BALKANMINE 2007

2nd Balkan Mining Congress
Book of Proceedings

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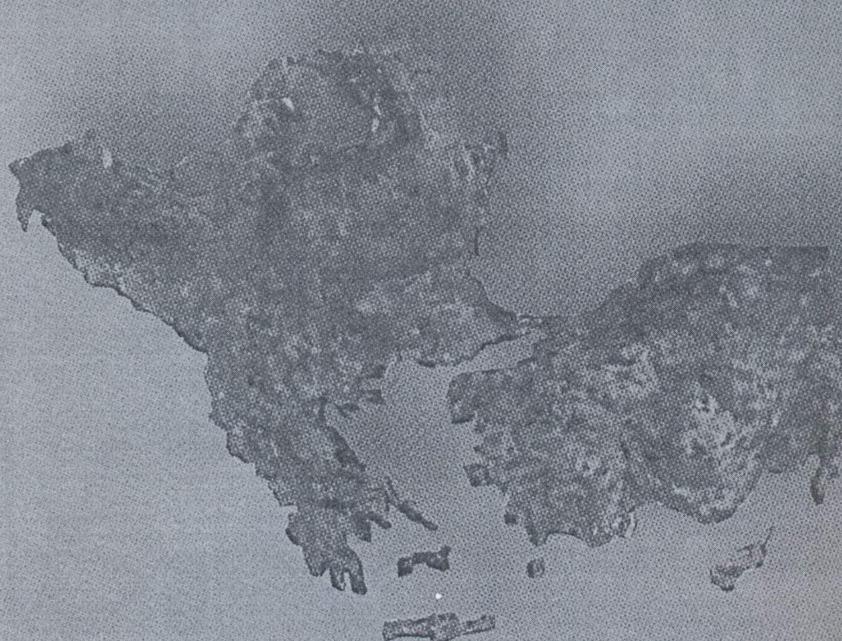
Slobodan Vujić



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BOOK OF PROCEEDINGS

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Heavy metals in the water of the river Zletovska and the vicinity

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Faculty of Mining and Geology - Stip, Republic of Macedonia

Abstract: *The paper presents the results and conclusions from the investigations carried out on the water contamination with heavy metals in the River Zletovska and its vicinity. The examinations are an attempt to determine the real and the physical state of heavy metals in the river water and its tributaries. Seventeen samples were collected from the Zletovska and several smaller rivers in the surrounding. Samples were analyzed with AES-ICP method. Earlier experiences indicated that the following elements should be expected: Mn, Fe. Al. Zn, As. Cd, Cu, Ni, Co, Ag. Cr, Ti with possible occurrence of increased concentrations of maximum allowable amounts.*
Analysis and data interoperation yielded increased concentrations of Mn, Fe, Al, Pb, Zn, As, Cd and Cu. The entire drainage system in the Zletovska in the Municipality of Probistip has been polluted. The drainage system in the area consists of the Rivers Kiselica and Koritnica, Casicki Dol and Lojzanski Dol. It was found that the major pollutants are the Zletovo Mine and the discharge of waste waters containing heavy metals. The increased concentrations of some metals are often twice higher than the maximum allowable.

KEY WORDS: HEAVY METALS, POLLUTION, THE RIVER ZLETOVSKA, WATER, RIVERS KISELICKA AND KORITNICA.

1. Introduction

Over the past few decades environmental pollution was not given sufficient attention. However, the issue was given a priority over the few years. Heavy and toxic metals in drinking water has been of special concern. It is of note that the wells from which the population in several municipalities receive water for the water supply system are located in the River Zletovska alluvion or more precisely at the estuary to Koritnica and Zletovska. This has been a serious concern for the people in the Municipality of Probistip.

People in the area use the waters from several tributaries for drinking water and household needs. They also use the water for irrigation, agriculture particularly in the production of many kinds of vegetables. Investigations carried out so far point out possible water pollution.

Another reason for the implementation of the project is the strict laws on the quality of the human environment.

