Macedonian Journal of Ecology and Environment
Vol. 25, issue 1
pp. 43 - 55
Skopje (2023)
ISSN 1857 - 8330 (on-line)
ISSN 0354-2491 (print)
Original scientific paper
Available online at www.mjee.org.mk
DOI: https://doi.org/10.59194/MJEE23251043t

Distribution of chemical elements in surface waters from the Strumica River Basin, North Macedonia

Katerina Trajanova[1], Robert Šajn[2], Trajče Stafilov[1]*

[1]*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss Cyril and Methodius University in Skopje, Arhimedova 5, 1001 Skopje, North Macedonia;*

[2]*Geological Survey of Slovenia, Dimičeva ul. 14, 1000 Ljubljana, Slovenia*

Abstract

In this work, the distribution of chemical elements in samples of surface water from the Strumica River Basin, North Macedonia, was studied. The water samples were collected from a total of twelve sites. In addition to the Strumica River, samples were collected from its tributaries: Bansko, Dabile, Turija, Vodoča, Radoviška, and Injevska. The determination of the concentration of 21 elements (Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V, and Zn) was performed by inductively coupled plasma - atomic emission spectrometry (ICP-AES). All detailed information on the studied items was statistically processed using Stat Soft, 11.0 software. Using the obtained data on the concentration of the studied elements, descriptive statistical analysis of the values for the concentration of the elements was performed. A map of spatial distribution was obtained for each element. The obtained results show that the concentrations of the studied elements in the surface water samples are relatively low and the distribution of most of the elements follows the lithology of the study area.

Key words: rivers, surface water, heavy metals, Strumica River Basin, North Macedonia

Introduction

The demand for water increases day by day. This increase is due to the constant growth of the population, the enormous development and progress of industry, which requires large quantities of water in all its processes, and the intensive use of water for the irrigation of cereals and other crops. Today, it is quite obvious that water is a source of life, work, food, and energy, and that its scarity is a crucial factor for economic development (Kabata-Pendias & Mukherjee 2007). The growing world population, the development of industry, agriculture, and food technology, and urbanization, require ever-increasing amounts of water. Under these conditions of increased consumption, water pollution is also increasing. Natural or anthropogenic changes in water quality that make the water unusable or dangerous to humans, animals, and plants are considered pollution. Human activities are major contributors to water pollution. The cycling of matter and energy includes the cycling of pollutants that pollute the hydrosphere (Drever 2005; Naiman & Bilby 2007; Bhardwaj et al. 2008).

Surface waters are carriers of large amounts of various wastes. Pollution of surface waters is usually caused by wastewater from households, various industrial plants, and large urban agglomerations located on rivers or lakes. The introduction of new alien species, acidification from atmospheric sources, and the draining of agricultural lands are particular factors that negatively affect lake and river ecosystems and, consequently humans. Today's pollution problem is closely related to heavy metal pollution, which plays a significant role in the environment. The existing

Submitted: *02.02.2023;*
Accepted: *20.02.2023*

* Author for correspondence: *trajcest@pmf.ukim.mk*

heavy metals are deposited in the atmosphere, which contributes to the contamination of all components of the biosphere (water, soil, and vegetation). Therefore, in order to maintain or improve the quality of the environment, studies should be conducted to identify the pollutants and the extent of pollution, and then determine where and to what extent protective measures should be taken (Kabata-Pendias & Mukherjee 2007; Darby & Sear 2004; Ilić Popov et al. 2014).

The state of water quality in North Macedonia indicates an already disturbed natural balance in watercourses, due to pollution of rivers with organic matter and heavy metals. Water pollution in the environment is due to the release of wastewater from households, industry, mining, agriculture, untended landfills and roads. The amount of municipal wastewater is greatest in urban areas, so pollution is particularly high downstream of cities. In addition to the impact of human activities, water quality is directly related to the amount of water. The more water there is, the greater the ability of the water body to clean itself (Markoski 2006; Popovska & Geshovska 2014). About 2% of the territory of North Macedonia is under the water surface. There are about 35 rivers and 53 natural and artificial lakes. In terms of water quantity, Macedonia is an area with satisfactory water resources, but they are unevenly distributed. The rivers belong to 6 basins: the Vardar 20,546 km^2, the Crn Drim 3,355 km^2, the Strumica 1,520 km^2, the Dojran Lake 120 km^2, the Lebnička River 129 km^2, and the Binačka Morava River 44 km^2 (Popovska & Stavric 2004; Popovska 2014; Popovska & Geshovska 2014).

The Strumica River Basin ecosystem is vital for the population living in the area. It provides drinking and irrigation water for 124,500 people and is a natural habitat for many plants and animals. The Strumica River Basin is a particularly fragile ecosystem that is threatened by the effects of climate change, agriculture that affects water levels and quality, excessive use of fertilizers and pesticides, and the use of water for irrigation. Although the occurrence of various chemical elements in surface waters of other river basins in North Macedonia has been extensively studied (Pavlov et al. 2012; Ilić Popov et al. 2014; Balabanova et al. 2016; Vasilevska et al. 2018; Tomovski et al. 2018; Stafilov et al. 2021), no such study has been conducted for the Srumica basin. Most studies on the quality of water from the Strumica basin relate to groundwater and drinking water, and the presence of potentially toxic elements was found to be of lithogenic origin and mainly due to the geological composition of the area or agricultural activities (Kostik et al. 2014; Kovacevik et al. 2015, 2016; Boev et al. 2016).

Therefore, the main objective of this study is to determine the concentration of chemical elements and their distribution in surface water samples collected from different locations in the Strumica River basin. There are no data on the presence of various chemical elements in the Strumica River basin, except for parts of the basin that have already been partially studied. Along the Strumica River, water samples were collected at 12 locations in March-April 2015 as a part of a previously established network. The concentration of a total of 21 chemical elements (Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V and Zn) was analysed by inductively coupled plasma - atomic emission spectrometry (ICP-AES).

Basic descriptive statistics for the concentration of the analyzed elements were performed for the obtained results. In parallel, normalization tests were performed. Based on the obtained results and the distribution histograms for each analyzed chemical element, the distribution of the content of the elements was determined.

Materials and methods

Study area

The study area includes the catchment area of the Strumica River located in the southeastern part of North Macedonia (Figure 1). According to its formation, it is a tectonic rift with a Dinarid orientation, so it is naturally open to the Radoviš valley in the northwest and to the Petrič valley in the southeast. The natural boundaries of the valley are determined according to the principles of tectonics and catchment areas, which concern the Strumica Graben with the lower catchment area of the river. The Strumica valley is demarcated from neighboring valleys and catchments by mountain horsts (Manaković & Andonovski 1981; Cankov & Stojanov 2005; Pavlov & Vasilevski 2012).

