Mining and Metallurgy Institute Bor
West University Timisoara

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Environmental Impact Report

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Environmental Impact Report

Authors: Prof. Adriana Isvoran

PhD Zoran Stevanovic

Prof. Vasile Ostafe

Cornel Popovici Sturza

West University Timisoara	**Mining and Metallurgy Institute Bor**
	Director Advisor
RORS-337 PM	RORS-337 TDM
PhD Adriana Isvoran	PhD Zoran Stevanovic

Cooperation beyond borders.
Interreg-IPA Cross-border Cooperation Romania-Serbia Programme is financed by the European Union under the Instrument for Pre-accession Assistance (IPA II) and co-financed by the partner states in the Programme.
Project RoRS 337- ROmania Serbia NETwork for assessing and disseminating the impact of copper mining activities on water quality in the cross-border area (RoS-NET2)

Contents

1. INTRODUCTION

Mining plays an important role in the global economy and allow access to the metals and the minerals that are much needed for the development of technology and life. The mining industry brings substantial economic growth and benefits to countries, generating revenues and creating jobs.

However, from the other side, mining operations have a huge impact on the environment and population. They produce many types of air, water and soil pollutants that may ultimately affect human health [1]. In Serbia and Romania, copper mineralization is mostly porphyry type of deposits containing sulphur minerals associated with pyrites that are one of the main sulphuric acid generators in contact with the atmosphere. Main mining wastes generated during the treatment of those kinds of copper deposits and which cause the major environmental pollution are: tailings generated during flotation processes containing a variety of metallic and non-metallic minerals and spent ores consisting of the material remaining in either dump or heap leach piles when leaching ceases.

The huge amounts of tailings that are created during the extraction and processing of ore represent a great danger to the environment and destroy agricultural land and forests. The dust that the wind disperses from the tailings represent environment hazard by pollution of heavy metals ions. Tailings are also a source of Acid Mine Drainages (AMD) that contains high concentrations of metal cations, especially iron, and often toxic chemical elements such as arsenic [2]. AMD are one of the most significant environmental risks globally because they could be transported by surface waters on wider area, sometimes even out of the country. Hundreds of thousands of hectares of land and thousands of kilometers of watercourses around the world are threatened by the runoff of AMD [3]. Abandoned mines and tailings can generate acidic water for tens, hundreds, even thousands of years. Abandoned Richmond pyrite mine in California (USA) is estimated to generate an extremely acidic solution for the next 3,000 years [4], while a small zinc and copper mine in northwestern Ontario (Canada) is estimated to generate acidic mine waters in the next 10,000-35,000 years [5]. Although these are extreme examples, it is not uncommon for abandoned mine shafts and tailings to have the capacity to form acidic solutions over a period of hundreds of years. Surface and underground ore mining generally have serious negative impacts on the environment such as air pollution, land use and biodiversity and water availability. Also, some effluents generated in the mining industry contain large amounts of toxic substances (cyanides, heavy metals and other harmful and dangerous substances), which have serious human health and environmental hazards [6-8]. Based on possible hazards, waste mine water generated from active as well as abandoned mines is one of the main chemical threats to environment.

According to a study prepared for DG Environment, the European Commission, more than 4.7 billion tons of mining waste and 1.2 billion tons of flotation tailings were disposed of across the European Union [9]. Ten thousand active and abandoned mines are source for $5\text{-}10\times10^9$ m^3 of highly polluted AMD annually [10]. Global mining activities with technological processes of mineral processing and metal production generate several billion tons of solid inorganic waste or by-products, including liquid waste [11]. Balkan Peninsula was generally the main area in Europe for supply of copper, lead and zinc until 1990 [12] and many mines still are operational. Also, in this area exist and many abandoned mines and tailings which represent continuous environmental threat.

