Macedonian Journal of Ecology and Environment
Vol. 26, issue 2
pp. 151 - 168
Skopje (2024)
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/MJEE24262151s

Distribution of chemical elements in river sediments and alluvial soils from the Strumica River basin, North Macedonia

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Abstract

The distribution of 20 chemical elements (Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) in river sediments and alluvial soils from the Strumica River basin in North Macedonia is presented. A total of 12 sediment and 24 soil samples were collected, from four locations of the Strumica River and eight locations of its main tributaries (Bansko, Dabile, Turija, Vodoča, Radoviška River and Injevska River). The content of the analysed elements was determined using inductively coupled plasma - atomic emission spectrometry (ICP-AES). All data obtained for the analysed samples were statistically processed using Stat Soft 11.0 software, whereby a descriptive statistical analysis of the element content values was performed. The maps of the spatial distribution of the content for each element with a minimum and maximum value of the content for each element were also created. The matrix of correlation coefficient for the sediments and soil samples from the entire study area shows that there is a strong correlation between the contents of the elements: V-Fe (0.97), V-Cr (0.94), Fe-Cr (0.91), Mn-Fe (0.85), Sr-Ba (0.83), Mg-Ca (0.83), Mg-Li (0.82), Ni-Cr (0.81) and P-Sr (0.80). There are three factors in the matrix of loading factors for the elements in the sediment and soil samples. Factor 1 includes the chemical elements V, Cr, Ge, P, Cu, Ni and Pb, Factor 2 comprises the chemical elements Sr, Ba, Al, Zn and Mn and Factor 3 includes Mg, Li and Ca. The comparative statistics using three methods [t-test, F-ratio and R(T/B)] showed no difference between the distribution of the different chemical elements in the topsoil and subsoil samples. The results obtained show that the content of potentially toxic elements in the river sediments and alluvial soil is low and it can be concluded that the Strumica catchment is not polluted with heavy metals.

Keywords: Strumica, North Macedonia, river basin, sediment, soil, heavy metals, distribution

Introduction

Sediments, which are formed by soil erosive, physical and chemical processes due to changes in river conditions, vary in different watercourses. Over millions of years, entire mountain ranges have been flattened by these processes and the sediments that enter the watercourses are transported across them. In addition to the transport of these sediments, the forces with which the water flow acts on the bed edges and the bottom, through which it flows cause the separation of particles and their transport, or sediments from the external environment can be deposited on the bottom and the bed edges. In this way, rivers can deepen and widen these beds or fill them up over time. The erosion of the sides or bottom of a riverbed can occur in different ways. If the boundary material consists of soluble rock such as limestone, dissolution in the flowing water is very likely. In addition, sediment carried by water can lead to erosion, especially if large pieces slide off and roll over the bottom, scouring can occur. Studies have

Submitted: 07.08.2024;
Accepted: 02.09.2024

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shown that watercourses that carry a lot of sediment have a greater erosive force than those that have a lower sediment content. When large pieces begin to slide and roll on the bottom due to changes in velocity, the effect can be so great that entire pieces of bed material can be torn off. Although rivers constantly erode the bed through which they flow, internal scour processes refer to the ability of rivers to „pick up" loose pieces of material from the bed through the direct hydraulic action of the flowing water. As the water flows, the resulting forces act on the surface of the bed. If these forces are greater than gravity, which tends to keep the particles at the bottom, the particles are „collected" and incorporated into the water flow (Baker & Ritter 1975; Ritter et al. 1995).

Experiments with other reservoirs through which water flows, which simulate the flow of water through the troughs, show that with increasing speed, larger parts are lifted, driven, from the ground. The total amount of sediment carried by the watercourse is called the load. The sediment load can be divided into three types, depending on the method and processes of transfer. The dissolved load is completely dissolved in the water. A large part of the dissolved load is „captured" by the bottom of the watercourse, i.e. it is carried from the underground part of the entire watercourse. During the relatively long period of resistance of the groundwater flow, solids that react chemically with the groundwater through a series of physical and chemical processes caused by weathering are carried into the surface waters. The surface component of the dissolved material is much smaller due to the short flow time of the groundwater. From the undissolved load in the rivers, the small particles are transported as „bound" load. This type of transport indicates that the particles are prevented from settling to the bottom of the watercourse by the water movement (Ritter et al. 1995; Förstner & Owens 2007).

River sediment is not only the largest water pollutant by weight and volume, but also serves as a catalyst, carrier and reservoir for other forms of pollution. In general, the higher the sediment concentration, the poorer the water quality. Sediment alone degrades water quality, especially for urban supply, recreation, industrial consumption and cooling, hydropower facilities and aquatic life. In addition, chemicals and wastes are taken up on and in sediment particles (Yang et al. 2003). Sediments in rivers and lakes play an important role in determining water quality. Suspended sediments adsorb pollutants from the water and thus reduce the concentration of pollutants in the water. However, pollutants can also be released if the sediment is disturbed. Benthic sediments also provide habitats and a food source for benthic fauna. Pollutants can be directly or indirectly toxic to aquatic flora and fauna. The effect of pollutants can also be detected on land due to the effects of bioaccumulation and bioconcentration in the food chain (Yang et al. 2003; Kaletova et al. 2022).

In the context of river hydrology, sediment is inorganic and organic material that is transported, suspended or deposited by rivers. Sedimentation is a process in which particles are transported from one place by natural or induced processes and deposited elsewhere on the banks of a river. The sediment load is the amount of sediment transported by a river and depends on the flow, river bottom and structure, weather conditions and many other factors (Selley et al. 2005). The sediments carried by rivers can be deposited in fine or coarse material. Sediment yield is the sum of sediments transported from the river to the shore at a given place and time. Low sediment yields are the result of low erosion rates. Porous soils and low topographic relief contribute to the reduction of erosion material or sediment. If the relief is steeper and the soil is erosive, sedimentation is accelerated. The human factor is also the cause of accelerated sedimentation. The alluvial plain occurs in the lower reaches of the river, where the gradient is low, lateral erosion is high and the accumulation of river material is pronounced because the transport capacity of the water in this area has decreased. The alluvium in the sediment is deposited on the surface of the reservoir. This is a tip for the sediment to transport the rock from the site to the weather you have already received the product and the fraction on the sand and stones.

Water pollution in North Macedonia is linked to industrial development, agricultural activities, illegal landfills or uncontrolled wastewater discharges (Dimitrovska et al. 2012; Stafilov 2014). The largest central water ecosystem, the Vardar River basin, has already been studied (Stafilov & Levkov 2007; Serafimovska et al. 2011; Ilić Popov et al. 2014, 2016), including the catchments of its main tributaries, the Bregalnica River (Stafilov et al. 2014, 2015; Balabanova et al. 2015, 2016; Krstić et al. 2016) and the Crna Reka River (Stafilov et al. 2013; Tomovski et al. 2018, 2019). The second river basin is that of the Crn Drim River, which was also investigated for possible pollution of its waters or sediments with heavy metals (Vasilevska et al. 2018, 2019).

The aim of this work is to show the condition of the sediments and alluvial soils in the part of the Strumica River in North Macedonia, which is the third catchment area in the country. The results of the study on the concentrations of chemical elements in the surface water samples are relatively low and the distribution of most elements follows the lithology of the study area (Trajanova et al. 2023). The main objective of the present study is to investigate the distribution of 20 chemical elements (Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V и Zn) in sediments and alluvial soil samples collected from different locations in the Strumica river basin, to interpret their contents and relate them to the lithogenic occurrence and possible anthropogenic influences.

Materials and methods

Study area

About 2% of the territory of North Macedonia is under water. There are about 35 rivers and 53 natural and artificial lakes. As far as water resources are concerned, Macedonia is an area with satisfactory water resources, but they are unevenly distributed. The rivers belong to 6 river basins: the Vardar 20,535 km^2, the Crn Drim 3,350 km^2, the Strumica 1,535 km^2, the Dojran Lake 120 km^2, the Lebnička River 129 km^2 and the Binačka Morava River 44 km^2 (Dimitrovska et al. 2012).

The study area of the Strumica River Basin, which belongs to North Macedonia, covers the catchment area of the Strumica River in the south-eastern part of the country (Fig. 1). The Strumica valley is delimited from the neighbouring valleys and catchments by high-mountain ridges (Manaković & Andonovski 1981; Pavlov & Vasilevski 2012; Trajanova et al. 2023). Detailed data on the studied area with its geographical, geological, climatic and hydrographic features can be found in our previously published data (Trajanova et al. 2023).

Fig. 1b shows a land use map indicating that the central part of the study area is used for agriculture, followed by grassland and pasture, scrub and herbaceous vegetation and forest. This can be clearly seen on the satellite image of the North Macedonia region in the visible and infrared spectrum (Fig. 2).