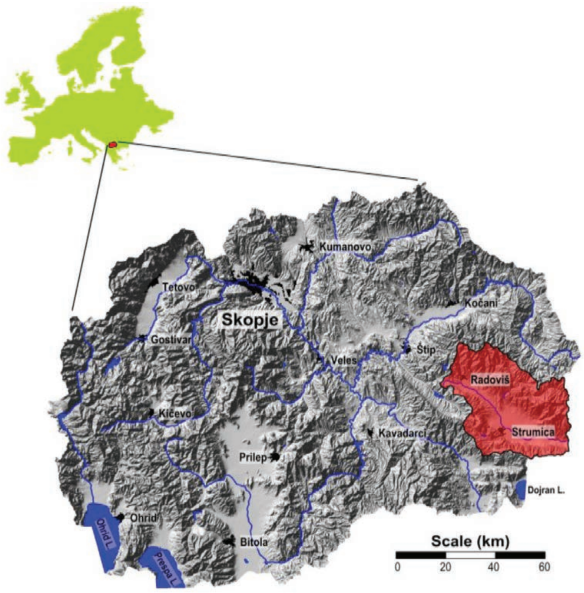

Figure 1. Map of the Republic of North Macedonia with the Strumica River Basin

Geological composition is an important factor in hydrological characteristics. In the Strumica River

Basin (in the Strumica Valley part), there are magmatic, metamorphic, and sedimentary rocks of different ages from the Precambrian to the youngest forms of the Holocene. Tectonically, the Strumica Valley belongs mainly to the Serbian-Macedonian Massif which is characterized by two structural complexes. These are the lower highly metamorphic complex with amphibolite facies and the upper metamorphic complex of green slate facies (Arsovski 1997).

The geological map of the study area is shown in Figure 2. In the northern part, i.e. along the Radoviška River, Quaternary alluvial sediments and Neogene classical sediments dominate, while Quaternary deluvial/proluvial sediments are less common. The central part is dominated by similar formations, with Paleozoic igneous rocks present in some parts. Mount Plačkovica in the northern part of the basin consists mainly of Proterozoic metamorphic rocks, while mount Ogražden on one side and Belasica on the other side in the southern part consist mainly of Paleozoic igneous rocks and Proterozoic metamorphic rocks. The western part of the basin represents the ridges of the Plavuš, Gradeška, and Smrdeš Mountains, and consists mainly composed of Neogene clastitic sediments (Gaševski 1975; Rakičević et al. 1980; Arsovski 1997; Stafilov & Šajn 2016; Petrušev et al. 2021).

Climate properties

The particular geographical and topographical position of the Strumica region is characterized by two climatic zones: the sub-Mediterranean climate and the continental climate. The sub-Mediterranean climate is characterized by long, hot summers with high average daily temperatures and lower annual precipitation, while in winter temperatures drop and winds come from all directions (Lazarevski 1993). The duration of solar radiation for the Strumica Valley was calculated on the basis of cloud cover, and the following results were obtained: the average annual duration of solar radiation is 2472 hours (Lazarevski 1993). It is longest in July with 340 hours, and shortest in January with 108 hours. As for the air temperature, the average monthly and annual temperatures from various measurements ranges from 12.4°C to 13.4°C (Gaševski 1975; Lazarevski 1993).

In the Strumica Valley, winds blow most frequently from the northwest (166‰), with an average annual speed of 2.1 m/s. The second most common is the southwest wind with 92 ‰ and an average speed of 1.7 m/s. The third most common is the south wind with an average annual frequency of 87‰ and an average speed of 1.8 m/s. The values for the winds from the other directions are west wind (frequency 72 ‰; the average annual speed of 1.9 m/s); north wind (frequency 71‰; the average annual speed of 1.8 m/s); southeast wind (frequency 62‰; the average annual velocity of 1.6 m/s); east wind (frequency 49 ‰; the average annual velocity of 1.3 m/s); northeast wind (frequency 34 ‰; the average annual velocity of 1.3 m/s) (Lazarevski, 1982). The average annual relative humidity in the Strumica Valley is 69%. Humidity decreases from January to July, when it is minimal, and then increases until December (Lazarevski 1993; Zikov 1995).

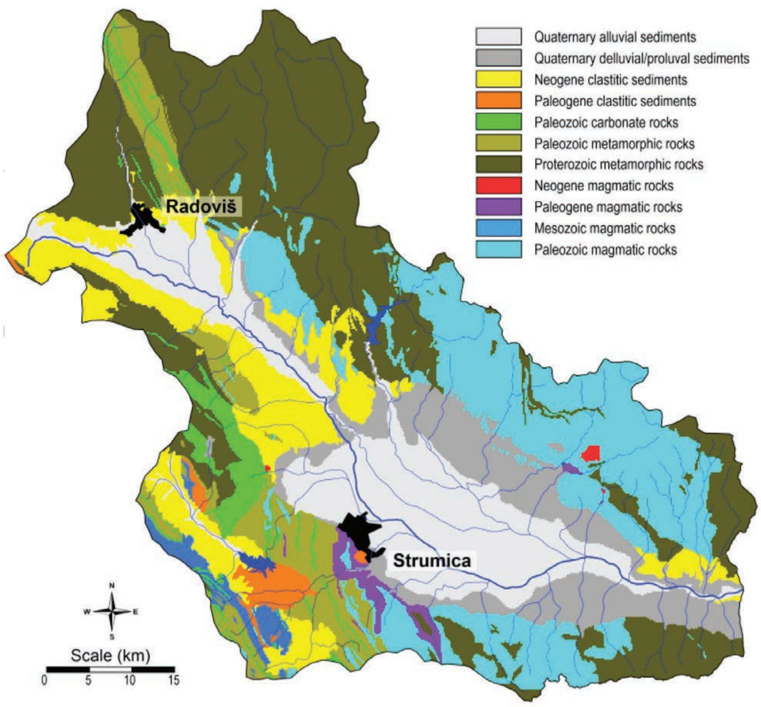

Figure 2. Geological map of the study area

Hydrographic features

The total area of the Strumica River basin in the Strumica Valley is 999.4 km^2. Most of the total catchment area (75%) is located in the Republic of North Macedonia, the rest in the Republic of Bulgaria and the Republic of Greece. The Strumica River has a total length of 114 km, of which 81 km are in North Macedonia and 33 km in Bulgaria. It is the largest tributary of the Struma River. The source of the Radoviška River is at 1540 m.a.s.l. After the confluence with the Oreovačka River through the Radoviš Valley, it is called Stara Reka, where it takes the first major tributary, the Plavia (Sermeninska River), from the left side. On its way through the Dervenska gorge downstream from the village of Radičevo, it enters the Strumica Valley, where it is called Strumica. In this part, the Strumica takes in the largest tributaries: Turia, Vodočnica and numerous torrential streams coming from the high parts of Belasica and Ogražden mountains. Downstream from Novo Selo, the Strumica River leaves the Strumica field and flows through the narrow Ključ Gorge into neighboring Bulgaria (Pavlov & Vasilevski 2012; Popovska & Geshovska 2014).