Due to a great negative impact of mining industry on water system, one of objectives of cross-border collaborative project, ***Romania Serbia NETwork for assessing and disseminating the impact of copper mining activities on water quality in the cross-border area (ROSNET2)***, was to perform the monitoring of waters, soil and river sediments close to active and abandoned mines in cross border area. Considered Romanian Serbian Cross border area is presented in Figure 1. Project includes area of mine Moldova Nouă from the Romanian side and Eastern Serbia area from the active copper mine in Bor, all the way to the confluence of the Timok into the Danube near Radujevac. This area was chosen because both mine locations have negative impact on environment. Rivers Bosneag, Radimna and Nera from the Romanian side in Caras Severin County near Moldova Noua are tributary of Danube River and flow in area which is affected by spreading of dust from the abandoned flotation tailing of copper mine. Bor, Krivelj, and Bela Rivers in Eastern Serbia belong to the watershed of Timok River, which is also a tributary of Danube River. All mentioned Rivers flow near to the largest mining complex in Republic of Serbia where mining activities continuously exist for more than 115 years.

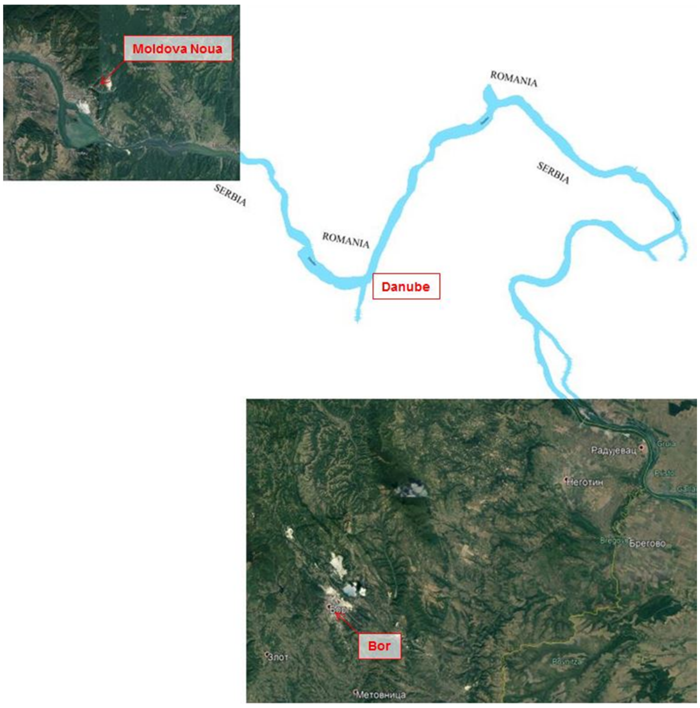

Figure 1. Romanian Serbian Cross border ROSNET2 Project area

The main goal of monitoring was to gain a complete insight into the state of the environment and determine the need to take protection measures depending on the degree of threat and type of pollution. Knowledge of water and soil quality from the point of view of the content of organic and inorganic pollutants is reflected in the possibility of risk assessment, location and remediation of polluted areas as well as urban planning in terms of identification and relocation of pollution sources. In order to find measures and solutions for the reduction, remediation and elimination of pollutants, it is necessary to have a true picture of the consequences of more than a century of continuous mining and metallurgical activities. In this study, aiming to assess the risk of mining activities in the vicinity of the Bor copper mine from Serbia and the Moldova Noua closed copper mine from Romania, on the pollution of surface waters, wells, sediments and soil, physico-chemical analysis of the collected samples were performed. In Serbia, sampling was performed quarterly, with 14 previously defined profiles of the Bor River (W5-1-W5-14), as well as from locations upstream and downstream of the Bor River (marked W1-W4, W6-W10). In addition, samples collected from locations on the Timok River (marked W11-W15) were analyzed. In Romania, surface water, well water, sediment and soil samples were collected in four sampling campaigns. The surface water (W18-W23) and sediment (S82-S84) samples were collected from three rivers, Radimna, Bosneag and Nera, the soil samples

(S85-S88) were collected from the vicinity of the tailing pond and the well water samples (WU11-WU14) were collected from localities in the area of Moldova Noua. Having on mind that copper mine from Romanian side is not in operational stage, water samples were taken for monitoring purposes at first. Sampling locations were chosen to cover surface waters in surrounding area where could be expected pollution by spreading of dust from the abandoned flotation tailing. Sequence of sampling was scheduled to cover different weather condition and seasons [13].