The area studied included the River Stalkovica, Koritnica, Kiselica and Zletovska as far as its estuary to the Bregalnica (fig. 1). The area marked with an oblong is the place where water samples were collected.

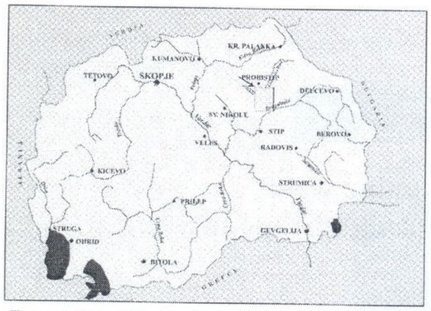

Figure 1. Map of the Republic of Macedonia with location of investigated area

2. Methods of work

Preliminary field activities were carried out in order to obtain data on the situation of the terrain.

Field sampling also defined measurement points and cross-section lines. Topography of sampling stations was defined including the cross section lines for sample collection. In this stage the Zletovska and its tributaries from Stalkovica across Bunecki Dol as far as the estuary to Kiselica and Zletovica going further to Kocani (the course of the Zletovska from the village of Lepopelci to Ziganci to Ularci and at estuary to Zlretovska and Bregalnica) were analysed.

The initial phase consisted of collecting water samples in the middle of the river course in a 1-l. clean plastic vessel. Sample collection also included filtering through paper the openings being 45 μm. Before closing the vessel acidifying with 0.4ml nitric acid (HNO_3) of 50% was done to avoid possible metal settling on the wall and the bottom of the vessel. Sample collection was accompanied with precise determination of sampling points using a 1: 50 000 scale topographic map. Laboratory examinations included AES-ICP method and their interpretation.

3. Results and discussion

Samples were collected from the middle of the river course and places where water flows slowly. Samples were denoted with numbers, and the places were marked on the topographic map (fig. 2).

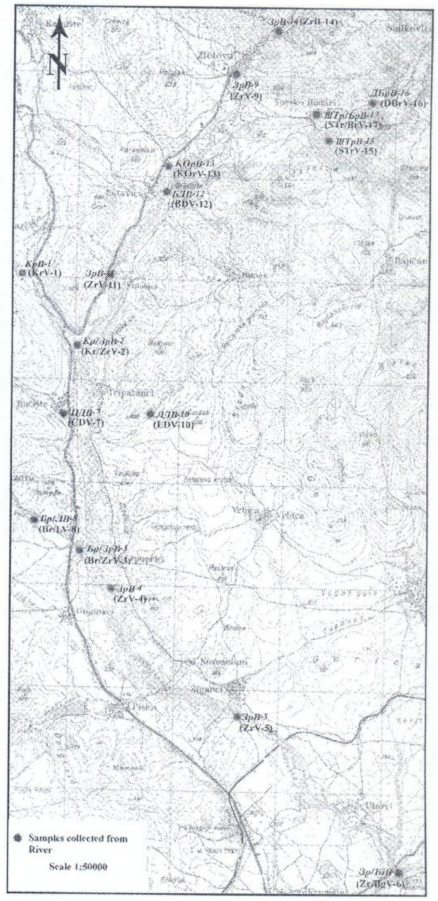

Figure 2. Topographic map with places where samples were collected

Tables 1 and 2 and the results or the heavy metals contents in river waters and pH value.

Data shown in Tables 1 and 2 make it possible to define the amount of heavy metals in the Zletovska River water and its tributaries and the reasons for their occurrence.

Calcium is lower than the maximum allowable. The highest concentrations were found in samples Kr-1, Cd-7, Br-8, Kor-13. The lowest concentration was found in samples nos. Zr-9 and ZrV-14.

Magnesium in all samples is lower than the maximum allowable. The highest concentrations were found in samples BDV-12 (39,64 mg/l) and Kr-13 (40,44 mg/l).

The lowest magnesium concentrations were found in samples nos. Zr-9 and Zr-14. pH value of the media is from 4,21 and 7,71.

