Determination of heavy metals in water and sediments of Drini river, Buna River and Lake Shkodra

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Abstract

Lake Shkodra is located on the border between Montenegro and Albania at 40º 10' North latitude, 19º 15' East longitude.The lake water level alsovaries seasonally from 4.7 to 9.8 m above sea level. The largest inflow is the Moraca river (Montenegro),which provides more then 62% of the lake water and the outflow is Buna River.
The aim of this study was the monitoring of heavy metal levels in water and sediment samples from Drini river, Buna River and Lake Shkodra.
From the results of analysis of sediments from Skodra lake, River Drini and River Buna by using two methods of extractions and analysing them in ICP –MS for total concentration of toxic metals as Cr and Ni, we concluded that sites in river Drini and Buna are the most contaminated from these metals which indicate in water quality of Shkodra Lake and posed a risk for lake biota. The most probably reasons of those results are, geological construction of north Albania and the existence of the considered number of mines of chromium, and nickel very near to Drini river.

Keywords: ICP –MS, toxic metals

Introduction

Lake Shkodra is located on the border between Montenegro and Albania at 40º 10' North latitude, 19º 15' East longitude.The lake water level alsovaries seasonally from 4.7 to 9.8 m above sea level. The largest inflow is the Moraca river (Montenegro), which provides more then 62% of the lake water and the outflow is Buna River.
The Buna-Bojana River originates from Lake Shkoder it is joined by the Drin River and is a potential outflow between the Adriatic Sea and the lake. Lake Shkoder receives water from the Drini River during the winter. When the water level in the lake is low compared to the water level in the Drin, Drin water enters into the lake. This inflow takes place only within a period of about three months: from December to February.
During the last decades the anthropogenic pollution is going to be significant in this area.The Moraca River, the main tributary of the lake, brings most pollutants into the lake from Aluminium company (KAP), agricultural plantations complex Podgorica landfill, the city drainage collector etc (Misurovic.A 2002).
During the period 1974- 1975 the concentration of in Trace elements (Mn, Ni, Zn, Cr, Co,Pb, Cd, Fe, Hg etc.) in lake Skadar water has been 0.02-4.6 mg/l (Filipovic at al)
The recent analysis of lake water and sediments show significant increase in concentrations of these heavy metals (Filipovic. S 2002)
After the years 90 the activity of mines and chemical industry in Albania has been minimal but the residues of them in environment posed a risk for the human health (A.Miho 2005).
The increase in the 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 Albanian and Montenegrin part of the lake area, and the increasing population.
In the Albanian part of the lake Shkodra there is not existing any industry but the residues of mines in the north Albania has their indication in the increasing of the pollution from heavy metals in this area.

