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WATER MONITORING AROUND THE BUCHIM COPPER MINE DRAINAGE SYSTEM

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ABSTRACT

Two hot-spot sources are representative for the Buchim mine drainage system. The first one is the waste dump, which produces an average flow of 15-20 l/s with low pH value (3,6-5,5) and 450-850 mg/l Cu. The second source one is the hydrotailing dam near the Topolnica River where monitored parameters of waters distinguish themselves by increased pH values from 6.2 up to 7.6 and increased concentrations of suspended matters (7-466 mg/l) while the copper concentration remained below the MDK limits at 0.01-0.048 mg/l Cu. Environmental conditions regarding the ground and surface water drainage system around the Buchim mine conditions have changed dramatically after 2010 with the construction of the copper leaching facility. Namely, the results from the newest monitoring in 2012 have shown range of pH 3.60÷7.95 and copper concentrations of 0.01÷0.68 mg/l Cu. According to the monitoring in 2012, beside the copper and pH, other parameters were close to the maximally allowed limits for such or similar waters.

Keywords: copper mine, waste dump, drainage, tailing dam, monitoring.

INTRODUCTION

During the three decades of continuous exploitation around the Buchim Mine was created surface waste dump were have been stored more than 140 Mt of material and more than 120 Mt material within the hydrotailing dam. These secondary landfills for years have been considered as basic sources of anthropogenic influences and contamination of air, soil and especially water. In this period, around the Buchim mine has been determined significant contaminations of groundwater and surface water in which the content of the copper was over 800 mg/l Cu. During the 2011 in the adjacent vicinity of the waste dump was built copper leaching facility, which catches all the drainage waters. Also, around the leaching facility and continuous watercourse have been established monitoring points for quality determination of groundwater and surface water. These are basic goals within the frame of this paper, where we are going to preview the contamination of the drainage system before and after construction of the installation.

Some of the preliminary publications that have studied the issues of mine pollution at the territory of the Republic of Macedonia, including area around the Buchim Mine, can be found in [1], [2], [3], [4], [5], [6], [7], [8]. After that period studies around the Buchim Mine have been intensified and have been set monitoring points for particular hot spots around waste dump and tailing dam with associated water drainage, ambiental dust monitoring, monitoring of soil contamination etc. Considering that issue there have been completed some significant studies of soil contamination [9], [10], [11].

METHODOLOGY

Samples were collected during the continuous monitoring in 2008-2010 and 2012 from the most environmentally threatening hot spots within the Buchim mine drainage system outlined below. Water was collected in polythene syringes, passed through a 0.45μm filter and transferred into polythene tubes. Water was acidified with 0.4 ml of 50% nitric acid. Conductivity and pH were measured in the field for all water samples. Samples were stored in a cool and dark place until they were returned to the laboratory analysis. Solutions were analysed by ICPAES or ICPMS, depending on concentrations. A large number of analytes were determined but only those that are likely mining related and environmentally significant are presented and discussed here. The concentrations were compared to reference guidelines (Maximally Allowed Concentrations-MDK) to assess their significance.

ACID MINE DRAINAGE SYSTEM

There are several areas at the Buchim Mine system that are of particular environmental concern: the open pit, the heap leach pad, waste dump, tailing dam and the system of underground fractures that control groundwater movement. Short term environmental concerns include the presence of cyanide and metal rich solutions in the leach pad, while the long term environmental concern is acid mine drainage. Acidic drainage is caused by the oxidation of sulfide minerals exposed to atmospheric oxygen. Although acid drainage is commonly associated with the extraction and processing of sulfide-bearing metalliferous ore deposits, acidic drainage can occur wherever sulfide minerals are excavated and exposed to atmospheric oxygen [12]. BuchimMine is especially vulnerable to the environment danger of acid mine drainage because all of the rocks there have lost their capability to buffer acids due to acid sulfide hydrothermal alteration. In fact, the rocks of Buchim deposit contain less than 7%, sulfides, but because no carbonates are present to counteract the acid waters that have passed through the ore body, the pH remains very low. The acid mine drainage has the most potential to affect water quality in the downstream agricultural and wetland areas of the Damjan Field and Kriva Lakavica Valley. Within this paper has been performed systematization of an array of studies of ground and surface waters that are draining the mine, mine waste dump and tailing dam, which have been separated into separate segments. Within the first one were considered waters draining mine waste dump where as main drainages is stream Jasenov Dol and so called Buchim Lake. The second one considered outflow waters from the tailing dam near the Topolnica village and their flow along the Topolnica River.

