THE ASSESSMENT OF HEAVY METALS IN SEDIMENTS OF VIROI LAKE IN GJIROKASTRA DISTRICT, ALBANIA

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Abstract

Sediments can be sensitive indicators for monitoring contaminants in aquatic environments. The sediments can be polluted with various kinds of toxic substances, including heavy metals. In this study we have assess heavy metals in the sediments of Viroi lake in Gjirokastra district. There is no scientific information on affecting degree by heavy metals of sediments in this location. Seven samples of sediments were collected in 15cm depth and the concentration of Ni, Cr, Pb, Cu, and Cd were determined. Samples were digested with a mixture of HNO_{3cc} and H_2O_2 30% and analyzed by atomic absorption spectrophotometry. The average concentrations of the heavy metals analyzed are listed as the following decreasing order: Ni>Cr>Cu>Pb, whereas Cd was not detected in all sediment samples. The result showed that the total contents of Ni, Cr, Cu, and Pb, varied with respective mean values of 198, 75 (± 113.2), 86.36 (± 39.2), 62.89 (± 40.1), 59.69 (± 20.4). The processed sediment samples were also analyzed for pH, carbonate, C.E.C and total nitrogen, using standard methods. pH_{CaCl2} value ranged from 7.30-8.30, $CaCO_3$ (12.8%-47.8%), C.E.C. (29.1 meq/100g-44.1meq/100g) and TN (0.096%-0.224%). Background values given as 90^{th} percentile were used to evaluate the sediment pollution with heavy metals. Correlation coefficient (*r*) among heavy metals and between those and sediment properties were also determined. Assessment of sediment pollution from heavy metals using sediment quality guideline SQG of USEPA, classified the sediments as non-polluted and heavily-polluted.

Keywords**:** *heavy metals, Viroi lake, sediments, sediment quality guideline SQG, background values*

