QUALITY ASSESSMENT OF VALEA ȘESII STREAM NEAR A COOPER MINE TAILING POND

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Abstract. Roşia Poieni, a large copper mine from Arieș basin, produces tons of copper/year.The resulted sterile are deposited in Geamăna tailing pond located in the vicinity of Valea Şesii stream, one of the Arieş River tributaries, contributing decisively to the quality of its water. The study aims to assess the quality status of Valea Șesii stream using a complex green technology, combining chemical analysis and biomonitoring methods in order to establish the environmental trend of the catchment.The quality of the surface water is considered relatively good, with a circum-acid pH (4.5), electrical conductivity of 1677 µS/cm , 1742 ppmfor the total dissolved solids, 7.64 mgO_2/L for the biological oxygen demandand rather small values of nutrients. The presence of chlorophyll α and β was noticed (0.374 µg/mL and 0.998 µg/mL). A correlation between the nutrients content and the chlorophylls values was observed, while the chlorophylls values increases, the content of nutrients decreases.

Keywords: Roșia Poieni, Geamăna tailing pond, surface water, quality assessment, chlorophyllα, β

INTRODUCTION

Being a vital aspect of life on Earth, water must meet the highest quality standards in order to be considerate safe for human or animal consumption. The use of surface waters as a drinking water source is a worldwide issue and therefore, the presence of pollutants in the environment has been seriously investigated and monitored (Santos et al., 2017, Rahman and Singh, 2018).

Industrial and mining wastewaters discharged into the watercourses can cause huge damage on the quality states of the surface water. The activities conducted in the Rosia Poieni mining centre have major implications regarding the contamination of the Valea Șesii's surface water, and therefore, the whole Arieș River basin (Bird et. al., 2005). Other studies conducted in the Arieș catchment had indicated high levels of heavy metals, cyanides and other pollutants in the vicinity of all mining centres within the catchment (Butiuc-Keul et. al., 2012, Levei et. al., 2014, Priotr et. al., 2017).

The presence of high content of heavy metals, cyanides, pesticides and an inconsistent pH level may affect the human health (Hu et al., 2020; Zhao et al., 2020) and could induce negative effects on the aquatic flora and fauna. An indicator of the surface water quality may be the presence of some plants, algae and bacteria (Huang et al., 2019, Hinojosa-Garro et al., 2020), presence proved by the content of *Chlorophyll α* and *β*. The chlorophylls are a group of pigments involved in the photosynthesis of plants, algae and some species of bacteria. *Chlorophyll α* and *chlorophyll β* are two major light-adsorbing pigments with a very similar chemicals structure coexisting in many oxygenic photosynthetic organisms (Scheer, 1991).

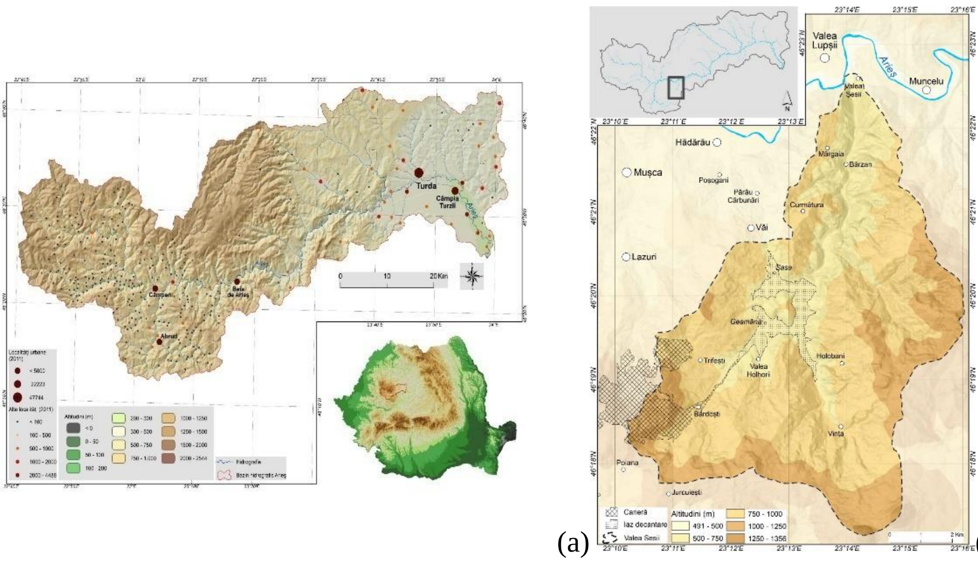
The aim of this study was to (1) asses the quality status of Valea Șesii stream and (2) to demonstrate that a connection between the level of water contamination and the presence the *chlorophyll α* and *chlorophyll* β exists, hence, a correlation and influence between the pollution degree and the aquatic flora and fauna.

