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CHEMICAL PARAMETERS OF BLOAJA VALLEY WATER AFFECTED BY ACID ROCK DRAINAGE, BĂIUȚ MINING AREA, ROMANIA

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ABSTRACT. Mining areas are among the most polluted industrial sites, the surface waters being often affected by acid rock drainage. Mine and processing wastes represents one of the main sources of acidic waters. The seepages form Bloaja tailings management facilities have a low pH and increased total dissolved solids. Chemical analyses show high Zn, Cu and Pb concentrations of the contact water with the pyrite concentrate deposited on Bloaja Old tailings management facility. These polluted waters are discharged in the watercourses, decreasing the quality of surface water. Despite of the remediation of Bloaja New tailings management facility, the waste waters seepages have a conspicuous environmental impact on watercourses from Lăpuș River basin.

Key words: *mining area, tailings, acid rock drainage, pyrite concentrate, heavy metals, water pollution.*

INTRODUCTION

The development of human society through history is strongly associated with complex materials made from mineral resources. Mining is one of the most polluting industries, with serious effects on human health (Candeias et al., 2018). In mining regions, the risks related to the management of mine wastes and tailings are very high both in the operational phase and in the post-closure time (Kossoff et al., 2014). A difficult environmental issue occurring in mining regions is acid rock drainage characterized by elevated metals concentrations of underground and surface waters (Nordstrom, 2011).

Finding a control and/or treatment strategy of these phenomenon for a certain mining region is a complex task due to the diversity of factors on which the formation depends (Skousen et al., 2019). The geochemical background of the studied area is important in order to assess the contribution of acid rock drainage to the water chemistry (Matschullat et al., 2000).

The century-old mining of the non-ferrous metals ore deposits in Baia Mare region, one of the most famous mining region from Romania, has led to a heavy legacy for all environmental components: air, water and soil. Some heavy metals pollution problems have been attenuated by the closing of mining activities which begins in 2006 and by some rehabilitations measures implemented on the most severely affected areas. However, the management the waters affected by the acid rock drainage has not been addressed properly in order to minimize the associated risks (Costin and Baciu, 2010).

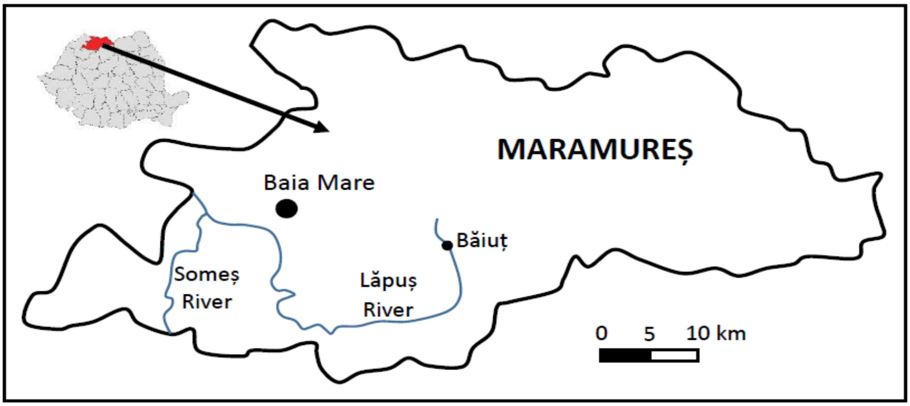

Fig. 1. *Location of Băiuț mining area in Maramureș County*

This paper is focused on some aspects of environmental impact of processing wastes from Băiuț mining area, a mining district of Baia Mare region. The aim of this study is to evaluate the consequences of the acid rock drainage discharged from Bloaja Valley tailings management facilities on the chemistry of surface waters in order to facilitate the finding of better remediation methods.

STUDY AREA

Băiuț area is located at 80 km south-east of Baia Mare city, in easternmost part of Oaș-Gutâi-Țibleș volcanic mountains, geographical unit belonging to East Carpathians (figure 1). Considering the values of the landscape fragmentation density and the maximum elevations, this area has sub-mountain characteristics. Lăpuș River springs from this region and downstream it collects a relative large number of small creeks forming the main watercourse of the Lăpuș sedimentary basin. The landscape formation was strongly influenced by the complex geological structure.

