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Original Article

Environmental Impact of Valea Vinului (Romania) Closed Mine Acid Mine Drainages (AMDs) on Surface Water Quality

MIHAIESCU Radu[1], Tania MIHAIESCU[1*], Antonia ODAGIU[2], Andras-Istvan BARTA[3], Francesco TADDEI[1]

[1]*Babeş-Bolyai University, Faculty of Environmental Science and Engineering, Fantanele St., No 30, 400294, Cluj-Napoca, Romania*

[2]*University of Agricultural Sciences and Veterinary Medicine, Faculty of Agriculture, 3-5 Manastur St., 400372, Cluj-Napoca, Romania*

[3]*Babeş-Bolyai University, Faculty of Geography, 5-7 Clinicilor St., 400006 Cluj-Napoca, Romania*

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Abstract

Economic reasons and environmental concerns led since 2005 to a substantial decrease of the mining activities for complex minerals in Romania. Valea Vinului mining area, located in the National Park Rodnei Mountains was subjected, as the majority of mining operations in Romania, to closure and conservation programs. Although, since 2007 mining activities ceased in this area, and measures to contain the pollution were applied, acid mine drainage (AMD) still remains a problem, contributing to the deterioration of the surface water quality. The study was focused on assessing the impacts of the collected and treated mine waters, on the chemical quality of Valea Bailor River, tributary of Somes Mare River. The results of the analyses were revealed based on the variation of the main mine waters indicators, namely, the water quality was characterized on the basis of the Fe, Pb, Zn and Cu contents and on the basis of the pH and electrical conductivity. For interpretation, the obtained values were related to the limits imposed by the Romanian Legislation.

Keywords: mining activities, acid mine drainage, environmental impact, water quality, heavy metals.

1. Introduction

Pollution destroys natural ecosystems affecting water resources, soil and atmospheric air. A lot of these problems occurred due of the application of some development methods which are destructive for environment and due to the miseducation concerning surface water protection, underground water, soil and atmospheric air. The consequences of these problems are measured by their effects on environment and their effect on public health.

* Corresponding author.
Tel: +40-264-596384
Fax: +40-264-593792
e-mail: tania.mihaiescu @usamvcluj.ro

Mining operations usually create a negative environmental impact, both during the mining activity and after the mine has closed.

Hence, most of the world's nations have passed regulations to decrease the impact. the European Mine

Waste Directive [1] has introduced new requirements for mine waste management, including that resulting from historical mining.

The challenge in implementing the European Directive is to develop a pan-European risk-based inventory of abandoned mines, in order to select sites for remediation based on a common set of criteria.

The characterization of the mine waste and its transformations in the short and long term, forms the basis for a risk-based classification of abandoned mine sites [2].

The focus of 2006/21/EC is on:

- the prevention or reduction of extractive waste generation and of its harmfulness,
- the recovery of extractive waste (by recycling, re-use or reclaiming),
- the assurance of short- and long-term safe disposal of extractive waste.

Monitoring and assessment of the water pollution has become a very critical area of study because of direct implications of water pollution on the aquatic life and the human beings. Spatial variation and source apportionment characterization of water quality parameters can provide a detailed understanding of environmental conditions and help researchers to establish priorities for sustainable water management [3].

Heavy metals are among the most common environmental pollutants because of their toxicity, persistence and non-degradability in the environment and their occurrence in water and biota indicate the presence of natural or anthropogenic sources [4]. The contamination of surface water by heavy metals is a serious ecological problem as some of them like Hg and Pb are toxic even at low concentrations, are non-degradable and can bio-accumulate through food chain.

Abandoned mine drainage is water that is polluted from contact with mining activity. It is a common form of water pollution in areas where mining took place in the past. There are several issues with abandoned mines that impact water quality:

- acid mine drainage (the most prevalent);
- alkaline mine drainage (this typically occurs when calcite or dolomite is present);
- metal mine drainage (high levels of lead or other metals drain from these abandoned mines).

Acid mine drainage is the formation and movement of highly acidic water rich in heavy metals. This acidic water forms through the chemical reaction of surface water (rainwater, snowmelt, pond water) and shallow subsurface water with rocks that contain sulfur-bearing minerals, resulting in sulfuric acid. Heavy metals can be leached from rocks that come in contact with the acid, a process that may be substantially enhanced by bacterial action. The resulting fluids may be highly toxic and, when mixed with groundwater, surface water and soil, may have harmful effects on humans, animals and plants [5].

