RESEARCH ARTICLE **(Open Access)**

Water and Sediment Heavy Metal Pollution in Ereniku River of Kosovo

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Abstract

Soil, water and sediment samples were collected in 13 sampling stations along Erenik River, in the western part of Kosovo in order to assess heavy metal pollution. The concentration of hevy metals as Cd, Hg, Pb, Cr, Cu and Zn were determinated in water, soil and sediment samples. The concentration of heavy metals in water samples was measured using the flame atomic absorption spectrophotometer (AAS), while for sediment and soil samples was used inductively coupled plasma mass spectrometry (ICP-MS). Obtained results showed that the concentrations in soil of heavy metals Cd, Pb, Cu and Zn were under the proposed limit values by the European guideline for "soil background", while the obtained values of Cr in all stations were higher than proposed limit values. The concentrations of heavy metals in sediment were often higher than the values determined with low action on the biological systems of the river ecosystem (ERL Effect Range Low) but smaller than the values that negatively affecting the extent > 50% of organisms on core Effect Medium Range - ERM (Cu, Pb and Ni). The total values of Cr were higher than ERM but its origin is mainly geological more than human activities, thus the biological effect of this element can be probably low. Our results indicated that heavy metals as Pb, Zn and Cu were found in high portion in fine sediment fraction (<0.2 mm), while Cr, Ni and Co were in low amount in this sediment fraction. The concentrations of all analyzed heavy metals in the water were generally low at the beginning of the flow, average in middle stations and higher in secondary stations. Furthermore, the values for Pb, Cd, Cu and Zn were higher than international standards in some stations, showing the influence of highly polluted streams that join Erenik River flow in these stations.

Keywords: Heavy metals, pollution, water, sediment, soil.

1. Introduction

Heavy metals (HM) enters in aquatic ecosystems by altered geological layers and the anthropogenic sources through several pathways, for example leaching processes that reach aquifer waters, run-off, atmospheric deposition, point and non-point pollution sources [12, 4].

Heavy metals released in water are eventually accumulated in the sediment and can be as indicator of heavy metals pollution [5, 15]. Protection of water ecosystems from heavy metal pollution requires knowledges about their content levels in soil and the contribution of point sources on this pollution. The behaviour and effects of heavy metals in water are complex and difficult to be defined, although there is a correlation between their water contents and the applied pressure to ecological receptors and human health. Their mobility in the ecosystem and transfer in the food chain is one of the key issues of the environmental research [16, 1, 7]. Due to their long-standing toxicity, a special attention to heavy metals have to take place when they exceede specific thresholds [8, 10]. Dynamic and uncontrolled development, agriculture, urbanization and a lack of policies and money cash flow investments can accelerate the input of heavy metals into the environment in many countries especially in not developed countries as Kosovo. Many scientific researches have been performed to identify of the sources, types, extent pollution, acts and effects of heavy metals in different pools of ecosystems [17, 9].

Erenik River is one of the main branch of the Drini Bardhe River, which is one of the two main branches of the Drini River whose flow begins to the east of the Albanian Alps, in the town of Junik

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and descends; it crosses the city of Gjakova and pours into the river in front of the Drini Bardhe close to Prizren city. Its watershed is about 88 km^2 and includes mountains up to 2000 m altitude, steep surfaces and forested valleys and fields as part of the Dukagjini plain. Environmental problems related to the quality of water and sediment discharges are untreated wastewater of urban centers, erosion of organic matter or humus and its derivatives due to steep slopes and leaching of nutrients and pesticides from agricultural activity.

Water quality of Erenik River is very important not only because of the negative impact in the river ecosystem sustainability but also because the quality of water affects the Drini River. Drini River is the longest river in Albania (278 km) and the largest watershed (about 19,000 km^2) and its use is intensive water for drinking, energy production, irrigation, fishing and recreation as well regulate hidric regime of Drini watershed. The objective of current study was to evaluate heavy metals pollution and to estimate the pressure level of agriculture, industry and urban on Erenik River Basin.

2. Material and Methods

Soil samples were collected in five locations and 100-200 m from the river bed, on the surface soil horizon in order to estimate heavy metals concentrations. The sediment samples were taken at nine stations along the length of the river. The water samples were collected in 13 stations (Figure 1). The number of samples for soil, sediment and water were different based on physical and geographical characteristics and importance of source pollution which was preliminary identified. Water samples were taken in three periods of 2011 (fall) and 2012 (spring and summer) at 30 cm depth of surface water, in 1.5 liter plastic bottles, stored in cool boxer at 4 ^{0}C temperature till storing in the laboratory. Heavy metals analyses were carried out using flame atomic absorption spectrophotometer (GBC Avanta version 1.31). The calibration curves were prepared separately for all the metals by running different concentrations of standard solutions (Pb 0.0-50 µg L^{-1}, Cd 0.0-1.6 µg L^{-1}, and Cu and Cr 0.0-300 µg L^{-1}). The instrument was set to zero by running the respective reagent blanks. Average values of three replicates were taken for each determination.