From the geological point of view, the Strumica Valley is mainly part of the Serbian-Macedonian Massif,

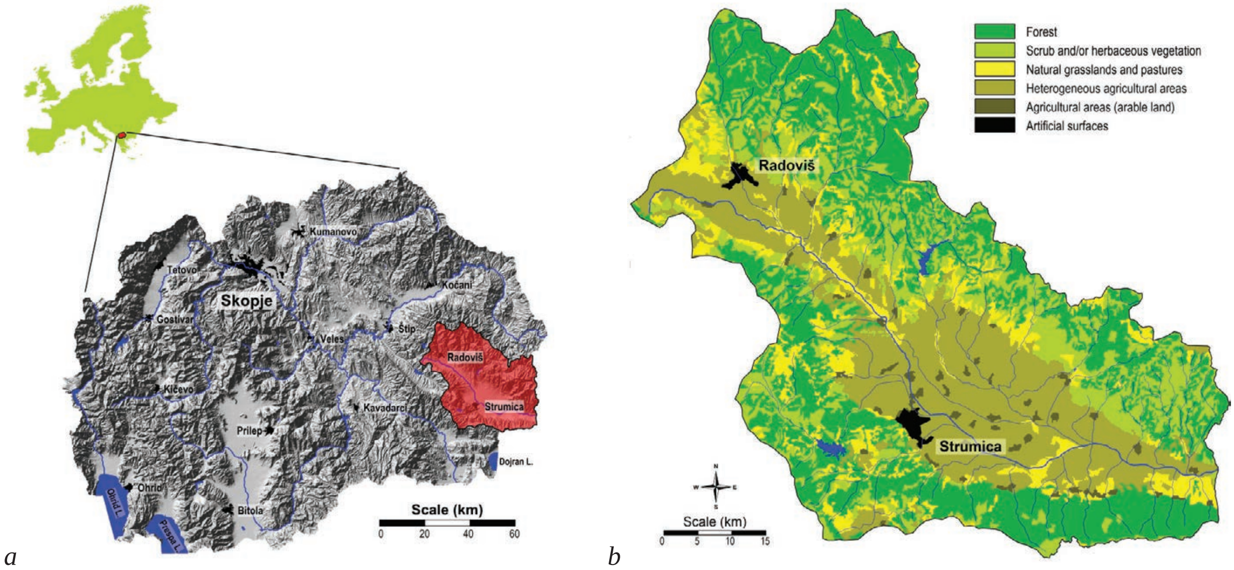

Figure 1. Map of the Republic of North Macedonia with the study area (a) and land use map (b) of the Strumica river basin

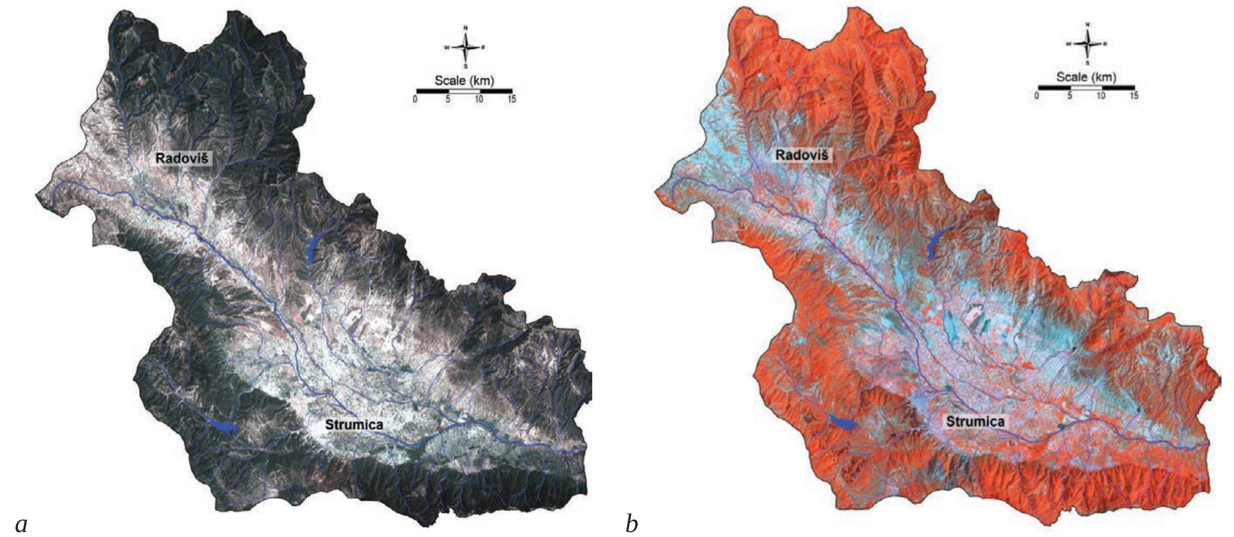

Figure 2. Satellite image of the territory of the Strumica River basin in the visible (a) and infrared spectrum (b)

which is characterised by two structural complexes. These are the lower highly metamorphic complex with amphibolitic facies and the upper metamorphic complex with greenschist facies (Arsovski 1997). The geological map of the study area (Fig. 3a) shows that Quaternary alluvial sediments and classic Neogene sediments predominate in the northern part, while Quaternary deluvial/proluvial sediments are less common. The central part is dominated by similar formations, with Paleozoic igneous rocks present in some parts. The northern part of the basin (Plačkovica Mountains) consists mainly of Proterozoic metamorphic rocks, while the Ogražden and Belasica Mountains in the southern part consist mainly of Paleozoic igneous rocks and Proterozoic metamorphic rocks. (Trajanova et al. 2023).

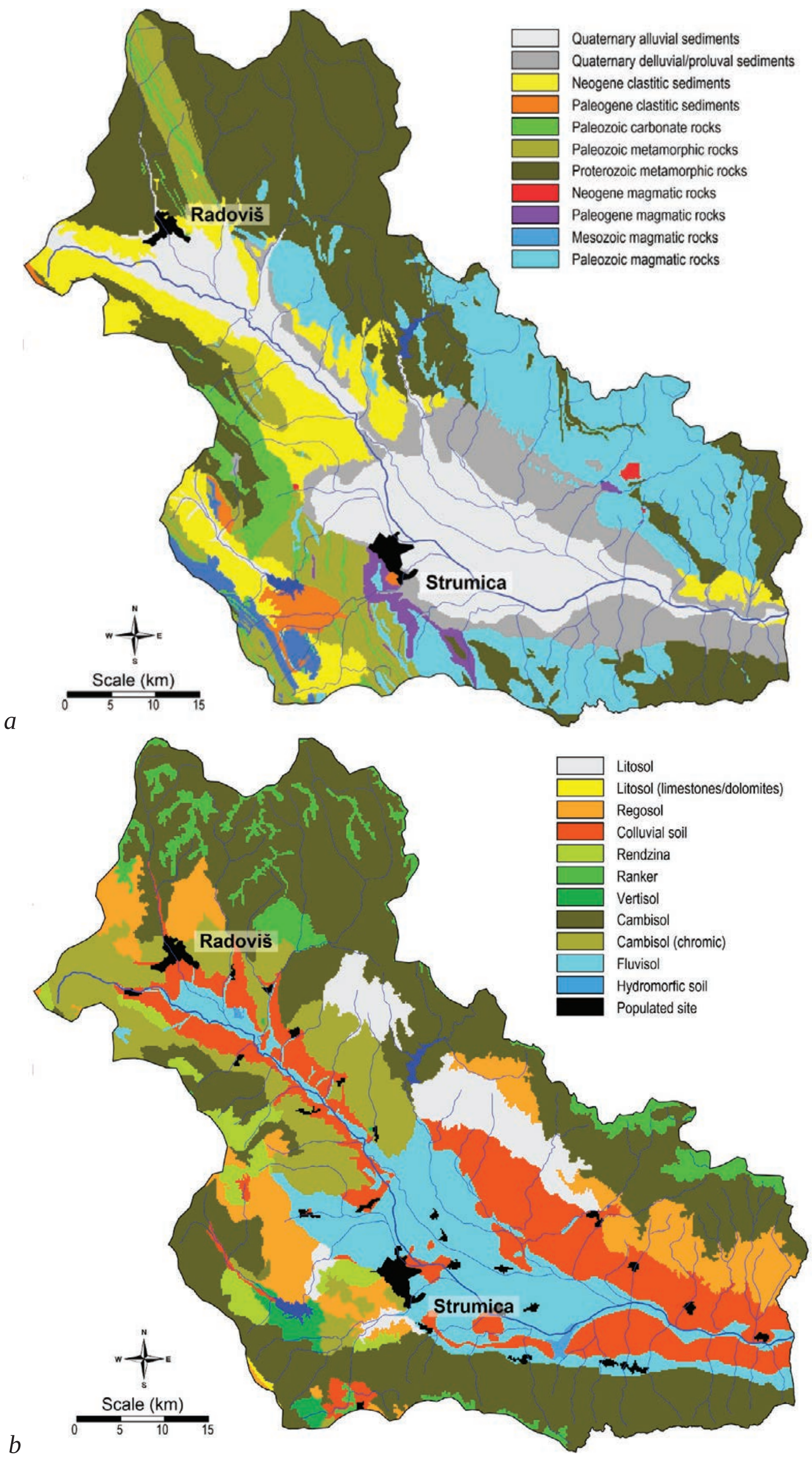

Figure 3. Geological (a) and pedological (b) maps of the Strumica River basin

The pedological map of the study area (Fig. 3b) shows that most of the waterlogged soils along the Strumica River valley are fluvisols. In the other part of the Strumica valley, mainly colluvial soils and cambisols (chromic) are represented, while in the plateau and mountain areas litosols, regosols, cambisols and rankers dominate (Filipovski et al. 2015).

