Assessment of Heavy Metal Pollution in Ibër River Sediment, Kosova

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Abstract

Natural environment which is polluting by heavy elements is considered as a universal problem. The heavy metals released in the environment as the result of human activities, atmospheric depositions and erosions would finally enter in to the aqua systems. Since, heavy metals are toxic, stable in the environment and potential to combine with the nutritive continuum. Thus, they are considered as one of the most significant pollutant in aqua systems.
The aim of this study was the monitoring of heavy metal levels in sediment samples from Ibër River. Sediment samples were chemically analyzed in order to determine the concentration, and origin of heavy metals (Pb, Cd, Cu, and Zn). Concentrations of lead, cadmium, copper, and zinc were determined in sediment samples collected in 2008 at four sites places in the Ibër River between Montenegro and Serbia. The concentration of these elements was determined by using Differential Pulse Anodic Striping Voltammetry (DPASV) in universal cell three electrode systems with HDME. All the determined parameters with DPASV are compared with the results of ICP/MS method.
Concentrations of metals generally decreased with distance downstream, with highest values occurring in the industrial upper stream of Ibër River. Concentrations of cadmium, copper, and zinc in 2008 were lower at most sites than those in previous years. Unlike, the lead concentration was generally higher in 2008. The most probably reasons of these results are soil geological composition of north Kosova, the existence of the considered number of mines of lead and zinc (Pb-Zn-mining), smelting and chemical industry at Zvecan and Mitrovica, located very close to Ibër river.

Keywords: Ibër River, Sediment, Heavy metals, DPASV, ICP/MS and Kosova

Introduction

The River Ibër flows up in the Montenegro and is characterized with a low hydrological regimen, with an average flow of 33 m^3/sec. Since historically this river is surrounded by a lot of dwellings, River Ibër is an important factor for their development. Until lately, the water of this river was an important flow for them and was used for different purposes like, water supply, irrigation, fishing and recreation (Anonim, 2003).
After the years 90 (last century) the activity of mines and chemical industry in Kosova has been minimal but the residues of them in environment posed a risk for the human health. Increasing of pollution in the recent time would be generally expected, because of poor management of industrial and municipal wastes, the development in the last decade on both Serbian and Montenegrin part of the former Yugoslavia, and the increasing population.
In the Montenegro's part of the Ibër River there does not exist any industry but the residues of mines in the north Kosovo has their indication in the increasing of the pollution from heavy metals in this area (Anonim 1989).
Natural water contains low concentrations of eco-toxic metals and any contaminations may present a severe hazard to the normal functioning of the aquatic ecosystem. Something like that is happening with the water of the River Ibër.
Trace metals are not biodegradable and are involved in biogeochemical cycles by which they are concentrated in sediment and biota, by very high distribution coefficients.
Different anthropogenic and biogeochemical sources indicate in the content of trace metals in different aquatic surfaces and that: (i) by, direct input of the pollutants that contain metals, or by inputting other reactive reagents (ii) which have an indication in spreading trace metals within chemical types and their surfaces in the aquatic system (organic ligands, active superficial material, redox reagents) and indirect, like thermal pollution (iii) (Branica et al., 1988). When it comes to the point of River Ibër, in which discharged all used waters from Mineral and Metallurgic Complex "TREPÇA" (MMCT) where collected all water of residual postindustrial something like this is evident (Arbneshi, et al., 2007).
Direct input of different pollutants in aquatic system indicates in the content of the general amount of metals within the entire system, while two others (ii) and (iii) show how evidently can be indicated in the amount and spreading of ionic types in different surfaces of the aquatic system (Branica et al., 1988).

