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Spatial Variation of Water Chemistry in Aries River Catchment Western Romania

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Abstract: This study aims to investigate the quality and vulnerability of surface water (Aries River catchment) in order to identify the impact of past mining activities. For this purpose, the pollution and water quality indices, Piper and Durov plots, as well vulnerability modeling maps were used. The obtained results indicate that the water samples were contaminated with As, Fe, Mn, Pb and have relatively high concentrations of SO_4^{2-}, HCO_3^-, TDS, Ca, K, Mg and high values for the electrical conductivity. Possible sources of the high content of chemicals could be the natural processes or the inputs of the mine drainage. Generally, according to the pollution indices, which were correlated to high concentrations of heavy metals, especially with Pb, Fe and Mn, the water samples were characterized by heavy metals pollution. The water quality index classified the studied water samples into five different classes of quality, namely: unsuitable for drinking, poor, medium, good and excellent quality. Similarly, medium, high and very high vulnerability classes were observed. The Durov and Piper plots classified the waters into Mg-HCO_3^- and Ca-Cl^- types. The past and present mining activities clearly change the water chemistry and alter the quality of the Aries River, with the water requiring specific treatments before use.

Keywords: water quality; mining areas; pollution indices; Piper diagram; HCA

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1. Introduction

Worldwide, wastewaters resulted from mining operations (metal oRes. exploitation) are released directly into the river catchments. According to a UNESCO report, 80% of the wastewaters are discharged directly into the environment without any previous treatments [1,2]. The anthropogenic activities influence and alter the quality of water systems, generating negative effects on the aquatic flora and fauna. Hence, the well-functioning of the water system is affected. The presence of high concentrations of heavy metals, organic compounds, insecticides and different other chemical compounds in drinking water sources in waters used in agricultural and household activities affect the human health [3]. These organic and inorganic contaminants are found in different toxic and mobile forms. According to the chemistry and dynamics, they act differently and attach easily to the water ecosystems, influencing the quality and the natural flows of the water systems [4–6].

In Romania, mining activities were blooming during the last 30 years, together with the pollution levels in water, soil and air. The discharge of industrial and mining

wastewaters directly into the water streams, without any pretreatment, and the hazards caused environmental disasters (the cyanide spill near Baia Mare, poisoning animals and inducing cancer cases in the area of the "Black Town", Copsa-Mica) [7].Since the disaster of Baia Mare area, the mining activities still continued with major impacts on groundwater and surface waters. The Aries River presents a higher vulnerability due to mining activities [8]. The main pollutants of the Aries River are Cu, Pb, Zn and cyanides, due to the acid mine drainage in the mining centers situated along the Aries River [8–10]. Different studies on the Aries River catchment revealed that the areas near the mining centers are still highly polluted and implicitly affected [9–12]. Moreover, the areas crossed by the Aries River represent a petrographic mosaic where the karst landscape is dominant in the upper and middle river catchment (e.g., Bihor Mountains and Muntele Mare areas).

Hence, information regarding the current status of the Aries River is still considered to be essential in order to define and process a suitable decontamination treatment before using the water for drinking purposes, agricultural practices and industrial usages. A part of the water sources monitoring is represented by different and efficient tools such as the water quality indices Appl. to specific points of the water bodies. Two of the most common methods are theHeavy Metal Pollution Index (HPI) and the Heavy Metal Evaluation Index (HEI), used to establish the pollution status of water ecosystems, considering the heavy metals content [13–15]. In order to evaluate the water quality regarding different types of physico-chemical characteristics, Horton proposed the Water Quality Index (WQI) [16]. The WQI is widely used to characterize all types of water bodies. Adimala et al. [17], Wang et al. [18] and Sener et al. [19] assessed the quality of various water systems (in Nanganur, South India and in different areas of China and Turkey) by using the WQI.The results were useful in order to assess the quality of surface water resources as an alternative drinking water possibility.

The aim of this study was: (1) to obtain new and valuable data regarding the current quality status and vulnerability of the Aries River, which is situated near the mining areas; (2) to study the impact of historical mining centers on the surface water quality in all the catchment areas, by determining the physico-chemical properties of waters; and (3) to assess the water quality using various heavy metal pollution indexes.

2. Methodology

2.1. Geological Settings and Description of the Study Area

The Aries River catchment is part of the Romanian Golden Quadrangle, recognized for the Au, Ag and porphyry copper deposits from Rosia Poieni [20,21]. The Aries River catchment has more than 60% of its surface developed in the Apuseni Mountains and ~40% on the Transylvanian Plateau and Feleacului Hills [22]. The Apuseni Mountains are particular mountains in western Romania, characterized by diverse and unique landforms belonging to the Western Carpathians. The Transylvanian Plateau is represented by three distinct units (Somes Plateau, Transylvanian Plain and Tirnavelor Plateau),defined mostly by depressions, low plateaus and hills (the transition areas near mountains) with different geological structuRes. [23]. Feleacului Hills cover only a small area of the Aries River catchment (north-eastern part), where marly to sandy clay soils appear, intercalated with sands and sandstones. The Aries River springs from Bihor Mountains (near VirfulVirtopu, 1294 m) and flows into the MuRes. River (near GuraAriesului village, 317 m), with a total length of ~166 km. The Aries River catchment covers several landscapes and landforms of Apuseni Mountains and Transylvanian Plateau (Bihor Mountains in the west part of the country; Metaliferi Mountains in thesouth-central area, Gilau-Muntele Mare in thenorth-central area of the catchment, Trascau Mountains in the south-east area,Feleacului Hills in the north-east area and Transylvanian Plateau in the east part of the country) [22].

The geological framework is diverse and represented by a variety of formations (from north to south), with basement tectonic units (metamorphic rocks and granites),

sedimentary and volcanic cover in the northern area, while Middle Jurassic ophiolites, Late Jurassic volcanic rocks and Late Cretaceous sedimentary deposits dominate the southern part of Apuseni Mountains. Moreover, the groundwater resources in the Aries River catchment are mostly related to karst aquifers developed in limestones or fissured rocks, being part of local or discontinuous aquifers (southern part of the basin), while the northern area of the basin is characterized by formations with deep aquifers or without aquifers (Figure 1).

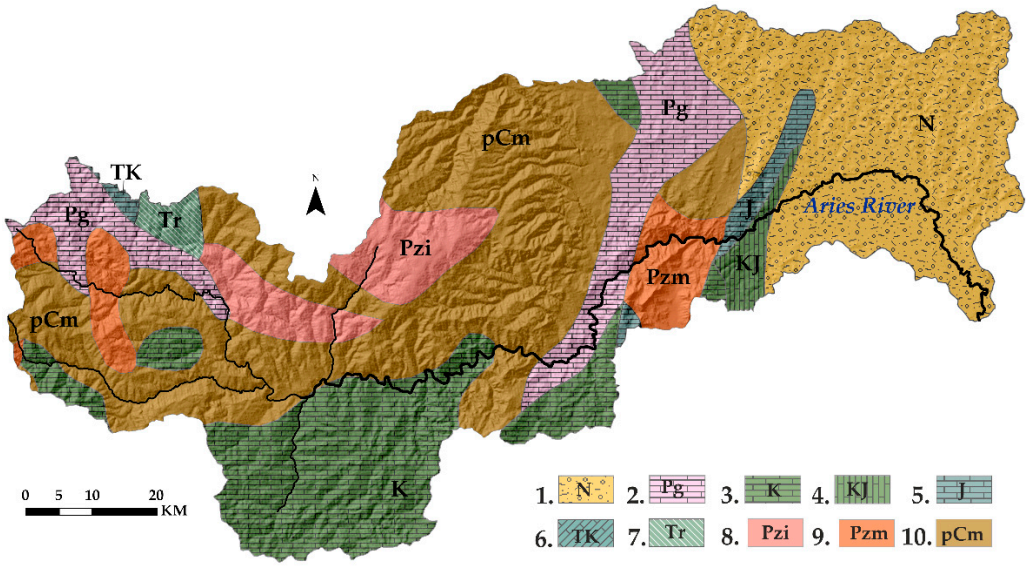

Figure 1. Geologic map of the Aries catchment (modified after Pawlewicz et al., 2002 [24]).1. Neogene; 2. Paleogene; 3. Cretaceous; 4. Cretaceous–Jurassic; 5. Jurassic; 6. Triassic–Cretaceous; 7. Triassic; 8. Paleozoic intrusive rocks; 9. Paleozoic metamorphic rocks; 10. Undivided Precambrian.