2. MATERIALS AND METHODS

During sampling was recorded GPS data for each sampling point and for water samples was additionally noted: sampling method, time, air and water temperature, color and odor of water, redox potential, pH value, DO (dissolved oxygen) and electro conductivity. Samples are taken in prepared bottles, water samples are stored in bottles treated with 3% HNO_3 (30-40 ml) during 6 days. Samples were sealed and labelled and transferred to chemical laboratory. Samples were analyzed in chemical laboratory of Mining and Metallurgy Institute Bor with ICP-MS (Agilent Technologies 7700 Series, Singapore, Republic of Singapore); ICP-OES (Spectro Arcos, Kleve, Germany) and FIMS (Flow Injection Mercury System) 100 (Perkin Elmer, Norwalk, USA). Used techniques per elements with operating conditions are given in Table 1.

Table 1. Operating conditions for the analysis of the elements

Determined elements	**Technique**	**Operating conditions**	
Hg	FIMS-AAS	Integration time (s)	20
		Data Processing	Peak Height, Smoothing: 0.5 s or 19 points
		Lamp	HCL
		Slit (nm)	0.7
		Wavelength (nm)	253.7
Cr, Cu, Fe, Mn, S, Zn	ICPOES	RF Power (W)	1450
		Coolant flow (L/min)	13
		Nebulizer flow (L/min)	0.75
		Auxiliary flow (L/min)	1.0
		Plasma, torch	Quartz, demountable, 2.0 mm injector tube
		Spray chamber	Scott
		Nebulizer	Cross-flow
		Sample aspiration rate	2 mL/min
		Wavelength (nm)	Cr-267.716 nm; Cu-324.754 nm; Fe-259.941; Mn-257.611; Mo-202.095 nm; Se-196.090 nm; S-180.731 nm; Zn-213.856 nm
As, Cd, Ni, Pb	ICPMS	RF Power (W)	1550
		RF matching (V)	1.8
		Sample depth (mm)	10
		Carrier gas (L/min)	1.0

		Nebulizer pump speed (L/min)	0.1
		Spray chamber temperature (^0C)	2.0
		Peak pattern (point)	1.0
		Reaction gas cell flow (mL/min)	He-4.5
		Mass/Cell mode	As-75 He; Cd-111-No gas; Ni-60-No gas; Pb-208-No gas

The accuracy and the precision of the ICPMS and ICPOES methods were investigated analysing the two Standard Reference Material, NIST 1640a (Trace elements in natural water) and LGC Standard Reference Material VHG-QWPTM-15 (Water Pollution Trace metals).

There also was an alternative monitoring of the environment, the information being perceived at the level of the basic human senses. The process of alternative environmental monitoring is, first and foremost, an environmental education activity for young people, especially students. Through this activity, young people acquire skills to collect useful information about the phenomenon of water and soil pollution with heavy metals in the area of mining activities.

3. RESULTS

Locations of sampling were presented on Figures 2 and 3 while summary results during the Project are presented on Tables 2 – 8 [13].

