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Assessment of heavy metal contamination in water and sediments of Trepça and Sitnica rivers, Kosovo, using pollution indicators and multivariate cluster analysis

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Abstract The concentrations of As, Cd, Cr, Co, Cu, Ni, Pb, and Zn in water and sediment samples from Trepça and Sitnica rivers were determined to assess the level of contamination. Six water and sediment samples were collected during the period from April to July 2014. Most of the water samples was found within the European and Kosovo permissible limits. The highest concentration of As, Cd, Pb, and Zn originates primarily from anthropogenic sources such discharge of industrial water from mining flotation and from the mine waste eroded from the river banks. Sediment contamination assessment was carried out using the pollution indicators such as contamination factor (*CF*), degree of contamination (*Cd*), modified degree of contamination (*mCd*), pollution load index (*PLI*), and geo-accumulation index (I*geo*). The CF values for the investigated metals indicated a high contaminated nature of sediments, while the *Cd* values indicated a very high contamination degree of sediments. The *mCd* values indicate a high degree of contamination of Sitnica river sediment to ultrahigh degree of contamination of Trepça river sediment. The *PLI* values ranged from 1.89 to 14.1 which indicate that the heavy metal concentration levels in all investigated sites exceeded the background values and sediment quality guidelines. The average values of Igeo revealed the following ranking of intensity of heavy metal contamination of the Trepça and Sitnica river sediments: Cd>As>Pb>Zn>Cu>Co>Cr>Ni. 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 form waste from a zinc mine plant. In order to protect the sediments from further contamination, the designing of a monitoring network and reducing the anthropogenic discharges are suggested.

Keywords Heavy metal · Trepça and Sitnica rivers · Pollution indicators · Multivariate cluster analysis · Water and sediment contamination

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Introduction

Today, the contamination of rivers and sediment 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, persistent and abundant that can accumulate in aquatic ecosystems. The most toxic heavy metals arsenic, cadmium, and lead are carcinogenic and can have health effects even at very low concentrations. Although some heavy metals such as Fe, Mn, Co, Cu, and Zn are essential micronutrients for fauna and flora, they are dangerous at high levels (Nagajyoti et al. 2010). Thus, for organisms living in rivers, the high concentration of heavy metals may impart a significant impact on health, reproduction, and survival (Moore et al. 2009). The heavy metals are released directly from industrial and municipal waste dischargers and from polluted runoff in urban and agricultural areas (EPA 1999).

Heavy metals discharged into rivers are likely to be scavenged by particles leading to their accumulation in sediments (Ideriah et al. 2012). A sediment as a large reservoir of metals can potentially lead to adverse ecologic effects. Several studies have demonstrated that the pollution of rivers and sediments with heavy metals increased at global scale over the last few decades (Özkan 2012; Nagajyoti et al 2010; Li et al 2000). The evaluation of metal distribution in river sediments is useful to assess the evidence of the anthropogenic impact on river water quality as well as for local communities and the whole ecosystem.

In many countries, the environmentalists are working very closely to provide adequate education program to the population in increasing the awareness, preventing the pollution, and, at the same time, establishing proper management of ecosystems (Demirak et al. 2006; Gashi et al. 2011). As reported by Gashi et al. (2011), the river water quality in Europe is one of the most eminent concerns for the future. The Water Framework Directive (WFD 2000) requires European Union (EU) member states to develop and implement an integrated system of water protection, improvement, and sustainable use. Under the WFD, all water bodies are expected to reach good ecological status (GES) or good ecological potential and good chemical status (GCS) by the end of 2015. But, as reported by Brills (2008), there is still a concern on the lack of uniformity in the methods and guideline values used to assess and estimate the overall amount of contaminated sediment in Europe.

Kosovo as a new country aiming the EU integration has harmonized the national water legislation with EU Water Framework Directive. There are a very few references to waters and sediments in Kosovo; however, these are all in respect of the chemical quality (Bacaj and Branica 1983; Rugova et al. 1989; Berisha et al. 2008 and Gashi et al. 2011). The authors reported the level of heavy metals in rivers of Kosovo, mainly in water and sediments of Sitnica river, are very high due to the inputs of industrial discharge, mining waste erosion, and sewage runoff. No studies have been reported on the assessment of ecological status of the rivers and sediments in Kosovo.

In general, to assess the metal contamination in river sediment, different pollution indicators such as contamination factor (*CF*), contamination degree (*Cd*), pollution load index (*PLI*), the geo-accumulation index (I_{geo}), and the enrichment factor (*EF*) are often used (Ideriah et al. 2012; Özkan 2012; Moore et al. 2009; Li et al. 2000).

Since many of these pollution indicators are very popular all over the world, in assessing the sediment contamination posed by heavy metals, we hope to provide the first and useful information about the application of these indicators for Trepça and Sitnica river sediments, where other researchers in Kosovo can refer to.

The aim of the current work is (i) to determine the levels and distribution of the toxic heavy metals in water and sediment of two very important rivers in the northern part of Kosovo and Trepça and Sitnica rivers; (ii) to explore the degree of contamination and pollution impacts by using the following pollution indicators such as: contamination factor (*CF*), degree of contamination (*Cd*), modified degree of contamination (*mCd*), pollution load index (*PLI*) and geo-accumulation index (I*geo*); (iii) to investigate the polluted nature of sediments by using multivariate cluster analysis; (iv) to establish baseline data on the present status of the rivers that can be used by relevant authorities and other researchers, and (v) to suggest a regular monitoring network in line with proper water management.

