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FACULTY OF ENVIRONMENTAL
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DOCTORAL SCHOOL OF ENVIRONMENTAL SCIENCE

PhD THESIS
SUMMARY

Geochemical features of the hydrologic system from Roșia Montană mining area

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LIST OF PAPERS

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7. Goldschmidt Conference Abstracts (2016) 2430. Isotopes as tracer for groundwater – surface water – mine water interactions in post-mining environments: the case study of Zlatna mining area (Romania), in: Goldschmidt Abstracts, 2016 2430. Delia Cristina Papp, Ioan Cociuba, Călin Baciu, **Alexandra Cozma**.

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9. Rn SEERAS, Second East European Radon Symposium: **Alexandra Iulia Cozma**, M. Moldovan, C. Baciu, B. Burghele. Radon and radium monitoring in several groundwaters from Rosia Montana area, Romania. Rn SEERAS, Second East European Radon Symposium, Nis, Serbia, 27 – 30 mai 2014- **poster.**

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12. European Geoscience Union General Assembly, International Conference, 12 – 17 aprilie 2015, Vienna. **Alexandra Iulia Cozma**, Calin Baciu, Adriana Olenici, Dorian Brahaita, Cristian Pop, Laura Lazar, Carmen Roba, Gabriela Popita. Characterizing the hydrological system in Rosia Montana mining area for AMD mitigation- **oral presentation.**

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15. ECOSMART International Conference, 12 – 15 Nov 2015, București: **Alexandra Iulia Cozma**, Baciu C., Moldovan M., Pop C. Using natural tracers to track the ground water flow path and the residence time in a mining area- **oral presentation.**

16. ELSEDIMA International Conference, 26 – 28 may 2016, Cluj-Napoca: Alexandra Iulia Cozma, Baciu C., Pop C., Lazar L., Popita G. The impact of the past mining activity on the water resources in Rosia Montana mining area- **poster.**

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18. 15^{th} International Symposium on Water-rock interaction, 16 – 21 October 2016, Evora, Portugal. Papp D.C., Cociuba I., Baciu C., **Cozma A.** Composition and origin of mine water at Zlatna gold mining area (Apuseni Mountains, Romania).

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21. Simpozion Geo 2015, Electrical Signatures of Groundwater, 20 Nov, Bucuresti. A. Ionescu, B.M. Kis, C. Baciu, **A.I. Cozma**, A. Sciarra, M. Moldovan, G. Etiope. First Assessment of the flux and origin of methane at the Ciomadu post-volcanic area (Romania)- **oral presentation.**

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23. XIV[th] Edition of Isotope Workshop ESIR 2017, Băile Govora, România 25 – 29 June 2017. Calin Baciu, Delia Papp, **Alexandra Cozma**. Application of Stable Isotopes for Investigating the Dynamics of Waters in Rosia Montana and Zlatna Mining Areas **oral presentation.**

24. 12[th] International Conference Environmental Legislation, Safety Engineering and Disaster Management ELSEDIMA 2018, 17 – 19 May 2018, Cluj-Napoca, Romania. **Alexandra Iulia Cozma**, Calin Baciu, Nicoleta Brisan. Hydrogeochemical features of the mineral waters from Ciomadul volcanic area, Eastern Carpathians, Romania) – **prezentare**.

CO-AUTHOR IN TECHNICAL REPORTS WITHIN INTERNAȚIONAL PROJECT FP 7

1. Environmental risk assessment practices and applications for gold mines in EU - Assessing environmental risks at three mine sites: Kittilä mine in Finland and Roșia Montană and Zlatna mines in Romania. C. Baciu, L. Lazăr, **A. Cozma**, A. Olenici, I.C. Pop, C. Roba, D. Costin (Babes Bolyai University): Roșia Montană case, D. C. Papp, I. Cociuba (Geological Institute of Romania): Zlatna case. ERA-MIN –SUSMIN Project Deliverable D5.4.
2. Prediction of long-term impacts using environmental monitoring and modelling tools at two mine sites: Kittilä mine in Finland and Roșia Montana in Romania. T. Lahtinen, K. Turunen, E. Hämäläinen, M. Hämäläinen, S. Nieminen, T. Forsman, (Geological Survey of Finland): Kittila case and Rosia Montana case, C. Baciu, **A. Cozma**, I.C. Pop, C. Roba, D. Costin (Babes Bolyai University): Rosia Montana case. ERA-MIN –SUSMIN Project Deliverable D5.3.
3. Use of geochemical characteristics and isotopes for assessing migration of harmful substances at three mine sites: Kittilä mine in Finland and Roșia Montană and Zlatna mines in Romania. D.C. Papp, I. Cociuba (Geological Institute of Romania): Zlatna case,

C. Larkins, I. Mänttäri, K. Turunen, Y. Lahaye, N. Hendriksson, P. Forsman, S. Nieminen (Geological Survey of Finland): Kittila case and Rosia Montana case, C. Baciu, **A. Cozma**, L. Lazar, I.C.Pop, C. Roba (Babes Bolyai University): Rosia Montana case. ERA-MIN –SUSMIN Project Deliverable D5.1.

SUMMER SCHOOLS, SEMINARS AND FORMATIVE COURSES

1. National Workshop on Implementation of Basic Safety Standards on Public Exposure due to Radon and Building Materials. Organized by National Commission for Nuclear Activities Control (CNCAN) and Babes Bolyai University Cluj-Napoca (UBB) in co-operation with International Atomic Energy Agency (IAEA) Within the framework of the TC National Project ROM/0/008 *"Further Development of Romanian Nuclear Regulatory Authority Capabilities" – period 23 – 27.01.2017.*
2. Organizer at the național competition *" Să păstrăm un mediu sănătos", ediția a IV-a, concurs aprobat de Ministerul Educației Naționale cu nr. 46761/21.11.2016.*
3. Organizer at the național competition *" Să păstrăm un mediu sănătos", ediția a VI-a, concurs aprobat de Ministerul Educației Naționale cu nr. 377683/23.10.2018.*
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5. Summer school participant: *"The impact of mining activities on the environment ERASMUS IP"- Certificate of attendance. Spisska Nova Ves, Slovacia, period: 1 – 12. July 2013.*
6. Summer school participant: *"Environmental Technologies in mining and waste management ERASMUS IP"- Certificate of attendance. Kosice, Slovacia, period: 30 June – 11 July 2014.*
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RESEARCH EXPERIENCE

Researcher in three national and international projects:

1. Project TOOLS FOR SUSTAINABLE GOLD MINING IN EU (SUSMIN) 3-005/ 24.03.2014.
2. Project number 2090 G TA 101 –Reduced Carbon in Earth: Origin, Form, Quantities and Movements.
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Contents

Key words: mining, acid mine drainage, groundwater, Roșia Montană, stable isotopes, geochemistry, residence time.

I. INTRODUCTION

„He provides rain for the earth and he sends water on the countryside."

Job 5:10

The oldest writings in the world, including the Holy Bible, are describing the relationship between people and environment. In time, the philosophical knowledge and science have developed and the human society has become more and more interested by the state of the environment. Hence, it is our moral responsibility to maintain a good state of the environment, both for ecosystems and the human society. The concept of sustainable development is clearly explained by a simple sentence that has seen a global dissemination: *„sustainable development is development that meets the needs of the present, without compromising the ability of future generations to meet their own needs"* (WCED, 1994).

The present work entitled ***Geochemical characteristics of water system from Roșia Montană mining area*** synthesize data from previous studies regarding the state of the environment in the area Roșia Montană, to which a substantial personal contribution focused on the state of the aquatic resource in the study area is added. Mining activities disturb the nature and normal functionality of a specific area through the several changes on the soil, water, vegetation and air. Untreated mine waters released into natural streams is a problem for each mining area and at the same time, a challenge in finding solutions to neutralize them.