MAJOR WATER CONTAMINANTS AROUND THE BUCHIM MINE

In the adjacent vicinity of the Buchim Mine have been located the few important hydrological objects (Figure 1).

Figure 1. Topographic map of the Buchim Mine area with monitoring points

Buchim Lake, to the west from the open pit, located in its vicinity (S-1). Draining waters from the mine waste are composed of meteoric waters flowing from upper parts above the mine waste pile (mine yard and Buchim village area) and passing through the mine waste, rain waters passing though the mine waste dump and flowing further downstream and ground waters infiltrating through the mine waste dump. Buchim Dol (Buchim Lake)-before the start of mine production it was built drainage system/collector with channels around the location perimeter planned for the mine waste dump (Figure 2).

Figure 2. Buchim Lake and Buchim Dol (drainage waters under the mine waste dump, left); Topolnica River before the bridge, on the road Stip-Radovish, during increased water level (pH = 5.1; Cu in solution 80 mg/l) with a characteristic blue coloring of the water (right).

This system collects part of draining waters from the mine waste dump and guide them to the Buchim Dol. Beside these waters, this gully constitutes of atmospheric waters re-directed from open pit and ground waters under the mine waste. With the latest improvements, waters at the bottom of open pit have been pumped into the pools for industrial water because they are unpolluted and can be used again. The water samples analyses in

2008-2010 have been characterized by 30-45 mg/L Cu), low pH value (3,6-5,5) and average flow of 15-20 l/s (Table 1).

Table 1. Descriptive statistics of chemical and geochemical analyses of water samples from monitoring point Buchim lake, drainage from dam (period 01.2008 - 07. 2010).

Parameters	X_a	X_g	Md	min	max	s	CV	MKD 3rd class	Samples above limit values
Temperature,°C	15.25	13.30	14.4	4	27	7.35	48.22	-	-
pH	4.13	4.90	4	3.3	6.86	0.65	15.83	6.0 - 6.3	30 under 6.0 1 over 6.1
HPK KMn04, mg/l	10.42	10.14	10.96	6.2	13.21	2.27	21.76	5.01-10.0	20
Total dry residue at 105^{O}C, mg/l	9749.9	7605.9	6624	1975	29722	7257.6	74.44	-	-
Dissolved matters, mg/l	9340.4	7225.9	6389	1829	28874	7126.9	76.30	1000	31
Suspended matters, mg/l	597.52	216.75	195	28	8430	1489.8	257.07	30 - 60	27
Copper, Cu^{2+}, mg/l	88.51	60.80	51.6	12.6	341	83.11	93.9	0.05	31
Silver, Ag^{2+}, mg/l	0.021	0.021	0.022	0.01	0.045	0.0074	33.83	0.02	19
Ammonia, NH_4^+, mg/l	10.25	3.36	4.32	0.015	137.67	24.06	234.78	10.0	7
Nitrates, NO_3^-, mg/l	12.84	12.49	12.34	6.81	25.2	3.22	25.08	15.0	5
Nitrites, NO_2^-, mg/l	0.055	0.017	0.01	0.001	0.67	0.126	227.60	0.5	1
Total phosphate, PO_4^{3-}, mg/l	0.035	0.021	0.022	0.001	0.23	0.043	123.21	0.0071-0.01 0.011 - 0.02*	24

*lake water and accumulations; the numbers marked in red are out of the frame of the allowed values. n -number of measurements; X_a - arithmetical mean; X_g - geometrical mean; Md - median; s - standard deviation; CV - coefficient of variation.