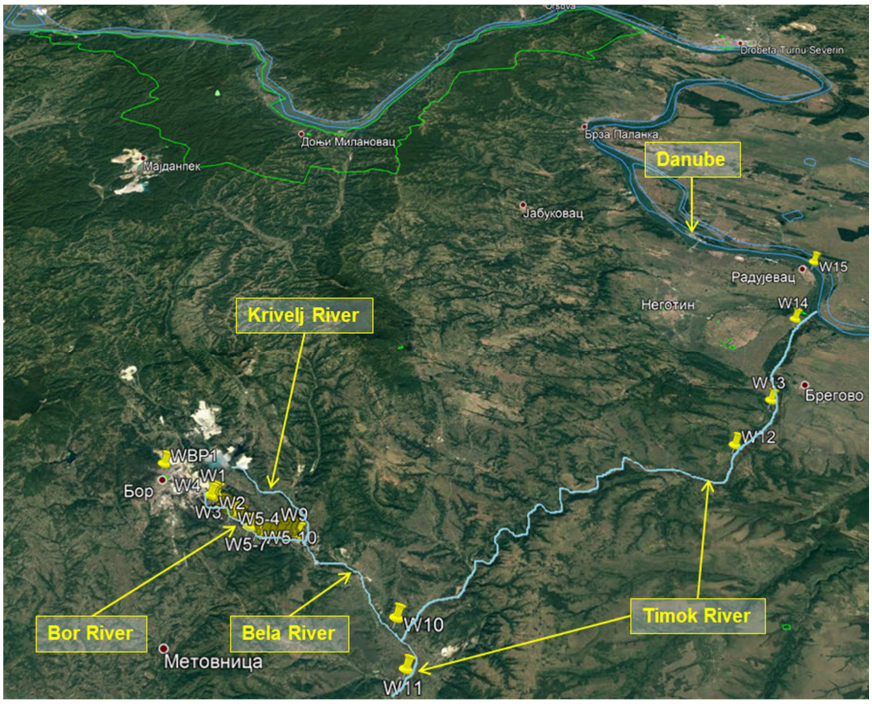

Figure 2 - Eastern Serbia side

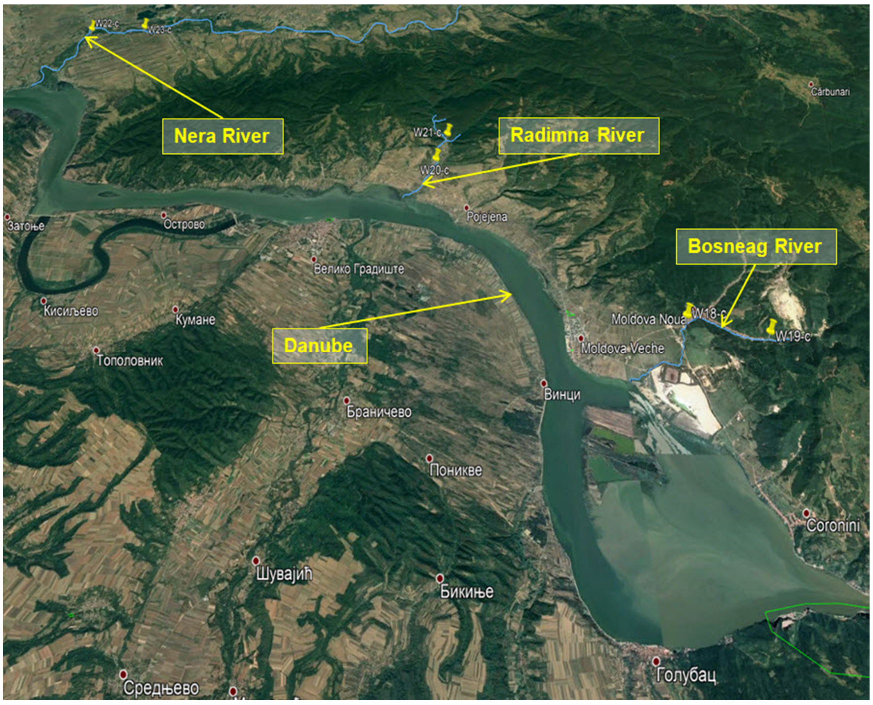

Figure 3 - Romanian side

Table 2 – Summary results for surface water samples sampled from Serbian side

Category of surface water / Location	Parameter	Range (min-max)	Median	MAC
IV From Bor city to the confluence Bor and Timok River Samples (W1 – W10)	Fe (mg/l)	0.069-1368.1	116.3	2
	Mn (mg/l)	1.5-115.8	6.1	1
	Cu (mg/l)	0.089-318.7	46.4	1
	Zn (mg/l)	0.28-43.2	7.1	5
	As (µg/l)	<2.1-25991.3	279.2	100
	Ni (µg/l)	38-16200.0	1676.9	34
	Pb (µg/l)	<2.1-3718	471.0	14
	Cd (µg/l)	8.0-5375	508.3	0.9
	Cr (mg/l)	<0.005-0.16	0.021	0.25
	Hg (µg/l)	N.D. (<0.5)	N.D. (<0.5)	0.07
	SO_4^{2-} (mg/l)	744.1-13964.3	2404.4	300
III From the confluence Bor and Timok River up to the confluence of Timok and Danube River Samples	Fe (mg/l)	<0.007-0.35	0.067	1
	Mn (mg/l)	<0.006-0.78	0.17	0.3
	Cu (mg/l)	<0.005-0.33	0.059	0.5
	Zn (mg/l)	<0.005-0.76	0.026	2
	As (µg/l)	<2.1-4.7	3.5	50
	Ni (µg/l)	5.3-551.9	29.3	34
	Pb (µg/l)	<2.1-5.9	5.9	14
	Cd (µg/l)	<0.14-47.0	3.0	0.6
	Cr (mg/l)	<0.005	-	0.1

(W12 – W14)	Hg (μg/l)	N.D. (<0.5)	N.D. (<0.5)	0.07
	SO_4^{2-} (mg/l)	82.2-691.6	161.8	200
