ASSESSMENT OF SURFACE WATER QUALITY IN JIU VALLEY MINING AREA

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***Abstract**: The main objective of the present study was to perform a general screening of surface water quality in Jiu Valley mining rea. Surface waters were collected from West Jiu river and some of its tributaries (Căprişoara creek; Baleia creek; Bărbăteni creek; Vacii Valley creek; Tusu creek; Bulzu creek) to analyze several general physico-chemical and some specific chemical quality parameters. The general physico-chemical parameters: pH, redox potential (ORP), salinity, total dissolved solids (TDS), electrical conductivity (EC) and dissolved ions were analyzed.*

The analyzed water samples had a neutral pH, with a relatively low content of dissolved salts, except for Căprişoara creek. Based on their dissolved ions content, most of the analysed waters correspond to I^{st} quality class, which reflect a very good ecological status. Because of the high content of sulphate, calcium and magnesium, water sampled from Căprişoara creek corresponds to V^{th} class (based on SO_4^{2-} content), IV^{th} class (Ca^{2+} level) and III^{rd} (Mg^{2+} concentration) class, indicating a bad / low / moderate ecological status. The water quality degradation of Căprişoara creek in the investigated area may be associated with several anthropic activities identified in the area, but to confirm this sources further investigations are needed.

Keywords: Jiu Valley, mining units, water quality.

INTRODUCTION

Degradation of surface water quality due to anthropogenic activities (agriculture, industry, urbanization, deforestation, etc.) or natural factors (soil erosion, meteorological phenomenon-rain, climate change, etc.) represents a global problem (Munabi et al., 2009). Surface water pollution leads to equilibrium perturbation of the ecosystem and can have a negative impact on public health (Dalakoti et al., 2017).

Mining industry represents one of the most important pollution sources of the environment, generating high amounts of waste during ore extraction, processing, transport and deposition. It can have a major impact on the landscape, soil or surface and underground water quality, leading to aquatic and terrestrial ecosystems degradation (Fodor, 2006). Generally, the mining activities are associated with four major effects on the environment, as was mentioned by Rybicka (1996): (i) changes in hydrogeological system; (ii) hydrological modifications of soils and surface water flux; (iii) contamination of soils and surface water basins and (iv) atmosphere pollution. The additional impacts are: reduced biodiversity, modifications of ecosystem functioning and structure, modifications of soil stratigraphy (Almas et al. 2004; Jason, 2012).

The present study was performed in a former mining area from Romania, namely in the mining basin of Jiu Valley, where the largest coal deposit from Romania was exploited during the XIX century. The extraction technologies used in the Jiu Valley were adapted to the geological mining characteristics, being conditioned, first of all, by the thickness and slope of the layer (Neagu et al., 2015). In 1840 the first surface operations began in the area, by the exploitation and coal processing within the Vulcan, Petroşani and Petrila mines (Faur et al., 2017). Coal exploitation intensified over time in the area, so that at the beginning of the '90s there were 14 mine perimeters put into operation in the Jiu Valley. The coal production declined in the area since 1996, when started the restructuring process (closure of some mining units), the decline accelerating after 2000 in the area. Because of the lack of a visionary policy in the energy sector, the future of coal exploitation in Jiu Valley is uncertain (Faur et al., 2017).

Due to the intense mining activities carried out in the area in the past, it is possible that the environment is still facing a negative impact caused by the discharge of improperly treated wastewater, or by the hydrotechnical activities performed for permanent or torrential water courses regularization in interior or exterior of the mining perimeter, or by the leaching from the cool deposit (Almas et al., 2004; Jason, 2012).

The main objective of the present study was to perform a general screening of surface water quality in Jiu Valley mining rea. Surface waters were collected from West Jiu river and some of its tributaries (Căprișoara creek; Baleia creek; Bărbăteni creek; Vacii Valley creek; Tusu creek; and Bulzu creek) to analyze several general physico-chemical and some specific chemical quality parameters.

STUDY AREA

The investigated area is located in Hunedoara County, in the coal mining perimeter of Jiu Valley, Petroșani depression. A total of seven surface water samples were collected in October 2020 (Fig. 1). The sampling points are located on three territorial administrative units, respectively: Uricani, Lupeni and Vulcan.