The most significant exploitations conducted in the catchment area are Rosia Montana, Rosia Poieni, Baia de Aries and Iara (Table 1) [21,25,26]. Tailings resulting from the oRes. extractions were stored in several tailing ponds, while all the wastewaters resulted from the mining activities and secondary processing of the oRes. are discharged into the tributaries of the Aries Rivers (Figure 2).Most of the mining and ore processing facilities were demolished or conserved;however, some of them were simply abandoned [27].At present, the open-cast mine Rosia Poieni is the only unity in operation, although reopening the exploitation of gold and silver oRes. at Rosia Montana has been largely debated during the last few years.

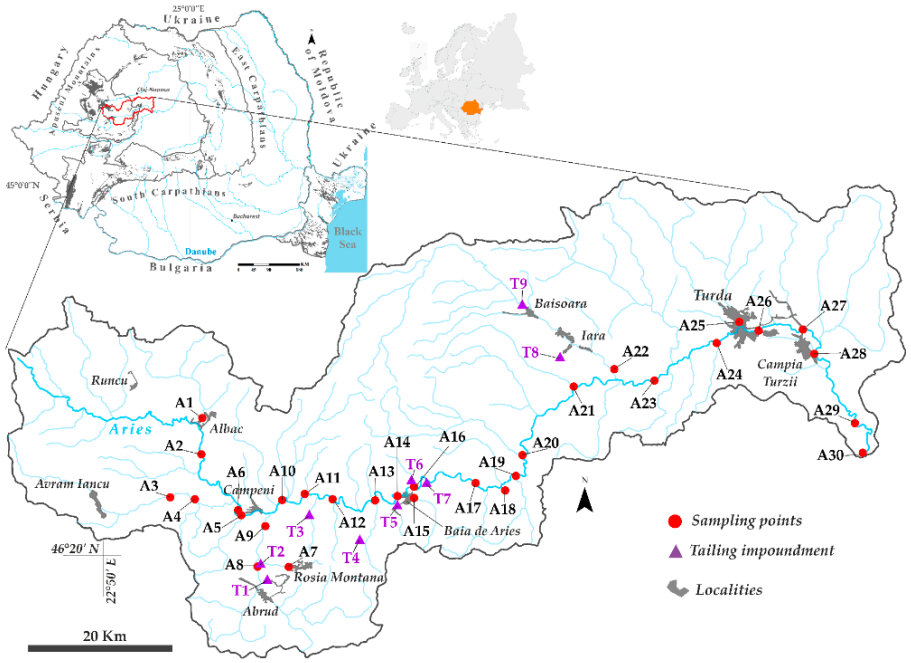

Figure 2. Location of the sampling points and the main tailings impoundments in the Aries River catchment.

Table 1. Characteristics of the main tailing impoundments located in the Aries Rciver catchment [27].

	Deposit Type	Extraction Technique	Current Status	Tailing Impoundment	Deposit Volume (mil m³)
Rosia Montana	Au ores Ag ores Cu ores	Open-pit gold mine	Closed since 2006	Seliste	6.60
				Gura Rosie	5.80
Rosia Poieni	Porphyritic Cu	Open-pit copper mine	Open	Stefanca	11.0
				Sesei	66.0
Baia de Aries	Lead-zinc ferrous Gold-silver ferrous	Gallery mine	Closed since 2004	Cutii	1.62
				Sartas	2.86
				Brazesti	3.47
Iara	Fe ores Mg ores	Open pit mine	Closed since 2005	Baisoara	3.33
				FagetulIerii	1.56

Over the years, several remediation measuRes. were taken, but the resulting wastes of the long periods of mining activities and their poor management have led to a significant deterioration of the quality of the natural environment[9,10,27,28].

2.2. Sampling and Analytical Procedures

The study area was selected based on the impacts generated by the mining and industrial activities on the water resources (Figure 2). To evaluate the quality of the surface water, a field survey was conducted across the Aries River catchment. A number of 30 samples were collected from the mainstream (17 samples—A6, A12, A15-A30) and from the tributaries (13 samples—A1-A5, A7-A11, A13, A14) in November 2018.

The samples were collected with a "Grab" device submerged at 20 cm under the water in polyethylene bottles pre-washed with 0.1N HNO_3.The water samples were kept at 4 °C until the physico-chemical analysis, but no longer than 24 h.

The pH and electrical conductivity (EC) were measured on-field by using a portable 350I multiparameter (WTW, Weilheim, Germany). The total dissolved solids (TDS) were

determined by gravimetry, while bicarbonates (HCO_3^-) were determined by titration with 0.1 N HCl in the presence of bromocresol green indicator. The anions (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) concentration was measured by ion chromatography using an IC 761 Compact equipment (Metrohm, Herisau, Switzerland) after filtering the samples with 0.45 μm cellulose acetate membrane filters(Isolab, Eschau, Germany), used with no further purification treatments. Samples were directed injected into the equipment, characterized by a flow of 0.7 mL/min, 7.5 mPa pressure and 15.0 μS/cm electrical conductivity. Anions were separated through the anions exchange column and detected with the help of a conductivity detector [29].

For the determination of metals, the samples were filtered with 0.45 μm cellulose acetate membrane and acidified with 65% HNO_3. The major cations (Fe, Na, Mg, K and Ca) were analyzed through an inductively coupled plasma optical emission spectrometer(ICP-OES, Perkin Elmer, Waltham, MA, USA), while the trace metals (Ni, Cr, Co, Cu, Zn, Cd, Pb, Mn, Ba, Al, Sr and As) were analyzed through an inductively coupled mass spectrometer (ELAN DRC II ICP-MS, Perkin Elmer, Waltham, MA, USA), due to the very low sensitivity of the equipment [29]. The instruments calibration was performed using analytical curves prepared with a multi-element standard solution from ICP Multi-Element Standard Solution IV (CertiPUR Merck, Darmstadt, Germany) in case of the ICP-OES and PerkinElmer Instrument Calibration Standard 3 in case of the ICP-MS.

In order to ensure the quality of the results, calibration standards, duplicate samples and procedural lab blanks were prepared and determined, in concordance with Moldovan et al. [30]. The accuracy of the metal determinations was tested using the 1643f NIST certified reference material (National Institute of Standards and Technology, Gaithersburg, MD, USA), while the anions were determined according to the IC1 Multi-element standard (CertiPUR Merck, Darmstadt, Germany). The mean recoveries ranged between 94% and 105% for the metals and between 89% and 102% for the anions.

All reagents were of analytical grade and were used without any further purification. Ultrapure water from a Millipore system (Molsheim, France) was used for all dilutions.

2.3. Pollution Assessment

The Heavy Metal Pollution Index (HPI) is a rating model that provides the aggregate influence of individual heavy metals on the overall quality of different water types [31,32]. Seven heavy metals (Cd, Cu, Fe, Mn, Ni, Pb and Zn) were used for the calculation of HPI. The HPI was computed in two steps, according to Equations (1) and (2) [33]:

$$HPI = \frac{\sum_{i=1}^{n}(Q_i W_i)}{\sum_{i=1}^{n} W_i} \quad (1)$$

$$Q_i = \frac{M_i}{S_i} \times 100 \quad (2)$$

where, Q_i is the sub-index of the ith parameter, W_i is the unit weightage of the ith parameter and n is the number of the considered chemical parameters. M_i and S_i are the concentration of the monitored ith parameter and the standard maximum allowable values (mg/L), according to the Romanian Regulation and to the European Directive concerning water quality [34,35].

HPI scoRes. below the threshold (HPI <100) indicate low pollution with heavy metals, while scoRes. higher than 100 (HPI >100) suggest that the water is unsuitable for consumption and, when consumed, it causes harmful health consequences. The case of an HPI > 100 indicates pollution with heavy metals [36].

