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ASSESSEMENT OF THE MINING PRACTICES EFFECTS ON THE WATER QUALITY IN THE IBAR RIVER WITHIN THE LEPOSAVIĆ MUNICIPALITY

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Abstract: Exploitation, development and primary extraction of the minerals result in release of the harmful substances, e.g. heavy metals, toxic gases, dirt, etc, that are often uncontrolled deposit in the environment. Those deposited and overlooked substances remain as a heritage and challenge for the coming generations that would involve abundant human, technical and financial resources for the environmental reclamation. The mining activities of the Trepča – RIF Kopaonik has both positive and negative influences within the Leposavić municipality, i.e., industrial development and environmental degradation. As a result of the mining activities the air, land and water resources both surface and underground are severely polluted. The main objective of this paper is to present adverse effects of the mineral resources (lead and zinc) exploitation and primary extraction on the Ibar River water quality degradation mainly by heavy metals. Since the heavy metals are frequently ingested by the people through the food chain and given the high toxicity of them they are crucial parameters for the water quality monitoring practices that should be carefully assessed and controlled. Thus this paper includes comprehensive analyses of the heavy metals concentration (Pb, Zn, Cu, Cd and Fe) in the Ibar River within the Leposavić municipality

Keywords: Lead and zinc extraction, flotation, mine water pollution, flotation separation landfill, water, heavy metals

Introduction

Leposavić municipality is located on the northern part of the Autonomous Province of the Kosovo and Metohija (Republic of Serbia) within the narrow corridor in the Ibar valley between Kosovska Mitrovica and Raška district, and it is bounded by the municipalities of Raška, Kuršumlija, Zvečan, Kosovska Mitrovica and Podujevo. The total area of the municipality is 530 km^2, with 14.503 inhabitants. The administrative centre of the municipality is Leposavić, with 5957 inhabitants, which is located 35 km north of the Kosovska Mitrovica within Ibar valley.

Elevation of the town is between 445 and 500 m a.s.l. In the Leposavić municipality lead and zinc deposits are located within the Rogozna and Kopaonik mineral deposits with major deposits locations: Belo Brdo, Crnac, Koporić, Žuta

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Prlina and Jelakce. In 1999 the exploitation of the mineral resources has been terminated. At this moment, the mining activities exist in Belo Brdo and Crnac and transported from there to Leposavić for flotation. The pulp of the flotation is deposited in the flotation landfill which is located close to the town of Leposavić on the left bank of the Ibar near by the riverbed.

For the comprehensive analyses of the Ibar River pollution by the heavy metals this paper evaluates main characteristics of the industrial polluters, namely mining practices within the company Trepča – RIF Kopaonik. The water quality monitoring has been done at 3 locations: Leposavić – entrance (LS), Leposavić – exit (LN) and Tvrđanski potok. The main water quality parameters and heavy metals i.e. Pb, Zn, Cu, Cd and Fe concentrations were quantified.

Cadastre of polluters

There are many companies in the Leposavić municipality (Table 1) that are releasing harmful substances during their industrial practices. Those substances have adverse effects on the water quality in the Ibar (Milentijević, 2005 b).

Table 1. Cadastre of the surface water industrial polluters within the Leposavić municipality

No	Polluter title	Polluter Characteristics	Remarks	Discharge Location
1.	Timber industry Hrast, Leposavić	Complex chemical pollution by ants' acid, lacquer.	Temporary pollution	Ibar River
2.	Glass Industry Kristal, Leposavić	Complex chemical pollution Hydrofluoric acid	Temporary pollution	Ibar River
3.	Mining waste water Pit: Jakce	Complex chemical pollution by heavy metals	Permanent pollution	Dobravska River
4.	Mining waste water Pit: Žuta Prlina	Complex chemical pollution by heavy metals	Permanent pollution	Leposavska River
5.	Mining waste water Pit Koporić	Complex chemical pollution by heavy metals	Permanent pollution	Leposavska River
6.	Leposavić flotation	Complex chemical pollution by heavy metals	Plant works Temporary	Tvrđanska River
7.	Flotation landfill Tvrđanski Do	Complex chemical pollution by heavy metals	Permanent pollution	Ibar River
8.	Flotation landfill Bostanište	Complex chemical pollution	Permanent pollution	Ibar River
9.	Mining waste water pit Crnac – adit Gnježdane	Complex chemical pollution by heavy metals	Permanent pollution	Jošanička River
10.	Mining waste water Pit: Belo Brdo	Complex chemical pollution by heavy metals	Permanent pollution	Drenska River