From the short review of the results in Table 1 and their comparison with maximally allowed concentrations it was determined that all of them differ at least for one of the three values (arithmetical mean, minimum and maximum) while four of them are out of limits for all three values. Drainage water from open pit and waste dump are highly contaminated. Those waters (especially surface ones) during their movement are getting into contact with rocks that are containing easily soluble compounds, first of all Cu- sulfide minerals (chalcopyrite associated with pyrite and magnetite), which causes oxidation of sulfide minerals and results in decrease of pH values down to 3.3 and increase of copper and other metals solubility. Also, these waters were characterized by significantly increased concentration of dissolved and suspended matters, which made possible transfer of Fe, Al, heavy metals in solid state to greater distances [13]. Copper content in these waters is quite high reaching range of 450-850 mg/l Cu, with pH values in the range of 3.4-4.5 and average water flow of 5-20 l/s.

River Topolnica, directly receives waters from the drainage system of the hydrotailing dam, as well as all other waters in the zone of mine operations. This water flow also receives waters from the Jasenov Dol (Figure 2). The review of the results and their comparison with MDK values, confirmed that only five parameters of ten are above limits at least for one (arithmetic mean, maximum, minimum) while no one is above all three values. However, the waste waters from the tailing dam are contaminated, but not at high levels. There have been determined numerous specifics, which compared to normal waters distinguish themselves by increased pH values from 6.2 up to 7.6 and increased concentrations of suspended matters (7-466 mg/l) while the copper concentration remained below the MDK limits (0.01-0.048 mg/l Cu).

Sampling point at the the *Topolnicka River before the bridge* on the regional road Shtip-Radovish (Figure 2), was subject of continuous monitoring during the years. Analysis data review of this sampling point have shown that only two of ten parameters are within allowed limits while the rest of them are out of the MDK limits (Table 2). Waters of this part of the Topolnica River are highly polluted. The concentration of contaminants varies during the year and is dependant of quantity of atmospheric precipitation (rain and snowfall).

Table 2. Descriptive statistics of chemical and geochemical analyses of water samples from monitoring point Topolnica River before the bridge, road Stip-Radovish (period 01.2008-07. 2010) (n=31).

Parameters	X_a	X_g	Md	min	max	s	CV	MKD 3rd class	Samples above limit values
Temperature,°C	13.45	12.2	13.5	4.7	23	5.4	39.9	-	-
pH	5.1	5	5	3.9	6.93	0.8	15.8	6.0 - 6.3	28 under 6.0 3 over 6.3
HPK KMn04, mg/l	9.43	9.4	9.23	7.15	12.03	1.13	12.01	5.01-10.0	9
Total dry residue at 105°C, mg/l	3522.4	2840.6	2755	830	12352	2606.6	73.9	-	-
Solved matters, mg/l	3150.6	2435.1	2395	579	12129	2574.6	81.7	1000	27
Suspended matters, mg/l	373.4	175.7	202	11	5606	962.2	275.7	30 - 60	28
Copper, Cu^{2+}, mg/l	58.3	28.1	43.3	0.3	376	71.5	122.5	0.05	31
Silver, Ag^{2+}, mg/l	0.02	0.01	0.02	0.001	0.05	0.01	56.5	0.02	7
Ammonia, NH_4^+, mg/l	1.8	0.98	1.05	0.01	7.35	1.9	102.5	10.0	0
Nitrates, NO_3^-, mg/l	11.3	9.99	9.7	4.07	49.9	7.9	70.2	15.0	3
Nitrites, NO_2^-, mg/l	0.09	0.06	0.07	0.001	0.43	0.09	90.1	0.5	0
Total phosphate, PO_4^{3-}, mg/l	0.04	0.02	0.02	0.001	0.17	0.04	101.8	0.0071-0.01 0.011- 0.02*	20

*lake water and accumulations; the numbers marked in red are out of the frame of the allowed values. n -number of measurements; X_a - arithmetical mean; X_g - geometrical mean; Md - median; min -minimum; max - maximum; s - standard deviation; CV - coefficient of variation.