II Danube Sample (W15)	Fe (mg/l)	<0.007-38.4	0.081	0.5
	Mn (mg/l)	<0.006-4.3	0.26	0.1
	Cu (mg/l)	<0.005-0.58	0.025	0.005(T=10) 0.112 (T=300)
	Zn (mg/l)	<0.005-0.40	0.031	0.3 (T=10) 2(T=500)
	As (μg/l)	<2.1-31.2	3.9	10
	Ni (μg/l)	<3.6-388.2	16.8	34
	Pb (μg/l)	<2.1-7.1	5.6	14
	Cd (μg/l)	<0.14-35.3	0.45	0.45
	Cr (mg/l)	<0.005	0.022	0.05
	Hg (μg/l)	N.D. (<0.5)	N.D. (<0.5)	0.07
	SO_4^{2-} (mg/l)	26.7-1950.6	73.5	100

Table 3 – Summary results for wells sampled from Serbian side

Element/ Parameter	**Range (min-max)**	**Median**	**MAC for drinking water**
Mn (mg/l)	<0.006-26.6	0.057	0.05
Cu (mg/l)	<0.005-13.6	0.040	2
Zn (mg/l)	<0.005-2.3	0.056	3
As (μg/l)	<2.1-162.6	4.8	10
Ni (μg/l)	<3.6-629.5	5.9	20
Pb (μg/l)	<2.1-29.2	2.4	10
Cr (mg/l)	<0.005-0.022	0.015	0.05
Mo (mg/L)	<0.007	-	0.07
Hg (mg/l)	<0.0005	-	0.001
SO_4^{2-} (mg/l)	52.7-4387.1	446.1	250

Table 4 – Summary results for soil sampled from Serbian side

Element/ Parameter	**Range (min-max)**	**MAC soil**
Cu (mg/kg)	215.4-12478.6	110
Zn (mg/kg)	51.1-6009.3	430
As (mg/kg)	30.3-959.1	42
Ni (mg/kg)	1.7-47.7	44
Pb (mg/kg)	41.1-1322.6	310
Cr (mg/kg)	33.7-308.0	240
Cd (mg/kg)	0.1-5.3	6.4
Hg (mg/kg)	0.1-1.5	1.6