Materials and methods

Study area

The study area was conducted at designated points along rivers of Trepça and Sitnica in Mitrovica, Kosovo, as shown in Fig. 1. Mitrovica is located on lat. 42,53° N and long. 25,52° E in north of Kosovo. 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 (Kerolli-Mustafa et al. 2015). It was one of the most important industrial areas of Kosovo as well as one of the most

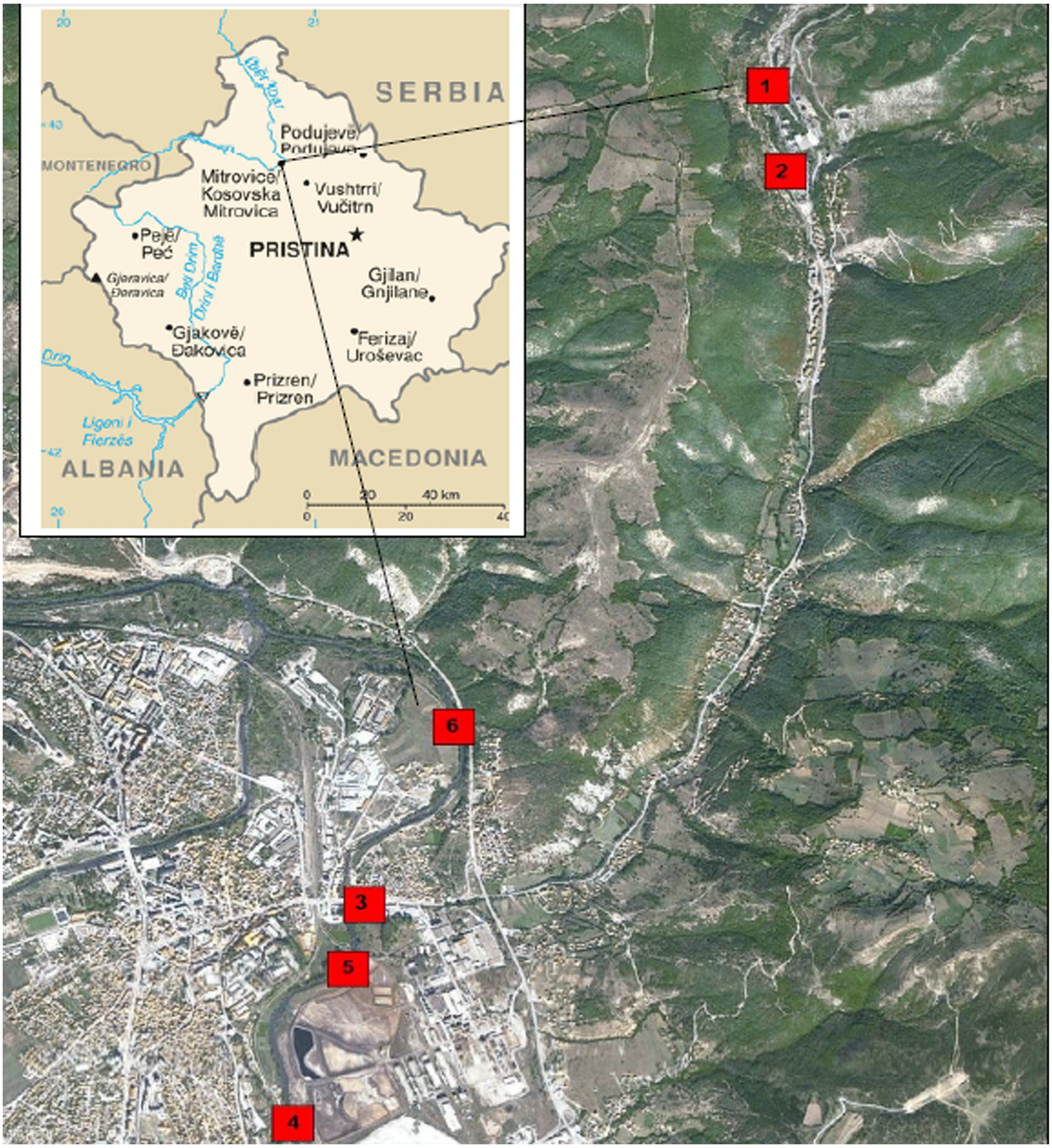

Fig. 1 Location of different sampling sites of Trepça and Sitnica rivers in Mitrovica, Kosovo

important mining districts of Europe. The industrial zone of Mitrovica is situated 20 m next to the banks of Sitnica river and very close to the residential area and to the banks of Trepça river. For water and bed sediment sampling, six sampling points were chosen at the banks of Trepça and Sitnica rivers. The sampling points were located at four drain outfalls (P1, P3, and P4) and three industrial outfalls (P2, P5, P6) along Trepça and Sitnica branches. The samples P1, P2, and P3 are collected in Trepça river, while P3, P4, and P6 are collected in Sitnica river as shown in Fig. 1. These drains were chosen because they receive considerable amounts of waste water from industrial areas as well as from domestic wastes from the city and surrounding villages.

Water and sediment sampling

Six water and six sediment samples were collected during the period from April to July 2014. Water samples were taken by using Van Dorn plastic bottles (1.5-L capacity) in accordance with standard method ISO 5667-1(2006). The water samples were collected after recording the pH in situ using portable digital pH meter (PH-ECTDS-Meter HJ-991301 Hanna Instruments). Samples after collection were stored in the refrigerator at about 4 °C prior to analysis. The sediment samples were collected (ISO 5667-15 2009) by sediment collector with an acid-washed plastic scoop up to 10 cm of the bed sediment from 5 m away from the riverbank. Sediment samples were returned to the laboratory in polyethylene bags. In the laboratory, the samples were naturally dried at room temperature (25 °C±2) and passed through a 2-mm sieve prior to analysis. The sediment pH was measured in accordance with ISO 10390 (2005) standard procedure using Eutech Instruments pH 1500.

Chemical analysis

As soon as the water samples were brought on the laboratory, they were preserved with 1 mL of concentrated nitric acid (HNO_3), filtered, and stored in the dark at ambient temperature until microwave acid digestion following EPA method 3015 (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 standard method US Environmental Protection Agency 6010C (2007).