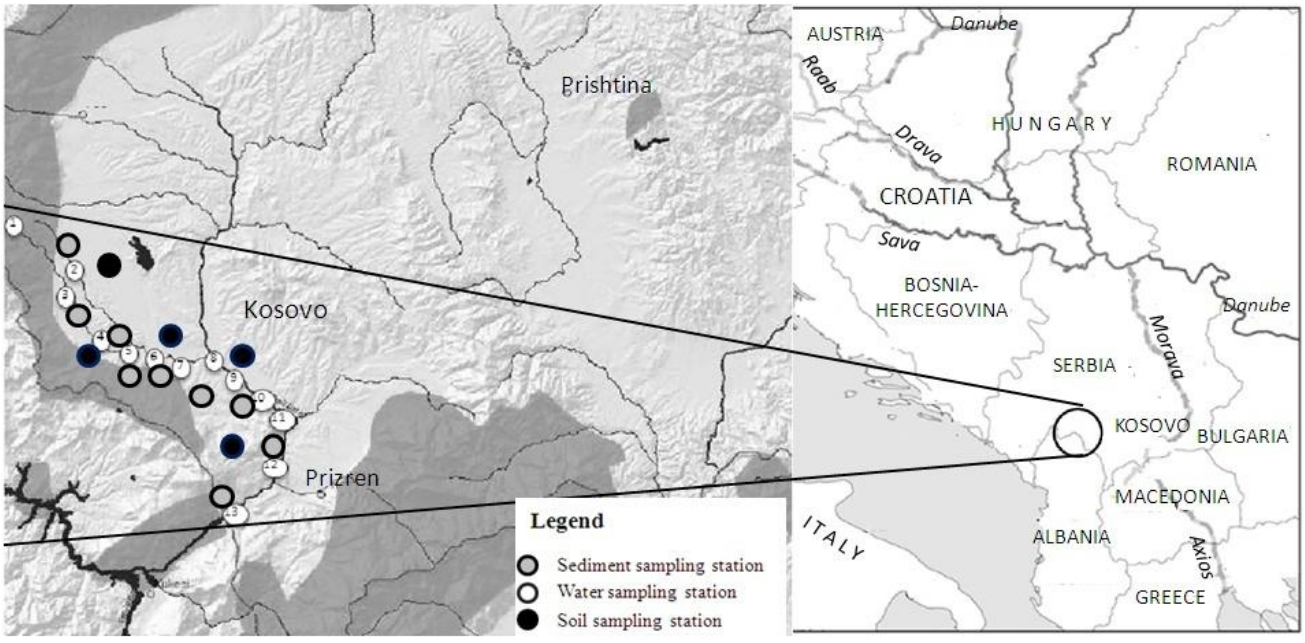

Figure 1. Water, sediment and soil sampling stations

Sediment samples were collected at bottom of the river, up to 15 cm depth, in 9 stations along the river. For each sample were taken three sub-samples within an area of 1 m² and placed in cool boxer in 4 ^{0}C until they were send to the laboratory. Samples were air dryied in room temperature, grinded and sieved in two consecutive sieves: 2.0 and 0.2 mm, on receiving respectively three fractions: > 2 mm, 2-0.2 mm and < 0.2 mm. Soil samples were collected at the surface horizon (0-30 cm) in 5 sampling stations, were air dryied and sieved on sieve of Ø =

2.0 mm and the fraction < 2 mm were used for further analysis.

The concentration of Cd, Hg, Pb, Cr, Cu and Zn were analyzed in water, soil and sediment samples by using EPA 3052 method in mass spectrometry (Inductively coupled plasma mass spectrometry (ICP-MS) type Perkin Elmer-ICP OES OPTIMA 2100 DV (Vetlab-Prishtinë). Reading ICP samples was made according to the EPA 6010c method.

3. Results and Discussion

3.1. Heavy metals in soil

The Europian Council Directive 86/278 EEC [3] regarding the limit value of heavy metals concentrations in the soils-Annex II C, expressed in mg kg^{-1} dry soil, it defines follwing limits for heavy metals: Cd: 1-3; Hg: 1-1.5; Cu: 50-140; Ni: 30-75; Pb: 50-300; Zn: 150-300.

The content of Cd in soil was <0.1 mg/kg for all types of soils. This value was under the limit value of Europeans standards (3 mg kg^{-1} soil). In Comparison with contaminated soil near the "Trepçe" Combine of Kosovo this value was up to to ten times higher [13].

The Cr is not determed as a limit value on EEC [6] but as a guide proposal from the European Commission, thus the proposed limit value for Cr is 50 mg kg^{-1} soil. The obtained value for Cr, in all analysed samples were higher then 50 mg; they varies from 117 (station 4) to 179 mg kg^{-1} dry soil (station 1 and 3). High concentration value of Cr in Kosovo and in Northen Albanian soils are due to specific geological soil formation, as they are developed on top of serpentine magmatic rocks. The Cu, Hg, Pb and Zn valuess were lower than the allowed limits determined on the Directive. Generally, the first two stations (1 and 2) have the highest content of Cu, Pb and Zn compared with other stations, allthough not statistically significant ($p<0.05$).

3.2. Heavy metals in sediment

The concentrations of heavy metals in sediment, expressed in mg for kg dry sediment, vary from one sampling station to the other. The values of Ni varies from 151 (station 7) to 494 (station 4). At the bigining of the river flow the obtained values were higher than other stations. The difference between these stations can be described as "natural enrichment" made to the sediment from the near by lands as a result of erosion.

The average concentration value of lead in sediment was 14.8 mg kg^{-1}, the minimum value was detected in the last station (number 9 with 7 mg kg^{-1}) and the maximum in station number 4 (27mg kg^{-1}). The highest values were found in station 4 and 5. The concentration values of Pb in sediment were much higher than in soil, as a conseguence of pollution then other sources except the “natural enrichment” or erosive proceses. The enrichement ratio values for Pb (ER^{Pb}) varie from 1.8 to 2.2 in all investigated stations. The average value of Zn in the sediment was 157 mg kg^{-1} sediment, with minimum value of 113 (station 6) and maximum of 203 (station 4) mg kg^{-1} sediment. In comparison with the soil, the content of Zn in sediment were 2-3 times higher, much higher in stations 8 and 9, this fact can be explained with double origin: anthropogenic and natural sources. The Cu values (in mg kg^{-1} dry sedediment) varie from 30.0 (station 1) to 94.5 (station 5). As in the case of Zn, the obtained concentration values of Cu in sediment are 1-3 times higher than obtained concentration values in soil. The enrichement ratio (ER_{Cu}) was higher in the middle sampling stations while in the last stations these values were near 1.0 or the concentration values of Cu in soil and sediment were almost equal. The concentration values of Cr in sediments were from 2 to 7 times higher than in soil. The average concentration value of Cr was 625, while the minimum and maximum values were 331 and 887 mg kg^{-1} for stations 7 and 6, respectively. The average concentration value of Co in sediment was 196.7 ± 21.0 kg^{-1} μg dry sediment. The lowest value was in station 1 (171 μg kg^{-1}) and highest in station 4 (232 μg kg^{-1}). The statistical analysis showed no significant variability between obtained values in all stations.