Source: Milentijević, 2005b

Short description of Trepča – RIF Kopaonik pits that have adverse effects on the Ibar water quality are presented in the succeeding paragraphs.

Lead and Zinc pits: Belo Brdo, Žuta Prlina, Koporić i Crnac

Mining pits Belo Brdo, Žuta Prlina, Koporić are located on the south slopes of mountain Kopaonik while the pit Crnac is situated on the eastern slopes of mountain Rogozna. Chemical composition of the ores for these 4 deposits is shown in Table 2.

Table 2. Lead and Zinc deposits chemical composition for pits Belo Brdo, Žuta Prlina, Koporić and Crnac

Chemical composition	Žuta Prlina	Belo Brdo	Crnac	Koporić
Pb - total (%)	3,64	4,01	4,01	1,71
Pb – oxides (%)	0,25	0,27	0,26	0,33
Zn - total (%)	2,52	3,94	1,95	0,50
Zn - oxides (%)	0,26	0,20	0,25	0,15
Fe - total (%)	14,00	19,45	11,30	12,20
S (%)	16,10	21,00	13,54	2,12
As (%)	0,36	1,18	0,28	0,32
Cu (%)	0,03	0,10	0,02	0,07
SiO_2 (%)	29,48	19,58	31,55	45,45
Al_2O_3 (%)	2,74	4,31	9,20	7,32
MgO (%)	3,90	1,20	2,86	6,28
CaO (%)	0,018	5,72	7,48	2,11
Ag (g/t)	43,00	62,00	46,00	23,00

Source: Milentijević *et al.*, 2009

Ores from all before mentioned pits have significant portion of the silver (30 - 80 gr/t), that increase their economical value.

Based on the minerals analyses the main minerals in the individual pits are (Milentijević *et al.*, 2009):

- Žuta Prlina - pyrite, sphalerite, galenite as a primary minerals, and smithsonite and cerussite as secondary minerals;
- Belo Brdo - pyrite, pyrhotine, sphalerite (marmatite), galenite and arsenopyrite as primary minerals;
- Crnac - pyrite, sphalerite and galenite as primary minerals;
- Koporić - galenite, sphalerite, pyrite and marcasite as a primary minerals while limonite, cerussite, anglesite and smithsonite are secondary minerals.

The presence of the other ores chalcopyrite, cubanite, jamesonite and tetrehedrite is insignificant. It is noteworthy to mention significant deposits of quartz, dolomite and siderite. The highest economical values have galenite, sphalerite and pyrite. Minerals processing is in Leposavić flotation plant before this plant was built minerals had been processed in flotation plant RMHK Trepča – Zvečan.

Mining Waters

It was detected on field that from the before mentioned mineral deposits due to mining activities significant amount of water occurs. Those waters drain to the surrounding terrain and discharge into the clear mountain rivers, tributaries of the Ibar.

Within the area of the pit Crnac fissure- permeable aquifer exists. Adit Gnježdane drains all waters from the pit from the present and former mining activities. The estimated quantity of the water ranging from 8 l/s (minimum) to 30 l/s (maximum). Measured water is temperature is 16^0C, pH is 8 (Milentijević, 2005a), and heavy metal concentrations are: Cu - 0,06mg/l, Fe - 13,8mg/l, Pb - 0,99mg/l, Cd - 0,0036mg/l and Zn - 1,4mg/l. Finally, detected sulphate concentration is 321, 3 mg/l (Milentijević *et al*., 2009). Mining waters directly discharge in to the Jošanička River, left tributary of the Ibar.