The flow regime in the Strumica River basin in the Strumica Valley corresponds to the pluviometric regime, the type of substrate, vegetation, and evapotranspiration, on which the runoff depends. The lowest average monthly flow in the period 1991-2000 was measured in August (0.32 m^3/s), when the average monthly precipitation has the lowest value of 28.1 mm in the central part of the valley at the monitoring station in the town of Strumica. The highest flow at the measuring station near the village of Novo Selo was registered in 1996 (5.41 m3/s), which is considered one of the wettest years, when 679.1 mm was discharged in Strumica, when it is known that the average is 524.7 mm (Gaševski 1975; Pavlov & Vasilevski 2012).

The regime of runoff in the Strumica River basin in the Strumica Valley corresponds to the pluviometric regime, the type of substrate, vegetation and evapotranspiration, on which the runoff depends. The lowest average monthly runoff in the period 1991-2000 was measured in August (0.32 m^3/s), when the average monthly precipitation in the central part of the valley has the lowest value of 28.1 mm at the measuring station in the town of Strumica. The highest discharge was recorded at the gaging station near the village of Novo Selo in 1996 (5.41 m^3/s), which is considered one of the wettest years, when 679.1 mm was discharged in Strumica, while it is known that the average is 524.7 mm (Gaševski 1975; Pavlov & Vasilevski 2012).

Sampling

In the period from March to April 2015, 12 surface water samples were collected from the Strumica catchment (Figure 3). Depending on site conditions and availability, samples were collected in the immediate vicinity at the locations indicated in Table 1. Two water samples were collected at the first location at the border crossing with Bulgaria. The second site is also located on the Strumica River near the village of Novo Selo. The next location where the samples were taken is the Strumica River near the village of Bansko. The samples from the river Turija were taken just before the confluence with the river Strumica. This is followed by the samples from the Vodochnica River, 100 m from the Vodoča Monastery. The eleventh site is the Stara Reka River, which flows through the town of Radovish

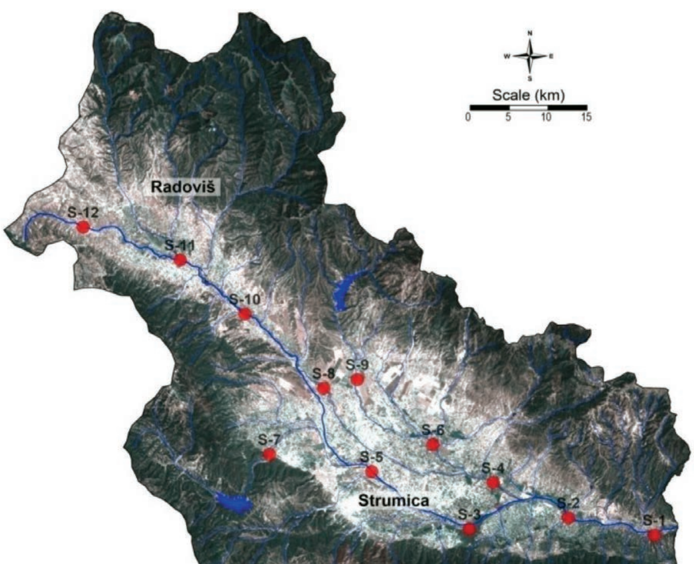

Figure 3. Topographic map of the studied catchment area with the locations of the water samples

Table 1. Data of the sampling location

No.	River	Location	N/°	E/°	Class*
S-1	Strumica	Border crossing with Bulgaria	41.38900	22.94555	III
S-2	Strumica	Village Novo Selo	41.40358	22.86572	III
S-3	Bansko	Village Bansko	41.39584	22.77472	II
S-4	Strumica	Village Turnovo	41.42838	22.79751	III
S-5	Strumica	Village Dabile	41.43828	22.68498	III
S-6	Turija	Village Petralinci	41.45800	22.74213	II
S-7	Vodoča	Village Vodoča	41.45138	22.59097	III
S-8	Strumica	Village Vasilevo	41.49882	22.64234	III
S-9	Turija	Village Dobrašinci	41.50463	22.67255	II
S-10	Radoviška River	Village Dukatino	41.55184	22.57091	III
S-11	Radoviška River	Village Syurdulci	41.59205	22.51158	III
S-12	Injevska River	Village Injevo	41.61688	22.42244	II

*Class according to the Decree on Water Classification of the Republic of Macedonia (Official Gazette of the Republic of Macedonia, No. 18, 1999).

and divides the town into two parts. The last site is the Injevska River near the village of Injevo, from which it takes its name.

During sampling, geographic coordinates were recorded using a global positioning system, and each sample was labeled with the sample marker, sample type, and date of sampling. At each site, a water sample was collected in a completely sterile plastic bottle with a plastic cap. The surface water and urban water samples were processed immediately upon arrival at the laboratory, filtered through a filter paper with a porosity of 2-3 µm, and acidified with 1 ml of concentrated nitric acid (HNO_3, 69%, high purity). Thus, the preserved samples were stored in the refrigerator until analysis.

Instrumentation

Water samples were analysed by inductively coupled plasma - atomic emission spectrometry (ICP-AES), Varian model 715 ES, according to the optimal parameters given by Balabanova et al. (2010). A total of 21 chemical elements were analysed in all samples: Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V, and Zn. All data on the concentration of the studied elements were statistically processed using the software Stat Soft, 11.0.

Results and discussion

Twelve samples of surface water from the catchment area of the Strumica River were collected in the study area. The results of the analysis of 21 elements analysed in these samples (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, V and Zn) are presented in Table 2, while Table 3 contains the descriptive statistics of the values for the concentrations of the elements with a concentration above the detection limit (Al, Ba, Ca, Cu, Fe, K, Li, Mg, Mn, Na, Sr and Zn). Table 3 shows the values for the arithmetic mean, Box-Cox transformed mean, median, minimum and maximum, 10th percentile, 25th percentile, 75th percentile, and 90th percentile, arithmetic standard deviation, standard deviation, coefficient of variation, asymmetry, and kurtosis.

Tables 2 and 3 show that the highest values for the arithmetic mean, Box-Cox transformed mean and median for calcium were 55 mg/L, 54 mg/L, and 52 mg/L, respectively. The highest calcium concentration of 96 mg/L was determined in the water sample from the Radoviška River. It was found that the concentrations for Ag, Cd, Co, Cr, Ni and Mo were below the detection limit of 0.001 mg/L, as well as for V with 0.005 mg/L and for As and Pb with 0.01 mg/L. According to the Regulation on Classification of Rivers, Lakes, Reservoirs and Surface Waters of the Republic of Macedonia (Official Gazette RM, No. 18, 1999), the waters in the catchment area of the Strumica River belong to the second class and in some areas to the third class (Table 1).

