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CHEMICAL CHARACTERISATION OF ACID MINE DRAINAGE FROM VALEA ȘESEI TAILING DAM (NW OF ROMANIA) AND ITS IMPACT ON SURFACE WATER QUALITY

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ABSTRACT. The acid mine drainage (AMD) can be a major source of water and soil pollution. To evaluate the chemical composition of the AMD and its impact on surface waters, a total of 132 water samples, both surface and waste waters, were collected during four field campaigns in November 2018, December 2018, March 2019 and April 2019. There were also collected several samples from the tailing dam material and sediments from the rivers where acidic waters are discharged. The physico-chemical parameters (pH, redox potential, electrical conductivity, total dissolved salts and salinity) were measured by a portable multiparameter (WTW multi350i, Germany), while the dissolved ions (NO_2^-, NO_3^-, Br^-, F^-, Cl^-, PO_4^{3-}, SO_4^{2-}, Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were analysed by ion chromatography and the metal content (Cu, Zn, Fe, Cr, Cd, Ni, Pb) was determined by atomic absorption spectrometry. Most of the water samples had an acidic pH, with high electrical conductivity values (up to 9,360 µS/cm). The waters had a high level of SO_4^{2-} (up to 8141.8 mg/l), Fe (up to 1,216.2 mg/l), Cu (up to 71.9 mg/l) and Zn (up to 61.98 mg/l). The tailing dam material was characterised by high levels of Fe (39.87 – 40.72 g/kg), Zn (81.3 – 241.1 mg/kg), Cu (343.5 – 942.3 mg/kg) and Pb (41.4 – 77.1 mg/kg). The analyses indicated the negative impact of AMD discharge in surface waters, which proved to have high levels of SO_4^{2-} and heavy metals.

Key words: *acid mine drainage, heavy metals pollution, tailing dam, Valea Șesei.*

INTRODUCTION

Mining activities represents a major source of pollution for the environment, generating pollutants, like heavy metals, which can have a significant negative impact on the environment and human health (Hadzy et al., 2015; Islam et al., 2015; Linkuku et al., 2013). Roșia Poieni (Alba County) is the largest copper ore exploitation from Romania and the second largest in Europe, consisting of more than a billion tonnes of porphyry-type ore, with an average of 0.36% Cu (Milu et al., 2002; 2004; Rzymski et al., 2017). The exploitation of the copper ore is carried out in the open pit manner and all the generated wastes are deposited at Valea Șesei tailing pond, situated on the valley with the same name, which is the right affluent of Arieș River (figure 1). The dam is built from limestone blocks and gravel and it has a height of 118 m and an inclination of 33° (Duma, 1998; Melenti et al., 2011). Downhill from the dam, at approximately 1.2 km, is the confluence between Valea Șesei and Arieș River (Melenti et al., 2011). The acid mine drainage (AMD) generated by the tailing pond, can be a major source of water and soil pollution in the area.

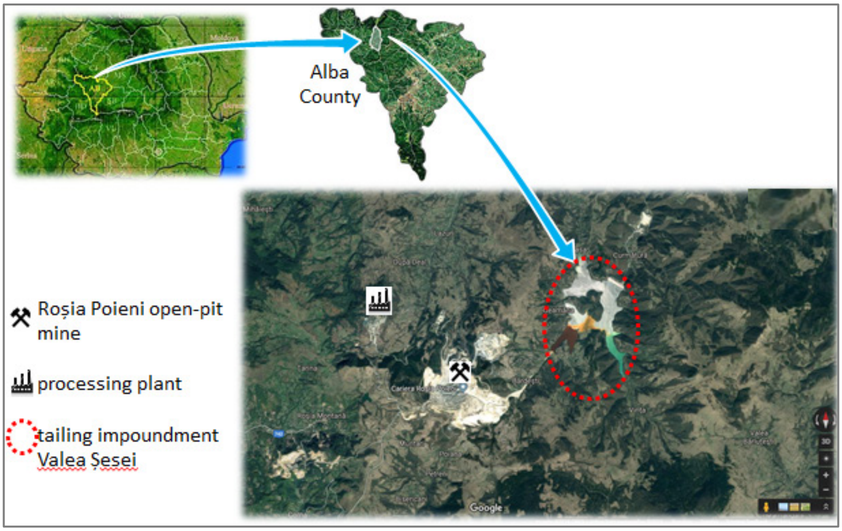

Fig. 1. *Location of Valea Șesei tailing impoundment*

The main purposes of the present study were: (1) to evaluate the chemical composition of sterile deposited on the tailing impoundment; (2) to evaluate the chemical composition of wastewaters generated by the tailing impoundment; (3) to evaluate the impact of acidic mine drainage (AMD) on surface water downstream from Roșia Poieni mine and (4) to assess the seasonal fluctuation of chemical parameters.