Contents of individual metals in samples (mg/l) and pH values *Table 1.*

	Kr-1	Kr/Zr-2	Br/Zr-3	Zr-4	Zr-5	Zr/Bg-6	Cd-7	Br-8
Ca	102,01	10,85	16,36	13,55	14,74	15,97	97,47	86,77
Stand.	200,00	200,00	200,00	200,00	200,00	200,00	200,00	200,00
Mg	26,61	3,64	5,39	4,37	4,79	5,05	28,35	32,99
Stand.	150,00	150,00	150,00	150,00	150,00	150,00	150,00	150,00
Na	78,16	4,79	8,34	6,19	6,78	6,94	62,03	72,77
K	10,73	2,68	2,72	3,05	3,27	2,84	10,74	4,86
Al	0,020	0,112	0,237	0,378	0,968	0,275	0,083	0,033
Stand.	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Fe	0,133	0,234	0,284	0,637	0,824	0,478	0,096	0,050
Stand.	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Mn	3,76	0,088	0,142	0,108	0,110	0,114	0,008	0,008
Stand.	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
P	0,037	0,060	0,017	0,026	0,028	0,030	0,171	0,013
Sr	1,25	0,074	0,145	0,112	0,121	0,132	0,994	1,12
Ba	0,0062	0,014	0,019	0,020	0,024	0,021	0,102	0,052
Zn	0,831	0,034	0,056	0,047	0,045	0,039	0,0011	0,0015
Stand.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ni	0,0093998	0,0175464	0,0062502	<0.005	0,0078789	<0.005	<0.005	0,0107007
Stand.	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Pb	0,016	<0.005	0,006	0,007	0,005	<0.005	<0.005	0,014
Stand.	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cu	0,0006674	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0,0052188
Stand.	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cr	0,0010686	<0.001	<0.001	0,0014843	0,0005917	0,0019112	0,0023861	<0.001
Stand.	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Co	0,0039099	0,0038699	0,0049624	0,0050927	0,007	0,0074101	0,0054583	0,0041125
Stand.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cd	0,0014868	<0.001	<0.001	<0.001	<0.001	0,001663	<0.001	<0.001
Stand.	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
V	0,0015555	0,0045983	0,0042702	0,001267	0,0038584	0,0013832	0,0147871	0,0017323
Stand.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
As	<0.005	0,0550656	0,0570838	0,0304566	0,0704608	0,0410018	0,3641202	0,1801498
Stand.	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Ag	<0.002	0,0065238	0,0044616	0,0038663	0,0040006	0,0039995	<0.002	0,0049686
Stand.	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Ti	0,0025607	0,0025625	0,0025491	0,0025344	0,0027656	0,0025355	0,0025525	0,0025499
Stand.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
PH	6,94	7.24	7,09	7,03	7,02	6,99	7,33	7.48

Content of metals in individual samples taken from river course (mg/l) and pH values *Table 2.*

