



Distribution of trace elements in sediments and soil from Crn Drim River Basin, Republic of Macedonia

Silvana Vasilevska¹ · Trajče Stafilov¹ · Robert Šajn²

© Springer Nature Switzerland AG 2019

Abstract

A systematic study was carried out to investigate the distribution of chemical elements in the sediment and soil samples collected from Crn Drim River Basin, Republic of Macedonia. For this purpose, 18 samples of river sediment, 19 samples of lake sediment, 16 samples of surface (0–5 cm) and 16 samples of bottom (20–30 cm) soil were collected within the basin. From the sewerage systems in the towns of Resen, Ohrid, Struga and Debar, 11 samples of urban sediment were collected. The determination of the content of 22 elements was performed by using inductively coupled plasma atomic emission spectrometry. Cluster and factor analyses were applied in order to show the associations of chemical elements. According to a correlation coefficient matrix of all sediment samples, a strong correlation (over 0.70) was identified between the content of the following elements: Zn–Cu, Ni–Cr, V–Fe, Sr–Ca, Fe–Cr, P–Cu, Ni–Cu, Zn–P and V–Cr. Factor analysis of the data resulted in three factors: Factor 1 (Fe, V, Al, Mn, Li), Factor 2 (Zn, Cu, Ag, Pb) and Factor 3 (Co, Ni, Cr). The elements included in factors F2 and F3 were internally correlated and belong to one cluster. Comparative statistics with three methods [*t* test, F ratio and R(T/B)] showed no difference between the distribution of various chemical elements in top (T) and bottom (B) soil samples. The results show that the samples of urban sediment have a high content of heavy metals, which represent a risk to the environment and the river basin of Crn Drim, especially for the natural Prespa and Ohrid lakes.

Keywords Soil · Heavy metals · Urban sediment · Crn Drim River Basin · Republic of Macedonia

1 Introduction

Pollution and protection of the environment are a global problem. The increase in population, industry, traffic, landfills of various waste materials and wastewater cause pollution of the environment, within air, water, soil, plant and animal life habitat. Surface waters are carriers of large quantities of various waste materials. Concentrated pollutants of surface water are usually wastewaters from households, industrial facilities and large urban agglomerations which are located near rivers or lakes [1].

Sediment is part of the environment that provides essential environmental information and is increasingly recognized as carriers and as a potential source of

contamination of aqua systems. Metals dissolved in soil solution, surface waters and those adsorbed in the sediment with the cation exchange process are usually available for aquatic and benthic organisms, as well as for plants. The acidification of atmospheric sources and the drainage of agricultural land are special types of factors that influence the degradation of lake and river ecosystems, and consequently human health. The anthropogenic elements accumulated in alluvial soils pose a danger because they accumulate in all agricultural products that are grown on that soil. Water used for irrigation from the rivers, also contaminated by anthropogenic elements, contributes to the production and distribution of agricultural products that are potentially dangerous to human health [2].

✉ Trajče Stafilov, trajcest@pmf.ukim.mk | ¹Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University, Arhimedova 5, 1000 Skopje, Republic of Macedonia. ²Geological Survey of Slovenia, Dimičeva ulica 14, 1000 Ljubljana, Slovenia.



The growth of population in urban areas and the impacts of industries and other human activities have resulted in the distribution and accumulation of metals in urban soils. These can remain for centuries and may become concentrated due to supplements from domestic, commercial or industrial sources, with long-term risks to human health and the environment [3–6]. The metals present in the environment are susceptible to atmospheric deposition which contributes to the contamination of all components of the biosphere (water, soil and vegetation) [7, 8]. Because of this, and in order to maintain or improve the quality of the environment, research should be carried out to determine the pollutants and the level of pollution and then assess where and what protection measures should be taken.

More research on the rivers in the Republic of Macedonia indicates the presence of heavy metals in the waters [9–19]. Primary sources of heavy metal contamination in the Republic of Macedonia are lead and zinc mines and flotation plants, Pb–Zn, steel and ferronickel metallurgical activities, different industrial activities and urban waste. There are three active Pb–Zn mines and flotation plants situated in the eastern part of the country, and their activities pollute the environment with Pb, Zn, Cd and some other heavy metals, which can be found in the soil [13, 20] and river waters [15–17]. Studies also found an influence of the thermoelectric power plant near the city of Bitola, producing about one million tons of fly ash per year, deposited on the surface close to the plant. This plant pollutes soil, air and water with Pb and Zn [13, 15, 16, 19]. The study on the impacts of the Pb and Zn smelter plant in the city of Veles detected soil pollution with potentially harmful elements (As, Cd, Cu, Hg, In, Pb, Sb, Zn) exceeding the intervention values [13, 20]. Similar effects were detected in an area with ferronickel metallurgical activities near the city of Kavadarci regarding the contamination of soil [21]. The arsenic–antimony abounded mine “Allchar” near the city of Kavadarci also affects the environment, with the main pollutants As, Sb and Tl in the soil [13, 20, 22] or in the river waters and sediment [13, 19, 22].

The aim of this work is to present data about the spatial distribution of chemical elements in samples of sediment and soil collected from different locations in the Crn Drim River Basin, Republic of Macedonia, as well as samples of urban sediment collected from the sewerage systems in the towns of Resen, Ohrid, Struga and Debar from this water basin. By determining the concentration of chemical elements in the soil and sediment samples, their interpretation and correlation will provide information on the presence of potentially toxic metals in the sediment and soil from the Crn Drim River Basin.

2 Materials and methods

2.1 Study area

The investigated region includes the basin of the river Crn Drim which is in the southwestern part of the Republic of Macedonia (Fig. 1). The River Crn Drim flows through two valleys, the Ohrid–Struga and the Debar–Rekanska Valleys. This basin also includes two natural lakes, Prespa and Ohrid lakes. Prespa Lake is located at the bottom of the Prespa Valley at an altitude of 856 m [23]. The water from Lake Prespa has no surface runoff, but through the limestone composition of the mountains Galičica and Suva Gora, it flows out of the underground waters into the Ohrid Lake [18, 24–26]. Besides these two lakes, two artificial lakes, Debar and Globočica, exist along the river Crn Drim, and in the northern part of the investigated region, there is another artificial Lake Mavrovo.

A geological map of the investigated area is shown in Fig. 2. In the northern part of the investigated area, that is, downstream of the river Radika, the geological formations are dominated by Mesozoic tributaries and Paleozoic metamorphic sediment, and sporadically Mesozoic carbonate rocks. In the central part of the investigated area, similar formations are predominant with certain parts in which Mesozoic magnetite rocks are represented. The mountains of Karaorman, Kopanica, Istok and part of Plačanska are composed of Paleozoic metamorphic rocks with the

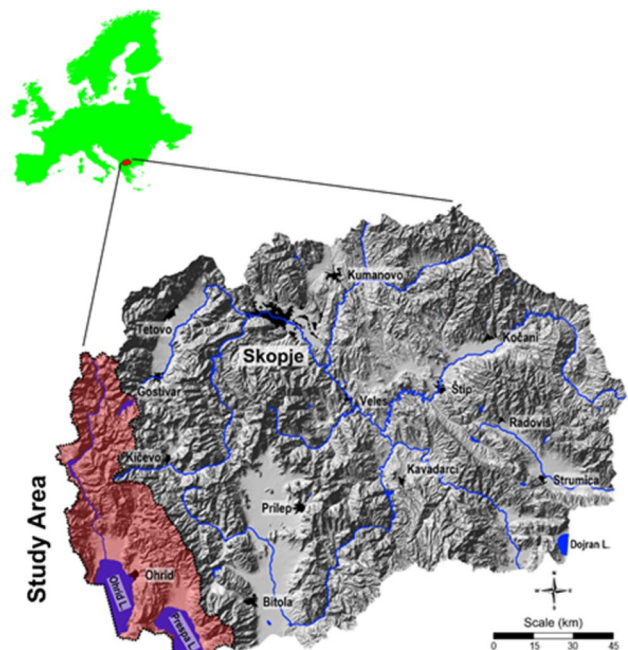


Fig. 1 Location of the investigated region within the territory of the Republic of Macedonia