The Heavy Metal Evaluation Index (HEI) is another tool for assessing water quality, offering an insight into the overall quality of water sources with respect to the heavy metals content, which is consistent with the HPI method. The HEI iscalculated based on Equation (3), according to Bhuiyan et al. [37],Edet and Offiong[38]. The surface water can

be classified based on the HEI scores, as follows: surface waters with a low degree of pollution (HEI < 10), waters with a medium degree of pollution (10<HEI< 20) and waters with a high pollution level (HEI > 20) [39].

$$HEI = \sum_{i=1}^{n} \frac{M_i}{S_i} \quad (3)$$

whereM_i is the determined concentration of the ith parameter and S_i represents the maximum allowable concentration (MAC) of the parameters. In the present study,S_i values were considered according to the Romanian and International Regulations, namely the Minister Order 161/2006/OD and Directive 2008/32/CE, regarding the quality of surface water resources [34,35]

2.4. Water Quality Index (WQI)

One of the most effective tools in evaluating the quality of waters is represented by the Water Quality Index (WQI), showing the risk posed by the pollutants present in the water constituents matrix [16]. This method provides an overview of the quality status characterizing various water resources. The WQI is computed in four steps: (a) the assignment of the weights (w_i) for each physico-chemical parameter based on its importance for the quality of the surface water (Table 2); (b) the calculation of the relative weight (W_i) using Equation (4); (c) establishing the quality rating (q_i) according to Equation (5); (d) the calculation of the subindex for each physico-chemical parameter (SI_i) and aggregation into the WQI. Equations (6) and (7) are Appl. in the last step of the method [16].

Table 2. List of the parameter values (S_i), weights (w_i)and relative weights (W_i) used for the calculation of the WQI.

Parameter	Unit	S_i*	w_i	W_i
pH	-	6.5–8.5	3	0.06
TDS	mg/L	1300	5	0.10
Ca	mg/L	300	4	0.08
Mg	mg/L	200	4	0.08
Na	mg/L	200	2	0.04
Cl^-	mg/L	300	4	0.08
NO_3^-	mg/L	11.2	5	0.10
SO_4^{2-}	mg/L	300	3	0.06
As	mg/L	0.100	3	0.06
Mn	mg/L	0.100	3	0.06
Fe	mg/L	0.200	3	0.06
Pb	mg/L	0.050	3	0.06
Ni	mg/L	0.100	3	0.06
Zn	mg/L	1.00	3	0.06
Cu	mg/L	1.00	3	0.06
			$\sum w_i = 51$	$\sum W_i = 1.00$

*Ministerial Order 161/2006/OD and Directive 2008/32/CE [34,35].

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \quad (4)$$

$$q_i = \frac{C_i}{S_i} \times 100 \quad (5)$$

$$SI_i = W_i \times q_i \quad (6)$$

$$\text{WQI}=\sum_{i=1}^{n} SI_i \quad (7)$$

where, $w_i$is the weight of each parameter, W_i is the relative weight,q_i represents the quality rating for each physico-chemical parameter, C_i and S_i represent the concentration and the guideline value according to the drinking water quality guidelines established by the Minister Order 161/2006/OD and the Directive 2008/32/CE [34,35], SI_i represents the subindex of the ith parameter.

The WQI scoRes. classify the studied waters into five different quality categories: (a) excellent—suitable for drinking, irrigation and industrial usages, WQI = 0–25; (b) good—suitable for domestic, irrigation and industrial usages, WQI = 26–50; (c) poor—suitable for irrigation and industrial usages, WQI = 51–75; (d) very poor—suitable for irrigation usage, WQI = 76–100 and (e) unsuitable for drinking purposes and restricted for irrigation, WQI > 100 [40,41].

2.5. Graphical Approaches of the Quality Status

Piper and Durov diagrams were generated by using AqQa software (free version). The studied water samples were classified, based on the specific concentrations of physico-chemical parameters. For the Piper diagram, specific indicators such as Cl^-, SO_4^{2-}, Ca, Mg, Na, K, HCO_3^- and CO_3^{2-}, concentrations were used, while for the Durov plot, the pH and TDS content were added [42,43].

To highlight the correlations and similarities among the physico-chemical indicators, the agglomerative hierarchical cluster analysis (HCA) based on the Ward method (Euclidean distance) was assessed. The method was Appl. using XLSTAT software.

2.6. Interpolation Methods Used for Representation of HPI, HEI and WQI

In order to assess the polluted areas, several interpolation methods from ArcGis 10.1 spatial analyst were used: IDW, Ordinary Kriging (OK) and Empirical Bayesian Kriging (EBK). From these methods, only the EBK method was appropriate to represent the contaminated areas regarding the number and the distribution of the sampling points in the Aries catchment. EBK was reported to have good results with small datasets regarding the contaminated areas [44]. However, in order to reduce the bias, the EBK was Appl. only to the mainstream and to the floodplain area around the Aries River (and few tributaries) for determining the polluted areas.

3. Results

3.1. Water Quality Assessment

The monitoring study was conducted in the rainy season (November 2018), which is more susceptible to indicate the actual values of the studied physico-chemical indicators, compared to the warm season, when due to the drought, the concentrations are higher. This season was not characterized by high precipitation amounts; therefore, the dissolution of the physico-chemical compounds and the low concentrations of the chemicals due to the washing by precipitations should be avoided. The total number of sampling sites was set to 30 points, randomly chosen, in order to analyze a number of 27 physico-chemical parameters. The obtained results, along with their statistical data, are presented in Tables 3 and 4.

The pH of the water samples (7.2–8.7) was within the normal limits except for three sample points: A3 (9.0), A7 (2.8) and A13 (5.2), which were indicating a strong variation of the water character. The slightly alkaline pH values are explained by the dissolution of carbonate minerals [29], while the strong acid character can be attributed to the drainage of the acid mine wastewaters near two mining areas. Acid mine drainage is an important source of surface water pollution worldwide. Luis et al. (2009) reported the effects of the

mine drainage into a hydrographic river catchment, in an area characterized by the abundance of sulfide ores, in Portugal [45].

Generally, tailings coming from mineral extraction areas are considered major sources of heavy metals and other chemical compounds (cyanide, sulfuric acid, ammonium nitrate). These chemicals are used during the separation processes of sterile from the ore and excavating machines. However, the natural geological units could also be the source of high amounts of toxic metals (e.g., Cd from sphalerite, Zn from sphalerite and As from oxidation of sulfide minerals pyrite) [46].

The analyzed surface water samples showed a low spatial variation of heavy metals (such as Cd, Mn, Ni and As). However, important differences were observed in the cases of the Fe, Cr, Co, Zn, Sr, Ba, and Al variability. It was observed that the metal concentrations varied in different sampling locations (Figure 3). Samples A9–A13 were characterized by the highest concentrations of As, Fe, Mn and Pb, exceeding the thresholds up to four times. The waters were sampled next to the tailing impoundments and connected to Rosia Montana and Rosia Poieni mining areas, indicating a significant impact on the chemical composition of the Aries River catchment over time. In the proximity of ValeaSesii tailing impoundment, A12 has the highest As, Fe and Mn concentrations, exceeding the thresholds. All samples were contaminated with Pb, with values ranging between 0.041 and 0.227, except for A19, which has a significant concentration of Pb as well, but below the threshold.