Sampling and analysis

The topographic map of the study area with the sampling locations is presented in Fig. 4. Two sediment samples were collected from each of the 12 sampling sites, one on each side of the river of the sampling site. Soil samples were collected from two layers, the topsoil (0-5 cm) and subsoil (20-30 cm), and collected from both sides of the river at each sampling site. Five separate soil samples were taken from each soil layer in a square with a length of 10 m. All five subsets were mixed to obtain a representative sample (Stafilov & Šajn 2016).

The river sediments and soil samples were dried in the laboratory at room temperature and then cleaned, crushed and sieved through a 125 µm sieve. The samples were then digested with a mixture of concentrated mineral acids according to the international standard ISO 14869-1: 2001 (2001) using concentrated HNO_3, HF, $HClO_4$ and HCl. The digested samples were analysed with an inductively coupled plasma atomic emission spectrometer (ICP-AES, Varian, 715ES). The standard solutions of the elements were prepared by dilution of 1000 mg/l solutions (11355-ICP multi-element standard solution). The quality control of the applied techniques was performed using the standard addition method and it was found that the recoveries for the analysed elements were between 98.0% and 101.5%. Certified reference material (CRM) was also used for the quality control of the analytical method. Both certified reference materials (NIST-SRM 2711a, Montana II Soil, National Institute of Standards & Technologies, USA) and spiked in-house laboratory samples were analysed at a combined frequency of 20% of the samples. The recovery rate for all analysed elements ranged from 87.5% for Na to 112% for P.

All data on the contents of the analysed elements were statistically evaluated using Stat Soft, 11.0 software. A basic descriptive statistical analysis of the element concentration values was performed for all sediment samples as well as for the upper and lower alluvial samples. Using bivariate statistics with a significance level $p < 0.05$; $p > 0.01$, the degree of correlation of the values of the chemical element contents in the samples is estimated and the correlation coefficients are presented in the correlation matrix.

Results and discussion

As part of this research, 12 samples of river sediments and 24 samples of alluvial soils were taken from 12 locations in the Strumica river basin, of which 12 samples were taken from the topsoil (0-5 cm) and 12 samples from the subsoil (20-30 cm) of the alluvial soil from the two river locations. The content of the elements in the analysed samples was determined to assess their impact on the environment in this river catchment.

The sediment and soil samples were analysed for the following chemical elements: Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, and Zn. The basic descriptive statistics of the values for the content of the analysed chemical elements in these samples are shown in Tab. 1 and 2.

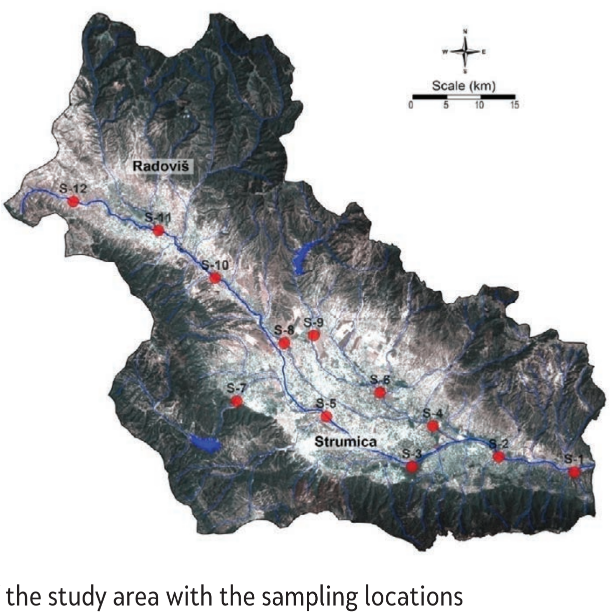

Figure 4. Topographic map of the study area with the sampling locations

Table 1. Descriptive statistics of the content of the analyzed elements in sediment samples collected from the Strumica River basin in North Macedonia, *n*=12

Element	Unit	Optimum	Action	X	$X_{(BC)}$	Md	Min	Max	P_{25}	P_{75}	S	Sx	CV	A	E	$A_{(BC)}$	$E_{(BC)}$
Ag	mg/kg			1.7	1.7	1.5	0.56	3.0	1.3	2.2	0.71	0.20	40	0.47	-0.13	0.09	0.17
Al	%			3.1	2.9	2.9	1.5	6.3	2.1	4.1	1.4	0.40	44	0.99	1.11	0.18	-0.51
Ba	mg/kg	200	625	240	180	200	58	520	130	330	140	42	61	0.71	-0.28	-0.75	-0.18
Ca	%			0.72	0.58	0.65	0.10	1.8	0.36	1.0	0.49	0.14	68	0.89	1.05	-0.50	-0.19
Cd	mg/kg	1	12	1.9	0.82	0.90	0.25	9.8	0.41	1.7	2.7	0.79	144	2.57	6.96	-0.05	-0.95
Co	mg/kg	20	240	1.1	0.75	0.50	0.50	4.2	0.50	1.2	1.2	0.35	109	1.98	3.39	1.46	0.42
Cr	mg/kg	100	380	39	36	38	17	62	26	50	15	4.4	39	0.19	-1.19	-0.23	-1.08
Cu	mg/kg	36	190	22	20	18	12	40	15	31	9.3	2.7	42	0.86	-0.59	0.46	-1.16
Fe	%			2.3	2.2	2.4	0.83	3.7	1.7	2.8	0.77	0.22	34	-0.14	0.04	-0.62	0.60
K	%			1.9	1.8	1.8	1.2	2.7	1.6	2.2	0.46	0.13	25	0.01	-0.47	-0.43	-0.35
Li	mg/kg			13	10	11	2.7	33	6.3	20	9.7	2.8	72	0.85	-0.32	-0.32	-0.78
Mg	%			0.38	0.19	0.32	0.02	1.1	0.05	0.64	0.37	0.11	97	0.76	-0.80	-0.45	-1.27
Mn	mg/kg			400	360	370	160	680	270	530	170	49	42	0.52	-0.71	-0.39	-0.15
Na	%			2.5	2.4	2.6	1.2	3.9	1.8	3.2	0.86	0.25	34	0.07	-0.96	-0.45	-0.77
Ni	mg/kg	35	210	17	15	14	7.4	32	8.8	23	8.5	2.5	51	0.51	-1.17	0.14	-1.61
P	mg/kg			480	470	520	150	760	340	620	180	52	37	-0.32	-0.61	-0.70	0.14
Pb	mg/kg	85	530	9.3	6.7	7.5	0.50	23	3.1	15	7.8	2.2	83	0.58	-0.73	-0.45	-0.96
Sr	mg/kg			62	53	55	13	150	36	79	38	11	61	1.13	1.99	-0.30	0.09
V	mg/kg			58	57	61	16	98	43	72	22	6.3	38	-0.09	0.23	-0.38	0.49
Zn	mg/kg	140	720	98	63	59	31	420	45	110	110	31	108	2.95	9.37	0.00	-0.29

*Optimum and action values according to the New Dutch standards; 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; BC – Box-Cox transformed values

Table 2. Descriptive statistics of the content of the analyzed elements in top- and bottom alluvial soil samples collected from the Strumica River basin in North Macedonia, n=24

Element	Unit	Optimum	Action	X	$X_{(BC)}$	Md	Min	Max	P_{25}	P_{75}	S	Sx	CV	A	E	$A_{(BC)}$	$E_{(BC)}$
Ag	mg/kg			2.1	1.9	1.9	0.60	3.4	1.6	2.7	0.93	0.19	45	0.32	0.61	-0.20	0.14
Al	%			2.8	2.3	2.0	0.84	6.7	1.7	4.0	1.8	0.37	64	1.39	2.65	0.13	-0.56
Ba	mg/kg	200	625	200	160	140	89	580	110	210	160	32	79	1.98	3.25	0.54	-0.11
Ca	%			0.58	0.39	0.51	0.11	1.4	0.26	0.63	0.47	0.10	80	1.66	2.92	0.18	-0.21
Cd	mg/kg	1	12	0.90	0.70	0.38	0.25	1.7	0.25	1.7	0.79	0.16	88	0.78	-0.96	0.24	-1.90
Co	mg/kg	20	240	2.3	1.4	2.4	0.50	4.5	0.50	3.2	1.7	0.34	71	0.53	-0.38	-0.48	-1.53
Cr	mg/kg	100	380	35	32	32	19	57	26	45	12	2.3	33	0.40	-0.78	0.00	-0.99
Cu	mg/kg	36	190	21	19	20	14	31	16	28	6.9	1.4	33	0.24	-1.03	-0.33	-0.64
Fe	%			2.1	2.0	2.1	1.3	3.4	1.5	2.5	0.62	0.13	30	0.60	0.04	0.30	-0.50
K	%			1.8	1.6	1.7	1.4	2.3	1.4	2.1	0.35	0.07	20	0.42	-1.08	0.22	-1.13
Li	mg/kg			11	7.7	8.9	4.3	24	5.0	16	7.1	1.5	64	0.81	-0.66	0.19	-1.47
Mg	%			0.25	0.10	0.14	0.04	0.78	0.05	0.29	0.29	0.06	118	1.88	3.27	0.19	-0.71
Mn	mg/kg			330	310	300	200	530	230	420	130	26	38	0.82	0.07	0.14	-0.95
Na	%			2.5	2.1	2.3	1.4	3.7	1.9	2.7	0.92	0.19	38	1.15	1.34	0.20	0.23
Ni	mg/kg	35	210	15	12	12	6.6	28	9.6	22	7.7	1.6	51	0.61	-0.73	-0.11	-0.50
P	mg/kg			410	390	370	250	720	340	470	140	28	34	0.75	0.78	0.28	0.43
Pb	mg/kg	85	530	8.4	6.8	6.8	0.50	27	2.1	10	7.8	1.6	93	1.23	1.10	-0.10	-0.78
Sr	mg/kg			48	40	36	11	110	24	63	31	6.3	65	1.05	0.64	0.08	-0.65
V	mg/kg			53	52	54	31	85	40	65	16	3.3	31	0.26	-0.44	0.11	-0.54
Zn	mg/kg	140	720	92	62	65	37	250	44	100	84	17	92	2.83	9.10	0.30	-0.92