From the data given in Table 2, it can be seen that the concentrations of 9 elements were below the detection limit: 0.001 mg/L for Ag, Cd, Co, Cr, Mo, and Ni; 0.01 mg/L for As and Pb; and 0.05 mg/L for V. Therefore, the results for the concentrations of the remaining elements (Al, Ba, Ca, Cu, Fe, K, Li, Mg, Mn, Na, Sr, and Zn) are discussed in the following text.

Aluminum is one of the most abundant metals in the earth's crust. It is assumed that 8% of the earth's crust consists of aluminum. Aluminum does not occur in nature in elemental form but is always associated with various substances in rocks and soil. Higher concentrations of aluminum can negatively

Table 2. Concentrations of analysed elements in surface water samples from 12 locations in the Strumica River basin (in mg/L)

Element	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10	S-11	S-12	MAC*	MAC**
Ag	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	0.02
Al	0.37	0.40	0.16	0.30	0.11	0.35	0.21	0.15	0.45	0.18	0.12	0.34	1.5	1.5
As	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	0.05
Ba	0.035	0.034	0.031	0.033	0.016	0.029	0.022	0.038	0.034	0.049	0.034	0.046	1.0	4.0
Ca	46.4	52.1	76.7	37.8	44.1	21.7	67.9	51.3	19.3	96.5	69.1	76.3	-	-
Cd	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	0.01
Co	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.1	2.0
Cr	<0.001	<0.001	<0.001	0.002	<0.001	0.001	<0.001	<0.001	0.001	<0.001	0.001	<0.001	0.05	0.1
Cu	0.015	0.011	<0.001	0.004	0.005	0.003	0.005	0.009	0.016	0.009	0.007	<0.001	0.01	0.05
Fe	0.69	0.66	0.31	0.47	0.14	0.52	0.17	0.24	0.51	0.25	0.23	0.32	0.3	1.0
K	3.29	3.38	3.73	2.83	1.53	2.95	1.86	2.91	2.91	3.35	3.13	2.21	-	-
Li	0.004	0.004	0.003	0.004	0.002	0.004	0.003	0.002	0.004	0.003	0.002	0.008	-	-
Mg	11.5	11.7	16.4	9.2	8.9	7.2	12.4	11.8	6.9	16.9	14.6	25.9	-	-
Mn	0.052	0.063	0.092	0.044	0.044	0.053	0.014	0.025	0.020	0.071	0.075	0.024	0.05	1.0
Mo	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.5	0.5
Na	12.88	13.59	15.44	13.79	8.47	7.57	8.34	11.45	6.03	12.77	16.36	42.73	-	-
Ni	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.011	<0.001	0.008	0.012	<0.001	<0.001	0.05	0.1
Pb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.03
Sr	0.20	0.23	0.32	0.17	0.17	0.09	0.23	0.26	0.08	0.40	0.41	0.41	-	-
V	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.005	<0.005	0.1	0.2
Zn	0.006	0.010	0.006	0.002	0.009	0.013	0.016	0.003	0.007	0.023	0.007	0.003	0.1	0.2

*MAC - Maximal allowed concentration for the II class and **MAC - Maximal allowed concentration for the III class according to the Decree on Water Classification of the Republic of Macedonia (Official Gazette of the Republic of Macedonia, No. 18, 1999).

Table 3. Descriptive statistics of concentrations of the analysed elements in surface water samples collected from the Strumica River Basin (n=12)

Element	Unit	X	X(BC)	Md	Min	Max	P_{25}	P_{75}	S	Sx	CV	A	E	A(BC)	E(BC)
Al	mg/L	0.26	0.24	0.26	0.11	0.45	0.15	0.36	0.12	0.03	45	0.16	-1.65	-0.1	-1.71
Ba	µg/L	33	34	34	16	49	30	37	9.0	2.6	27	-0.09	0.60	-0.02	0.58
Ca	mg/L	55	54	52	19	96	41	73	23	6.7	42	0.07	-0.52	-0.13	-0.53
Cu	µg/L	7.1	6.1	5.9	0.28	16	3.7	9.9	5.2	1.5	73	0.54	-0.41	-0.3	-0.41
Fe	mg/L	0.4	0.34	0.32	0.14	0.69	0.23	0.51	0.19	0.05	50	0.51	-1.09	-0.03	-1.19
K	mg/L	2.8	2.9	2.9	1.5	3.7	2.5	3.3	0.66	0.19	23	-0.91	0.11	-0.27	-0.37
Li	µg/L	3.7	3.3	3.5	2.0	8.2	2.6	4.1	1.6	0.47	44	2.10	5.81	0.02	0.26
Mg	mg/L	13	12	12	6.9	26	9.0	15	5.3	1.5	41	1.44	2.76	0.04	-0.25
Mn	µg/L	48	45	48	14	92	25	67	24	7.1	51	0.25	-0.79	-0.1	-1
Na	mg/L	14	12	13	6.0	43	8.4	15	9.6	2.8	68	2.76	8.65	0.01	0.59
Sr	mg/L	0.3	0.24	0.23	0.08	0.41	0.17	0.36	0.12	0.03	47	0.21	-1.09	-0.1	-0.89
Zn	µg/L	8.7	7	6.7	2.1	23	4.3	12	6.3	1.8	72	1.29	1.52	-0	-0.61

X - average; X(BC) - Box-Cox transformed average; Md - median; Min - minimum; Max - maximum; P_{25} – 25th percentile; P_{75} – 75th percentile;
S – arithmetic standard deviation; Sx - standard deviation; CV – coefficient of variation; A - asymmetry; E - distribution; BC - Box-Cox transformation.

affect plants and animals in various ways. The spatial distribution of Al in surface water samples is shown in Figure 4. The mean value of Al concentration in surface water samples from the Strumica River Basin is shown in Table 2 and is 0.262 mg/L. The highest concentration was found in the surface water sample from the Turia River near the village of Dobrašinci in the Vasilevo municipality (0.45 mg/L), and this increase is most likely due to the drainage water from Mount Goten, where the soils have high aluminum content (Stafilov & Šajn, 2016; Čančalova et al., 2017). A high Al concentration (0.40 mg/L) was also registered in the water samples from the Strumica River, most likely due to leaching of the geological composition of the Ogražden and Belasica mountains, where the soils have a high aluminum content (Stafilov & Šajn, 2016). The lowest value of Al concentration (0.115 mg/L) was found in the sample from the Strumica River near the town of Strumica. Aluminum is naturally present in water in very low concentrations. The determined aluminum concentrations (Table 2) in the surface water samples do not exceed the maximum permissible concentration for aluminum for the first and second class of water bodies (1500 μg/L) according to the Regulation on Water Classification of the Republic of Macedonia (Official Gazette of the Republic of Macedonia, No. 18, 1999).