	Zr-9	LD-10	Zr-11	BD-12	Kor-13	Zr-14	Str-15	Kp-16	St-17
Ca	6,00	55,00	7,56	68,89	121,26	5,79	7,74	40,38	12,28
Stand.	200,00	200,00	200,00	200,00	200,00	200,00	200,00	200,00	200,00
Mg	2,35	34,51	2,89	39,64	40,44	2,43	3,30	18,23	4 ,55
Stand.	150,00	150,00	150,00	150,00	150,00	150,00	150,00	150,00	150,00
Na	3,14	35,99	3,55	20,90	27,10	2,89	3,13	12,00	4,60
K	2,29	19,34	2,32	5,49	5,12	2,53	2,01	12,16	1,87
Al	0,351	0,010	0,316	0,104	0,271	0,217	0,039	6,566	0,052
Stand.	0,500	0,500	0,500	0,500	0,500	0,500	0,500	0,500	0,500
Fe	0,472	0,024	0,469	0,021	0,575	0,420	0,096	0,591	0,160
Stand.	0,300	0,300	0,300	0,300	0,300	0,300	0,300	0,300	0,300
Mn	0.4	0,028	0,053	0,002	9,811	0,030	0,013	0,612	0,013
Stand.	0,050	0,050	0,050	0,050	0,050	0,050	0,050	0,050	0,050
P	0,042	0,018	0,039	0,038	0,011	0,019	0,014	0,032	0,018
Sr	0,039	0,622	0,054	0,872	1,560	0,039	0,056	0,201	0,087
Ba	0,014	0,091	0,016	0,053	0,022	0,014	0,006	0,032	0,005
Zn	0,0013	0,0012	0,011	<0.004	2,047	<0.004	<0.004	0,113	<0.004
Stand.	0,1000	0,1000	0,1000	0,1000	0,1000	0,1000	0,1000	0,1000	0,1000
Ni	<0.005	<0.005	<0.005	0,0075304	<0.005	<0.005	0,0055675	0,0124651	<0.005
Stand.	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05
Pb	<0.005	0,005	0,0143372	<0.005	0,0117824	<0.005	0,005	0,0139975	0,013
Stand.	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
Cu	<0.005	0,0059946	<0.005	<0.005	<0.005	0,0104641	<0.005	0,0128693	0,024
Stand.	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
Cr	0,003693	<0.001	0,001512	0,0063078	0,0023163	0,0043941	0,003059	0,0036845	<0.001
Stand.	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,01
Co	0,0073429	0,0039126	0,0037496	0,0037829	0,0191652	0,0062968	0,007422	0,0317927	0,0041
Stand.	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
Cd	<0.001	<0.001	<0.001	<0.001	0,0175587	0,0017301	<0.001	<0.001	<0.001
Stand.	0,0001	0,0001	0,0001	0,0001	0,0001	0,0001	0,0001	0,0001	0,0001
V	0,0044486	0,0123124	0,0046584	0,0068081	0,0018207	0,0025281	0,0055056	0,0047782	0,0037
Stand.	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
As	0,1372717	0,0860884	0,1924279	0,0415724	0,1757859	0,2402934	0,2195517	0,1773075	0,011
Stand.	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05
Ag	0,0052604	0,0034328	0,0034897	<0.002	0,0032724	0,0047801	<0.002	0,0019969	0,0085
Stand.	0,012	0,012	0,012	0,012	0,012	0,012	0,012	0,012	0,012
Ti	0,0025248	0,0025673	0,0025631	0,0025664	0,0025689	0,0025396	0,0025435	0,0025331	0,0068
Stand.	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
pH	7,71	7,5	7,64	7,65	7,52	7,68	7,54	4,21	6,03

Unlike calcium and magnesium which occur in concentrations lower than the maximum allowable, aluminium in sample Zr-5 (sample was taken in the Zletovska between Ziganci and Ularci) occurs in concentration twice higher than the maximum allowable, whereas in sample no. Kr-16 (collected from the Kosol stream near Tursko Rudari) aluminium concentrations are thirteen times higher than the maximum allowable limit. Aluminium in other samples occurs in concentrations close or lower than maximum allowable. The increased aluminium concentrations in Tursko Rudari are due to the silicate minerals in the area.

Data on iron concentrations (table 1 and 2) point out increased amounts in most of the samples. The highest iron concentrations were found in sample Zr-5 of 0.824 mg/l. Increased iron concentrations were found in samples Zr-4, Zr/Bg-6, Zr-9, Zr-11, Zr-13, Zr-14, Zr-16. In other samples iron occurs in amounts close or lower than maximum allowable limits.

It can be generally said that the entire area is contaminated with iron and that the increased concentrations are due to sulphide and oxide (pyrite and limonite) presence.

Of special interest are the increased manganese concentrations in samples Kr-1 (3.76 mg/l) and Kor- 13 (9.811 mg/l). One sample was collected downstream the river Kiselicka near Neokazi, and the other from Koritnica near Ratavica. The reason for the high manganese occurrences is the River Kiselicka, which flows near the waste pile. The high manganese concentrations in the Koritnica are due to the waste waters discharged from the Zletovo Mine.