Similar studies have been conducted in the area, like the ones performed by Melenti et al. (2011), Milu et al. (2002, 2004), Rzymski et al. (2017), or Ștefănescu et al. (2010).

MATERIALS AND METHODS

A total of 12 sterile samples were collected during November 2018 and March 2019, from six sampling points: S1 – S5 (tailing impoundment) and S6 (tailing pipe). Supplementary, 132 water samples were collected in triplicate, during November 2018, December 2018, March 2019 and April 2019. The water samples consisted of surface waters from Valea Holhorii creek (SW1), Valea Șesei creek (SW2 – SW8), Arieș River (SW9 – SW10) and wastewaters (W1 – W6).

The investigated physico-chemical parameters (pH, Eh – redox potential, EC – electrical conductivity, TDS – total dissolved salts and salinity) were measured using a portable multiparameter (WTW Multi 350i). In the case of water samples, these parameters were measured *in situ*, while for sterile samples they were measured in the laboratory, after the extraction with distilled water (ratio 1:5) (SR 7184-13/2001; Mofor et al., 2017).

The water samples used for the analysis of major dissolved ions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}) were filtered (0.45 μm), kept in the refrigerator (at dark and 4°C) and analysed using an ion chromatograph system (Dionex 1500 IC, USA).

The heavy metals (Pb, Fe, Zn, Ni, Cd, Cu, Cr) analyses were performed by atomic absorption spectrometry (AAS), by using a ZEEnit 700 system (Analytik Jena) equipped with air – acetylene burner, a graphite furnace, and a special hollow – cathode lamp for each metal. Before AAS analyses, the soil samples were dried in oven at 105°C for 24 hours, ground and sieved through 250 μm sieve, then were mineralized with *aqua regia* overnight at room temperature, then heated to reflux on sand bath for 2 h, filtered (0.45 μm) and diluted to 100 ml with HNO_3 (0.5%). The water samples were acidified at a pH ≈ 2 with HNO_3 (65%) and filtered (0.45 μm).

RESULTS AND DISCUSSIONS

Sterile samples

The results for the analysed physico-chemical parameters (figure 2) indicated the heterogenic character of the analysed samples. The sterile from sampling points S2 and S3 proved to be acidic, while the rest of the samples had an alkaline pH. The acidic nature of samples S2 and S3 is a consequence of the location of these two sampling points in the vicinity of the acid mine drainage inflowing from Roșia Poieni copper mine to Valea Șesei. The rest of the samples had an alkaline pH, because they were samples close to the pipe which transports sterile and wastewaters from processing plant, which uses lime as flotation reagent and from the vicinity of the pipe which transports slaked lime for neutralization.

Samples S2 and S3 proved to have the highest EC and salinity, reflecting the high amounts of salts. The seasonal fluctuations indicated that the pH and Eh levels were generally higher during March 2019, while the EC and salinity were higher during November 2018, comparing to March 2019 (figure 2).