Barium is the 14th most abundant element in the Earth's crust and its compounds, soluble in water and acids, are toxic. Barium and its compounds are used in various industries, medicine, and mining, and enter urban waters through wastewater. Figure 4 shows the spatial distribution of Ba in the water bodies of the study area. The lowest mean value of Ba concentration was determined in the water sample from the Turia River (16 μg/L), and the highest in the water sample from the Strumica River (49 μg/L). In the waters of the Strumica River and its tributaries, barium is present only at low levels. The values of Ba concentrations in the water samples from individual areas are presented in Table 2. The concentration values for Ba in the surface water samples from the Strumica River basin are very low and are below the maximum allowable Ba concentration (1000 μg/L) according to the Decree on Water Classification of the Republic of Macedonia (Official Gazette of the Republic of Macedonia, No. 18, 1999).

Calcium is an essential element for plants, animals, and humans and is abundant in the earth's crust. The average value of Ca concentration in surface water samples in the Strumica River basin is 54.9 mg/L and ranges from 19 to 96 mg/kg. The highest value of 96 mg/L was measured in samples from the Strumica River between the towns of Radoviš and Strumica, and the lowest in surface water samples from the Tuia River (19 mg/L) (Figure 5). The higher calcium concentration in the region between Radoviš and Strumica is most likely due to atmospheric waters that washed away calcium from construction works in the area.

The spatial distribution of Cu in the surface water samples is shown in Figure 5. The highest copper concentration was found in the water sample from the Turija River near the dam of the Turia reservoir. Most likely, this is due to the presence of copper in the construction material of the built dams. The determined concentrations of Cu in the surface water samples ranged from 0.28 μg/L to 16 μg/L (Figure 5). A high concentration of Cu was also found in the sample from the Strumica River taken near the border crossing with Bulgaria (15 μg/L). Sources of copper in surface water are industrial wastewater, wastewater containing copper chemicals, and agricultural wastewater, some of which is not treated at all and as such flows into rivers.

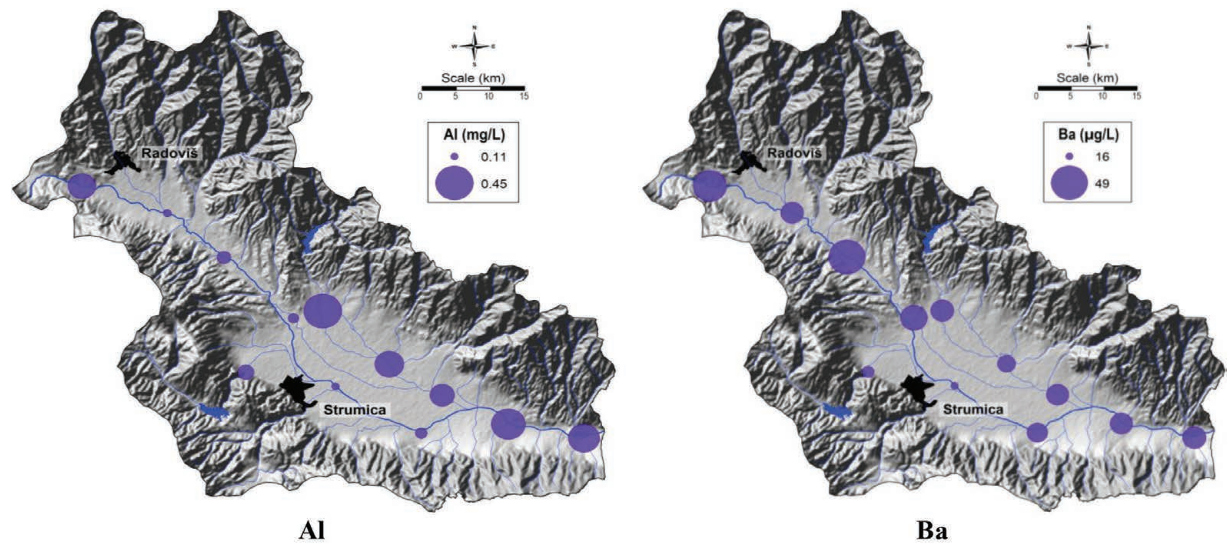

Figure 4. Spatial distribution of Al and Ba in surface water samples from the Strumica river basin

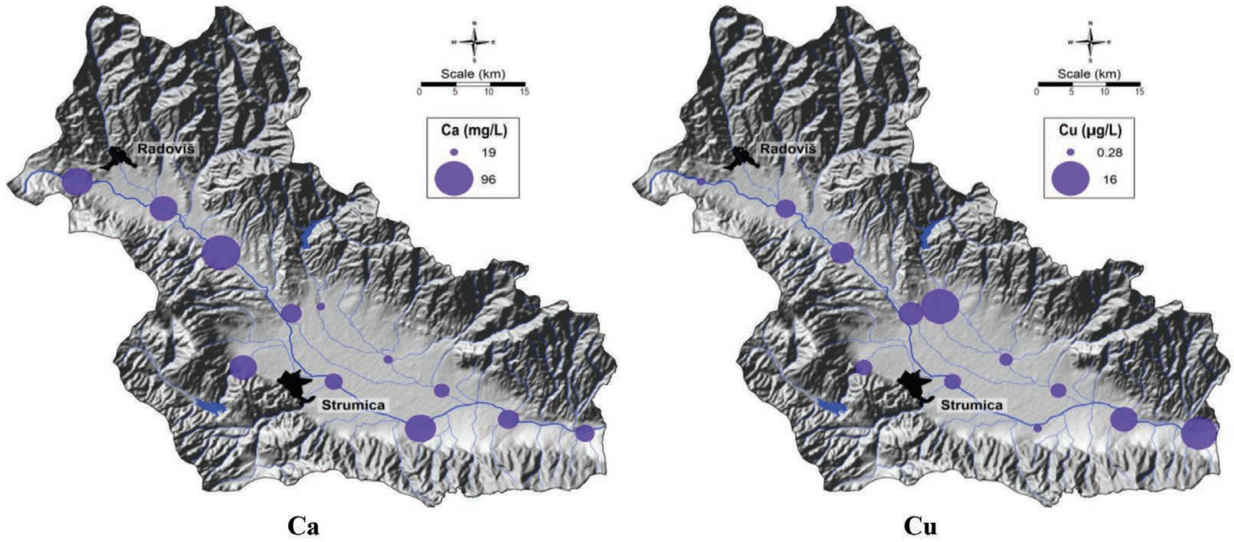

Figure 5. Spatial distribution of Cu in surface water samples from the Strumica river basin

However, in all other water samples from the Strumica River Basin copper concentrations are below the maximum permissible copper concentration (10 µg/L).