Repeated mobilization of previous deposed metals in the lower levels of the aquatic system causes increase of risky indication in human nutrition especially with its concentration in the food chain.
Statistical analysis of heavy metal concentrations in sediment was studied to understand the interrelationship between different parameters and also to identify probable source component in order to explain the pollution status of selected estuaries.
Natural environment which is polluting by heavy elements is considered as a universal problem. The heavy elements released in the environment as the result of human activities, atmospheric depositions and erosions would finally enter in to the aqua systems. Since, heavy metals are toxic, stable in the environment and potential to combine with the nutritive continuum. Thus, they are considered as one of the most significant pollutant in aqua systems (Desya *et al*., 2002; Smecka-Cymerman and Kempers, 2001).
Because of the importance of sediments to the overall quality of aquatic system, sediment analysis is often included in environmental assessment studies (Adekola and Eletta, 2007).
Sediments can also be a potential reservoir of metals, by releasing them to the water column under changing physical and chemical conditions (Karbassi *et al*., 2007).
Geochemical studies on sediment contents of aqua systems such as rivers, estuary and river beds may be an effective measure to find the origin and scatter pattern of elements and to bio environmentally evaluate the current situation of an area (Paul, 2001).
Methods of multivariate analysis have been widely used to identify pollution sources and to apportion natural and anthropogenic contribution (Mico *et al*., 2006).
Mining operation is an important industry in Kosova. Many of them are near rivers. It is essential to closely investigate the heavy metals concentrations in river sediments in these regions of the country.
In this research, the concentration of heavy metals has investigated via chemical analysis of Ibër River bed sediments and determining the origin of heavy metals.

Study Field and Methodology

Sampling locations

The purpose of this study was determination of the quantity of lead, cadmium, copper and zinc in the sediment of the Ibër River as well as identification of the potential pollutants of this water. Along the flow in the bed of the River Ibër considerable amounts of urban and industrial waters discharge straight from dwellings and different industries.
Sampling was performed during vintner, spring, summer and fall periods, in 2008. Samples were taken in four following points Zhabare (I-1) before entering to the town of Mitrovica, Suhodoll (I-2) in the enter of the town of Mitrovica, Mitrovica 1 (I-3) in the town of Mitrovica, and Mitrovica 2 (I-4) closeness to the city of Mitrovica, before the reunion of River Sitnica with River Ibër. The sampling areas are shown in Figure 1.
Sediment samples were collected using a grab sampler, preserved according to standard methods (Dlmacija, 2000). During the sampling campaign in Ibër River, in 2008, 16 sediment samples were collected around the Mitrovica city, Kosovo.

Analysis of Heavy Metals

Analyses of the heavy metals (Pb, Cd, Zn and Cu) in sediments collected in 2008 were performed at the Chemistry Department of FNS, University of Prishtina, Kosovo. The sediment samples were held at room temperature until analysis. Air-dried sediment samples were used after being sifted through 0.063 mm sieves. The samples were prepared and analyzed according to standard methods (Dlmacija, 2000). Sediments were analyzed for total concentration of heavy metals in extracts. For total concentration in extract was used 1g of sediment. Heavy metals are determined from the acidic aquatic solutions with anodic stripping voltametry (Branica, M., et al., 1998). All the determined parameters with DPASV are compared with the results of ICP/MS method. Samples were injected in ICP-MS (HELWETT PACKARD 4500 SERIES, Autosampler Cetac Technologies, carrier gas argon).

