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CHEMICAL CHARACTERISATION OF ACID MINE DRAINAGE AND ITS IMPACT ON SURFACE WATER QUALITY IN THE FORMER MINING AREA OF VALEA VINULUI (BISTRIȚA COUNTY – ROMANIA)

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ABSTRACT. Acid mine drainage (AMD) represents a major source of environment pollution in both active and former mining areas. AMD have a high acidity and high levels of sulphate and toxic metals. The present study was focused on assessing the chemical caracterisation of AMD generated Gheorghiu gallery - Valea Vinului minining area and to evaluate the impact of AMD disposal onto surface water by calculating relevant water index. The AMD samples proved to be highly acidic (pH between 2.6 and 4.0) and contaminated with Zn, Cu, Al and Mn. The discharge of untreated acidic waters has a negative impact on Valea Băilor creek by increasing the content of Zn and Mn. The values of both HPI and MI confirm the negative impact of AMD discharge on the quality of surface water.

Key words: *acid mine drainage, mining area, Valea Vinului mine, heavy metal pollution index, metal index.*

INTRODUCTION

Once exposed to water and oxygen, most sulphide minerals are oxidised and form sulphuric acid, metals ions or sulphate, generating acid mine drainage (AMD) (Akcil and Koldas, 2006; Skousen et al., 2018; Skousen et al., 1999). The AMD are characterised by low pH, high conductivity and high levels of alkaline-earth metals, iron, aluminium, manganese, sulphate, bicarbonate and various toxic metals (Pb, Ni, Cd, As, etc.) (Equeenuddin et al., 2010). AMD is one of the severe environmental problems, which once generated is difficult to control and treat (Kefeni et al., 2017). When acidic waters reach surface or underground waters, they can contaminate the water body with toxic metals and making it unsuitable for domestic, agricultural or industrial usage (Skousen et al., 2018; Evans et al., 2015; Hogsden and Harding, 2012). The AMD can also degrade the soil quality by contaminating the soil with sulphate or heavy metals. The abandoned mines represent the main contributor of AMD.

In recent years, much attention has been paid to the assessing of water heavy metal contamination through specific indexes like heavy metal pollution index (HPI) and metal index (MI) (Pal et al., 2017; Mohan et al., 1996; Reddy, 1995; Balakrishnan and Ramu, 2016). HPI is reflecting the composite influence of different heavy metals present in water samples and it is calculated considering the suitability of water for human consumption. The critical HPI value for drinking water should be less than 100. Metal index (MI) is useful in evaluating the overall quality of drinking water, by taking into account the possible additive effect of heavy metals on human health (Balakrishnan and Ramu, 2016).

The present study was focused on assessing the chemical caracterisation of AMD generated in Valea Vinului minining area and to evaluate the impact of AMD disposal onto surface water by calculating relevant water index. The results of the preliminary study conducted in the area were published last year by the authors (Roba et al., 2017). In order to improve the investigation, the study continued during 2017 and 2018 by analizing new chemical parameteres. Few recent studies were conducted in the area (Maicaneanu et al., 2013; Nimirciag, 2012).

Valea Vinului village is located in Rodna commune (Bistrița Năsăud County, Romania) close to Rodnei Mountains National Park. Valea Vinului mining area is situated at about 13 km from Rodna. The mineral exploitations dates back to the Roman times and it was focused on iron and lead extraction, while during the medieval times, the gold and silver were mainly extracted (Maghiar and Olteanu, 1970; Nimirciag, 2012).The complex ore contains high amounts of Zn (5–15%), Pb (up to 4%) and Ag (30–40 g/t) (Mârza, 1977; Maicaneanu et al, 2013), the minerals being extracted from adits located between 665 and 1225 m in depth. In 1996 Valea Vinului mine was declared as being in conservation and in 1998 the mine was closed by a Government decision.

MATERIALS AND METHODS

Sampling

A total of 24 samples were collected from the acidic mine drainage generated by the Gheorghiu Gallery (Valea Vinului mine), from six sampling points (P1 – P6), over a distance of 100 m (figure 1). The AMD are discharged in Valea Băilor creek and then later in Someșul Mic River. In order to evaluate the impact of AMD discharge onto surface water quality, 12 samples were collected from Valea Băilor creek, from one sampling point (P7) located 100 m upstream of the acidic mine discharging site and two sampling points (P8 and P9) located 100 m and 200 m respectively, downstream of the acidic mine discharging site (figure 1). The waters were sampled during summer (June 2017, July 2017) and spring season (April 2018, May 2018).