MATERIAL AND METHODS

Study area and water sampling

Arieș River is one of the most polluted rivers in Romania, due to the intensive industrial activities conducted in the area (Constantin et. al., 2015). Roșia Poieni is the largest unexploited gold deposit in Europe, located in the Apuseni Mountains, near the Roșia Montană gold mine, in the northern part of the Bucium–Roșia Montană metal district. The copper deposit in this area represents about 65% of the total copper reserve of the country (Luca et. al., 2006). A quantity of 5000 tons of cooper is extracted annual. The waters from the quarry perimeter are collected by four of the Aries River tributaries: Valea Strigoi, Valea Şesii, Valea Muscanilor and Valea Fântânilor (Rzymski et al., 2017).

In order to assess the quality status of Valea Șesii stream, a sampling campaign was organized alongside the water body, during the cold season of 2019, when a total number of 7 samples were collected from randomly selected sampling locations. The water samples were collected in polyethylene bottles, which were pre-washed with 0.1N HCl and kept at 4°C until the chemical analysis.



(a) (b)

Fig. 1. (a) The Arieș River basin and (b) Valea Șesii stream catchment

Analytical methods and materials

The biological oxygen demand *(BOD)* was analysed from freshly sampled waters according to SR EN 1899-2:2002.

To determine the content of *chlorophylls*, 5mL of sample was centrifuged at 3500rpm for 8min with an Universal 320 centrifuge (Hettich, Germany). The growth medium was removed and 5mL methanol was added; then, the samples were placed for 3min in a water bath with a constant temperature of 70°C (Memmert, Germany) and afterwards centrifuged. The absorbance (A) of the supernatant was measured at 652.4 and 665.2nm using a Lambda 25PerkinElmer UV/VIS spectrophotometer (USA). The obtained values were used to calculate the contents of *chlorophyll α* and *chlorophyll β* with the help of equations (1) and (2)(Kim et al., 2019).

$$Chlorophyll\ \alpha = 16.72\ A_{665.2} - 9.16\ A_{652.4} \quad \text{(Eq.1)}$$

$$Chlorophyll\ \beta = 36.09\ A_{652.4} - 15.28\ A_{665.2} \quad \text{(Eq.2)}$$

The *heavy metals, micro*-and *macro-nutrients* concentrations were determined by ICP mass spectrometry (ICP-MS) using an ELAN DRC II Spectrometer (Perkin-Elmer, Canada). Previously, the samples were filtered by using 0.45 μm filters and mineralized with 5 mL ultrapure grade 65% HNO_3 (Merck, Germany) to 100 mL water sample, according to ISO 17294-2:2016.

The *pH* and *electrical conductivity (EC)* were measured in situ by using a portable WTW 350I multiparameter (Xylem, USA).

The *total dissolved solids (TDS)* were determined gravimetrically by evaporating 100 mL of filtered water samples at 180°C. To remove the particles from the water samples, 0.45 µm membrane filters were used (Atekwana et. al., 2004). After cooling, the samples were weighted.