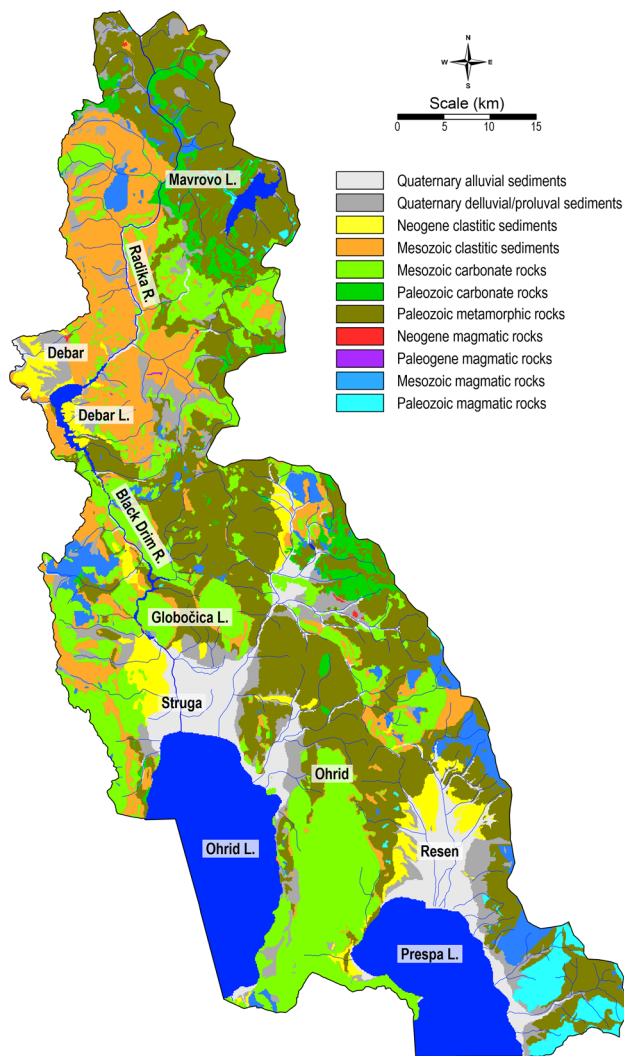


Fig. 2 Geological map of the investigated region

presence of Mesozoic magmatic rocks. Galičica Mountain mainly consists of Mesozoic carbonate rocks, while Paleozoic metamorphic rocks, Paleozoic magmatic rocks and Mesozoic magmatic rocks are present in the western part of Mountain Baba. Debar Field, Ohrid Field, Resen Field and Struga Field consist of quaternary alluvial and diluvial/proluvial sediment, and the upper zones of the respective valleys consist of Neogene clastic sediment.

Agricultural areas dominate the towns of Struga, Debar, Resen and Ohrid. The pedological map of the investigated region (Fig. 3) shows that lithosols (dolomites/limestones) are most present in the hill–mountain zones of Galičica, Jablanica, Korab and Bistra. Cambisol soil dominates the mountains Baba, Bigla, Plančenska, Ilinska, Stogovo and around the Mavrovo Lake, and a small part of the mountains Jablanica and Korab. On the Stogovo and Ničpur mountains, there is a ranker soil along with lithosol, colluvial and regosol. In the settlements of Resen, Ohrid

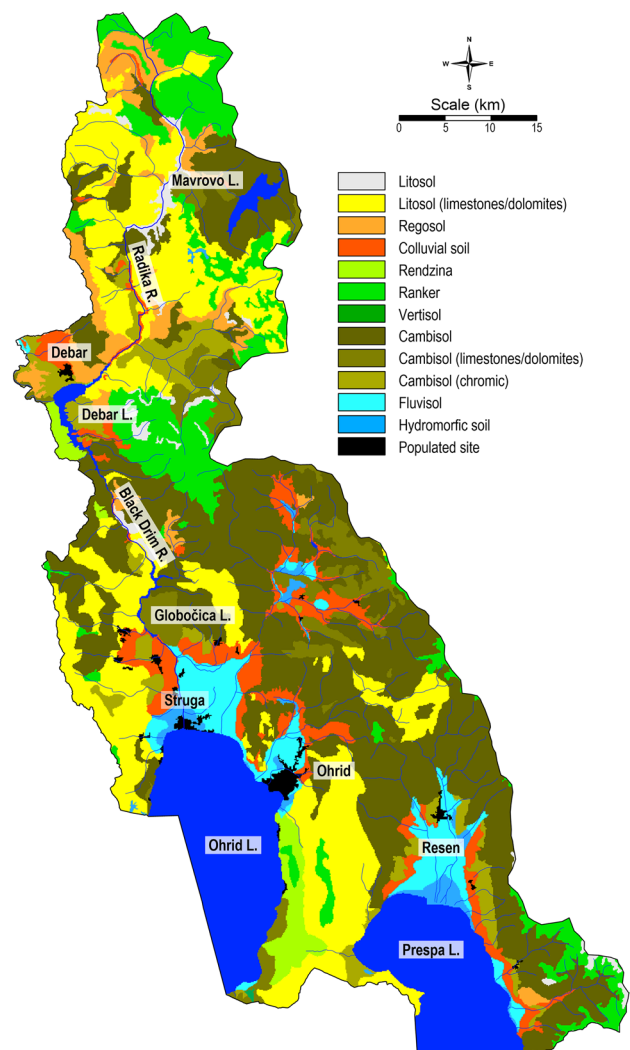


Fig. 3 Pedological map of the investigated region

and Struga there is a fluvial soil with areas composed of hydromorphic soil near the lake shores, and in the higher zones of their respective valleys, there is the colluvium soil. Various types of soils are represented in the Debar Valley: colluvial, chromicambisol, regosol, fluvial and cambisol.

2.2 Sampling and sample preparation

Sediment and soil samples were collected in the period from June to September 2015, along the river basin Crn Drim and the towns of Resen, Ohrid, Struga and Debar. First, a sample collection network of 47 locations was prepared across the entire study area shown in Fig. 4. Depending on site location and availability, samples were collected in immediate proximity to the specified locations. In the basin of the River Crn Drim, 18 samples of river sediment and 19 samples of lake sediment were collected. Also, 16 samples of surface soil (0–5 cm) and 16 samples of

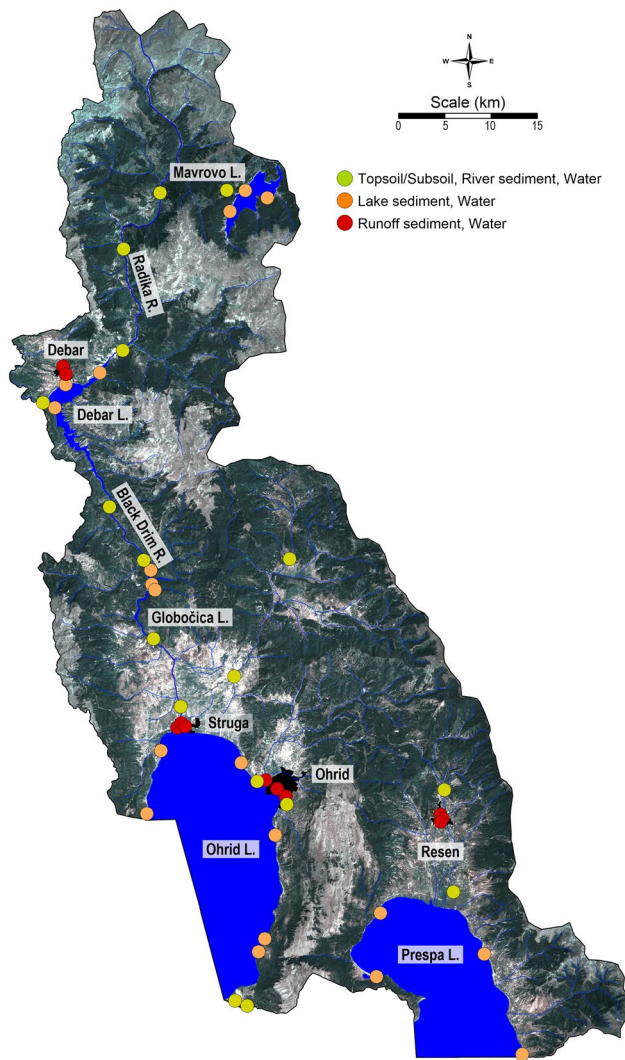


Fig. 4 Map of locations of sediment and soil samples

bottom (20–30 cm) soil were collected in the basin of the river Crn Drim. From the sewerage systems in the towns of Resen, Ohrid, Struga and Debar, 11 samples of urban sediment were collected (Fig. 5).

The samples of river and soil sediment were collected from rivers Golema, Koselska, Cerava, Sateska and Radika. Three samples of lake sediment were collected from Globočica, Debar Lake and Mavrovo Lake. Five samples of lake sediment were collected from Lake Prespa, and six samples of lake sediment were collected from Lake Ohrid. One sample of river sediment was taken from St. Naum Springs and Biljana’s Springs. In the upstream of the Crn Drim River, samples of river and soil sediment were collected in several locations, several kilometers apart. Samples of urban sediment were collected from the towns of Resen, Ohrid, Struga and Debar. Samples of urban sediment consist of mud taken from the pipes from before

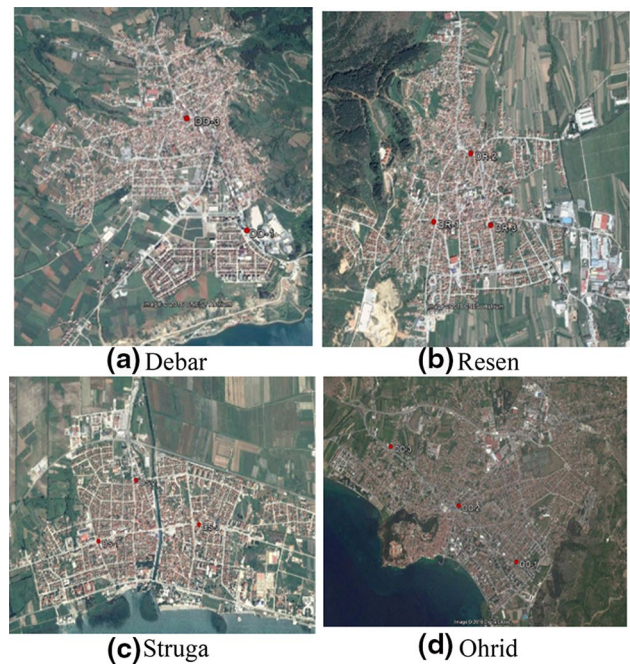


Fig. 5 Locations of urban samples in the towns from the investigated river basin

and after the sewage treatment stations in the cities of Resen, Ohrid and Struga, apart from the city of Debar, where there are no wastewater treatment stations and the samples were collected directly from the wastewater discharge system.