High zinc concentrations were found in the samples taken from Kiselica and Koritnica. The high concentration comes from the Zletovo lead and zinc mine, or more precisely, the waste pile located near the Kiselica and the waste water discharge from the Zletovo Mine into Koritnica.

Increased lead concentrations were found in samples Kr-1 (0.016 mg/l), Br/L-8 (0.014 mg/l), Zr-11 (0.0143372 mg/l). Kor-13 (0.0117824) mg/l), Kr-16 (0.0139975 mg/l), Sr/Sr-17 (0.013 mg/l).

It is obvious that lead was found in most of the samples. However, the highest lead concentrations were found in samples in which increased amounts of manganese and zinc were also found. This confirms the enormous effects of the tailing pond and the operation of the Zletovo mine on the pollution in the area.

Copper occurs in amounts lower than the allowable. Increased concentrations were found only near Tursko Rudari and Zletovo owing to the presence of copper mineralization there. The low copper concentration is also due to the effects of the medium, which is close to neutral (pH of amount 7).

Chromium was found in amounts lower than the maximum allowable and was not defined as water contaminant in the Zletovska.

Cobalt like chromium was found in concentrations lower than the allowable limit and does not represent an important contaminant in the Zletovska drainage system.

Of special attention are the cadmium, arsenic and silver concentrations.

In three samples cadmium was found in extremely high concentrations. Increased concentrations were found in Kiselicka, Koritnica Zletovska and between Ziganci and Ularci and at the estuary to Zletovska and Bregalnica.

Increased cadmium concentration was found in parts contaminated with zinc.

Arsenic was found in all samples, particularly in Casicki Dol and in the part between the River Stalkovska and Tursko Rudari. Increased arsenic concentrations are due to arsenic in the copper mineralization in the area of Tursko Rudari.

Data obtained for silver (Table 1 and 2) point out that silver contaminates the entire drainage system of Zletovica. It is clear that increased silver concentrations occur in all samples occurring along with lead.

Vanadium was found in concentrations lower than maximum allowable and is not a contaminant in the Zletovo drainage system.

4. Conclusion

Data obtained with laboratory examinations on heavy metal contents in the waters of the

Zletovica and its tributaries indicate that a number of heavy metals occur in increased amounts, some of them in amounts lower than the maximum allowable.

The most important contaminants are lead, zinc, cadmium, silver, arsenic and silver.

The major contaminant is the tailing pond with the waste material discharged after lead and zinc processing (the part of Kiselicka), the operation of the Zletovo lead and zinc mine (the upper course of the river Zletovska), the presence of copper mineralization accompanied with arsenic in Tursko Rudari and the transport of lead and zinc concentrate to the Vanco Prke railway station (the area between the villages of Ziganci and Ularci and the estuary to the Zletovska and Bregalnica).

The metal concentration in flowing waters is also influenced by their geochemical characteristics and pH and eH factors.

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Mine waters of the Buchim deposit and the effects on the human environment

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Abstract: *Removal of natural resources has an adverse effect on the landscape, destroys the bio-chemical balance and degrades the environment which as an open, dynamic and integrated system is closely related to the excavation of mineral resources.*
Mining activities have an effect on the environment in all phases of mining cycle - the preparation of the site, digging, removal and ore processing as far as water evacuation that is done in order to provide uninterrupted mine operation and waste water drainage from the tailing pond.
Environmental pollution resulting from mining activities includes contamination with acidic mine waters, heavy metals, chemical reagents, suspended materials, percolating and overflow waters from tailing pond.
Cessation of mining activities does not mean cessation of pollution. It is the other way round, it may continue years after mine closure.
Mine waters contaminated with heavy metals pose risk to water resources, land, people and premises in the area. The major problem related to this kind of pollution affecting quality of life and health of people and their safety consists of health risks from heavy metals in the water, contamination of water courses in terms of change of the colour as a result of introduction of hydroxide salts of iron, copper, aluminum, or arsenic. These destroy water life and prevent the use of water for water supply, recreational use; large-scale risks to health owing to waste water outflow and risks from the use of wastewaters and soils in agriculture.
The state of the matter regarding contamination of the environment determined through numerous earlier geological and ecological research works entails the need of greater concern and problem analysis.
The issue of heavy metal concentration in waters was given greater attention over the past few years due to the scientific development and the higher awareness with the people for the need of environmental protection. The development of analytic technique and methodology, which make possible better measurements of their concentration is an important contribution to unravel the issue of heavy metals in mine waters.
The paper will present the state of the matters regarding the content and distribution of heavy and toxic metals in the waters of the Buchim mine area.