Iron is the fourth most abundant element in the Earth's crust. The iron concentration in the surface water samples from the studied area ranges from 0.14 mg/L to 0.69 mg/L. Its spatial distribution is shown in Figure 6. The southeastern region of northern Macedonia is characterized by high iron content (Stafilov & Šajn 2016; Čančalova et al. 2017), which also leads to elevated Fe concentrations in the surface water samples from the Strumica River Basin (0.693 and 0.655 mg/L). The determined Fe concentrations in the water samples from 5 of the 12 sites (S-1, S2, S3, S4, S6, and S9) exceed the maximum allowable Fe concentration in surface waters (0.300 mg/L) according to the Regulation on Water Classification of the Republic of Macedonia. The lowest concentration (0.14 mg/L) was found in the sample from the Dabile tributary. Potassium concentration in the water of the studied area ranges from 1.5 mg/L to 3.73 mg/L (Table 2, Figure 6). The highest K concentration was measured in the sample from a tributary of the Strumica River near the village of Bansko (3.73 mg/L), followed by a very similar concentration in a sample from the Strumica River near the village of Novo Selo and on the border with Bulgaria (3.38 mg/L and 3.29 mg/L, respectively)

The concentration of Li ranges from 2.0 µg/L to 8.2 µg/L (Figure 7). Higher concentrations were found in the northern part of the Strumica River Basin, with the

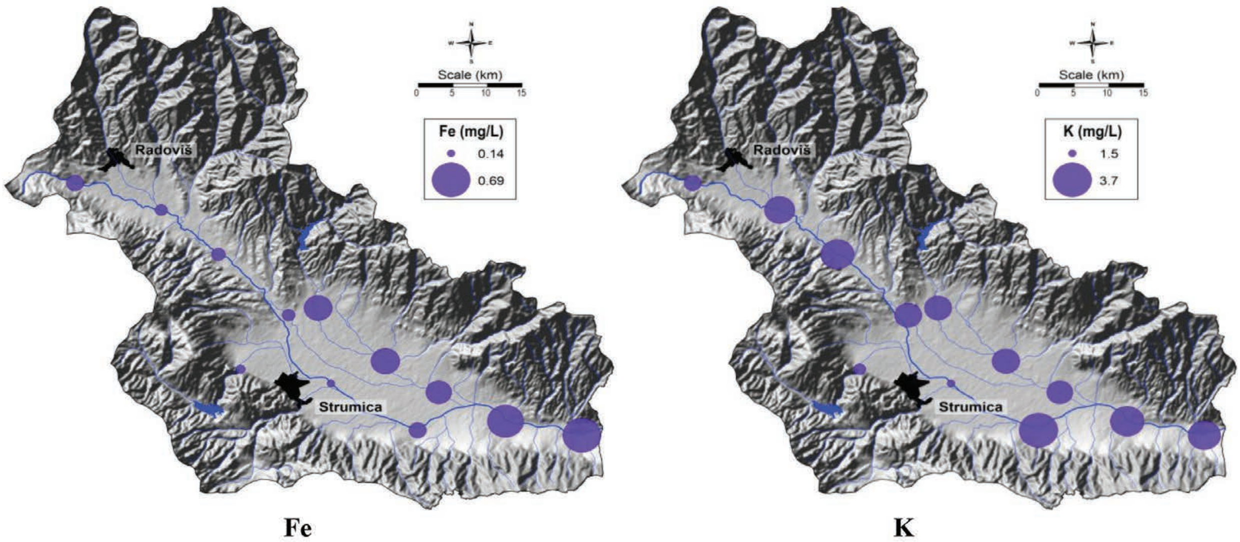

Figure 6. Spatial distribution of Fe and K in surface water samples from the Strumica river basin

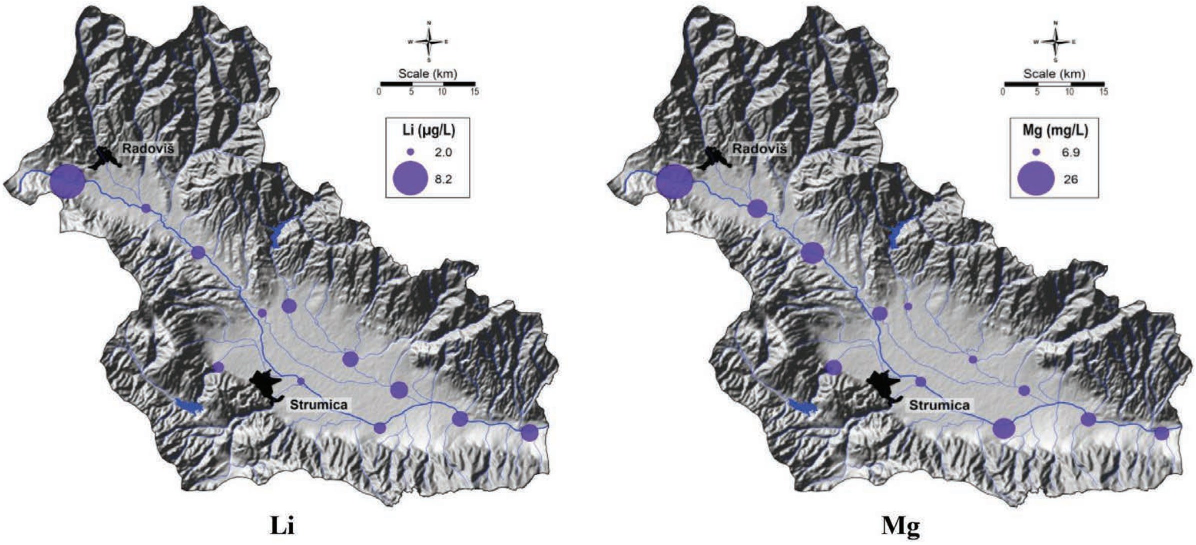

Figure 7. Spatial distribution of Li and Mg in surface water samples from the Strumica river basin

maximum value reached in the sample from Injevska Reka (8.2 µg/L). The concentration of Li in the other samples is quite low, ranging from 2 µg/L to 4 µg/L (Table 3).

Magnesium is an alkaline earth metal found in dolomite, magnesite, epsomite, and other minerals. Figure 7 shows a map of the spatial distribution of magnesium concentrations in the water samples from the studied area. The highest Mg concentration is found in the samples from Injevska Reka (25.9 mg/L) and the lowest in the samples from Turia River (6.9 mg/L). The mean value of Mg concentration in the surface water samples is 12.8 mg/L.