Within the area of the Jelakce, from fissure- permeable aquifer through the cracks, fissures, faults and fault zones water amount of more than 50 l/s discharges uncontrolled. Measured water is temperature is 14^0C, pH (Milentijević, 2005a) is 6, and heavy metal concentrations are: Cu - 0,01mg/l, Fe - 4,0mg/l, Pb - 0,03mg/l, Cd - 0,003mg/l and Zn - 1,6mg/l (Milentijević *et al*., 2009). As a final point determined sulphate concentration is 63, 4 mg/l. Mining waters discharges directly into Dobrovska River, right tributary of the Ibar River.

Within the area of the pit Žuta Prlina, fissure- permeable aquifer drains water from the deposits through the cracks, fissures, faults and faults zones. Mining waters enter in the level entry, galleries and appears on the adit and finally drains directly to Leposavska River, right tributary of Ibar. Quantity of the water is approximately 21 l/s with temperature of 10^0C and pH = 6, 9 (Milentijević, 2005a). Measured heavy metals concentrations are: Cu - 0,01mg/l, Fe - 10,4mg/l, Pb - 0,03mg/l, Cd - 0,0044mg/l and Zn - 10mg/l and sulphate concentration is 298, 2 mg/l (Milentijević *et al*., 2009).

Within the area of the open-pit surface mine Koporić during the exploration period (before 1999) excavated ore was transported by the system of ore chute and adit. The length of the adit is 1000 m and central ore cute is 100 m high. At the moment central ore cute is filled. Due to that an artificial lake has been formed in the open-pit surface mine Koporić. The lake waters occur at the adit Water temperature is 8^0C, pH is 7, 4 (Milentijević, 2005a) and measured water quantity that drains through ore chute is approximately 20 l/s. Heavy metal concentrations are: Cu - 0, 03mg/l, Fe - 3,1mg/l, Pb - 0,03mg/l, Cd - 0,003mg/l and Zn - 0,11mg/l. Lastly, sulphate concentration is 124,8 mg/l (Milentijević *et al*., 2009). Mining waters drains to the Koporićka River that discharges into the Leposavska River, the right tributary of the Ibar River.

Within the area of the pit Belo Brdo, mining waters are moving through gravitational channel, occur at the adit and drain directly to the Drenska River the right tributary of the Ibar. Measured water quantity is 116 l/s, temperature is 14^0C and pH = 7, 4 (Milentijević, 2005a). Determined heavy metal concentrations are: Cu - 0, 03mg/l, Fe - 3,1mg/l, Pb - 0,03mg/l, Cd - 0,003mg/l and Zn - 0,69mg/l. Finally, sulphate concentration is 288, 51 mg/l (Milentijević *et al*., 2009).

Figure 1. Photo of the waters discharge from
the pit Žuta Prlina into the river (Milentijević, 2005a)

The characteristics of the sulphide deposits mining waters are the high sulphate concentration, low pH (acid water) and high concentration of the heavy metals (Dragišić, 2005). Results of the mining waste water research for pits Crnac, Jelakce, Žuta Prlina, Koporić and Belo Brdo in generally indicate high concentrations of the heavy metals and sulphate, while pH values are not low.

Leposavić Flotation plant

Leposavić flotation plant has operated since 1972 with designed capacity of 400,000 t ore per year. Excavated ore is transported from the pits to the flotation plant by tracks. Flotation discharge is conveyed by the centrifugal pump to the hydrocyclon at the flotation landfill. Hydrocyclon sand is used for a dike build at the flotation landfill while the discharge is gravitationally sent to a lake for sedimentation. Liquid substance drains to the Ibar River through the system of manholes and collectors (Nedeljković *et al*., 2007a).