The sediment samples were digested using microwave digestion system (model: BERGHOF speedwave MWS-3+) in accordance with US Environmental Protection Agency 3051A (2007) in which 0.5 g of sample was placed in a Teflon vessel with 2 mL HNO_3 65 %, 6 mL HCl 35 %, and 0.5 mL HF 40 %. An aliquot of the filtration of the samples was taken (about 100 mL). Digestion solutions were measured for total heavy metals (As, Cd, Cr, Co, Cu, Ni, Pb, and Zn) using ICP–OES (US Environmental Protection Agency 6010C 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 (SRM-143d for water and CRM-277 for sediment) with the same procedure. All reagents used in this work were analytical or HPLC grade and used without any further purification.

Methods for estimating pollution indicators

To determine the magnitude of the investigated heavy metals in sediments of Trepça and Sitnica rivers the contamination factor, degree of contamination, modified degree of contamination, pollution load index (*PLI*), and geo-accumulation index (I*geo*) were employed.

Determination of contamination factor

The contamination factor (CF) of a single trace element was calculated as suggested by Min et al. (2013) and Kerolli-Mustafa et al. (2015). It was used to evaluate the contamination of the single heavy metal in our samples. The formula for calculation of contamination factor (CF) used to evaluate the pollution of the single heavy metal in our sediment samples is

$$CF = C^i_{\text{sample}} / C^i_{\text{re ference}}$$

where CF is the contamination factor for a heavy metal; C^i_{sample} is the measured value of the heavy metal in the sediment; $C^i_{\text{reference}}$ is the parameter for calculation, with reference to the background values for heavy metals in sediment recommended by Burton (2002), Table 3.

Degree of contamination and modified degree of contamination

The degree of contamination (Cd) in river sediment is defined as the sum of all contamination factors of the investigated heavy metals (Özkan 2012):

$$C_d = \sum_{i=1}^{n=8} \mathrm{CF}_i$$

The following classification proposed by Håkanson (1980) is adopted to describe the contamination degree for analyzed elements: $Cd<6$: low contamination degree, $6\leq Cd<12$: moderate contamination degree; $12\leq$

$Cd<24$: considerable contamination degree; $Cd\geq24$: very high contamination degree.

In order to provide an overall average value for a range of pollutants in river sediments, the modified degree of contamination (mC_d) was calculated using generalized formula suggested by Abrahim and Parker (2008)):

$$mC_d = \frac{\sum_{i=1}^{n=8} \mathrm{CF}i}{n}$$

where n is the number of analyzed elements and CFi is the contamination factor. Abrahim and Parker (2008) proposed the following modified degree of contamination (mCd) in sediments:

$mCd<1.5$	Nil to very low degree of contamination
$1.5\leq mCd<2$	Low degree of contamination
$2\leq mCd<4$	Moderate degree of contamination
$4\leq mCd<8$	High degree of contamination
$8\leq mCd<16$	Very high degree of contamination
$16\leq mCd<32$	Extremely high degree of contamination
$mCd\geq32$	Ultrahigh degree of contamination

Determination of pollution load index

The *PLI* proposed by Tomlinson et al. (1980) provide understanding on the area about the quantity of analyzed element in the environment. The *PLI* of a single site is the n root of n number of multiplied together contamination factor (*CF*) values. The *PLI* formula will be calculated as suggested by Tomlinson et al. (1980) and Mohiuddin et al. (2011) is

$$PLI = (CF1 \times CF2 \times CF3 \times CFn)^{1/n}$$

where *CF* is the contamination factor and n is the number of metals. According to Mohiuddin et al. (2011), when *PLI* is greater than 1, it means that contamination exists and if *PLI* is less than 1, there is no metal contamination.

Determination of geo-accumulation index

In order to assess the contamination impact of heavy metals in river sediments a common approach such as the geoaccumulation index (I*geo*) proposed by Müller (1969) was used to calculate the metal concentrations above background or baseline concentrations. The method assesses the degree of metal contamination in terms of seven classes based on the increasing numerical values of the index. This index is calculated as follows:

$$\mathrm{I}geo = \log2 \ C_n/1.5 \ B_n$$

where C_n is the concentration of the element in the enriched samples, and the B_n is the background or pristine value of the element. The factor 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments (Abrahim and Parker 2008). Müller (1969) proposed the following descriptive classes for increasing Igeo values (Table 1).

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 sediment samples. Evaluations of similarity were based on the average linkage between groups of cluster analysis (CA) (Ameh et al. 2011).

The method detection limit (MDL) is used as well to define the minimum concentration of analyzed elements in water that can be measured and reported with 99 % confidence. The MDL was determined from seven replicate measurements as described from the US Environmental Protection Agency (EPA) procedure 40 CFR Part 236 Appendix B (2003). The MDL is primary calculated as suggested by Georgian and Osborn (2003) using the formula:

$$\mathrm{MDL} = \ t_{(1-p,\ n-1)}s$$

Table 1 Descriptive classes for Igeo values (Müller 1969)

I*geo* value	I*geo* class	Designation of sediment quality
>5	6	Extremely contaminated
4–5	5	Strongly to extremely contaminated
3–4	4	Strongly contaminated
2–3	3	Moderately to strongly contaminated
1–2	2	Moderately contaminated
0–1		Uncontaminated to moderately contaminated
≤0	0	Uncontaminated

Table 2 Heavy metal concentrations in water samples from Trepça and Sitnica rivers and national limited values (concentration unit is in milligrams per liter)