To obsereve long-term impact of heavy metals in sediment to biological organisms, mainly to the zoobenthos and higher organisms is used the guide according the National Oceanographic and Atmospheric Administration [1]. The reference guide classifies the contents of metals and their influence towards the biological systems at different effect range: Effect Range Low - ERL and Effect Range Medium - ERM.

The Cu values were in accordance with the impact on biological systems as they are between ERL and ERM (34 and 270 mg kg^{-1} sediment) with the exeption of the value of the station 1 (<34 mg kg^{-1}) and on this case the concentration of Cu was not harmful to organisms. All other values were ERM < than the values of Cu in sediment > ERL and its impact on organisms were up to 29 %.

However values were <94 mg kg^{-1} or close to three times lower than the upper ERM maximum value and often its impact on biological systems is not seen as prohibitor; in agricultural activity but it is considered like micro nutrients.

For Ni, the values in the sediment were much higher than ERL, than the interval ERL - ERM and the limit values of ERM. All values for all stations were much higher than 51.6 mg kg^{-1} sediment and they vary from 151 to 494 mg kg^{-1}. This content as well as the Cr content can be explained with serpentine geological formations of soils. However the impact on biological systems is relatively low even when passing sensitive ERM. This impact is only 16.9%.

The values of Pb in the sediment, for all stations, were slightly above the value of the ERL (8 mg kg^{-1}); they vary from 7 to 24 mg kg^{-1}, while the value of the ERM was 217 mg kg^{-1}. The Zn values in sediment vary from 113 to 186 mg kg^{-1} while the ERL and ERM values were 150 and 410 mg kg^{-1} sediment. The values in stations 1, 2, 6 and 7 were lower than the values of ERL and their influence on organisms was neglicted while in other stations they were slightly above the ERL value but however much smaller than the ERM. The influence on these last stations was between 4.7 and 41%. The limit influence values for Cr are respectively 81 and 370 mg kg^{-1} for the ERL and ERM. Exept the values of the station 7 (331 mg kg^{-1}) all values in the other stations were higher and much higher than the ERM, which means that the influence of Cr in biological systems is very high (around 95%).

Table 1. The content of heavy metals in soil samples

Heavy metal	Unit	Method	Sampling Stations				
			1	2	3	4	5
Cd	mg kg^{-1} soil	EPA 3052:1996	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Cr			179.66	137.37	179.68	117.34	134.4
Cu			21.51	36	22.9	20.4	13.26
Fe			17655.32	18589.55	19612.9	16632.89	17712
Hg		EPA 6010C:2007	< 1	< 1	< 1	< 1	< 1
Pb			3.09	4.31	7.1	3.4	3.9
Zn			60.1	69.51	51.94	54.91	61.

Table 2. The content of heavy metals in sediment (mg kg^{-1}, for Co are expressed in μg kg^{-1})

HM/Station	1	2	3	4	5	6	7	8	9	Average	SDV	Diferences.
Ni	432	429	459	494	398	297	151	310	229	355.4	115.3	d*
Pb	12	10.8	9	27	24	15	18	10	7	14.8	6.9	a
Zn	135	143	151	203	191	113	124	167	186	157.0	31.5	c
Cu	30	41.8	45.8	80.7	94.5	73.3	84.4	60	79	70.6	20.8	b
Cr	581.3	718	683	662.7	711	887	331	587	467	625.3	159.8	e
Co	171	213	196	232	218	181	178	201.3	179.9	196.7	21.0	c

Student-Newman-Keuls test where statistically proving differences marked with different small letters (a, b, c, d for $p<0.05$). When difference are not statistically significant there are the same letters.

Table 3. Ecological values guide of heavy metals [11]

Chemical element	Guide (mg/kg dry matter)		Percentage incidence on organisms *		
	ERL	ERM	<ERL	ERL-ERM	>ERM
Arsenic	8.2	70	5	11.1	63
Cadmium	1.2	9.6	6.6	36.6	65.7
Chromium	81	370	2.9	21.1	95.0
Cooper	34	270	9.4	29.1	83.7
Lead	8.0	217	35.8	90.2	
Mercury	0.15	0.71	8.3	23.5	42.3
Nickel	20.9	51.6	1.9	16.7	16.9
Zinc	150	410	6.1	47.0	69.8

*The ERL and ERM are general guidelines for evaluating sediment contamination, and the sediment toxicity test uses one organism as a screening tool. This design ensures that a consistent metric is applied across the nation, but the results do not necessarily reflect the extent to which sediments may be toxic to the biota that actually inhabit any particular sampling location.

3.3. Heavy metals in sediment fractions

As described above, in the method, the sediment was divided in three factions: the fine fraction (<0.2 mm), medium fraction (2.0-0.2 mm) and coars fraction (> 2.0 mm). Therefore, determination of heavy metals concentrations in each sediment fraction can help to evaluate the importance of each sediment fraction on heavy metal content, to judge about their origins and to asses their possible movement on river ecosystems.

The contents of heavy metals as discussed above (in absolute value) show different trends according to samplig stations.