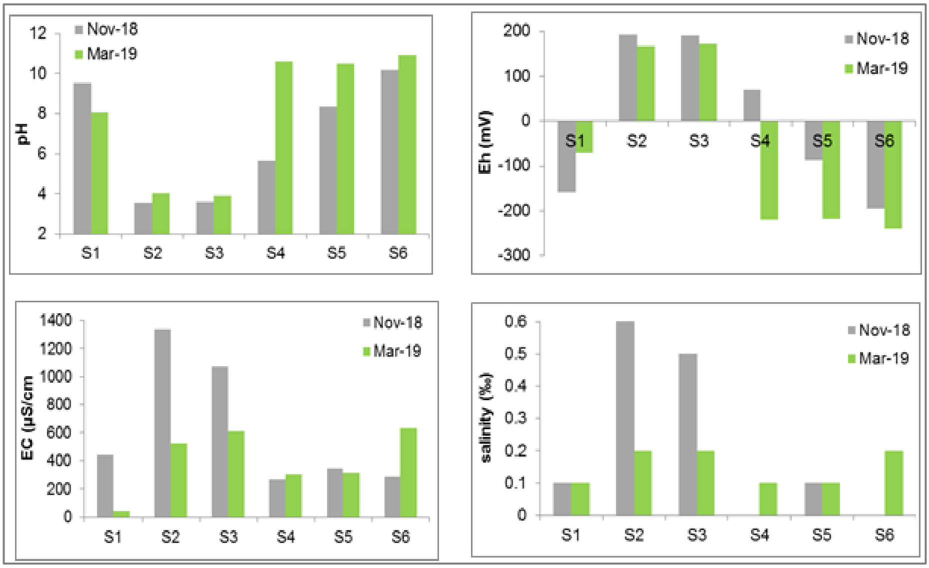

Fig. 2. *The physico-chemical parameters of the sterile samples*

The metals distribution in sterile samples was dominated by the presence of Cu (278 – 942 mg/kg), Zn (48 – 230 mg/kg) and Pb (23 – 77 mg/kg), which had higher concentrations than Cr (2 – 10 mg/kg), Ni (2.6 – 6.9 mg/kg) and Cd (1.3 – 2.2 mg/kg) (Fig 3). The highest concentrations were registered in S6 point, where the sterile and waste water are discharged.

Generally, the average levels were slightly higher in November 2018 than during March 2019 (figure 3).

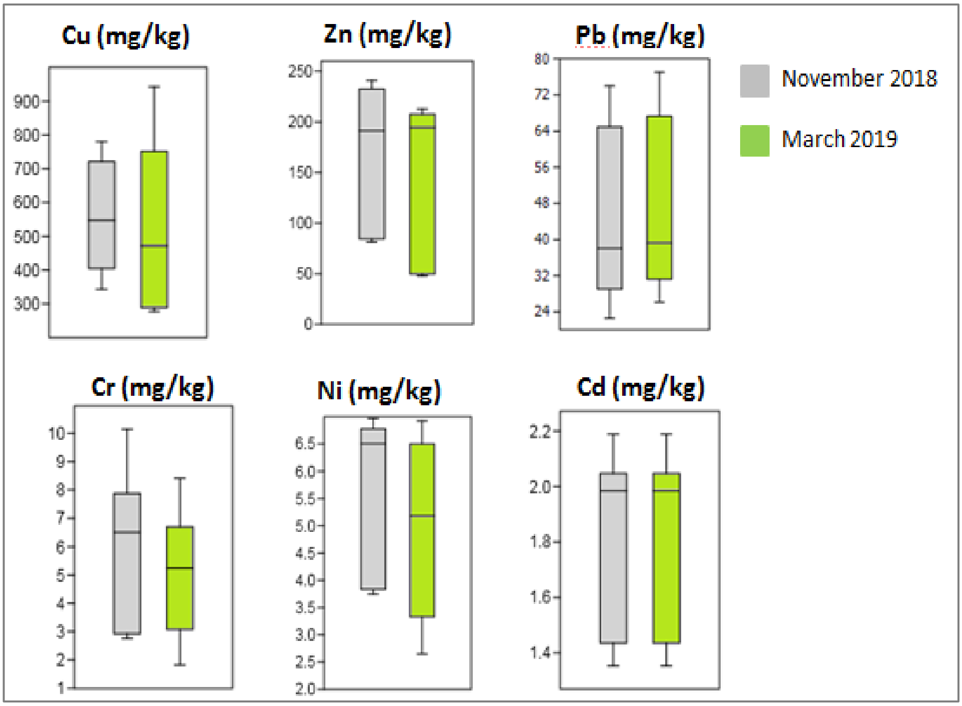

Fig. 3. *Seasonal fluctuation of metals content in sterile samples*

To have an over role image of the quality of the sterile samples, there were calculated two specific indices: Enrichment factor (EF) and Geo-accumulation index (I_{geo}). Enrichment factor was calculated based on the method proposed by Sinex and Helz (1981), using iron as reference metal:

$$EF = \frac{\frac{C_n}{C_{Fe}} sterile}{\frac{C_n}{C_{Fe}} crust}$$

where, C_n is the heavy metal concentration (mg/kg) in sterile and in the upper continental crust, while C_{Fe} is the iron concentration in both sterile and in the upper continental crust (mg/kg).