Soil samples were taken from two layers, topsoil (0–5 cm) and bottom soil (20–30 cm), and also from both sides of the river at each sampling site. From each soil layer, five separate soil samples were collected within a radius of 10 × 10 m according to the appropriate standards for taking this type of sample. Four samples were collected from the corners of the surface square, and the fifth sample was collected from the intersection of the diagonals of the square. All five subsets were mixed, and a representative sample was obtained [27–31].

The preparation of river, lake, urban and soil sediment samples for laboratory analysis was carried out by cleaning and drying for several days at room temperature and not directly in the sun. During drying, trimming and homogenization of the samples were done so that if there were lumps in the sediment, they were crushed to smaller parts using a rubber hammer. After drying, the river, lake and urban sediment were sifted through a 0.125-mm sieve. Surface and deep soil samples were sifted through a 2-mm sieve and then were ground into fine material (below 100 μm).

Such prepared samples were digested by applying mixtures of mineral concentrated acids according to

international standard ISO 14869-1: 2001 [32]. A precisely measured mass of 0.25 g with the accuracy of 0.0001 g was placed in Teflon vessels, and 5 ml of concentrated nitric acid was added to each vessel and heated on a hot plate, and as soon as steamed vapors were evaporated from nitrogen oxides, new amounts of concentrated nitric acid were added. Then, 5 ml of concentrated hydrofluoric acid was added to each sample, for complete decomposition of inorganic components. When the solution was completely cleared, 2 ml of concentrated perchloric acid, analytical purity (Alkaloid, Skopje), was added. Then the containers were stored for another 15 min, and then 2 ml of concentrated hydrochloric acid and 5 ml redistilled water were added for a complete dissolution of the sample.

The analysis was performed using atomic emission spectrometer with inductively coupled plasma ICP-AES, model 715ES (Varian, USA). The instrumental and operational working conditions were given in our previous paper [33]. In all of the samples, the contents of the 22 chemical elements were analyzed: Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V and Zn.

The quality control of the applied techniques was performed by standard addition method, and it was observed that in the recovery of the analyzed elements, ranges for ICP-AES 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 and Technologies, USA) and spiked intra-laboratory samples were analyzed at a combined frequency of 20% of the samples. The recovery for all of the analyzed elements ranged from 87.5% for Na to 112% for P (for ICP-AES measurements).

3 Results and discussion

3.1 Trace elements in sediment

The basic descriptive statistics of the values for the content of the analyzed chemical elements in 37 samples of river and lake sediment are presented in Table 1. Values of Al, Ca, Fe, K, Mg and Na are in % and remaining elements (Ag, As, Ba, Cd, Co, Cr, Li, Mn, Mo, Ni, P, Pb, Sr, V, Zn) in mg/kg. Highest values for the arithmetic mean (2.4%), Box-Cox transformed mean (2.3%), median (2.4 mg/kg), 10th percentile (0.56%), 25th percentile (1.8%) and 75th percentile (3.2%) were obtained for Al in lake and river sediment of the Crn Drim River Basin. The content of Al in the soil from the southwestern part of the Republic of Macedonia was 6.6% [20]. The highest value for the minimum

Table 1 Descriptive statistics on the values for the content of the analyzed elements in 37 samples of river and lake sediments from the investigated region

E	MU	X	X _(BC)	Md	Min	Max	P ₁₀	P ₉₀	P ₂₅	P ₇₅	S	Sx	CV	A	E
Ag	mg/kg	0.71	0.44	0.59	0.050	3.0	0.05	1.4	0.29	0.81	0.67	0.11	93	1.99	4.72
Al	%	2.4	2.3	2.4	0.19	4.0	0.56	3.4	1.8	3.2	0.99	0.16	42	-0.63	-0.34
Ba	mg/kg	200	180	190	41	450	87	320	140	230	92	15	47	1.13	1.86
Ca	%	2.0	1.4	1.5	0.039	8.5	0.12	5.5	0.72	2.6	1.9	0.32	95	1.70	3.03
Co	mg/kg	5.1	2.8	4.5	0.50	19	0.50	13	0.50	6.9	5.3	0.87	103	1.30	1.15
Cr	mg/kg	57	44	45	9.6	160	20	120	33	75	38	6.3	67	1.07	0.42
Cu	mg/kg	23	18	19	3.9	45	7.5	39	14	33	12	1.9	52	0.28	-1.02
Fe	%	2.0	1.9	2.1	0.14	4.8	0.41	3.3	1.3	2.5	1.0	0.17	53	0.35	0.37
K	%	1.5	1.5	1.6	0.24	2.7	0.56	2.1	1.3	1.8	0.54	0.089	36	-0.36	0.81
Li	mg/kg	19	17	18	2.9	39	5.3	30	13	25	9.1	1.5	49	0.10	-0.53
Mg	%	0.24	0.19	0.18	0.074	1.0	0.09	0.41	0.13	0.32	0.17	0.028	74	2.67	9.68
Mn	mg/kg	450	390	400	62	1300	170	940	280	530	280	45	61	1.31	1.75
Mo	mg/kg	1.1	0.34	0.25	0.25	7.1	0.25	4.1	0.25	0.76	1.9	0.30	163	2.27	4.36
Na	%	0.72	0.70	0.61	0.26	1.6	0.36	1.3	0.49	0.92	0.36	0.059	50	1.24	0.95
Ni	mg/kg	40	27	25	6.6	130	12	110	19	43	36	5.9	89	1.63	1.51
P	mg/kg	580	400	410	200	3500	230	660	320	540	640	106	112	3.85	14.82
Pb	mg/kg	10	7.0	5.0	5.0	33	5.0	27	5.0	15	8.4	1.4	80	1.43	0.92
Sr	mg/kg	52	42	39	2.3	290	19	91	26	68	48	7.9	93	3.64	17.28
V	mg/kg	60	56	56	8.0	170	16	87	43	72	32	5.2	53	1.33	3.71
Zn	mg/kg	69	64	70	27	100	48	88	60	78	17	2.8	25	-0.47	0.86

E—analyzed element, MU—measuring unit, X—arithmetic mean, X_(BC)—arithmetic mean obtained with Box-Cox method, Md—median, Min—minimum, Max—maximum, P₁₀—10 percentiles, P₉₀—90 percentiles, P₂₅—25 percentiles, P₇₅—75 percentiles, S—standard deviation, Sx—standard deviation (standard error), CV—coefficient of variation, A—asymmetry, E—distribution

was obtained for Na, which was 2600 mg/kg. The highest value for the maximum (8.0%) and the highest value for the 90th percentile (5.5%) were obtained for the element Ca in the sediment of the Crn Drim River basin. Spatial distribution of the content of K in the samples of the river, lake and urban sediment from the investigated region was almost uniform across the whole range with values ranging from 0.5 to 2.6%. The content of Mg in the samples of sediment from the investigated region was in the range of 0.09–0.77%. The content of the major elements in the samples of river and lake sediment was the most frequent, as a result of the dominant geological formations of the area.

Lowest values for arithmetic mean (0.71 mg/kg), ranging from 0.05 mg/kg to 3.0 mg/kg, were obtained for Ag. The mean value of the content of Ag in the samples of lake and river sediment was below 0.6 mg/kg. While in all samples of urban sediment, the mean value of the content of Ag was higher than 0.7 mg/kg, the highest with a value of 5.70 mg/kg was found in urban sediment from the city of Ohrid which is probably due to anthropogenic pollution. The lowest registered values for Box–Cox transformed mean of 0.34 mg/kg and median of 0.25 mg/kg were for Mo in the lake and river sediment. The content of Mo in the samples of river, lake and urban sediment from the investigated region is not exceeding the background limit for Mo (10 mg/kg). Strontium was widely distributed throughout the investigated region with content in the river, lake and urban sediment samples ranging from 7.5 to 100 mg/kg. In the soil from the southwestern part of Macedonia, the average value of Sr was 22 mg/kg [20]. The content of P in the soil from the southwestern part of the Republic of Macedonia had an average value of 0.074%. The high content of P in the urban sediment of the city of Ohrid and Struga (2300–3000 mg/kg) is due to communal and industrial waste as well as household waste rich in phosphorus compounds.