Sample	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	pH
P1	<MDL	<MDL	0.042±0.003	<MDL	0.046±0.007	<MDL	<MDL	<MDL	8.04±0.02
P2	0.076±0.002	0.071±0.004	0.046±0.009	0.035±0.001	0.054±0.002	<MDL	0.288±0.01	7.994±0.05	7.06±0.01
P3	<MDL	<MDL	0.044±0.01	<MDL	0.032±0.003	<MDL	0.103±0.021	0.876±0.03	8.29±0.01
P4	0.046±0.01	0.045±0.002	0.044±0.06	<MDL	0.038±0.004	<MDL	<MDL	0.029±0.006	7.96±0.01
P5	0.084±0.009	0.081±0.002	0.042±0.003	0.054±0.03	0.034±0.003	0.058±0.003	0.448±0.028	0.260±0.01	7.93±0.06
P6	<MDL	0.017±0.001	0.044±0.003	0.051±0.028	0.050±0.002	<MDL	<MDL	0.336±0.04	8.07±0.01
MDLs	0.05	0.012	0.028	0.031	0.012	0.01	0.031	0.022	
UA 13/2008[a]	0.05	0.01	0.5	0.5	0.1	0.5	0.2	0.5	
75/440/EEC[b]	0.05	0.005	–	0.05	0.02	–	0.05	0.5	
Back. world average[c]	–	*0.3*	*7.1*	*90*	*45*	68	*20*	*95*	

MDL=$t_{(1-p,\, n-1)}s$ where s is standard deviation and t is the correct Student's t value

MDL method detection limits

[a] Republic of Kosovo/Ministry of Environment and Spatial Planning (2008): Administrative instruction No. 13/2008

[b] European Council Directive 75/440/EEC of 16 June 1975

[c] Turekian and Wedepohl (1961)

The factor $t_{(1-p,\, n-1)}$ denotes the $_{(1-p)}$ 100th percentile of the Student t distribution with $_{n-1}$ degrees of freedom, where p=0.01; s denoted the standard deviation for a set of n replicate measurements (n≥7).

Results and discussions

Metal concentrations in water and sediment samples are presented in Tables 2 and 3, which include mean concentrations with standard deviation values.

Water

The water sample results presented in Table 2 showed that most of the heavy metal concentrations in water of Trepça and Sitnica rivers were found within the permissible limits of both European Legislation—75/440/EEC and Kosovo National Administrative Direction UA13 (2008). The method detection limit (MDL) is used as well to define the minimum concentration of analyzed elements in water measured with 99 %. The low concentration of analyzed elements compared with MDL levels were reported as ‘ MDL’. Arsenic concentrations were below permissible limit for many of the sampling sites 1, 3, 4, and 6. Site 2 registered a concentration value of 0.076 mg L^{-1} for As, while site 5 registered a concentration of 0.084 mg L^{-1}. Generally, the highest As concentration was at site 5, Fig. 2a. The concentration for Cd varies; it is under the MDL values (0.012 mg L^{-1}) at sites 1 and 3 and exceeds the MDL values with 0.071 mg L^{-1} at site 3 and 0.081 mg L^{-1} at site 5. The highest concentration of Cd was registered at site 5, Fig. 2b. The concentrations of Co, Cr, and Ni were below the permissible values. The highest concentrations for Co and Cu were registered at site 2, Fig. 2c, d, while the highest concentrations of Cr and Ni were registered at site 5, Fig. 2d, f. The concentrations of Pb and Zn were above the permissible limits in sites 2, 5. Zn showed high concentration in the site 3 as well. The high levels of concentration of As, Cd, Pb, and Zn in the site 2 originate primarily from anthropogenic sources such as discharge of industrial water from mining flotation, whereas the concentration of heavy metals in sites 4 and 5 is originating from the mine waste eroded from the river banks. The mining waste deposited in the tailing dams in Mitrovica Industrial Park is very close to the river banks of Sitnica river. Mine waste eroded from the river banks contribute to entrainment of

Table 3 Heavy metal concentrations in sediment samples from Trepça and Sitnica rivers and limited values (concentration unit is in milligrams per kilogram dry weight)

Sample	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	pH
P1	632.27±0.56	632.08±0.62	10.67±0.20	43.61±0.34	187.60±0.40	35.19±0.22	3249.50±0.64	2069.20±0.51	7.5±0.01
P2	1699.42±0.54	1691.93±0.50	18.38±0.20	112.94±0.55	367.21±0.21	93.42±0.46	5834.7±0.67	5954.75±0.58	7.4±0.05
P3	156.79±0.41	155.82±0.45	14.57±0.45	69.94±0.59	66.06±0.58	73.05±0.24	897.61±0.36	1933.16±0.45	7.8±0.01
P4	53.78±0.43	53.39±0.43	22.12±0.10	162.09±0.13	48.44±0.53	147.79±0.81	219.30±0.26	451.95±0.55	7.7±0.02
P5	89.29±0.68	55.65±0.38	22.85±0.56	178.20±0.35	52.68±0.55	180.13±0.59	697.17±0.36	2555.16±0.39	7.3±0.01
P6	76.01±0.56	2.91±0.26	12.41±0.49	136.16±0.29	26.18±0.87	152.61±0.52	2555.16±0.34	2483.44±0.59	7.4±0.05
TEL[a]	5.9	0.6	–	37.3	35.7	18	35	123	
SQO[b]	2.9	0.8	–	–	36	–	85	140	
Back. world average[c]	*5*	*1.4*	*55.3*	*126*	*122.9*	*102.2*	*230.75*	*303*	

[a] TEL refers to threshold effect level, Burton (2002)

[b] SQO Netherlands limit refers to the sediment quality objective, Burton (2002)

[c] Klavins (2000)

