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Multivariate Statistical Analysis for the Surface Water Quality of Trepçaand Sitnica Rivers, Kosovo

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Abstract: The study was performed to investigate the concentration of toxic heavy metals like As, Cd, Cr, Co, Cu, Ni, Pb and Zn in the water of Trepça and Sitnica Rivers. It was observed that the concentration of most of the analyzed heavy metals was much higher than the European and Kosovo permissible limits. Water quality parameters including DO, BOD, conductivity, temperature, TDS, pH, and turbidity were measured in samples collected from 6 stations. The highest concentration of As, Cd, Pb and Zn originate primarily from anthropogenic sources such as discharge of industrial water from mining flotation and from the mine waste eroded from the river banks. Multivariate statistical analyses, such as cluster analysis (CA) were applied to evaluate water quality and to identify potential pollution sources of Trepça and the Sitnica River. Cluster analysis suggests that As, Cd, Cr, Co, Cu, Ni, Pb and Zn are derived from anthropogenic sources, particularly discharges from mining flotation and erosion from waste from a zinc mine plant.

Keywords: *heavy metal, Trepça and Sitnica Rivers, multivariate cluster analysis, quality of water.*

Introduction

Rivers are important sources of water that can be used for industry, agriculture and households. Despite their importance rivers are imperiled by pollution from human activities. The contamination of rivers with different pollutants presents a complex long-term environmental problem, particularly in areas with high anthropogenic pressure. Heavy metals are one of the most serious environmental pollutants due to their toxic effects. The heavy metals released from industrial and municipal waste dischargers and from polluted runoffs can accumulate in aquatic ecosystems (Öztürk *et al*., 2009; Odu *et al*., 2011).

The most toxic heavy metals such as arsenic, cadmium and lead are carcinogenic andcan have a health effects even at very low concentrations. Therefore, at high concentration the heavy metals may impart a significant impact on health, reproduction, and survival (Mohiuddinet al.2011).Several studies have demonstrated that the pollution of rivers and sediments with heavy metals increased on a global scale over the last few decades (Mohiuddin *et al*.2011, Reza et al. 2010, Demirak et al. 2006). The industrial processes applied in "Trepca" Mining complex in Kosovo have resulted in enormous environmental pollution with heavy metals. According to the latest publications (Bacaj *et al*.1983; Rugova *et al*., 1989; Berisha *et al*., 2008) the quality of rivers in Kosovo is not satisfactory because of the water pollution with heavy metals, which presents one of the biggest environmental problems in the region. There are no water treatment plants and industrial waste, and hereby rivers are used as sinks for industrial emissions. For these reasons, the Sitnica River and streams of the Trepça River are classified as dead rivers, because of the high pollution. Thus, these rivers cannot be used for recreational purposes without prior treatment.

The main goal of this study is: *i*) to determine the level of concentration of heavy metals including: As, Cd, Cr, Co, Cu, Ni, Pb and Zn in river water of the Sitnicia and Trepca; *ii*) to explore the nature of water pollution using multivariate analysis (cluster analysis) of all parameters evaluated; *iii*) to assess the quality of water in the two rivers by physico-chemical parameters (conductivity, DO, BOD, temperature, TDS, pH, and turbidity); *iv*) to present the current state of the rivers and to recommend to the relevant authorities the measures that can be taken and to improve the quality of these waters. Multivariate statistical analyses, such as cluster analysis (CA) were applied to identify potential pollution sources of the Trepça and Sitnica River. The multivariate statistical methods have

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an extensive application in characterization and evaluation of surface water quality and are useful for the evaluation of temporal and spatial variations caused by natural and anthropogenic factors (Zhao *et al*., 2009).