*Optimum and action values according to the New Dutch standards; 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; BC – Box-Cox transformed values

The values for the content of Al, Ca, Fe, K, Mg and na are given in %, those of the other elements in mg/kg. The decrease in the content of the most frequently occurring elements is in the following order: Al > Na > Fe > K > Ca > Mg. The mean and median values of the content of Al, Na, Fe, K, Ca and Mg in the sediments are as follows: 3.1 % and 2.8 %, 2.5 % and 2.5 %, 2.3 % and 2.4 %, 1.9 % and 1.8 %, 0.72 % and 0.58 % and 0.28 % and 0.25 %, respectively, while these values in the alluvial soils are as follows: 2.8 % and 2.0 %, 2.5 % and 2.3 %, 2.1 % and 2.1 %, 1.8 % and 1.7 %, 0.58 % and 0.51 % and 0.25 % and 0.14 %, respectively. Other elements show significantly lower values in both types of samples. Of these, however, P, Mn and Ba show higher concentrations, while the content of all others is below 100 mg/kg.

The results in Tab. 1 and 2 show that the contents of all elements in the samples of sediments and soils from the Strumica catchment area do not exceed the action value according to the Dutch standards (http://www.contaminatedland.co.uk/std-guid/dutch-l.htm). The results show that only a few sediment and soil samples exceed the optimum value for the content of Ba, Cd and Zn, which is due to the lithological origin.

Tab. 3 shows a comparison of the content of the analysed elements in river sediments and alluvial soils from the catchment area of the Strumica River with their content in the topsoil of the entire Strumica region. It can be seen that the content of most elements in the sediments and alluvial soils along the Strumica River and its main tributaries is similar. However, the higher values for Na and the lower values for Pb and Zn differ in the samples from the river catchment. This is probably due to the higher Na content in the Strumica valley compared to the rest of the Strumica region, i.e. the higher Pb and Zn content in the mountainous parts of the region that are not exposed to the transfer of the material in the river beds (Čančalova 2017; Čančalova et al. 2017).

To determine whether there is a significant difference in the distribution of elements in the topsoil and the lower alluvium, as well as whether there is a difference in the distribution of elements between the sediments and the surface alluvium (topsoil), comparative statistics were performed using a specific loading coefficient and three methods [t-test, F-quotient and EF(T/B)] (Tab. 4 and 5). The F-quotient and t-test as well as EF(T/B) show that there is no significant difference in the distribution of elements between the analysed soil and surface samples (Tab. 4). In addition, the same statistical analysis was performed to compare the results of the sediment and surface soil samples (Tab. 5). Significant differences were only found in the distribution of Cr from all elements in the three tests, due to its higher content in the surface soil samples (1.9 mg/kg on average) compared to the lower content of Cr in the sediments (0.75 mg/kg). The enrichment factor as

Table 3. Comparison of the content of the analysed elements in river sediments and alluvial soils from the Strumica River basin with their content in the soil of the entire Strumica region

Element	Unit	River sediment (this study); *n*=12		Alluvial topsoil (this study); *n*=24		Topsoil from Strumica region (Čančalova et al., 2017); *n*=66	
		Md	Min-Max	Md	Min-Max	Md	Min-Max
Ag	mg/kg	1.5	0.56-3.0	1.9	0.60-3.4	0.93	0.040-5.9
Al	%	2.9	1.5-6.3	2.0	6.7	2.0	0.46-5.7
Ba	mg/kg	200	58-520	140	89-580	220	38-420
Ca	%	0.65	0.10-1.8	0.51	0.11-1.4	0.63	0.047-8.3
Cd	mg/kg	0.90	0.25-9.8	0.38	0.25-1.7	-	-
Co	mg/kg	0.50	0.50-4.2	2.4	0.50-4.5	-	-
Cr	mg/kg	38	17-62	32	19-57	43	8.6-98
Cu	mg/kg	18	12-40	20	14-31	21	5.9-58
Fe	%	2.4	0.83-3.7	2.1	1.3-3.4	2.6	0.78-5.5
K	%	1.8	1.2-2.7	1.7	1.4-2.3	1.6	0.47-3.5
Li	mg/kg	11	2.7-33	8.9	4.3-24	12	4.0-51
Mg	%	0.32	0.02-1.1	0.14	0.04-0.78	0.54	0.099-0.99
Mn	mg/kg	370	160-680	300	200-530	450	81-2200
Na	%	2.6	1.2-3.9	2.3	1.4-3.7	1.4	0.27-2.6
Ni	mg/kg	14	7.4-32	12	6.6-28	18	1.6-54
P	mg/kg	520	150-760	370	250-720	510	150-1400
Pb	mg/kg	7.5	0.50-23	6.8	0.50-27	17	2.5-170
Sr	mg/kg	55	13-150	36	11-110	49	3.0-220
V	mg/kg	61	16-98	54	31-85	66	11-200
Zn	mg/kg	59	31-420	65	37-250	90	39-1200

Table 4. Comparative statistics with three methods [t-test, F-ratio and R (T/B)] for the results obtained for the top and bottom alluvial soil from the Strumica River basin

Element	Unit	Subsoil (B)	Topsoil (T)	EF(T/B)	*t*-test	Sign	F-ratio	Sign	R(T/B)	Sign
Ag	mg/kg	1.9	2.1	1.07	0.36	NS	1.11	NS	0.62	*
Al	%	2.3	2.5	1.11	0.39	NS	1.07	NS	0.65	*
Ba	mg/kg	160	150	0.94	-0.26	NS	1.22	NS	0.63	*
Ca	%	0.39	0.54	1.37	0.98	NS	1.47	NS	0.43	NS
Co	mg/kg	0.70	0.40	0.57	-1.58	NS	1.10	NS	-0.01	NS
Cr	mg/kg	1.4	1.9	1.33	0.75	NS	1.13	NS	0.31	NS
Cu	mg/kg	32	35	1.07	0.48	NS	1.09	NS	0.44	NS
Fe	mg/kg	19	21	1.12	0.77	NS	1.64	NS	0.43	NS
K	%	2.0	2.0	1.01	0.09	NS	1.13	NS	0.62	*
Li	%	1.6	1.8	1.13	1.57	NS	1.03	NS	0.55	NS
Mg	mg/kg	7.7	10	1.37	1.21	NS	1.07	NS	0.44	NS
Mn	%	0.10	0.19	1.80	1.25	NS	1.21	NS	0.27	NS
Mo	mg/kg	310	310	1.00	0.02	NS	1.06	NS	0.45	NS
Na	%	2.1	2.6	1.26	1.65	NS	1.34	NS	0.58	*
Ni	mg/kg	12	15	1.24	1.00	NS	1.93	NS	0.74	*
P	mg/kg	400	410	1.03	0.18	NS	1.07	NS	0.52	NS
Pb	mg/kg	6.8	5.1	0.74	-0.62	NS	1.56	NS	0.43	NS
Sr	mg/kg	40	40	1.00	-0.02	NS	1.43	NS	0.69	*
V	mg/kg	52	53	1.02	0.14	NS	1.05	NS	0.46	NS
Zn	mg/kg	62	65	1.05	0.22	NS	1.54	NS	0.61	*

EF(T/B) - enrichment factor, ration between the content in surface and deep soil, Sign - significance,

NS - the difference is not significant, * - the difference is significant

Table 5. Comparative statistics with three methods [t-test, F-ratio and R(S/T)] for the results obtained for the samples of top alluvial soil and river sediments from the Strumica River basin