The study area

The studied area, Valea Vinului is situated at about 13 km from Rodna in Curatel west mountainside on Valea Bailor River. From a geological point of view, the area consists of mica schists and crystalline limestones intercalations. All these rocks are crossed by Neogene andesites, which gave rise to columns of volcanic breccias. Valea Vinului, a complex hydrothermal ore, mainly consisting of pyrite – FeS_2, sphalerite – (Zn, Fe)S and galena – PbS, subordinately chalcopyrite – $CuFeS_2$, magnetite – Fe_3O_4, arsenopyrite – FeAsS and tetrahedrite – $(Cu, Fe)_{12}Sb_4S_{13}$ [6], has been submitted to a long-term mining processes since 1235 [7]. The complex ore contains 5–15% Zn, up to 4%Pb, 30÷40 g $tonne^{-1}$ Ag [8]. Other minerals present are jamesonite ($Pb_4FeSb_6S_{14}$), bournonite ($PbCuSbS_3$) and gangue minerals (calcite, quartz). The minerals were extracted from adits situated from 665 to 1225 m. After 1989, the production started to decrease, the mining activity became unprofitable and in 2006 the mine was closed [9].

The hydrographic network of the Valea-Vinului perimeter consists of the Valea Bailor River, in which the streams on both sides are drained, and upstream of the Valea Vinului locality, its tributary are the Izvorul Rosu River and Izvorul Bailor River.

The surface water network from the Valea Vinului perimeter is supplied by precipitation, melting snow and partly by underground springs. During periods of heavier rainfall, water flows from abandoned mining works increase due to surface and field infiltration, and due to the specific geomorphological characteristics of the area: rugged terrain, steep slopes, brooks with steep slopes and high runoff, determine creating strong torrents.

The ongoing issue is the regular discharge of acid mine drainage from the galleries which, during raining periods, exceeds the volume that can be treated in the wastewater treatment plant, leading to contamination of the soil, groundwater and Somes Mare River.

The old mining entails 7 coastal galleries, these constituting the main exploitation horizons: Horizon I- elevation +800 m, New Gallery elevation +840 m, Gallery 7 November- elevation +908 m, Gallery 23 August- elevation +968 m, Gallery V. Roaita- elevation +1017 m, Nepomuc- Gallery elevation +1071 m and Zapp Petru- Elevation Gallery +1118 m.

During the closure of the Valea Vinului mining perimeter, works were carried out towards restricting access to the former galleries and collecting the mine waters at the final elevation +720 m, Izvorul Rosu Gallery collected mine waters are temporarily stored in a concrete open reservoir, connected by a pipeline to the wastewater treatment plant (WWTP). Once subjected to the treatment process, the water is discharged into Valea Bailor River, a tributary of Somesul Mare River.

Surveys were carried out in the period 2018-2020, on summer time and five representative sampling points of the water quality were chosen, respectively: four surface water sampling points (SW1: Izvorul Rosu River - reference section; SW2: Izvorul Bailor River - reference section; SW3: Valea Bailor River - upstream WWTP; SW4: Valea Bailor River - downstream WWTP 2 Km) and one acid mine drainages sampling point AMD1: Collector reservoir Izvorul Rosu Mine Gallery (Fig. 1 and Table 1).