A geological succession of Mesozoic, Paleogene and Neogene sedimentary formation (clays, marls, sandstone and limestone) was partially covered by volcanoclastics and volcanic rocks (mainly andesite) and pierced by subvolcanic bodies (Aroldi, 2001). Associated with volcanic activity, a metallogenetic episode has generated ore deposits (Borcoş and Gheorghiţă, 1976). Veins are the main orebody type of these deposits, having a polymetallic character (lead, zinc, copper) with significant amounts of precious metals (gold and silver). The geological and geochemical characteristics of the ore deposits define its assignment to the epithermal type (Costin, 2000; Costin and Vlad, 2005).

The valorization of mineral resources has a long tradition in Băiuț area, the first mining activities being carry out in the Middle Age time (Achim and Ciolte, 1991). The awareness of environmental problems associated with mining has begun to emerge in the last few decades. The main sources of acid rock drainage are the discharged waters from the closed underground works and in conservation tailings management facilities. Băiuț area is considered one of the most important pollution point in the north-western Romania (Bird et al, 2003). Some preliminary data were presented by Costin and Marina (2006) and Costin (2007) regarding the pollution associated with acid rock drainage occurring in one of the ore extraction field. Detailed studies were conducted in Băiuț area in order to assess the heavy metals pollution effects on the soil quality (Chira et al., 2014; Doroțan et al., 2015; Doroțan et al., 2018). Maramureș County Committee for Emergency Situations (2016) included Băiuț area on the list of the main areas of the Maramureș County potentially generating pollution on watercourses due to the existence of the closed mine facilities and mine wastes.

Bloaja Valley belongs to the upper basin of Lăpuș River. This typical mountain v-shape valley with a length of approx. 3 km is a left tributary of Lăpuș River. Two tailings management facilities (TMF) were built up in this area: Bloaja New cross-valley type tailings impoundment and Bloaja Old side-hill type tailings impoundment. The area is located at 7 km downstream of the former flotation plant.

Bloaja New TMF has an area of 15.30 ha, a length of 525 m, an average width of 217 m, and a capacity of 2.46 million m^3. Due to the small slope of the natural terrain (1.2%), two dams were gradually raised in order to create the necessary space to tailings deposition in the pond: a smaller upstream dam and a larger downstream dam. The height of the downstream dam is 44.50 m. Upstream of the TMF, the diversion of Bloaja Valley was made through a visiting canal with a length of 517 m, built of reinforced concrete. In the extension of the canal, a tunnel with a length of 243 m was excavated in the slope hill on the left side of the valley.

In the operational phase, the freewater from the pond that resulted after the tailings sedimentation was evacuated by three decant wells connected to a pipe laid on the bed of the TMF. The surface water runoff which passes through the upstream tailings dam is released at the base of the dam diffusely forming a swampy area. Drain pipes were installed at the bottom of the downstream dam in order to control the seepage outflow. The collected water is spilled into Bloaja Valley, downstream of the tunnel.

The commissioning of the pond was carried out in 1975 and it was operational until 2007 when Băiuț mine was closed. During this time, there were no damages that would endanger the stability of the pond and the safety of its operation. In the post-closure period, a reclamation and ecological rehabilitation program has been carried out on the surface of the pond and the two dams. The main objectives of the works were to control the runoff and erosion, the infiltration, and the seepage. After the compaction and levelling of the tailings, the surface of the TMF was covered with geomembrane. Geotextile materials added on top of this impermeable level provided the foundation of the topsoil which has been cultivated with local vegetation. On the reclaimed TMF, a surface water diversion system composed by a network of concrete channels has been installed. A complex system of drains linked to the surface water channels is used to manage the seepages. There is no water treatment facility downstream of the reclaimed TMF

Located at 450 m SW from Bloaja New TMF, was in operation between 1972 and 1975. After its closure, initially these impoundments were managed as an emergency facility in case of unforeseen events that would occur at the deposition to the tailings in the new TMF. Due to the short time of operational phase, a small amount of tailings was deposited (approximately 91,000 m^3) on a surface area of 5.20 ha. The height of the dam is 10 m. Later, a concrete wall was built on the northern and western sides of Bloaja Old TMF to store the pyrite concentrate which could not be marketed as piles. No maintenance and remediation works were done on this TMF. Rills and gullies are created by the surface water that runoffs freely over the concentrate and the tailings, transporting these mineral materials outside the TMF and covering large areas of flat terrain in the nearby. The contact water forms small pool on the surface of the TMF or it is collected in a small channel made on the bottom of the dam from where it is discharged into Bloaja Valley.