Based on EF level, the sterile samples can be classified in five quality classes as follows: unpolluted ($0 < EF < 1$), minor polluted ($1 < EF < 3$), moderate polluted ($3 < EF < 5$), moderately to severe polluted ($5 < EF < 10$), severe polluted ($10 < EF < 25$) and very severe polluted ($25 < EF < 50$) (Simex and Helz, 1981).

Geo-accumulation index, was calculated based on the formulae proposed by Muller (1981):

$$I_{geo} = ln\frac{C_n}{1.5 \cdot B_n}$$

where, C_n is the concentration (mg/kg) of heavy metal in sterile sample, B_n is the concentration (mg/kg) of heavy metal in the upper continental crust and 1.5 is the correction factor.

By calculating I_{geo}, the sterile samples can be classified as: unpolluted ($I_{geo} \leq 0$), unpolluted to moderately polluted ($0 < I_{geo} < 1$), moderately polluted ($1 < I_{geo} < 2$), moderately to heavily polluted ($2 < I_{geo} < 3$) and heavily polluted ($3 < I_{geo} < 4$).

The values of the calculated indices are presented in figure 4 and figure 5. The results indicated that based on EF values, the analyzed sterile samples are unpolluted with Ni, Cr, minor polluted with Pb, Zn, Cd, moderate polluted with Pb and severe to very severe polluted with Cu (Fig. 4). These results were confirmed by calculating the I_{geo}, which indicated that the investigated sterile samples are unpolluted with Ni and Cr, unpolluted to moderately pollute with Pb, Cd, Zn, and moderately to heavily polluted with Cu (figure 5).

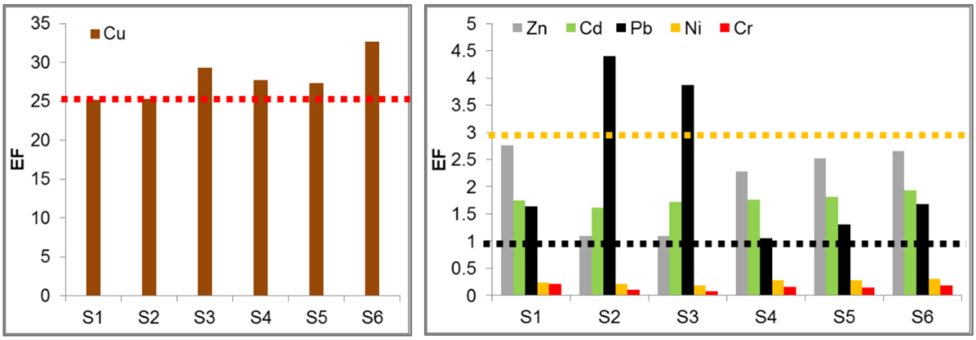

Fig. 4. *Heavy metals pollution degree of sterile samples, based on the Enrichment Factor (EF) values (unpolluted 0 < EF < 1, minor polluted 1 < EF < 3, moderate polluted 3 < EF < 5, moderately to severe polluted 5 < EF < 10, severe polluted 10 < EF < 25 and very severe polluted 25 < EF < 50)*

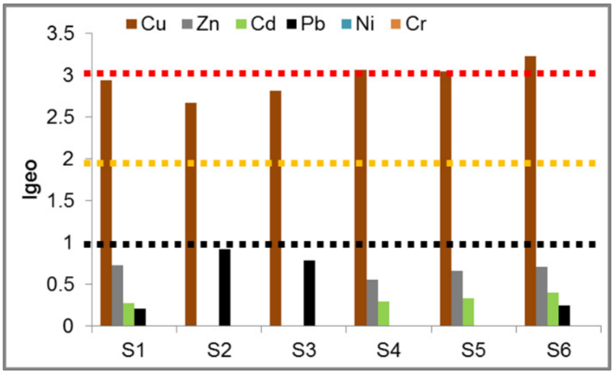

Fig. 5. *Heavy metals pollution degree of sterile samples, based on Geo-accumulation index (I_{geo}) values (unpolluted $I_{geo} \leq 0$, unpolluted to moderately polluted $0 < I_{geo} < 1$, moderately polluted $1 < I_{geo} < 2$, moderately to heavily polluted $2 < I_{geo} < 3$, heavily polluted $3 < I_{geo} < 4$)*