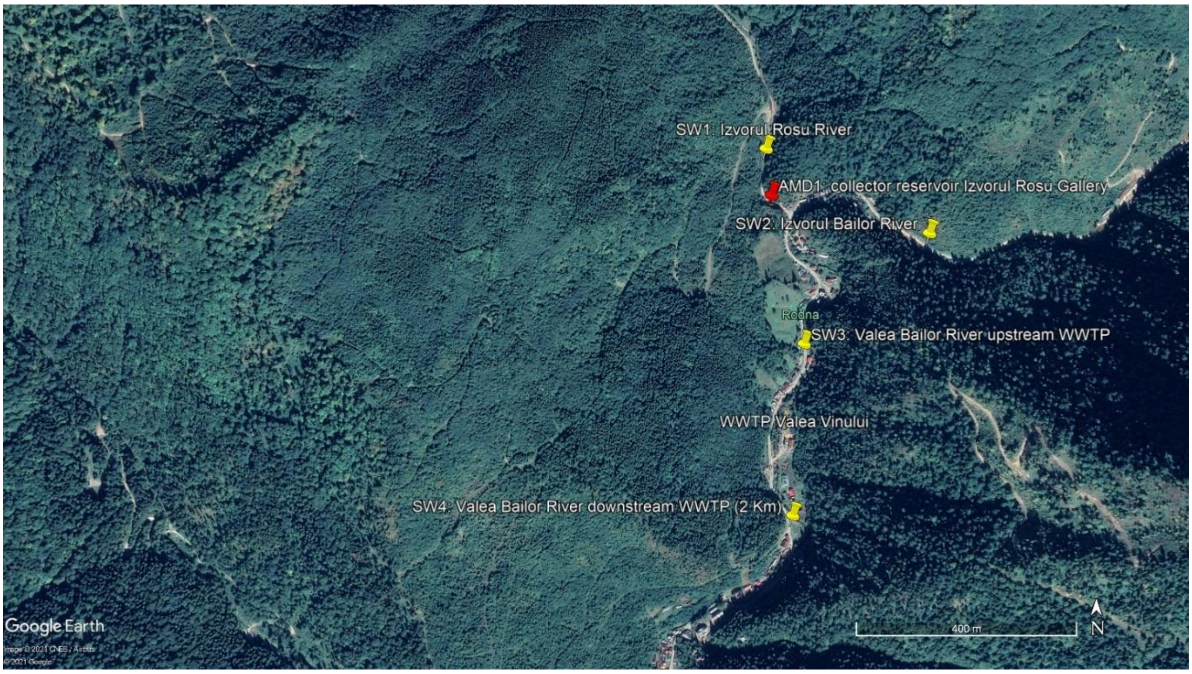

Figure 1. Location of the studied area
(Source: Google Earth)

Table 1. Water sampling points

Sample point	Sample code	Water type	Geographic coordinates
Izvorul Rosu River (reference section)	SW1	surface water	47°29'51,18''N; 24°49'30,85''E
Izvorul Bailor River (reference section)	SW2	surface water	47º29,4'27''N;24°49'44,41''E
Collector reservoir Izvorul Rosu Mine Gallery	AMD1	acid mine drainages	47°29'32''N; 24°49'66''E
Valea Bailor River upstream WWTP	SW3	surface water	47º28'48,66''N; 24º49'44,57''E;
Valea Bailor River downstream WWTP (2 Km)	SW4	surface water	47°26'35,07''N; 24°48'24,45''E

WWTP – waste water treatment plant

2. Material and Method

Water samples were analyzed for a pre-defined set of physical and chemical indicators to allow the buildup of a meaningful database that can be used for comparative assessment and trend delineation.

In-situ measurements

Water temperature, pH (at 25°C) and electrical conductivity (at 25°C) were measured in-situ, using a WTW 350i Handheld Multi-Parameter Instrument (WTW, Germany). Analyses were made in triplicate and the mean values are reported.

Heavy metals quantification by FAAS

The water samples were digested using a Speedwave MWS-2 Microwave Pressure Digestion microwave digestion system (Berghof Products + Instruments, Germany). 20 mL of the sample was digested in a duplicate with 3 mL of nitric acid 65% (Suprapure, Merck, Darmstadt, Germany) in pre-cleaned HF100 PTFE vessels. All samples were completely digested and diluted to a final volume of 50 mL deionized water (≥18 MΩ). Samples were further diluted as necessary in the same manner. Preparation blanks were taken through the same digestion and preparation process as the samples and analyzed accordingly. Details of the procedure are provided in Table 2.

Total heavy metals concentrations were measured using an ZEEnit 700 atomic absorption spectrometer (Analytik Jena GmbH) according to SR ISO 8288: 2001. Water quality. Determination of the content of cobalt, nickel, copper, zinc, cadmium and lead. Flame atomic absorption spectrometry method. The instrumental conditions for AAS are listed in Table 3.

Table 2. Program used for the digestion of water samples

Step	1	2	3
Temperature [°C]	200	130	100
Power [%]	60	40	40
Time [min]	20	5	5

Table 3. Operation conditions for the analysis of heavy metals by atomic absorption spectrometry

Parameter		Zn	Cu	Pb	Fe
Spectrometer	Wavelength (nm)	213.9	324.8	283.3	248.3
	Slit width (nm)	0.5	1.2	1.2	0.2
	HCL current (mA)	5	3	3	3
	Integration time (s)	3	3	3	3
	Replicate	3	3	3	3
Atomizer	Flame	Air-acetylene			
	Gas flow rate (l/h)	50	50	65	50
	Burner height (mm)	5	5	6	5

HCL hollow cathode lamp

The instrument response was periodically checked with known solution standards. The experiments were performed in triplicate and the samples were analyzed in triplicate as well.

For each set of data present, standard statistical methods were used to determine the mean values and standard deviations.

Confidence intervals of 95% were calculated for each set of samples in order to determine the margin of error.