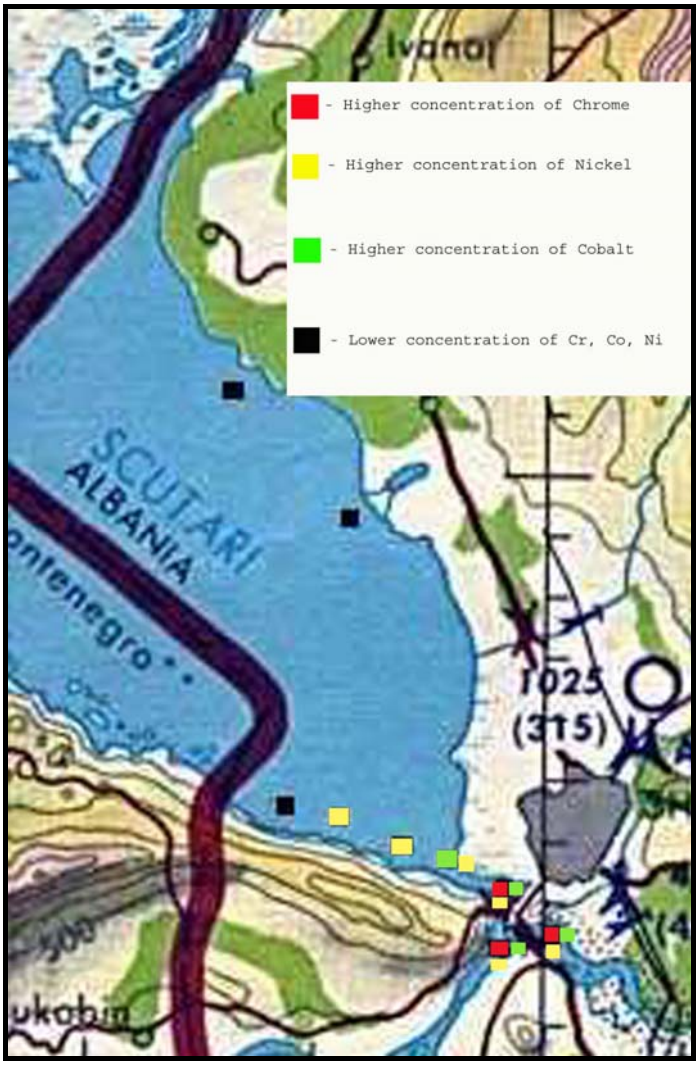

Figure1 Map for distribution of Cr, Ni, Co in 9 sampling sites

Materials and methods

Sampling

The water samples were collected in the surface waters in the 6 sampling points (Ura e Bunes, Ura e Bahcallekut, Dajlon,Zues, Shiroka, Peshkimi) in May 2003. They were treated with concentrated nitric acid and stored in refregerator.The surface sediment samples were collected in April 2003 and dried in the room temperatures. Sampling sites of sediment samples are presented in the Figure 1 (Peshkimi, Kamicë, Dajlon, Ura e Bahçallëkut, Ura e Bunës, Zues, Sterbeq, Shiroka, Zogaj).

Water analysis

1 ml water from each sample was diluted with 10 ml distilled water. The prepeared standart solutions were (multielement + Hg ;Sb ;Sn): 0,1ppb, 1 ppb, 5 ppb ,10 ppb, 50 ppb, 100 ppb. The standart reference material were diluted 1 ml in 10 ml water. Standart Reference Material 1640 TRACE ELEMENTS IN WATER U.S Department of Comerce National Institute of Standarts and Technology GAITHERS BURG MD 20899. Samples were injected in ICP-MS (HELWETT PACKARD 4500 SERIES, Autosampler Cetac Technologies, carrier gaz argon).

Sediment analysis

Sediments were analysed for total concentration of heavy metals in extracts and metals present as mobil forms which can released in water. For total concentration in extract was used 1g of sediment sample which was digested with 5 ml of nitric acid in PTFE epruvetes at microwave sistem for two hours. After digestion samples, reference material (STANDART REFERENCE MATERIAL 2711 MONTANA SOIL ,Baseline Trace Elements Concentrations) and blanks were diluted in 50 ml water. Standart solutions were prepeared from 0.1-10 ppb. 1 ml of each sample were diluted in 10 ml of water. Samples were injected in ICP-MS (HELWETT PACKARD 4500 SERIES, Autosampler Cetac Technologies, carrier gaz argon).
For determination of metals which released in water 1g sediment sample were diluted in 10 ml of water and stirred for 24 hours and then centrifuged for 10 minutes. 5 ml of extract was diluted it with 5 ml distilled water. Standard solutions were (multielement + Hg,Sn, Sb): 0,1ppb,1ppb, 5ppb, 10ppb, 50ppb, 100ppb. Samples were injected in ICP-MS (HELWETT PACKARD 4500 SERIES, Autosampler Cetac Technologies, carrier gaz argon).