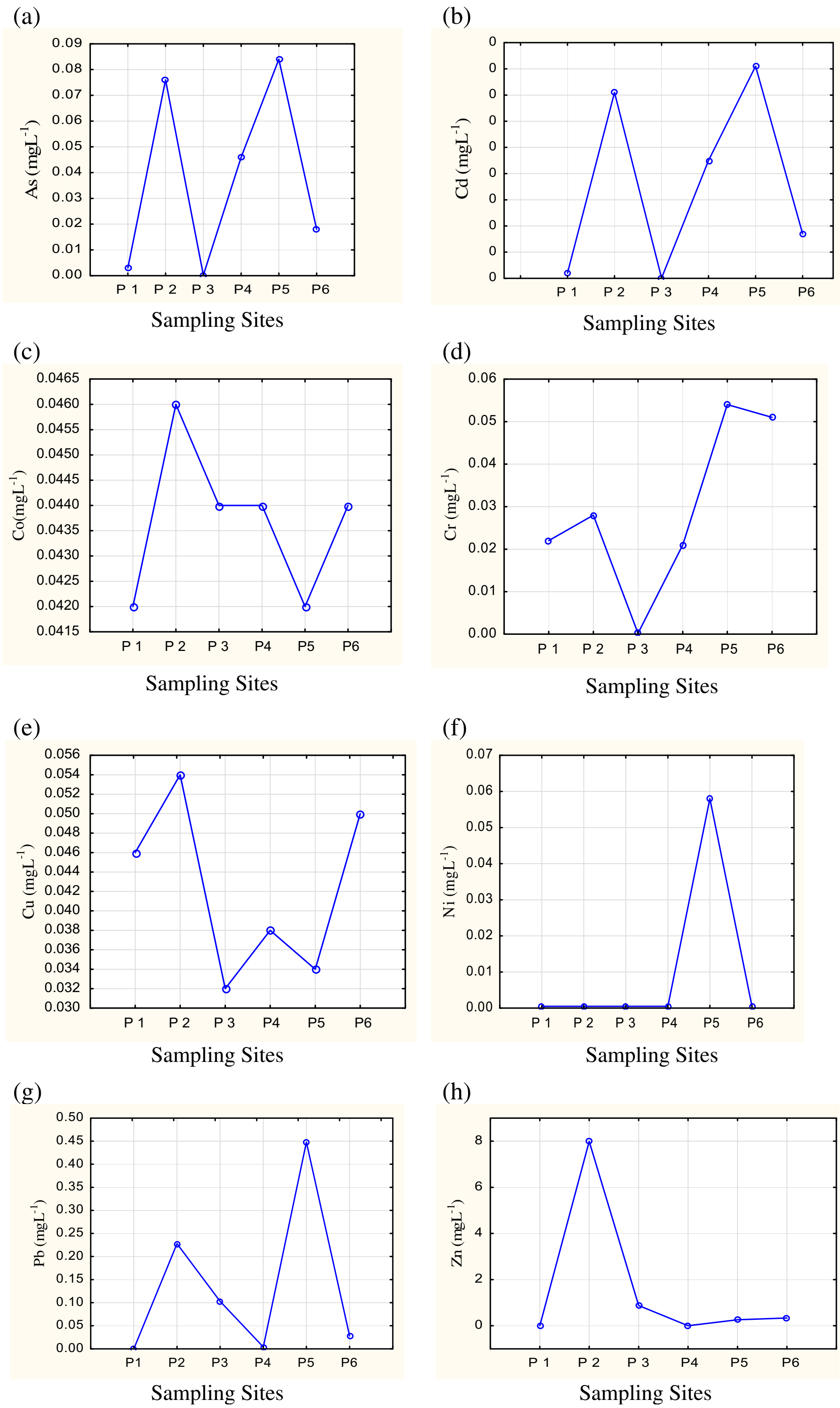

Fig. 2 Heavy metal concentrations in Trepça and Sitnica rivers

the dissolved metals into the river, while the discharge of untreated water from mining flotation into the Trepça river increases the metal content in sites 2 and 3.

Table 4 presents the classification of river waters at each sampling location, based on concentrations of heavy metals. The classification of waters was tentatively performed using available standards in Kosovo (UA13/2008). The location P2 having category V is in accordance with the determination of a high concentration of zinc as a result of discharge of mining zinc flotation waters in Trepça river. For most other metal concentrations, waters are from II to III categories. Also, there is a good agreement with earlier results of Gashi et al. (2011) and Rugova et al. (1989) with respect to Sitnica river. By comparing our results with world average background values of heavy metals in river water (Turekian and Wedepohl 1961), Trepça and Sitnica rivers show a much lower concentration of heavy metals. The pH range of 7.06–8.29 was determined in the water and 7.3–7.8 in the sediment. The lower limit of the pH in water was determined at site 2 and the upper limit at site 3. The lower limit of the pH in the sediment was determined at site 5 and the upper limit at site 3. The pH of water was higher in the water than in the sediment (Tables 2 and 3).

Sediments

Sediment contamination presents one of the biggest environmental concerns. The heavy metal concentrations in sediment act as a transport agent into the aquatic system. The level of contamination of sediment is considered at least three orders of magnitude higher than the same metals in surrounding water (El Bouraie et al. 2010). The contamination of river sediments is a result of urban discharge and industrial waste water beside of natural sources. The analysis of heavy metals in sediment provides information about the water system pollution and "critical sites." The results presented in Table 3 showed variations in the contents of studied elements in the Trepça and Sitnica river sediments. The following results were observed: As 53.78–1699.42 mg kg^{-1}, Cd 2.91–1691.93 mg kg^{-1}, Co 10.67–22.85 mg kg^{-1}, Cr 43.61–178.20 mg kg^{-1}, Cu 26.18–367.21 mg kg^{-1}, Ni 35.19–180.13 mg kg^{-1}, Pb 219.30–5834.7 mg kg^{-1}, and Zn 451.91–5954.75 mg kg^{-1}. The highest concentration values of most of the elements were observed in site 2 at the point of discharge from mining flotation and at sites 5 and 6 (Fig. 3a–h). Surprisingly, the sediment from site 1 where there is no industrial discharge denotes high concentrations of As, Cd, Cu, Pb, and Zn (Fig. 3a, b, e, g, h). Zinc and Pb contents in the sediment profiles reflect a combination of the natural geochemical background, anthropogenic influences, and the mixing effects within the estuary (Li et al. 2000). The distribution of As, Cd, Cu, Pb, and Zn in the sediments may originate from terrestrial (rock and soil) weathering; however, it may have had some anthropogenic sources such possible weeping groundwater from mining. Further investigation on groundwater and soil structure is in process. On the other hand, the levels of As, Cd, Cu, Ni, Pb, and Zn exceed the threshold effect levels and sediment quality objective (SQO) and background world average values. The results show that Trepça and Sitnica river sediments are heavily contaminated. The main anthropogenic