3. Results and Discussions

The results of are presented in Table 4.

Table 4. Basic statistics for pH determination

Sample point	Sample code	Sample size	Mean± $SE_{\bar{x}}$	Median	Minimum	Maximum
Izvorul Rosu River (reference section)	SW1	9	6.70±0.08	6.55	6.52	7.02
Izvorul Bailor River (reference section)	SW2	9	6.84±0.02	6.89	6.73	6.89
Collector reservoir Izvorul Rosu Mine Gallery	AMD1	9	3.55±0.15	3.56	2.9	4.2
Valea Vinului River upstream WWTP	SW3	9	6.73±0.05	6.62	6.58	6.99
Valea Vinului River downstream WWTP (2 Km)	SW4	9	7.83±0.05	7.73	7.73	8.04

Indicator	MAC* (according to NTPA002/2002)[10]	Quality Class (Permissible values according to Order no. 161/2006)[11]				
		I	II	III	IV	V
*p*H	6.5 – 8.5	6.5 – 8.5				

The pH values of all the surface water samples ranged between 6.52 (slightly acidic pH) and 8.04 (basic pH).

Normal values of pH in surface water systems range from 6.5 to 8.5 (Order No 161/2006). Lower pH values in the upper basin may be due to fermentation processes developed on peat-covered areas, but there is an assumption of a decrease in pH due to oxidative processes that can occur on naturally exposed rocks.

There is a significant decrease in pH in the case of acid mine waters due to the biological oxidation processes of sulphides in the minerals exposed as a result of former ore mining works. The pH at the discharge of the treatment plant is within the normal limits for watercourses, being an indicator of the operation of the treatment plant within the normal technological limits. By dilution with unpolluted water the pH values are also maintained within normal limits downstream of the treatment plant.

Table 5. Basic statistics for Electrical conductivity [μS cm^{-1}]

Sample point	Sample code	Sample size	Mean± $SE_{\bar{x}}$	Median	Minimum	Maximum
Izvorul Rosu River (reference section)	SW1	9	257±17.5	289	184	297
Izvorul Bailor River (reference section)	SW2	9	176±8.4	176	141	212
Collector reservoir Izvorul Rosu Mine Gallery	AMD1	9	1912±31.6	1254	1100	1382
Valea Bailor River upstream WWTP	SW3	9	237±9.5	253	189	269
Valea Bailor River downstream WWTP (2 Km)	SW4	9	269±32.7	323	112	340

The conductivity of the water samples from the unpolluted areas was low, proving the absence of pollution sources. Relatively high values of electrical conductivity measured in water samples taken from acidic mine discharges may reflect a charge in various ions due to both longer residence time and oxidative processes., Downstream of the treatment plant the measured conductivity values returns to normal values, characteristic of these types of water bodies.

The results obtained from the determination of heavy metals concentrations are presented in Table 6.

Table 6. Basic statistics for Heavy metals concentrations [mg L^{-1}]

Sample point	Sample code	HM	Sample size	HM conc [mg L^{-1}]				Class
				Mean± $SE_{\bar{x}}$	Median	Min.	Max.	
Izvorul Rosu River (reference section)	SW1	Cu	9	0.017±0.001	0.017	0.015	0.0176	I
		Fe	9	0.307±0.050	0.29	0.23	0.4	II
		Pb	9	0.009±0.001	0.0094	0.007	0.01	II
		Zn	9	0.162±0.010	0.16	0.145	0.18	II
Izvorul Bailor River (reference section)	SW2	Cu	9	0.009±0.001	0.01	0.007	0.01	I
		Fe	9	0.303±0.024	0.29	0.27	0.35	II
		Pb	9	0.008±0.002	0.008	0.006	0.01	II
		Zn	9	0.114±0.009	0.112	0.101	0.13	II
Collector reservoir Izvorul Rosu Mine Gallery	AMD1	Cu	9	0.120±0.094	0.032	0.008	0.04	-
		Fe	9	18.93±6.78	6.43	4.5	24.98	-
		Pb	9	0.151±0.068	0.08	0.052	0.28	-
		Zn	9	19.83±1.38	5.162	0.65	21.89	-
Valea Vinului River upstream WWTP	SW3	Cu	9	0.012±0.001	0.012	0.0104	0.013	I
		Fe	9	0.268±0.125	0.354	0.0213	0.43	II
		Pb	9	0.009±0.001	0.0078	0.0072	0.0115	II
		Zn	9	0.162±0.008	0.1620	0.148	0.175	II
Valea Vinului River downstream WWTP (2 Km)	SW4	Cu	9	0.0232±0.001	0.023	0.0215	0.0251	II
		Fe	9	0.237±0.104	0.32	0.031	0.36	I
		Pb	9	0.009±0.001	0.01	0.007	0.01	II
		Zn	9	0.201±0.011	0.21	0.18	0.213	II