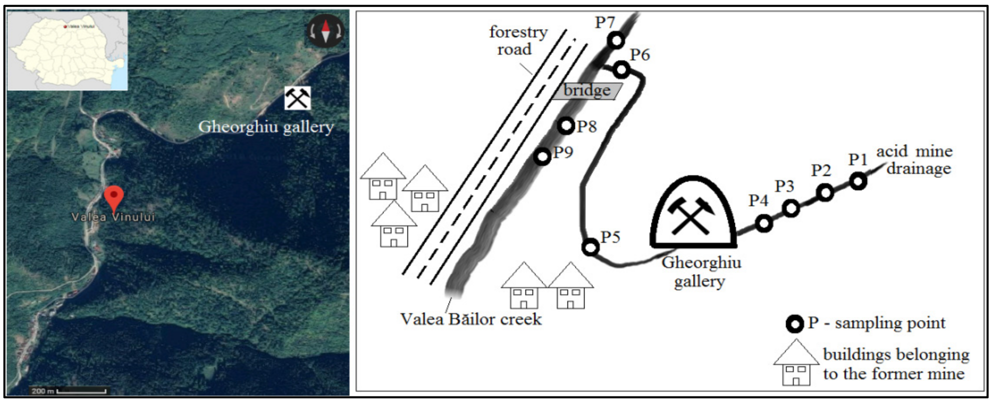

Fig.1. *Location of the investigated area (left) (modified after Google Earth) and sketch with the position of the sampling points (right).*

Analysis of the quality parameters

In order to assess the water quality, a total of 17 physicochemical and chemical parameters were analysed for each sample.

The investigated physico-chemical parameters were: pH, redox potential (ORP), electrical conductivity (EC), total dissolved solids (TDS), and salinity. These parameters were measured *in situ* using a portable multiparameter (WTW multi350i, Germany). Chemical parameters included twelve metals (Na, Al, Mn, Zn, Mg, Ca, Ni, Pb, Cu, Cd, Ti and Sr), which were analysed by inductively coupled plasma mass spectrometry (ICP-MS) by using an Perkin Elmer ELAN DRC-e instrument, equipped with a Meinhard nebulizer and a glass cyclonic spray chamber for pneumatic nebulization. The operating conditions were: nebulizer gas flow rates, 0.92 /min; auxiliary gas flow, 1.2 l/min; plasma gas flow, 15 l/min; lens voltage, 7.25 V; radiofrequency power, 1100 W; CeO/Ce ratio = 0.030; and Ba++/Ba ratio =0.026.

Before ICP-MS analysis, the water samples were filtrated (0.45 μm) and acidified to pH≈2 (with HNO_3 65%). The samples were stored in the laboratory at dark and 4ºC, and analysed within three days from sampling.

Heavy metal pollution index (HPI) and metal index (MI)

HPI was calculated based on the equation given by Mohan et al. (1996):

$$HPI = \frac{\sum_{i=1}^{n} W_i \cdot Q_i}{\sum_{i=1}^{n} W_i}$$

where: W_i is the unit weightage of the i^{th} parameter defined as reciprocal value of S_i (Pal et al., 2017) (S_i is the maximum permissible limit for drinking water given by national legislation – Law 458/2002 regarding the quality of drinking water) and Qi is the sub quality index and is calculated using the formulae (Mohan et al. 1996; Pal et al., 2017):

$$Q_i = \sum_{i=1}^{n} \frac{M_i}{S_i} \cdot 100$$

where: M_i is the monitored value of heavy metal, S_i is the standard value (maximum permissible limit for drinking water given by national legislation)

MI was preliminarily defined by Tamasi and Cini (2004) as follows:

$$MI = \sum_{i=1}^{n} \frac{C_i}{MAC_i}$$

where: C_i is the concentration of each metal in the sample, MAC_i is the maximum allowed concentration for each element (maximum permissible limit for drinking water given by national legislation).