In comparison with the other two factions, the metal content in the small fraction (silt and clay) is also often greater than the sum of two other factions. This finding can be explained by the fact that metallic fine structures but especially their oxide and hydroxide traits are chemically and physically connected with clay. Similar tests are carried out in the sediments of wetlands in Greece (Eastern Macedonia) [2]. Christophoridis [2] show that the concentartions of heavy metals in fractions (> 1mm) ranged from 20 to 25 % of total content while the concentartions of heavy metals in small fraction (<0.01 mm) were between 35 and 55% of total content. Thus, small fraction (<0.01 mm) is the most important fraction which help to evaluate the influence of soil, geology and anthropogenic factors. The resulst of heavy metal concentrations from current study are presented in the Table 3.

In our study the calculation of the metal fractions content is based on:

$$Y = \{[FP] \times [Cm]\}/\{[TCm] \times [100]\} * 100$$

Y - The percentage of metal content in the fraction;

FP - Protion of fraction in total sediment analyzed;

Cm - The metal concentration in the respective fraction;

TCm - total concentration of the metal in the sediment (all fractions included).

Expressed as a percentage of total metals in the sediment contents of Ni in the small fraction (< 0.2 mm) of stations varies from 39.5 (station 8) to 48.1 (station 4).

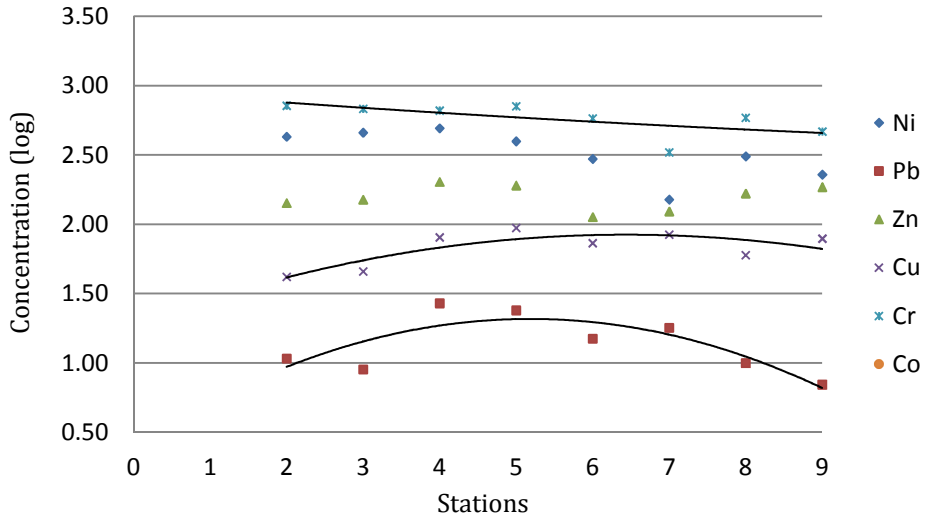

Figure 2. The havy metals concentration (log) in sediment samples according to sampling stations

Presented as logaritm values (log_{10}), given for all metals on all stations (figure below) indicated that:

a) Lead and Copper have the same growing trend in middle stations, and show it through polynomial curve (the degree was 2).

b) Other metals do not have a distribution nomocracy but nevertheless they have the tendence that on last stations the values were higher compared to those of beginnings; while the cobalt there has no any trend.

Table 3. Heavy metal concentration in fine fractions < 0.2 mm on % of total concentration in sediment

	Stations								
Metals	1	2	3	4	5	6	7	8	9
Ni	43.1	40.5	41.6	42.7	48.1	45.0	40.8	39.4	42.4
Pb	81.8	66.7	70.8	66.7	69.6	43.8	33.3	46.2	70.0
Zn	56.7	57.3	60.4	62.2	69.7	56.9	56.9	58.1	55.4
Cu	41.7	45.3	41.5	53.8	54.8	40.5	52.1	60.0	50.6
Cr	34.8	30.1	33.3	29.8	30.0	32.7	31.4	38.4	33.5
Co	48.3	42.2	54.6	47.9	53.2	49.9	48.8	47.2	44.4

More than 50% of the Ni content is associated with coarse fractions, with the exception of the values of two stations (station 5 and 6) which are statistically different. At stations 5 and 6, the sediments are supplied by waste and urban waters with small diameter fractions, therefore the relative high content of Ni in fine sediment fractions of these stations can be explained with these anthropogenic amendments and their deposition.

The concentrations of Pb in the small sediment fraction were higher than 50%, in most of the stations. The minimum value was at station 7 (33.3%) and the maximum value was at station 1 (81.8%). The values in the upper and middle-flow were significantly higher and can be explained by the fact thatPb is much more stable in small fractions than in coarse fractions and it is an important chemical component of water urban and sewages. Its highest value in the station 9 (Fierza lake) (70%) may be explained with other impacts from different flows that join at the downstream of the flow.

The presence of Zn in the fine sediment fraction, in all stations was higher than 50%, which shows its high water solubibility when it is not chemically linked with clay particles. The obtained values varie from 55.4% (station 9) to 69.7% (station 5). The stations 3, 4 and 5 have significatively a higher

value than other stations. The Cu values were lower than those of Zn. They vary at a minimumof 41.5 % (station 3) and a maximum of 60.0% (station 8). Generally, the stations on the downstream flow have higher values compared to stations in the upper and middle part of the river flow. Generally, low values were due to its solubility and its deposition in sediment mainly fine fractions.