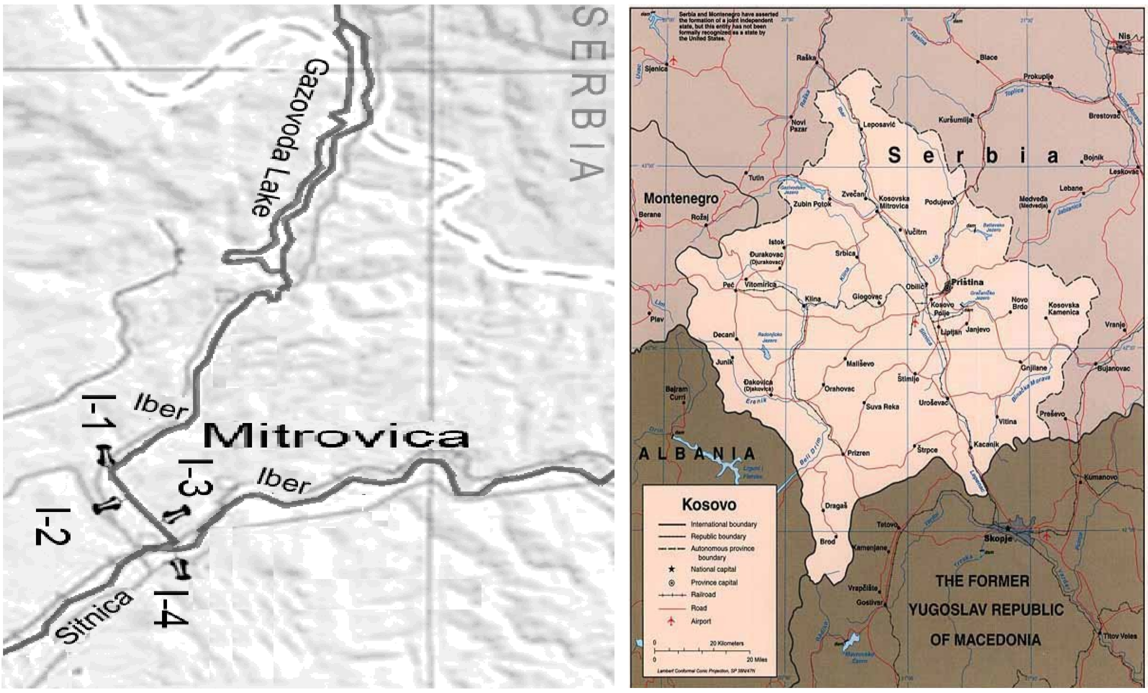

Figure 1. Map showing location of sampling area in Ibër River at Mitrovica region, Kosovo

Results and Discussion

The quality of sediment in the river system is seriously affected by pollutants which enter through drains that bring domestic as well as industrial effluents. These industrial and domestic waste waters, besides other pollutants also contain high concentration of heavy metals. Because of adsorption, hydrolysis and co-precipitation only a small portion of free metal ions stay dissolved in water and a large quantity of them get deposited in the sediment (Beg and Ali, 2008).

Heavy Metal Concentrations in the Ibër River bed sediments as analysis of the metal content in separated fine fraction gives an opportunity for the comparison of sediment pollution in different rivers. Heavy metal concentrations in the fine fraction of investigated sediments can be compared with sediments of the other rivers. However, the metal content in bulk sample better reflects pollution of sediments.
Ibër river bed sediments consist exclusively of medium grained sands <1 mm and just this fraction were analyzed for metal content. The sediment from of Ibër River was analyzed for four selected metals (Zn, Pb, Cd and Cu). The measured concentrations of heavy metals in sediments on individual stations are given (depicted) in table 1 and figures 2-5.

Table 1. Heavy metal concentrations in river sediments (see map for numbers of sampling points).

Sampling Times	Sampling Places							
	I-1	I-2	I-3	I-4	I-1	I-2	I-3	I-4
	Lead (μg/g)				Zinc (μg/g)			
February	20.5	75.45	114.3	133.8	55.8	188.3	288.6	325.4
May	21.5	78.35	115.45	134.3	56.2	189.4	270.4	321.5
August	21.8	79.45	116.8	135.45	56.05	190.1	278.7	331.2
November	20.3	73.25	113.25	133.05	55.9	187.7	275.3	338.7
Sampling Times	Cadmium (μg/g)				Copper (μg/g)			
	I-1	I-2	I-3	I-4	I-1	I-2	I-3	I-4
February	0.23	0.49	3.95	5.35	7.05	25.4	69.7	79.5
May	0.24	0.51	4.25	5.6	7.1	25.8	78.5	81.2
August	0.25	0.53	4.45	5.5	7.2	26.05	79	83
November	0.22	0.5	4.35	5.25	6.9	28.35	67.2	80.5

In this paper the sediments were classified:
a) According to the Criteria for the characterization of sediment quality according to Canadian sediment quality standards (Table 2).
(https://www.pla.co.uk/display_fixedpage.cfm/id/2468/site/environment.), and
b) According to the Criteria for the characterization of sediments quality according to concentration of Cadmium, and Copper. Assessment criteria elaborated by the Oslo and Paris Commission 1994, Table 3. http://www.pbl.nl/en/publications/1994/index.html
The two guideline values TEL and PEL delineate three concentration ranges for a particular chemical:
1. Concentrations below the TEL value represent concentrations, which are not expected to cause any adverse biological effects.
2. Concentrations equal to and above TEL, but below the PEL represent a range of concentrations within which effects may occasionally occur on sensitive organisms, but there is only a slight risk.
3. Concentrations equivalent to and above the PEL value represent a probable-effects range within which adverse biological effects would frequently occur.