SAMPLING AND ANALYTICAL METHOD

In order to evaluate the quality of the surface water in the area of the two TMF, a sampling network with ten points was chosen. The location and the description of the sampling points are presented in figure 2 and table 1.

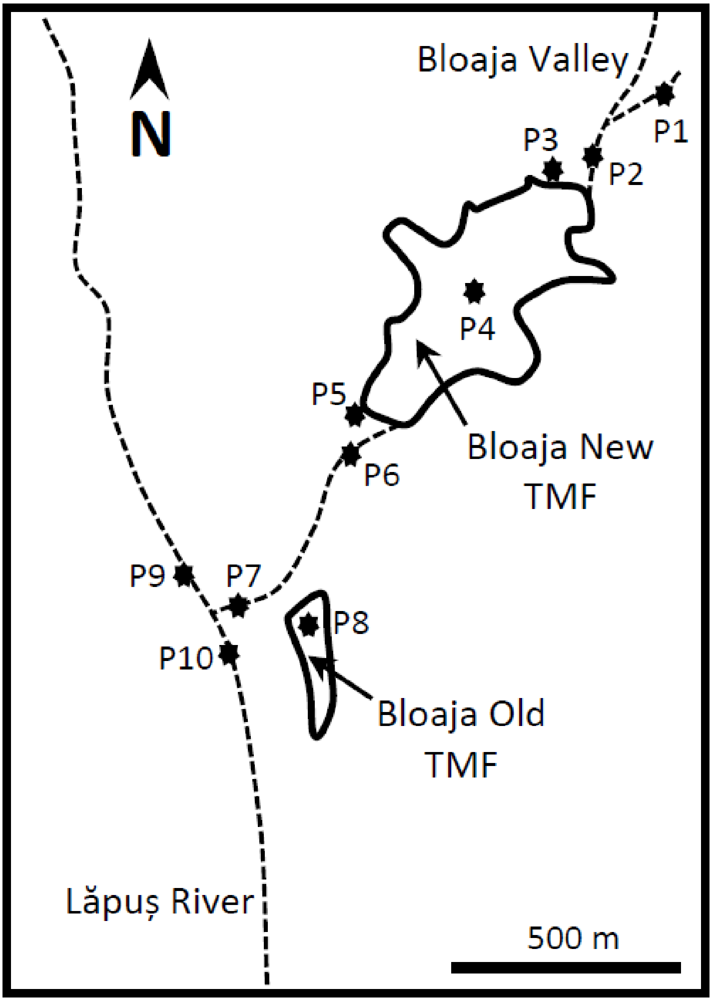

Fig. 2. *Map of the sampling points from Bloaja Valley area*

Table 1. *The site characteristics of water samples*

Sample	Description
P1	Small creek, left tributary of the Bloaja Valley, 200 m upstream of the Bloaja New TMF
P2	Surface water from the Bloaja Valley, 50 m upstream Bloaja New TMF
P3	Seepage water from the upstream dam of the Bloaja New TMF
P4	Surface water collected in the main channel of the diversion system constructed on the reclaimed pond
P5	Seepage water from the downstream dam of the Bloaja New TMF
P6	Surface water from the Bloaja Valley, 100 m downstream Bloaja New TMF
P7	Surface water from the Bloaja Valley, 50 m before the confluence with the Lăpuș River
P8	Surface water from the small pool located on the surface of the Bloaja Old TMF
P9	Surface water from the Lăpuș River, 100 m upstream to the confluence with the Bloaja Valley
P10	Surface water from the Lăpuș River, 100 m downstream to the confluence with the Bloaja Valley