Element	Unit	Sediment (S)	Topsoil (T)	EF(S/T)	*t*-test	Sign	F-ratio	Sign	R(S/T)	Sign
Ag	mg/kg	1.7	2.1	0.83	1.01	NS	1.79	NS	0.12	NS
Al	%	2.9	2.5	1.16	-0.65	NS	2.17	NS	0.52	NS
Ba	mg/kg	180	150	1.21	-0.75	NS	1.51	NS	0.23	NS
Ca	%	0.58	0.54	1.08	-0.24	NS	1.04	NS	0.12	NS
Co	mg/kg	0.82	0.40	2.05	-1.93	NS	1.23	NS	**-0.64**	*
Cr	mg/kg	0.75	1.9	0.40	**2.66**	*	1.25	*	-0.23	NS
Cu	mg/kg	36	35	1.05	-0.33	NS	1.62	NS	0.40	NS
Fe	mg/kg	20	21	0.97	0.21	NS	1.72	NS	0.25	NS
K	%	2.2	2.0	1.09	-0.63	NS	1.61	NS	0.52	NS
Li	%	1.8	1.8	0.99	0.11	NS	1.80	NS	0.52	NS
Mg	mg/kg	10	10	0.97	0.10	NS	1.52	NS	-0.06	NS
Mn	%	0.19	0.19	1.03	-0.05	NS	1.88	NS	-0.35	NS
Mo	mg/kg	360	310	1.17	-0.96	NS	1.40	NS	0.46	NS
Na	%	2.4	2.6	0.93	0.50	NS	1.02	NS	0.36	NS
Ni	mg/kg	15	15	0.99	0.07	NS	1.53	NS	**0.62**	*
P	mg/kg	470	410	1.15	-0.91	NS	1.59	NS	0.44	NS
Pb	mg/kg	6.7	5.1	1.33	-0.55	NS	1.13	NS	0.32	NS
Sr	mg/kg	53	40	1.32	-0.97	NS	1.14	NS	0.53	NS
V	mg/kg	57	53	1.08	-0.52	NS	1.70	NS	0.44	NS
Zn	mg/kg	63	65	0.96	0.18	NS	1.55	NS	0.33	NS

EF(T/B) - enrichment factor, ration between the content in sediment and surface soil, Sign - significance,

NS - the difference is not significant, * - the difference is significant

Table 6. Matrix of correlation coefficients for the analyzed elements in the sediment and alluvial soil samples from the Strumica River Basin in North Macedonia (n=36). Values in the range 0.5–0.7 (good association) are underlined and in the range 0.7–1.0 (strong association) are in bold; Box-Cox transformed values were used.

	Ag	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	Sr	V	Zn
Ag	1.00																			
Al	-0.31	1.00																		
Ba	-0.35	0.48	1.00																	
Ca	-0.02	0.27	0.47	1.00																
Cd	0.05	0.05	0.05	-0.10	1.00															
Co	0.03	-0.19	-0.30	-0.26	-0.29	1.00														
Cr	0.05	0.31	0.43	0.64	0.04	-0.50	1.00													
Cu	0.07	0.16	0.39	0.44	-0.04	-0.23	0.59	1.00												
Fe	-0.09	0.44	0.55	0.63	0.01	-0.60	**0.91**	0.57	1.00											
K	0.12	0.43	0.48	0.23	0.06	-0.20	0.36	0.41	0.34	1.00										
Li	0.28	0.20	0.54	**0.70**	-0.12	-0.32	0.62	0.43	0.61	0.58	1.00									
Mg	0.15	-0.01	0.41	**0.83**	-0.21	-0.34	0.57	0.44	0.55	0.32	**0.82**	1.00								
Mn	-0.24	0.41	0.61	0.69	0.02	-0.46	0.69	0.45	**0.85**	0.21	0.56	0.55	1.00							
Na	0.46	-0.19	-0.12	0.23	0.00	0.02	-0.05	-0.32	-0.10	-0.01	0.41	0.32	-0.01	1.00						
Ni	0.14	0.18	0.44	0.64	-0.03	-0.44	**0.81**	0.69	**0.71**	0.56	**0.73**	0.68	0.54	0.00	1.00					
P	0.15	0.28	0.24	0.64	0.08	-0.30	**0.80**	0.52	**0.74**	0.23	0.57	0.46	0.64	0.08	0.62	1.00				
Pb	-0.07	0.38	0.25	0.22	-0.06	-0.20	0.27	0.41	0.40	0.25	0.11	0.16	0.27	-0.49	0.27	0.24	1.00			
Sr	-0.33	0.65	**0.83**	0.67	-0.03	-0.25	0.48	0.28	0.63	0.26	0.55	0.46	**0.75**	0.08	0.37	0.41	0.28	1.00		
V	0.00	0.36	0.47	0.62	0.06	-0.54	**0.94**	0.58	**0.97**	0.31	0.59	0.55	**0.78**	-0.08	**0.74**	**0.78**	0.40	0.55	1.00	
Zn	-0.25	0.23	0.69	0.37	-0.10	-0.45	0.54	0.45	0.66	0.27	0.40	0.36	0.64	-0.15	0.53	0.29	0.35	0.59	0.60	1.00

a ratio between the content of the elements in sediments and topsoil [EF(S/T)] also shows the difference between the distribution of some other chemical elements in the sediment and surface soil samples (Co and Ni). However, in general, these differences are not significant and, in most cases, it is less than 1.

To determine the degree of correlation between the analysed elements in the samples of river sediments and soils in the study area, the bivariate statistic was used, according to which there is a good correlation between the analysed elements if the absolute value of the correlation coefficient is between 0.3 and 0.7, and a strong correlation between the analysed elements if the correlation coefficient is between 0.7 and 1. Tab. 6 shows the matrix of correlation coefficients for 12 samples of river sediments and 24 soil samples in all zones of the study area. There is a strong correlation between the content of the following elements: V-Fe (0.97), V-Cr (0.94), Fe-Cr (0.91), Mn-Fe (0.85), Sr-Ba (0.83), Mg-Ca (0.83), Mg-Li (0.82), Ni-Cr (0.81) and P-Sr (0.80). There is a weaker correlation between the contents of the following elements: Cr-Co (0.50), P-Cu (0.52), Zn-Ni (0.53), Li-Ba (0.54), V-Mg (0.55), V-Sr (0.55), Mn-Li (0.56), P-Li (0.57), Li-K (0.58), V-Cu (0.58), Zn-Sr (0.59), Zn-V (0.60). The elements Na and Pb show no or a very weak correlation with the contents of the other elements.

The multivariate factor analysis of the content of chemical elements in all samples of river sediments and soils resulted in a matrix of loading factors, which is listed in Tab. 7. The factor analysis shows three factors, of which factor 1 (F1) has the highest loading value of 4.47 and a variability of 29.78% of the total variability, corresponding to 76.5%. The first factor associates the elements V, Cr, Fe, P, Cu, Ni and Pb. The highest charge value in this geochemical association of elements was found for vanadium (0.81), the lowest for lead (0.57). Factor 2 (F2) has a charge value of 3.42 and a variability of 22.83% and associates the following elements Sr, Ba, Al, Zn and Mn. The highest charge value in the second geochemical association of elements was obtained for strontium (0.87) and the lowest for manganese (0.58). The third factor (F3) represents 23.84% of the total variability of the matrix with the lowest loadvalue 1.27 and associates the elements Mg, Li and Ca. The highest loadvalue in the third geochemical association is magnesium (0.87) and the lowest is calcium (0.74).

The results obtained with the multivariable factor analysis were verified by applying a multivariable cluster analysis. The resulting dendrogram of the interdependence of the analysed elements in the samples of river sediments and soils from the Strumica river catchment is shown in Fig. 5. Two clusters with subclusters are formed in the dendrogram. In the first cluster, one subcluster contains the elements from factor 2 (Al, Ba, Sr, Zn) and the second subcluster contains the elements from the geochemical association of factor 3 (Ca, Li, Mg). The second cluster contains the elements from the geochemical association of factor 1 (Cr, Fe, V, P, Cu, Ni).