Results and discusion

The results of analysis of water and sediments samples of Shkodra lake, River Drini and River Buna are presented in Table 1.2.3. The concentrations of heavy metals in water are within the permissible limits of the EU Standards Table 1 and Figure 2. The total concentration of heavy metals in sediments are presented Table 2 and Figure 4. Total concentration level of Ni and Cr resulted higher than limits of the EU standards in sampling sites Ura e Bahcallëkut, Zues and Dajlon see Map 1.The most probably reasons of these results are geological and geochemical structure of north Albania and the existence of the considered number of mines of chromium, iron and nickel very near to Drini river see Figure 5. The concentrations of heavy metals released in water are presented in Table 3 and Figure 4. The highest concentrations of Cr, Ni have been dedected in the same sampling sites Ura e Bahcallëkut, Zues and Dajlon. All three the most polluted sampling sites are in River Drini and river Buna and in the other sites from Lake Shkodra the total concentration of heavy metals in sediments were lower than limits of the EU standards. The outflow of lake Shkodra sites (Shiroka, Ura e Bunës) are indicated from the phenomen of inflow of Drini water into the lake during the winter. The concentration of Cr and Ni in Shiroka and Ura e Bunës is higher than in sites of the lake far from outflow.

Table 1 The concentrations of heavy metals in water (µg/l)

Sample	Cr	Co	Ni	Cu	Zn	As	Cd	Sn	Hg	Pb
ura e bunes	1,5	0,2	1,9	1,4	1,64	0,6	< 0,1	< 0,1	< 0,1	0,8
ura e bahcall	1,8	0,3	4,1	1,5	< 0,1	1,7	< 0,1	< 0,1	< 0,1	< 0,1
dajlon	1,4	0,2	1,6	0,3	< 0,1	0,3	< 0,1	< 0,1	< 0,1	< 0,1
zus	1,4	0,2	1,7	0,4	< 0,1	0,2	< 0,1	< 0,1	< 0,1	< 0,1
shiroka	1,6	0,2	1,6	2,7	5,6	0,2	< 0,1	< 0,1	< 0,1	0,6
peshkimi	1,6	0,2	1,5	1,6	< 0,1	0,4	< 0,1	< 0,1	< 0,1	0,1
refer water	3,35	1,92	2,5	8	4,6	2,67	1,61	0,16	0,18	2,58

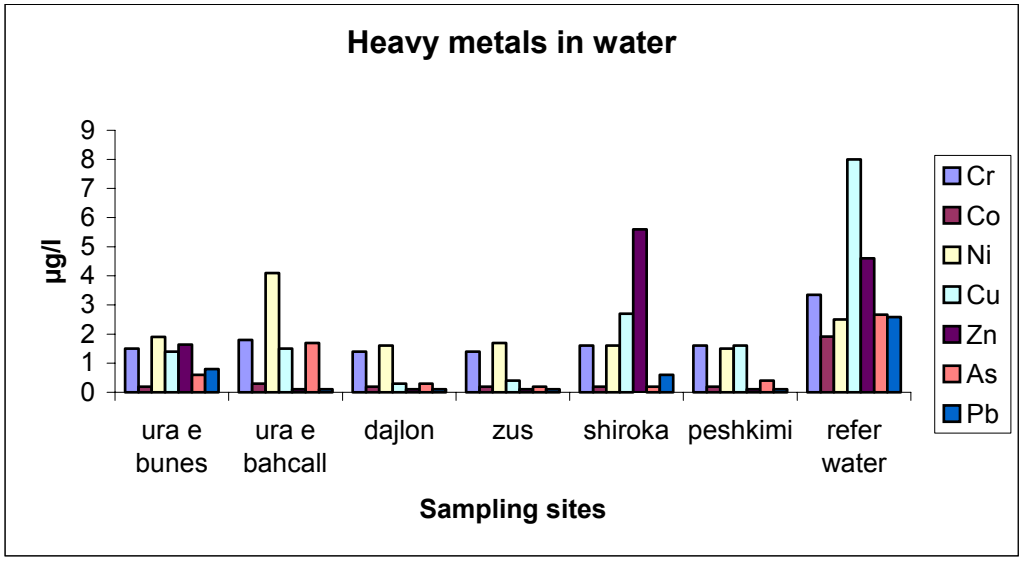

Figure 2 Concentrations of heavy metals in water

Table 2 The total concentrations of heavy metals in sediments (mg/kg dry weight)