The matrix of the correlation coefficients for 48 samples of the river, lake and urban sediment in all zones of the investigated region is presented in Table 2. There is a strong correlation between the content of the following elements: Zn–Cu (0.91), Ni–Cr (0.81), V–Fe (0.80), Sr–Ca (0.77), Fe–Cr (0.75), P–Cu (0.75), Ni–Cu (0.73), V–Cr (0.70) and Zn–P (0.72). A weaker correlation exists between the contents of the following elements: Ca–Ag (0.53), Cr–Al (0.56), Cu–Cr (0.52), Fe–Al (0.69), K–Al (0.67), Mg–Ca (0.50), Mg–Cu (0.57), Mn–Cr (0.51), Mn–Fe (0.61), Ni–Fe (0.51), P–Ag (0.51), P–Ca (0.60), P–Mg (0.65), Pb–Ba (0.69), Sr–P (0.57), V–Al (0.69), V–Mn (0.65), V–K (0.50), Zn–Ni (0.64), Zn–Pb (0.54). Elements Na and Mo do not show or have very poor correlation with the contents of the remaining elements.

From the multivariate factorial analysis of the content of chemical elements in the 48 samples of river, lake and

urban sediment, the matrix of load factors was obtained, which are presented in Table 3. Factor matrix distinguishes three factors from which Factor 1 (F1) has the highest load value of 4.58 and variability 32.2% of the total variability that is 70.4%. The F1 associates elements Fe–V–Al–Mn–Li. The highest load value in this geochemical association of elements was obtained for Fe (0.90) and the lowest for Li (0.62). Factor 2 (F2) has a load value of 2.46 and variability of 20.9% and associates the following elements Zn–Cu–Ag–Pb. The highest value of the load in the second geochemical association of elements is for Zn (0.82), and the lowest is for Pb (0.68). Factor 3 (F3) represents 17.3% of the total variability of the matrix with the lowest load value 1.41 and associates Co–Ni–Cr. The highest load value in the third geochemical association is Co (0.85), and the lowest is Cr (0.76).

The dendrogram of the interdependence of the analyzed elements in the samples of the river, lake and urban sediment from the basin of the river Crn Drim is shown in Fig. 6. Two clusters with subclusters have been formed in the dendrogram. In the first cluster, one subcluster contains the elements of F2 (Ag, Pb, Cu, Zn), and the second subcluster contains the elements of the geochemical association of F3 (Co, Cr, Ni). According to the cluster analysis, the elements of F2 and F3 have an interrelated internal correlation and belong to one cluster. The second cluster contains the elements of the geochemical association of F1 (Al, Fe, V, Mn, Li).

Histograms and spatial distribution maps show factor standard values of F1, F2, F3 for the distribution of elements in all zones of the investigated region. Figure 7 presents the spatial distribution of factor scores F1 in sediment samples and the factor values of F1 by zones: rivers Crn Drim and Radika, Ohrid Lake, tributaries of Ohrid lake, Prespa Lake and tributaries of Prespa Lake as well as runoff sediment samples from the towns of Debar, Struga, Ohrid and Resen. A higher factor value for F1 was registered for river sediment samples from the northern tributary of Crn Drim, River Radika. The lowest factor value of F1 was registered in the samples of lake sediment from Lake Ohrid. Factor values for the chemical elements from F1 were much higher in samples of urban sediment from the town of Struga than other urban sediment.

The spatial distribution of the elements of Factor 1 (Fe–V–Al–Mn–Li) in the sediment is the result of the lithogenic association of the elements. Their occurrence is a characteristic of the geological composition of the soil from the investigated region. Iron is naturally present in the basin of the Crn Drim River with a soil content of 3.8% [20]. The first geochemical association of elements includes V, which was found in all sediment of the investigated region and was most present in the sediment of the area of the river Radika, due to the presence of V in the soil

Table 3 Load factor matrix—factor analysis of the contents of chemical elements in 48 examples of river, lakes and urban sediments

Element	F1	F2	F3	Comm.
Fe	0.90	0.26	-0.02	88.2
V	0.89	-0.06	0.16	82.6
Al	0.80	-0.07	-0.24	70.0
Mn	0.67	0.09	0.20	49.6
Li	0.62	0.04	0.04	38.4
Zn	0.14	0.82	0.24	74.9
Cu	0.29	0.80	0.33	83.0
Ag	-0.17	0.71	-0.07	54.4
Pb	0.05	0.68	0.02	46.9
Co	-0.30	0.01	0.85	80.2
Ni	0.40	0.33	0.80	91.0
Cr	0.51	0.20	0.76	85.6
Prp.Totl	32.2	20.9	17.3	70.4
EigenVal	4.58	2.46	1.41	
Expl.Var	3.86	2.51	2.07	

F—values for factors of overload, F1, F2, F3—values of load factor, respectively, 1, 2 and 3, Comm—communality in %, Prp.Totl—total variants of the system, EigenVal—eigenvalue, Expl.Var—variants of a separate component

Bolded numbers refer to the rotated factor loadings for the elements that belong to the corresponding factor

in the southwestern part of Macedonia with a content of 100 mg/kg [20]. The highest content of Al was obtained in the samples of river sediment from the tributaries of Prespa Lake, which is a result of the geological composition of the environment. Mn was found in the samples of river and lake sediment with the highest content in the sediment of the river Radika as a result of the naturally present Mn in the surrounding area. Li was mostly found

in river sediment from the tributaries of Lake Ohrid and least in the sediment of Prespa Lake. This is due to the geological composition of the area, which contains Li with an average value of 38 mg/kg [20]. The content of elements of Factor 1 in sample sediment was the highest in the urban sediment of the city of Ohrid.

The spatial distribution of F2 and factor values for F2 for samples of river, lake and urban sediment (Fig. 8) show that the factor values for Zn, Cu, Ag, Pb in lake and river sediment have a downward trend from left to right, while their values in urban sediment are much higher, especially in the towns of Ohrid and Struga. The elements of the second geochemical association Zn–Cu–Ag–Pb are much more prevalent in the urban sediment of the cities, and much less in river and lake sediment, indicating the pollution with Zn, Cu, Pb and Ag in urban sediment in the cities. Low content of Ag was common in river and lake sediment, while higher content of Ag was obtained in samples of urban sediment, with the highest being in the city of Ohrid, which is probably a result of pollution from industrial wastewater and wastes. In river and lake sediment samples, Zn had a low content as a result of being naturally present in the soil with an average value of 110 mg/kg [20]. The content of Zn in urban sediment was higher with the maximum in urban sediment from Ohrid, followed by Struga. The content of Zn in the urban sediment of the cities of Ohrid, Struga and Resen exceeds the background value for the content of Zn (140 mg/kg) according to the Dutch standards [34], while the urban sediment from Struga and Ohrid is very close to the intervening limit for the content of Zn (720 mg/kg). These results indicate that the sewerage systems in the cities of Resen, Ohrid and Struga are affected by Zn pollution from industrial wastewater and wastes.

Fig. 6 Dendrogram of the mutual dependence of the analyzed elements in the samples of river, lake and urban sediments from the investigated region

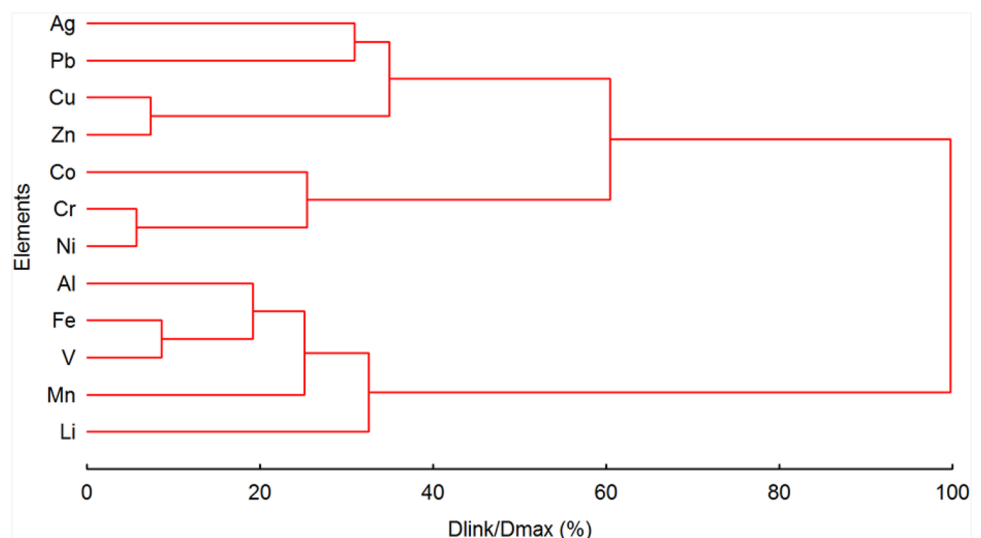


Fig. 7 Spatial distribution of factor scores of F1 (Fe–V–Al–Mn–Li) (a) and their average values according to the zones and type of sediments (b)

