J. Int. Environmental Application & Science, Vol. 11(2): 166-169 (2016)

The Pollution of River Trepça with Heavy Metals as a Result of Exploitation and Processing of Pb-Zn Ore

Sadija Kadriu, Mehush Aliu*, Milaim Sadiku, Mensur Kelmendi, Ismet Mulliqi, Sabri Hajdini

University of Mitrovica "Isa Boletini" Faculty of Food Technology, 40000, Mitrovicë, KOSOVË

Received March 12, 2016; Accepted June 03, 2016

Abstract: Intensive exploitation of Pb-Zn ore in "Trepça" mine during years 60-90, but since 2000 it has continued to cause serious problems of environmental pollution in general, but in particular on river Trepça, since this mine is located on one side of the banks of this river. After discharge process of untreated waters from mine galleries, the pollution with heavy metals of this river continues also during flotation process of Pb-Zn ore. Building object in one side of river Trepça, in which occurs the flotation process of this ore, located near the residence of the First Tunnel around 2 km below the Stari Terg mine. Our work based on laboratory analysis is focused on the degree of pollution with heavy metals of waters of the river Trepça, as a result of the impact of these two polluting sources.

Keywords: *"Tepça" mine, flotation, Pb-Zn ore, waters, Trepça River, heavy metals, pollution*

Introduction

Immediately after the constitution of Trepça combine with the aim of achieving the most underground mineral resources, it emerged as a necessity opening of galleries rich with heavy metals, but for the purpose of cleaning the galleries from excessive waters, the amount of which reached the value of 80 dm^3/s, their discharge done into the river Trepça.

Industrial effluents and industrial waste sludge can greatly affect in environmental pollution with different metals. (Connell *et al*, 1984). Besides waters emerging from galleries which in themselves have heavy metals, pollution of the river Trepça with these metals become even untreated waters, emerging during the flotation of Pb–Zn ore, in location located near the First Tunnel.

Heavy metals dissolved in water quickly, then precipitate on end of the river beds as carbonate, sulfate and sulfide that are less soluble. (Goletić, 2005). Therefore, in order to determine the degree of water pollution with heavy metals we have seen fit to take samples for laboratory analysis of the water of this river, which after passing the First Tunnel and villages Reka and Shupkovc flows into river Sitnica.

Material and Methods

With the aim of reflecting more accurate of degree of content and contamination with heavy metals of waters in river Trepça we set two points of monitoring: UT_1 (waters of the river Trepça under flotation of the First Tunnel) and UT_2 (waters of the river Trepça before joining with the waters of the river Sitnica). The taken samples for each monitoring point are made during winter and summer season 2014/2015. The sampling method, the amount of sample collected and the mode of transport and the maximum time that can stand the sample before chemical analysis were made in accordance with paragraph 5.4 of norms EN ISO/CEI 17025. Samples were divided into separate containers and their conservation is done in accordance with the procedure of conservation of American Public Health Association, 2005. (APHA, 2005) Preparation of water samples for measurement of heavy metals based on mineralisation of samples on applying the methods EPA 3015 and 3051. (H, 1994)

Table 1. Sampling points and their coordinates

River	Site-sampling	Latitude	Longitude	Sea level (m)
TrepçaUT_1	Under flotation	42°55'1.15"	20°54'1.89"	582
TrepçaUT_2	Before joining with river Sitnicë	42°53'21.48"	20°52'50.13"	506

*Corresponding: E-Mail: mehush.aliu@umib.net; Tel: +37744-633-263;

In these samples was determined the concentration of metals Pb, Zn, Cd, Hg, Cu, Mn and Sb in the waters of the river Trepça, and other indicative parameters of water, such as temperature, turbidity, pH, electrical conductivity, nitrates, nitrites, ammonium ion, phosphate ion, sulphate ion and total phosphorus. For the determination of heavy metals in taken samples, implemented two techniques of measurements, measurement techniques with SAA-F and techniques of measurement with ICP-OES, conducted laboratory analyzes environmental IHMK and private laboratory "Agrovet" accredited by the Kosovo Accreditation Agency.