In Roșia Montană mining area 140 km of galleries were inventoried, that means a system where water mixing and transfer processes are particularly complex. Mobilization of metals occurs mainly through the action of acid waters formed by oxidation of sulphides in the deposit, by the contact with atmospheric air and meteoric waters. As a result of oxidation, sulphur produces sulfuric acid, which drastically reduces the pH of mine water, which frequently reaches values of 2 or 3. Acid waters exhibit increased aggression towards rock, which leads to its weathering, with the mobilization of metals. The expansion of pollution along water courses makes the environmental impact due to mining operations extend over tens of km downstream. As a result, one of the conditions necessary for the operation of mining is a good management of acid waters, minimizing their development and proper treatment prior to their discharge.

The present thesis aims to better understand the generation of mine waters and their underground dynamics in order to develop the most efficient management strategies. Hydrogeochemical techniques based on the assessment of water chemistry and isotopic analysis will be used for this scope.

1. The goals of the thesis

The objectives of the present study are:

- ***understanding the changes that the mining workings introduce to the natural cycle of surface and groundwater at local scale;***
- ***understanding the dynamics of water bodies in a mining area;***
- ***creating a conceptual water circulation model at local scale based on interpretation of physical and geochemical data;***
- ***better understanding the dynamics of water by comparing the isotopic features of running waters and groundwaters (drinking/mine waters) with the meteoric water, by using the LMWL;***
- ***establishing a geochemical database, useful for the future remediation actions.***

The geochemical study was focused on the analysis of heavy metals (Ni, Cu, Cd, Pb, Zn, Cr), respectively major ions. The approach was based on the rigorous monitoring of the seasonal variations of the chemical composition of the waters. It has been set up a monitoring network including running waters, lakes, wells, springs and mine waters. Water samples were collected at and around the former Rosia Montana mining site, from August 2013 to August 2015 for 24 months, on the same period of the month. The samples were analysed chemically and isotopically. The radioactive potential of the area was estimated by analysis of radionuclides Rn ^{222} and Ra ^{226}.

Mine water genesis studies including isotopic measurements, especially using stable isotopes of oxygen and hydrogen, sulphur, strontium are timely. The dynamics of water in polluted areas is essential and stable isotopes of oxygen and hydrogen in water have the potential to clarify the dynamics and geochemical processes (Leybourne et al. 2006; Leybourne et al. 2007). Stable isotopes of oxygen and hydrogen provide substantial scientific contribution to the study of the distribution of water in the atmosphere and the hydrosphere (Clark & Fritz, 1998).

It is necessary to use a multidisciplinary approach to evaluate the water resource, including knowledge of genesis, hydrodynamics, hydrogeochemistry and pollutants in the proximity of the watershed. In areas with acidic waters where the leakage occurs, the water-rock interaction is mainly controlled by the pH and ORP (oxidation-reduction potential).

Isotopic analysis can provide useful information with respect to the: residence time, water-rock interaction, geochemical evolution, etc (Ghomshei & Allen, 1999; Seal II et al. 2008). Oxygen and hydrogen isotopes are natural tracers of water dynamics, which are very useful to improve knowledge about the transfer between surface water and groundwater. From an international perspective, there are several works that were carried out in mining areas for better understanding the genesis of mine waters, dynamics, mixing and solutions using stable isotopes and trace elements (Melchiorre et al. 2005; Hazen et al. 2001; Gammons et al. 2010; Gammons et al. 2013; Sracek et al. 2004; Caruso et al. 2011; Hem, 1985; Hofmann et al. 2008), but also using stable isotopes to identify the groundwater recharge (Oiro et al. 2018).

The interpretation of isotopic data for all water bodies in the mining area is based on the LMWL (local meteoric water line) built for Roșia Montană Meteorological Station.

The present thesis is developed in two main parts, as follows:

The first part presents the physico-geographical framework of the area, general features of the watershed based on the bibliography, being divided in chapters and subchapters regarding the history of mining activities in Roșia Montană mining area, the impact of mining activities on the ecosystems, similar studies in the world, the types of mining activities carried out in Roșia Montană mining area, genesis of mine waters and considerations on tailings ponds and deposits.

The second part of the thesis, which is the most extensive, describes personal contributions for a better understanding of the state of the environment, especially the water component. For this purpose geochemical analyses and interpretations were included. A conceptual model of water circulation was developed in Roșia Montană mining area considering the interaction between surface waters and groundwaters.

Chapter 1 describes the research methodology for each parameter and the sampling method. **Chapter 2** describes the methodology of the laboratory analyses for heavy metals, major ions, stable isotopes, the equipment and work protocols. Atomic Absorption Spectrometer Zeenit 700, Dionex Chromatograph and Picarro Isotope Analyzer CRDS were used. At the same time, this chapter describes the processing of the results. **Chapter 3** presents the results of the measured parameters considered for this study and also the descriptive statistics. This chapter includes graphs that show seasonal variations of some parameters: pH, temperature, turbidity, stable isotopes of oxygen and hydrogen in water. **Chapter 4** describes the correlation between stable isotopes of oxygen and hydrogen, pH and TDS in order to elucidate the mixing water processes and dynamics. The isotopic composition of precipitation from Roșia Montană and Cluj-Napoca according to the procedures established by IAEA Vienna has been analysed. This chapter is less detailed because the data were published in an ISI paper. **Chapter 5** presents considerations about the radioactive potential of the area, and all the data including interpretations and graphs are published in a BDI paper. **Chapter 6** refers to the applicability of natural tracers used for the mining area, and also the quality of the water bodies. **Chapter 7** presents the dynamics of groundwater based on the analyses and data used for this research, as well as the residence time of it. In **chapter 8** four conceptual 3D models based on the obtained information and pre-existing data for Roșia Montană, Corna and Săliște valleys were included. **Chapter 9** summarizes the conclusions of the study, limitations for the present research and future directions.

2. General considerations

2.1. Relief and climate

The relief is strongly influenced by the river network, especially the Roșia valley, but also the other ones: Corna, Săliște and Abruzel. The altitude varies between 550 meters (Arieș valley) and 1256 meters (Curmătura).

The climate in Roșia Montană area is temperate continental with few exceptions in the higher altitude areas where a specific microclimate dominates, with cool winters and significant snow cover, ranging from 4 to 6 months (RMGC, 2006). Spring and autumn seasons are relatively cold with high humidity as a consequence of heavy rain. The warm season is short with medium temperatures. The average annual temperature is 7.38°C, with an average monthly maximum of 18.6°C recorded during the warm season in August, and with an average monthly minimum of -2.4°C during the winter season recorded in January (Roșia Montană Meteorological Station).

The vegetation in Roșia Montană area is characteristic of the Mountain climate, with several forests and alpine surfaces.

2.2. Geology

From a geological and structural point of view, the Apuseni Mountains, are divided into two major units with different evolution and distinct characteristics, the Northern Apuseni Mountains and the Southern Apuseni Mountains.

The southern part of the mountains, including the area of the present study, represents the result of the operation of major the Tethysian sutures, which probably began before the Jurassic and lasted until the end of the Cretaceous.

It is well-known the Golden Quadrilateral, which defines a particularly rich metalogenetical district, known for over two millennia, especially for its precious metal resources. The ore in the area is represented by Au-Ag type (eg Roșia Montană), Au-Cu type (eg Rovina) and porphyry copper type (eg Roșia Poieni), to which deposits with common non-ferrous metals (lead, zinc) are added.

The spatial arrangement is split into three belts of Neogenic magmatites, rich in mineralizations, Roșia Montană belonging to the northern most part (Mutihac, 1990).

Roșia Montană is a maar-diatreme structure, included in a mass of Cretaceous sediments (**Figure 1**). The structure is dominated by freatomagmatic products, volcanoclastic rocks, with intercalated subvolcanic porpyhric dacites, dacitic dykes, and late freatomagmatic breccias. The mineralization of interest in Roșia Montană area is interpreted as an epitermal system of moderate to low depth (Tămaş, 2007).