Table 4 Classification of Trepça and Sitnica river waters based on heavy metal concentrations

Parameter (mg L^{-1})	Category II	Category III	Category IV	Category V
As	0.05	0.1	0.2	0.2
	P2, P4, P5			
Cd	0.01	0.05	0.1	0.2
	P2, P4, P5, P6	P2, P5		
Co	0.5	1	1.25	1.5
Cr	0.5	1	1.5	1.75
Cu	0.1	0.25	0.4	0.5
Ni	0.5	1	1	1.5
Pb	0.2	0.5	0.75	1
	P2, P4			
Zn	0.1	1	1.5	2
	P2, P3, P5, P6			P2

Fig. 3 Heavy metal concentrations in Trepça and Sitnica river sediments

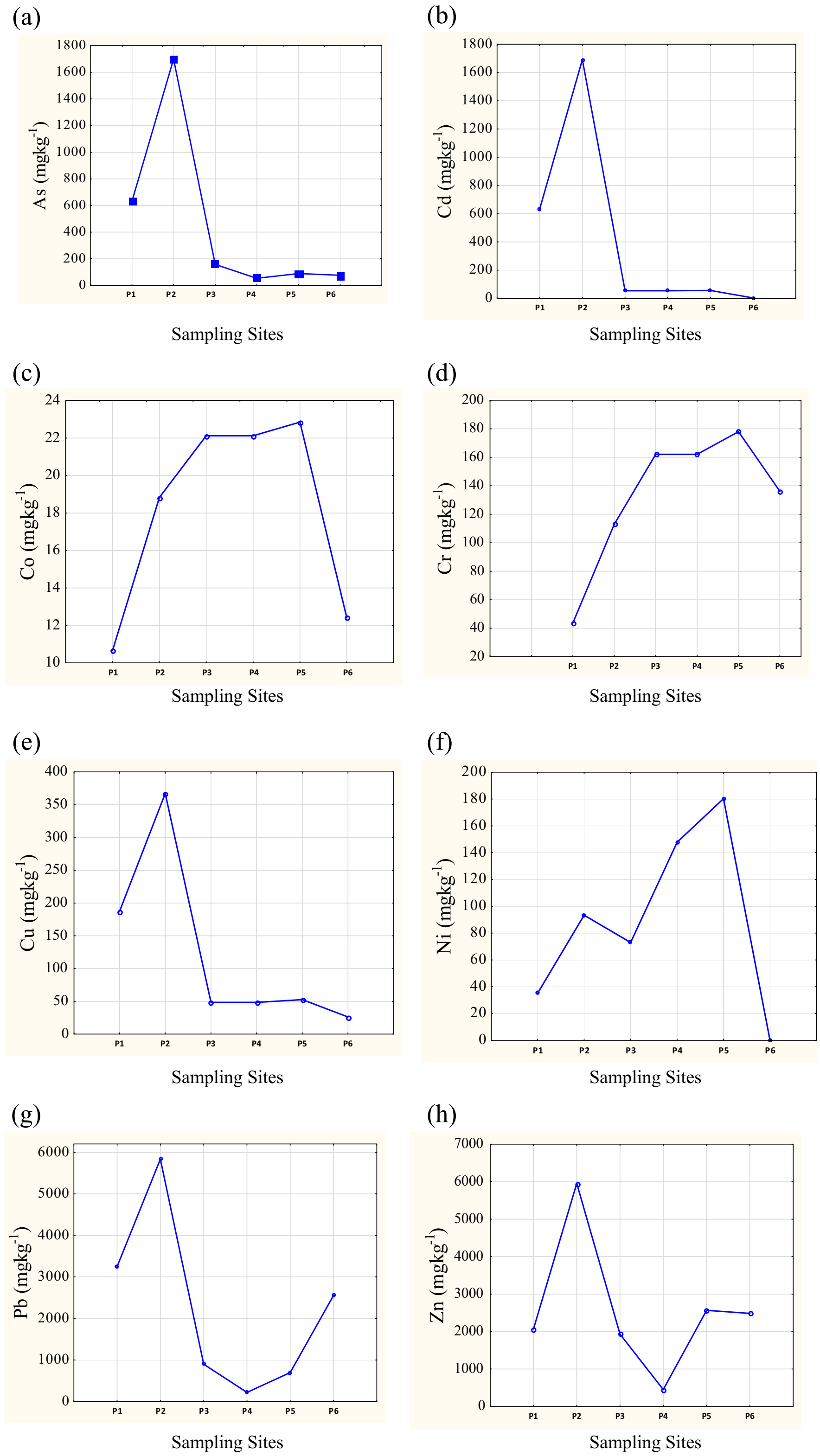

Table 5 Contamination factors (CFs)

Sample	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
P1	126.24	451.48	0.19	0.34	1.52	0.34	14.08	6.82
P2	339.88	1208.52	0.33	0.89	2.98	0.91	25.28	19.65
P3	31.35	111.3	0.26	0.55	0.53	0.71	3.88	6.38
P4	10.75	38.13	0.4	1.28	0.39	1.44	0.94	1.49
P5	17.85	39.75	0.41	1.41	0.42	1.76	3.02	8.43
P6	15.2	2.07	0.22	1.08	0.21	1.49	11.07	9.19

sources are coming from the mining and lead and zinc metallurgy in the region.