Table 7. Factor analysis (n=36)

	F1	F2	F3	Comm
V	**0.81**	0.34	0.35	90.6
Cr	**0.80**	0.23	0.43	87.7
Fe	**0.75**	0.46	0.36	90.1
P	**0.74**	0.11	0.39	70.2
Cu	**0.72**	0.11	0.23	58.5
Ni	**0.68**	0.11	0.56	78.9
Pb	**0.57**	0.37	-0.28	54.1
Sr	0.13	**0.87**	0.40	93.8
Ba	0.10	**0.81**	0.37	81.1
Al	0.21	**0.77**	-0.15	66.6
Zn	0.39	**0.59**	0.24	55.4
Mn	0.48	**0.58**	0.44	76.6
Mg	0.29	0.10	**0.87**	84.6
Li	0.31	0.24	**0.81**	80.8
Ca	0.35	0.32	**0.74**	77.6
EigenVal	8.51	1.69	1.27	
Expl.Var	4.47	3.42	3.58	
Prp.Totl	29.78	22.83	23.84	76.5

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

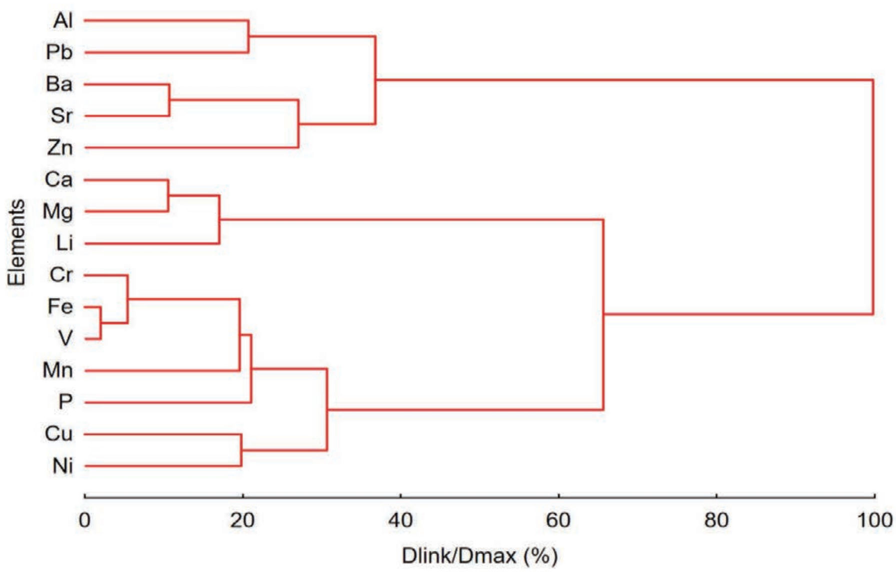

Figure 5. Dendrogram of the interdependence of the analysed elements

Factor 1 (**F1**) comprises V, Cr, Fe, P, Cu, Ni and Pb and accounts for 16.3% of the total variability. The spatial distribution maps of the factor score values of factor 1 and the spatial distribution of the contents of the individual elements belonging to this factor are shown in Fig. 6. A higher factor score of factor 1 was registered for river sediments and soils from the Strumica River and a lower factor score for river sediments from its tributaries. The lowest factor value of factor 1 was recorded in river sediments and soils from Injevska Reka and Stara Reka.

The first geochemical association of elements (F1) includes vanadium. Its spatial distribution in river sediments and alluvial soils in the study area is shown in Fig. 6. The content of vanadium in these samples ranges from 16 mg/kg to 98 mg/kg. It is mainly present in the sediments and soils of the Strumica River. The spatial distribution map shows that the V content in river sediments and alluvial soils is highest in the samples from the vicinity of Novo Selo (98 mg/kg) and lowest in the samples from Injevska Reka (16 mg/kg)

The map of the spatial distribution of chromium content in the studied area shows that chromium is more abundant in the sediment and soil samples from the Strumica River, which were taken along its course from the town of Strumica to the border with neighbouring Bulgaria (Fig. 6). The Cr content in sediments and alluvial soils from the study area is between 17 mg/kg and 62 mg/kg. The highest value of Cr content is found in river sediments and alluvial soils from the Strumica River (62 mg/kg), but still does not exceed the optimum limit (100 mg/kg) for Cr according to Dutch standards. The lowest value of Cr content is found in river sediments and soils from Injevska Reka (17 mg/kg).

Iron and aluminium belong to the first factor of the geochemical association and show a similar distribution of their content in the sediments and alluvial soils of the studied area. The map of the spatial distribution of Fe content in river sediments is shown in Fig. 6. The Fe content in river sediments and soils increases from north to south. The map of Fe content in the sediment samples from the study area shows that the highest Fe content is found in the sediments and soils of the Strumica River near Novo Selo (2.6%), followed by the sediments and soils of the Strumica River near the village of Bansko.

Phosphorus is present in all sediment samples from the analysed area with different contents in the sediments and alluvial soils (Fig. 6). The average value of phosphorus content in this analysed catchment is 434 mg/kg. The river sediments and alluvial soils from the Vodoča River have a higher content (765 mg/kg). The lowest phosphorus content was found in the sediments and soils from Injevska Reka (150 mg/kg). The higher phosphorus content is due to municipal and industrial waste and the use of phosphate fertilisers in agriculture.

The copper content in the sediments and soils of the study area is between 12 mg/kg and 40 mg/kg (Fig. 6). The map of the spatial distribution of Cu content shows that the content in river sediments and alluvial soils is low, with the exception of the sample from the Strumica River near the village of Bansko (40.1 mg/kg), which exceeds the optimal limit (36 mg/kg) according to Dutch standards. Anthropogenic sources of Cu are municipal and industrial waste, various copper-containing chemicals, agricultural wastewater, etc. The lowest Cu content was found in river sediments and soils from the Turia River (11.8 mg/kg).

The spatial distribution of nickel in the river sediments and soils shows a low Ni content in the river

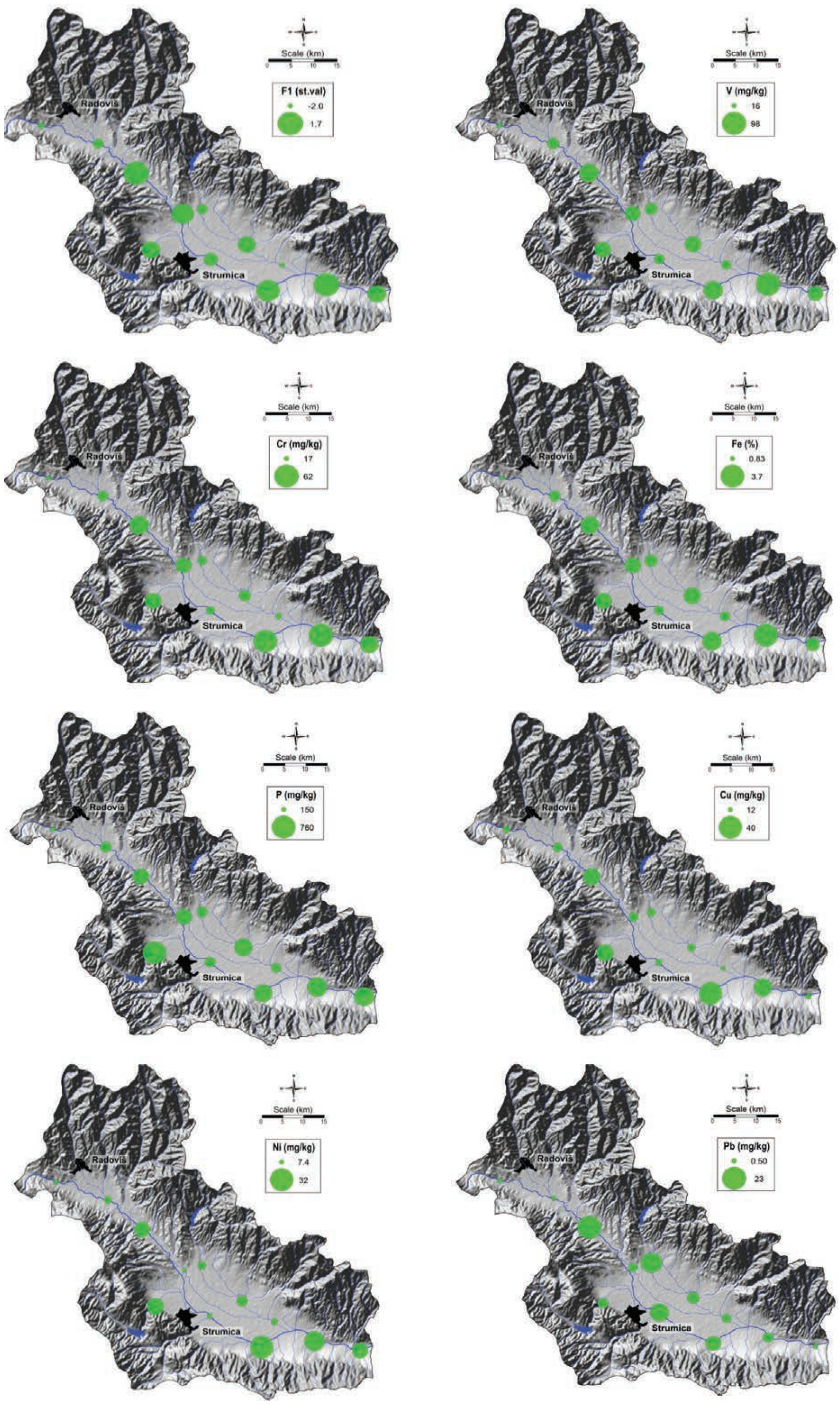

Figure 6. Spatial distribution of factor scores of Factor 1 and of the content of the elements inclided in F1 (V, Cr, Fe, P, Cu, Ni and Pb)

sediments along the course of the Strumica river (Fig. 4). The Ni content in river sediments and alluvial soils from the study area shows an increasing trend from the sources towards the Bulgarian border (Fig. 6). The results obtained for the river sediments and soils are consistent with the nickel content in the geological composition of the soil in the south-eastern part of the Republic of Macedonia. The highest mean value of Ni content was found in the sediments and soils of the Bansko River (31.8 mg/kg), a tributary of the Strumica River. The Ni contents determined in the sediments and soils of the Strumica River do not exceed the optimal limit value for Ni (35 mg/kg).