Uricani town is located in the north of Jiu Valley, with Brazi Valley and Câmpu lui Neag as component localities. Uricani town was part of the Jiu Valley coal basin, located in its western part and bounded by the former mining perimeters from Bărbăteni (east) and Brazi Valley (west), having an area of 1548.6 ha. Currently, the Uricani mine is closed, as remedial and reintegration activities have been started in the natural landscape of the area occupied by the constructions specific to the activities of the past (Buliga, 2017).

Lupeni mining perimeter is located in the central-western part of the Petroșani depression, being adjacent to the east of the Vulcan mining perimeter and to the west of the former Bărbăteni mining field. The mining perimeter has an area of 1334.7 ha, where the Lupeni Mining Exploitation operates, whose object of activity is the extraction of energy coal contained in layer 3 (Buliga, 2017). The main water course is represented by West Jiu, which collects the tributaries from the slopes of the depression. The water samples were taken mainly from the areas downstream from the mining units or fields, respectively the samples from Pâraiele Tusu (sample no. 6) and Vacii Valley (sample no. 5), being downstream from the former exploitations from Uricani, the sample from the Bărbăteni stream (sample no. 4) being taken from downstream of the former Bărbăteni exploitation.

Figure 1. Location of the surface water sampling points – Jiu Valley mining area (1 – West Jiu river; 2 – Căprișoara creek; 3 – Baleia creek; 4 – Bărbăteni creek; 5 – Vacii Valley creek; 6 – Tusu creek; 7 – Bulzu creek) (modified after Google Erath).

Vulcan mining perimeter is located in the central area of the West Jiu Valley and covers an area of 12.6 km^2. Vulcan perimeter is bounded to the east by the Aninoasa mining perimeter, and to the west by the Paroșeni and Lupeni mining perimeters. The mining activity is managed by Hunedoara Energetic Complex S.A. Company. At the level of 2014, the Vulcan mine had two production sectors, one electro-mechanical sector, one transport sector and a ventilation sector (Buliga, 2017). In addition to the DN 66A national road, access to the premises is via the Petroșani-Livezeni-Lupeni railway. The hydrographic network in the described perimeter is tributary to the West Jiu River. Samples were collected from tributaries of the Jiu River that either cross areas affected by both current and historical mining activities or affected by industrial activities such as the Paroșeni thermal power plant. As it can be observed in Fig. 1, the samples were taken both upstream (upstream-sample no. 2 Căprișoara creek) and downstream of the mining units (downstream E.M. Lupeni- sample no. 3, Baleia creek and E.M. Vulcan- sample no. 1 Jiu).

MATERIALS AND METHODS

With the help of the multiparameter WTW Multi 350i, the following physico-chemical parameters were measured *in situ*: electrical conductivity (EC), total dissolved solids (TDS), salinity, pH, redox potential (ORP). Before the field measurements, the equipment was calibrated using standard buffer pH solutions (pH = 4.01; 7.00; 10.01) and standard solution with an electric conductivity of 1278 µS/cm (20°C), respectively 1413 µS/cm (25°C).

The samples destinated for major dissolved ions analyses were collected in sterile polyethylene vials, with a volume of 120 ml. The collection and preservation of water samples was carried out according to national and international standards (ISO 5667-1/2023, ISO 5667-3/2024). The samples were filtered in the field by using syringe filters with pore size of 0.45 µm. The vials were labelled and transported to the laboratory in dark at cold (5°C) condition. The analyses were performed within 48h from sampling by using an ion chromatography system (model IC 1500 Dionex – SUA), which allows the analyse of the following ions F^-, Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, Li^+, Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}. The qualitative analysis was performed based on retention times for each ion present in the standard solution, while the quantitative analysis was carried out based on the external standard method, using the previously calibration curves plotted for each ion. The sensitivity of IC method was estimated based on the limit of detection (LOD) and the limit of quantification (LOQ). The results showed that ion chromatographic method had an adequate sensitivity, the LOD values ranged between 0.001 and 0.02 mg/l, and the LOQ values were in the range of 0.003 – 0.065 mg/l, depending on the ion. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated based on the standard deviation of the response – σ (10 repeated measurements of the blank sample) and the slope of the calibration curve – S, according to the formulas below:

$$LOD = \frac{3.3\times\sigma}{S}; LOQ = \frac{10\times\sigma}{S}$$

The content of carbonates and bicarbonates was measured by titration with HCl, in the presence of phenolphthalein and methylorange as indicators.