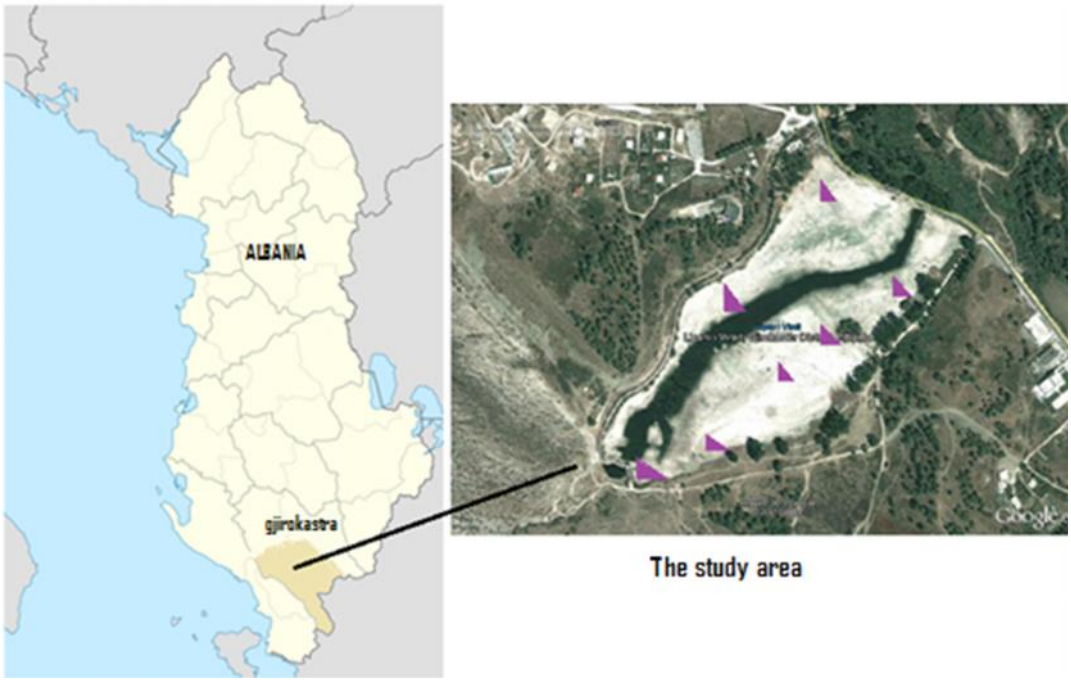
Introduction

Sediments can be sensitive indicators for monitoring aquatic environments. The sediments were polluted with various kinds of hazardous and toxic substances, including heavy metals (Harikumar, et al. 2009), which can be originated from human activities, weathering, air polluted, etc. Sediments give good information for the quality of aquatic ecosystems. Through pollution of sediments by heavy metals, the historical pollution of those ecosystems is defined as the metals cannot degrade and continuously keep on depositing in sediments.
The objective of this study was to evaluate the pollution degree by heavy metals of the samples from Viroi lake (Gjirokastra district). In the absence of the study for this area and specifically on sediments of the lake, in 2012 a study was carried out whose purpose was to determine the range of heavy metals and background values in the sediments of this lake. Such assessment would define the situation of this ecosystem, because heavy metals are serious pollutants in aquatic environments, in terms of their toxicity and ability to be incorporated in food chains (El Nemr, 2003).

Materials and methods

The study area

The study area is located in the district of Gjirokastra (south of Albania). Viroi Lake has a water area of 17 ha and its surrounding area of tens of hectares, which is mainly wooded with pine. The source that supplies the artificial lake is called the Mother of Viroi, a karstic source. Viroi lake with coordinates 40^{o} 06’00.93’’N, 20^{o} 07’22.93’’E, is situated near the national road of Gjirokastra district. The area is characterized by continental climate with hot summers which affects the partial drying of this lake, thus causing direct impact in human and natural activities in the sediment of lake.



The study area

Sample collection and preparation

Seven sediment samples were collected during August 2012 at a depth of 0-15 cm. All samples were stored in polyethylene bags making it easier for transporting them to the laboratory. Sediment samples were air dried, sieved with a 2 mm sieve and the fractions samples < 2mm were used for further analysis.
Sediment samples were analyzed for total concentration of Cd, Cr, Ni, Cu, Pb. The sediment samples were also analyzed for pH, $CaCO_3$, total nitrogen and CEC.
The pH of the sediment was measured in the supernatant suspension of rate 1:5 sediment: liquid (v/v) mixture, with a pH-meter. This liquid is made up of a 0.01 mol/l solution of calcium chloride in water pH ($CaCl_2$).
The nitrogen content in sediment was determined by heating to a temperature of at least 900 °C in the presence of oxygen gas. Mineral and organic nitrogen compounds are oxidized and/or volatilized. The combustion products are oxides of nitrogen (NOx) and molecular nitrogen (N_2). Nitrogen forms are transformed all into N_2, the content of total nitrogen is measured using thermal conductivity (method ISO 13878).
The carbonates were determined by the gas volumetric method using a calcimeter, following the method ISO 10693. CEC was determined by treating the sediment with 0.1mol/l $BaCl_2$ solution.
For the determination of the heavy metals the sediment samples were mixed with 0.3g, HNO_3cc acid and H_2O_2 33%. The mixture of samples was carried in microwave for 25 minutes in 180^oC. The concentrations of heavy metals were determined by atomic absorption spectrometer (AAS).

Metal contents are presented in mg/kg in dry weight. Background values were given as 90th percentile and the correlation coefficients between heavy metals and metals with physico-chemical parameters were used to explain the origin of heavy metals and the mechanisms of deposition in the sediments (Gjoka et.al.2010).

Results and discussions

Chemical properties of sediment

The physico-chemical properties of sediment samples from this study are shown in Table 1. The pH values were in the range from 7.3-8.3. The carbonates are highly variable (12.8%-47.8%), where the highest value is near the source, which differs for its karstic origin.

Total nitrogen was in the range from 0.096% to 0.224%, on classifying this sediments moderate to rich with nitrogen. CEC values range from 29.1-44.1 meq/100g of soil.