Table 2. Criteria for the characterization of sediment quality according to Canadian sediment quality standards. (https://www.pla.co.uk/display_fixedpage.cfm/id/2468/site/environment).

Metal (μg/g) DW*)	TEL (Threshold effect level)	PEL (Probable effect level)
Cadmium	0.7	4.2
Copper	18.7	108
Lead	30.2	112
Zinc	124	271

*DW=dry weight

Table 3. Criteria for the characterization of sediments quality according to concentration of Cadmium, and Copper. Assessment criteria elaborated by the Oslo and Paris Commission 1994. http://www.pbl.nl/en/publications/1994/index.html

Metal	*Very Good*	*Good*	*Fair*	*Poor*	*Very Poor*
Cadmium ((μg/g DW)*	*Background levels*	*< 0.34*	*0.34 -0.68*	*0.68 - 4.21*	*> 4.21*
Copper ((μg/g DW)*	*Background levels*	*< 9.35*	*9.35 – 18.7*	*18.7 – 108*	*> 108*

Generally, concentrations of heavy metals in fine fraction of the investigated bed sediments are very high. Particularly, high zinc, lead, and copper content in the sediment of Ibër River suggests that the lead zinc smelter in Mitrovica still discharges strongly polluted effluents into this Stream. However, the high metal content could also reflect the accumulation of fine, strongly polluted particles in the river bed for a fairly long time. This could have taken place because rare, high water discharges in mainly artificially swelled streams, makes the erosion and winnowing of fine polluted sediments episodic. The zinc, lead and cadmium leaching can also be confirmed by the high percentage of these elements in easily mobile exchangeable form.
In the surrounding of the chemical industry very high content of zinc and lead were found in the sediment of Ibër River. Concentrations of zinc ranged from 55.8 μg/g dry weight in sampling place Zhabare on February 2008, to 338.7 μg/g dry weight in sampling place Mitrovica 2 on November 2008. The highest concentrations of zinc have been detected in the same sampling sites Mitrovica 1 (270.4 - 288.6 μg/g dry weight) and Mitrovica 2 (321.5 - 338.7 μg/g dry weight), (table 1 and figure 2). Particularly high is the zinc content which, in last sample place, varies between 321.5 - 338.7 μg/g (ppm). It is much higher than the pollution of larger European rivers (Helios-Rybicka et al., 2000 and Vink, et al., 1999). Similar contamination occurs in rivers receiving effluents from zinc and lead mines (Warren, 1981).
As can be seen from the graph in Figure 2 the amount of zinc at sampling point Zhabare isn't exceed the values of standard TEL, situation has changed in Suhadoll samples, they significantly exceeds its values. Also in two other sample places (Mitrovica 1 and Mitrovica 2) level of concentration of zinc is higher than the standard PEL, as a result of this, the quality of Sediment in these two sample places is not satisfactory.