Water samples

The monthly fluctuation of the physico-chemical parameters for the analysed water samples is presented in Fig. 6. The waste waters sampled from points W3 – W5 proved to be highly acidic, exceeding the limits (6.5 – 8.5) imposed by national legislation (GD 352/2005) for the discharge of waste waters into surface waters. Generally, the waste waters sampled from sampling points W1, W2 and W 6 were alkaline, because they were sampled from the pipe which transports lime for neutralisation and from the pipe which that transports sterile and wastewaters from the processing plant, where lime is used as flotation reagent. The data reflected the impact caused by the discharge of acidic waste waters onto the surface waters, most of them being more acidic than the national recommendations (Order 161/2006) (figure 6).

The waste waters sampled from points W3 – W6 had a high EC and salinity, which reflects the high amounts of dissolved salts. The discharge of these waters into surface waters leads to high levels of EC and salinity for Valea Holhorii creek (SW1) and Valea Șesei creek (SW2 – SW8); only the high dilution with Arieș River (SW9 – SW10) decreases the levels of EC and salinity.

The monthly fluctuation showed that the waters were generally more acidic during April 2019 than in March 2019, while the EC and salinity were slightly higher during April 2019 than in March 2019. These fluctuations can be correlated with the high amounts of precipitations from April 2019.

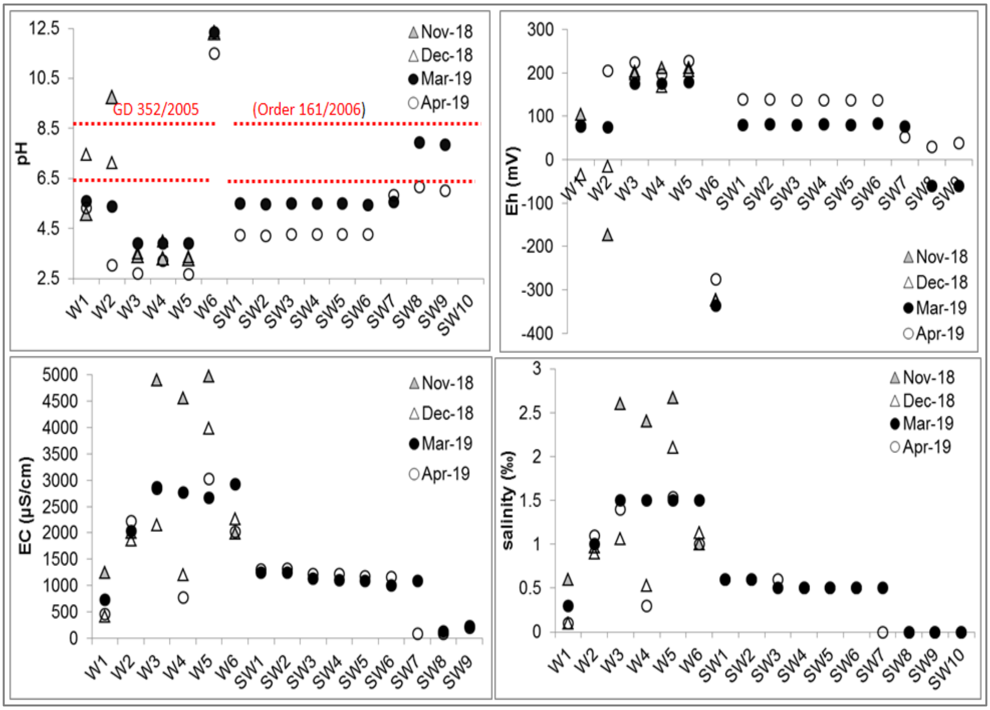

Fig. 6. *Monthly fluctuation of the physico-chemical parameters for the analysed water samples*

The analysed waters proved to have high levels of calcium, magnesium and sulphates, for waste waters these parameters exceeded the limits imposed by national legislation for their discharge into surface waters (figure 7). As a consequence, the discharge of these waste waters had a negative impact on the quality of surface waters, which due to the high content of SO_4^{2-}, Ca^{2+} and Mg^{2+}, can be classified as having a bad or poor ecological status (S 1 – 7) (Order 161/2006). The content of sodium, potassium, chloride and nitrate, proved to be considerably lower than the other ions (figure 7).