The Mn concentrations in the water samples are listed in Table 2, and their spatial distribution is shown in Figure 8. The highest Mn concentration was found in the water samples from the Bansko tributary near the village of Bansko (92 µg/L) and the lowest value in the samples from the Vodoča River (14 µg/L), while the mean value for the manganese concentration from the Strumica catchment is 48 µ/L. Manganese concentration in the water samples does not exceed the maximum allowable value for Mn concentration (1000 µg/L) for the third water class according to the Regulation on Water Classification (Official Gazette of the Republic of Macedonia, No. 18, 1999), while it is higher than the maximum allowable concentration in the water samples from the rivers of water class II (0.05 mg/kg), such as the river near the village of Bansko and the river Turija.

Sodium is an alkali metal and the sixth most abundant element in the Earth's crust. The spatial distribution of sodium in the water samples from the studied sub-basin is shown in Figure 8. A higher sodium

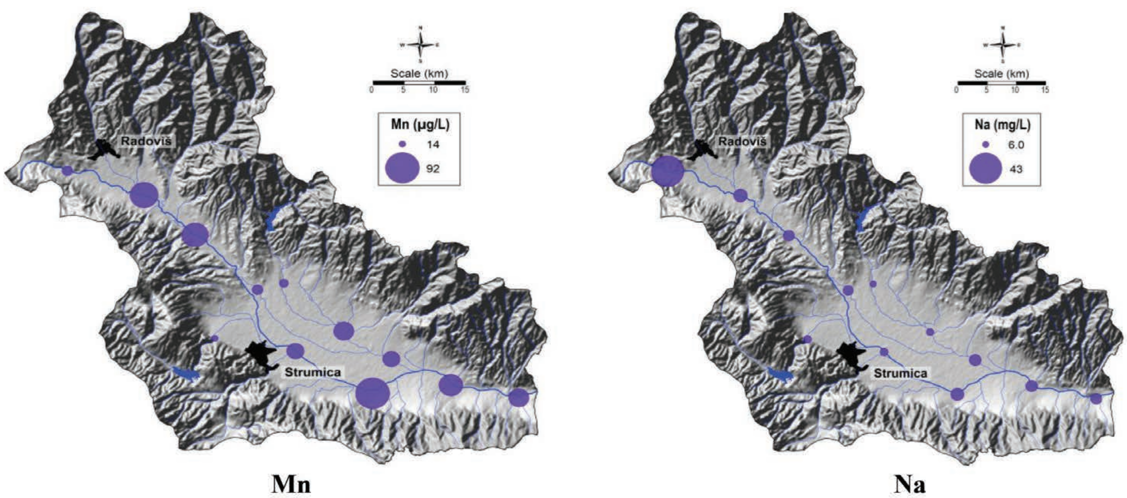

Figure 8. Spatial distribution of Mn and Na in surface water samples from the Strumica river basin

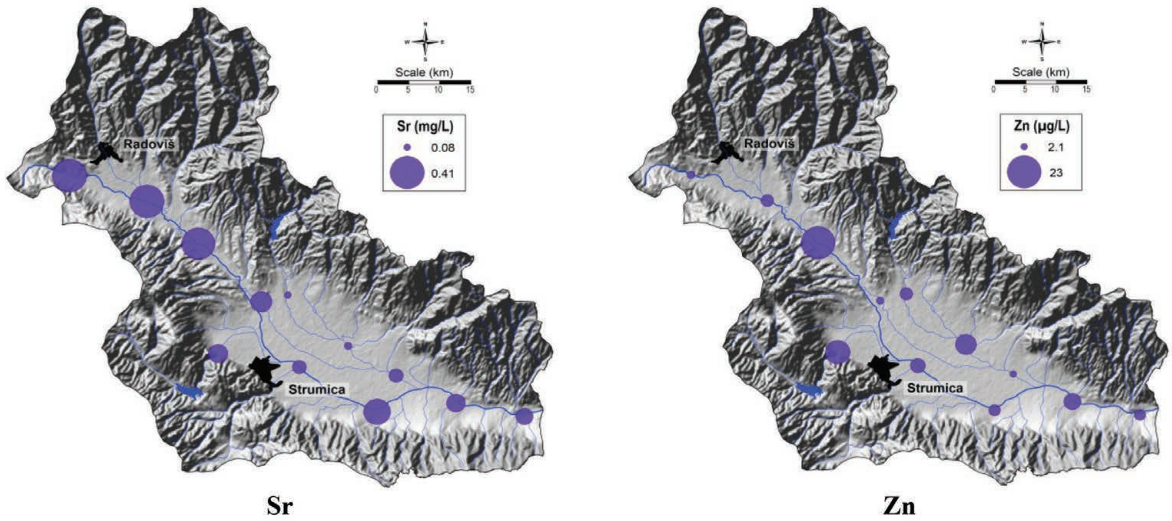

Figure 9. Spatial distribution of Sr in surface water samples from the Strumica river basin

concentration was found in the water sample from Injevska Reka (43 mg/L), which is most likely due to the presence of Neogene igneous rocks in this section (Čančalova et al. 2017). The lowest sodium concentration in the waters of this catchment is found in the sample from the Turia River (6.03 mg/L), collected near the village of Dobrašinci. The mean value of sodium concentration in the water samples is 14.12 mg/L.

The spatial distribution of strontium concentrations in surface water samples is shown in Figure 9. The highest Sr concentrations are found in the samples from Radoviš valley, namely: Injevska Reka (41 µg/L), Radoviška Reka (40 mg/L and 41 µg/L). The lowest Sr concentration (8 µg/L) was found in the sample from the Turia River. The rather high Sr concentrations in the surface water samples from the rivers of the Radoviš Valley are probably the result of the high Sr content in the surrounding soils, which are dominated by Quaternary alluvium and deluvium formations (Stafilov & Šajn 2016).

The main anthropogenic sources of zinc in the environment are the metal-processing industry, coal-burning industry, industrial wastes, and tire wastes, while low concentrations of zinc are naturally derived from the Earth's crust. From the spatial distribution of Zn concentrations (Figure 9), it is evident that the lowest value of Zn concentration is found in the water samples from the river Turia, taken just before the confluence with the river Strumica (2.1 µg/L). The highest Zn concentration was determined in the water samples from the Strumica River (23 µg/L). The mean value of the determined Zn concentrations in the water bodies of the study area is 9 µg/L (Table 2). The values for Zn concentration in the waters of the Strumica River basin are below the maximum permissible concentration (200 µg/L) according to the Regulation on the Water Classification in the Republic of Macedonia (Official Gazette of the Republic of Macedonia, No. 18, 1999).

Conclusion

The distribution of various chemical elements in surface water samples from the catchment area of the Strumica River, North Macedonia, was evaluated by the analysis of 21 elements (Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V, and Zn) using inductively coupled plasma atomic emission spectrometry (ICP-AES). In addition to the samples from the Strumica River, samples were also collected from its tributaries: Bansko, Dabile, Turija, Vodoča, Radoviška River, and Injevska River. The results for the presence of potentially toxic elements in the water samples from the entire study area show that their concentrations are mostly below the maximum permissible concentrations according to the Regulation on the Classification of Water in Macedonia. In general, it can be stated that the distribution of most elements follows the lithology of the study area.

