water samples is 40 mg/l ranging from 19.3 mg/l to 100 mg/l (Tables 1 and 2). The highest in sample from Tabanovska River near the village of Tabanovce (100 mg/l), while the lowest in Pčinja River near the village of Katlanovo (19.3 mg/l) before its inflow into the river Vardar (Figure 8).

The spatial distribution of copper in the water samples is given in Figure 8. The results obtained for the whole region are probably due to the relatively increased content of copper in the soils in this region (Stafilov & Šajn, 2016), as well as the use of copper as a pesticide, insecticide and as a fertilizer in the treatment of arable land. The average concentration of copper is 0.024 mg/l ranging from 0.001 mg/l to 0.48 mg/l). The concentrations of Cu in all river water samples are below the maximal permitted concentration according to the Macedonian legislation for river waters (0.05 mg/l) while its concentration in the lake's water samples is higher than the maximum permitted concentration for copper for the lake waters (0.01 mg/l) (Tables 1 and 2).

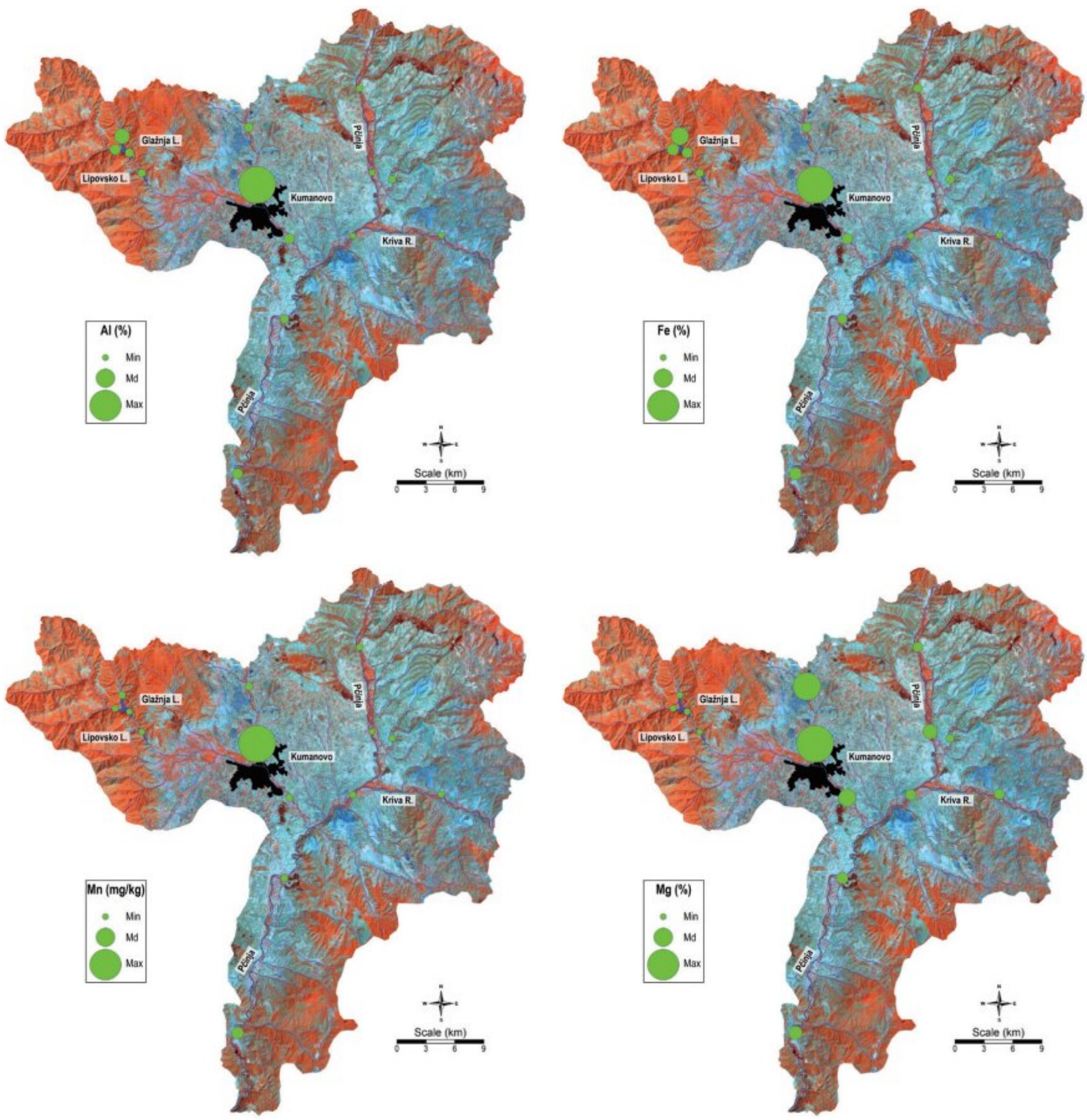

Figure 7. Spatial distribution of the elements from F2 (Al, Fe, Mn and Mg) in water samples