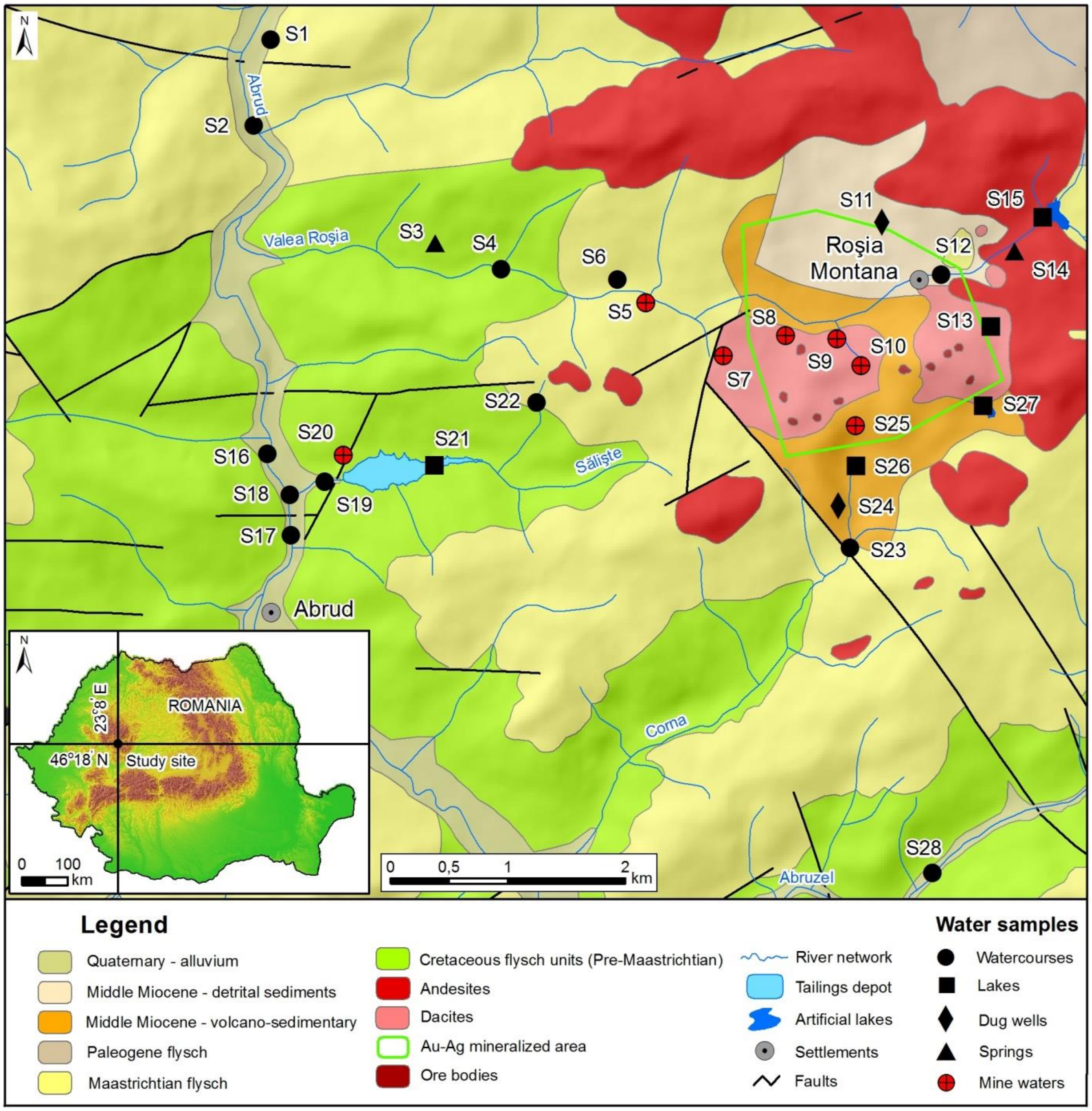

Figure 1. Geology map of Roșia Montană (after Geology Map scale 1:50.000, paper Abrud, Bordea et al., 1979).

2.3. River network

The most important water resource from Apuseni Mountains is Arieș river. It flows at 10 km north from Roșia Montană and collects the majority of the streams from the area, Abrud being one of the rivers that Arieș collect. Abrud collects all the courses that come from Roșia Montană mining area (**Figure 2**). In Roșia Montană, the Roșia stream is the main stream flowing from east to west, taking the waters that flow in the area. Its flow is dependent on the amount of precipitation, the storage of water from the lakes that are placed in the upstream, but also by the amount of water discharged by the mining works. The stream takes all the acid waters coming from the mining works (RMGC, 2006).

The sampling points selected for the present study are located on the Rosia, Corna, Saliste, Abruzel and Abrud water courses. The artificial lakes dug nearby the ore extraction are fed with water the grinding facilities (”steampuri”). Currently there are 8 lakes in the area, out of total of 110 historically documented lakes, the largest ones being Tău Mare, Tău Țarina, Tău Brazi, Tău Anghel, Tău Corna, and the smallest ones are Tău Cartuș, Tău Găuri and Tău Țapului.

Four of them were selected for monitoring within our research. The lakes will be briefly described in the sampling chapter.

Figure 2. The confluence between Arieș river (right) and Abrud river (left).

3. Mining activity and results of the mining operations producing environmental impact

3.1. Underground mining workings

The first gold extraction operations in Roșia Montană mining area were performed in outcrops, after which the works were pursued in depth, as underground workings, continuing in this form for almost 2000 years.

The underground workings form a complex network of tunnels, shafts, and large voids. The underground network consists of 140 km of mining workings, a situation favouring a complex hydrogeochemical system.

3.2. Tailings ponds

Two tailings ponds functioned in Roșia Montană mining area, Gura Roșiei and, respectively Săliște. Their operation ceased in 2006. Gura Roșiei tailings pond is situated along the Abrud River with an area of 230.000 m^2**.** At present, the deposit is reclaimed, with geometric correction of the slopes, geomembrane and soil coverage, and grass plantation. As a consequence, the tailings ponds Gura Roșiei is isolated by the external environmental factors and has not been included in this study.

Săliște tailings pond generated a stailings deposit (approximately 4.000.000 m^3) located on Săliște valley, occupying a big part of the valley. The surface of the tailings pond is 16.1 ha (Raport la studiu de impact, 2014). Its construction follows the general principles used for the valley tailings ponds. The water of Săliște stream is directed through a bypass tunnel that avoids the contact of water with the tailings. Săliște pond was reclaimed following a similar procedure to that used at Gura Roșiei pond.

All water samples for the current study were collected before the beginning of the reclamation operations. At the time of the monitoring, most of the deposit was dry, with a small pond in the upstream part of the structure.

3.3. Tailings dumps

In Roșia Montană area there are several dumps (**Table 1**), generally small, resulting from the different stages of the mining operations. The majority are slope dumps, deposited at the outlet of the mine galleries or in the proximity of the open pits. As a result of natural vegetation covering, some of the old dumps are difficult to recognize in the field.

The waste rock dumps are located in the proximity of Cetate and Cîrnic open pits, and in the Orlea and Jig mining fields. In 2012, the General Directorate for Mineral Resources made an inventory of all inactive waste dumps in Romania, resulting in a total of 627 dumps. In Roșia Montană mining area 33 dumps were identified, and the main features are presented in **Table 1**.

As a consequence, these forms of waste storage (waste rock dumps and tailings ponds) are likely to generate significant environmental impacts, primarily on surface and groundwater, but also on soil, land and air. To highlight the influence of mining waste deposits on the status of aquatic resources in Roșia Montană area, several monitoring points that have an influence from these deposits, have been included in the monitoring network. Several images of the waste material are shown in **Figure 3**.