Table 5 – Summary results for sediments sampled from Serbian side

Element/ Parameter	**Range (min-max)**	**MAC sediments**
Cu (mg/kg)	59.8-7225.5	110

Zn (mg/kg)	38.2-6562.5	430
As (mg/kg)	9.9-945.4	42
Ni (mg/kg)	14.2-71.5	44
Pb (mg/kg)	19.7-1150.5	310
Cr (mg/kg)	83.7-413.4	240
Cd (mg/kg)	0.1-26.0	6.4
Hg (mg/kg)	0.1-0.32	1.6

Table 6 – Summary results for surface water samples sampled from Romanian side

Category of surface water / Location	**Parameter**	**Range (min-max)**	**Median**	**MAC**
II Bosneag River Samples (W18– W19)	Fe (mg/l)	0.0087-0.8903	0.4782	0.5
	Mn (mg/l)	<0.0016-0.0583	0.0583	0.1
	Cu (mg/l)	0.0284-0.1158	0.069	0.03
	Zn (mg/l)	0.0252-0.0549	0.0472	0.2
	As (µg/l)	<2.1-3.7	3.0	20
	Ni (µg/l)	<3.6-4.2	4.2	25
	Pb (µg/l)	<2.1-3.7	3.7	10
	Cd (µg/l)	<0.14-0.39	0.26	1
	Cr (mg/l)	<0.0017	/	0.05
	Hg (µg/l)	N.D.	N.D.	0.3
	SO_4^{2-} (mg/l)	78.5-295.8	133.7	120
II Radimna River Samples (W20 – W21)	Fe (mg/l)	0.1310-0.2652	0.2397	0.5
	Mn (mg/l)	0.0106-0.0326	0.0230	0.1
	Cu (mg/l)	0.0376-0.0546	0.0474	0.03
	Zn (mg/l)	0.0176-0.0333	0.0216	0.2
	As (µg/l)	<2.1	/	20
	Ni (µg/l)	<3.6	/	25
	Pb (µg/l)	<2.1	/	10
	Cd (µg/l)	<0.14	/	1
	Cr (mg/l)	<0.0017	/	0.05
	Hg (µg/l)	N.D.	N.D.	0.3
	SO_4^{2-} (mg/l)	21.9-30.3	24.8	120
II Nera River Samples (W22 – W23)	Fe (mg/l)	0.9895-1.1643	1.0292	0.5
	Mn (mg/l)	0.0423-0.0524	0.0497	0.1
	Cu (mg/l)	0.0136-0.0460	0.0317	0.03
	Zn (mg/l)	<0.0062-0.0232	0.0109	0.2
	As (µg/l)	<2.1	/	20
	Ni (µg/l)	<3.6	/	25
	Pb (µg/l)	<2.1	/	10
	Cd (µg/l)	<0.14	/	1
	Cr (mg/l)	<0.0017	/	0.05
	Hg (µg/l)	N.D.	N.D.	0.3
	SO_4^{2-} (mg/l)	21.6-29.6	24.8	120

Table 7 – Summary results for wells sampled from Romanian side

Element/ Parameter	Range (min-max)	MAC for drinking water
Mn (mg/l)	<0.001-0.583	0.05
Cu (mg/l)	<0.003-0.435	2
Zn (mg/l)	<0.005-0.28	3
As (µg/l)	<2.1-6.9	10
Ni (µg/l)	<3.6	20
Pb (µg/l)	<2.1	10
Cr (mg/l)	<0.017-0.087	0.05
Mo (mg/L)	<0.0023	0.07
Hg (mg/l)	<0.0005	0.001
SO_4^{2-} (mg/l)	17.0-121.4	250