Indicator	Quality Class (Permissible values according to Order no. 161/2006)					MAC* (according to NTPA002/2002)
	Class I	Class II	Class III	Class IV	Class V	
Copper [mg L^{-1}]	0.02	0.03	0.05	0.1	> 0.1	0.1
Iron [mg L^{-1}]	0.3	0.5	1.0	2	> 2	-
Lead [mg L^{-1}]	0.005	0.01	0.025	0.05	> 0.05	0.2
Zinc [mg L^{-1}]	0.1	0.2	0.5	1	> 1	0.5

*MAC - maximum allowable concentration

Collected AMD measured in the collector reservoir presents increased concentrations of heavy metals highlighting the necessity of maintaining the integrity of the mine closure works and drainage collector network.

Regarding heavy metal concentration, the measured values in surface water samples, usually correspond to Class II of water quality. The measured values for iron and lead are situated within the limits of the Class II water quality both for the selected reference sections and sections downstream the identified possible pollutant discharges. Contribution of the natural background concentrations or of possible still undetected acid mine drainage can be taken in consideration. Cooper concentrations show a of slight increasing trend downstream the waste water treatment plant, possible due to the limited efficiency of the treatment technology.

During heavy rain episodes the treatment capacity of the acid mine drainage and water treatment plant system can be exceeded and heavily polluted waters can be spilled untreated into the receiving river.

4. Conclusions

The obtained results showed that even after the cessation of mining activity, the improperly closed mines and poorly managed tailing deposits still generate a significant heavy metal pollution of surface waters due to uncontrolled leaching processes. The pollutant removal efficiency of the waste water treatment plant can be affected by episodes of massive rains leading to possible pollutant discharges. The analyzed data reveal signs of environment recuperation followed by episodes of remobilization of pollutants dispersed in soil, barren heaps, and possible uncontained acid mine drainages.

Further monitoring actions are needed in order to identify and design strategies of containment the remaining pollution sources which become active during precipitation events.

References

[1] European Commission, 2006, Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the management of waste from extractive industries and amending Directive 2004/35/EC - Statement by the European Parliament, the Council and the Commission, Official Journal of the European Union, L 102/15, 15-34.

[2] Servida D., G. Grieco, L. De Capitani, 2009, Geochemical hazard evaluation of sulphide-rich iron mines: The Rio Marina district (Elba Island, Italy), J. Geochem. Explor., 100(1), 331–333.

[3] Popa G., T. Mihaiescu, A. Odagiu, R. Mihaiescu, C. Balint, 2018, Assessment of Surface Water Quality of Upper Basin of Lapus River (Romania) Postmining Closure Operation, ProEnvironment, 11(35), 204-209.

[4] Majhi A., S. K. Biswal, 2016, Application of HPI (Heavy Metal Pollution Index) and correlation coefficient for the assessment of ground water quality near ash ponds of thermal power plants, International Journal of Science Engineering and Advance Technology (IJSEAT), 4(8), 395-405.

[5] EPA, 2020, Polluted Runoff: Nonpoint Source (NPS) Pollution, https://www.epa.gov/nps/abandoned-mine-drainage.

[6] Udubasa G., 1980, Lithology controls of ore localization: Blazna Valley stratabound ore deposit, Eastern Carpathians, Reports of the Geological and Geophysical Institute, LXV, 113-130.

[7] Nimirciag R., 2012, Heavy metals in the soils of Rodna mining area, Romania and zeolite efficiency for remediation, Environmental Engineering and Management Journal, 11(2), 421-426.

[8] Marza, I., 1977, Geologia zacamintelor de minereuri. Romania, Babes-Bolyai University, Cluj-Napoca.

[9] Maicaneanu A., H. Bedelean, M. Ardelean, S. Burca, M. Stanca, 2013, Hanes and Valea Vinului (Romania) closed mines Acid Mine Drainages (AMDs)-Actual condition and passive treatment remediation proposal, Chemosphere, 93(7), 1400-1405.

[10] Romanian Goverment, 2002, Normativ NTPA-002 privind conditiile de evacuare a apelor uzate in retelele de canalizare ale localitatilor si direct in statiile de epurare, Monitorul Oficial, Part I no. 187.

[11] MMGA, 2006, Order no 161, Monitorul Oficial, 511.