Materials and Methods

Study area

The study area was conducted at designated points along rivers of Trepça and Sitnica in Mitrovica, Kosova as shown in Figure 1. Mitrovica is located at a Lat. 42.53 ° N and a Long 25.52 °E in the north of Kosova. The city is about 508-510 m above sea level. The average monthly temperatures range between 15 and 25°C. Mitrovica city has a long history of lead and zinc metallurgy productions where unfortunately these mining operations have resulted in negative environmental impacts (Dekonta, 2009). It was one of the most important industrial areas of Kosova as well as one of the most important mining districts of Europe. The industrial zone of Mitrovicais situated 20 m next to the banks of Sitnica River and very close to a residential area and to the banks of the Trepça River(Kerolli -Mustafa et al. 2015, Ferati et al. 2015). For water sampling, sampling points were chosen on the banks of the Trepça and Sitnica Rivers. The sampling points were located at four drain outfalls (L1, L3, L4) and three industrial outfalls (L2, L5, L6) along the Trepça and Sitnica Branches. The sample L1, L2 and L3 are collected in the Trepça River, while L4, L5 and L6 are collected in the Sitnica River as shown in Figure 1. These drains were chosen, because they receive considerable amounts of waste water from industrial areas as well as domestic waste from the city and surrounding villages.

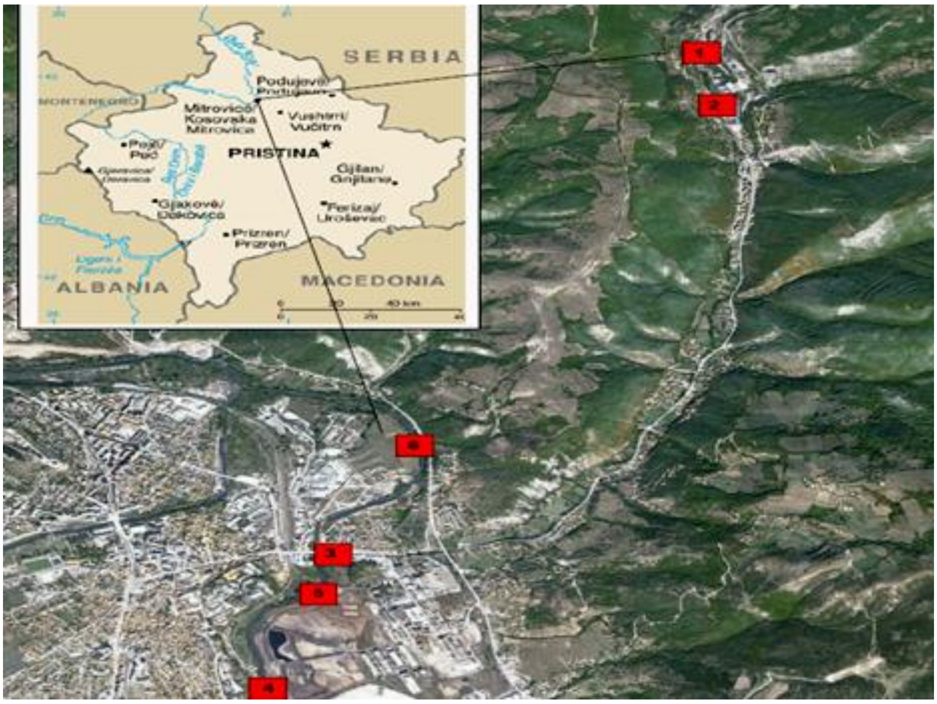

Figure 1. Location of different sampling sites of the Trepça and Sitnica Rivers in Mitrovica, Kosovo

Water sampling

Six water samples were collected during the period from April to July 2015. Water samples were taken by using Van Dorn plastic bottles (1.5 liter capacity) in accordance with standard method ISO 5667-1(ISO 2006).The water samples were collected after recording the pH, water temperature (T), total dissolved solids (TDS) and electrical conductivity (EC) in-situ using portable digital pH meter (PH-ECTDS-Meter HJ-991301 Hanna Instruments). Dissolved oxygen (DO), biochemical oxygen demand (BOD) were measured with Winkler azide method. The samples, after collection were stored in the refrigerator at about 4 ˚C prior to analysis. Meters and probes were calibrated with standard solutions as suggested by the manufacturers. Most of parameters are expressed in milligrams per liter (mg L-1), except pH, EC (µS cm^{-1}) and temperature (^{o}C).