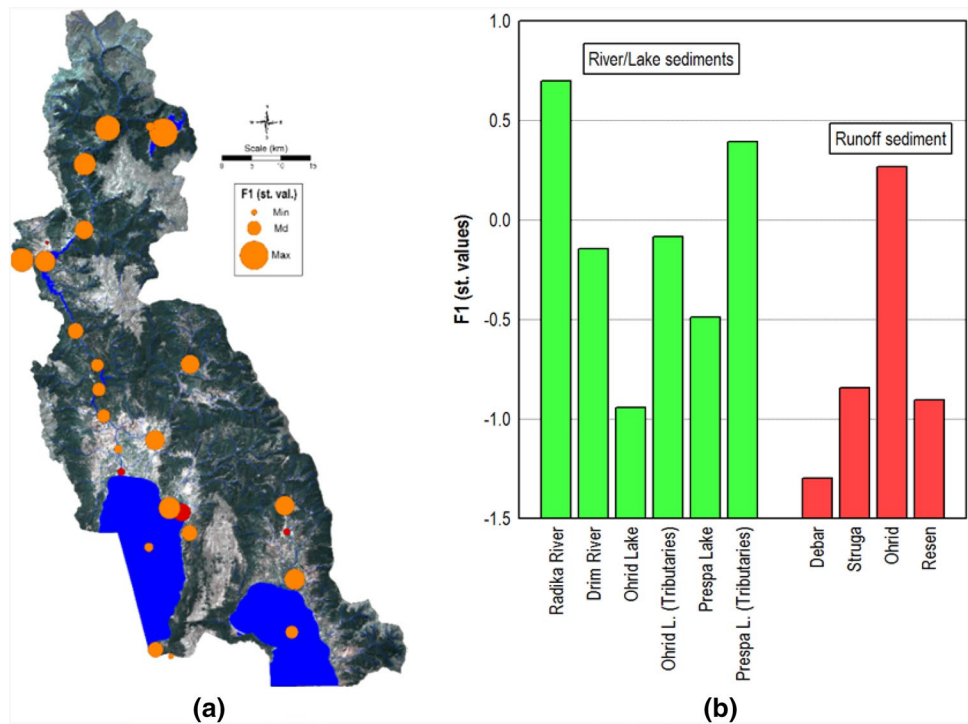
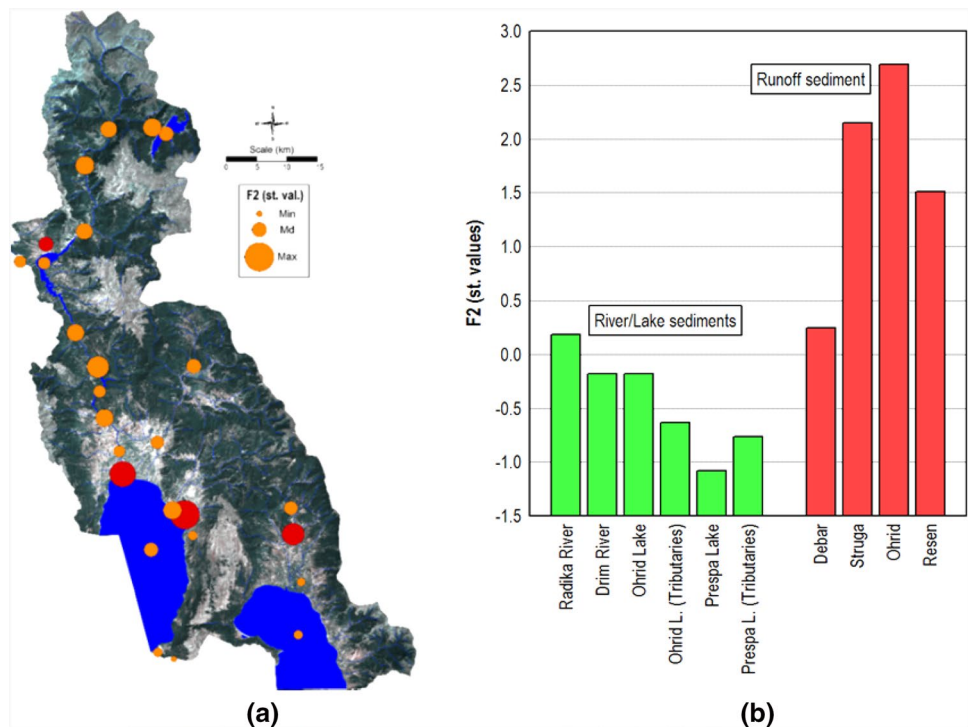


Fig. 8 Spatial distribution of factor scores of F2 (Ag, Pb, Cu, Zn) (a) and their average values according to the zones and type of sediments (b)



The content of Cu in the urban sediment of Resen, Ohrid, Struga and Debar exceeds the background value for the content of Cu (36 mg/kg), and the content of Cu in the urban sediment of Ohrid (230 mg/kg) exceeds the intervention limit (190 mg/kg) for Cu according to the

Dutch standards. The sewage systems in the cities of Ohrid, Struga, Resen and Debar are probably due to the influence of external pollution by industrial Cu, industrial dust, various chemicals with Cu and agricultural drainage waters. The distribution and the content of Pb in the sediment

samples were similar. The highest content of Pb, which was very close to the optimum content of Pb (85 mg/kg) was found in the urban sediment of the city of Ohrid (84 mg/kg), which is probably the result of pollution from industrial wastewater and wastes.

The geochemical association of F3 from Co–Ni–Cr has a uniform distribution and was prevalent in the fifth and sixth zone of the investigated region, and also in the urban sediment (Fig. 9). The third geochemical association has the highest factor value in the river sediment of the Crn Drim River and a very high factor value in the urban sediment of the towns of Debar, Resen and Ohrid (Fig. 9). The F3 geochemical association (Co–Ni–Cr) has the highest factor value in the river sediment of the Crn Drim River, which is in line with the geological composition of the area. However, there is also a high factor value in urban sediment from the cities. The highest content of Co was determined along the course of the Crn Drim River, which originates from the lithologic composition of the environment containing 17 mg/kg. The content of Ni in river and lake sediment shows an increasing trend from the first to the sixth zone, which is a result of the naturally occurring Ni in the geological composition of the soil from the southwestern part of the Republic of Macedonia at 55 mg/kg. Higher content of Ni was determined in the urban sediment of Ohrid and was well above the background content for Ni (35 mg/kg) indicating pollution with industrial wastewater and wastes in the sewage system of the city of Ohrid. The highest content of Cr was determined in the urban sediment of the city of

Ohrid, which exceeds the background value (100 mg/kg) for Cr; this strongly indicates that there is probably pollution from industrial waste and wastewater from the sewerage system in the city of Ohrid.

In most of the samples, the content of As and Cd was below the detection limit, and therefore, these elements were not included in the statistical processing. However, in some of the samples of the lake, river and urban sediment content of As and Cd was registered, and the values obtained for their contents are given in Table 4. In samples of the river and lake sediment from the investigated region where As was detected, its content ranges between 10 and 152 mg/kg. The content of arsenic is related to its lithogenic presence in the soil with a value of 11 mg/kg according to the geochemical atlas of the Republic of Macedonia [20]. In the samples of urban sediment from the towns of Ohrid, Struga, Debar and Resen, content of As was determined to be within the limits of 10–134 mg/kg. Potentially toxic content of As in the samples of sediment was found in the urban sediment of the towns of Ohrid and Struga, as well as in the river sediment of the river Crn Drim and Radika. Compared with the Dutch standards, the mean value of content of As in urban sediment from Ohrid (71.8 mg/kg) and river sediment from Crn Drim (55.1 mg/kg) exceeds the background value (29 mg/kg)). It also exceeds the intervention limit for content of As (55 mg/kg), which requires urgent intervention.

The content of Cd in the samples of sediment of the investigated region ranges from 0.1 to 6.7 mg/kg. Higher

Fig. 9 Spatial distribution of factor scores of F3 (Co, Cr, Ni) (a) and their average values according to the zones and type of sediments (b)

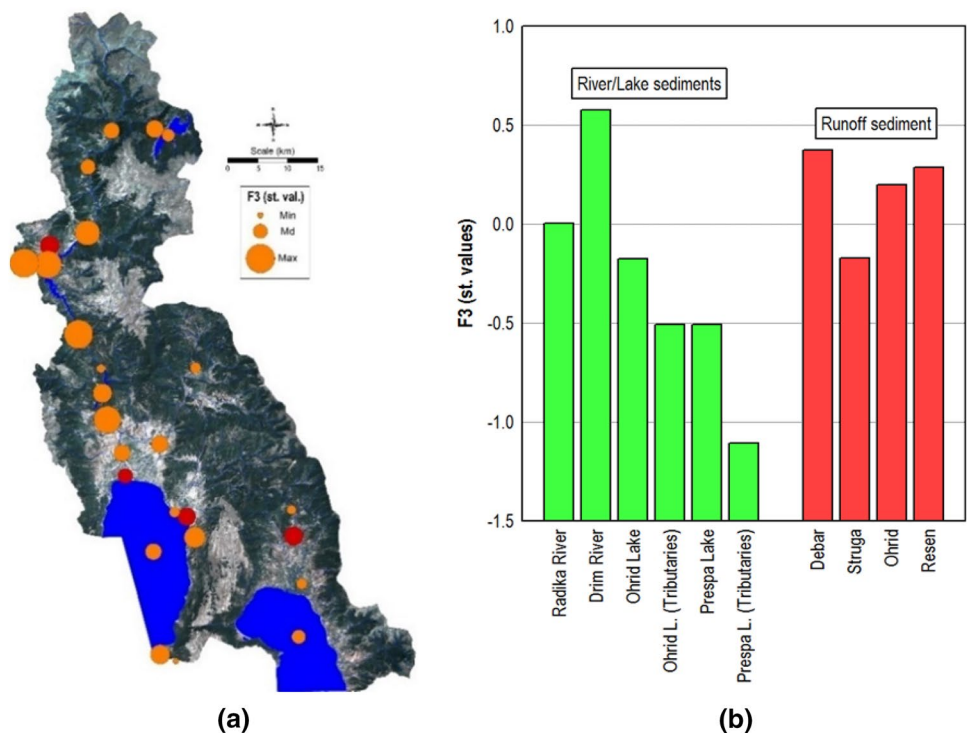


Table 4 Mean values of the content of As and Cd in samples of river, lake and urban sediments in the investigated region (in mg/kg)