Table 1. Inventory of waste rock dumps from Roșia Montană, according to General Directorate of Mineral Resources, Romania (www.minind.ro).

No.	Tailings dumps name	The law of closure	Surface ha	Volume thousands of cubic meters	The tailings is influenced by the Wind YES/NO
1	VERKEȘ	644/2007	1,26	6	YES
2	IRINA RACOȘI	644/2007	0,30	26,85	YES
3	IULIANA	644/2007	1,49	9,50	YES
4	AFINIȘ	644/2007	1,96	9,40	YES
5	AURORA	644/2007	0,20	8,00	YES
6	GĂURI	644/2007	0,20	13,60	YES
7	VALEA VERDE	644/2007	5,75	30,60	YES
8	GALERIA 23 AUGUST	644/2007	0,12		YES
9	CÎRNICEL	644/2007	0,10	9,58	YES
10	GALERIA NAPOLEON +984 m	644/2007	0,20	5,54	YES
11	GALERIA NAPOLEON +954 m	644/2007	0,20	8,62	YES
12	MĂNEȘTI	644/2007	0,81	4,50	YES
13	GAL. +887m	644/2007	0,20	9,65	YES
14	GAL. +938 m	644/2007	0,20	20,15	YES
15	PÂRÂUL CORBULUI	644/2007	0,10	6,36	YES
16	PIATRA CORBULUI	644/2007	0,10	4,23	YES
17	HOP	644/2007	4,58	23,70	YES
18	ZONA GĂURI	644/2007	1,83	12,20	YES
19	RÂPA ALBĂ	644/2007	1,41	8,60	YES
20	RAKOȘI	644/2007	0,43	3,20	YES
21	GAL DE COASTĂ	644/2007	0,61	4,18	YES
22	GĂURI 1	644/2007	0,80		YES
23	GĂURI 2	644/2007	0,21	2,10	YES
24	PIATRA CORBULUI 1A	644/2007	0,31	2,72	YES
25	PIATRA CORBULUI 1B	644/2007	0,75	7,00	YES
26	PIATRA CORBULUI 2	644/2007	0,62	5,40	YES
27	ROSTOGOL COLECTOR NAPOLEON	644/2007	0,56	4,50	YES
28	IPEG (+895 și +907)	644/2007	1,16	9,28	YES
29	VOLBURA CANTALIȘTE ȘI CORNURI	644/2007	3,98		YES
30	VOLBURA CANTALIȘTE EST	644/2007	1,85	11,00	YES
31	CÎRNICEL ORIZ+941	644/2007	0,52	3,40	YES
32	CÎRNICEL ORIZ +907	644/2007	0,59	4,00	YES
33	CÎRNICEL ORIZ+885	644/2007	0,36	2,60	YES

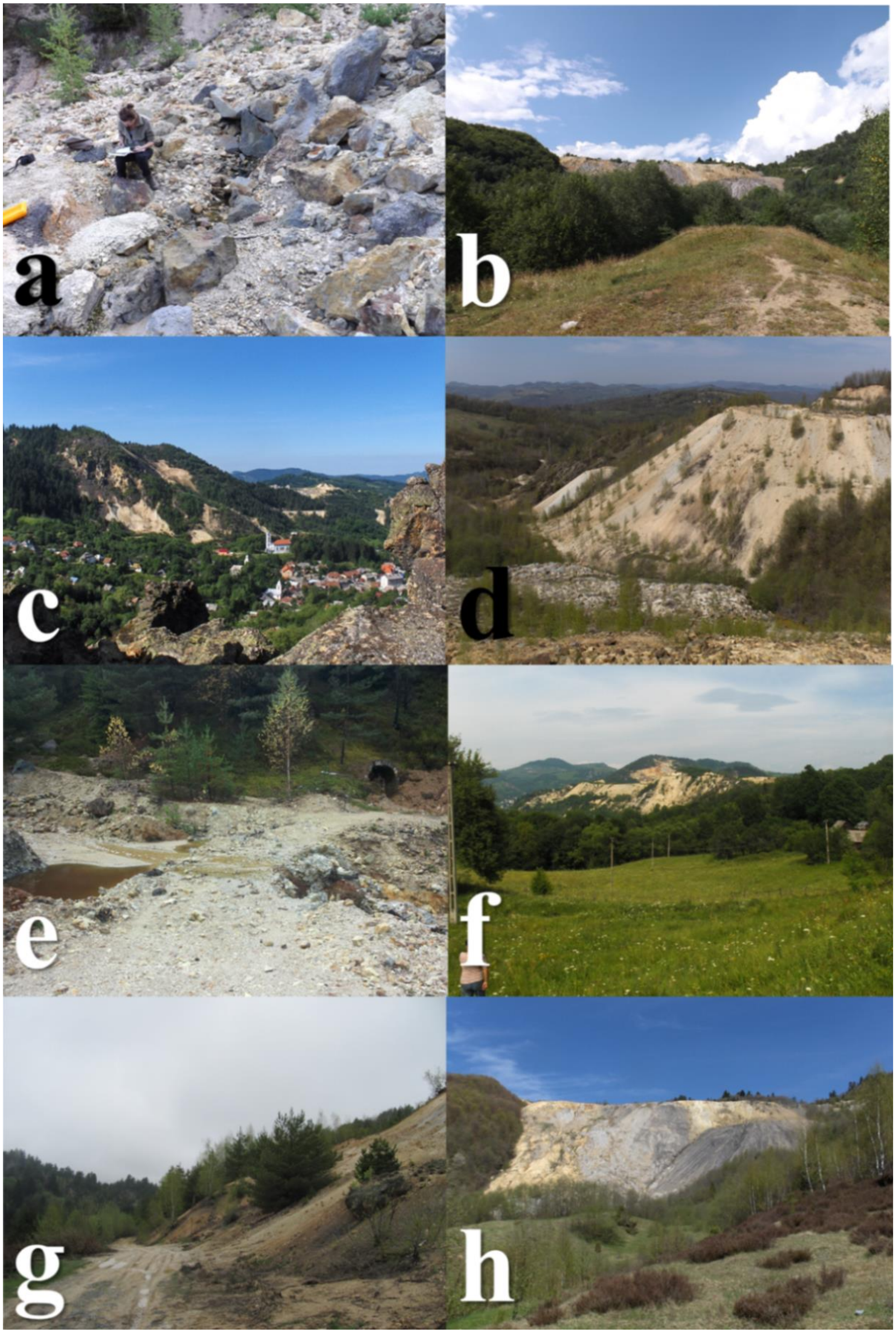

Figure 3. (a -Cetate); (b, h – Verde valley); (c, f –general view); (d -Cetate west); (e -Cetate); (g -Cârnic). Waste deposits near the mining area Roșia Montană.

3.2.5. Genesis of acid mine drainage and its interaction with water bodies

As a consequence of mining operations, especially for coal and metalliferous ores, acid mine drainage frequently occurs. Several chemical reactions are initiated spontaneously, due to the material exposed to an oxidizing environment (Deutsch, 1997). The formation of acid waters is common within underground workings and open pits, and the process develops when the ore is exposed to atmospheric oxygen. In the presence of water and oxygen, bacteria favour an acidic environment (Baciu & Costin, 2008), in which sulphides decompose and release sulfuric acid and dissolved metals.