Leposavić Flotation Landfill

Flotation Landfill Tvrđanski Do (Figures 2 and 3) is located east of the highway Kraljevo – Kosovska Mitrovica, close to the town of Leposavić at the Ibar right river bank. This landfill has been used for dispose of the pulp from the flotation plant where the ore from the mining pits: Crnac, Jelakce, Žuta Prlina, Koporić and Belo Brdo was processed. The total area of the landfill is about 7 ha and approximately 2.600.000 t of pulp is disposed there. Based on the pulp analyses lead concentration ranging from 0,26 % to 0,32% is noticed, of which 0,18% lead oxide, pyrite 19,27%, pyrrhotite 10,025% and Zinc from 0,16 to 0,23% (Milentijević, 2005a).

Figure 2. Photo of Tvrđanski Do flotation landfill (Nedeljković *et al.*, 2007b)

Dam includes several steep slopes, and the steepest one is the eastern part of the dam which descends to the railways just before the tunnel entrance at the northern side of the dam. Western side is shorter with evident erosion processes. The pulp moves down to the foot of the slope where tree allay exists near by the Ibar. Given that landfill recultivation has not completely finished during the windy events a certain amount of the dust from the landfill spreads over the Leposavić and puts town in risk of the pollution. Sunken water from the landfill is conveyed by the collector to the Ibar River. Pulp surface is read and oxidized. On the dam perimeters even hard parts are visible. Since the increase in dam elevation was not feasible disposal of the pulp stopped and new flotation landfill Bostanište has been built (Nedeljković *et al*., 2007a).

Figure 3. Photo of arsenic - trioxide at the flotation landfill Tvrđanski (Milentijević, 2005a)

Landfill Bostanište (Figure 4) is located south of the landfill Tvrđanski Do, where the northern dam perimeter leans on the end of the western part of the old dam. The major part of the landfill is bordering with the Ibar River, i.e. approximately 1 km and has natural limits by the hill on the eastern side. Landfill is characterized by the relatively steep dam slopes on the northern and western sides with surface partly covered by sand and the rest is covered by oxidized pulp with deep erosion canals drills. Landfill recultivation has not been done so there are no plants or grass on the surface.

Figure 4. Photo of Bostanište flotation landfill dam (Milentijević, 2005a)

As a result, during the windy events the dust from the landfill is spread around and presents potential risk for the town of Leposavić and surrounding villages. The border between dam foot and the Ibar is scant tree alley with bushes around. Along the steep slopes of the dam drills are visible as a result of the erosion. Drainage of the precipitation is by the drainage pipe network that conveys water to the collector which is located on the perimeter of the stockpile. Based on the chemical analyses of the flotation landfill Bostanište the chemical composition of the pulp has been detected as follows: Zr - 107,7 ppm, Sr-121,7 ppm, Rb - 71,8ppm, Pb - 2136 ppm, As - 3566 ppm, Zn - 1948 ppm, Cu - 117,3, Ni - 115,78 ppm, Fe - 107587,2 ppm, Mn - 8321,47 ppm, Cr - 341,93 ppm (Nedeljković *et al.*, 2007b).

Ibar River water quality

During the year of 2007 from January till December monitoring program for water quality was completed on the following locations: Leposavić -entrance, before flotation landfill Bostanište (LS), Leposavić - exit, after flotation landfill Bostanište (LN) and Tvrđanski potok (flotation). Water samples have been collected monthly and concentrations of the following heavy metals were assessed: Cu, Fe, Pb, Cd and Zn and concentration of the basic parameters for water quality evaluation: pH, sediments, dissolved maters, total solids, SO_4 and Ca (Nedeljković *et al.*, 2007b). Chemical analyses have been completed for all monitoring locations and results are exhibited in Figures 5 to 15.