RESULTS AND DISCUSSIONS

Determination of physico-chemical parameters

Seven surface water samples were taken from the mining perimeter of Jiu Valley, in order to determine their physico-chemical parametes (the values are presented in Table 1).

Table 1. Values of physico-chemical parameters for the collected surface water samples

Sample	pH	ORP (mV)	EC (µS/cm)	TDS (mg/l)	Sal. (‰)
1. West Jiu river	7.74	-61.9	175.1	112	<0.01
2. Căprișoara creek	7.48	-49.5	665.0	425	0.3
3. Baleia creek	7.57	-54.4	68.2	44	<0.01
4. Bărbăteni creek	7.62	-55.1	192.0	123	<0.01
5. Vacii Valley creek	7.80	-61.9	59.4	38	<0.01
6. Tusu creek	7.73	-60.3	97.5	62	<0.01
7. Bulzu creek	7.72	-61.2	122.4	78	<0.01

The pH indicates the hydrogen ions concentration, which determines the acid or basic character of water. The water pH change is related to the formation and decomposition processes of organic substances, on which the decrease or increase of carbonic acid concentration depends. The development and vital activity of aquatic organisms, as well as the stability and migration of chemical elements depend on the pH (Puri, 2015). The analyzed water samples had a neutral pH (between 7.48 and 7.80) (Table 1), being within the limits (6.5 – 8.5) imposed by the national legislation (Order no. 161 from 16.02.2006).

The redox potential presented negative values (between -49.5 and -61.9 mV), being indirectly correlated with pH values. There are studies that have highlighted the correlation between the redox potential and the abundance of nitrate ion, namely the fact that the depletion of nitrite correlates with switching from a positive to negative ORP gradient (Weißbach et al., 2018). Therefore, the negative values of the potential could be a possible reason why the nitrite content in all the analysed samples was below the detection limit.

Electrical conductivity is an important parameter, being an indicator of the level of dissolved salts, including magnesium, sulphate, sodium, chloride, or calcium. Depending on EC values, the water can be used in irrigation, recreational, industrial or other purposes. The surface water samples had a low EC, between 68.2 and 665.0 µS/cm. The highest EC value was registered in Căprișoara creek, which has the confluence with West Jiu river, downstream of Vulcan mining exploitation area. Considering that surface water is an important resource for agriculture, the EC value of the investigated waters is suitable for agricultural usage. Generally, water with EC <750 µS/cm is safe so be used for irrigation (Kadhem, 2013).

The total dissolved solids TDS (mg/l) in water include, generally, inorganic salts (as carbonate, bicarbonate, chloride, sulphate, nitrate, sodium, potassium, calcium and magnesium) and a small quantity of organic material (Puri, 2015). Thus, the values for the total dissolved solids are between 38 mg/l for Vacii Valley creek and 425 mg/l for the sample number 2, collected from Căprișoara creek.

The analysed water samples had a low salinity, the values being below the detection limit of the equipment (<0.01‰), with the exception of Căprișoara creek, where the salinity was 0.3‰ (Table 1).

Ions concentration in surface water samples

Concentrations of dissolved ions for the investigated water samples are presented in Figure 2 and the quality classes can be determined according to the present legislation (Order no. 161 from 16.02.2006). The ions concentrations F^-, NO_2^-, Br^-, PO_4^{3-}, K^+, Li^+, NH_4^+ were under the detection limit of the equipment.