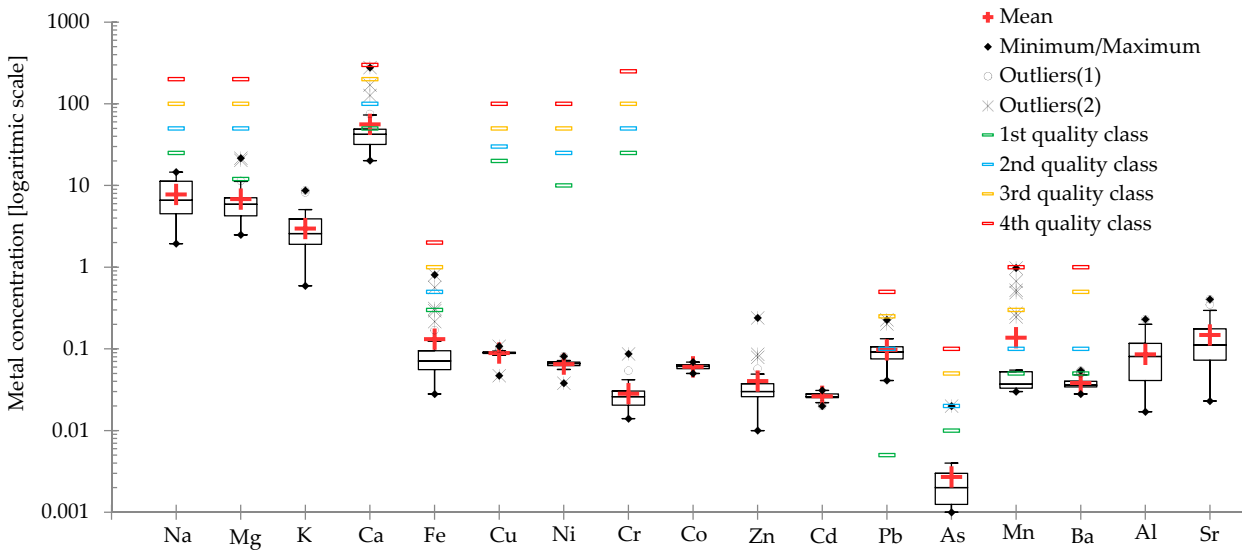

Figure 3. The variation of elements in the sampling sites.

Cr, Co and Zn concentrations were below the limits established by the Romanian and European Regulations regarding the quality of water resources [34,35]. The highest Cr concentration was 0.087 mg/L (A14) nearby Baia de Aries (a former mine that stopped its activity in 2004). There are no available data of environmental quality remediation attempts in that area. The Cu and Zn concentrations have a low degree of variation: Cu was in the range of 0.088–0.108 mg/L, and Zn ranged between 0.010 and 0.240 mg/L. Pb (0.041–0.227 mg/L) was identified in samples connected to the tailing impoundments (A7, A9–A15).

Ni, Co and Cd concentrations had a very low spatial variation, indicating no anthropogenic interference in the water chemistry main processes. Ni ranged from 0.038 to 0.081 mg/L, Co from 0.050 mg/L to 0.069 mg/L, with the highest value in A11, while Cd concentrations ranged between 0.020 mg/L and 0.031 mg/L (A17).

In all studied samples, Ba and Al were within the normal limits, Ba ranged between 0.028 mg/L and 0.054 mg/L (A11) and Al between 0.033 mg/L and 0.230 mg/L (A20). Sr had the maximum value of 0.405 mg/L in A14, nearby Baia de Aries.

It was noticed that most of the contaminated sampling points with heavy metals were A7, A9, A12 and A13. The water samples sites were connected to Rosia Montana and Rosia Poieni mining areas, indicating a significant impact on the chemical composition of the Aries River catchment over time.

Table 3. Trend of spatial variation of the physico-chemical parameters analyzed in the Aries River water samples.

	pH	CE (μs/cm)	TDS (mg/L)	HCO_3^- (mg/L)	F^-	Cl^-	NO_3^-	SO_4^{3-}
A1	7.6	188	167	87.6	0.06	8.09	1.18	4.78
A2	7.5	202	154	97.6	0.06	8.22	1.22	5.82
A3	8.7	173	162	94.2	0.08	8.61	1.02	6.83
A4	8.3	140	159	73.6	0.06	1.91	0.99	5.67
A5	8.2	157	168	84.5	0.07	2.13	1.08	5.74
A6	9.0	168	178	80.6	0.06	6.52	1.22	5.13
A7	2.8	901	952	302	0.15	42.9	0.67	465
A8	7.2	824	485	122	0.15	12.8	0.77	6.82
A9	5.2	494	414	277	0.12	14.3	0.92	214
A10	7.2	620	412	62.4	0.12	15.0	0.88	202
A11	7.4	576	405	79.3	0.11	15.5	0.50	194
A12	7.6	222	231	90.7	0.08	7.65	2.33	32.2
A13	5.2	1348	712	262	0.33	45.8	2.45	208
A14	8.0	495	408	171	0.13	19.1	0.58	93.2
A15	8.0	357	312	72.1	0.12	14.2	1.11	87.3
A16	8.1	287	249	83.6	0.11	8.21	1.27	56.0
A17	8.0	309	246	89.8	0.13	8.41	1.19	62.5
A18	7.9	318	258	88.4	0.13	8.77	1.20	66.2
A19	8.0	320	263	84.2	0.12	9.00	1.13	68.0
A20	8.0	251	197	109	0.09	10.8	1.38	17.4
A21	8.1	244	202	74.2	0.12	9.56	1.45	50.8
A22	8.1	283	227	98.7	0.10	6.82	1.41	43.8
A23	8.1	328	234	113	0.10	9.26	1.53	56.4
A24	8.2	322	274	108	0.10	17.6	1.72	59.8
A25	8.4	414	303	126	0.11	21.5	1.99	66.5
A26	8.5	478	278	123	0.11	21.5	1.91	68.3
A27	8.4	417	287	131	0.12	21.7	1.88	66.0
A28	8.5	405	273	114	0.12	20.8	1.64	66.3
A29	8.6	384	267	108	0.11	18.8	1.26	67.7
A30	8.3	368	262	117	0.13	14.6	1.37	63.5
Min	2.8	140	154	62.4	0.06	1.91	0.50	4.78
Max	9.0	1348	952	302	0.33	45.8	2.50	465
Average	7.7	400	305	118	0.11	14.3	1.31	80.5
MAC*	6.5–8.5	-	1300	-	-	300	11.2	300

* Ministerial Order 161/2006/OD and Directive 2008/32/CE [34,35].

Table 4. The element concentrations (mg/ L) in the surface water samples (A1–A30).