Chemical analysis

As soon as the water samples were brought to the laboratory they were preserved with 1mL of concentrated nitric acid (HNO_3), filtered and stored in dark at an ambient temperature until microwave acid digestion following EPA method 3015(US EPA, 1994).The digestion of 50 mL was performed with 4-5 mL HNO_3 65% and 1 mL HCl 35%. Total metal samples were filtered through 0.45 µm nylon filters after digestion. The concentrations of As, Cd, Cr, Co, Cu, Ni, Pb and Zn were measured using inductively coupled plasma - optical emission spectrometry (ICP–OES Optima 2100 DV) in accordance with the standard method US EPA 6010C (US EPA, 2007). Three independent replicates were performed for each sample and blanks were measured in parallel for each set of analyses using the same procedure. In order to evaluate the stability and accuracy of the procedure in all samples, the reference material was used for water SRM-143d with the same procedure. All reagents used in this work were analytical or HPLC grade and used without any further purification.

Statistical analysis

Microsoft Excel and SPSS 10 software was used to perform statistical analyses. Cluster analysis was also used for investigating the similarities between major variables and heavy metals from the water samples. Evaluations of similarity were based on the average linkage between groups of Cluster analysis (CA) (Zhao et al. 2009, Ferati *et al*., 2015).

Results and Discussions

Metal concentrations in water samples are presented in Table 1, which include mean concentrations with standard deviation values. Values of physical-chemical parameters of water samples from the Trepça and Sitnica Rivers are presented in Table 2.The water sample results presented in Table 1 show that, most of the heavy metal concentrations in water of the Trepça and Sitnica Rivers were found within the permissible limits of both European Legislation-75/440/EEC and Kosovo National Administrative Direction UA13/2008 (75/440/EEC 1975, UA 13 2008). Arsenic concentrations were below permissible limit for the sampling locations 1, 3, 4, 6. While, in locations 2 and 5 the concentration values were much higher with 0.089 mgL^{-1} and 0.092 mgL^{-1}, respectively. Generally, the highest As concentration was at site 5, Figure 2(a). The concentration for Cd varies from 0.003 to 0.098 mgL^{-1}. The highest concentration of Cd was registered in location 5, Figure 2(b). The concentration of Co, Cr and Ni was below the permissible values. The highest concentration of Co and Cu was registered at site 2, Figure 2(c), (d), while the highest concentration of Cr and Ni was registered at site 5, Figure 2(d), (f). The concentration of Pb and Zn were above the permissible limits in the sites 2, 5. Zn showed high concentration in site 3 as well which exceeds the limited values. The high level of concentration of As, Cd, Pb and Zn in location 2 originate primarily from anthropogenic sources such as discharge of industrial water from mining flotation, whereas the concentration of heavy metals in locations 4 and 5 are originating from the mine waste eroded from the river banks.

Table 1. Heavy metal concentrations in water samples from the Trepça and Sitnica Rivers and national limited values (concentration unit is in mgL^{-1})