Table 1. Physico-chemical properties of sediment samples

Sampling points	pH	CaCO3 (%)	TN (%)	CEC (meq/100g)
S1	**7,3**	**47,8**	**0,096**	**29,1**
S2	**7,4**	**21,75**	**0,182**	**44,1**
S3	**7,4**	**28,44**	**0,224**	**41**
S4	**7,61**	**43,6**	**0,21**	**40,9**
S5	**7,52**	**46,7**	**0,224**	**39,1**
S6	**8,3**	**12,8**	**0,126**	**43,09**
S7	**8,2**	**30,4**	**0,154**	**41**
Average	**7,675714**	**33,07**	**0,173714**	**39,75571**
Stdev	**0,405457**	**13,42393**	**0,050245**	**4,972765**
Max	**8,3**	**47,8**	**0,224**	**44,1**
Min	**7,3**	**12,8**	**0,096**	**29,1**

The total of heavy metals contents in sediment samples of this study are presented in the Table 2. Seven sediment samples were collected and each sample was analyzed with three repetitions, thus a total of 21 extracted samples were analyzed. In this study were determined heavy metals as Cd, Cr, Cu, Ni and Pb. Heavy metals content, expressed on mg/kg, were as follow: Cr (8,64-156,35), Ni(25.453-410.5), Cu (8.675-141.51) and Pb (42.525-138.53), whereas Cd was not detected.

Table 2. Total heavy metals contents in sediment samples

Sampling points	Ni mg/kg	Cr mg/kg	Pb mg/kg	Cu mg/kg
S1_1	45,703	42,72	45,584	23,388
S1_2	45,226	43,197	52,982	17,827
S1_3	25,453	37,219	48,209	8,675
S2_1	161,941	75,883	57,089	42,675
S2_2	189,779	77,126	51,62	48,893
S2_3	193,029	88,587	45,445	46,505
S3_1	156,243	58,548	51,084	82,207
S3_2	183,064	70,908	59,187	102,408
S3_3	191,053	70,418	74,367	98,642
S4_1	318,307	116,37	46,71	68,51
S4_2	61,267	112,95	138,53	40,72
S4_3	286,492	115,3	42,525	66,3
S5_1	181,88	97,62	46,22	34,65
S5_2	167,81	99,91	50,57	30,49

S5_3	149,82	85,09	57,11	34,71
S6_1	404,26	154,26	59,04	141,51
S6_2	410,5	156,35	75,23	138,74
S6_3	406,56	153,69	73,28	139,86
S7_1	214,02	8,64	55,27	48,35
S7_2	211,41	80,55	63,93	62,61
S7_3	170,11	68,28	59,58	43,18
Mean	**198,7584**	**86,36267**	**59,69343**	**62,89762**
STDEV	**113,271**	**39,27422**	**20,43844**	**40,15668**
Maximum	410,5	156,35	138,53	141,51
Minimum	25,453	8,64	42,525	8,675

Background values

The background values determined in the sediments of lake were given as 90th percentile of the obtained values. Indication of 90th percentile means that statistically 9 of 10 soils exhibit low or the same substance contents (Gjoka et.al. 2010). The background values of heavy metals in sediment samples collected in this study are generally higher than those reported from other authors (De Vos & Tarvainen, 2006, Gjoka et. al., 2010), also maximum values of Cr, Ni, Cu, and Pb concentration were higher than those reported in other studies (Crommentuijn et al., 2000, Ramos et al., 1999, Bryan & Hummerstone, 1977).
The maximum values of heavy metals in sediment of this study compare with values of heavy metals determined in sediment sample of Albania rivers (Gjoka et.al., 2010), were lower for Cr, Ni, Cu, but were higher for Pb (Table 3).
According to the European legislation for soil with pH>7, the sediments in this study (alkaline sediments), are polluted with Cr and Ni, while others were near maximum values of this legislation. The total contents of heavy metals given as 90th percentile are proposed as background values for the sediments of Viroi lake. These values were much higher than those reported in the literature, indicating that the levels of these metals were naturally higher. The high content of Pb in this study, compare with the Pb level of river sediments in Albania, may be as a result of air pollution, because this lake is near to the national road. Also, an increase of these metals in the sediments comes from the soil erosion of the surrounding areas.

Table 3. Comparison of heavy metal concentrations in sediment samples collected in this study (mg/kg of dry weight) with those published in literature.