Results and Discussion

During the experimental phase of the research is defined the concentrations of heavy metals Pb, Zn, Cd, Hg, Cu, Mn and Sb and indicative parameters in water samples of river Trepça.
The results obtained from these tests are given in Tables 1-10.
Based on the results obtained is made the assessment of the presence of heavy metals in the waters of the river Trepça as basic values of reference are taken, Directive 75/440/EEC on surface waters intended for production of drinking water and Instruction Kosovo No.13 /2008 which relates to effluent discharged into bodies of water and sewerage.

Table 2. Concentration of indicative parameters in sampling UT1- by months, year 2014/2015

	Unit	MPV	July	September	November	March
Physical parameters						
Water temp–T_w	^{0}C	25	24.1	25.8	18.3	7.3
Turbidity- TUR	NTU		19.0	16.9	84	2.6
Electr. Cond.– χ	µS/cm	1000	1023	1163	1046	539
Chemical parameters						
pH	1-14	6.5-8	8.26	8. 6	8.54	7.90
Nitrate - NO_3^-	mg/dm^3	30	0.2	0.0	1.2	5.5
nitrite ion NO_2^-	mg/dm^3	0.2	0.2	0.04	0.114	0.20
Ammonia NH_4^+	mg/dm^3	0.2	2.16	0.38	0.39	0.23
Phosphate-PO_4^{3-}	mg/dm^3	1.0	<0.01	<0.001	0.002	0.724
Total phosphate -P_{Tot}	mg/dm^3	1.0	<0.01	<0.001	0.002	0.322
Sulphate -SO_4^{2-}	mg/dm^3	150	261	316	182	136

Table 3. Concentration of indicative parameters in sampling UT2- by months, year 2014/2015

	Unit	MPV	July	September	November	March
Physical parameters						
Water temp.- T_u	C^0	25	19.1	22.6	11.6	6.5
Turbidity- TUR	NTU		15.7	12.3	16.0	9.0
Electr. Cond.– χ	µS/cm	1000	803	488	946	581
Chemical parameters						
pH	1-14	6.5-8	7.93	7.34	8.03	8.00
Nitrate- NO_3^-	mg/dm^3	30	2.4	25.5	1.7	6.2
Nitrite NO_2^-	mg/dm^3	0.2	0.41	0.46	0.42	0.06
Ammonia NH_4^+	mg/dm^3	0.2	1.15	2.03	2.01	0.17
Phosphate-PO_4^{3-}	mg/dm^3	1.0	0.03	0.695	0.598	0.332
Total phosphor -P_{Tot}	mg/dm^3	1.0	0.02	0.326	0.315	0.169
Sulphate -SO_4^{2-}	mg/dm^3	150	268	60	60.1	136.7

Table 4. Concentration of Pb (mg/dm^3) by site-sampling and monitored during the months of the year 2014/2015

Pb (mg/dm^3)	UT_1	UT_2
June ICP-OES	0,701	0,32
July, SAA-F	<0,05	<0,05
September ICP-OES	0,724	0,216
November, SAA-F	0,904	<0,05
March IP-OES	0,755	0,224
Direc.75/440EEC	0,05	0,05
UA,13/2008, Kosovë	0,2	0,2

The results obtained regarding the concentration of indicative parameters result with exceeded the maximum allowable sulfate ions from metal salts and electrical conductivity. Therefore, based on these results we think the presence of heavy metals in these site-sampling. The results obtained reflect the concentration of Pb on-UT_1 and UT_2 beyond the reference values.

Table 5. Concentration of Zn (mg/dm^3) by site-sampling and monitored during the months of the year 2014/2015

Zn(mg/dm^3)	**UT_1**	**UT_2**
June ICP-OES	0,99	0,508
July SAA-F	2,35	0,095
September ICP-OES	0,95	0,146
November, SAA-F	5,491	2,78
March ICP-OES	1,148	0,164
Direc.75/440EEC A2/G	1	1
UA,13/2008, Kosovë	0,5	0,5

From the table we see that we have exceeded the reference values of the Zn on sampling points in this river.

Table 1-6. The concentration of Cd (mg/dm^3) by site-sampling and monitored during the months of the year 2014/2015.