Sample	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
L 1	0.001 ±0.0005	0.003 ±0.005	0.048 ±0.0030	0.019 ±0.003	0.032 ±0.0025	0.0005 ±0	0.0001 ±0	0.0001 ±0
L 2	0.089 ±0.0075	0.065 ±0.000	0.068 ±0.0090	0.031 ±0.0030	0.064 ±0.0025	0.0005 ±0	0.309 ±0.0165	8.034 ±0.0541
L3	0.0002 ±0	0.0001 ±0	0.042 ±0.0101	0.0002 ±0	0.028 ±0.0030	0.0005 ±0	0.123 ±0.0030	0.793 ±0.0336
L4	0.051 ±0.0105	0.057 ±0.005	0.036 ±0.0068	0.018 ±0.0025	0.031 ±0.0045	0.0005 ±0	0.005 ±0.0010	0.0002 ±0
L 5	0.092 ±0.0091	0.098 ±0.005	0.058 ±0.0030	0.084 ±0.0037	0.052 ±0.0030	0.061 ±0.0035	0.539 ±0.0126	0.398 ±0.0195
L 6	0.015 ±0.0025	0.022 ±0.01	0.029 ±0.0030	0.043 ±0.0026	0.038 ±0.0025	0.0005 ±0	0.032 ±0.0035	0.296 ±0.0400
UA 13/2008*	**0.05**	**0.01**	**0.5**	**0.5**	**0.1**	**0.5**	**0.2**	**0.5**
75/440/EEC**	**0.05**	**0.005**	**---**	**0.05**	**0.02**	**---**	**0.05**	**0.5**