Pollution indicators

Contamination factor

In order to assess the pollution load of Trepça and Sitnica river sediments with respect to heavy metals, the contamination factor is used. *CF* values for heavy metals recorded at different sampling locations are presented in Table 5.

According to Håkanson (1980) classification, $CF<1$ points to low contamination factor, $1\leq CF<3$ points to moderate contamination factor, $3\leq CF<6$ points to considerable contamination factor, and $CF\geq 6$ points to a very high contamination factor. Considering this classification, all sites along Trepça and Sitnica rivers indicated a high contaminated nature of sediments. The variation of contamination factor of each investigated elements is presented in Fig. 4.

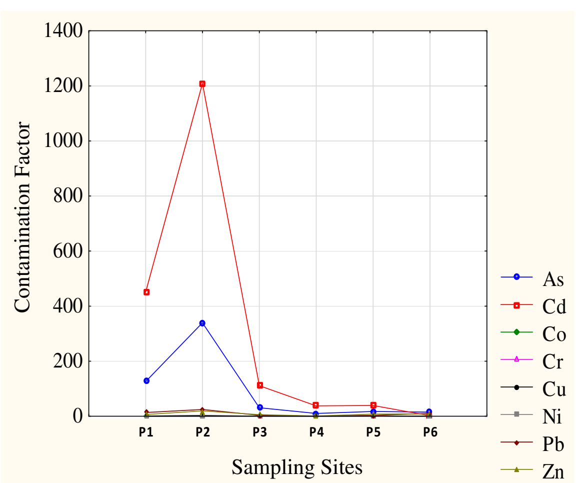

Fig. 4 Contamination factor (*CF*) of heavy metals in Trepça and Sitnica river sediments

The contamination factor resulted to be very high for As and Cd followed by Pb and Zn, while for Cr, Co, Cu and Ni the values are much lower. The values for As ranges from (10.75–339.88), Cd (2.07–1208.52), Pb (0.94–25.28) and Zn (1.49–19.65).

Contamination degree and modified contamination degree

The contamination degree is the sum of all *CF* of a particular site. The results of contamination degree for the investigated sites are presented in Table 6. Based on Håkanson (1980), the *Cd* values range from 40.53 to 1598.44 which indicate a very high contamination degree of sediments.

The *mCd* for the six sites lie in the range from 5.07 to 189.91 as shown in Table 6. Two of the six sites (P4 and P6) have *mCd* values above 5, and one site (P5) has values above 9. These sites can be classified into the high degree of contamination (P4, P6), respectively, and

Table 6 Average of C_d, mC_d, and pollution load index (*PLI*) of Trepça and Sitnica river sediments

Samples	C_d	mC_d	*PLI*
P1	601.01	75.13	4.54
P2	1598.44	199.81	14.1
P3	154.96	19.37	2.87
P4	54.82	6.85	1.89
P5	73.05	9.13	3.06
P6	40.53	5.07	1.98

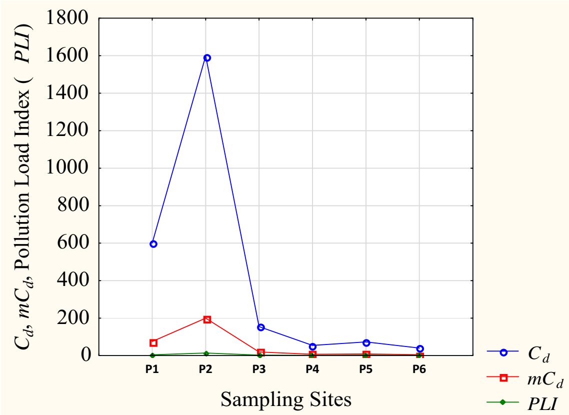

Fig. 5 C_d, mC_d, and pollution load index (*PLI*) of Trepça and Sitnica river sediments

very high degree of contamination (P5) (Fig. 5). P3 site can be classified into the extremely high degree of contamination, while the site P1 and P2 lies into the ultrahigh degree of contamination (Fig. 5). The mCd data indicate significant anthropogenic impact in all sites. Using the classification system proposed for the modified equation (Abrahim and Parker 2008), the overall range of *mCd* values indicate a high degree of contamination of Sitnica river sediment to ultrahigh degree of contamination of Trepça river sediment.

Pollution load index

Another method used to evaluate the heavy metal contamination in sediments is the pollution load index (*PLI*). Barakat et al. (2012) reported that the *PLI* represents the number of times by which the metal content in the sediment exceeds the background concentration and gives a summative indication of the overall level of heavy metal toxicity in a particular sample. The values of *PLI* obtained are summarized in Table 6. They ranged from 1.89 to 14.1 indicating that the heavy metal concentration levels in all investigated sites exceeded the background values (Klavins et al. 2000), TEL threshold values, and SQO Netherlands limits (Burton 2002) that have been used in the absence of sediment quality guidelines in Kosovo. Compared to these values, the Trepça and Sitnica river sediments are having serious anthropogenic pollution as shown in Fig. 5.