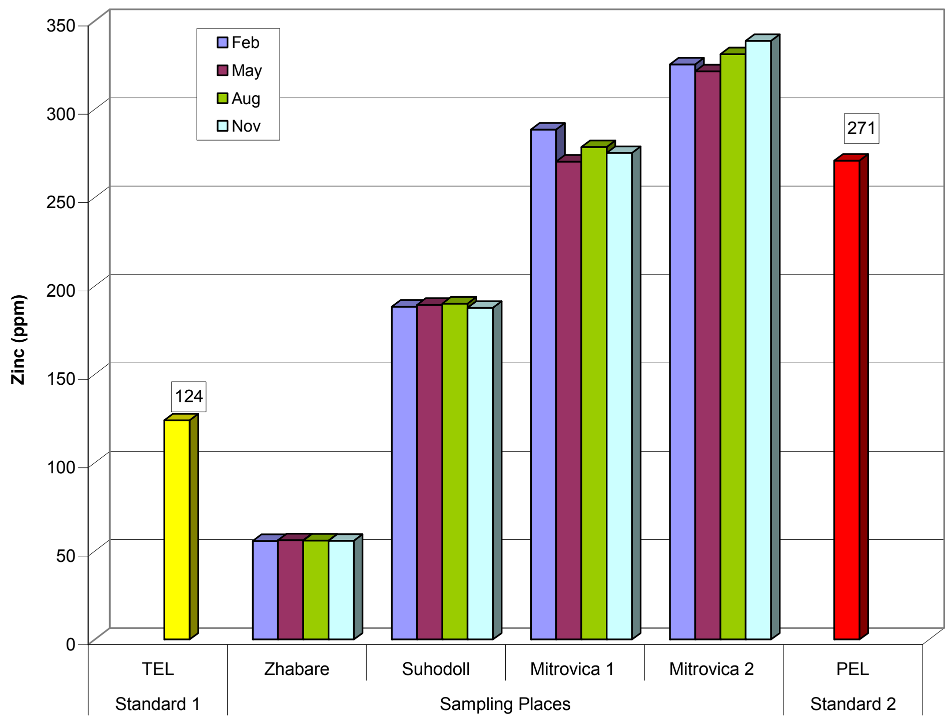

Figure 2. Changes of the zinc concentration in sediment

Concentrations of lead ranged from 20.3 μg/g dry weights in sampling place Zhabare on November 2008, to 135.45 μg/g dry weights in sampling place Mitrovica 2 on August 2008. The highest concentrations of lead have been detected in the same sampling sites Mitrovica 1 (113.25 -116.8μg/g dry weight) and Mitrovica 2 (133.05 - 135.45 μg/g dry weight), (table 1 and figure 3).

As can be understood from the graph in Figure 3, the amount of lead in sampling point Zhabare is lower than the standard value TEL, while in Suhadoll point they are approximately twofold higher. In two other sample places (Mitrovica 1 and Mitrovica 2) level of lead concentration is higher than the PEL standard. This implies that in these two samples, sediment is charged with considerable quantities of lead and his quality is threatened.

High content of zinc and lead in sampling points very close to the zinc-lead mines, lead smelter and zinc refinery (sampling places I-3 /Mitrovica 1 and I-4/Mitrovica 2) suggests leaching of these elements from sandy soils, which have been severely polluted by dust emission since 1980.

The level of concentration of cadmium in the first two samples is relatively low and ranges from 0.22 to 0.25 μg/g dry weights in Zhabare and from 0.49 to 0.53 μg/g dry weights, these values significantly lower than the standard TEL (Figure 4). It should be noted that the level of concentration of cadmium in Mitrovica1 sample place ranges near PEL standard values (exactly from 3.95 – 4.45μg/g dry weight) while sample place Mitrovica 2 values recorded in all cases exceed the standard value PEL and range from 5.25 - 5.6 μg/g dry weight. As seen from Figure 4 levels of cadmium concentration tends to increase the flow of the river Ibër lower reaching higher values in my last sample place (Mitrovica 2).

Concentrations of copper ranged between 6.9 (Zhabare) and 83 μg/g dry weight (Mitrovica2.) The highest value found in the Mitrovica 2 was higher compared to levels encountered in the Zhabare and Suhodoll range: 6.9 -7.2 μg/g dry weight respectively 25.4 -28.35 μg/g dry weight), table 1 and figure 5.