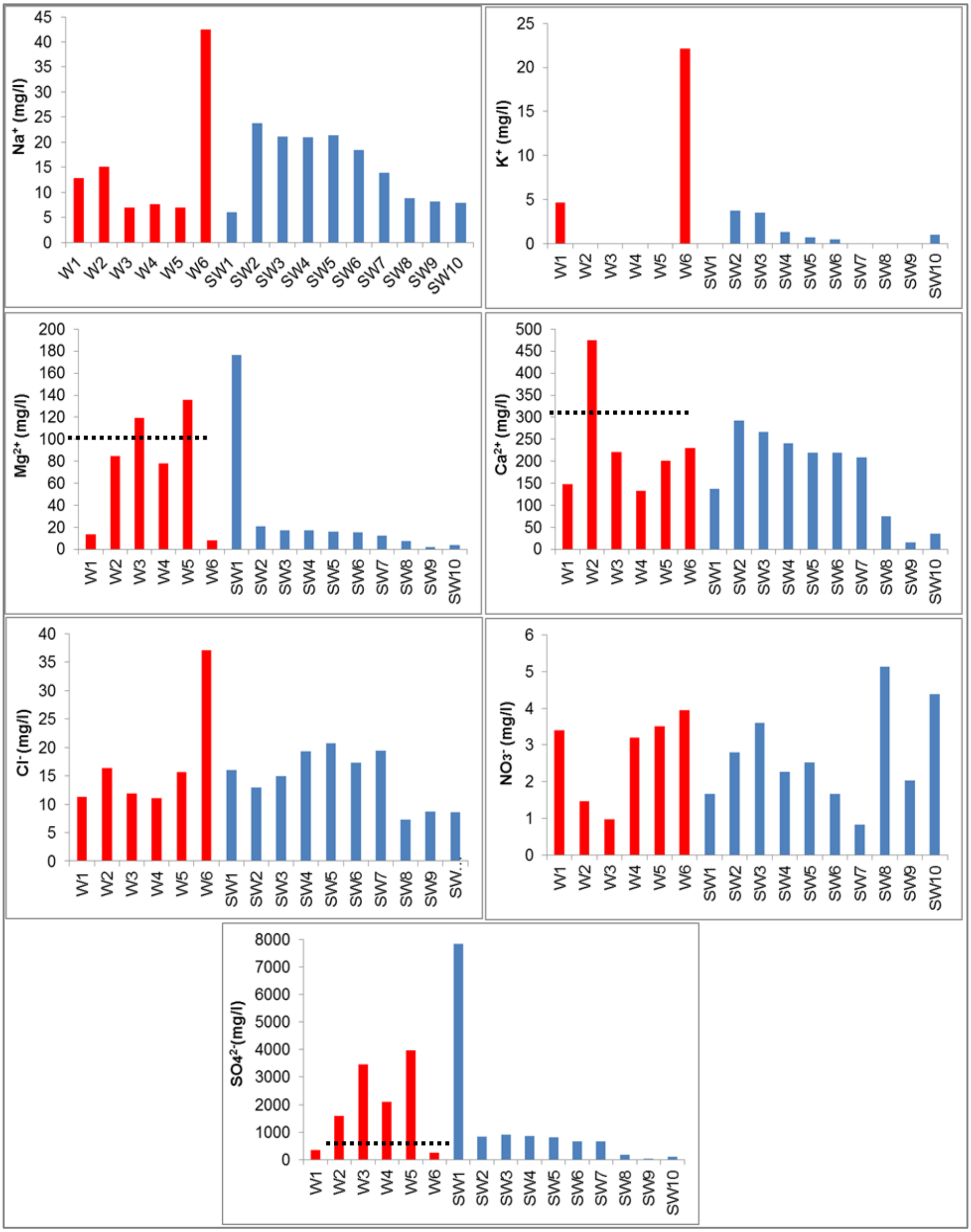

Fig. 7. *The content of dissolved ions in both waste waters and surface waters*

The waste waters proved to be highly contaminated with copper and zinc, having values (1.7 – 45.6 mg/l, for Cu and 0.1 – 18.7 mg/l for Zn) considerably higher than the maximum permissible limit (MPL) (0.1 mg/l for Cu and 0.5 mg/l for Zn) imposed by national legislation for waste water discharge into surface waters (GD 352/2005). The content of Pb and Cd were close to the MPL, while the content of Cr and Ni were lower than the national legislation requirements.