RESULTS AND DISCUSSIONS

Chemical characterisation of acid mine drainage and Valea Băilor creek

The AMD samples (samples P1 – P6) were highly acidic having the pH between 2.6 and 4.0 (Fig. 2), being considerably lower than the permissible limit (6.5 – 8.5) imposed by national legislation for wastewaters discharged into natural surface waters (Government Decision no. 352/21 April 2005). The most acidic values were registered during April 2018, fact that can be correlated with the snow melting process and the high amount of precipitation which has increased the acidic mine drainage. Based on the previous study (Roba et al., 2017), the waters proved to be more acidic in April 2018 (pH between 2.6 and 3.2) than in April 2017 (pH between 3.1 and 3.4). These acidic waters are discharged into Valea Băilor creek without any prior chemical treatment. As a consequence, in some sampling intervals, the creek water had a pH lower than 6.5 – 8.5, which is the permissible limit impose by national legislation (Order no. 161/16 February 2006) (Fig. 2). It is necessary to treat these AMD waters in order to reduce their impact on Valea Băilor creek, Someșul Mic River, or onto underground water and the soil from the area.

Because of the low pH, the AMD waters had a positive ORP, between +169.2 and +228.8 mV, comparing to Valea Băilor creek, where the ORP was lower (-14.6 and +43.6 mV) (Fig.2). The AMD samples had high levels of EC (1426 – 2490 μS/cm), TDS (892 – 1556 mg/l) and salinity (0.7 – 1.3 ‰), reflecting the high amount of dissolved salts (figure 2). Generally, these parameters were higher during April 2018 (Fig. 2), fact that can be correlated with the snow melting and the high amount of precipitation registered during that period, which increased the acidic mine drainage and the dissolution of ions especially sulphates. After the discharge of AMD, there was a slightly increasing of EC, TDS and Salinity levels between the upstream (P7) and downstream (P8 - P9) sampling points (figure 2).

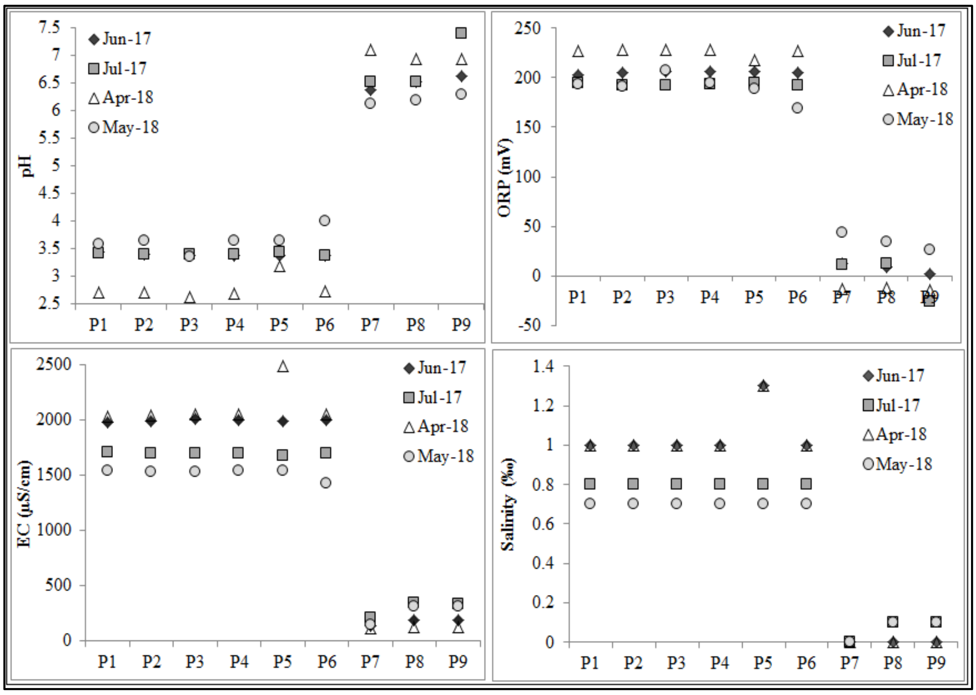

Fig. 2. *Seasonal fluctuation of physico-chemical parameters in acid mine drainage (P1 - P6) and surface waters (P7 - P9).*

All the parameters showed a relatively homogenous distribution for both AMD and surface water samples (figure 2).

The AMD samples proved to have high levels of metals, the total content of metals ranged between 210.6 and 217.2 mg/l, comparing to Valea Baii creek (26.7 and 34.1 mg/l) (figure 3). By comparing the total content of metals registered upstream and downstream of AMD discharging point, the results confirm the impact of AMD on the quality of Valea Băii creek.