Lead is also a geochemical compound of elements. Its content in the samples of river sediments and soils in the study area ranges from 0.50 mg/kg to 23 mg/kg and its spatial distribution is shown in Fig. 6. Of all sediments, the Pb content in river sediments and soils in the Radovishka River is the highest (23 mg/kg), but does not exceed the optimal limit for lead (85 mg/kg) according to Dutch standards. The average value of Pb content in river sediments is below 10 mg/kg.

Factor **2** (**F2**) has a variability of 22.83% and associates the following elements Sr, Ba, Al, Zn and Mn. The spatial distribution of Factor 2 and the content of the elements of this factor in river sediment and alluvial samples (Fig. 7) is similar to factor 1. The difference is that a higher factor value is observed for river sediments from the Turia River. The strontium content in river sediments and alluvial soil samples is between 13 mg/kg and 150 mg/kg (Tab. 1 and 2). The highest Sr content is found in the river sediments and soils from the Turia River (150 mg/kg), the lowest content (13 mg/kg) in the samples from Injevska Reka (Fig. 7). In the river

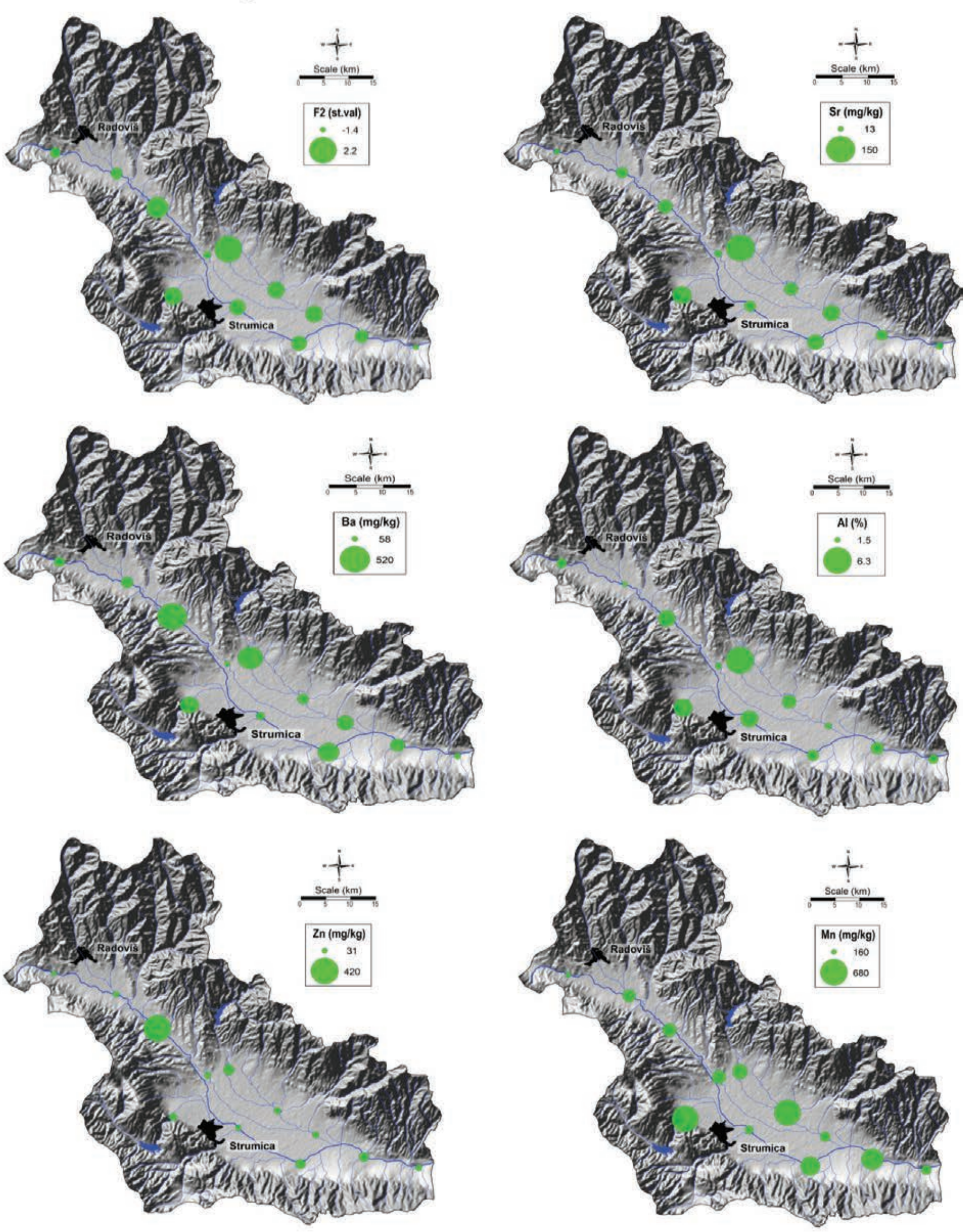

Figure 7. Spatial distribution of factor scores of Factor 2 and of the content of the elements inclided in F1 (Sr, Ba, Al, Zn and Mn)

sediments sampled after the dam near Turia and on the Strumica River after the town of Radovish, a higher barium content was found compared to other samples of river sediments and soils (Fig. 7). The mean values of Ba content in river sediments and soils in the study area range from 58 mg/kg to 520 mg/kg (Tab. 1 and 2). The values for Ba content in the river sediments and soils from the Strumica River basin exceed the optimal value according to the Dutch standards for Ba (200 mg/kg), which is due to a higher natural occurrence of barium in Macedonian soils (Stafilov & Šajn 2016; Čančalova et al. 2017). The spatial distribution of the aluminium content in river sediment and alluvial samples from the study area is shown in Fig. 7. The content ranges from 1.5% to 6.3% (Fig. 7). The highest Al content (6.3%) was found in a sample of river sediment and soil from the Turia River, while in river sediment the highest content was found in sediment from the Strumica River (4.1%). Thus, the increased Al content in the samples from these rivers is the result of the geological composition of their environment (Stafilov & Šajn 2016; Čančalova et al. 2017).

The distribution of zinc content in the river sediments and soil samples throughout the study area is relatively low (31 mg/kg to 250 mg/kg) and uniform (Fig. 7), with the exception of the river sediments and soils from the Radoviška River near the village of Dukatino, where the Zn content is higher (420 mg/kg). Here, the optimal value for zinc (140 mg/kg) according to Dutch standards is exceeded, but the intervention value is not exceeded (720 mg/kg). The reason for the elevated values of zinc content is most likely the deposition of erosive material from the Plačkovica Mountains, where elevated values for its content were found in the soils (Stafilov & Šajn 2016; Čančalova et al. 2017). The spatial distribution of manganese in the river sediments and soils in the study area is shown in Fig. 7. The Mn content determined in the samples of river sediments and soils along the course of the Vodoča River, a tributary of the Strumica (680 mg/kg), is higher than the other values. The Mn content in all samples of river sediments and soils is close to each other at around 300 mg/kg, except in river sediments and soils from the Turija and Vodoča rivers (over 600 mg/kg), which have higher values. This is most likely due to the sediments from the western part of Belasica Mountain and Plauš Mountain, in whose areas an increased manganese content in the soils was found (Stafilov & Šajn 2016; Čančalova et al. 2017).

The third factor (**F3**) accounts for 23.84% of the total variability and combines the elements Mg, Li and Ca. The spatial distribution of the factor values of F1 and the content of the individual elements of this factor are shown in Fig. 8. It can be seen that these elements have a certain increased content in the sediments and