KEY WORDS: HEAVY METALS, MINE WATERS, POLLUTION, THE BUCHIM DEPOSIT, TAILING POND, TOPOLNICA, RIVER MADENSKA, KRIVA LAKAVICA.

1. Introduction

The Buchim-Damjan-Borov Dol ore region occupies the middle parts of the Lece-Halkidiki metallogenetic zone. With an area of 150 km^2 it is one of the smallest ore regions in the zone. However, its specific metallogenetic features make it fairly versatile.

The Buchim deposit occupies the northern parts of the region. It is located some 10 km west of Radovis (fig. 1). The geology consists mainly of Precambrian metamorphic rocks (gneisses and amphibolites) and Tertiary volcanics (andesites and latite andesites).

The porphyry copper mineralization in the Buchim deposit has been determined in an area of 1.5 km^2 300 m to depth.

Earlier investigations carried out on the geology and pollution in the Buchim-Damjan-Borov Dol area indicated naturally increased concentrations of some elements and increased contents of some elements caused by anthropological activities.

Figure 1. Map of the Republic of Macedonia with the location of the area under investigation

Investigations have shown that the Buchim and adjacent deposits contain copper mineralization. In addition to the major minerals such as Cu, Au, Ag, Mo, Fe, S a number of microelements have also been determined: Ni, Co, Cr, Ti, V, Sb, As, Pb, Zn, Bi, Se, Te, Ga, Ge, Mn, Ba, Sr, B, B, Sc, Zr. The increased contents of these elements have been found in individual samples in the so called secondary hellos of dissemination, especially in stream sediments, which points out that in the vicinity of the Buchim deposit there is natural contamination of the waters drained from the terrain. The active watreflows are the River Topolnica, the Buchim Mine drainage stream, the Madesnka, Kriva Lakavica and some other smaller streams comprising the drainage system.

The highest contamination is caused by the mine and its tailing pond located above the village of Topolnica. Investigations included part of the River Topolnica, which receives the wastewater from the tailing pond, a stream coming from the mine, the part where they join and flow into Madenska as far the estuary in the Kriva Lakavica. Data obtained during the examinations are to give additional information on the components that were transported by water flows.

2. Methods of work

Preliminary field investigations were carried out in order to obtain essential data on the terrain. It included obtaining data on the Rivers Topolnica, Madenska and Kriva Lakavica water courses selected as possible stations for sample collection.

Samples from water flows and springs were collected in order to obtain data on the most critical points in terms of heavy metal contamination and how to direct future sampling and analyses.

Water samples were collected below the flotation tailing pond whose drainage waters flow into the Topolnica, then the drainage water from the mine, the part where they join and flow into the Madenska along the entire course to the estuary in the Kriva Lakavica (fig. 2). The aim was to determine the effect that the mining activities and the tailing pond have on the distribution of heavy and toxic metals in waters.

Water sampling was done with plastic syringe from the middle part of the water flow. The 50 ml of water from the syringe was transferred into a plastic vessel. It is of note that when the water is transferred from the syringe to the vessel it is filtered through a paper filter the openings 45 μm. Acidizing with 0.4 ml of 50% nitric acid is done before closing the vessel. This is done to avoid settling of metals on the wall and bottom of the vessel.