**Kosovo National Administrative Instruction No. 13/2008; **European Council Directive 75/440/EEC of 16 June 1975.*

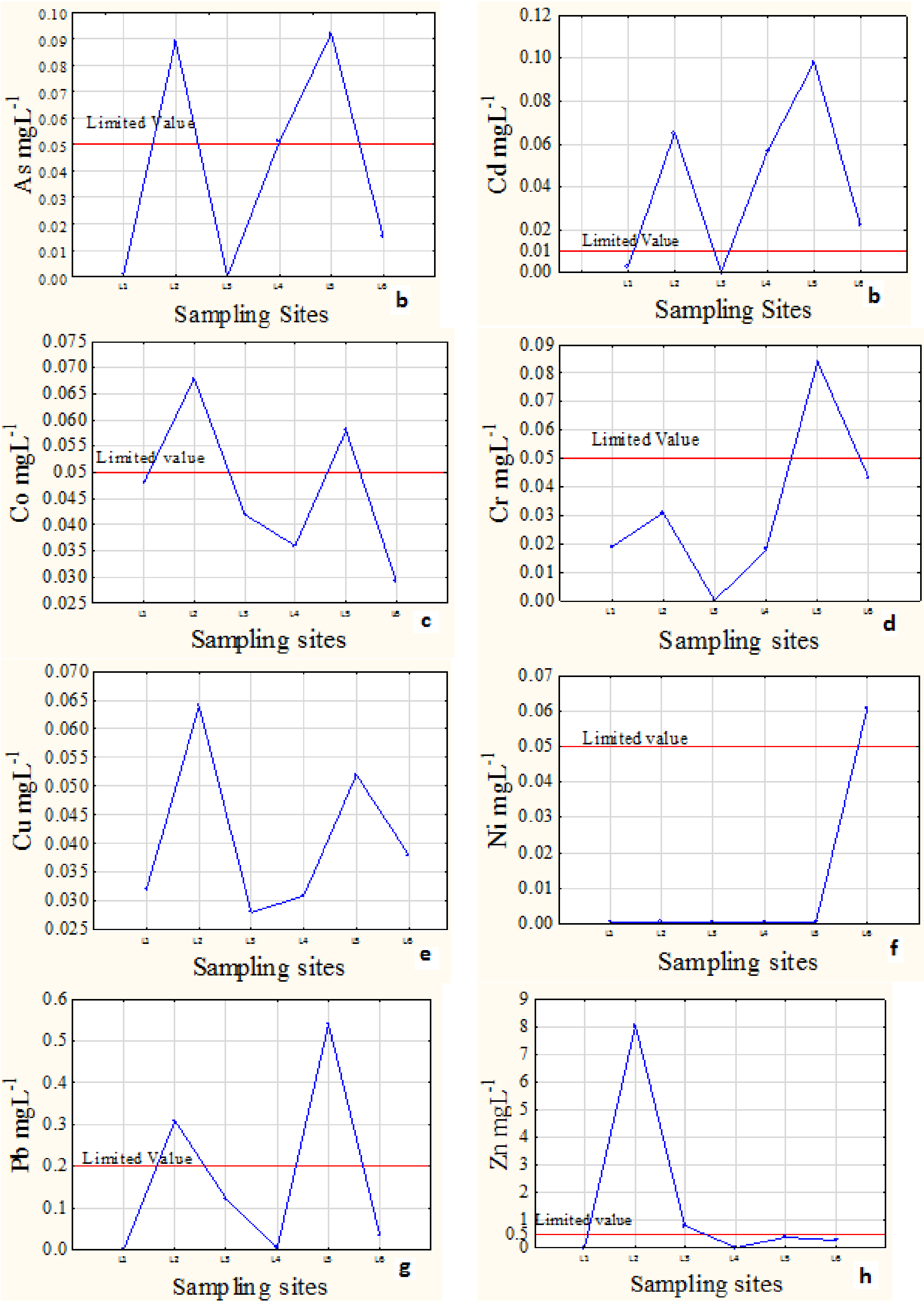

Figure 2. Heavy metal concentration in Trepca and Sitnica Rivers

The mining waste deposited in the tailing dumps in Mitrovica Industrial Park is very close to the river banks of the SitnicaRiver(Ferati et al.2015). Mine waste eroded from the river banks contribute to entrainment of the dissolved metals into the river. Therefore, the discharge of untreated water from mining flotation into the Trepca river increases the metal content in locations 2 and 3(Feratiet al.2015). Thus, location 2 was characterized as one of the most polluted locations due to the high concentration of toxic metals.

The results of mean values of physico-chemical parameters are given in Table 2.Conductivity is an important and fast method that measures the total dissolved ions and is directly related to total solids. The electrical conductivity (EC) of water samples in the Trepça and Sitnica Rivers ranges from 760 to 1210 μS cm^{-1}. Conductivity is also affected by temperature. The warmer waters have higher values of the conductivity.The water temperature is also a significant parameter that controls the inborn physical qualities of the water. In this study, the water temperature ranged between 17.7 °C and 24.8°C. The maximal temperatures were recorded in location 2 during the dry season.The pH is a measurement of the acidity or basic quality of water. Extremely high or low pH levels have a significant effect for most aquatic organisms. The pH of the water changes even slightly. In our case the pH levels range from 7.62 to 8.06.

Table 2. Physico-Chemical values of Trepça and Sitnica Rivers

Parameters	Unit	L 1	L 2	L 3	L 4	L 5	L 6
EC	μS cm^{-1}	760±4.5	1210±1.5	1070±3.5	850±5.5	820±3.5	840±5.0
Temperature	˚C	17.7±0.1	24.8±0.05	19.8±0.15	18.3±0.15	18.7±0.2	18.8±0.25
pH		7.81±0.01	8.06±0.01	7.92±0.02	7.67±0.03	7.62±0.04	7.68±0.04
Turbidity	NTU	8.9±0.15	86±1.5	112±1.5	39±1.5	70±2.08	58±2.51
TDS	mgL^{-1}	380±1.5	610±2.5	540±2.5	430±3.05	440±3.6	420±3.6
DO	mgL^{-1}	9.66±0.03	7.77±0.02	8.7±0.1	4.34±0.04	4.8±0.1	4.3±0.2
DO5	mgL^{-1}	6.14±0.01	5.75±0.01	2.16±0.01	0.26±0.02	0.34±0.03	0.33±0.04
BOD	mgL^{-1}	3.52±0.03	2.02±0.03	6.54±0.1	4.08±0.03	4.46±0.08	3.97±0.19

Total dissolved solids (TDS) are the measurements of dissolved matter (salts, organic matter, minerals, etc.) in water. TDS can be naturally present in water or the result of mining or other industrial discharge. TDS can be toxic to aquatic life through increases in salinity. According to the US EPA Guidelines the recommended value for TDS is 50 mgL^{-1}(US EPA 2009, U.S. Geological Survey). The present study shows that the average value of TDS varies from 380 to 610 mgL^{-1}.