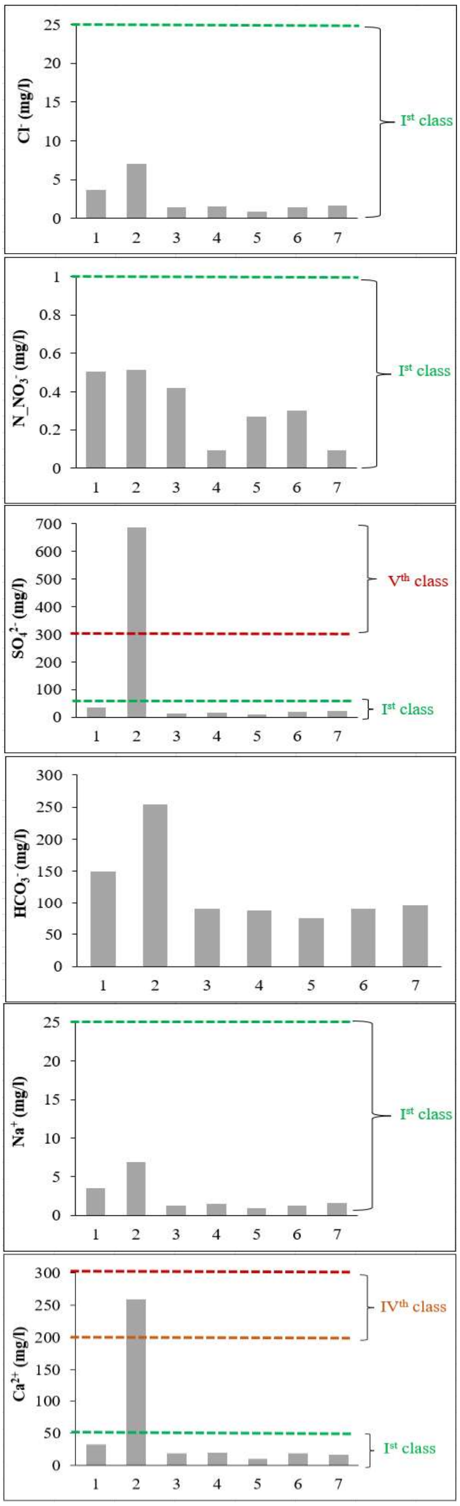
The distribution of major dissolved ions was dominated by the presence of SO_4^{2-}, HCO_3^-, Ca^{2+} and Mg^{2+} (Fig. 2). The surface waters had a low Cl^- content, between 0.91 and 7.04 mg/l, which corresponds to Ist quality class "very good ecological status". Similar to Cl^-, the NO_3^- content was low, the values for $N\_NO_3^-$ ranged between 0.09 – 0.51 mg/l, all the samples being classified as Ist quality class "very good ecological status". The nitrates content was slightly higher in samples 1-3 compared to the rest of the samples. Nitrates presence in surface waters can be associated with natural and anthropic sources (agriculture by manure elimination, food production and deposit activities of household and industrial waste) (Puri, 2015).

Except for sample no. 2, the sulphate content was low, corresponding to Ist quality class "very good ecological status" (Fig. 2). In sample 2, the sulphate was abnormally high, the water sample being classified as Vth quality class "bad ecological status". The high content of sulphate from Căprișoara creek (sample no. 2) reflected an anthropic impact, which can be correlated with possible leachate of pollutants from the household waste dumps located upstream from the sampling point, or with the aerial dispersion of pollutants from the surface of the ash pits generated by Paroșeni Plant, located at approximately 500 m from the sampling point. Therefore, through the action of rainwater, leachate appears, which can negatively influence the quality of underground and surface water from their perimeter. Further investigation is needed to assess the water quality of this particular tributary of West Jiu river and to confirm the impact of the above mention anthropic activities.

High concentrations of SO_4^{2-} in surface water, can disturb the equilibrium and the ionic exchange processes, which can have a negative impact on aquatic organisms (Qian et al., 2017). Sulphates, sulfides and sulphurate hydrogen represent the sulphur combinations. Sulphates have a low stability, being a substrate for oxido-reduction bacteria and transform them into sulphurate hydrogen or soluble sulphides. Thus, in oxidation reactions, in the water presence, the sulfoxidant bacteria transform H_2S or elemental sulphur into sulphates. On the other hand, in reduction reactions, bacteria transform sulphates in H_2S which is obtained or in the iron presence can form pyrites FeS (Bech et al., 2017).

The carbonate was not detected in the analysed water, while the bicarbonate content ranged between 75 and 254 mg/l. The highest bicarbonate levels were registered in sample no. 1 – West Jiu river (150 mg/l) and in sample no. 2 – Căprișoara stream (254 mg/l). The presence of bicarbonates in surface waters can be correlated with the geological features of the aquifers, namely to the presence of limestone and dolomite. Thus, the presence of carbon in dolomite and calcite is responsible for the presence of almost half of the bicarbonate ions content from solution. The presence of these minerals determines an increase of calcium, magnesium and bicarbonate ions concentration in water (Gastmans et al., 2010; Khashogji et al., 2013). Possible sources for carbonates and bicarbonates in surface waters can include the presence of organic material in aquifer, which is oxidized and produces CO_2, favoring mineral dissolution.