The P1 and P2 samples were collected from pristine streams unaffected by the mining or other human activities and can be considered as reflecting the geochemical background of the study area. In order to assess the chemistry characteristics of the water due to the water-tailings interaction, three samples were analysed: P3, P5 are the seepages from the dams and P4 represents water drained from the surface of Bloaja New TMF in diversion channel. The P6 water was sampled from Bloaja Valley downstream Bloaja New TMF, considering that this sample reflects the impact of the flotation wastes on surface water. Located at 500 m downstream of the previous sample, the P7 comprise surface water from Bloaja Valley prior to the confluence with Lăpuș River. The sample water P8 was collected from a small pool formed by the accumulation on the surface of Bloaja Old TMF of meteoric water which interacted with the pyrite concentrate along the slope of the piles. Two samples of surface water (P9 and P10) from Lăpuș River were collected in order to evaluate the possible influence of Bloaja Valley tributary on the chemistry of river water.

Given the characteristics of the samples and their location, P1, P2, P6, P7, P9, and P10 can be considered as surface water samples. P3, P4, P5, and P8 are wastewater samples because the chemical characteristics of these waters resulted from the interaction with waste materials deposits: tailings facility and pyrite concentrate piles. To evaluate the quality of water samples, appropriate national regulations must be applied: Order 161/2006 for surface water and NTPA 001-2002 for wastewater.

In each sampling point, two subsamples were collected: one for pH, redox potential (Eh), electrical conductivity (EC), total dissolved solids (TDS) using a portable multiparameter (WTW Inolab 320i), the other was passed through a 0.2 μm filter and acidified with $HNO3$ to pH < 2 for metal analysis. A ZEEnit 700 atomic absorption spectrometer using an acetylene–air flame, a graphite furnace and the adequate cathode lamps at the recommended current and conditions (specified in the FAAS Operators Manual) was used to determine the heavy metals content of four samples.

RESULTS AND DISCUSSION

The values of physico-chemical parameters for the investigated water samples are presented in table 2.

Table 2. *The physico-chemical parameters of water samples*

Sample	pH	ORP (mv)	EC (μS/cm)	TDS (mg/l)
P1	6.26	16.9	165	82.5
P2	6.78	-2.8	265	132.5
P3	6.50	13.7	1997	998.5
P4	6.52	6.8	1039	519.5
P5	6.61	1.2	1782	891
P6	6.73	-3.2	481	240.5
P7	7.12	-26.8	470	235
P8	2.59	228.9	1564	782
P9	5.85	46.2	137	68.5
P10	6.31	21.3	171	85.5

All the samples except one show an acidic environment, the pH values ranging from 2.59 to 7.12 (figure 3). The slight acidic values are due to the geochemical background of the study area (P1, P2), the acid rock drainage caused by water-tailings interaction (P3, P4, P5, P6), and to the combination of the geochemical background and the mine wastes pollution (P9, P10). The lower value of pH (2.59 for P8) is the consequence of the intense acid rock drainage generated by the meteoric water which percolates the pyrite concentrate (a very rich sulphide material). A neutralization process is responsible for the neutral value of the pH for the P7 sample, the acidic water downstream Bloaja New TMF being diluted by small tributary creek of Bloaja Valley, unaffected by acid rock drainage.

Comparing P9 and P10 sampled from Lăpuș River (figure 4), it can be observed a slight increase of the pH, caused by the neutral water influx of Bloaja Valley tributary. The mixing of acidic water from Lăpuș River with neutral water from Bloaja Valley has a limited neutralization effect due to the lower water flow of the valley compared to the river. The pH values measured in all samples fall within the limits (6.5 – 8.5) provided by national legislation (Order 161/2006, NTPA 001-2002).