Graphical approaches of the quality assessment

The corellation beetwen the total contamination of the surface water samples and the presence of *chlorophyll α* and *β*was assessed using the *contamination index (C_d)*. $C_d$was computed using the equations Eqs. (3) and (4).

$$C_d = \sum_{i=1}^{n} (c_f) \quad \text{(Eq.3)}$$

$$C_f = \sum_{i=1}^{n} \left(\frac{C_{Ai}}{C_{Ni}} - 1\right) \quad \text{(Eq.4)}$$

where C_{Ai} represents the amount of the determined chemical indicator and C_{Ni} is the maximum allowable concentration (MAC) of the determined parameter, according to the Romanian legislation (Hakanson, 1980).

In order to highlight the correlations and similarities among the chemical indicators, the agglomerative hierarchical cluster analysis (***HCA***) and the principal component analysis ***(PCA)*** were performed with the help of XL STAT software.

Table 1

The bio-chemical and chemical characteristics of the analysed surface water samples

							Heavy metals				Micronutrients					Macronutrients			
	BOD [mg/L]	Ch. α [µg/L]	Ch. β [µg/L]	pH [pH units]	EC [µS/cm]	TDS [ppm]	Cd [mg/L]	Pb [mg/L]	Cr [mg/L]	As [mg/L]	Zn [mg/L]	Mn [mg/L]	Cu [mg/L]	Ni [mg/L]	Co [mg/L]	Mg [mg/L]	Ca [mg/L]	K [mg/L]	Na [mg/L]
S1	7.64	0.097	0.286	4.52	1677	1742	<0.01	0.122	0.044	<0.001	1.60	1.06	2.02	0.107	0.102	12.3	230	8.57	11.5
S2	7.51	0.102	0.305	4.64	1632	1735	<0.01	0.116	0.044	<0.001	1.51	1.04	1.89	0.091	0.095	11.9	228	8.43	11.2
S3	8.20	0.163	0.458	4.93	1234	1730	<0.01	0.089	0.035	<0.001	0.927	0.739	1.59	0.088	0.087	9.76	167	6.16	8.08
S4	8.31	0.194	0.522	5.02	1206	1534	<0.01	0.072	0.035	<0.001	0.920	0.739	1.42	0.086	0.086	9.63	165	5.85	7.79
S5	8.39	0.198	0.564	5.34	1193	1182	<0.01	0.080	0.035	<0.001	0.917	0.739	1.22	0.083	0.086	9.44	157	5.66	7.31
S6	8.52	0.374	0.998	5.50	1193	1190	<0.01	0.093	0.035	<0.001	1.23	0.755	1.18	0.081	0.083	8.53	165	5.39	7.48
S7	8.57	0.204	0.582	6.50	1251	1175	<0.01	0.060	0.030	<0.001	0.917	0.739	1.14	0.082	0.086	9.00	147	5.88	7.06
MAC*	20.0	250	-	6.5-8.5	-	1300	0.005	0.050	0.250	0.010	1.00	1.00	0.250	0.100	0.100	200	300	-	200

*according to Order no. 161/2006 for the approval of the Norm regarding the classification of surface water quality in order to establish the ecological status of the water bodies SR EN 27888-1997

RESULTS AND DISCUSSIONS

The results of the analyses for chemical and biochemical tested parameters are presented in table 1.

The *BOD* and *EC* of the samples were in the normal limits. All the samples had *BOD* values lower than the MAC, ranging from 7.51 – 8.57 mg/L. The *pH* ranged between 4.52 – 6.50 pH units, indicating a certain level of acidity. Hence, a negative influence of acid mine draining was observed. The *EC* was varying between 1677 – 1175 µS/cm, while the MAC for the *TDS* (1300 mg/L) was exceeded for sample S1 with 34%, S2 and S3 with 33% and S4 with 15%.