Literature	**Cr**	**Ni**	**Cu**	**Zn**	**Pb**	**Cd**
Gjoka et. al., 2010	56-375.8	20,9-736	200-1167	113-618	9,9-26,1	0,12-0,83
Crommentuijn et al., 2000	100	35	36	140	85	0,8
Ramos et al., 1999	-	-	2,23-37,4	20,6-198,5	2,82-69,7	0,23-1,25
Bryan & Hummerstone, 1977	59	57	65	329	155	1,3
De Vos & Tarvainen, 2006	48^{a}/1750^{b}	46^{a}/1200^{b}	34^{a}/998^{b}	141^{a}/11400^{b}	39^{a}/4880^{b}	0,821^{a}/43,1^{b}
Max value for soil with pH >7, by European legislation (Sofianska, 2008)	62	110	150	300	200	- - -

This study	**153.69[a] 156.35[b]**	**404.26[a] 410.5[b]**	**138.74[a] 141.51[b]**	- - -	**74.367[a] 138.53[b]**	**n.d.**

[a]90th percentile; [b]Maximum

Based on SQG of USEPA (Harikumar et.al., 2009) presented in the Table 4, these sediments due to the concentration of heavy metals can be classified as moderately polluted to heavily polluted in Ni, Pb and non polluted to heavily polluted in Cr and Cu.

Table 4. Classification of heavy metals according SQG of USEPA

Element mg/kg	SQG, non-polluted	SQG, moderate polluted	SQG, heavily polluted
Cu	<25	25-50	>50
Zn	<90	90-200	>200
Mn	-	-	-
Cr	<25	25-75	>75
Cd	-	-	-
Pb	<40	40-60	>60
Ni	<20	20-50	>50

Correlation analysis

In table 5 and 6 are given correlation coefficients among heavy metals and heavy metals with physico-chemical parameters.

Table 5. Correlation coefficients (r) among heavy metals

	Ni	Cr	Pb	Cu
Ni	**1**			
Cr	**0,762**	**1**		
Pb	**-0,035**	**0,297**	**1**	
Cu	**0,847**	**0,672**	**0,203**	**1**

Positive significant correlations resulted among three heavy metals Ni, Cr and Cu, which means the increase of concentration of one element is accompanied with the increased of concentration of the other elements. Thus, these data showed that the elements in study sediments have the same natural origin. Pb element in these sediments has weak correlations with other heavy metals Ni, Cr, and Cu, therefore, this element has different origin from the other measured heavy metals in study sediments. Thus, can be assumed that Pb element in these sediments can be originated from human activities, urban waste, air polluted with emitted Pb by vehicles that drive in the national road near to the study area.

Table 6. Correlation coefficients (r) between heavy metals and physico-chemical properties

	pH	CaCO3	CEC
Ni	0,77017	-0,73744	0,7206
Cr	0,4839	-0,4462	0,5592
Pb	0,4856	-0,2565	0,453
Cu	0,596	-0,7811	0,5766

Positive correlations resulted between the content of Ni, Cr, Cu, Pb and the measured pH values. The correlations were stronger for Ni (0.77017) and Cu (0.596) than for Cr (0.483) and Pb (0.485) which had weak correlations.

A negative correlation is obtained between heavy metals and content of $CaCO_3$. The heavy metals Ni (-0.737) and Cu (-0.781) have stronger negative correlations, which means that heavy metals contents are decreased, whereas carbonates or carbonate minerals contents are increased. This fact suggests that heavy metals have the origin from non-carbonate minerals.

Positive correlations of heavy metals with CEC show that these elements exist as exchangeable ions absorbed on the surface of sediments (Gjoka et.al, 2010).

Conclusions

- Heavy metals determined in sediment samples of Viroi lake were Ni, Cr, Cu, Pb whereas Cd was not detected.
- The average concentrations of the analyzed heavy metals are listed as in the following decreasing order: Ni>Cr>Cu>Pb
- Positive correlations exist between heavy metals and pH and CEC, but negative correlations with metals and $CaCO_3$, indicating that these metals come from non-carbonate minerals and rocks.
- Total heavy metals contents given as 90^{th} percentile are proposed as background values for sediments of Viroi lake, which were for Cr: 153.69; Ni: 404.26; Cu: 138.74 and Pb: 74.367.
- The parameters of heavy metals in some sediments of the study area were above background values, suggesting heavy metal pollution.

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