Zones in the investigated region	As	Cd
River Radika	32.9	1.4
River Crn Drim	55.1	3.0
Lake Ohrid	28.2	1.8
Tributaries of the Ohrid Lake	28.0	1.6
Lake Prespa	28.6	4.0
Tributaries of the Prespa Lake	21.8	2.6
Debar	10.9	0.76
Struga	32.5	0.98
Ohrid	71.8	4.57
Resen	29.7	0.76

values of Cd were obtained in the urban sediment of the city of Ohrid, sediment of Prespa Lake and river Crn Drim. The average value of the content of Cd in the soil in the southwestern part of the Republic of Macedonia was 0.54 mg/kg [20]. Compared to the Dutch standards, most of the mean values for the content of Cd exceed the background value (0.8 mg/kg), but does not exceed the intervention limit (12 mg/kg).

From the obtained results for the chemical elements in the samples of the lake, river and urban sediment from the investigated region, it can be concluded that the river and lake sediment have a composition according to their geological environment, while the urban sediment in the collector system, especially from the cities of Ohrid and Struga, is under anthropogenic influence.

3.2 Trace elements in soils

Descriptive statistics on the values of the contents of the 20 analyzed elements in 32 soil samples are given in Table 5. The highest content was found for Al, Ca, Fe and K. Thus, the average content of Al was 2.9%, ranging from 0.53 to 5.4%. The average for Ca was 1.8% ranging from 1.1 to 5.8%. The average for Fe was 2.5% ranging from 0.78 to 4.5%. The average content for K was 1.6% ranging from 0.50 to 2.7%. The content of Cu in the Crn Drim River Basin was within the range of 11–80 mg/kg. The highest presence of Cu was recorded in the first zone of the investigated region. In the samples of the deep soil of Golema River, the mean value of the Cu content was 45.7 mg/kg which exceeds the background value for Cu (36 mg/kg) according to the Dutch standards. The average value of the content of Cu in the samples of soil from

Table 5 Descriptive statistics on the values for the content of the analyzed elements in 32 samples of soil from the investigated region

E_x	MU	X	X(BC)	Md	Min	Max	P_{10}	P_{90}	P_{25}	P_{75}	S	Sx	CV	A	E
Ag	mg/kg	0.54	0.44	0.56	0.050	1.4	0.19	0.88	0.32	0.73	0.30	0.053	55	0.62	0.95
Al	%	2.9	2.8	2.9	0.53	5.4	1.3	4.3	1.8	3.6	1.3	0.22	44	0.05	-0.42
Ba	mg/kg	210	200	200	69	330	130	290	160	270	65	12	31	0.07	-0.61
Ca	%	1.8	1.1	1.1	0.10	5.8	0.14	4.5	0.32	2.8	1.7	0.31	98	0.97	-0.18
Co	mg/kg	5.7	2.8	3.2	0.50	28	0.50	12	0.50	8.0	7.2	1.3	125	1.99	4.10
Cr	mg/kg	80	57	56	17	340	26	140	32	100	77	14	97	2.54	6.74
Cu	mg/kg	27	24	27	11	80	12	38	18	29	15	2.7	56	2.03	4.93
Fe	%	2.5	2.4	2.5	0.78	4.5	1.4	3.3	1.9	3.0	0.86	0.15	35	0.06	-0.27
K	%	1.6	1.6	1.5	0.50	2.7	0.78	2.4	1.4	1.8	0.55	0.097	35	0.03	0.39
Li	mg/kg	21	20	17	8.8	49	9.0	33	13	30	11	1.9	52	0.81	-0.14
Mg	%	0.48	0.28	0.31	0.054	2.3	0.11	0.93	0.17	0.52	0.55	0.096	115	2.54	6.60
Mn	mg/kg	500	470	460	230	1100	270	870	360	530	230	40	45	1.49	1.81
Mo	mg/kg	1.0	0.36	0.25	0.25	6.8	0.25	3.0	0.25	1.3	1.5	0.27	145	2.39	6.23
Na	%	0.77	0.74	0.78	0.018	1.3	0.49	1.1	0.55	1.0	0.31	0.055	40	-0.58	0.35
Ni	mg/kg	72	36	33	11	500	14	120	19	67	110	20	158	3.26	10.40
P	mg/kg	390	360	350	190	770	270	530	300	450	130	23	34	1.36	2.24
Pb	mg/kg	11	7.1	5.0	5.0	54	5.0	24	5.0	16	11	1.9	94	2.28	6.52
Sr	mg/kg	44	39	40	12	93	17	75	21	63	24	4.3	55	0.29	-1.27
V	mg/kg	63	61	64	16	90	32	83	55	80	19	3.4	31	-0.73	0.08
Zn	mg/kg	71	66	65	36	150	55	92	61	78	21	3.7	30	1.61	4.53

E —analyzed element, MU —measuring unit, X —arithmetic mean, $X(bc)$ —arithmetic mean obtained with Box-Cox method, Md —median, Min —minimum, Max —maximum, P_{10} —10 percentiles, P_{90} —90 percentiles, P_{25} —25 percentiles, P_{75} —75 percentiles, S —standard deviation, Sx —standard deviation (standard error), CV —coefficient of variation, A —asymmetry, E —distribution

the Crn Drim River was 37.4 mg/kg which exceeds the background value for Cu. These high contents of Cu are due to the geological composition of the soil, which in the southwestern part of Macedonia is quite rich naturally with copper. In 32 samples of soil from the basin of Crn Drim River its content was in the range of 17 mg/kg to 340 mg/kg. The highest mean value for the content of Cr (140.83 mg/kg) was obtained in the soil samples from the course of the river Crn Drim. In samples of soil from the investigated region, Ni was in the range of 11 mg/kg to 500 mg/kg. The average value of the content of Ni in the soil samples along the Crn Drim River was 161 mg/kg, and in the soil samples along the river Radika was 50.2 mg/kg. In both zones the content of Ni exceeds the background value of Ni (35 mg/kg) according to the Dutch standards. Ni is present naturally in the soil with an average value of 55 mg/kg. The mobility of Ni depends on pH and redox conditions in the area. Thus, Ni with soil erosion passes into alluvial soils and river sediment from the river Radika and Crn Drim. As a result, high content of Ni in the samples of the river and alluvial soil in the corresponding sites has been obtained. The content of Pb in soil samples from the basin of the river Crn Drim was in the range of 5–54 mg/kg and does not exceed the background value of Pb (85 mg/kg). The highest average value for the content of Pb (18.7 mg/kg) was obtained in

the soil samples along the course of the Crn Drim River. The content of Zn in soil samples from the basin of river Crn Drim was in the range of 36 mg/kg to 150 mg/kg. The highest average value of the content of Zn (81.5 mg/kg) was in soil samples collected along the course of the Radika River but does not exceed the background value for Zn (140 mg/kg) according to the Dutch standards. The maximum value of the content of Zn obtained for the sample deep soil taken from St. Naum Springs exceeds the background value of Zn as a result of the geological composition of the surrounding soil. Heavy metals Cr, Ni, Pb and Zn are naturally present in the soil from the investigated region, with higher content along the course of the rivers Crn Drim and Radika. With soil erosion, they pass into alluvial soils and river sediment from the river Radika and Crn Drim, and as a result, higher content of these elements in the samples of sediment and soil in the corresponding sites has been obtained.