Table 8 – Summary results for soil and sediments sampled from Romanian side

Element/ Parameter	Range (min-max)	MAC
Cu (mg/kg)	26.8-6018.2	110
Zn (mg/kg)	28.9-3333.5	430
As (mg/kg)	5.2-236.3	42
Ni (mg/kg)	5.4-59.6	44
Pb (mg/kg)	12.2-2326.3	310
Cr (mg/kg)	9.4-113.2	240
Cd (mg/kg)	0.1-2.7	6.4
Hg (mg/kg)	0.1-0.3	1.6

The alternative monitoring process of the Tăuşani - Boşneag pond made by volunteers on revealed air pollution as dust storm on the pond transported polluting mining waste over a distance of about 800 m outside the pond.

4. CONCLUSIONS

The presented researching under RORS-337 Project was one of the broadest environmental investigations of the multi-element content in considered mining area from Romanian and Serbian side.

It is important to underline that samples of surface waters were taken on rivers close to mining facilities and upstream and downstream of mining facilities, well waters were taken in surrounding area, sediments were taken downstream on river beds while soil were taken in area of highly polluted surface waters. Even it is well known that soil around highly polluted surface waters like Borska River is polluted, this approach was selected for measurements of ranges and limits of concentrations per sampling points during 2 years period on different weather conditions.

In Eastern Serbia, pH values for surface water samples from Bor city to the confluence of Bor and Timok River range from 1.77 to 7.72 indicating that most of the analyzed surface waters are strong acid water with pH values lower than 3.0 [14, 15]. According to Serbian legislation for surface water, in rivers from Bor city to the confluence Bor and Timok (IV water category), the content for almost all of the analyzed elements and sulfate are above the MAC [16].

Surface waters from Bor mining complex up to confluence with Timok River are extremely enriched with toxic elements such as arsenic and cadmium [17]. The manganese and cadmium concentrations in surface water samples from this area were above the MAC in most of analysed samples as well as sulphate content. Exceeding the MAC values in large numbers of samples were also recorded for Cu, Fe, Ni, Zn, Pb and As. The only element with content below the MAC was chromium. As particular concern is the data for cadmium, the maximum detected value of this highly toxic metal is almost 5500 times higher than the MAC. Fe was the most abundant element in IV class of surface water samples with median value of 116 mg/L. The Median value [18, 19] is presented to indicate the central tendency of these highly scattered data. High presence of copper in IV class of surface water is also recorded with median value of 46.4 mg/L. Considering recorded content and median value, pollution main hazards are Cd, Mn, Cu, Fe, Ni, Zn, Pb and As. However, with addition consideration on pollutants impact on human health, the main risk is caused by Cd, As, Pb and Cu pollution. One of the highest pollution hazards represents Cadmium (Cd) with maximum recorded value of 5375 µg/L which is more than 5500 times higher than allowed concentration.

Samples from surface waters from rivers that belong to the III category (from the confluence Bor and Timok River to the confluence of Timok and Danube River) show that most of the elements and sulfates are below the MAC for the given category of surface waters. The manganese and sulphate content was exceeded in half of the analysed samples. The content of nickel and cadmium for this category of surface waters was exceeded in 66.67% and 58.33% of the analysed samples, respectively. The recorded concentrations of other considered elements were below the MAC values for this category of surface waters. Content of the main heavy metal polluter were dropped by increasing of distance from mining complex and by mixing of Bela River with Timok River. However, even in these surface waters, Cd was recorded with maximum concentration of over 70 times higher than MAC for this category of surface waters. Nickel was recorded with maximum concentration of over 17 times higher than MAC.

The situation is even better with II category surface waters (Danube River) in which all median values were below MAC.

Decreases in the concentrations of Fe, Cu, As, and Pb in surface river waters from confluence of Bela and Timok river were mainly due to precipitation of this metal ions on the river bed. On the other hand, Cd, Ni and Mn stayed in increased concentrations even in III category surface waters indicating dilution of this elements and longer transportation by water ways.