The genesis of acid waters is described by the following reactions:

The classical reaction describing pyrite oxidation in the presence of oxygen and water has been reported by several researchers (e.g. Singer & Stumm, 1970; Nordstrom, 1979):

$$FeS_2 + 3{,}5\,O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

This bivalent form of iron usually oxidizes after the reaction:

$$14Fe^{2+} + 3{,}5O_2 + 14H^+ \rightarrow 14Fe^{3+} + 7H_2\text{O} \qquad (2)$$

In the process of pyrite oxidation and the generation of acid mine water, an important role is played by Fe^{3+}, which is able to oxidize pyrite in the anoxic environment under aqueous solution conditions with higher rate than that of molecular oxygen, according to the equation (Garrels & Thompson, 1960):

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (3)$$

In the initial stage, pyrite reacts with oxygen and water to produce ferrous iron, sulphate and acidity. The second step involves the conversion of Fe^{2+} into Fe^{3+}. The third reaction includes hydrolysis of ferric iron with water to form solid ferric hydroxide and release of additional acidity. At this stage, pH plays an important role. If the acidity is very high, for example pH lower than 3.5, solid minerals do not form and ferric iron remains in solution. At a higher pH, a yellow-brown precipitate called „yellowboy" is formed. The last step involves oxidation of the additional pyrite of ferric iron, generated by the oxidation reactions of the initial step 1 and 2. The cyclic diffusion of iron is rapid and continues until the supply of ferric iron or pyrite is exhausted.

The maximum acidity of a mining area in the most cases occurs at 5 to 10 years after the closure of mining, followed by a gradual decrease between 20 to 40 years (Ziemkiewicz et al., 1991; Hart et al., 1991). Several factors control the acidity of a mining area, for example lithology (Vasilatos et al., 2015), mineralogy, hydrological conditions and so on. The tailings ponds contain high quantities of waste resulting from ore processing. In the pond the sterile material is stored after separation. Generally the ponds contain also sulphides, which determine the acidic character of the mine waters.

The main source of acid mine drainage generation are the tailings ponds, waste dumps, surface runoff from active/inactive open pits, and underground mining workings (**Figure 4**).

II.

Figure 4. a,b,c,d – mine waters from Rosia Montana mining area (a – T.M.F. exfiltration Saliste pond, b – RO88 gallery, c – Cetate gallery, d – 714 gallery).

II. PERSONAL CONTRIBUTION

1. Research methodology

The geochemical methods, including isotopic analyses have the most important role in this work, highlighting the toxic substances derived from mining activities in groundwater and surface water. The isotopic characteristics of oxygen and hydrogen in water were used to evaluate the flow paths of the groundwater, mixing processes and interaction between precipitation –surface water and groundwater. The radioactive potential of the area was investigated by measuring the concentrations of ^{222}Rn and ^{226}Ra in water.

1.1. Sampling network

In order to characterize and estimate the variability of the compositional parameters of the waters of the study area, a monitoring network was defined, including 28 points, and subsequently reconfigured to 24 points considered representative for our scope. The sampling was done monthly, approximately in the same period of each month, between August 2013 and August 2015. The water sources included in the study were classified into 5 types: 12 sampling points from water courses, 7 acid mine waters, 5 artificial lakes, 2 dug wells dug and 2 springs, in the initial configuration, and in the second phase 3 test points of surface water from rivers and 1 point corresponding to artificial lakes were abandoned. The samples were collected in an altitudinal range between 576 and 1077 meters (**Figure 5**).

The sample points were selected according to their position against the main pollution sources, so as to include potentially non-affected waters upstream of these sources (3 points), points downstream of the emergence of mine waters (8 points) and a reference point, located at a certain distance from the mining area. It were also selected groundwater points without a direct influence of the mining area, springs (2 points) and wells (2 points) used for water supply to the population. The mine waters come from a tailings pond (1 point), drainage from the waste rock dumps (2 points) and mining workings (4 points).

The artificial lakes used in the past as water reservoirs for washing the ore (4 points) were also selected.

Thus, the following types of measurements were made: pH, water temperature, electrical conductivity, turbidity, dissolved oxygen, redox potential, salinity, $\delta^{18}O$, $\delta^{2}H$, as well as major ion concentration (F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, Li^+, Na^+, K^+, Mg^+, Ca^+, NH_4^+, HCO_3^-) and heavy metals concentrations (Ni, Cd, Pb, Cr, Zn, Cu).

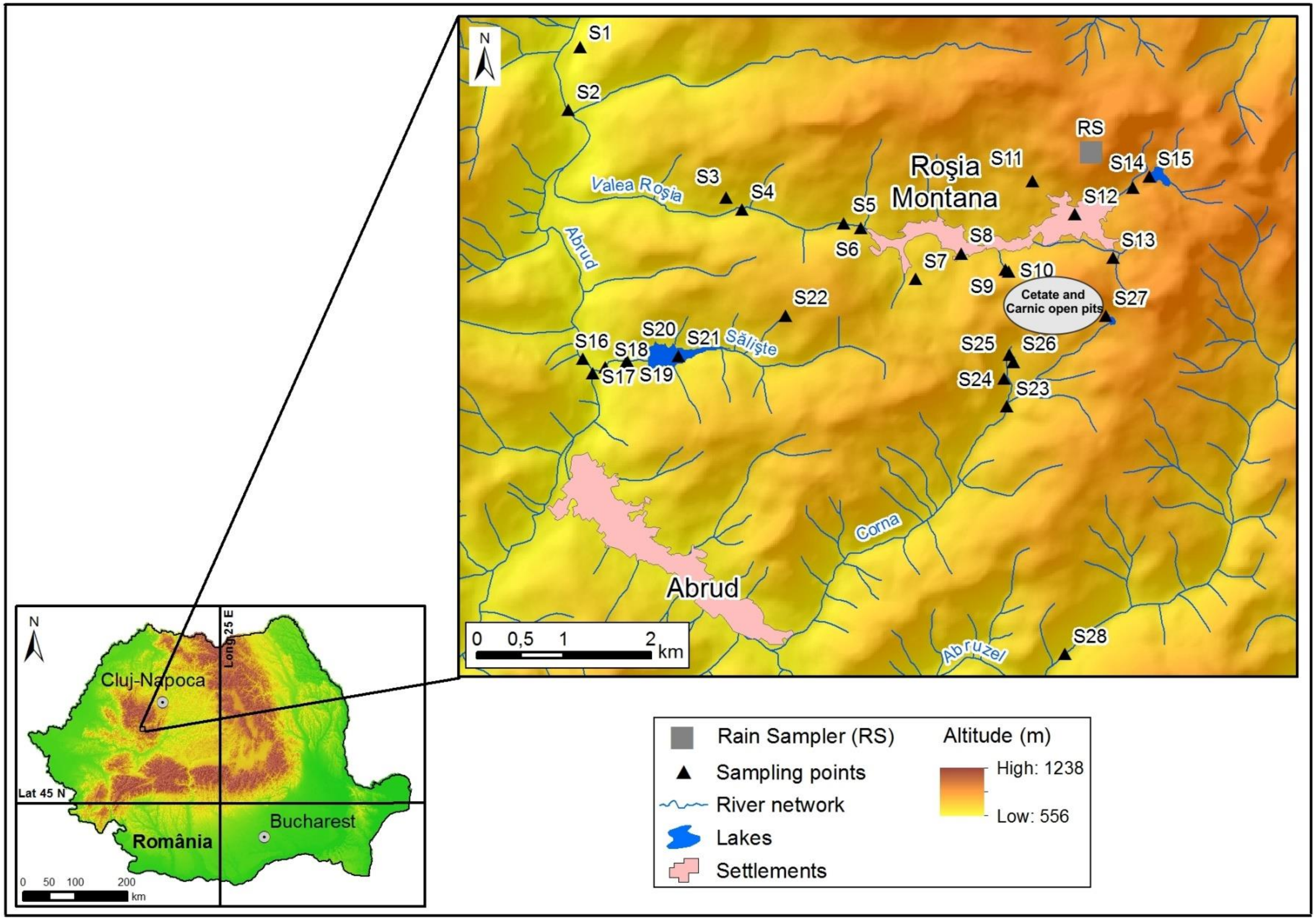

Figure 5. Location of the sampling points in the study area.