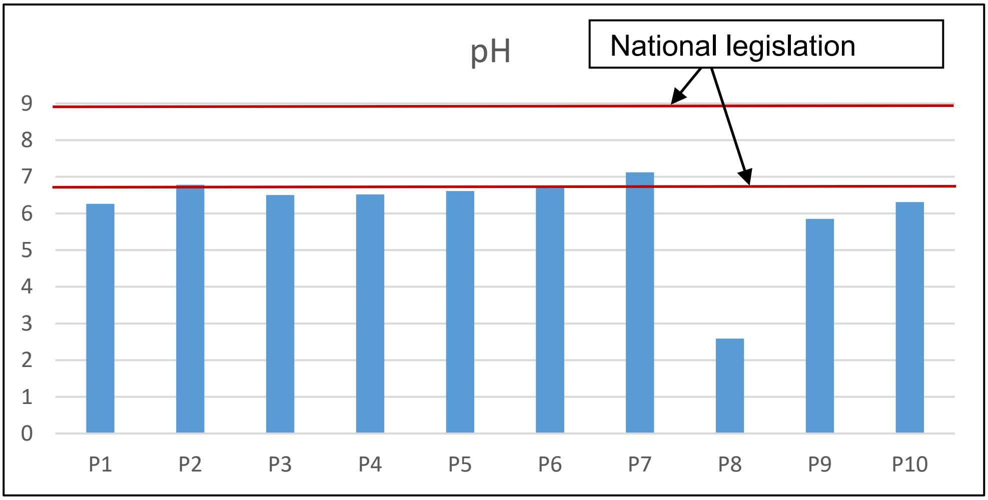

Fig. 3. *The pH values of analyzed samples*

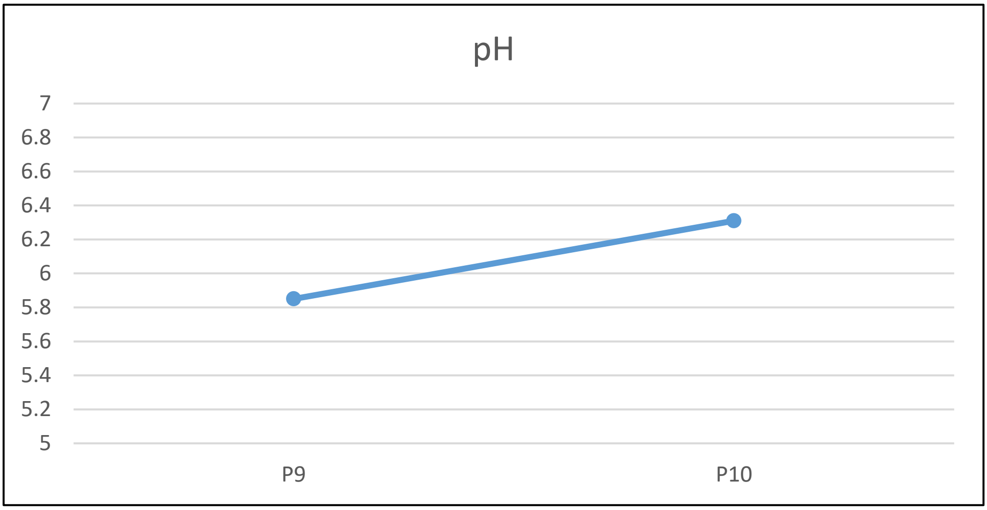

Fig. 4. *The pH variation of Lăpuș River samples, upstream and downstream of Bloaja Valley confluence*

The TDS values ranges from small values (68.5 mg/l for P9) to higher values (998.5 mg/l for P3) (figure 5). Small TDS concentrations (below 150 mg/l) are specific to unpolluted water (P1, P2) or to the diluted water as a consequence of the high water flow of the River Lăpuș (P9, P10). The medium values of the TDS (P6, P7) are due to the starting of a neutralization process as a result of mixing with unpolluted waters.

Acid rock drainage influenced waters (P3, P4, P5, P8) show the higher concentration of TDS, above 500 mg/l. It can be noticed that the TDS values of the seepages from the upstream dam (P3) and the downstream dam (P5) are higher than the TDS value of the water sample collected form the diversion channel (P4). This difference of the acid rock drainage concentration is due to the longer interaction time between tailings and water necessary to generate seepages than specific for runoff waters. The higher value of the TDS for P3 and P5 (tailings dam's seepages) comparing to the TDS value of P8 (small pool from pyrite concentrate piles) can be explained by the longer time of the water-tailings interaction than the water-pyrite concentrates as a consequence of the material volume which is bigger in the case of tailings.

A slight increase of TDS value can be reported in the case of the two samples collected form Lăpuș River, upstream (P9) and downstream (P10) of the confluence to Bloaja Valley (figure 6). The TDS concentration of Bloaja Valley water (P7) is higher than that of Lăpuș River water upstream of the confluence.