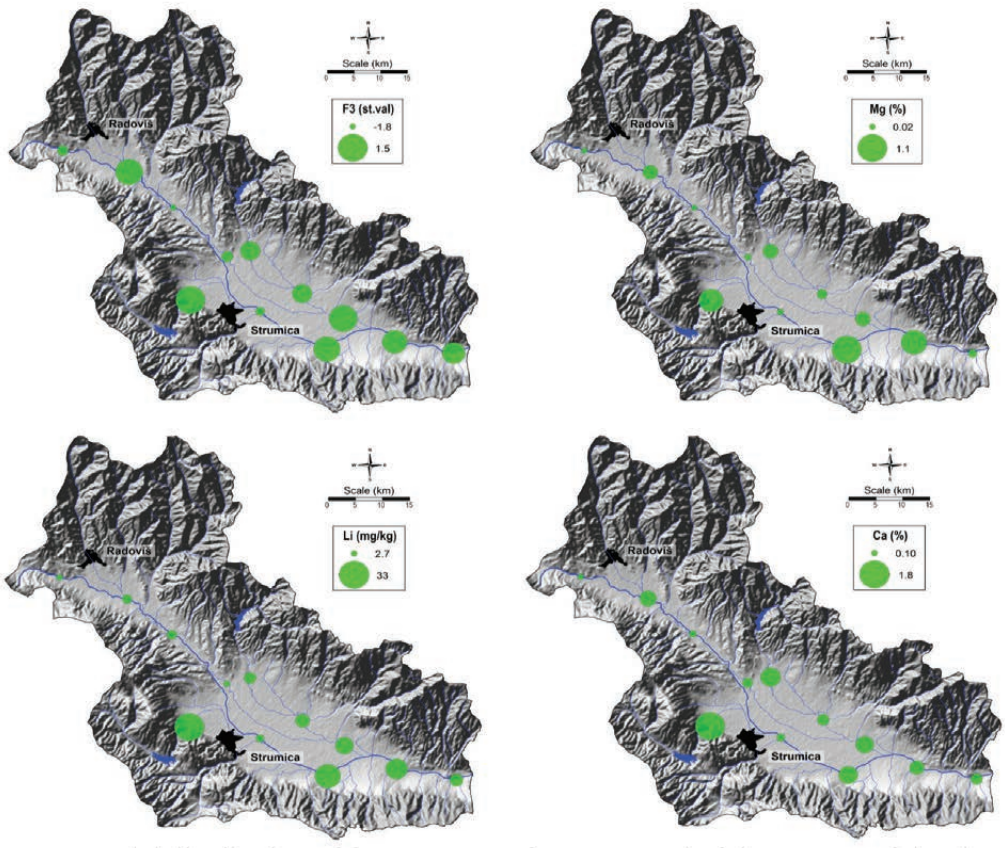

Figure 8. Spatial distribution of factor scores of Factor 3 and of the content of the elements inclided in F3 (Mg, Li and Ca)

alluvial deposits in the southern part of the analysed area (Strumica and Vodoča rivers).

The magnesium content in the sediments and soils of the analysed area is between 0.02% and 1.1%. Magnesium has a relatively high mobility in the environment. The highest magnesium content was found in the sediments and soils of the Strumica River near Bansko (1.1%). The presence of magnesium in the Strumica catchment area is due to its natural occurrence in the soils of this area. The contents of Li in sediments and soils from the study area range from 2.7 mg/kg to 33 mg/kg. A higher Li content was found in river sediments and soils from the Vodoča River. The Ca content in sediments and soils is between 0.10% and 1.8%. A higher Ca content was found in river sediments sampled near the Vodoča dam than in other river sediments and soils (1.8%)

Some of the analysed elements were not included in the factor associations (Ag, Cd, Co, K and Na) as they do not correlate with the other elements. The spatial distribution of these elements is shown in Fig. 9.

Silver is distributed in low concentrations in the sediments and soils of the entire study area, with the exception of river sediments and soils from the lower course of the Strumica posle gradot Strumica

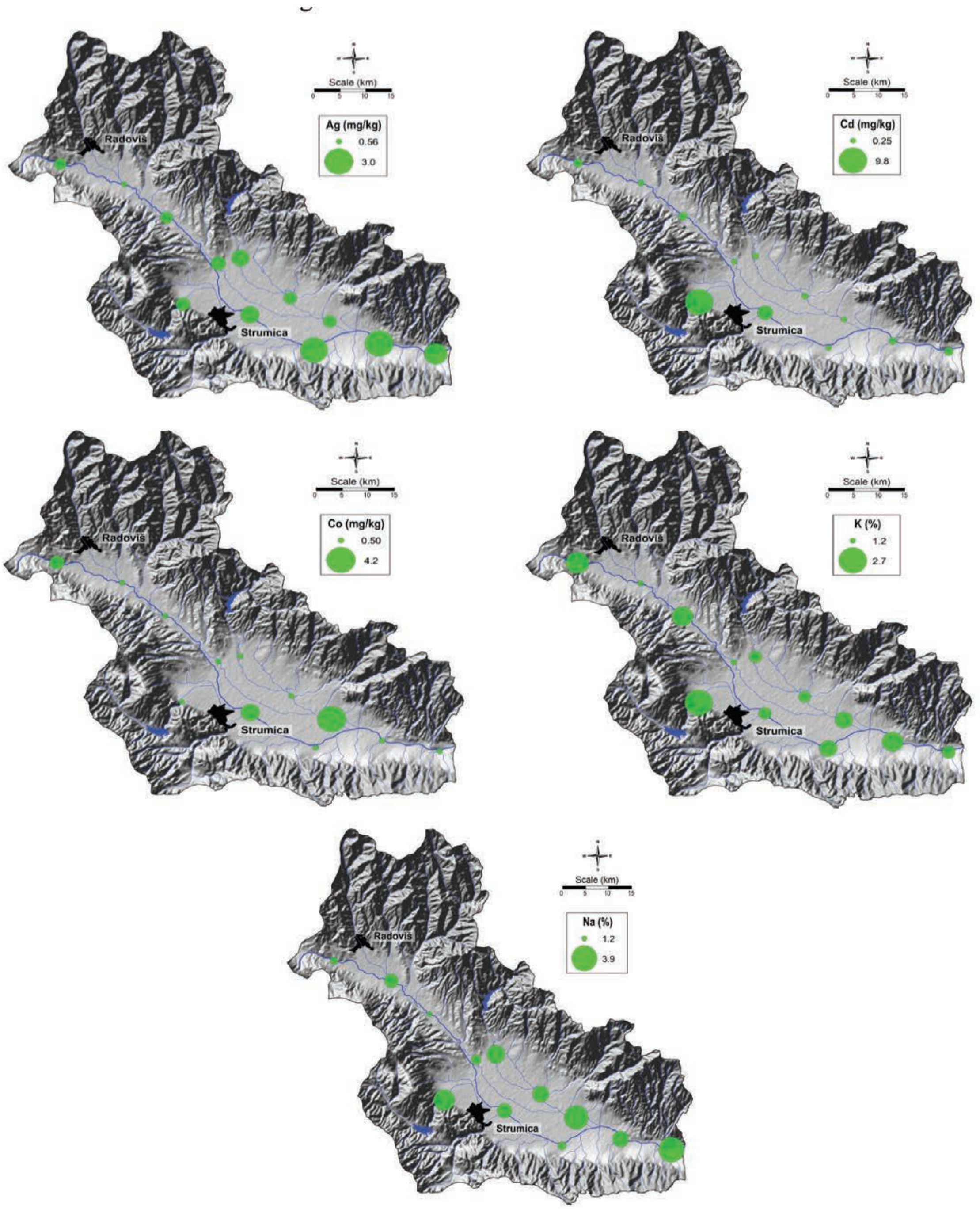

Figure 9. Spatial distribution of the content of Ag, Cd, Co, K and Na in sediments and soil

river, which is most likely the result of anthropogenic activities (Fig. 9). The silver content in the sediments ranges from 0.56 mg/kg to 3.4 mg/kg. The highest Ag content is found in the sediments and soils of the Strumica River near Novo Selo (3.4 mg/kg), the lowest in the samples from Stara Reka (0.56 mg/kg).

The Cd content in river sediments and soils from the study area ranges from 0.25 mg/kg to 9.8 mg/kg (Fig. 9). The values for Cd content in some of the river sediment samples from the Strumica river catchment exceed the optimal limit (0.8 mg/kg) according to Dutch standards. The highest Cd content was found in the river sediment samples from the Vodoča River (9.8 mg/kg), which is due to the characteristic composition of the soil in this part of the study area. The values for Co content in the samples of river sediments and soils from the study area are shown in Tab. 1 and 2. In the river sediment samples along the course of the Strumica River, a low Co content was found (0.5 mg/kg to 4.4 mg/kg), which does not exceed the optimal (20 mg/kg) and intervention value (240 mg/kg) according to Dutch standards.

The spatial distribution of K content in river sediment and soil samples from the area studied is almost evenly distributed over the entire area, with values ranging from 1.2 % to 2.7 % (Fig. 9). Potassium occurs naturally, but is often used as an artificial fertiliser in agriculture, which increases the potassium content in the environment. The highest K content is found in the river sediments and soils of Lake Vodoča (2.7 %), which is due to the agricultural plantations in the area. The sodium content ranges from 1.2% to 3.9%. A higher Na content was found in the river sediments and soil samples from the Strumica River, at the border crossing with Bulgaria (3.9%) and near the village of Turnovo (3.7%), while the lowest Na content was measured in the sediments and soils of Radovishka Reka.

From the results for the chemical elements in the river sediments and soil samples from the study area, it can be concluded that the river sediments and soils have a composition that corresponds to their geological environment.

Conclusion

The content of 20 chemical elements (Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) in river sediment and alluvial soil samples collected from 12 sites in the Strumica river basin in North Macedonia. A total of 12 river sediment samples and 24 alluvial soil samples were collected (12 samples from the surface layer and 12 from the deep layer). By applying a multivariate factor analysis, three associations of the elements were identified: Factor 1 (F1) associating the chemical elements V, Cr, Ge, P, Cu, Ni and Pb, Factor 2 (F2) associating Sr, Ba, Al, Zn and Mn and Factor 3 associating Mg, Li and Ca. The cluster analysis of the interdependence of the analysed elements in the samples from the Strumica river basin yielded the same results as the factor analysis. From the studies carried out and the results obtained, it can be concluded that the Strumica river basin generally follows the geology of its surroundings and that the partial contamination of certain parts of the area with some elements is the result of agricultural activities.

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