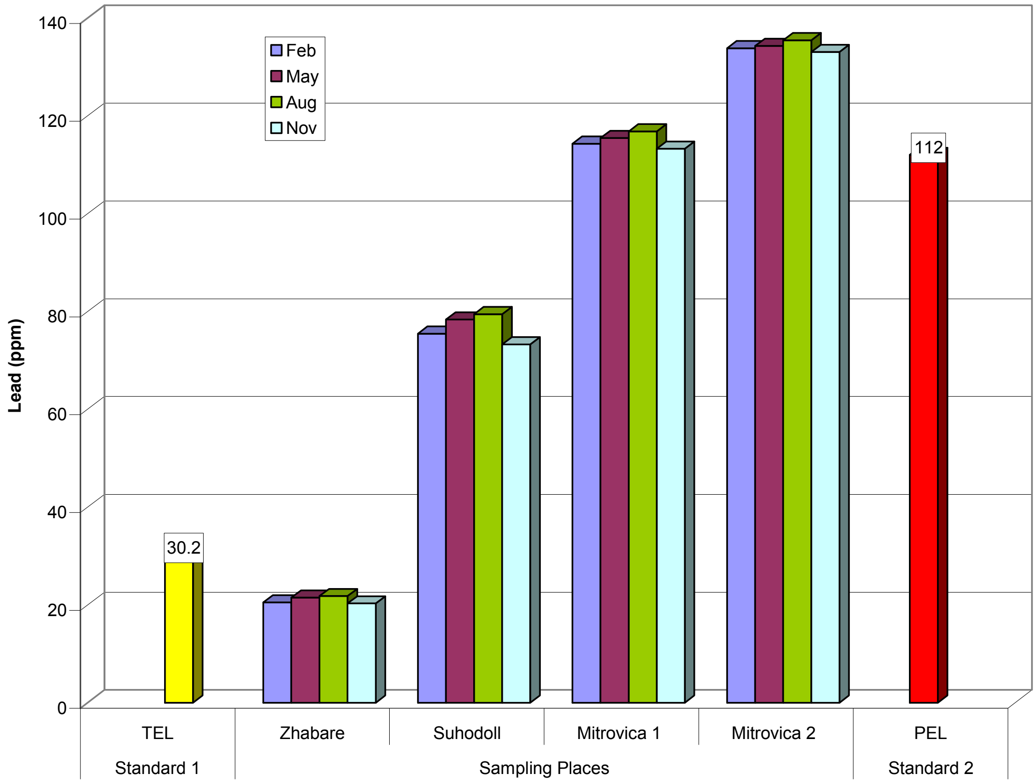

Figure 3. Changes of the lead concentration in sediment

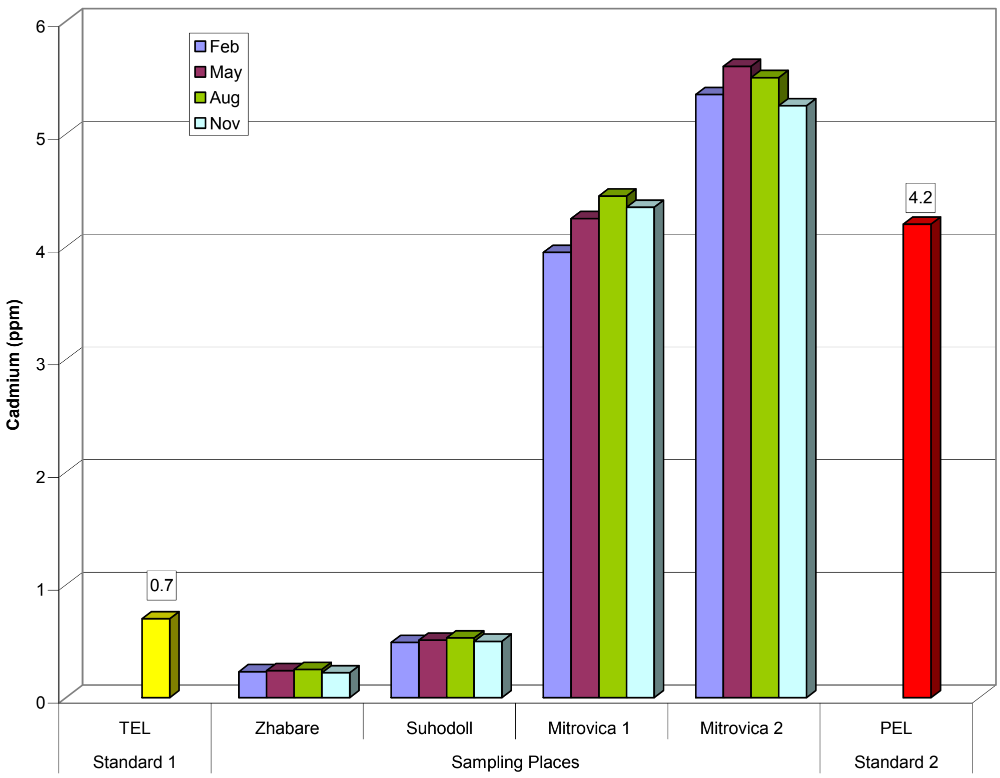

Figure 4. Changes of the cadmium concentration in sediment

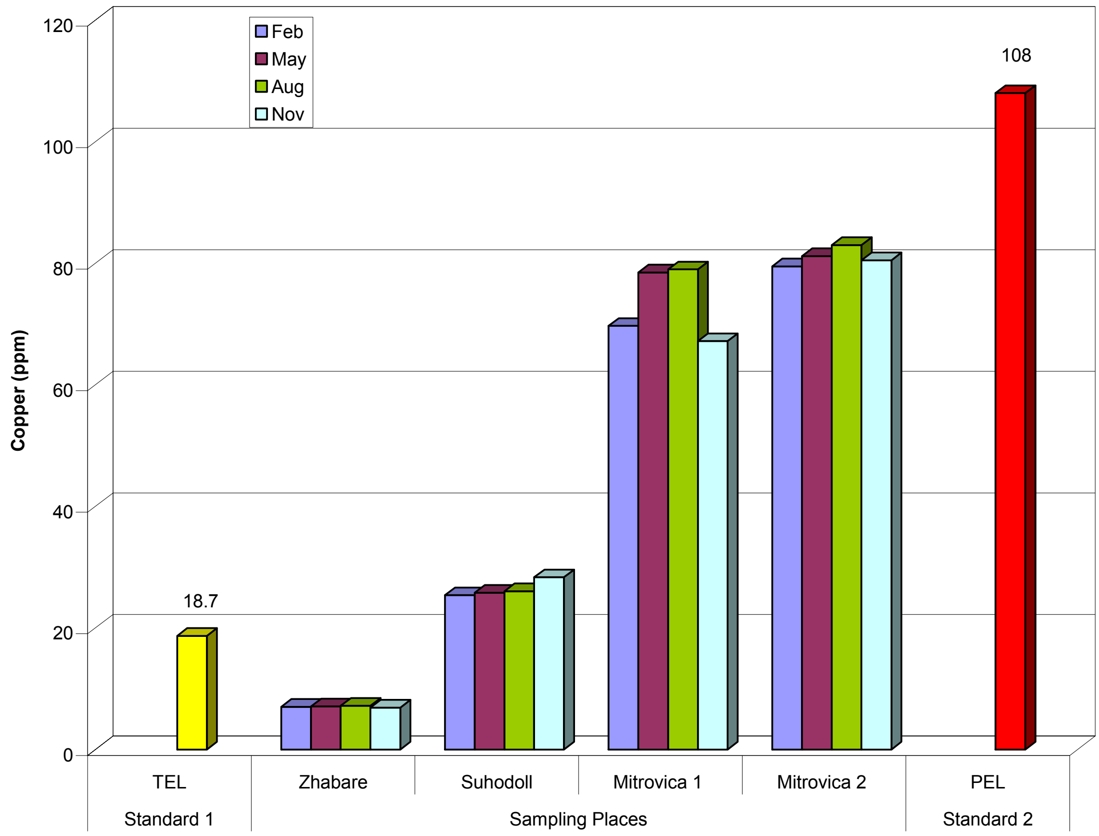

Figure 5. Changes of the copper concentration in sediment

As can be seen from Figure 5 the level of copper concentration, compared with the first two sample places (Zhabare and Suhodoll), has been relatively high even in sample place Mitrovica 1 (67.2 -79 µg/g dry weight) that is closely to that in Mitrovica 2 (79.5 - 83 µg/g dry weight). While the level of concentration in Zhabare brought under the standard values TEL in the other three sample places is between standards values TEL and PEL (Figure 5). According to this it appears that the level of copper concentration in any case has not exceeded the standard value of PEL.
Quality of sediments for Ibër River in different periods and sampling places were presented in tables according to the Criteria for the characterization of sediment quality according to Canadian sediment quality standards (Table 4), and according to the Criteria for the characterization of sediments quality according to concentration of Cadmium, and Copper. Assessment criteria elaborated by the Oslo and Paris Commission 1994, (Table 5).