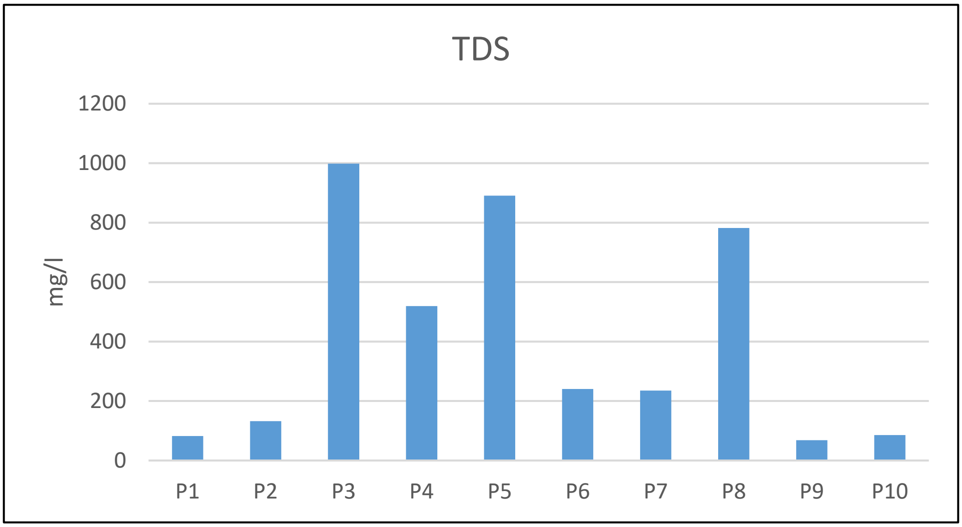

Fig. 5. *The TDS values of analyzed samples*

Due to the mineral characteristics of the tailings and pyrite concentrate, the Zn, Cu, Pb, Cd, and Ni contents in the waters that interacted with these wastes have been measured for P3, P4, P5, and P8. The metal concentrations of the seepages from the dams (P3, P5) and the water collected from diversion channel (P4) are low (table 3).

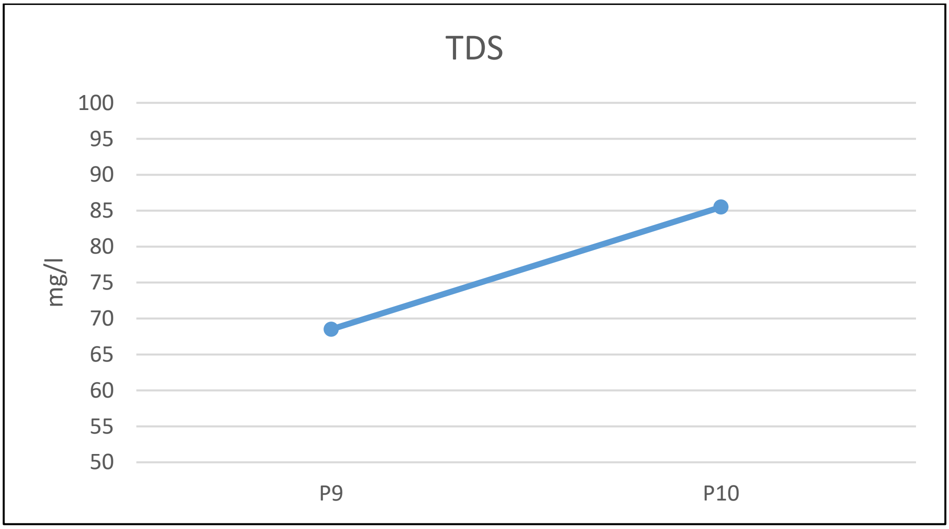

Fig. 6. *The TDS variation of Lăpuș River samples, upstream and downstream of Bloaja Valley confluence*

Table 3. *Metal concentrations of the contact water samples with mining wastes*

Sample	Zn (mg/l)	Cu (mg/l)	Pb (mg/l)	Cd (mg/l)	Ni (mg/l)
P3	0.129	ND	0.07668	ND	0.0440
P4	0.639	ND	0.03787	ND	0.0840
P5	0.197	ND	0.08614	ND	0.0212
P8	3.382	4.397	0.509	0.035	0.151
NTPA 001-2002	0.5	0.1	0.2	0.2	0.5

ND – non detected

The copper concentration for P4 is the only value which is higher than national standard NTPA 001-2002 and Government Decision 352/21.04.2005. Despite the fact that acid rock drainage is generated in the tailings, due to the small content of the sulphides in waste materials the metal concentration is low. Conversely, in the case of water sample which interacted with the pyrite concentrate (P8) the metal concentration is very high, especially for Zn, Cu, and Pb.