Samples	Cr	Co	Ni	Cu	As	Cd	Sn	Hg	Pb
Peshkimi	70.1	19.2	127	40.6	10.7	0.7	< 0.5	< 0.5	26.7
Kamice	19.6	5.4	22.8	10.1	4.1	0.5	< 0.5	< 0.5	10.1
Dajlon	117.7	22.5	221.7	28.8	8.6	0.3	< 0.5	< 0.5	14.6
Ura e Bah	159.5	24.0	321.2	25.7	5.7	0.2	< 0.5	< 0.5	6.0
Ura e Bun	92.6	22.7	176.5	38.9	9.6	0.4	< 0.5	< 0.5	27.3
Zues	195.8	35.4	385.8	36.5	6.9	0.2	< 0.5	< 0.5	18.8
Sterbeq	23.2	5.5	25.9	10.4	4.7	0.5	< 0.5	< 0.5	5.0
Shiroka	77.7	17.6	136.1	24.6	8.5	0.4	< 0.5	< 0.5	16.0
Zogaj	58.5	10.8	77.4	21.5	6.2	0.9	< 0.5	< 0.5	23.4
Reference materials	16.3	6.88	15.07	88.1	94.5	40.9	0.21	7.15	1078.6

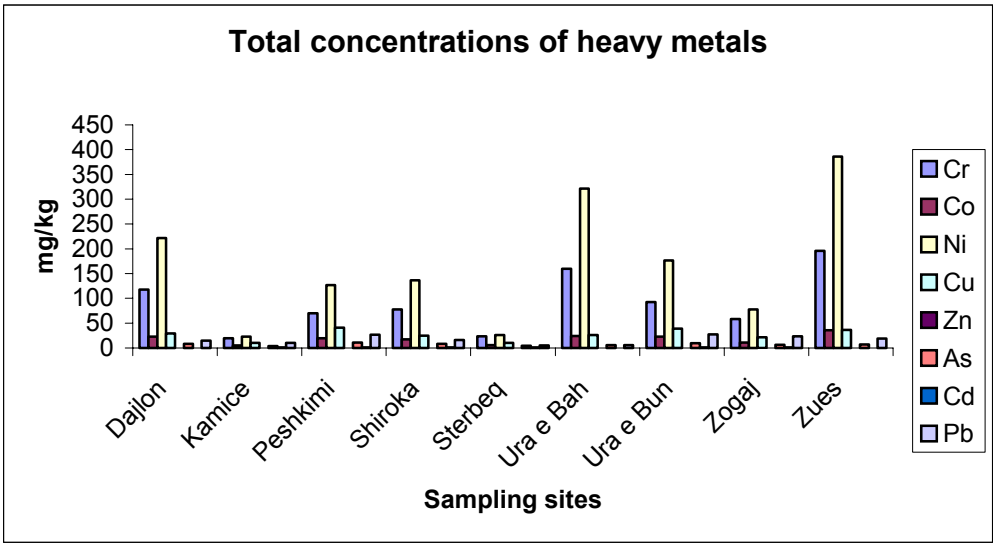

Figure 3 The total concentrations of heavy metals in sediments

Table 3 The concentrations of heavy metals released in water (µg/kg)

Sample	Cr	Co	Ni	Cu	Zn	As	Cd	Sn	Hg	Pb
dajlon	258,6	45,5	458	166	94.0	52,4	1,6	2,8	0,3	61,9
kamica	120,4	21,8	117,6	111,3	163,1	49	3,2	4,1	0,7	92,8
peshkimi	107,3	43,7	255,2	395,5	157,1	53,8	2,9	2,1	0,7	173,7
shiroka	105,8	31,8	258	212	63,5	49,1	1,7	1,3	1.0	74,6
sterbeq	60,6	18,8	65,8	83,5	63,6	44,6	2,4	1,8	0,3	114,2
ura e bahcall	197,8	66	563,9	90,4	53,2	33,6	0,9	0,6	0,2	24,1
ura e bunes	104,6	33,5	199	181,3	100,4	54,3	0,9	1,9	0,7	98,8
zogaj	178,6	26,1	217,3	140	117,9	34,5	1,9	3,76	0,6	46,8
zues	229,3	78,9	559,1	237,7	99,1	46,5	1,2	1,5	0,3	145,1