Table 4. Sediment quality according to the Criteria for the characterization of sediment quality according to Canadian sediment quality standards.

Sampling Times	Sampling Places							
	I-1	I-2	I-3	I-4	I-1	I-2	I-3	I-4
	Lead				Zinc			
Feb	< TEL	>TEL/<PEL	>PEL	>PEL	<TEL	>TEL/<PEL	>PEL	>PEL
May	< TEL	>TEL/<PEL	>PEL	>PEL	<TEL	>TEL/<PEL	>PEL	>PEL
Aug	< TEL	> TEL/<PEL	>PEL	>PEL	<TEL	> TEL/<PEL	>PEL	>PEL
Nov	< TEL	>TEL/<PEL	>PEL	>PEL	<TEL	>TEL/<PEL	>PEL	>PEL
	Cadmium				Copper			
Feb	< TEL	< TEL	>TEL/<PEL	>PEL	< TEL	>TEL	>TEL/<PEL	>TEL/<PEL
May	< TEL	< TEL	>PEL	>PEL	< TEL	>TEL	>TEL/<PEL	>TEL/<PEL
Aug	< TEL	< TEL	>PEL	>PEL	< TEL	> TEL	> TEL/<PEL	>TEL/<PEL
Nov	< TEL	< TEL	>PEL	>PEL	< TEL	>TEL	>TEL/<PEL	>TEL/<PEL

Table 5. Sediment quality according to concentration of Cadmium, and Copper. Assessment criteria elaborated by the Oslo and Paris Commission 1994.

Sampling Times	Cadmium (μg/g)				Copper (μg/g)			
	Sampling Places							
	I-1	I-2	I-3	I-4	I-1	I-2	I-3	I-4
February	Good	Fair	Poor	Very Poor	Good	Poor	Poor	Poor
May	Good	Fair	Very Poor	Very Poor	Good	Poor	Poor	Poor
August	Good	Fair	Very Poor	Very Poor	Good	Poor	Poor	Poor
November	Good	Fair	Very Poor	Very Poor	Good	Poor	Poor	Poor

Conclusions

The high level of concentrations for zinc, lead and cadmium were found in the sediments in the sampling point Mitrovica1 and Mitrovica2 (>PEL).While the concentration of copper in the same places was below PEL range (<PEL). However, according to the Canadian sediment quality standards the concentrations for Zn, Pb and Cd were over the PEL value (Table 4). Here, the sediment quality can be classified as very poor.

Significantly elevated concentrations of zinc, lead and copper were found in the sediments in the sampling point Suhodol (>TEL/<PEL). In this place concentration of cadmium was below TEL range. Based on concentration of Zn, Pb, and Cu the sediment quality in Suhodoll is also poor, but the levels are well below PEL so the risk of toxic effects due to heavy metals is small (Table 4).
According to the Canadian sediment quality standards, heavy metal concentrations (Zn, Pb, Cd and Cu) in the sampling point Zhabare were below TEL value (Table 4), which is not expected to cause any adverse biological effects.
According to concentration of Cadmium, and Copper, Assessment criteria elaborated by the Oslo and Paris Commission 1994 sediment quality for Ibër River can be classified as good in sampling point Zhabare to poor/very poor in sampling point Mitrovica 2, (Table 5).
Sediments in the middle part of the Ibër River represent Mitrovica's "hottest spot" with a possible long-term effect on the Ibër River water quality.
As you can see there is a decreasing trend in concentrations of heavy metals when moving from Zhabare to Mitrovica 2. (Figs 2-5). In general, trace metal levels in sediment collected from downstream Mitrovica area were higher than upstream area.
Generally, the sediment quality in terms of heavy metals can be classified as good in sampling place Zhabare, where the concentrations encountered are well below toxic levels; fair/poor in sampling place Suhodoll and poor/very poor in sampling places Mirovica 1 and Mitrovica 2, where the concentrations encountered are well over toxic levels (Table 1, 4 and 5).

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