Figure 2. Topographic map with sampling sites

Water sampling also included determination of the dissolved solid materials (TDS) and on conductivity.

The samples were taken to laboratory for chemical analysis for heavy metal and toxic metal determination with AEC-ICP.

3. Results and Discussion

The results obtained from flowing water samples are given in Table 1, with comparison between maximum allowable (MAC) concentration of heavy and toxic metals for I - II classes.

The analyses carried out on flowing water samples indicated that based on the MAC standards given for class I-II flowing water, individual heavy and toxic metals are in the span as follows: *Copper* did not indicate increased concentrations in the samples collected from the River Topolnica relative to MAC. This is due to the pH in the water which is within 6.48 and 7.1. In other words, it is a value that is close to neutral which is not favorable for dissolved Cu distribution.

The highest Cu concentrations were found in sample Mw5, collected from the mine drainage where it is several times higher relative to MAC. This is a consequence of the geology of the terrain (mineral assemblage) and due also to pH of the medium amounting to 3.89. High Cu concentrations were also found along the Madenska. Correlation dependence between Cu distribution and pH changes downstream the Madenska has also been found. In other words, Cu concentration reduces with the increase of pH of the medium. This finding is confirmed by the fact that the Kriva Lakavica, with pH of 7.8, contains lower Cu concentrations relative to MAC. At the estuary of Madenska in the Kriva Lakavica pH amounts to 5.07 which results in multifold increase of Cu concentration relative to MAC.

Iron, according to MAC standards, was found in lower concentrations. The highest concentration was found in the sample taken from point Mw8 at Madenska at Pilav Tepe. There, pH amounted to 4.44, which is a favorable medium for Fe distribution as dissolved concentration. The proximity of the Damjan mine is a possible cause for this.

Maximum zinc concentrations were found in sample Mw5 which is an immediate consequence of its association in the mineral assemblage as a sphalerite and the acidic nature of water. High concentrations were also found along the entire course of Madenska and at the estuary in the Kriva Lakavica.

Maximum nickel concentrations were found in sample Mw5. Higher concentrations relative to MAC were found in samples Mw6, Mw7, Mw8, Mw9, Mw10 and Mw12 as a direct consequence of pH and its presence as a microelement in the Buchim Mine.

In all samples Pb occurs in lower amounts than MAC, its maximum being in Mw5 owing to its presence in the Buchim deposit as galena and the pH in the medium.

Chromium was found in concentrations lower than MAC.

Lineite as a rare mineral occurs in the Buchim deposit. As a result, the highest cobalt concentrations were found in sample Mw5 occurring in concentrations that are several times higher than MAC. High Co concentrations were found along the entire course of Madenska and at the estuary in the Kriva Lakavica.

Contents of heavy and toxic metals in flowing waters in the surrounding of the Buchim Mine (mg/l) *Table 1.*