During the rainy periods it was noted that there is a process of dilution and were measured lower concentrations of the pollutants. Sudden increase of pollutants concentration has been measured after the confluence of acid drainage waste waters from the mine into the Topolnicka River. In that manner copper concentration increases 25-40 times.

RESULTS AND DISCUSSIONS FROM THE MONITORING IN 2012

The latest monitoring of the ground and surface waters around the Buchim mine has been established after the construction of the copper leaching facility. The leaching facility has been located under the main waste dump of the Buchim mine and encompasses all the drainage surface waters from the waste dump and the Buchim mine. There is closed circular system for treated waters and surface waters are completely encompassed within the system. Studied monitoring sites of established piezometers have shown significantly lower values for copper and other parameters measured in 2012 than those in period 2008-2010. These findings are given in the review below.

As may be seen from the Table above we have monitored several water parameters during the 2012. For the performed annual monitoring period measured parameters have shown wide range of values. For example: pH 3.60÷7.95 (std. 6.0÷6.3), height of water in piezometers 2.70÷7.70 m, HPK MnO_4 2.50÷97.90 mg/l (std. 5.01÷10.0 mg/l), total residue at 105^{O}C of 415÷8706 mg/l, dissolved mater 410÷8266 mg/l (std. 1000 mg/l), suspended mater 5÷1206 mg/l (std. 30÷60 mg/l), copper 0.01÷0.68 mg/l (std. 0.05 mg/l), silver 0.001÷0.02 mg/l (std. 0.02 mg/l), ammonia 0.06÷3.25 mg/l (std. 10 mg/l), nitrates 3.50÷43 mg/l (std. 15 mg/l), nitrites 0.07÷1.16 mg/l (std.0.5 mg/l) and total phosphates 0.01÷0.61 mg/l (std. 0.0071÷0.02). From the review of the monitoring of ground and surface waters, around the Buchim mine, for the 2012, can be concluded that in most of the examined parameters we have the continuity of the measured values does not drastically differ from the standards for ground and surface waters. Surely as a main parameter in these research is copper whose concentrations are still continuing to hold our statistical review and is expressed through diagrammatic presentation. It is evident that copper concentrations even in these samples shows increased values in terms of standards, but however those concentrations are significantly lower in comparison to ones determined in waters around the Buchim mine before the construction and putting into operation of the copper leaching facility.

By analogy to copper, continuously increased values, mainly in piezometers, have been determined for nitrates, phosphates, dissolved solids and partly HPK $KMNO_4$. One of especially remarkable parameters that is continuously measured and which contribute to the increased solubility of particular elements in solutions is the pH. Regarding this parameter we had certain decrease and deviation from neutral values. The lowest values of pH have been determined in piezometer S-3 during the monitoring in September, 2012, when the groundwater level was drastically low. During that period copper conce-ntrations usually have shown increased values, too. Especially, here we would like to point out copper values for the above mentioned monitoring period in 2012 (Table 3).

Table 3. Mointoring of the copper concentrations in waters around the Buchim Mine

	March, 2012 (mg/l)	June, 2012 (mg/l)	September, 2012 (mg/l)	December, 2012 (mg/l)	MDK (mg/l)
VP-1	0,048	0,035	0,011	0,012	0,05
VP-2	0,032	0,021	0,012	0,017	0,05
S-1	0,021	0,020	0,010	0,011	0,05
S-2	0,048	0,500	0,510	1,640	0,05
S-3	0,004	0,140	0,320	0,410	0,05
S-4	0,017	0,050	0,011	0,010	0,05
S-5	0,353	0,060	0,330	0,460	0,05
S-6	0,221	0,023	0,013	0,030	0,05
S-7	0,012	0,680	0,640	0,340	0,05

From the Table above it can be seen that in the majority of analyzed water samples have been determined higher concentrations than the maximally allowed concentrations

(MDK) for copper in class III waters That there is a correlation between the measuring points and obtained copper concentrations in different periods of 2012, can be seen at the diagram below (Figure 2).