Geo-accumulation index

Results of the mean geo-accumulation index are presented in Table 7. Based on Müller (1969) classification (Table 1), Trepça and Sitnica river sediments for geo-accumulation of metals, Cd and As belongs to class 6 (extremely contaminated), Pb belongs to class 5 (strongly to extremely contaminated in site P2), class 4 to strongly contaminated in site P1, and moderately to strongly contaminated class 3 and moderately contaminated class 2 in sites P6, respectively, P3 and P5. Zn belongs to class 4 in P2 (strongly contaminated) and to class 3 in sites P1, P3, P5, and P6 (moderately contaminated). Cu belongs to class 2 (moderately contaminated) in site P2, while in other sites resulted as uncontaminated. Co, Cr, and Ni belong to class 0 (uncontaminated). Negative geo-accumulation indexes revealed that the mean concentration of heavy metals in the river sediment is lower than their respective background and reference values. Sediments are the largest heavy metal sinks and reservoir in an ecosystem. Heavy metals are critical in the contamination of an ecosystem because of easy accumulation in the sediments and uptake into the

Table 7 Index of geo-accumulation (I*geo*) of heavy metals in Trepça and Sitnica river sediments

Sample	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
P1	6.3	8.2	−2.9	−2.1	0.02	−2.1	3.2	2.1
P2	7.8	9.6	−2.1	−0.7	1	−0.7	4	3.7
P3	4.3	6.2	−2.5	−1.4	−1.4	−1	1.3	2
P4	2.84	4.6	−1.8	−0.2	−1.9	−0.05	−0.6	−0.08
P5	3.5	4.7	−1.8	−0.08	−1.7	0.2	1	2.4
P6	3.3	0.47	−2.7	−4.1	−2.8	−0.06	2.8	2.44

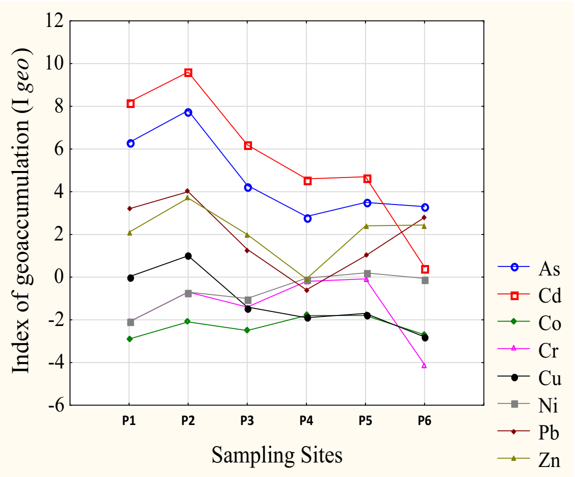

Fig. 6 Index of geo-accumulation (I*geo*) of heavy metals in Trepça and Sitnica river sediments

food. Figure 6 shows the range and average values of I*geo* values for each metal in the investigated sites. Based on average values of Igeo, the ranking of intensity of heavy metal pollution of the Trepça and Sitnica river sediments is as follows: Cd>As>Pb>Zn>Cu>Co>Cr>Ni.

Cluster analysis

Cluster analysis of the river sediments revealed several links between elements of interest. Eight variables (metal concentrations) were compared with the aim to find similarities and metal distribution of the investigated sites. The output of cluster analysis is given as a dendrogram (Fig. 7). The elements that are similar refer to the similar source of origin and the same mobility entrance in the environment. Following a dendrogram of investigated sediment samples was 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 three 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 and Zn are clustered into the third group, while no close similarity is shown with the rest of the group. The third group formed the second cluster. The relationship between two major clusters indicated strong anthropogenic inputs.

Conclusion

To investigate the level of metal contamination in Trepça and Sitnica river waters and sediments, the As, Cd, Cr, Co, Cu, Ni, Pb, and Zn concentrations were investigated in six selected sampling sites. The study revealed that the enhanced concentration of heavy metals in water and river sediments of Trepça and Sitnica rivers is due to the anthropogenic influences. International permissible limits (75/440/EEC) and Kosovo national limits (UA13/2008) were applied to assess the river water contamination. The result revealed that high levels of concentration for As, Cd, Pb, and Zn in the site P2 originate primarily from anthropogenic sources such as discharge of industrial water from mining flotation, whereas the concentration of heavy metals in sites P4 and P5 is originating from the mine waste eroded from the river banks. The water from the investigated sites is classified from II to III categories, except for the site P2 that is classified to category V. International sediment quality guidelines (TEL, SQO Netherlands limit), background world average values, contamination factor (*CF*), degree of contamination, modified degree of contamination, pollution load index (*PLI*), geo-accumulation index (I*geo*), and cluster analysis were applied for assessment of sediment contamination. The results revealed the sediments are heavily polluted. Considering all assessing methods, Cd and As are responsible for the significant amount of heavy metal contamination, followed by Pb and Zn. The results of this study provide baseline data which can be used by

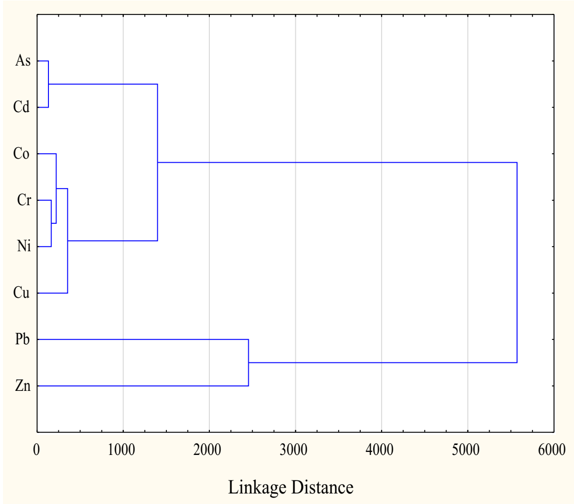

Fig. 7 Dendrogram obtained by cluster analysis of the sediment samples

Kosovo authorities for environmental management. It can be concluded that the input of 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 sediments and must be regarded as a major concern. In order to protect the water and sediment from further contamination, a designing of a monitoring network and reducing the anthropogenic discharges is suggested.

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