	Fe	Ni	Cr	Co	Cu	Zn	Cd	Pb	Na	Mg	K	Ca	Mn	Ba	Al	Sr	As
A1	0.041	0.069	0.017	0.064	0.088	0.032	0.028	0.080	4.19	2.92	0.639	25.3	0.032	0.034	0.038	0.023	0.001
A2	0.058	0.066	0.018	0.064	0.088	0.033	0.026	0.090	4.29	3.07	0.677	27.8	0.033	0.036	0.033	0.027	0.001
A3	0.169	0.065	0.020	0.064	0.087	0.038	0.027	0.093	4.36	3.32	0.689	26.3	0.036	0.038	0.121	0.035	0.001
A4	0.050	0.060	0.014	0.061	0.089	0.015	0.025	0.087	1.94	2.49	0.591	20.2	0.034	0.050	0.041	0.038	0.001
A5	0.077	0.066	0.015	0.063	0.092	0.011	0.026	0.074	2.04	2.61	0.682	22.4	0.033	0.040	0.038	0.027	0.001
A6	0.066	0.067	0.020	0.052	0.084	0.010	0.030	0.063	3.49	2.88	1.41	21.2	0.036	0.029	0.036	0.028	0.001
A7	0.807	0.064	0.035	0.065	0.084	0.038	0.028	0.227	7.63	21.6	8.69	278	0.038	0.039	0.041	0.292	0.002
A8	0.028	0.038	0.033	0.064	0.047	0.042	0.020	0.058	5.21	4.75	4.37	40.6	0.048	0.042	0.038	0.290	0.001
A9	0.313	0.069	0.022	0.064	0.108	0.086	0.026	0.132	11.4	20.4	8.19	127	0.490	0.048	0.200	0.289	0.001
A10	0.294	0.072	0.028	0.067	0.100	0.079	0.027	0.104	11.8	10.6	5.06	72.8	0.522	0.051	0.128	0.290	0.002
A11	0.076	0.081	0.031	0.069	0.091	0.240	0.026	0.110	12.1	11.2	4.76	75.1	0.672	0.054	0.083	0.296	0.002
A12	0.366	0.070	0.027	0.062	0.087	0.049	0.028	0.202	5.50	4.73	1.65	31.5	0.981	0.029	0.087	0.081	0.020
A13	0.070	0.066	0.028	0.060	0.090	0.057	0.026	0.133	10.2	5.88	1.88	170	0.273	0.028	0.071	0.088	0.002
A14	0.083	0.063	0.087	0.060	0.092	0.036	0.025	0.107	11.2	11.4	2.92	65.9	0.043	0.053	0.069	0.405	0.002
A15	0.072	0.063	0.027	0.061	0.090	0.030	0.026	0.100	5.88	8.16	3.04	42.7	0.055	0.042	0.062	0.348	0.002
A16	0.052	0.065	0.023	0.066	0.088	0.024	0.027	0.096	5.65	3.94	2.10	38.4	0.246	0.032	0.017	0.097	0.002
A17	0.099	0.069	0.016	0.062	0.092	0.027	0.030	0.113	6.43	4.10	2.48	41.9	0.046	0.032	0.142	0.104	0.002
A18	0.124	0.064	0.020	0.060	0.091	0.030	0.031	0.107	6.50	5.03	2.67	40.8	0.048	0.033	0.097	0.097	0.002
A19	0.216	0.056	0.036	0.058	0.092	0.028	0.030	0.041	6.69	5.29	2.35	40.0	0.054	0.033	0.041	0.091	0.003
A20	0.078	0.061	0.028	0.050	0.086	0.030	0.029	0.094	3.56	6.15	1.99	30.8	0.048	0.035	0.230	0.069	0.003
A21	0.064	0.060	0.054	0.055	0.090	0.027	0.028	0.088	4.22	5.87	2.02	32.7	0.042	0.035	0.062	0.070	0.002
A22	0.037	0.059	0.023	0.063	0.094	0.023	0.028	0.069	4.95	5.56	2.07	36.7	0.034	0.036	0.079	0.089	0.002
A23	0.075	0.058	0.023	0.060	0.090	0.027	0.022	0.093	6.78	5.74	2.47	43.3	0.033	0.035	0.119	0.119	0.003
A24	0.055	0.062	0.042	0.056	0.090	0.025	0.021	0.090	10.2	6.43	3.18	45.3	0.033	0.038	0.082	0.145	0.003
A25	0.042	0.068	0.031	0.051	0.091	0.026	0.022	0.090	14.1	7.17	4.11	48.5	0.033	0.040	0.094	0.176	0.003
A26	0.067	0.070	0.025	0.057	0.090	0.026	0.026	0.074	14.5	7.02	4.28	48.8	0.030	0.037	0.088	0.176	0.003
A27	0.078	0.070	0.029	0.061	0.089	0.029	0.026	0.050	14.6	7.09	4.24	48.9	0.033	0.035	0.109	0.176	0.004
A28	0.067	0.070	0.027	0.057	0.088	0.031	0.026	0.088	12.8	7.04	3.22	46.3	0.032	0.036	0.120	0.166	0.003
A29	0.067	0.069	0.025	0.057	0.088	0.036	0.025	0.104	11.3	6.29	3.24	45.8	0.034	0.039	0.132	0.157	0.003
A30	0.047	0.069	0.023	0.059	0.090	0.026	0.024	0.066	9.74	6.12	3.29	46.2	0.036	0.036	0.077	0.153	0.003
Min	0.028	0.038	0.017	0.050	0.047	0.010	0.020	0.041	1.90	2.50	0.59	20.2	0.030	0.028	0.033	0.023	0.001
Max	0.807	0.081	0.087	0.069	0.108	0.240	0.031	0.227	14.6	21.6	8.69	278	0.981	0.054	0.230	0.405	0.020
Average	0.124	0.062	0.036	0.061	0.093	0.044	0.026	0.102	7.77	6.99	2.96	56.0	0.143	0.042	0.091	0.154	0.003
MAC*	2.00	0.100	0.250	0.100	0.100	1.00	0.050	0.050	200	200	-	300	1.00	1.00	-	-	0.100

* Ministerial Order 161/2006/OD and Directive 2008/32/CE [34,35].

Previous studies conducted in the investigated area highlighted a high degree of pollution of the Abrud River (A9), emissary river of the Sesii Valley (A7) and of the Aries River, in the proximity of Baia de Aries (A13, A14) [10,47]. Relying on previous studies, it can be concluded that, even if the mining activity reduced or stopped operating in the studied area, the water quality did not present major improvements over time. Some studies indicated a long period of time until major improvements in the quality of the environment and surface waters in areas affected by mining activities are reached without any human intervention [48,49]. Thus, before overflowing into the effluent, wastewaters are highly recommended to be pretreated before being released into the environment in order to prevent the destruction of the natural water system and the imminent negative effects on human health. The nitrification, biochemical removal and thiocyanate processes are three successful wastewater treatment methods for addressing the sources of water contaminated by mining effluents [50]. Gonzalez-Merchan et al. [51] proposed an efficient treatment to neutralize the pH with wet Fe(VI) synthesized from $Fe(NO_3)_3$, $FeCl_3$, or $Fe_2(SO_4)_3$ and removing the toxic elements resulted from mining activities (gold extractions).

3.2. Cations and Anions Characteristics

The river chemistry is generally associated with human and atmospheric inputs: rock and soil weathering, evaporation and crystallization [42,52]. Ca (56.0 ± 52.1 mg/L) was the dominant major cation across the Aries River catchment, followed by Na (7.77 ± 1.98 mg/L), Mg (6.99 ± 4.52 mg/L) and K (2.96 ± 1.96 mg/L). Na concentration ranged between 1.90 and 14.6 mg/L, with the maximum concentration measured in A27 (Table 4). The highest levels of Mg, K and Ca were identified in A7 and A9. The Ca and Mg concentrations in the water samples from the Aries River catchment were higher than 75% of the total cation amount from the studied area, reflecting the predominance of carbonate weathering in the surface water. By contrast, HCO_3^-(118 ± 59.7 mg/L) and SO_4^{2-} (80.5 ± 94.8 mg/L) were the most abundant major anions in the surface waters. The main sources of bicarbonate are the weathering and dissolution processes of different rocks, such as calcite, carbonate, silicate and dolomite. The increasing trend of SO_4^{2-} concentration in A7 was not attributed to natural fluctuations but related to the industrial and agricultural activities in the Aries River catchment. The samples with the lowest SO_4^{2-}concentration are also associated with the lowest TDS values.

The NO_3^- concentrations ranged between 0.5 and 2.5 mg/L. Generally, the lowest values of NO_3^- are correlated to the highest TDS values, except for sample A13, which was the richest sample in NO_3^- and had a high value for the TDS.

Regarding the Cl^- concentration, high values were noticed in samples A7 (42.9 mg/L) and A13 (45.8 mg/L), while in the rest of the samples, Cl^-ranged between 1.19 and 20.8 mg/L. Furthermore, the chloride (Cl^-) concentration indicated a low atmospheric contribution in the river catchment area. The highest F^-concentration was determined in sample A13 (0.33 mg/L), while the lowest was in samples A1, A2, A4 and A6.

NO_2^- and PO_4^{3-} were lower than the quantification limits (0.05 mg/L) of the method. The low concentrations of anions in the samples A1–A6, A17–A24 were due to the lithology, low human interference and slow weathering rate. The high standard deviations of the anions indicated that the data were usually spread due to the spatial variations among all sites and possible anthropogenic impacts. Other surface waters from Europe are characterized by comparable concentrations of anions, ranging between 0.01 and 0.19 mg/L NO_2^-; 4.51 and 6.49 mg/L NO_3^-; 0.66 and 3.33 mg/L PO_4^{3-}; 23.5and 265 mg/L SO_4^{2-}in Coruh River Basin (Georgia and Turkey) and 30.0 and 2000 mg/L Cl^-, 0.1 and 30.0 mg/L NO_3^- and 550 and 1000 mg/L SO_4^{2-}in El Avenque River (Spain) [53,54].