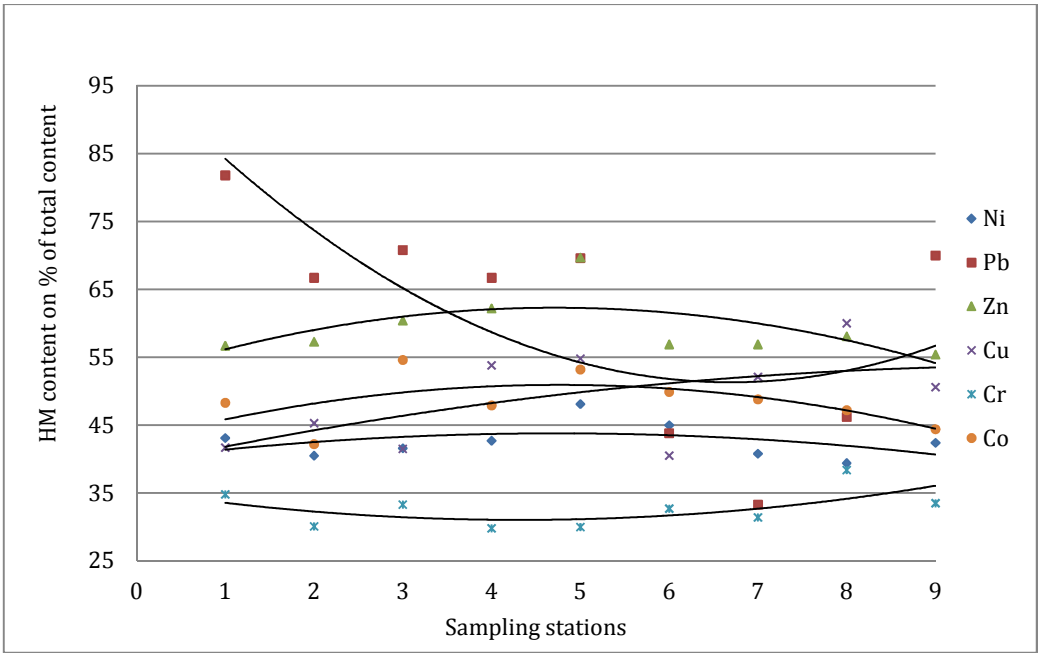

Figure 3. HM content in fine fractions of sediment samples

The Cr values were lower than 50% in all sampling stations. The occurrence of Cr in fine sediment fraction is smaller than the all other heavy metals. The lowest values were in station 4 and 5 (29.8 and 30.0, respectively) and the higher in station 8 (38.4%). The low values shows that the Erenik basin, part of which has a surface with rmagmatic rocks, the Cr is a mineral which crumbles and/or hydratate even on coarse fractions. The contents in fine fractions are the oxy-hydroxides associated with clay but in the upper part of the stream they are still in small quantities. The Co values are similar with those of Cu in fine fractions and in this case the highest values (more than 50%) are in the middle stations of the river flow.

3.4. Heavy metals in water

To clarify the behavior of metals in water and to put in evidence the contributors to them it was considered that the best period to measure heavy metals concentrations in water should be the evaluation of minimum and maximum of the river flow. Based on the flow dynamics of Erenik river, the heavy metals were measured in two periods within the minimum flow (August 2012) and the maximum flow (May 2012). Among them another evaluation was done when the rainy period begins in Kosovo (end of September 2011). The results of analysis for three periods are presented in the table below.

The average value of Pb for all stations was 0.014 ± 0.031 in September 2011. The average lead concentration in water was higher in two other periods, those of May and August 2012, with significant difference compared to the respectively above value (0.019 ± 0.039 and 0.040 ± 00:20). The standard deviation between the values to the same measurements shows big differences which reach several times between the stations. On the three cases the STDEV was almost two times higher of its value. The Pb maximum values for the three measurements results in station 4, significantly higher than the minimum values found in the station 1. The difference between the extreme values was about 50 to 70 times higher (0.05-0.072 vs. 0.001 mg L^{-1}).

The values presented in the above figure as the average of three measurements and compared with European standards, the US Environmental Agency - EPA-USA, the British standard GB3838-200 and the World Health Organization indicated that the values were generally lower than the maximum standards values, except that the Europeans.

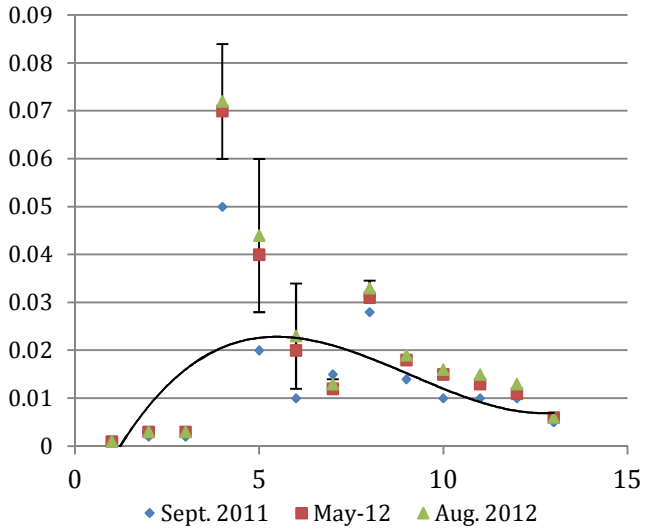

Figure 4. The values of Pb in the river water as average of three measurements (mg L^{-1})

According to the European standard the maximum limit value of Pb is ≤7.2 μg L^{-1}. Obtained values were not over limit value in first three stations, showing no impact of human activity (industrial, agricultural) and discharge of urban waters in the river. Compared with the limit values of the EPA and WHO (≤50 μg Pb L^{-1}) only the values of the stations 4 and 5 were higher by classifying the water quality as polluted (> 0.70 mg L^{-1}).