Turbidity is another important parameter of river pollution. The present study shows the turbidity in the range of 8.9 – 112 NTU. The highest desirable limits for turbidity are 5 NTU and maximum permissible limit 50 NTU (Mandal et al. 2012).In all locations the value of turbidity present are not within the desirable limit. It reveals that the river pollution is high and not at the safe level.

Dissolved oxygen in water is an essential and important parameter for aquatic life. Deficiency of dissolved oxygen comes as a result of anaerobic decomposition of organic waste(Mandal et al. 2012).DO in our study ranges from 4.3 to 9. 66 mgL^{-1}. The final Dissolved oxygen (DO_5) after five days ranges between 0.26 to 6.14 mgL^{-1}.

Biological Oxygen Demand (BOD) is an important parameter used to assess the organic pollution. According to the Royal Commission of sewage disposal water having BOD more than 5 mg/l is unsafe for domestic use(Mandal et al. 2012, Çullaj, 2010). In our case the BOD values ranges between 2.02 to 6.54 and exceeds the limits from 0.3 - 4.8 mgL^{-1}. Therefore, a high value of BOD confirms the present situation of highly contaminated rivers. The graphical presentation of physic-chemical parameters is presented in Figure 3.

The classification of river waters at each sampling location, based on concentrations of heavy metals is presented in Table 3. Classification of waters was tentatively performed using available standards in Kosovo(UA 13, 2008).The locations L2 having category V is in accordance with determination of high concentration of zinc as a result of discharge of mining zinc flotation waters in the Trepça River. For most other metal concentrations, waters are from II to III category.

Cluster analysis of the river waters revealed several links between elements of interest. The elements were compared with the aim to find similarities between metal distributions of the investigated locations. The output of cluster analysis is given as a dendrogram (Figure 4).The elements that are similar refer to the similar source of origin and the same mobility entrance in the environment. Following the dendrogram of investigated water samples were obtained with the help of Ward's method in order to define the similarities and dissimilarities of elements. The constructed dendrogram showed two major distinct clusters with six groups formed. As and Cd have good similarity and are clustered in one group, where the Ni, Cr, Co and Cu are clustered into another group. These two groups showed a close relationship in one of the major clusters. Pb is clustered with the group of Ni, Cr, Co and Cu, as well as with As and Cd while, Zn forms a separate cluster with no close similarities with other elements and with strong anthropogenic inputs.