The high values of EC and TDS and the high concentrations of HCO_3^-, SO_4^{2-}, Mg, K, Ca and Pb determined in samples A7, A9 and A13 clearly indicated an input of mine drainage from the mining-affected sites. Ca and HCO_3^-, K and NO_3^-, Mg and SO_4^{2-} were observed to have similar spatial variations (Figure 4). The trend of the highest composi-

tion of Ca and HCO_3^- in the Aries River was likely primarily derived from the dissolution of dolomite and from the dissolution of calcite (the upper and middle catchment area is represented mostly by karst landscape), while, based on the cation and anion concentrations, four different clusters were obtained. According to the hierarchical cluster analysis (HCA), four clusters were grouped, as indicated in Figure 4. Cluster 1 was formed by samples A7, A10 and A11, due to high values of Ca and SO_4^{2-}. Cluster 4 grouped samples A1, A2, A3, A4, A5, A6 and A10, based on the low concentrations of F^-, Cl^-, NO_3^-, SO_4^{2-}, Mg and K. A13 and A8 were not linked to a particular cluster, due to a main characteristic of the sample (in the case of A8, due to a high concentration of SO_4^{2-} and, in the case of A13, high concentration of HCO_3^-).

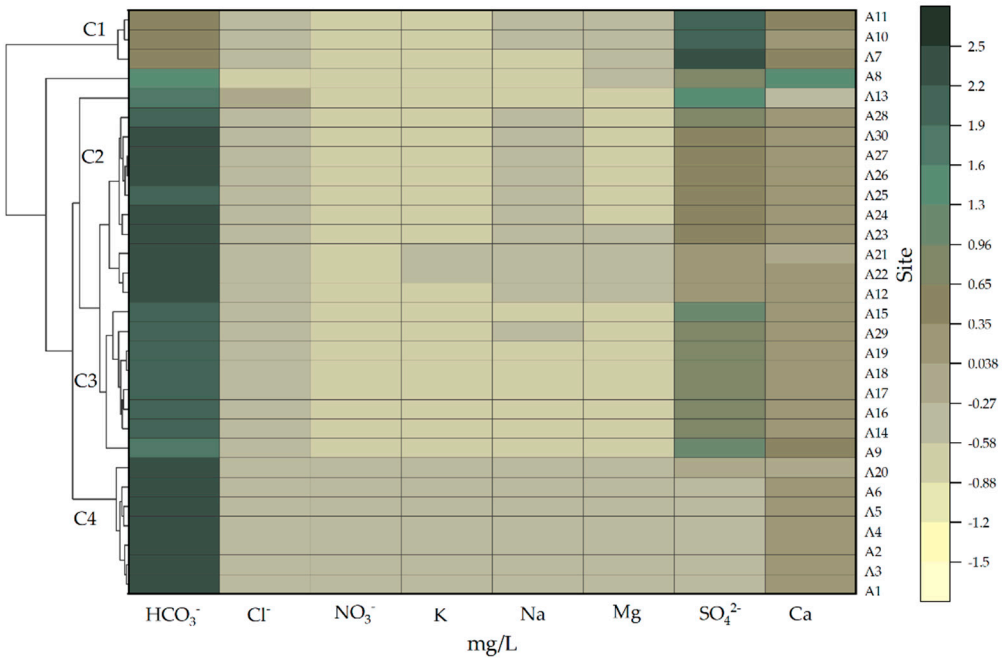

Figure 4. The logarithmic distribution of chemical parameters concentrations (HCO_3^-, Cl^-, NO_3^-, K, Na, Mg, SO_4^{2-}, Ca) among the sampling points with the corresponding dendrograms.

The correlations and similarities among the chemical indicators were established with the agglomerative hierarchical cluster analysis. The performed HCA classifies all 30 water samples (A1–A30) into four clusters (Figure 5). Cluster 1 (C1) included pH, NO_3^-, Al, Cd, Ni and Cu, Cluster 2 (C2) contained almost all of the anions (Cl^-, F^-, HCO_3^-, SO_4^{2-}), Ca, TDS and EC, while Cluster 3 (C3) included the rest of the cations (Mg, K, Na) and most of the metals (Sr, Cr, Ba, Fe, Pb, Co, Zn and Mn).

TDS, SO_4^{2-} and Ca were grouped, suggesting the same source. The high values of TDS were due to the natural dissolution of gypsum or due to anthropogenic activities. NO_3^-, Al, Cd, Ni and Cu (C1), and, respectively, Cr, Ba, Fe, Pb, Co, Zn and Mn (C3) were distant from EC/SO_4^{2-}, indicating that those parameters behave quite differently. Therefore, a possible mechanism of establishing the main processes controlling the chemistry of surface waters was established. Mining activities are a source of toxic metals, while natural processes, such as the weathering of gypsum, could be the main source of Ca and SO_4^{2-}[55]. NO_3^-, Mn and As were clustered in sample A12, indicating the same source and similar chemical behavior.

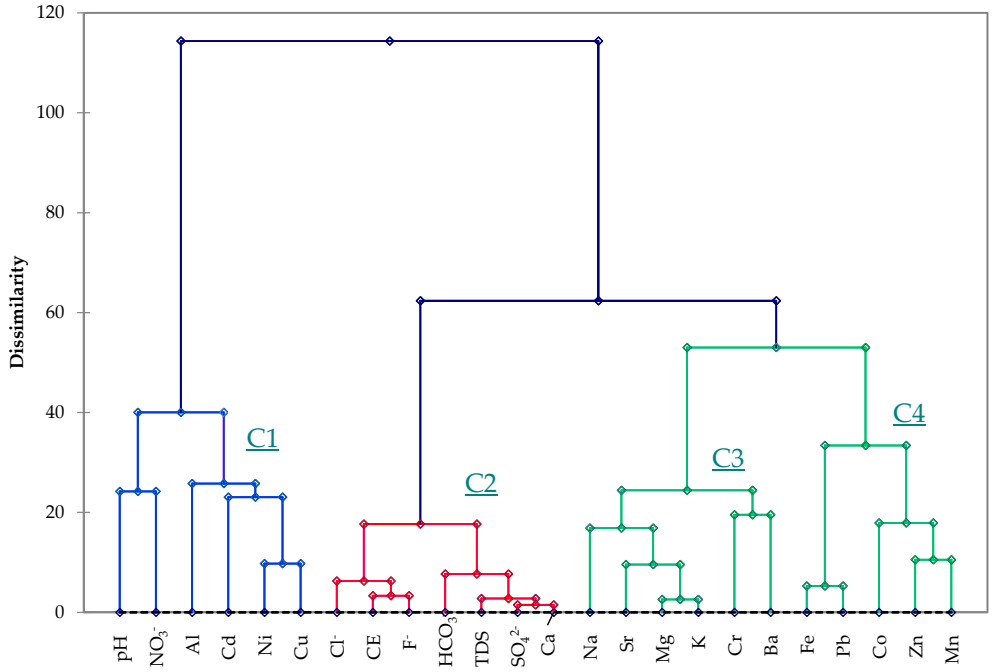

Figure 5. Hierarchical cluster analysis of the physico-chemical indicators for the studied samples.

The water types of the analyzed samples were determined using the Piper and Durov diagrams(Figure 6a,b). The hydrochemical facies and different types of waters were assessed based on the major cations and anions projected into the diamond field situated in the center of the Piper plot [32,42]. In the cation plot, most of the studied water samples were situated in the left corner, where the Ca concentration was high, indicating its dominance. In contrast, the anion diagram showed that most of the water samples were distributed in the lower-left corner, characterized by the dominance of HCO_3^- over Cl^- and SO_4^{2-}. However, two samples were situated in the upper corner and dominated by SO_4^{2-} over Cl^- and HCO_3^-.