The average concentration values of Cu (in mg L^{-1}) in water have the same trend as those of Pb; 0.044 ± 0.034 in 2011, 0.053 ± 0,041 in May 2012 and almost the same amount 0.056 ± 0.042 mg L^{-1} in September. Minimum and maximum values were achieved in the two measurements of 2012: 0:19 mg L^{-1} in station 5 and 0.009 mg L^{-1} in station 1. The highest values were achieved in stations 5 and 8, while the lowest values in the upper flow stations. The values in other stations were very lower compared with maximum values; four to ten times lower. At the last stations the average values were 0.020 ± 24 mg L^{-1}.

The average concentration values of Cu in four stations (of the upper part, station 1, 2, 3 and that of ended point - Lake Fierza) were lower than standard limit values set by all guidesThe Cu average values are higher in the stations 5 and 8. The trend of Cu is a arched curve with minimum in the extremes of river flow.

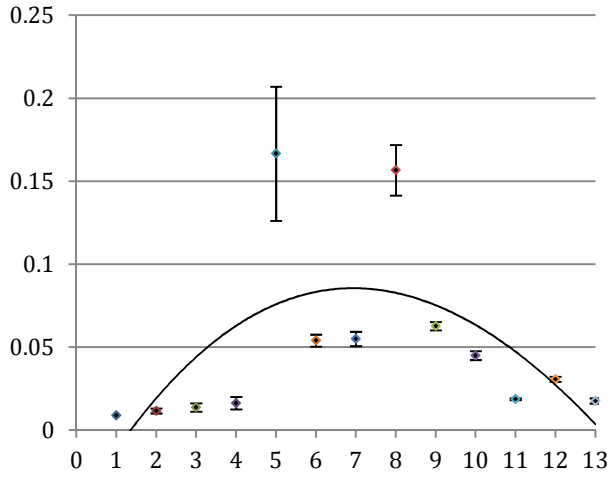

Figure 5. The values of Cu in the river waters as average of three measurements (mg L^{-1})

The average concentration values of Cr in water were significantly no different in all seasons; they varies from 0.029 ± 0.019 (2011) to 0.034 ± 0.031 (September, 2012). They vary from minimum value of 0.002 (first station) to 0.087 ± 0001 (stations 4 and 8). However, the variations between the stations were lower than Pb and Cu values; they were up to four times higher than the minimum value. This shows that Cr originated from geological layers is dominant on the water concentration.

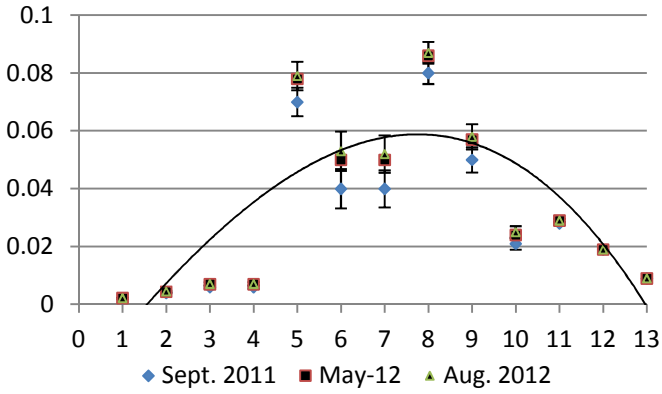

Figure 6. The values of Cr in the river water as average of three measurements (mg L^{-1})

Obtained values of Zn concentration in water does not exceed the limit of the European standard (100 μg L^{-1}).

Trend is identical with those of Cr and Cu. The average values were higher for all seasons in stations 5 and 8. The average values per seasons for all stations vary from 0.036 ± 0.042 (2011) to 0038 ± 0.035 mg L^{-1} for the other two seasons.

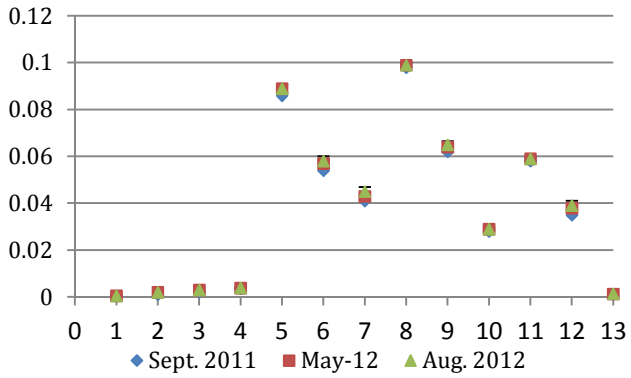

Figure 7. The values of Zn in river water, as an average of three measurements (mg L^{-1})

The only value that approaches the limit according to the European standard is achieved in station 8 (0.089 *vs* 0.100 mg L^{-1}).

The Cd average values in water were identical for the three seasons (0.004 mg L^{-1}) with SDEV from 0.004 to 0.008.

Large differences of Cd were observed in the stations 5-9, compared with end and begining stations; showing their origin mainly from the untreated urban waters of the city. The values however are relatively higher compared with European standards (≤0.005 mg L^{-1} or 5 µg L^{-1}).

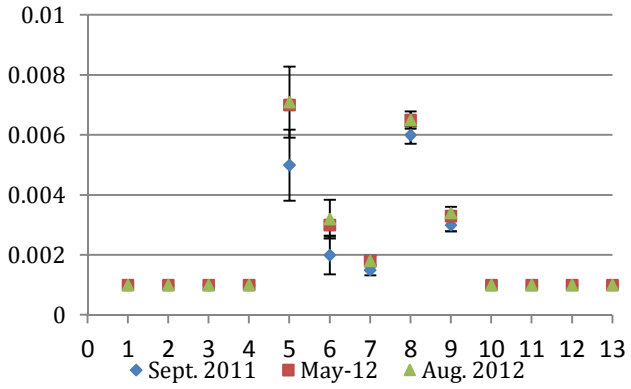

Figure 8. Cd values in river water, as average of three measurements (mg L^{-1})

The hierarchical clustering analysis was processed for the concentrations values of Cd, Pb and Cr in water (dendogram between squared linkage-SPSS [18]). The dendograms (Figure 8) shows that the relationship between the concentrations values on initial and last station were evident for Cd and Pb.