	Mw1	Mw'1	Mw2	Mw3	Mw4	Mw5	Mw5	Mw7	Mw8	Mw9	Mw10	Mw11	Mw12	Sred.	MDK
Ca	131,5	115,2	89,2	113,4	109,2	224,6	151,2	254,5	252,8	238.2	259,2	82,9	252,2	177,3	
Mg	30.97	27,31	20,19	29,72	29.51	550,0	209,9	250,3	251,2	228,1	237,9	50,56	235,3	157,0	
Na	130,4	101,0	133,6	87,22	85,54	105,8	102.5	91,70	81,89	83,87	101,4	48,79	109,3	97,17	
K	25.48	21,15	25,84	14,70	14.57	18,58	20,71	15,75	13,55	13,88	15,25	15,59	15,41	17,89	
Al	0,118	0,139	0,109	0,085	0,108	275,4	33,94	28,15	19.80	13,58	1,42	0.011	0,549	28,72	
Fe	0,053	0,074	0,035	0,058	0,050	0,023	0,121	0,134	0,179	0,175	0,020	0,025	0,017	0,075	0,500
Mn	1,33	0,149	1,37	0,035	0,025	180,7	41,31	47,43	40,82	39,72	24,54	0,055	22,12	30,74	
P	0,055	0,094	0,045	0,051	0.040	0,229	0,107	0.058	0,115	0,081	0,040	0,019	0,020	0,075	
Sr	0,27	0,27	0,25	0,21	0,28	0,87	0,45	0,85	0,88	0,85	0,99	0,55	1,04	0,500	
Ba	0,04	0,042	0,039	0,04	0.039	0,01	0,04	0,03	0,03	0,03	0,05	0,058	0,05	0,040	0,2
Zn	0,003	0,005	0,003	0,004	0,004	4,75	1,08	1,84	1,52	1,44	0,58	0,0004	0,51	0,919	0,2
Ni	0,003	0,006	0,006	0,002	0,004	2,57	0,52	0,72	0,53	0,59	0,38	0,004	0,32	0,458	0.05
Pb	0,002	0,004	0,001	0,004	0,014	0,025	0,004	0,009	0,005	0,015	0,012	0,011	0,008	0,009	0,05
Cu	0,004	0,008	0,013	0,009	0.021	509,8	112,5	85,35	74,47	77,22	47,21	0,050	22,83	71,58	0,1
Cr	0,001	0,0005	0,001	0,005	0,001	0,082	0,023	0,025	0,020	0,014	0,012	0,001	0,009	0,015	0,1
Co	0,005	0,005	0,004	0,007	0.004	4,89	1,11	1,17	0,94	0,88	0,59	0,004	0,54	0,782	0,2
Cd	0,001	0,0001	0,001	0,000	0,001	0,025	0,005	0,010	0,007	0.007	0,003	0,001	0,004	0,005	0,005
V	0,003	0,004	0,002	0,002	0,002	0,027	0,014	0,014	0,002	0,015	0,008	0,007	0,009	0,009	
As	0,17	0,20	0,17	0,29	0,080	0,25	0,23	0,30	0,21	0,17	0,025	0,088	0,14	0,180	0,05
Ag	0,0004	0,003	0,001	0,004	0,002	0,005	0,005	0,000	0,002	0.0001	0,003	0,0005	0,001	0,002	0,01
Ti	0,025	0,025	0,025	0,025	0,025	0,027	0,025	0,025	0,025	0,025	0,025	0,025	0,025	0,026	
pH	5,55	5,48	5,92	5,95	7,1	3,89	4,28	4,39	4,44	4,50	4,55	7,18	5,07		

Cadmium is a toxic metal. It was found in concentrations higher than MAC in sample Mw5. High concentrations were also found in Mw6, Mw7, Mw8, Mw9 owing to the pH value of the medium amounting from 3.89 - 4.50 or acid medium.

The increased *arsenic* concentrations exceeding the standard several times are due to this metalloid in the geological medium and pH of the media . It replaces sulphur in the crystal lattice of chalcopyrite and pyrite.

Silver is present in the Buchim Mine as one of the major elements being a characteristic element for porphyry deposits. Several silver minerals were determined such as krennerite, stephanite, and freibergite. However, although found in all samples collected from the river waters, they do not exceed the values defined by standards.

4. Conclusion

Based on the results obtained from the analyses of the samples collected along the River Topolnica, the drainage from the Buchim Mine, the Madenska and its flow into the Kriva Lakavica it can be inferred that the drainage area is highly contaminated.

The increased concentrations of heavy and toxic metals are a consequence of the geological composition of the terrain, anthropologic activities such as early mining and stockpiling of waste material, the use of fertilizers in agriculture as well as the physical and chemical character of the water solutes, first of all those of pH (acidity of the medium) and Eh (oxide-reduction potential of the medium).

It can be said in the end that the largest distribution and resulting contamination with heavy and toxic metals were found in the drainage stream leaving the mine and flowing into the Madesnka. From ecological point of view this entails the need of rehabilitation of the area in order to prevent flora and fauna intoxication in the water medium and the surrounding and prevent the negative effect on the health of the population.

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