The metals distributions fallowed the sequence: Ca>Mg>Zn>Mn>Al>Na>Sr>Ti>Cd>Cu>Pb>Ni (figure 4), the values being considerably lower in surface water than in AMD samples.

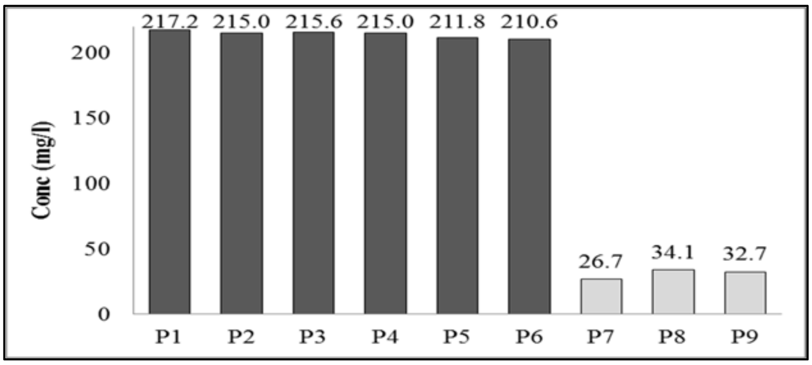

Fig. 3. *Total content of metals in acid mine drainage (P1 - P6) and surface waters (P7 - P9).*

The content of Ca (77.6 – 90.2 mg/l), Mg (61.1 – 79.6 mg/l), Cd (0.14 – 0.18 mg/l), Ni (0.042 – 0.047 mg/l), Pb (0.023 – 0.029 mg/l) from AMD samples was within the permissible limits (300 mg/l for Ca, 100 mg/l for Mg, 0.5 mg/l for Ni, 0.2 mg/l for Pb and Cd) imposed by national legislation for wastewaters discharge into natural surface waters (Government Decision no. 352/21 April 2005). The concentrations of Zn (39.66 – 45.57 mg/l), Cu (0.09 – 0.18 mg/l), Al (5.07 – 6.24) and Mn (7.57 – 8.04) in all acidic mine waters exceeded the national standards (0.5 mg/l for Zn and 0.1 mg/l for Cu, 5 mg/l for Al, 1 mg/l for Mn) imposed for wastewaters discharge into natural surface waters. The AMD samples had a relatively low content of Na (1.9 – 4.6 mg/l), Ti (0.38 – 0.39 mg/l) and Sr (0.35 – 0.45 mg/l).

Considering the low content of Ca (16.6 – 25.5 mg/l), Mg (6.1 – 7.1 mg/l), Na (0.7 – 3.7 mg/l), Cu (1.3 - 9.9 µg/l), Pb (0.1 – 2.1 µg/l) and Ni (1.7 – 2.7 µg/l), the Valea Băilor creek can be classified as 1st water quality class – very good ecological status) (Order no. 161/2006 for the approval of the Normative regarding the classification of surface water quality in order to establish the ecological status of the water bodies, elaborated by the Ministry of Environment and Water Management from Romania). The results obtained in the present study indicated the impact of AMD discharge onto the zinc and manganese level from Valea Băilor creek, which correspond to 5th water quality class (very poor ecological status) and 4th water quality class (poor ecological status).