Pb was the only heavy metal that had values higher than the MAC (0.05 mg/L). Regarding the micronutrients, they had values over the maximum limits and macronutrient had very low concentrations in the analysed samples. At such low content of macronutrients, Manisali et al., (2019) had demonstrated a decrease in the growth rate of the microflora. On the other hand, the *heavy metal* contented, especially *Pb* and *As* were reported by Evarsite et al. (2019) to produce enormous damage to the aquatic organism. The highest content of *heavy metals* was attributed to the sample S1, after that, a trend of heavy metal content decreasing with the growth of the distance from the source of pollution was noticed. S1 was characterized by the lowest values of *chlorophylls* (*chlorophyll α*– 0.097 µg/L and *chlorophyll β*–0.286 µg/L).

Table 2

The contamination index (C_d) computed for the analysed surface waters

	Contamination index (C_d)
S1	4.49
S2	4.38
S3	3.83
S4	3.35
S5	3.28
S6	2.76
S7	2.99

The correlation between the water quality and the presence of microorganisms is clearly showed in figure 2, indicating a directly proportional of the level of contamination with the *chlorophylls* content. Water sample S6 had the lowest contamination index (C_d = 2.76) and the highest *chlorophylls* content (chlorophyll α = 0.374 and *chlorophyll β* = 0.998). The connection is described by a linear function.

The C_d ranged between 2.76 and 4.49, as table 2 indicated. The highest value was attributed to S1, which is the closest location to the mining centre of Roșia Poieni.

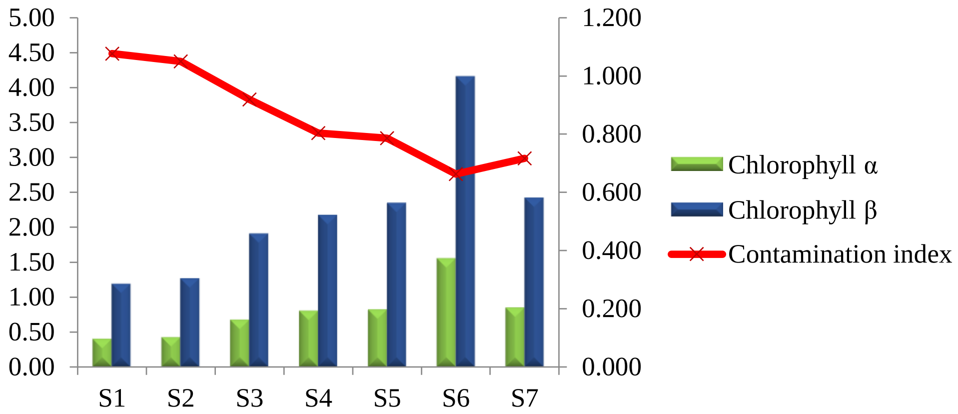


Fig. 2.The correlation between the presence of the *chlorophylls* and the Contamination index

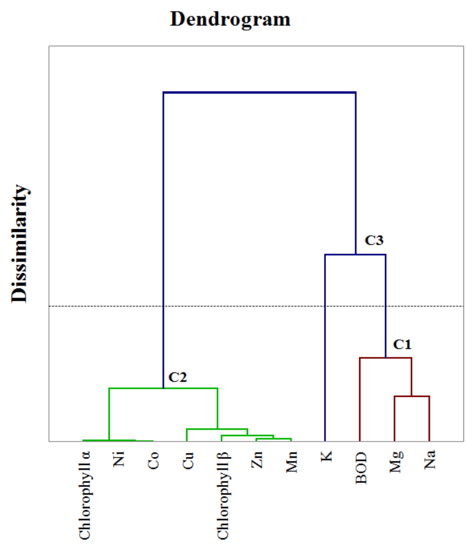


Fig. 3. The hierarchical cluster analysis for the analysed biochemical parameters analysed

To determinate the correlation between the *BOD*, *chlorophylls α* and *chlorophylls β*, *micro*- and *macronutrients*, an agglomerative hierarchical cluster analysis (HCA) according to Ward's method was conducted. The HCA was performed on the biochemical characteristics and the nutrients content as variables classifies all water samples chemical and biochemical analysis into 3 clusters:

- *cluster 1* (C1) containing *BOD*, *Mg* and *Na*;
- *cluster 2* (C2) containing *chlorophylls α* and *β* and all the *micronutrients* analysed (*Zn, Mn, Cu, Ni, Co*) and
- *cluster 3* (C3), which contains the *K* amount.