3.3 Comparison of trace elements distributions in sediments and soils

Comparative statistics were obtained using three methods [*t* test, F ratio and R(T/B)] in order to check whether there is a difference in the distribution of the elements in the surface and depth soil samples, and the results obtained

Table 6 Comparative analysis of the content of elements in 16 samples of surface and depth soil [*t* test, F ratio and R(T/B)]

E	MU	T	B	EF(T/B)	<i>t</i> test	Sig.	F ratio	Sig.	R(T/B)	Sig.
Ag	mg/kg	0.36	0.53	0.68	-1.42	NS	2.14	NS	0.06	NS
Al	%	2.8	2.8	1.01	0.05	NS	1.04	NS	0.29	NS
Ba	mg/kg	210	200	1.05	0.44	NS	1.13	NS	0.29	NS
Ca	%	1.1	1.2	0.92	-0.20	NS	1.11	NS	0.90	*
Co	mg/kg	2.9	2.8	1.04	0.07	NS	1.05	NS	0.63	*
Cr	mg/kg	57	56	1.03	0.12	NS	1.18	NS	0.96	*
Cu	mg/kg	24	23	1.08	0.44	NS	1.09	NS	0.49	*
Fe	%	2.5	2.4	1.04	0.28	NS	1.05	NS	0.78	*
K	%	1.5	1.6	0.95	-0.41	NS	1.27	NS	0.91	*
Li	mg/kg	20	20	1.00	-0.01	NS	1.03	NS	0.71	*
Mg	%	0.27	0.29	0.92	-0.24	NS	1.07	NS	0.78	*
Mn	mg/kg	480	450	1.07	0.48	NS	1.12	NS	0.78	*
Mo	mg/kg	0.33	0.40	0.83	-0.89	NS	1.10	NS	-0.28	NS
Na	%	0.73	0.76	0.96	-0.26	NS	1.04	NS	0.84	*
Ni	mg/kg	37	35	1.05	0.17	NS	1.09	NS	0.95	*
P	mg/kg	340	370	0.92	-0.78	NS	1.61	NS	0.84	*
Pb	mg/kg	6.5	7.8	0.83	-0.98	NS	1.50	NS	0.24	NS
Sr	mg/kg	39	38	1.03	0.12	NS	1.11	NS	0.73	*
V	mg/kg	61	61	1.01	0.05	NS	1.26	NS	0.90	*
Zn	mg/kg	67	66	1.01	0.13	NS	1.14	NS	0.49	*

E—analyzed element, *MU*—unit of measurement, *T*—surface soil (0–5 cm), *B*—deep soil (20–30 cm), *EF(T/B)*—enrichment factor, ration between the content in surface and deep soil, *Sig.*—significance, *NS*—the difference is not significant

*The difference is significant

Table 8 Comparative analysis of the content of elements in the samples of river/lake sediment and alluvial soil sediment [t test, F ratio and R(SR/AS)]

E	UM	SR	AS	EF(SR/AS)	t test	Sig.	F ratio	Sig.	R(SR/AS)	Sig.	Dutch criteria*	
											Background	Intervention
Ag	mg/kg	0.74	0.44	1.69	1.86	NS	2.99	NS	-0.04	NS		
Al	%	2.4	2.8	0.85	-1.33	NS	1.74	NS	0.28	NS		
Ba	mg/kg	200	200	1.01	0.07	NS	2.22	NS	0.00	NS	160	625
Ca	%	1.3	1.1	1.20	0.45	NS	1.08	NS	0.83	*		
Co	mg/kg	2.3	2.8	0.83	-0.38	NS	1.28	NS	0.53	*	9	240
Cr	mg/kg	48	57	0.85	-0.67	NS	1.07	NS	0.65	*	100	380
Cu	mg/kg	21	24	0.91	-0.50	NS	2.64	NS	0.75	*	36	190
Fe	%	2.0	2.4	0.83	-1.44	NS	1.07	NS	0.70	*		
K	%	1.5	1.6	0.97	-0.26	NS	1.25	NS	0.58	*		
Li	mg/kg	18	20	0.92	-0.53	NS	1.51	NS	0.85	*		
Mg	%	0.21	0.28	0.78	-1.19	NS	2.26	NS	0.31	NS		
Mn	mg/kg	430	470	0.92	-0.51	NS	1.55	NS	0.69	*		
Mo	mg/kg	0.34	0.36	0.95	-0.27	NS	2.66	NS	-0.02	NS	0.5	200
Na	%	0.77	0.74	1.04	0.26	NS	1.01	NS	0.34	NS		
Ni	mg/kg	30	36	0.85	-0.54	NS	1.02	NS	0.77	*	35	210
P	mg/kg	440	360	1.24	1.73	NS	1.48	NS	0.45	NS		
Pb	mg/kg	7.6	7.1	1.07	0.39	NS	1.36	NS	0.01	NS	85	530
Sr	mg/kg	45	39	1.16	0.74	NS	1.01	NS	0.57	*		
V	mg/kg	58	61	0.94	-0.47	NS	1.02	NS	0.66	*		
Zn	mg/kg	62	66	0.93	-0.65	NS	2.05	NS	0.78	*		

E—analyzed element, MU—unit of measurement, SR—river/lake sediments, AS—alluvial soil (0–30 cm), EF(SR/AS)—enrichment factor, ratio between the content in river sediment and alluvial soil, Sig.—significance, NS—the difference is not significant

*The difference is significant

*http://esdat.net/Environmental%20Standards/Dutch/annexS_I2000Dutch%20Environmental%20Standards.pdf

are given in Table 6. The F ratio and the t test show that there is no difference between the distribution of the various chemical elements in the samples of surface and deep soil. The ratio R(T/B) indicates the difference between the distribution of some chemical elements in the surface and depth soil samples, although this difference is insignificant because it is below 1. Because in the distribution of the elements in the soil samples no significant difference was found, the further statistical processing of the values of the elements in the soil refers to the average of the content of the elements in the surface and deep soil.

In order to find the correlation between the contents of the analyzed elements in 32 samples surface and depth soil, a bivariate analysis was performed using the correlation factor r, and the obtained matrix is given in Table 7. High correlation factors have been obtained for a small number of analyzed elements: Ni–Cr (0.96), V–Fe (0.81), Ba–Al (0.80), Sr–Ca (0.77), Zn–P (0.71), Mn–Cu (0.70). In contrast, a weak correlation exists between the following elements: Co–Al (0.50), Fe–Al (0.62), K–Al (0.65), Na–Al (0.65), K–Ba (0.51), Li–Ba (0.54), Co–Ca (0.55), K–Co (0.65), Cu–Cr (0.55), Mg–Cr (0.55), V–Cr (0.56), Fe–Cu (0.50), Ni–Cu

(0.57), Li–Fe (0.51), Na–K (0.68), Mg–Li (0.54), Ni–Mg (0.50), Ni–Na (0.52), Sr–Na (0.54).

The comparison of the mean values of the contents of the analyzed elements in the samples of river sediment, lake sediment and alluvial soil from the investigated region is given in Table 8. As can be seen, the values obtained for the contents of all the analyzed elements are very close in both types of samples river/lake sediment and alluvial soil. Also, the t test and the F ratio show that there is no difference between the distribution of the various chemical elements in the samples of river/lake sediment and alluvial soil. The R(SR/SS) method indicates the difference between the distribution of some chemical elements in the soil samples, but this difference is insignificant since the ratio is below 1.

In order to check whether there is a difference in the distribution of the elements in the samples of the river, lake, alluvial soil and urban sediment, comparative statistics have been applied. The obtained results are given in Table 9. As can be seen from the obtained values for the ratio of the content of the different elements in the samples of the river, lake, alluvial soil and urban sediment, the

Table 9 Comparative analysis of the elements in samples of surface and alluvial soil, river and lake sediment and urban sediment

E	UM	AS	SR	UR	S(FO)
Number of samples		32	37	11	
Ag	mg/kg	0.44	0.44	1.8	4.1
Al	%	2.8	2.3	1.8	0.8
Ba	mg/kg	200	180	279	15
Ca	%	1.1	1.4	7.7	5.6
Co	mg/kg	2.8	2.8	4.2	1.5
Cr	mg/kg	57	44	51	1.2
Cu	mg/kg	24	18	96	5.3
Fe	%	2.4	1.9	2.1	1.1
K	%	1.6	1.5	0.92	0.6
Li	mg/kg	20	17	14	0.8
Mg	%	0.28	0.19	0.38	2.0
Mn	mg/kg	470	390	326	0.8
Mo	mg/kg	0.36	0.34	0.48	1.4
Na	%	0.74	0.70	0.66	1.0
Ni	mg/kg	36	27	46	1.7
P	mg/kg	360	400	998	2.5
Pb	mg/kg	7.1	7.0	16	2.3
Sr	mg/kg	39	42	89	2.1
V	mg/kg	61	56	36	0.6
Zn	mg/kg	66	64	257	4.0

E—analyzed element, *UM*—unit of measurement, *AS*—alluvial soil sediment (0–30 cm), *SR*—river and lake sediments, *US*—urban sediment, *S(FO)*—enrichment factor for urban sediments relation to river and lake sediments

content of elements in urban sediment is higher than that in soil, river and lake sediment. Thus, the content of Ag is 4.1 times higher in urban sediment. The content of Ba is 15 times higher in urban sediment. The content of Zn in urban sediment is four times higher than that in soil and river sediment. The content of Cu is 5.3 times higher in urban sediment. The content of Pb is 2.3 times higher in urban sediment. The content of Ca is 5.6 times higher in urban sediment. Also, the ratio of the content of the following elements to the samples of urban sediment is over 2, which are: P, Mg, Sr.