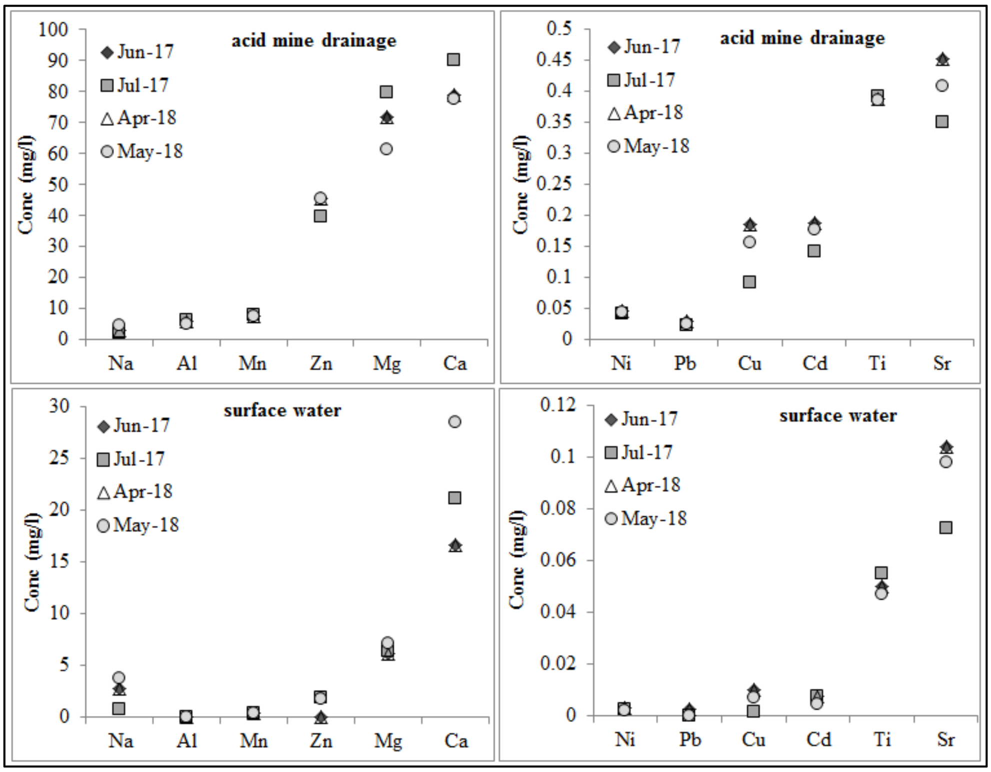

Fig. 4. *Seasonal fluctuation of metals in acid mine drainage (P1 - P6) and surface waters (P7 - P9).*

No significant fluctuation of metals content was observed during the four months.

The Heavy Pollution Index (HPI) and Metal Index (MI) of surface water

The HPI value for the waters sampled upstream of the AMD discarge point (P7) was below the critical index value of 100 (figure5), while the waters sampled downstream (P8 and P9) had the HPI above critical leveel, coresponding to a very poor quality.

Based on MI value, the water samples collected upstream of the AMD discharge (sampling point P7), correspond to class V – strongly affected with respect to metal pollution, having the MI level between 4 and 6 (Lyulko et al., 2001), while the samples collected downstream from AMD discharging point (P8 and P9) are classified as seriously affected, having the MI > 6 (Lyulko et al., 2001) (figure 5).

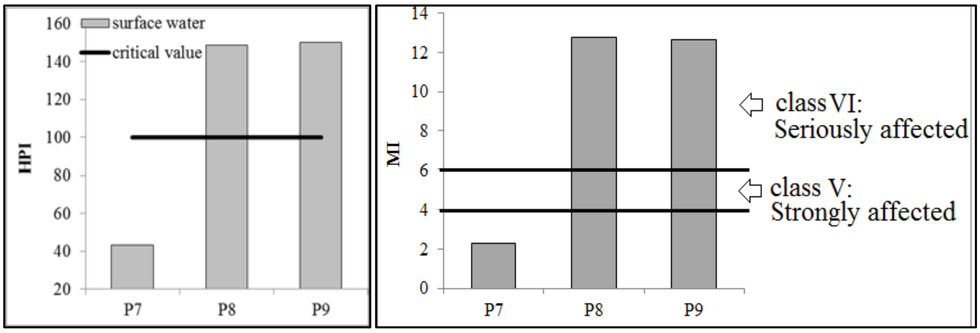

Fig. 5. *The average values for Heavy Pollution Index (**HPI**) and Metal Index (**MI**) for the analysed surface waters.*

The values of both HPI and MI confirm the negative impact of AMD discharge on the quality of Valea Băilor creek. In the proximity of AMD discharging point, the surface water dilution is not high enough to dominate the metal content from AMD. Future investigations should be performed in order to evaluate the quality of Valea Băilor creek on longer distances.

CONCLUSIONS

It can be concluded that the AMD from the Gheorghiu gallery are highly contaminated with Zn, Cu, Al and Mn. The discharge of untreated acidic waters has a negative impact on Valea Băilor creek by increasing the content of Zn and Mn, which correspond to 5th water quality class (very poor ecological status) and 4th water quality class (poor ecological status).

The values of both HPI and MI confirm the negative impact of AMD discharge on the quality of surface water. It is necessary to treat these AMD waters in order to reduce their impact on Valea Băilor creek, Someșul Mic River, or onto underground water and the soil from the area.

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