Consequently, the discharge of wastewater into Valea Holhorii creek (SW1) and Valea Șesei creek (SW2 – SW8) has led to their contamination with heavy metals. Based on Cu, Zn, Pb and Cd content, the surface waters sampled from S1 – S8 points correspond to a bad ecological status (figure 8). Only the high dilution with Aries River decreases the content of heavy metals corresponding to a very good to moderate ecological stats.

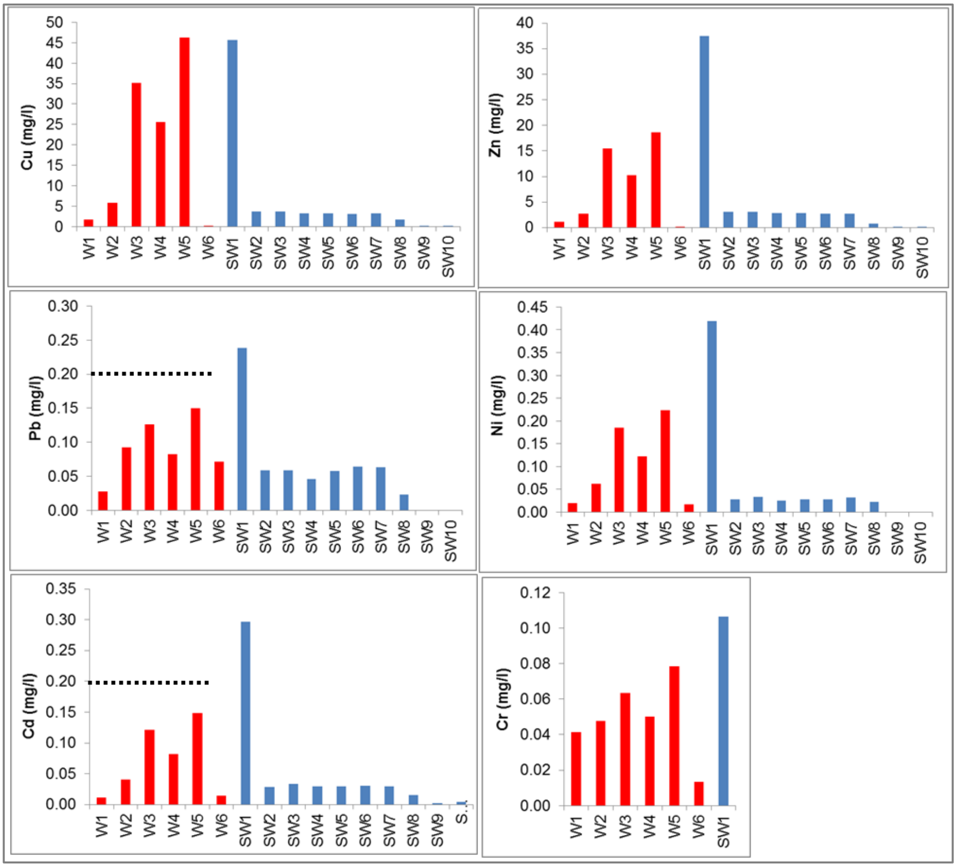

Fig. 8. *The content of metals in both waste waters and surface waters*

CONCLUSIONS

The results of the present study showed that the tailing dam material is characterised by high levels of Cu. Tailing impoundment from Valea Șesei represent a high risk for Cu contamination for soil and surface water.

The wastewaters deposited along with tailings in Valea Șesei represent a serious environmental and health risk, containing significant levels of copper, zinc and sulphates.

The analyses indicated the negative impact of AMD discharge in surface waters, which proved to have high levels of Cu, Zn and SO_4^{2-}.

Acknowledgments

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