The linkage was more significant for Pb compared with Cd. The differences were significant on the middle stations of the flow compared with others stations. They were higher for Cd and smaller for Pb. The dendograms graph for Cr had an inverse trend; the values at the middle stations were significantly smaller compared with all other stations.

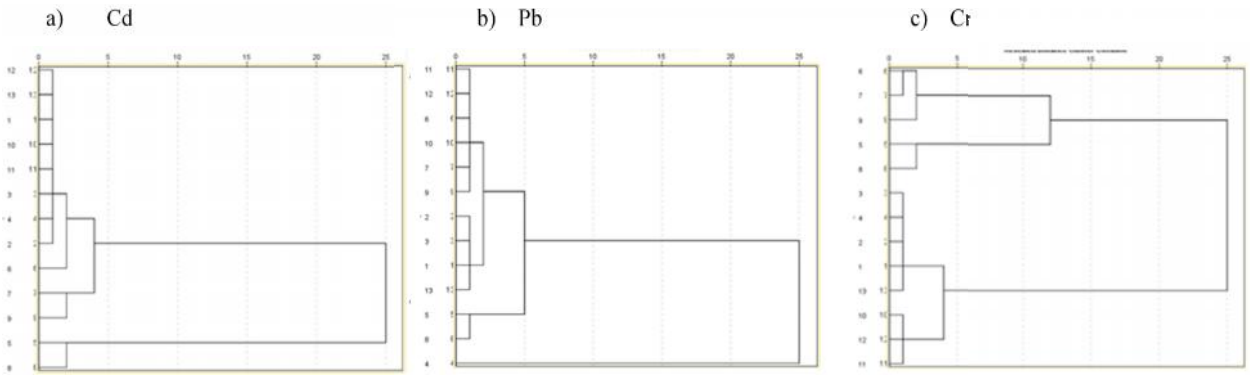

Figure 8. Dendogram clustering analyses (SPSS) of Cd (a), Pb (b) and Cr (c) soluble in water (August, 2012)

Table 4. Analysis of heavy metals (HM) in the river water of Erenik (three seasonal measurements) (mg/L)

HM analyzes, on 28.09.2011																		
HM/ Station	1	2	3	4	5	6	7	8	9	10	11	12	13	Average	SDV	Min.	Max.	Signific.
Lead -Pb	0.001	0.002	0.002	0.05	0.02	0.01	0.015	0.028	0.014	0.01	0.01	0.01	0.005	0.014	0.031	0.001	0.050	a
Copper- Cu	0.009	0.01	0.011	0.012	0.12	0.05	0.05	0.14	0.06	0.042	0.018	0.029	0.016	0.044	0.034	0.009	0.140	c
Chrome- Cr	0.002	0.004	0.006	0.006	0.07	0.04	0.04	0.08	0.05	0.021	0.028	0.019	0.009	0.029	0.029	0.002	0.080	b
Cadmium -Cd	<0.001	<0.001	<0.001	<0.001	0.005	0	0.002	0.006	0.003	<0.001	<0.001	<0.001	<0.001	0.004	0.007	0.002	0.006	a
Zinc- Zn	0.001	0.001	0.002	0.004	0.086	0.05	0.041	0.098	0.062	0.028	0.058	0.035	0.001	0.036	0.042	0.001	0.098	b
HM analyzes, on 31.05.2012																		
Lead -Pb	0.001	0.003	0.003	0.07	0.04	0.02	0.012	0.031	0.018	0.015	0.013	0.011	0.006	0.019	0.039	0.001	0.070	ab
Copper- Cu	0.009	0.012	0.014	0.018	0.19	0.06	0.057	0.16	0.063	0.046	0.019	0.031	0.018	0.053	0.041	0.009	0.190	c
Chrome- Cr	0.002	0.004	0.007	0.007	0.078	0.05	0.05	0.086	0.057	0.024	0.029	0.019	0.009	0.032	0.031	0.002	0.086	b
Cadmium -Cd	<0.001	<0.001	<0.001	<0.001	0.007	0	0.002	0.007	0.003	<0.001	<0.001	<0.001	<0.001	0.004	0.008	0.002	0.007	a
Zinc- Zn	5E-04	0.002	0.003	0.004	0.089	0.06	0.043	0.099	0.064	0.029	0.059	0.038	0.001	0.038	0.043	0.001	0.099	bc
HM analyzes, on 25.08.2012																		
Lead -Pb	0.001	0.003	0	0.072	0.044	0.02	0.013	0.033	0.02	0.016	0.015	0.013	0.006	0.020	0.040	0.000	0.072	ab
Copper- Cu	0.009	0.013	0.02	0.019	0.19	0.06	0.058	0.17	0.07	0.047	0.019	0.032	0.019	0.056	0.042	0.009	0.190	c
Chrome- Cr	0.002	0.005	0.01	0.007	0.079	0.05	0.052	0.087	0.06	0.025	0.029	0.019	0.009	0.034	0.031	0.002	0.087	b
Cadmium -Cd	<0.001	<0.001	<0.001	<0.001	0.007	0	0.002	0.007	0	<0.001	<0.001	<0.001	<0.001	0.004	0.004	0.000	0.007	a
Zinc- Zn	0.001	0.002	0.002	0.004	0.089	0.06	0.045	0.099	0.07	0.029	0.059	0.039	0.001	0.038	0.035	0.001	0.099	b

a, b and c, letters shows significant differences ($p<0.05$)

4. Conclusions

Heavy metal concentrations in investigated soils of the Erenik basin were within the norms determined or proposed by the European guideline for "Soil background", with exeption of the concentration values of Cr in all stations which were higher than the proposed limit value (EEC). High concentrations of Cr in soil are due to the geological fromation which characterize the river basin. Other metals as Cd, Pb, Cu and Zn were below the limit values.