2. Results and discussion

2.1. Geochemical characterization of the water bodies, genesis, dynamics and recharge of aquifers.

The hydrogeochemical facies of the water bodies from Roșia Montană is reflected in the Piper diagram (**Figure 6**). Mine waters (S20 – T.M.F. Sălişte, S25 - Gallery C122, S5 - Gallery 714, S9 - Cetate gallery, S7 - Haldă Cetate 2, S8 - Gallery RO88) are placed in the field of the Piper diagram characterized as SO_4-Ca-Mg. In the triangle of anions, the waters courses are positioned in the SO_4-HCO_3 field, being predominantly SO_4 those waters that were influenced by the mining works and predominantly HCO_3 those which are non-affected by the mining.

Regarding cations, water courses are Ca-Mg with low sodium and potassium. Artificial lakes (S13 - Tău Brazi, S15 - Tău Mare, S21 – Tailings pond Sălişte, S26 - Tău Cartuş, S27 - Tău Corna) are HCO_3-SO_4-Ca. Dug wells (S11 - RO78, S24 - C120) are HCO_3-Ca, and in the case of point S24 the influence of the mining works that generate a sulphate dominance is observed. The springs (S3 - RO11 and S14 - RO43) are HCO_3-Ca.

The Schoeller diagram is commonly used in hydrogeochemical investigations to assess the quality of groundwater and surface water. Schoeller (1955) proposed this type of diagram that describes the concentrations of the main ions (milliequivalents per litre) that are represented by six equally spaced logarithmic scales. Very high concentrations are observed for the main ions in the case of mine waters (**Figure 7**).

The lowest concentrations were observed in the case of springs and artificial lakes. The water courses show a large range of concentrations of the major ions, depending on their position, upstream or downstream from the sources of pollution, and on the mixture between the different categories of water.

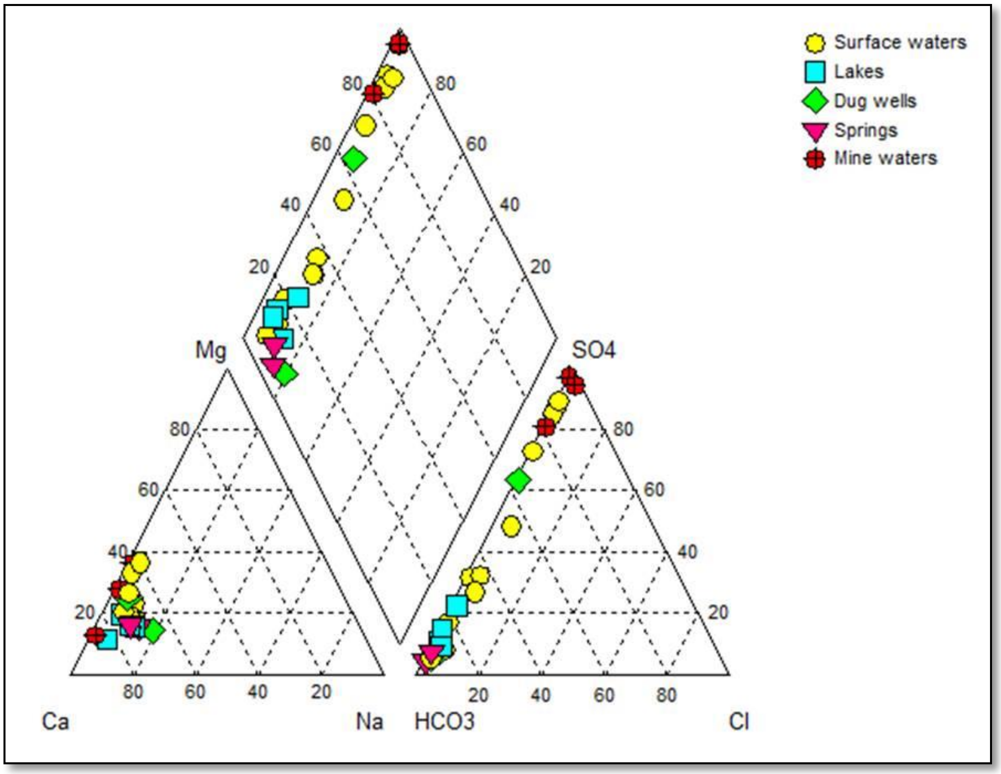

Figure 6. Piper diagram used to characterized the hidrogeochemical facies of the water bodies from Roșia Montană mining area.

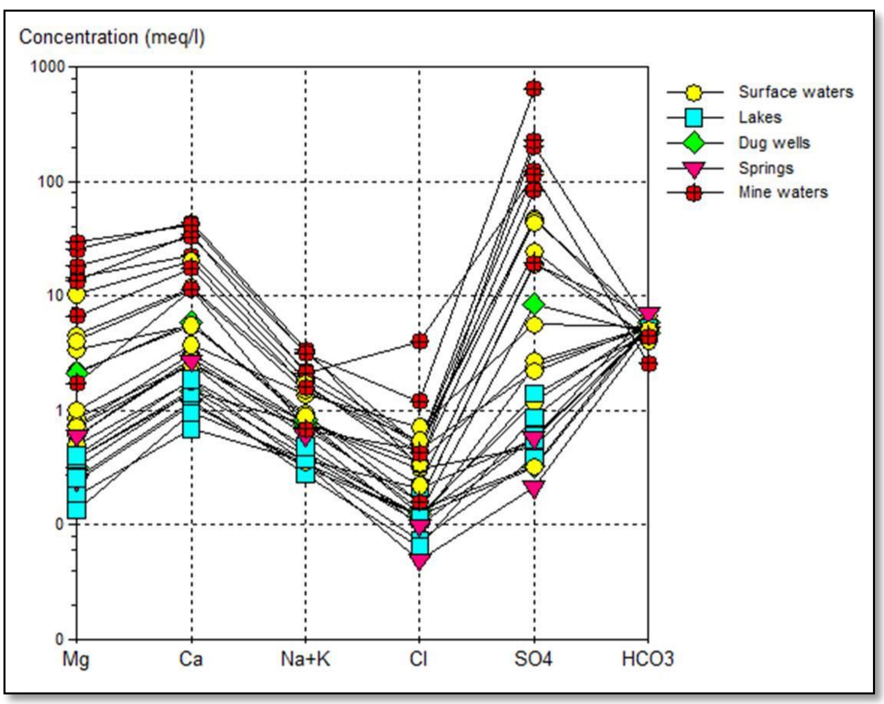

Figure 7. Schöeller diagram (average values of the main major ions for all water categories included in the study).

Mine waters in Roșia Montană mining area contain high concentrations of sulphates, as well as heavy metals (**Figure 8**) compared to the other water bodies. Especially 5 mine waters S9 (Cetate Gallery), S5 (Gallery 714), S25 (Gallery C122), S10 (Haldă Cetate 1) and S8 (Gallery RO88) are in direct contact with the mineralization and according to the Ficklin diagram, these waters are classified as ultra-acidic, in accordance with the sum of the trace metals. S9 has the highest metal concentrations and the lowest pH, being at the limit of the ultra-acid domain. Also points S5, S8, S10 and S25 show low pH (acid / ultra acid) and high values of metal concentration. Points S7 and S20 are in the acid domain with moderate concentrations of metals. Surface waters affected by mining (S4 and S28) may be located at the boundary between the acid and ultra-acid domains and may contain high concentrations of metals. As the influence of the mining works is reduced, the concentration of metals and the acidity decrease in the surface running waters. The lowest values of the metal concentrations are observed in the case of lakes and groundwater not influenced by the mining works. The pH values in this case are in the neutral range.