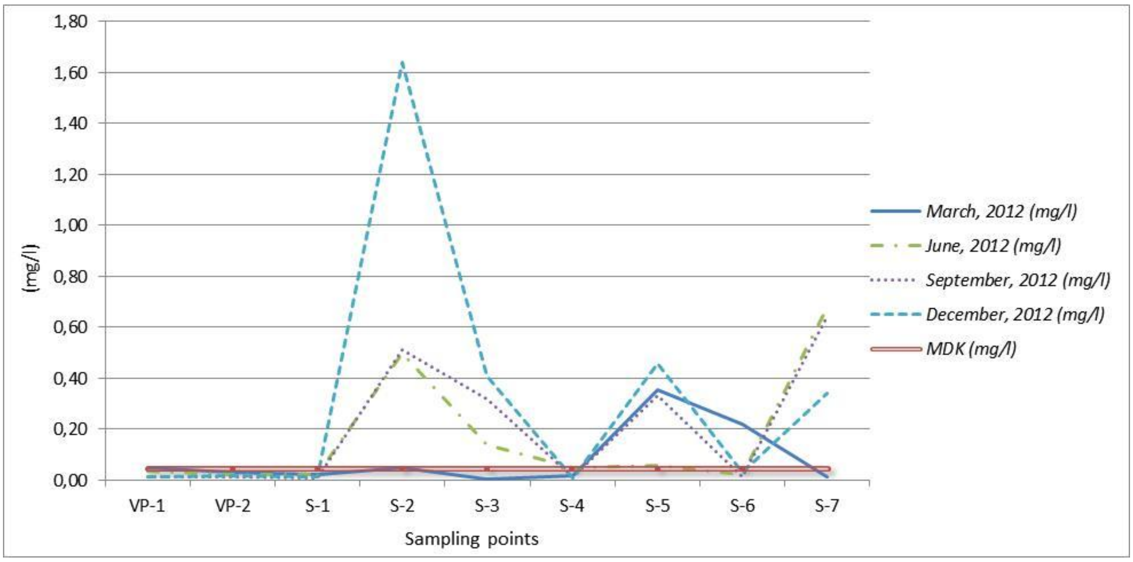

Figure 3. Diagram of copper distribution in the drainage mine waters around the Buchim copper mine

From the diagram above can be seen that values for all of the four monitoring of ground and surface waters in the adjacent vicinity o of the Buchim Mine remain synchronous. Joint feature of all samples that were analyzed is that the most of them had increased copper concentrations in comparison to the MDK values for the class III waters. At particular monitoring points such are S-2 and S-5, copper concentrations in all four monitoring periods have shown increased values. Also, it can be seen that at all four monitoring there is a continuity in copper values, which emphasizes the fact that the copper contaminations at certain points are directed by their persistent contamination sources.

This conclusion is confirmed by the fact (Figure 1), that monitoring point S-2 and S-5 are positioned at the locations in which there is a administered inflow-outflow of surface or ground water. For S-2 that is the stream, which represents the outflow of contaminated water from Buchim Lake, while the monitoring point S-5 is located within the drainage system of Jasenov Dol, which drains water from the main waste dump.

CONCLUSION

The drainage system around the Buchim copper mine manifested pronounced acidic character of mine waters (pH 3.6-5.5) and increased copper concentrations of up to 800 mg/l Cu. That was reason for construction of leaching facility for production of cathode copper, which have encompassed almost all the surface waters from the Buchim mine drainage system. The leaching facility is of closed type and surface waters around the Buchim mine occur only occasionally.

From the review of the monitoring of ground and surface waters, around the Buchim mine for the 2012, it can be concluded that for the most of studied parameters we have continuity of the measured values that does not drastically differ from the standards for ground and surface waters.

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