References

Arsovski, M. (1997). Tectonics of Macedonia. Faculty of Mining and Geology, Štip.

Balabanova, B., Stafilov, T., Bačeva, K., Šajn, R. (2010). Biomonitoring of atmospheric pollution with heavy metals in the copper mine vicinity located near Radoviš, Republic of Macedonia. *Journal of Environmental Science and Health, Part A*, **45**: 1504–1518.

Balabanova, B., Stafilov, T., Šajn, R., Tănăselia, C. (2016). Multivariate factor assessment for lithogenic and anthropogenic distribution of trace and macro elements in river water from Bregalnica River Basin, R. Macedonia. *Macedonian Journal of Chemistry and Chemical Engineering*, **34**(2): 235–250.

Bhardwaj, R. M., Chilton, J., van der Gun, J., Dieng, Y., Diop, S., Gaye, C., Hansen, A., Mtetwe, S., Natale, O., Neikerk, H., Neilsen, K., Rast, W., Toguebaye, B. (2008). Water quality for ecosystem and human health. GEMS Water Programme, Ontario, Canada.

Boev, I., Šorša, A., Kovačević, B., Mitrev, S., Boev, B. (2016). The use of factor analysis to distinguish the influence of parent material, mining and agriculture on groundwater composition in the Strumica valley, Macedonia. *Geologia Croatica*, **69**(2): 245–253.

Čančalova, S., Stafilov, T., Šajn, R., Alijagić, J. (2017). Spatial distribution of chemical elements in soil from the Strumica Region, Republic of Macedonia. *Geologica Macedonica*, **31**(2): 117-130.

Cankov, C. & Stojanov, K. (2005). Morphostructural peculiarities of Belasica complex horst mountain morphostructure, Proceedings of the Third Congress of Geographers of the Republic of Macedonia. Macedonian Geographical Society, Skopje, pp. 103-110. (in Bulgarian).

Darby, S., Sear, D. (2004). River restoration – Managing the uncertainty in restoring physical habitat. John Wiley & Sons, Chichester, UK.

Drever, J.I. (2005). Surface and ground water, weathering and soils, Elsevier, Amsterdam.

Gaševski, M. (1975). Strumica river basin and its regime. *Geografski razgledi*, **13**: 19-44. (in Macedonian).

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

Kabata-Pendias, A. & Mukherjee, A.B. (2007). Trace elements from soil to human. Springer, Berlin.

Kostik, V., Gjorgeska, B., Angelovska, B., Bauer, B., Petkovska, S. (2014). Distribution of the total arsenic content in drinking water obtained from different water sources in the Republic of Macedonia. *Journal of Food and Nutrition Sciences*, **2**(4): 146-155.

Kovacevik, B., Mitrev, S., Boev, B., Karov, I., Zajkova Panova, V. (2015). Groundwater quality as a source for irrigation in Strumica valley, Republic of Macedonia. *Agricultural Science and Technology*, **7**(3): 344–349.

Kovacevik, B., Boev, B., Zajkova Panova, V., Mitrev, S. (2016). Groundwater quality in alluvial and prolluvial areas under the influence of irrigated agriculture activities. *Journal of Environmental Science and Health, Part A*, **51**(14): 1197–1204.

Lazarevski, A (1993). Climate of Macedonia. Kultura, Skopje.

Manaković, D. & Andonovski, T. (1981). Morphological-topographic characteristic of Strumica valley. *Annual Proceedings of the Institute of Geography, Faculty of Geography, Skopje*, **26**: 5-38. (in Macedonian).

Markoski, A. (2006). Environmental protection. Faculty of Technical Sciences, St. Kliment Ohridsky University, Bitola.

Naiman, R., Bilby, R. E. (2008). River ecology and management. Wayerhaevser Company, Tacoma, USA.

Official Gazette (1999). Decree on Water Classification. Official Gazette of the Republic of Macedonia, No. 18, 1165-1179.

Pavlov, K. & Vasilevski, D. (2012). Strumica valley, natural and geographical characteristics. Skopje.

Pavlov, K., Bačeva, K., Stafilov, T., Vasileski, D., Toševska, S. (2012). Assessment of toxic metal pollution in some rivers in the Tikveš Basin, Republic of Macedonia. *International Journal of Environment Protection (IJEP)*, **2**(12): 9–16.

Petrušev, E., Stolić, N., Šajn, R., Stafilov, T. (2021). Geological characteristics of the Republic of North Macedonia. *Geologica Macedonica*, **35**(1): 49-58.

Popovska, C., Geshovska, V. (2014). Water balance model for vulnerability assessment of water resources in Strumica River basin. *Irrigation & Drainage Systems Engineering*, **3**(3): 1-9.

Popovska, C. (2014). Water resources. In: Zdraveva, P. (Ed.). Third National Communication on Climate Change, Ministry of Environment and Physical Planning, Skopje, pp. 1-60.

Popovska, C., Stavric, V. (2004). Transboundary river and lake basins in the Republic of Macedonia. UNESCO/INWEB Workshop on Development of an Inventory of Internationally shared Surface Waters in South-Eastern Europe, Thessaloniki, Greece, Proceedings, pp. 1-8.

Rakičević, T., Kovačević, M., Radović, N., Pendžerkovski, J. (1972). Interpreter of the basic geological map of SFRJ 1:100,000, Sheet Strumica. Professional Fund of the Geological Survey of Macedonia, Skopje.

Stafilov, T., Šajn, R. (2016). Geochemical Atlas of the Republic of Macedonia. Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University, Skopje.

Stafilov, T., Šajn, R., Bačvarovski, D. (2021). Multivariate factor assessment for lithogenic and anthropogenic distribution of macro and trace elements in water from Pčinja River Basin, North Macedonia. *Macedonian Journal of Ecology and Environment*, **23**(2): 73-84.

Tomovski, D., Stafilov, T., Šajn, R., Bačeva Andonovska, K. (2018). Distribution of chemical elements in surface waters from the Crna River Basin. *Contributions, Section of Natural, Mathematical* *and Biotechnical Sciences, Macedonian Academy of Sciences and Arts,* **39**(1): 31–49.

Vasilevska, S., Stafilov, T., Šajn, R. (2018). Distribution of chemical elements in surface water from Crn Drim River Basin, Republic of Macedonia. *Water Research and Management*, **8**(1): 3–15.

Zikov, M. (1995). Climate and climate regionalization in the Republic of Macedonia. *Geografski razgledi*, **30**: 13-22. (In Macedonian).