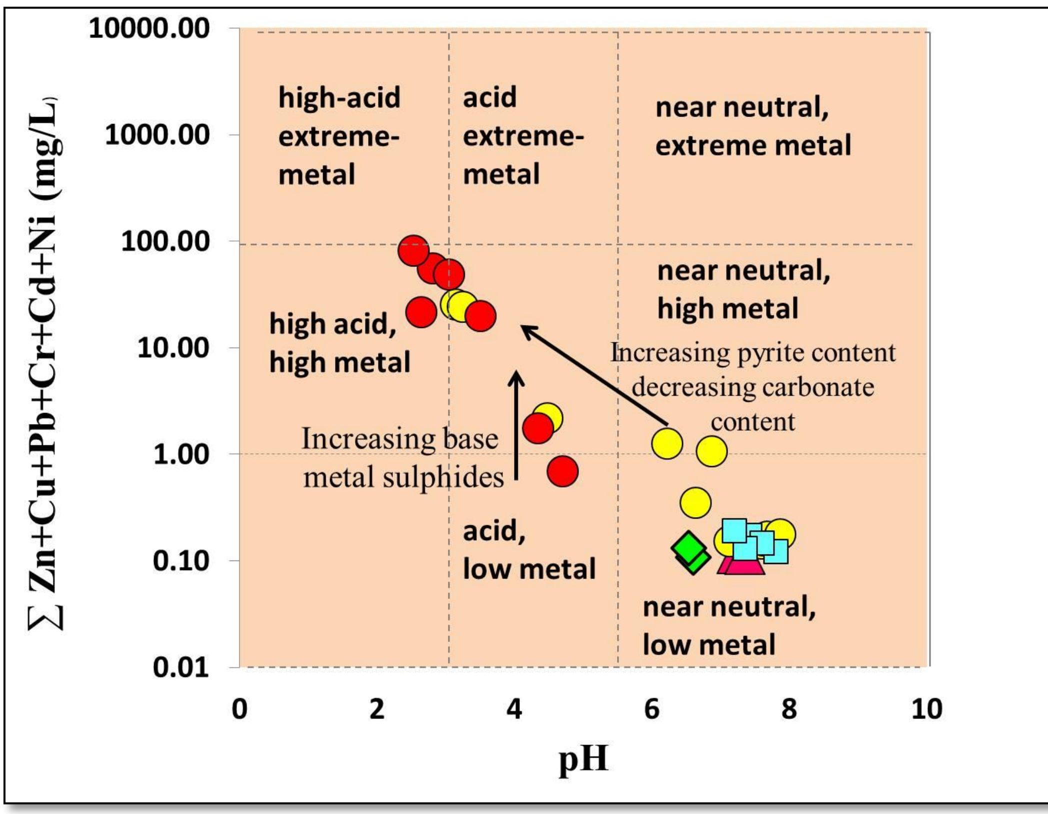

Figure 8. Ficklin (1992) diagram shows the sum of the heavy metals pursued in the area as a function of pH (the same symbols as in the Figure 4 and 5).

In order to identify the relationship between the investigated water sources, a *"Hierarchical Cluster"* analysis was performed, using 15 physico-chemical parameters (pH, electrical conductivity, Ni, Cu, Zn, Cr, Cd, Pb, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}). Cluster analysis was developed based on the above-mentioned standardized data, using Ward's (1963) method of Euclidean distances as a measure of similarity. The dendrogram (**Figure 9**) highlights three groups of sources that differ according to their common characteristics.

Therefore, group A1 corresponds to the points with the lowest metal concentrations, group A2 corresponds to the points with moderate contamination, and group A3 contains the points with the most intense contamination as a result of mining activities (**Figure 9**).

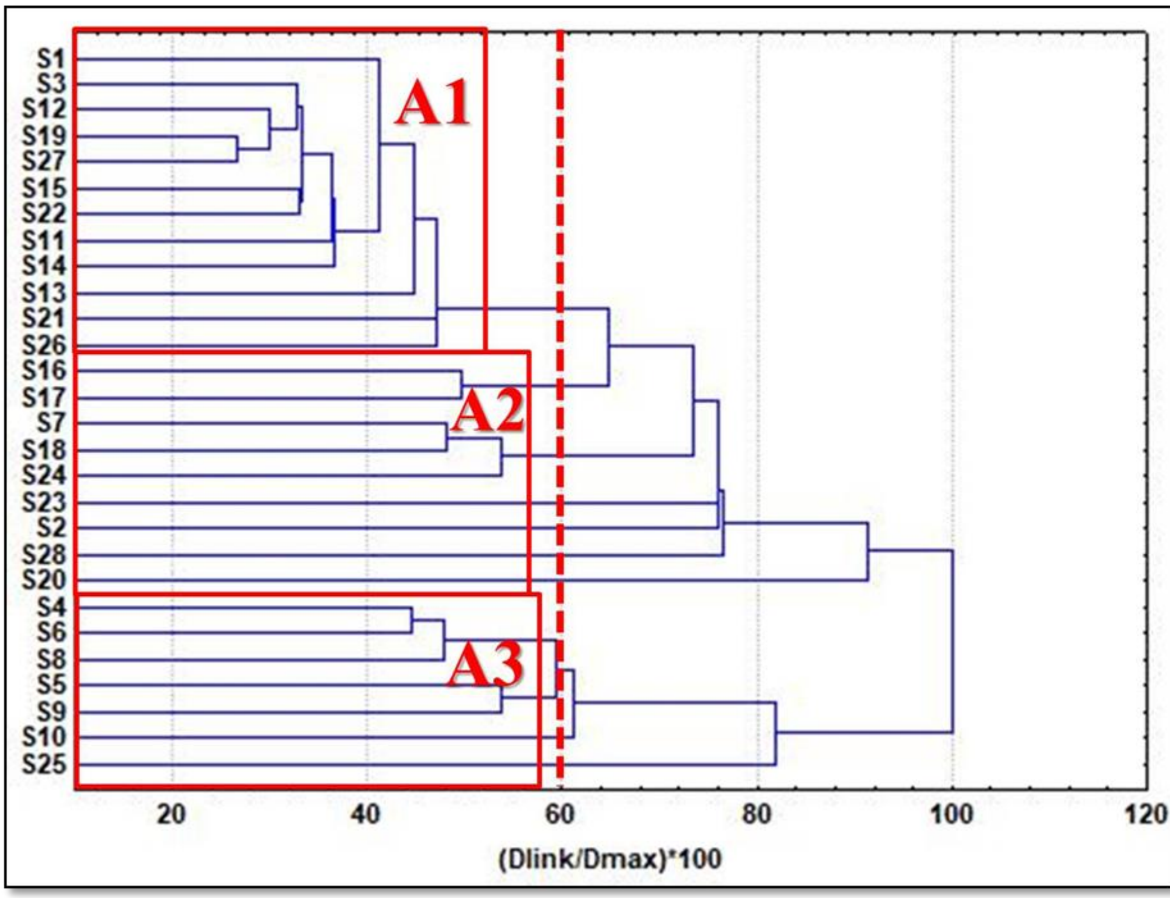

Figure 9. Hierarchical Cluster Analysis for all the categories of waters investigated in the present study.

2.2. Isotopic composition of all water bodies in the geochemical study

Stable isotopes of $\delta^{18}O$ and δD from water provide essential information about the water circuit. Stable isotopes are a useful tool in order to elucidate infiltration of precipitation within the watershed, surface runoff, evapotranspiration and other processes.