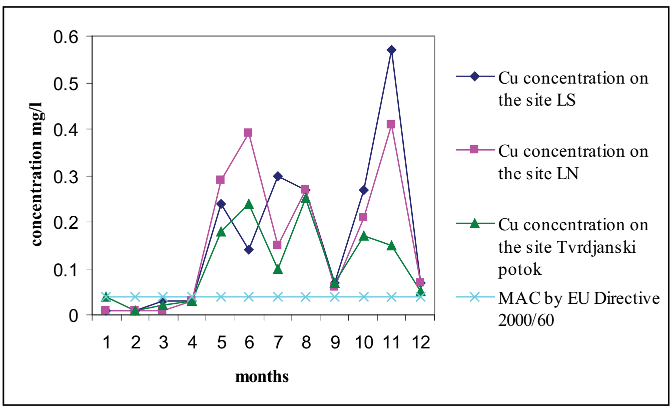

Figure 5. Cu concentration in the Ibar River - 2007

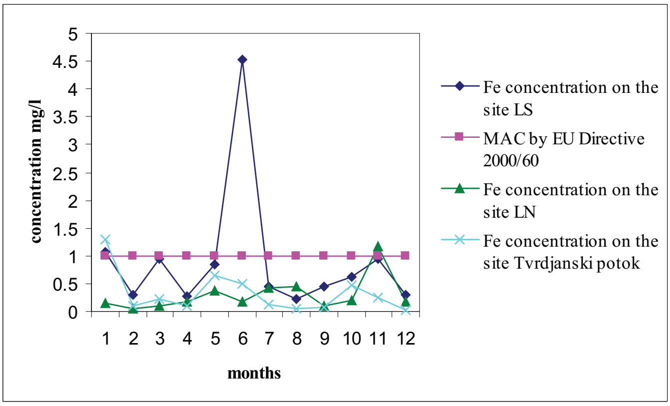

Figure 6. Fe concentration in the Ibar River - 2007

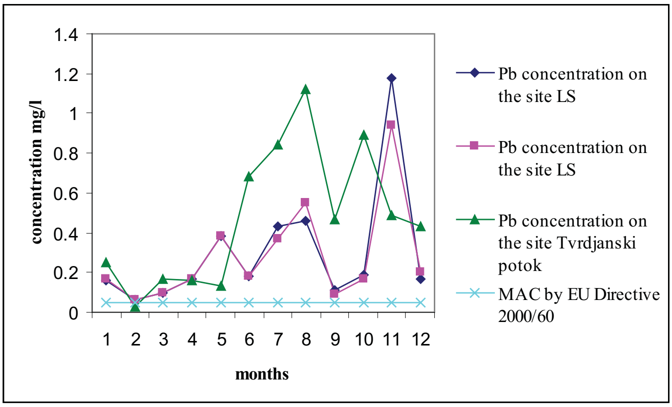

Figure 7. Pb concentration in the Ibar River - 2007

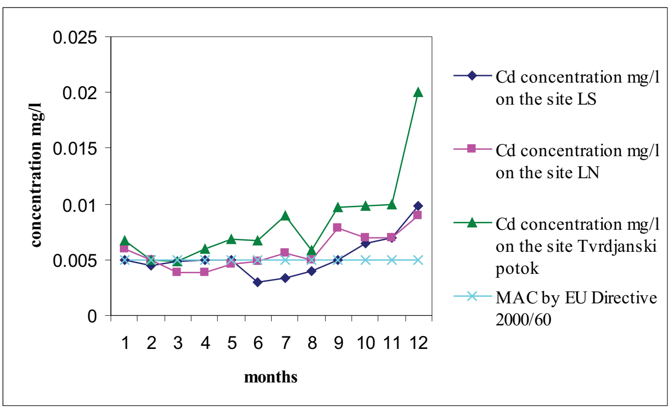

Figure 8. Cd concentration in the Ibar River - 2007

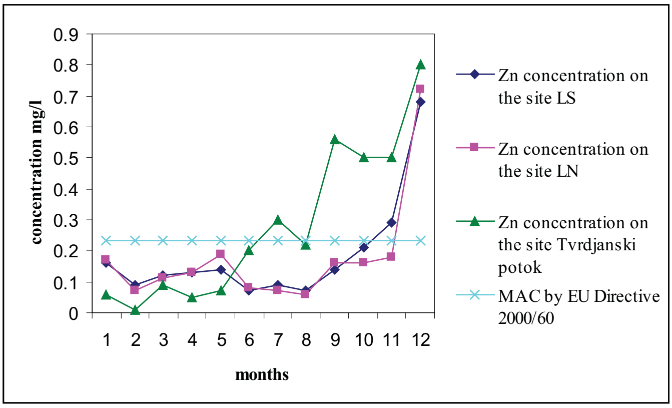

Figure 9. Zn concentration in the Ibar River - 2007

Figures 5, 6, 7, 8 and 9 display monitored values for heavy metals, namely Cu (mg/l), Fe (mg/l), Pb (mg/l), Cd (mg/l) and Zn (mg/l). Given that it has been concluded that these values are mainly above benchmarks proposed by the EU Directive 2000/60, based on UNECE, 1996 Guidelines on Water-Quality Monitoring and Assessment of Transboundary Rivers, and Pb values are persistently above MAC during the year.

Quantities for the basic water quality parameters pH, sediments (mg/l), dissolved mater (mg/l), total solids (mg/l), SO_4 (mg/l) and Ca (mg/l) are analyzed in accordance with the MACs based on JUS, while Ca concentration is compared with EU Directive water quality standards 2000/60. The results are presented graphically on Figures from 10 to 15.