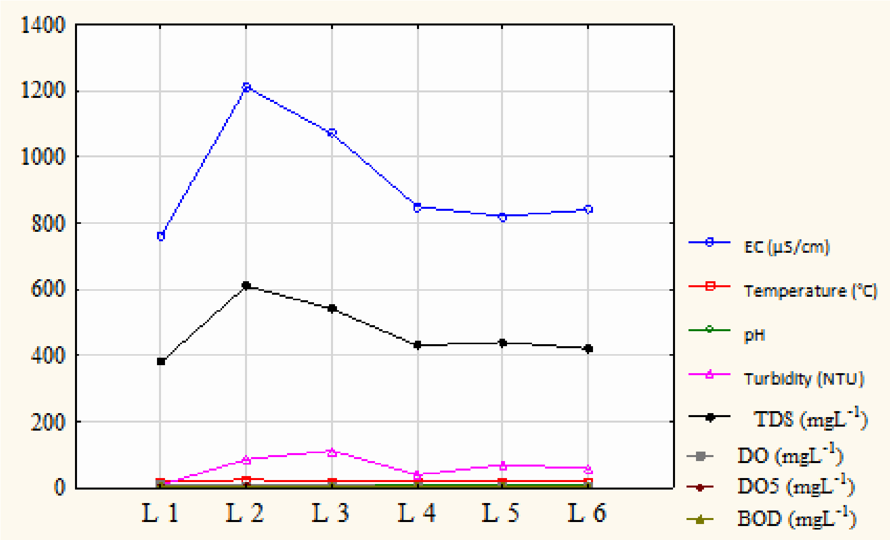

Figure 3. Physico-chemical parameters of Trepça and Sitnica Rivers

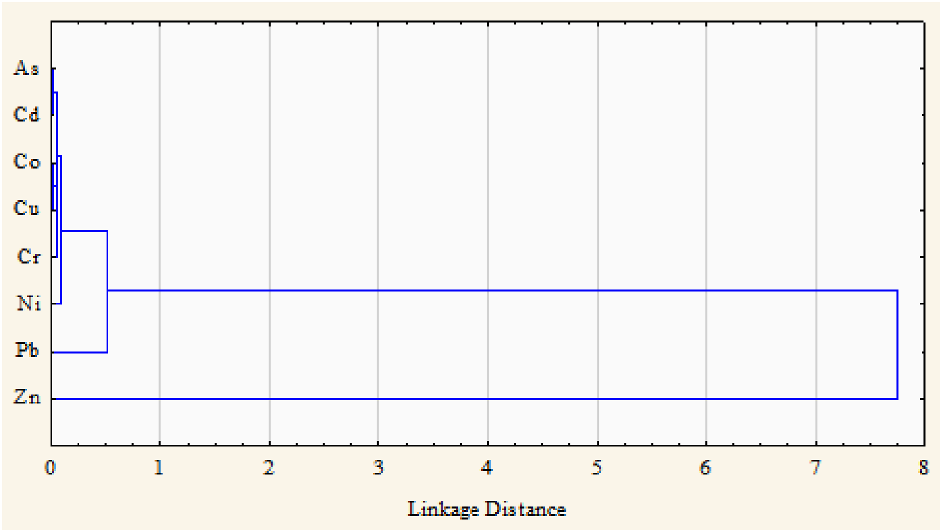

Figure 3. Dendrogram obtained by cluster analysis of the waters samples.

Table 3. Classification of Trepça and Sitnicariver waters, based on heavy metal concentrations (Ferati *et al*. 2015).

Parameter	Category II	Category III	Category IV	Category V
As , mgL^{-1}	0.05 L2, L4, L5	0.1	0.2	0.2
Cd, mgL^{-1}	0.01 L2,L4, L5, L6	0.05 L2, L5	0.1	0.2
Co, mgL^{-1}	0.5	1	1.25	1.5
Cr, mgL^{-1}	0.5	1	1.5	1.75
Cu, mgL^{-1}	0.1	0.25	0.4	0.5
Ni, mgL^{-1}	0.5	1	1	1.5
Pb, mgL^{-1}	0.2 L2, L4	0.5	0.75	1
Zn, mgL^{-1}	0.1 L2, L3, L5, L6	1	1.5	2 L2

Conclusion

This work has presented the levels of physicochemical parameters and the current state of the river water samples collected from the Rivers Trepça and Sitnica. The results revealed that there was an indication of water pollution with heavy metals as well as with some physic-chemical parameters, although some values of these parameters are within an acceptable range. The study further revealed that the water is not safe for use for recreational purposes or irrigation purposes. Considering all assessing methods, Cd and As are responsible for significant amount of heavy metal contamination, followed by Pb and Zn. Multivariate cluster analysis grouped the analyzed elements into two major distinct clusters with six groups formed based on the similarity between metal distributions of the investigated locations. Thus this work will serve as baseline information for Kosovo institutions and for our future work in terms of environmental management. It can be concluded that the industrial discharge of water from mining flotation and mining waste erosion into the Trepça and Sitnica Rivers are responsible for the intense contamination of the water and must be regarded as a major environmental concern. In order to protect the water from further contamination, a designing of a monitoring network and reducing the anthropogenic discharges is suggested.

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