Cluster 1 (C1) linked the *BOD* and some of the *macronutrients*, cluster 2 (C2) grouped the indicators of flora and fauna - *chlorophylls* and all the *micronutrients*. The relatively high values of micronutrients may be caused due to the low content of microorganisms. Cluster 3 (C3) included only the *K* content.The PCA reveals a strong correlation between the presence of all metals and the *BOD*, *pH* and *chlorophylls*.

Figure 4 shows the Spearman PCA applied tothe main biochemical and chemical parameters. As it is showed in the PCA, there are two direct correlations: on the 1st and 2nd quarters, all the *heavy metals* and *nutrients* content were grouped and positively correlated. In the 4th quarters, the *pH*, *BOD* and the *chlorophylls* content were integrated. The PCA highlights once more the strong relation between the *heavy metals* and the *nutrients* content and the presence of microorganism, therefore, the *BOD* values and the *chlorophylls* content.

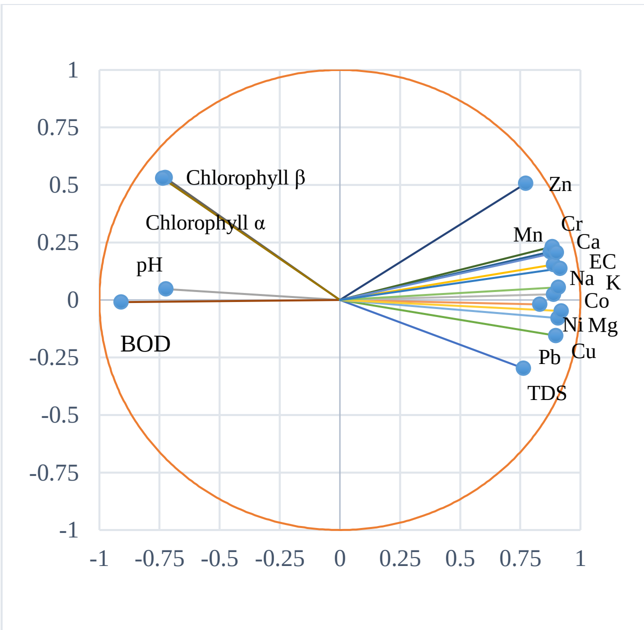


Fig. 4. Principal Component Analysis (PCA) for chemical and bio-chemical parameters

CONCLUSIONS

The quality of Valea Șesii stream was divided into two different categories: bad and relatively good. The first three water samples (S1-S3) exceeded the maximum values of concentrations of *pH, TDS, Pb, Zn, Cu* established by the Romania regulations and were enclosed in the 4th class of quality (bad water). The quality of the last four samples could be framed in the 3rd class of quality (relatively good water). The framing inclusion of waters in the quality categories has been indicated by the C_d values as well. The water samples were characterized by values attributed to the C_d that indicated moderate to considerate contamination among the Valea Șesii stream.

Getting further away from the copper mine, a significant increase of the *BOD*, *chlorophyll α*, *chlorophyllβ* and a decrease of the *heavy metals* content, *micro*- and *macronutrients* were noticed, those variations being a sign of an improvement trend of the water quality and of the dissolution of the chemical indicators in the water volume. The study showed a noticeable correlation between the water quality of the catchment and the organisms` bioactivity. A linear function between the two of them could be observed. The HCA of the bio-chemical parameters analyses divided them into three clusters, confirming once again the solid bond between water quality and the presence of the organisms within it. The PCA revealed a strong bond between the presence of all metals and *BOD*, *pH* and *chlorophylls*.

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