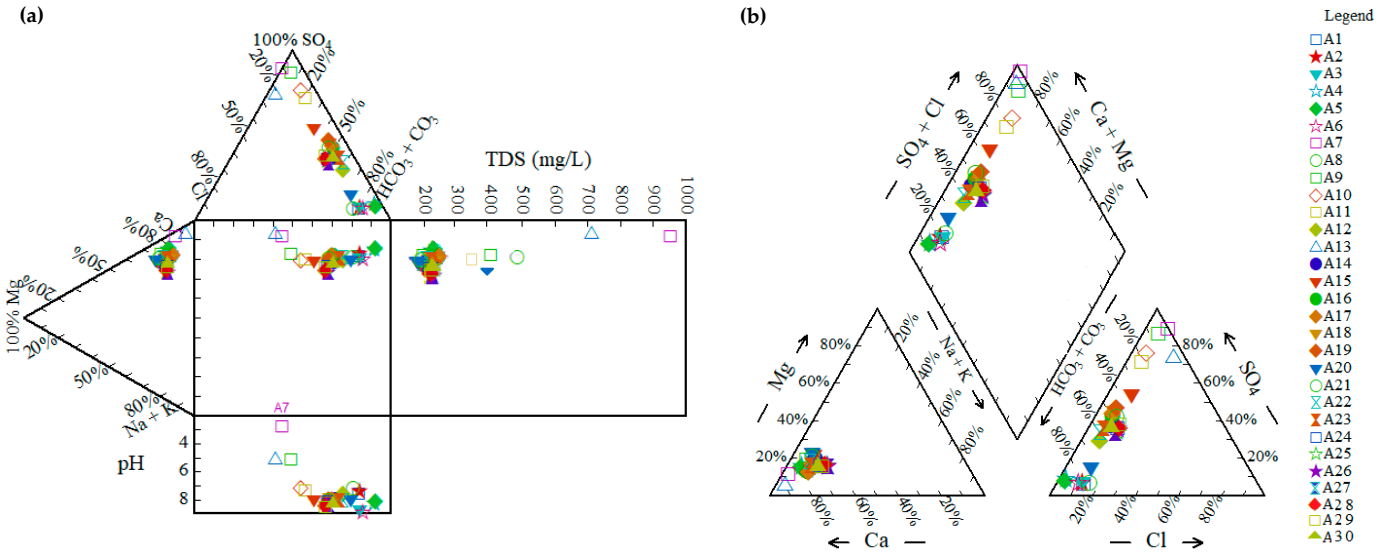

Figure 6. Durov (**a**) and Piper (**b**) diagrams describing the water facies of the studied surfacewaters.

The overall characteristics of the chemistry in the surface water samples, according to the Piper diagram, are the dominance of the alkaline earth elements (Ca and Mg) over

the alkaline elements (Na and K) and for the weak acids (HCO_3^-) over the strong acids (SO_4^{2-} + Cl^-).

The Piper and Durov diagrams showed that the water samples were divided into two main types: Mg-HCO_3^- type (A1–A6, A8, A12, A14, A16–A30), indicating their carbonate-dominant lithology and Ca-Cl^- type (A7, A9, A10, A11, A13, A15). The Durov plot also indicated that the majority of samples are alkaline, except for A7, A9 and A13, which were characterized by low pH values.

3.3. Pollution Index

The water quality of the study area was analyzed using several pollution indices. The HPI is used to characterize the potential environmental risk of heavy metals in water bodies, while HEI gives an overall quality of the water regarding the heavy metal concentration[13,38]. The spatial trends for the HPI and HEI in the Aries River catchment were calculated based on the following heavy metals: Cd, Cu, Fe, Mn, Ni, Pb and Zn. The number of heavy metals was reported to the standard values established by the Romanian Legislation, Order 161/2006/OD and Directive 2008/32/CE [34,35].

HEI ranged from 2.65 to 16.9, indicating a medium level of heavy metal pollution in 5 out of the 30 water samples. The highest HEI results were obtained in the case of A12 (HEI = 16.9), samples collected from the vicinity of Valea Sesii. Based on scaled HEI values, 83% of samples were classified as having low pollution levels and 17% with medium pollution levels (Figure 7b).

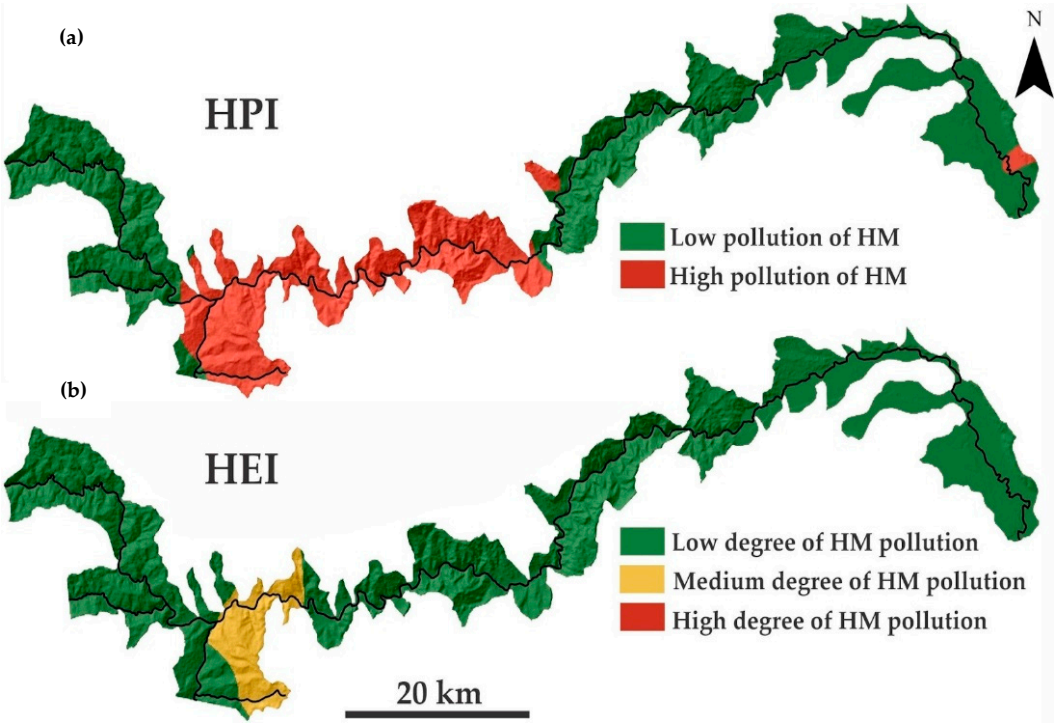

Figure 7. Spatial variation of heavy metal pollution index HPI (**a**) and heavy metal evaluation index HEI (**b**).

Studies from Africa indicated low and moderate–heavy metal pollution in the Malopane region (Dorpsrivier, Mogalakwena Deep pool, Dithokeng, Rooisloot, South Africa), a region with intensive agriculture and mining activities [56].

3.4. Water Quality Index and Vulnerability Assessment

The WQI provides a single value of expression, which outlines various parameters and gives a measure of the water quality. A number of 15 physico-chemical parameters were used for the calculation of the WQI (pH, TDS, Cl^-, NO_3^-, SO_4^{2-}, Na, Mg, Ca, Cu, Zn,

Pb, Fe, Ni, Mn and As). The results ranged from 17.7 to 103 with a mean value of 31.9 (for all 30 samples), and the mean water quality was rated as "good" in general. Spatially, 21 samples were ranked with excellent quality, three samples with good quality (A14, A15, A16), four with medium quality (A9, A10, A11, A13), one sample was characterized by poor quality (A7) and one sample unsuitable for usage (A12). Thus, the WQI scores. were significantly different among the four spatial groups (Figure 8).

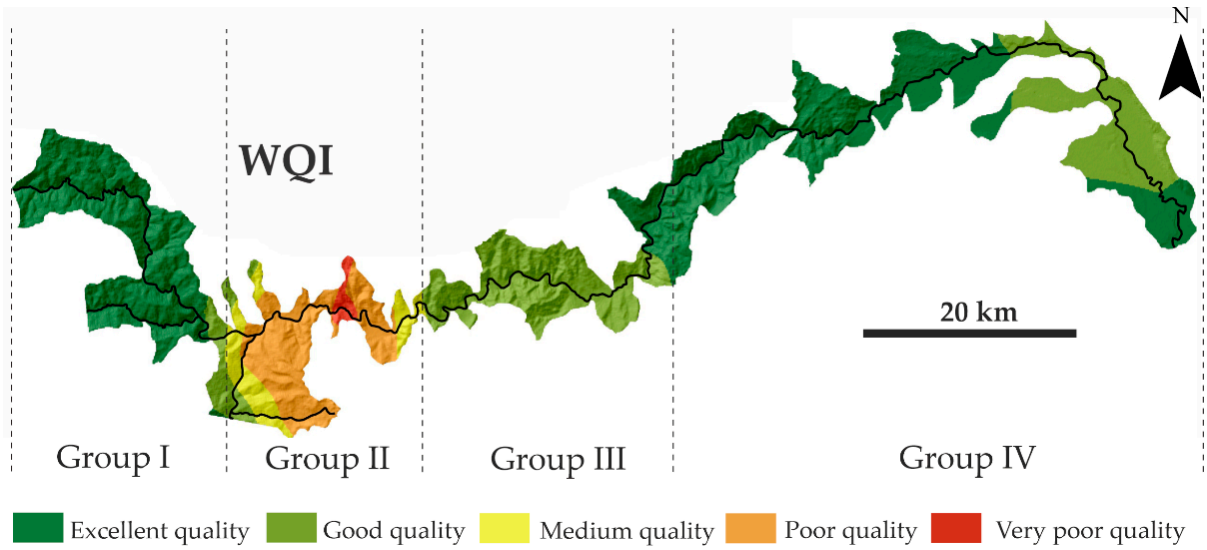

Figure 8. Spatial variation of the water quality index (WQI).