The sodium content was low (between 0.89 and 6.87 mg/l) for the analysed surface water samples, corresponding to I[st] quality class "very good ecological status" (Fig. 2). With the exception of sample no. 2, the rest of the samples had a low content of calcium and magnesium which correspond to I[st] quality class "very good ecological status" and respectively to II[nd] quality class "good ecological status" (sample 1 for Mg^{2+} content). The sample no. 2, collected from Căprișoara creek had a considerably higher magnesium (classified as III[rd] quality class "moderate ecological status") and calcium content (classified as IV[th] quality class "low ecological status") (Fig. 2). Such high levels of calcium and magnesium may be associated with anthropic sources, but in order to identify possible sources further investigations are needed.



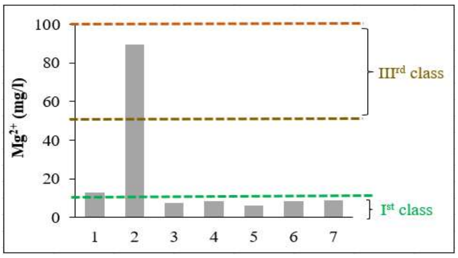


Figure 2. The content of major dissolved ions in the surface water samples and the corresponding water quality status according to national regulation (Order no. 161 from 16.02.2006).

Based on calcium and magnesium concentration, the water harness (HD) was calculated using the Water hardness calculator proposed by Lenntech. The results are presented in Fig. 3.

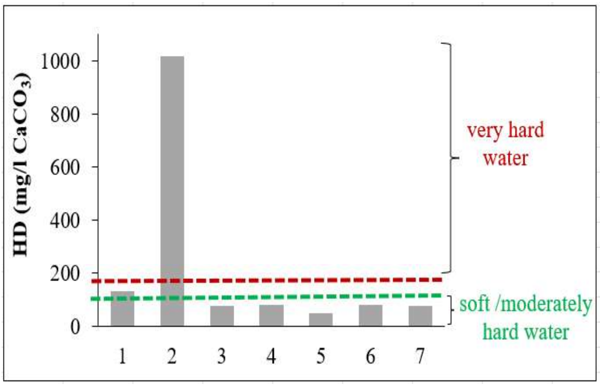


Figure 3. The hardness of the investigated surface waters.

Generally, the analysed waters can be classified as soft water (HD up to 60 mg/l $CaCO_3$) and moderately hard water (HD up to 120 mg/l $CaCO_3$). Sample no. 2 was again an exception, where the limit for very hard water (180 mg/l) was considerably exceeded. The water hardness from sample no. 2 - Căprişoara creek is caused by the high amount of dissolved calcium and magnesium salts in the water. Water hardness is a factor which restricts their usage in agriculture, industrial or recreational purposes. When passing through the pipes, the calcium and magnesium salts can form scale, which can reduce the life of equipment, raise the maintenance costs, lower the efficiency of electric water heaters, or lead to clog pipes. Too much salts in water used for irrigation can lead to accumulation of high amounts of salts in rootzone, which may reduce or even prohibit the crop production.

CONCLUSIONS

The main objective of this study was to evaluate the quality of surface water in the Jiu Valley, a mining area in southwest of Romania. Seven surface water samples crossing the territory of three territorial administrative units (Uricani, Lupeni, Vulcan) were analysed.

The analysed water samples had a neutral pH, with a relatively low content of dissolved salts, except for Căprişoara creek. Based on their dissolved ions content, most of the analysed waters correspond to Ist quality class, which reflect a very good ecological status. Căprişoara creek was an exception. Because of the high content of sulphate, calcium and magnesium, this water sample corresponds to Vth class (based on SO_4^{2-} content), IVth class (Ca^{2+} level) and IIIrd (Mg^{2+} concentration) class, indicating a bad / low / moderate ecological status. The contamination with these chemical compounds can be associated with possible anthropogenic sources, like leachate generated in the household waste dumps areas located upstream from the sampling point, or with the aerial dispersion of pollutants from the surface of the ash pits generated by Paroşeni Plant. To confirm this sources, further investigations are needed.

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ISSN 1582-1021
e-ISSN 2668-4764
Edited by "Aurel Vlaicu" University Publishing House, Arad, Romania

10.62591/Scien.Tech.Bull-Chem.FoodSci.Eng.2024.21.03