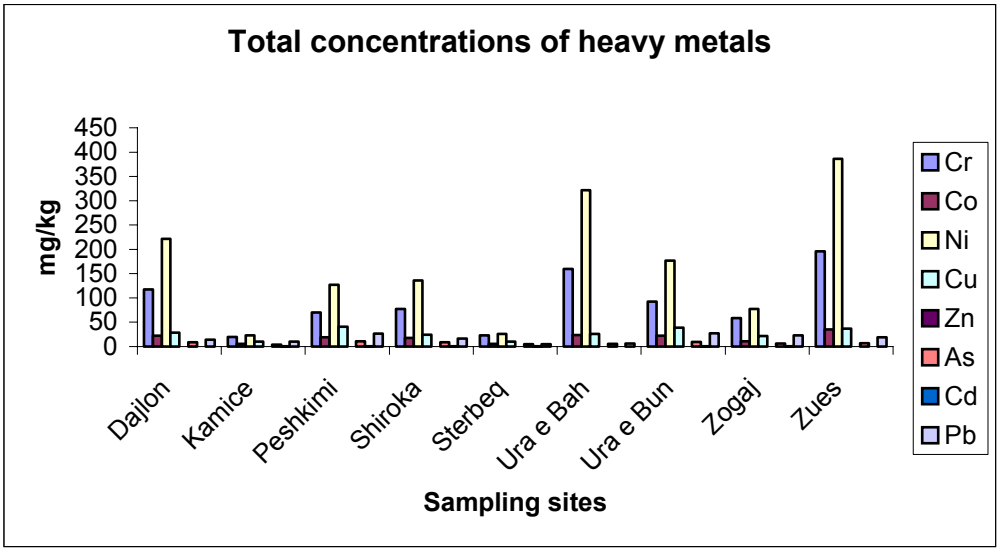

Figure 4 The concentrations of heavy metals released in water

Figure 5 Map of mines in the north of Albania near Drini river

The total concentration of the most toxic metals as Cd, Pb, Hg and As were found to be very low in all sampling sites. The distribution of heavy metals in environment and is well connected with the anthropogenic activity as mines and other industries rather than geological structure of sediments.

Conclusions

The concentrations of heavy metals in both the water and the sediments, in general, is still within the permissible limits of the EU standards. The high concentration of Cr and Ni in samples of Drini river is a result of existence of mines in North Albania and geological structure of sediments.
The indication of river Drini pollution in Lake sediment quality is connected with the inflow of Drini river in the lake and distribution of heavy metals in Lake water. From this natural transport of pollution is indicated River Buna and the outflow sector of Lake Shkodra.
In this study was confirmed the negativ indication of the inflow of River Drini in water and sediment quality of Shkodra lake. The future monitoring of heavy metal levels in water and sediment samples in River Drini. River Buna and Lake Shkodra is very important for evaluation of their environmental situation in this area.

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References

Bekteshi A. Beka I. & Neziri A. 2002*. The physico-chemical characteristics of waters of the Buna River. – Bul. Shkenc., 52: 35-41.*

Bekteshi A. & Mijovic S. 2003. *Preliminary data on the concentration of metals in the Shkodra Lake. Bul. Shk. Ser. Shk. Nat., 53: 293-34.*

Filipovic. P. S (1981)*Efects of pollution on lake skadar and its most important tributaries.The biota and limnology of Lake Skadar. p. 97 –108 (1981)*

Filipovic. P. S , Topaloviç. A , 2002 *Water quality assessment, physical- chemical investigations of Skadar lake. The Shkodra/Skadar Lake Project, Heidelberg, Conference report*
Misurovic.A , 2002 Environmental monitoring in Montenegro.The Shkodra/Skadar Lake Project, Heidelberg, Conference report

Miho, A, Cullaj, A, Hasko,A, Lazo, P,Kupe L, Bachofen,R, Brandl, H, Schanz, F, Baraj, B, 2005
Environmental state of some rivers of Albanian Adriatic lowland, 2005