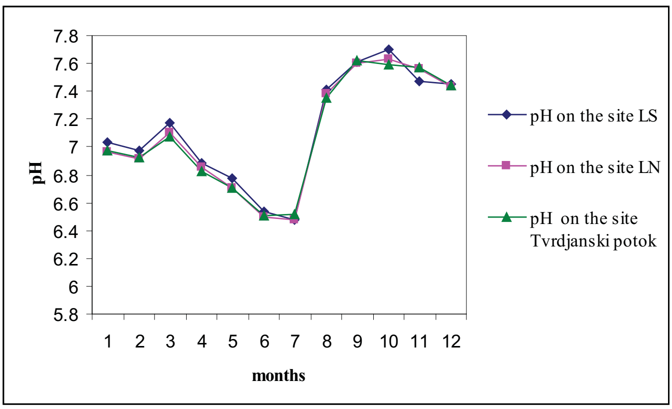

Figure 10. pH concentration in the Ibar River - 2007

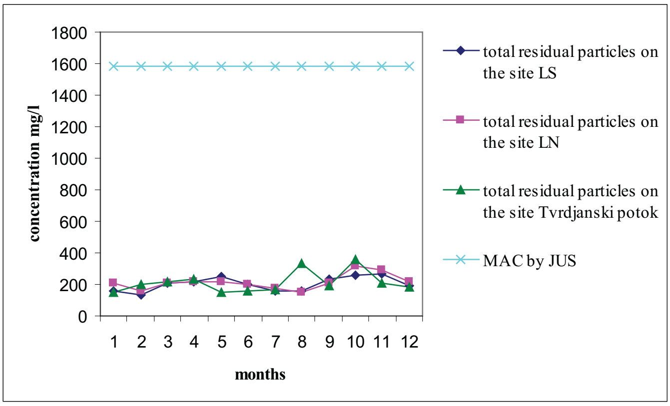

Figure 11. Sediment concentration in the Ibar River - 2007

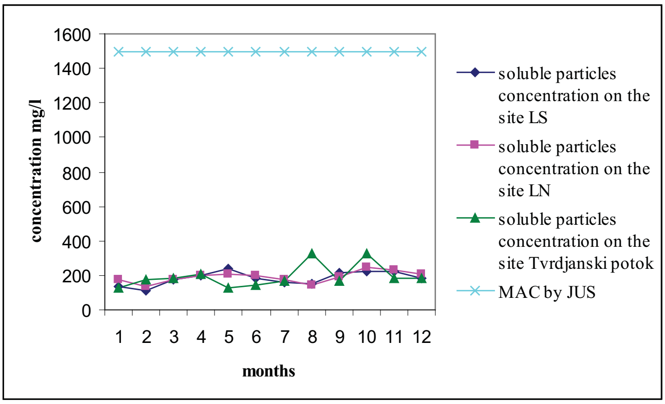

Figure 12. Dissolved matters concentration in the Ibar River - 2007

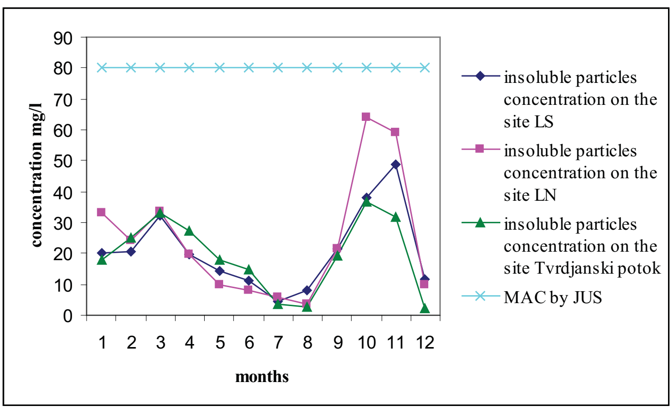

Figure 13. Total Solids concentration in the Ibar River -2007

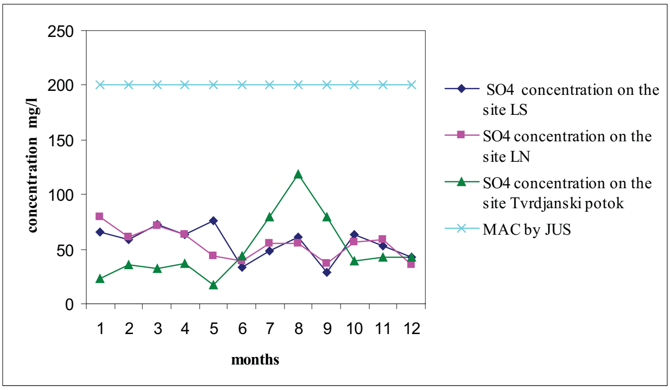

Figure 14. SO4 concentration in tthe Ibar River - 2007

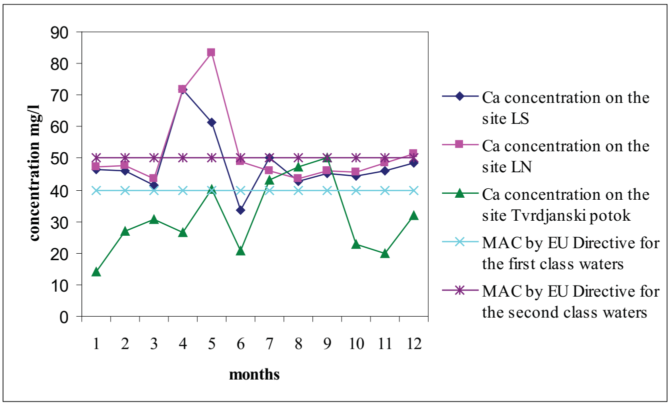

Figure 15. Ca concentration in the Ibar River - 2007

Based on assessment of the results for the basic water quality parameters and their comparison with JUS proposed benchmarks it can be concluded that concentrations are in line with MACs.

The analyses of the measurements emphasized necessity for the comparison with the EU standards for water quality since there is a tendency among the countries that have a goal to join EU to implement EU Directive and to modify of polices and regulation according to EU practices and regulations. Environmental Quality Standards (EQS) presented in Annex II EU Directive 2000/60 are stands for total concentration in water sample. For heavy metals concentration, EQS are related to the dissolved mater concentration, e.g., dissolved mater extracted by filtration.

EQS values for the heavy metals are associated with water hardness that is expressed based on the calcium concentration. Based on the EU Directive, Annex III there are five water hardness categories: (Category 1: <40 mg CaCO3/l, Category 2: 40 to <50 mg CaCO3/l, Category 3: 50 to <100 mg CaCO3/l, Category 4: 100 to <200 mg CaCO3/l and Category 5: ≥200 mg CaCO3/l). Given above categorization, Ibar River waters within the municipality of Leposavić can be in generally classified as II category. Hence, the quality standards for surface water category II have been applied.