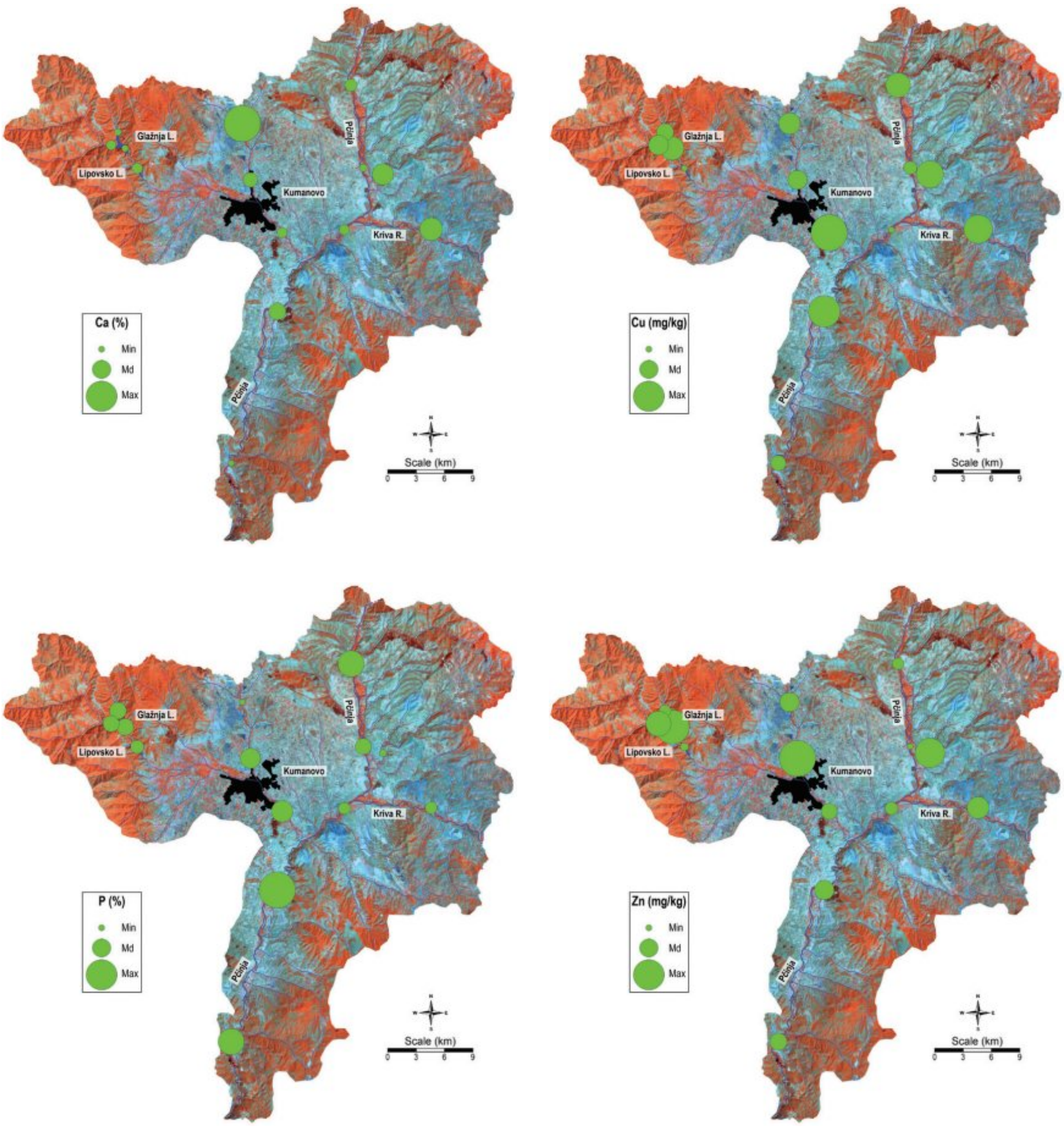

Figure 8. Spatial distribution of Ca, Cu, P and Zn

From the spatial distribution of phosphorus (Figure 8) it can be noticed that the its concentration is above the permissible limits in the samples of surface water of first and second class according to the Regulation, except for the water samples from Tabanovska River (RP-8) with a concentration of 0.048 mg/l (Table 1). The high concentration of phosphorus in the water samples is mostly as a result of wastewater from households, industries, municipal wastewater, as well as drainage water from agricultural areas.

The values for the concentration of Zn in the waters from Pčinja River basin and the Glažnja and Lipkovo Lakes (Figure 8) are significantly below the maximum allowed concentration of Zn of 0.2 mg/l (Official Gazette of the Republic of Macedonia, No. 18, 1999).

Conclusion

The distribution of different chemical elements in surface water samples from the basin of the river Pčinja River Basin, North Macedonia, was assessed using multivariate factor analysis, spatial distribution and correlation analysis. It was found that there is a strong correlation between the concentrations of the following elements: Fe-Al (0.99), Mn-Al (0.96), Sr-Ba (0.92), Fe-Mn (0.94) Sr-K (0.85), Na-K (0.84), Mn-Mg (0.79), Ba-K (0.78). There is a good correlation between the concentrations of the following elements: Mn-Al (0.71), Mn-Ba (0.56), Mg-Ba (0.64), Mg-Fe (0.66), Mg-Sr (0.63), Sr-Na (0.62), Na-P (0.59) and Na-Ba (0.57).

The obtained results for the presence of the potentially toxic elements in water samples from the whole study area, show that their concentrations are mainly below the maximum allowed concentration according to the Regulation on water classification of North Macedonia, except for the concentrations for Fe in the water of the river Pčinja immediately after the inflow Konjarska River, as well as the concentration of phosphorous in the samples from almost all locations which is much higher than the maximum allowed concentrations. In general, it could be concluded that the distribution of most of the elements follows the lithology of the study area, except for some elements (Cu, P) whose increased concentrations are as a result of urban and agricultural industrial activities.

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