Reporting these values to the relevant national legislation (NTPA 001-2002, Government Decision 352/21.04.2005), the Zn concentration is six times higher, the Cu concentration is forty-three times higher and the Pb concentration is two times higher than maximum allowable limits (figure 7). These values can be explained by the mineral composition of the pyrite concentrate. During the pyrite flotation process, small quantities of other metal sulphide are separated in addition to iron sulphide. Accordingly, the metal concentrations of acid rock drainage generated by the water percolation of the pyrite concentrate piles are higher than the contact water collected from the TMF.

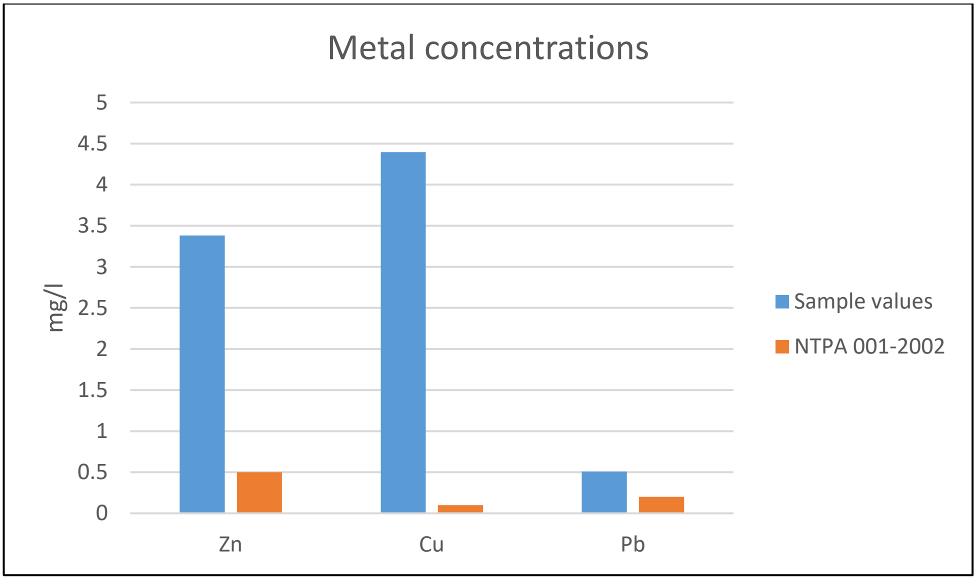

Fig. 7. *Zinc, copper, and lead concentrations of P8 water sample compared with maximum allowable limits from national legislation*

CONCLUSION

The historical mining activity in the Băiuț area has led to the accumulation of some environmental problems whose consequences are still present today. After the mine closure, some rehabilitation works were done in order to reduce the environmental impact of mine facilities (underground mine and tailings management facilities). However, these post-closure operations did not have a significant effect on acid rock drainage generated in underground mine works and mine wastes, Băiuț area being a surface waters pollution hotspot for Someș Basin. Such a source of pollution are the two tailings management facilities located on Bloaja Valley. The water which percolates the mining residues has a low pH and increased TDS values. Very high metal concentrations (Zn, Cu, Pb) were recorded for the contact water with the pyrite concentrate. All the acid rock drainage affected waters are discharged in Bloaja Valley, a left tributary of Lăpuș River. Due to the higher flow of the Lapuș River than that of the Bloaja Valley, the effect of the discharged waters from TMFs is not very conspicuous.

Further studies are necessary in order to determine the chemistry of water unaffected by human (especially mining) activities that is closely related to geochemical background. A new more complex rehabilitation program would reduce the environmental risk associated with acid rock drainage and its impact on the surface water.

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