Measured results for heavy metals: Cu, Fe, Pb and Zn in Ibar River, are unfavorable since almost all results are above EQS benchmarks. Sources of heavy metals pollution in the municipality of Leposavić are diverse. In this paper only a few of them have been introduced: lead and zinc mines, mining waste waters, flotation landfills, flotation plants, etc. Many rivers that have immense heavy metals concentrations are not exposed to waste waters from the mining industry. Many heavy metals could be detected in water due to the various circumstances and there are many different locations of the heavy metals discharge into the water bodies (Minić *et al.,* 2008).

Given the field observations, it can be concluded that flotation landfills Tvrđanski Do and Bostanište are the primary polluters of the Ibar River within the study area, namely, municipality of Leposavić. Before mentioned landfills are polluting water in many ways:

- By uncontrolled disposal of the pulp or during the accidental situations they cause both physical and chemical pollutions. Additionally they have adverse effects on the Ibar River water quality, flora and fauna within Ibar watershed.
- Through ground waters, water solutions that are generally saturated with heavy metals discharge into the river. There is real possibility of accidental situations occurrence due to severe flooding and improper landfill management. Those accidents can result in total destruction of the flora and fauna, risk for settlements and facilities downstream of the flotation landfills and permanent heavy metal contamination of the land and aquifers.
- Spreading of the dust particles by the winds and their deposition within the river bed and their flush from the soil surface. Geographical location of the town of Leposavić (North -South) and dominant air circulation pattern (North - South) makes the landfills the main polluter of the environment. These landfills are very harmful for the town and surrounding villages

especially during the windy days with main direction from the north which spreads huge amount of dust with gases, particularly sulphide dioxide, and immense amount of the specific metals (Pb, Zn, Cd) that are deposited in the human settlements, plants, animal and human bodies.

Given these conclusions the development of the appropriate environmental protection practices for the Ibar River watershed has started. To accomplish that comprehensive literature review was included. Based on the study (Dudka, Adriano, 1997) which correlate to our the results presented in this paper, it can be concluded that emission of the Pb, Zn, Cd and Cu have more adverse effects to the water resources than to the land. Comprehensive analyses of the possible industrial waste waters fitoremmedy and recultivation practices for the land contaminated by the heavy metals based on the best management practices Galiulin *et al.*, 2001) have been performed. Based on all activities for the protection of the Ibar River watershed the technical and biological recultivation of the flotation landfill is recommended.

Leposavić flotation landfills recultivation

To decrease the movement of the particles from the flotation landfills to the surrounding environment the biological recultivation of the landfill is recommended. At present, recultivation is possible for the flotation landfill Tvrđanski Do, since there is no more disposal of the pulp. During the years 2006 and 2007 for the implementation of the project: "Influence of the mining practices during the exploitation lead-zinc ore on the environment, geological characteristics and general health conditions within the Province Kosovo and Metohija registration *14026G",*the high rise plants had been planted especially acacia (*Robinia pseudoacacia*), pine (*Pinus nigra*) and grass. The lead concentrations have been monitored on pine trees (*Pinus nigra*) and on the acacia leaves (*Robinie pseudoacaci*e). Results had shown that acacia had developed better than pine in the areas of the flotation landfills (Nedeljković *et al.*, 2007b).

Conclusions

Results introduce concentration of the some heavy metals that are above proposed benchmarks at the monitoring locations in the Ibar River within the municipality of Leposavić. The main polluters of the Ibar River watershed are flotation plants, flotation landfills and mining waste waters. As primary polluters flotation landfills Bostanište and Tvrđanski Do have been recognized, and recultivation practices have been recommended where it is feasible. The future research should be focused on the finding solutions for appropriate monitoring, conservation and increase of the water quality in the Ibar River.

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