The WQI results were relatively high in Group I (with a mean of 19.1). The second group was characterized by a mean value of 62.9, with only one sample with a WQI score lower than 50 (WQI < 50). Group II area is localized nearby a tailing impoundment and an industrialized location. The WQI has a mean value of 28.2 in Group II. Water quality improves as the distance from mine drainage sources increases in Groups III and IV. According to the WQI classification, the general water quality state characterizes Group I with excellent quality, Group II with moderate quality and Groups III and IV with good and excellent quality.

The WQI scores obtained from different studies from Africa (Limpopo) range between 121 and 4644, indicating very poor quality water and not suitable for drinking due to the rich precipitation, high ionic activities and sedimentation [56]. In Turkey (Kirmir Basin), according to the WQI results, the studied water samples are characterized by very poor quality due to urbanization and anthropogenic activities; WQI ranged from 7.4 to 38.1 [57]. There were considerable spatial disparities in the assessed vulnerability of surface water resources in the study area.

Covering ≈ 68% of all the study area, the vulnerability level was generally reduced, especially in the western and eastern regions. In the central area of the Aries catchment, high and very high vulnerability levels were observed, overlapping with the discharge area of the tailing impoundments, washing water flux and all the streams influenced by their tributary's poor-quality status. Similar to the water quality classification based on the WQI, a medium vulnerability level was overlying the area characterized by a quality improvement trend (Group III).

Surface water resources in the Apuseni Mountains are abundant, while the ratio between regional supply and water demand in the study area was relatively small. Due to the historical and current mining activities, agricultural water consumption, and low efficiency of water use, the vulnerability of water resources in the Aries catchment remains high.

4. Discussion

On a global scale, acid mine drainage is an important source of surface water pollution. Luis et al. (2009) reported the effects of mine drainage to a hydrographic river catchment in an area characterized by an abundance of sulfide ore bodies from Portugal [45].

The degree of the mineralization process could be reflected by the EC and TDS, which showed variations. The EC and TDS were positively correlated. In the case of samples A7, A8 and A13, the EC and TDS values were in the range of 901–1348 μS/cm and 712–952 mg/L, respectively. Similar results of pH, TDS and EC were reported in the surface water resources nearby the gold mining areas in Tongon—an open-pit gold mine that produced between 2012 and 2015 about 1.356 × 107 tons of ores, located in Cote d'Ivoire Region, Africa [58]. In different parts of Europe (Georgia, Spain and Turkey), comparable results were obtained for Coruh and El Avenque Rivers with pH variation from 4.50 to 9.07, and EC from 114 to 1200 μS/cm [53,54].

In general, the sources of high amounts of heavy metals are industrial and mining activities [53,54]. Recent studies from Turkey and Georgia show relatively high amounts of heavy metals in surface waters, such as 0.33–2.88 μg/L Cd; 0.7–17.2 μg/L Co; 0.13–2.02 μg/L Cr; 0.06–895 μg/L Cu; 53.3–3140 μg/L Fe; 5.8–402 μg/L Mn; 1.4–21.0 μg/L Ni; 0.1–73.0 μg/L Pb and 7.6–537 μg/L Zn [53]. While in Spain (El Avenque River), the heavy metal content varied between 0.01 and 1.00 mg/L Cd, 0.01 and 0.15 mg/L Cu, 0.01 and 0.25 mg/L Pb, and 0.01 and 450 mg/L Zn [54].

In surface water in China, mining activities influenced the quality of water as well, by increasing the level of metals, the studied waters being characterized by relatively high concentrations of As (0.0–6.90 μg/L), Cr (0.95–42.9 μg/L), Cu (1.20–19.0 μg/L), Mn (2.65–168 μg/L), Ni (1.69–164 μg/L), Pb (0.91–28.2 μg/L) and Zn (2.74–490 μg/L) [59].

HPI results were ranging from 68.4 to 412, as indicated in Table 5, showing some pollution levels with the studied heavy metals. The spatial distribution of HPI results is presented in Figure 7a. The mean value of HPI results was 132, indicating a concerning risk of pollution with the analyzed heavy metals in the study area, more specifically with Pb, Mn and Fe. Different studies from Serbia (Ugljesnica River) and India (Bokaro River) indicated no heavy metal pollution with Cd, Cu, Fe, Mn, Pb, Zn with HPI scores. ranging from 66 to 90 and 2.0 to 26[14,15]although the rivers are located nearby mining areas. In Nigeria (Commodore channel) and China (Houjing River), the HPI results ranged between 985 and 5995, and 100 and 230, indicating high amounts of heavy metals due to industrial (wastewaters, landfill leachate) and household activities [60,61].

Table 5. Results of the calculated pollution and quality indices (HPI, HEI and WQI).

	HPI	HEI	WQI
A1	91.4	3.50	17.9
A2	100	3.72	18.4
A3	109	4.38	22.6
A4	96.2	3.53	17.7
A5	87.7	3.48	18.8
A6	78.7	3.31	19.4
A7	256	10.3	78.9
A8	68.9	2.65	18.8
A9	247	10.5	62.5
A10	229	10.2	63.0
A11	257	11.0	66.7
A12	412	16.9	103
A13	188	7.07	46.7
A14	117	4.24	25.1
A15	113	4.18	25.8
A16	150	5.94	33.6
A17	125	4.62	23.5
A18	121	4.62	24.2
A19	69.6	3.72	26.2
A20	107	4.06	21.1
A21	99.5	3.78	20.9
A22	80.2	3.17	19.4
A23	102	3.70	21.5
A24	99.3	3.56	22.1
A25	99.9	3.58	23.1
A26	87.5	3.45	23.4
A27	68.4	3.06	23.7
A28	99.7	3.75	23.3
A29	113	4.11	23.2
A30	80.7	3.24	21.8

5. Conclusions

According to the obtained results, the studied water system (Aries River) was characterized as vulnerable in the presence of mining activities and "historical" pollution.

The mean concentrations of the major ions were in the following order: Ca> Na> Mg> K, HCO_3^-> SO_4^{2-}> Cl^-> NO_3^-> F^-, indicating that both natural processes and anthropogenic activities conducted in the study area played an important role in the water quality.

Neutral–alkaline and acid waters characterized the studied water according to the Durov and Piper plots, indicating low water quality. The similarities among the studied physico-chemical indicators given by the HCA indicated the sources of water pollution (natural and anthropogenic) and the low quality of water, respectively.

Even if, in general, the heavy metals concentration was not considered to be higher than the MACs, except for Fe, Mn and Pb, the HPI scores. revealed a relatively high degree of heavy metals pollution in all the studied samples, while the HEI indicated low to high levels of heavy metal pollution in the studied water samples, due to high Fe, Mn and Pb concentrations. According to the WQI, the water quality was classified as excellent, good (A14, A15, A16), medium (A9, A10, A11, A13), poor (A7) and very poor (A12).

Generally, the obtained results showed contamination with metals, especially with As, Fe, Mn and Pb, indicating a degree of vulnerability for the water from the Aries River catchment in front of the mining activities, with historical pollution still present. Furthermore, the Aries River needs immediate quality monitoring and proper treatment in order to prevent hazards and human healthfrom being affected. Thus, the obtained results could be very useful to the local authorities in implementing a sustainable and appropriate management strategy, indicating the clear vulnerability of the water system.

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