Cd (mg/dm^3)	**UT_1**	**UT_2**
June, ICP-OES	<0,001	<0,001
July, SAA-F	<0,005	<0,005
September, ICP-OESa	<0,001	<0,001
November, SAA-F	<0,005	<0,005
March, ICP-OES	<0,001	<0,001
Direc.75/440EEC,	0,005	0,005
UA,13/2008, Kosovë	0,01	0,01

Unlike other metals, presence of excessive Cd in the sampling points of waters of the river Trepça is not recorded.

Table 7. Concentration of Hg (mg/dm^3) by site-sampling and monitored during the months of the year 2014/2015.

Hg (mg/dm^3)	**UT_1**	**UT_2**
June, ICP-OES	0,0055	0,0004
September , ICP-OES	0,0058	0,0062
March, ICP-OES	0,0063	0,0082
Direc.75/440EEC,A1/I	0,001	0,001
UA13/2008, Kosovë	0,005	0,005

Table 8. The concentration of Cu (mg/dm^3) by site-sampling and monitored during the months of the year 2015/2016.

Cu (mg/dm^3)	**UT_1**	**UT_2**
June, ICP-OES	0,033	0,004
July, SAA-F	<0,02	<0,02
September, ICP-OES	0,038	0,01
November, SAA-F	<0,02	<0,02
March, ICP-OES	0,039	0,013
Direc.75/440EEC,A1/I	0,02	0,02
UA 13/2008, Kosove	0,1	0,1

The presence of Cu above recommended values is found in sampling UT_1, in UT_2 have not encountered the excess of the allowed values.

Table 9. The concentration of Mn (mg/dm^3) by site-sampling and monitored during the months of the year 2015/2016

Mn (mg/dm^3)	**UT_1**	**UT_2**
June, ICP-OES	1,111	0,688
July, SAA-F	7,01	0,142
September, ICP-OES	1,113	0,742
November, SAA-F	3,41	0,924
March, ICP-OES	1,115	0,811
Direc.75/440EEC	0,05	0,05
UA 13/2008, Kosove	1,5	1,5

Analysis of water made for Mn show exceeded the reference in the two sampling points, however high concentrations observed in sampling UT_1 rather than UT_2.

Table 10. The concentration of Sb (mg/dm^3) by site-sampling and monitored during the months of the year 2015/2016

Sb (mg/dm^3)	**UT_1**	**UT_2**
June, ICP-OES	0,005	<0,002
July, ICP-OES	0,008	0,0022
March, ICP-OES	0,012	0,0028
Direc.75/440EEC	0,001	0,001
UA,13/2008, Kosove	0,001	0,001

Information gained from the results reflects the Sb excess on waters of the river Trepça in the two sampling points.

Conclusions

Based on the results obtained from laboratory analysis of water monitored through the four seasons of the years 2014/2015 and by comparing them with reference values arising from Directive 75/440 / EEC as Kosovo and Administrative Instruction No.13/2008 we can conclude that exceeded the reference in the river Trepça with heavy metals, with the exception of Cd, have on all samples taken. Laboratory tests indicate to us that the sources polluting the waters of the Trepça are untreated waters by underground galleries of combine "Trepça" and the untreated waters arising from the process of flotation ore located in the first tunnel.

Reference

American Public Health Association, (2005) *Standard methods for the examination of water and wastewater. 21st Edition*, New York, American Public Health Association.

APHA, AWWA, WEF, 2005, *Standard Methods for the Examination of Water and WasteWater. 21th Ed.* Washington, D.C. APHA.

Connell DW., Gregory J. Miller, *Chemistry and ecotoxicology of pollution, By* Connell et al, 1984.

Goletić Ś, (2005) :*Teški metali u okolišu*, Univerzitet u Tuzli.

H.M. (1994) *EPA Method 3015, Microwave assisted acid digestion of aqueous samples and extracts*, 'Skip' Kingston, Duquesne University, Pittsburgh, PA USA , Final Version September.

Nikshiq- Kadriu S, (2012) *Ndikimi i deponive metalurgjike–kimike në Shupkovc e Kelmend në ndotjen e lumenjve Sitnicë e Ibër me metale të rënda dhe përcaktimi i tye me metoda spektrofotometrike"*, Punim doktorature, Universiteti i Prishtinës.