4 Conclusion

The aim of this study was the systematic investigation of the spatial distribution of 22 chemical elements in 18 samples of river sediment, 19 samples of lake sediment and 11 samples of urban sediment from Crn Drim River Basin, Republic of Macedonia. The analyses were performed with atomic emission spectroscopy with inductively coupled plasma. The basic descriptive statistics and matrix of correlation coefficients have been developed. Factor analysis

with the multivariate R method was applied in order to show the associations of chemical elements in the samples. The significance of the factor analysis and the stability of the association of the elements were verified by cluster analysis. The multivariate factorial analysis of the content of chemical elements in 48 samples of river, lake and urban sediment, load factor matrix was obtained with three factors: F1 (Fe, V, Al, Mn, Li), F2 (Zn, Cu, Ag, Pb) and F3 (Co, Ni, Cr). In the obtained dendrogram of the interdependence of the analyzed elements in the samples of the river, lake and urban sediment from the river basin of the Crn Drim are forming two clusters with subclusters. Elements of F2 and F3 have an interrelated internal correlation and belong to one cluster, and in the second cluster are the elements of the geochemical association of F1. Comparative statistics with three methods show that there is no significant difference in the distribution of the elements in the samples of surface and depth soil from the river basin of Crn Drim. In the matrix obtained by the analysis of the correlation between the contents of the elements in 32 samples of surface and depth soil, high correlation factors were obtained for a small number of analyzed elements: Ni–Cr (0.96), V–Fe (0.81), Ba–Al (0.80), Sr–Ca (0.77), Zn–P (0.71), Mn–Cu (0.70).

The mean values of the content of the analyzed elements in the samples of the river and lake sediment, and the mean values of the content of alluvial soil from the investigated region, are very close in both types of samples. The results of the verification of whether there is a certain difference in the distribution of the elements in the samples river, lake, soil and urban sediment show that the content of elements in urban sediment is higher than that in the soil, river and lake sediment. The obtained results correspond to the high concentrations of heavy metals in urban water samples from the towns of Ohrid and Struga [18].

From the obtained results for the chemical elements in the samples of lake, river and urban sediment from the investigated region, it can be concluded that river and lake sediment have a composition according to their geological environment, while urban sediment in the collector system, especially from the towns of Ohrid and Struga, is under anthropogenic influence and represents potential pollutants of Lake Ohrid and river Crn Drim, which is why it is necessary for protective measures to be taken.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Bartram J, Balance R (1996) Water quality monitoring—a practical guide to the design and implementation of freshwater quality studies and monitoring programmes. UNEP/WHO, London
- Osakwe SA, Peretiemo-Clarke BO (2013) Evaluation of heavy metals in sediments of River Ethiope, Delta State, Nigeria. *IOSR J Appl Chem* 4:1–4
- Agarwal SK (2009) Heavy metal pollution. A.P.H Publishing Corporation, New Delhi
- Barakat A, Baghdadi ME, Rais J, Nadem S (2012) Assessment of heavy metal in surface sediments of day river at Beni-Mellal region, Morocco. *Res J Environ Earth Sci* 4:797–806
- Rouillon M, Damian BG, Taylor MP (2013) The nature and distribution of Cu, Zn, Hg, and Pb in urban soils of a regional city: Lithgow, Australia. *Appl Geochem* 36:83–91
- Ahmad S, Yousafzai AM, Bari F, Ullah T (2014) Assessment of heavy metal in surface water of river Panjkora Dir Lower, KPK Pakistan. *J Biodivers Environ Sci* 5:144152
- Petrović D, Todorović M, Manojlović D, Kršmanović VD (2010) A simulation experiment as a method for the investigation of the mobility of heavy metals from inundated land. *J Serb Chem Soc* 75:1005–1018
- Arpenti MB, Negreanu-Pirjol T, Ehlinger TJ, Paraschiv GM, Tofan L (2014) Heavy metal content analysis of Siutghiol Lake water and sediment. *Rev Chim-Buchar* 65:1108–1113
- Markoski B (2005) Cartographic defining and differentiating the valley spatial entities in the Republic of Macedonia. *Bull Inst Phys Geogr* 2:47–66
- Slavevska-Stamenković V, Stafilov T, Smiljkov S, Paunović M, Hristovski S (2009) Water quality characteristics of Mantovo reservoir, Republic of Macedonia. *Arch Biol Sci* 61:501–512
- Serafimovska JM, Arpadjan S, Stafilov T, Ilik Popov S (2011) Dissolved inorganic antimony, selenium and tin species in water samples from various sampling sites of river Vardar (Macedonia/Greece). *Maced J Chem Chem Eng* 30:181–188
- Dimitrovska O, Markoski B, Apostolovska Toshevska B, Milevski I, Gorin S (2012) Surface water pollution of major rivers in the Republic of Macedonia. *Procedia Environ Sci* 14:32–40
- Stafilov T (2014) Environmental pollution with heavy metals in the Republic of Macedonia. *Contrib Sect Nat Math Biotech Sci MASA* 35:81–119
- Vasilevska S, Veljanoska-Sarafiloska E (2015) State of water from littoral part of the Ohrid Lake based on physico-chemical parameters during 2013/2014 year—a review. *PSI Hydrobiol Inst Ohrid* 43:19–31
- Ilić Popov S, Stafilov T, Šajn R, Tănăselia C, Bačeva K (2014) Applying of factor analyses for determination of trace elements distribution in water from river Vardar and its tributaries, Macedonia/Greece. *Sci World J* 809253:1–11
- Ilić Popov S, Stafilov T, Šajn R, Tănăselia C (2016) Distribution of trace elements in sediment and soil from river Vardar Basin, Macedonia/Greece. *J Environ Sci Health A* 51:1–14
- 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. *Maced J Chem Chem Eng* 34:235–250
- Vasilevska S, Stafilov T, Šajn R (2018) Distribution of chemical elements in surface waters from the Crn Drim River Basin, Republic of Macedonia. *Water Res Manag* 8:3–15
- Tomovski D, Stafilov T, Šajn R, Bačeva Andonovska K (2018) Distribution of chemical elements in surface waters from the Crna River Basin. *Contrib Sect Nat Math Biotech Sci MASA* 39:31–49
- Stafilov T, Šajn R (2016) Geochemical Atlas of the Republic of Macedonia. Faculty of Natural Sciences and Mathematics, Sc. Cyril and Methodius University, Skopje
- Bačeva K, Stafilov T, Šajn R, Tănăselia C, Makreski P (2014) Distribution of chemical elements in soils and stream sediments in the area of abandoned Sb–As–Tl Allchar mine, Republic of Macedonia. *Environ Res* 133:77–89
- Stafilov T, Šajn R, Pančevski Z, Boev B, Frontasyeva MV, Strelkova LP (2010) Heavy metal contamination of surface soils around a lead and zinc smelter in the Republic of Macedonia. *J Hazard Mater* 175:896–914
- Jordanoski M, Mitić V, Lokoska L, Veljanoska Sarafiloska E, Patčeva S (2003) Anthropogenic impact on the water quality of the Macedonian part of the Lake Prespa. In: Proceedings of 32. conference on current problems of usage and protection of waters “Water 2003”. Zlatibor, pp 211–218
- Anovski T, Andonovski B, Minceva B (1992) Study of the hydrological relationship between Lake Ohrid and Prespa. In: Proceedings of symposium on isotope techniques in water resources development. Vienna, pp 737–740
- Sarafiloska VE, Patčeva S (2012) Trophic status of lakes Ohrid and Prespa during 2004–2006. *J Int Environ Appl Sci* 7:291–299
- Sibinović M (1987) The lakes Prespa and Ohrid. Water Management Institute of SR Macedonia, Skopje (**In Macedonian**)
- Salminen R, Batista MJ, Bidovec M, Demetriades A, De Vivo B, De Vos W, Duris M, Gilucis A, Gregorauskiene V, Halamic J, Heitzmann P, Lima A (2005) Geochemical Atlas of Europe. Part 1—Background Information, Methodology and Maps. Geological survey of Finland, Espoo
- Salminen R, Tarvainen T, Demetriades A, Duris M, Fordyce FM, Gregorauskiene V, Kahelin H, Kivisilla J, Klaver G, Klein H, Larson JO, Lis J, Locutura J, Marsina K, Mjartanova H, Mouvet C, O'Connor P, Odor L, Ottonello G, Paukola T, Plant JA, Reimann C, Schermann O, Siewers U, Steenfelt A, Van der Sluys J, de Vivo B, Williams L (1998) FOREGS geochemical mapping. Field manual. Geological Survey of Finland, Espoo
- Reimann C, Filzmoser P, Fabian K, Hron K, Birke M, Demetriades A, Dinelli E, Ladenberger A (2012) The concept of compositional data analysis in practice—total major element concentrations in agricultural and grazing land soils of Europe. *Sci Total Environ* 426:196–210
- Peh Z, Šajn R, Halamić J, Galović L (2008) Multiple discriminant analysis of the Drava River alluvial plain sediments. *Environ Geol* 55:1519–1535
- Šajn R, Halamić J, Peh Z, Galović L, Alijagić J (2011) Assessment of the natural and anthropogenic sources of chemical elements in alluvial soils from the Drava River using multivariate statistical methods. *J Geochem Explor* 110:278–289
- ISO 14869-1:2001. Soil quality—dissolution for the determination of total element content Part 1: dissolution with hydrofluoric and perchloric acids. International Organization for Standardization, Geneva
- 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. *J Environ Sci Health A* 45:1504–1518
- http://esdat.net/Environmental%20Standards/Dutch/annex_S_I2000Dutch%20Environmental%20Standards.pdf. Accessed 25 Feb 2019

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.