The obtained values of heavy metals in sediments were often higher than the values determined with low action on biological systems of river ecosystem - Effect Range Low ERL, but lower than the values which are affecting negatively then > 50% defined as ERM - Effect Range medium (Cu, Pb and Ni). The values for Cr were higher than the ERM but its origin on the sediment is mostly geological rather than from human activities.

The main contents (> 40% of total of heavy metals in sediments) that were found in the fine sediment fractions were for Pb, Zn and Cu, while for Cr, Ni and Co the values in this fraction were smaller. It seems that the metal with the highest solubility in water are hidden "prison" on the fine fractions (<0.2 mm diameter). Pb and Ni in investigated stations showed a trend by descending values from the beginning towards the end of the flow, while the other metal values were on the polynomial curve type with peaks in middle flow stations.

The obtained values of all estimated heavy metals in water were generally low at the begining of the flow, average values at terminal stations and higher at middle stations. The concentration values of Pb, Cd, Cu and Zn were higher than international standards (EEC, GB3838-200 WHO) in the stations 5 and 8, on showing high influence of polluted streams that are jointed in these stations along Erenik river flow.

5. References

1. Chander K., Dyckmans J., Joergensen R.G.J., Meyer B.G., Raubuch M. **Different sources of heavy metals and their long-term effects on soil microbial properties.** Biology and Fertility of Soils. 2001, **34:** 241–247.
2. Christophoridis A, Stamatis N, Orfanidis S. **Sediment heavy metals of a Mediterranean coastal lagoon: Agiasma, Nestos Delta, Eastern Macedonia (Greece).** Transitional Waters Bulletin. 4, 2007, **33-43**. ISSN 1825-229X, DOI 10.1285/i1825229Xv1. n.4, p.33.
3. Coskun M., Steinnes E., Viladimitrovna M., Sjobakk E., Demkina S. Heavy **metals pollution of surface soil in the Thrace region, Turkey**. Environmental Monitoring and Assessment. 2006, **119:** 545–556. DOI: 10.1007/s10661-005-9042-3.
4. Council **Directive 86/278/EEC** on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture as amended by Directive 91/692/EEC (OJ L 181, 04.07.86) and Regulation (EC) 807/2003 (OJ L 122, 16.5.2003, Regulation (EC) No 219/2009.
5. Dassenakis M., Degaita A., Scoullos M. **Trace metals in sediments of a Mediterranean estuary affected by human activities (Acheloos river estuary, Greece).** Science of the Total Environment. 1995, 168: 19-31.
6. Directorate Denerale-Joint Research Center. **Background values in European soils and sewage sludges**. 2006.
7. Frankowski M., Sojka M., Frankowska A.Z., Siepak M., Blazejewska S.M. **Distribution of heavy metals in Mala Welna River system (western Poland).** Oceanological and Hydrobiological Studies. 2009, **38**: 51–61.
8. Fytianos K., Katsianis G., Triantafyllou P., Zachariadis G. **Accumulation of heavy metals in vegetables grown in an industrial area in relation to soil.** Bull. Environ. Contam. Toxicol. 2001, **67**, 423–430.
9. Kendeler E., Kampichler C., Horak O. **Influence of heavy metals on the functional diversity of soil microbial communuties.** Biology and Fertility of Soils. 2012.**23**: 299–306.
10. Kumar Sharma R., Agrawal M., Marshall F. **Heavy metal contamination of soil and vegetables in suburban areas of Vanasi, India.** Ecotoxicology and Environmental Safety. 2007, **66**: 258–266.
11. Long Edward R., Donald D., McDonald Sherri L., Smith, and Fred D. Calder. **Incidence of Adverse Biological Effects Within Range of Chemical Concentrations in Marine and Estuarine Sediments.**

Environmental Management. 1995. **19.1**, 81-97.

12. Morton-Bermea O., Hernandez Alvarez E., Gaso I., and Segovia, N. **Heavy metal concentrationsin surface soil from Mexico city.** Bull. Environ. Contam. Toxicol. 2002. **68**, 383–388.
13. Musliu A. **Metalet e Rende ne mjeis dhe disa produkte ushqimorë ne zonen industriale te Mitrovices, Kosove**.2014.
14. NOAA. 1999. **Sediment Quality Guidelines Developed for the National Status and Trends Program**. http://www.ccma.nos.noaa.gov/publications/sqg.pdf. Accessed: June 4, 2012.
15. Stamatis N., Kamidis N., Sylaios G. **Sediment and suspended matter lead contamination in the Gulf of Kavala, Greece.** Environmental Monitoring and Assessment. 2006.**115**: 433-449.
16. Steinnes, E., Allen, R. O., Petersen, H. M., Rambek, J. P. and Varskog, P. **Evidence of large scale heavy-metal contamination of natural surface soil in Norway from long-range atmospheric transport**. Sci. Total. Envir. 1997, **205**, 255–266.
17. Wang Y.P., Shi J.Y., Wang H. **The influence of soil heavy metal pollution on soil microbial biomass, enzyme activity and community composition near a copper smelter.** Ecotoxicology and Environmental Safety. 2007, **67**: 75–81.
18. Chaper 8. **Cluster Analyses SPSS**. www.cs.uu.nl/docs/vakken/arm/SPSS/spss8.pdf.