The median values for almost all of the analyzed elements from wells from Serbian site were below the MAC except for the content of sulphate which was almost 2 times higher than MAC. The pH values for wells range from 5.76 to 7.82.

Copper content in soil samples, as expected due to sampling around Bor River, were high up to max value of 12478.6 mg/kg. Significantly higher content than MAC were recorded also for Zn, Pb and As while Cr and Ni were on limit values. Cd and Hg were below MAC. River sediments actually followed the trends of quality of surface waters. Therefore, increased concentrations were in sediments from IV category of rivers while with improving of quality of waters, sediments became cleaner.

Considered rivers in Caras Severin County near Moldova Noua in Romania mostly do not have acidic characteristics except slightly increased value than MAC for Bosneag River. This increased value (133.7 mg/l) is actually small and could not be stated as significant acidic characteristic. Probable reason for this value is vicinity of Bosneag River to flotation tailing. Other two rivers have significantly lower values than MAC. The main way of pollution of these rivers is by spreading of dust from nearby flotation tailing in windy conditions. According to Romanian legislation for surface water, in considered rivers, the content for almost all of the analyzed elements is below the

MAC [20] for this category of surface waters. The only exceptions are Fe and Cu which were with slightly increased concentrations probably because of windy weather before and during the sampling.

Median value for Fe was below MAC for Bosneag and Radimna River while for Nera River was two times higher but still with relatively low absolute concentrations. Possible reason for increased concentration of iron could be spreading of dust from nearby flotation tailing during windy weather. However, iron is not a strong hazardous element for human health, especially in recorded concentrations, but regarding of increased concentration it is expected that more attention will be given for clarification of noted increased transfer of Fe from soil to waters.

Increased copper concentrations were recorded in all considered rivers, with the highest content of Cu registered for Bosneag River, almost 4 times higher than MAC. However, median value was around 2 times higher than MAC. Having on mind that Bosneag River is closest to flotation tailing pond, probable reason for increased Cu concentration is spreading of dust from nearby flotation tailing during windy weather before and during sampling. Median values for Cu for Radimna and Nera River were just slightly over MAC. These two rivers are located farther than Bosneag River from the flotation tailing which indicate similar reason for the measured Cu concentrations. For the considered rivers on the Romanian side, it was important that no strong pollution with heavy metals was recorded. This is a consequence of the dominant dust pollution, and not AMD which is an incomparable higher danger than dust.

The values for almost all of the analyzed elements from wells in Romania were below the MAC except that for Mn and Cr was just few samples with slightly higher content than MAC.

Copper content in soil samples, as expected due to sampling around Bosneag tailing, were high up to max value of 6018.2 mg/kg. Significantly higher content than MAC were recorded also for Zn, Pb and As while for Ni were on limit values. Cr, Cd and Hg were below MAC.

Comparing pollution in rivers surrounding Moldova Noua in Romania where the largest environmental impact is spreading of the dust from flotation tailing and rivers surrounding Bor in Eastern Serbia with combined AMD, tailing leaking and dust spreading environmental impact, it is clear that strongest environmental impact on surface rivers have AMD. Moreover, due to mobility potential and water ways transportation of the diluted ions, AMD have the significant environmental impact on wider area, often on cross border area.

More details and information regarding the pollution of water, soil and sediment in this area can be found in the knowledge base created within the project [21].

5. ACKNOWLEDGEMENT

We acknowledge the financial support of the Project RoRS 337- ROmania Serbia NETwork for assessing and disseminating the impact of copper mining activities on water quality in the cross-border area (RoS-NET2), implemented under the Interreg-IPA Cross-border Cooperation Romania-Serbia Programme that is financed by the European Union under the Instrument for Pre-accession Assistance (IPA II) and co-financed by the partner states in the Programme.

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