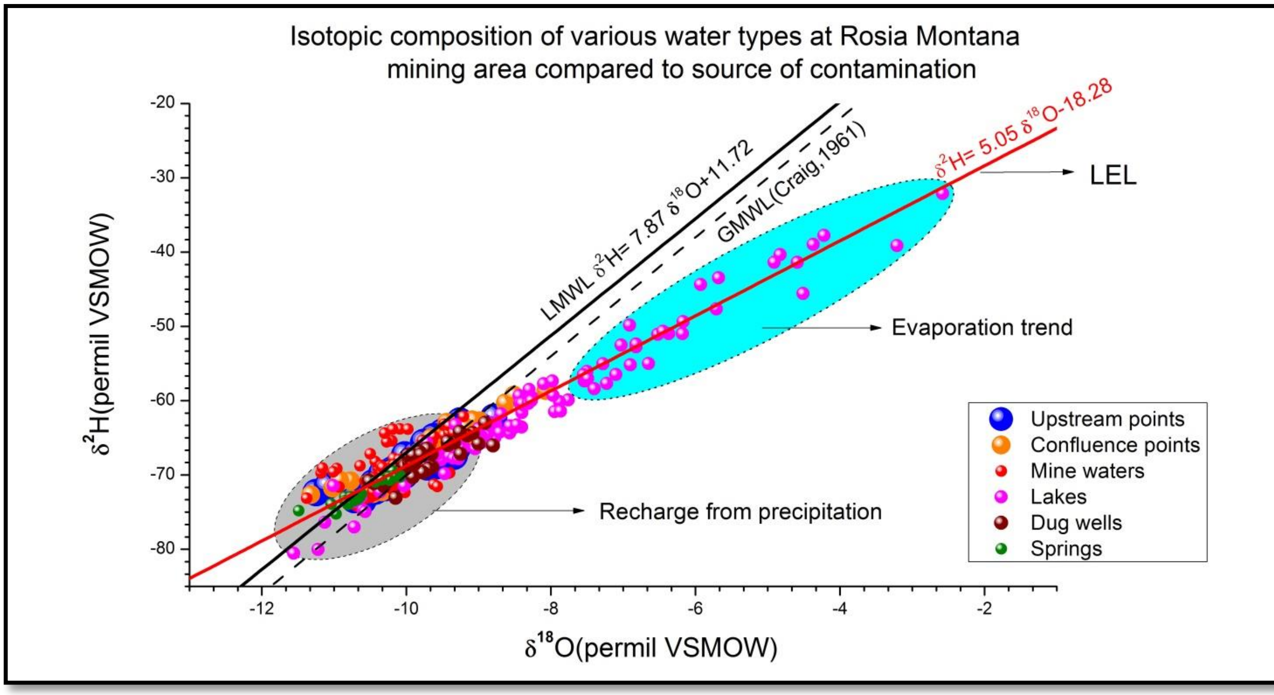

Figure 10. Isotopic composition of all water bodies against LMWL and GMWL, and the regression equation of the results for the present study.

All water types in the study area have meteoric origin, a fact that is highlighted by their position relative to the LMWL. In the case of lakes, there is an obvious tendency of evaporation.

The regression line of all the waters in Roșia Montană mining area is shown in figure 10:

$$\delta D = 5.05 \times \delta 18O - 18.28 \quad (4)$$

During evaporation, isotopic fractionation takes place, thus light isotopes concentrating in vapours, and the remaining water is enriched in heavy isotopes. This process is much more pronounced in the case of oxygen. The regression line is strongly deflected to the right due to the presence of lakes that exhibit an evaporation tendency (**Figure 10**).

The running and mine waters are located at the bottom of the regression line, whereas in the case of lakes evaporation produces an isotope enrichment, which places the points at the top of the regression line.

2.3. The radioactive potential in Roșia Montană mining area

Natural tracers used in the present hydrogeochemical study contribute to the elucidation of some geochemical features, of the origin and dynamics of waters. The radioactive isotopes (radon and radium) have been used, in order to estimate the radioactive potential in the area. Radon and radium isotopes are commonly used in hydrogeochemical studies in order to reveal the particular processes that occur in the water bodies, especially the interaction with the host rock.

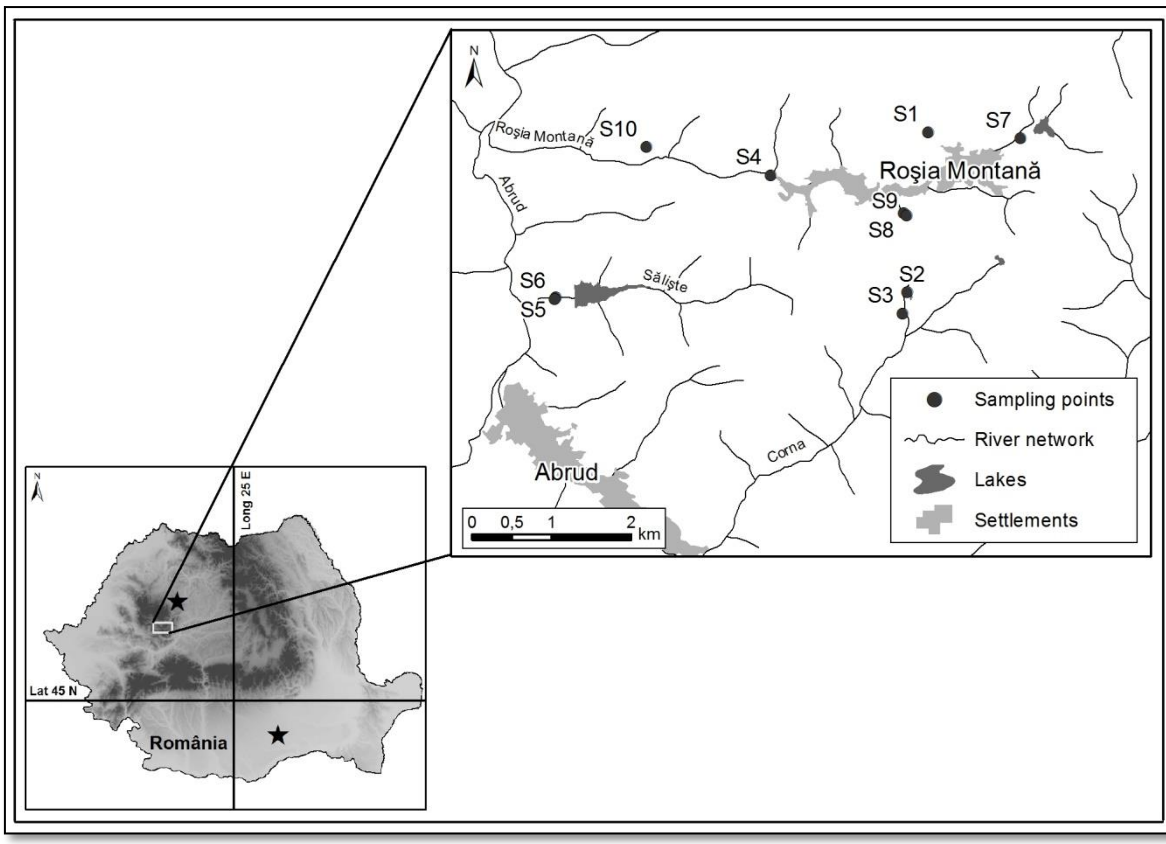

Figure 11. Map of the study area and the location of the 10 sampling points in order to estimate the radioactive potential (Cozma et al., 2016).

Figure 11 shows the 10 sampling points chosen in order to estimate the radioactive potential. The most representative points were selected (groundwater affected by the mining activity, respectively non-affected by the mining activity) over a 9 month monitoring period, November 2013 July 2014.

The results reflect a low level of radioactivity in the area. Radon and radium concentrations do not exceed the thresholds imposed by the international regulations (Cozma et al., 2016). Thus the highest concentrations were found in source S3 (RO11), with a value of 210 mBq / L in the case of Ra^{226} and 11.2 Bq / L in the case of Rn^{222}, the monitoring point, not being affected by the mining works (**figure 12**).

The northern part of the region indicates the highest concentrations, while the lowest concentrations are in the southern part of the study area (**Figure 12**) according to Cozma et al., (2016).

Despite the fact that in the Roşia Montană area there are several tailings dumps, and rocks exposed to external factors and a significant rock-water interaction, the concentrations of these radionuclides remain low in the area strongly affected by the mining activity. This is explained by the geology of the area that does not favour a high radioactive potential (Cozma et al., 2016).

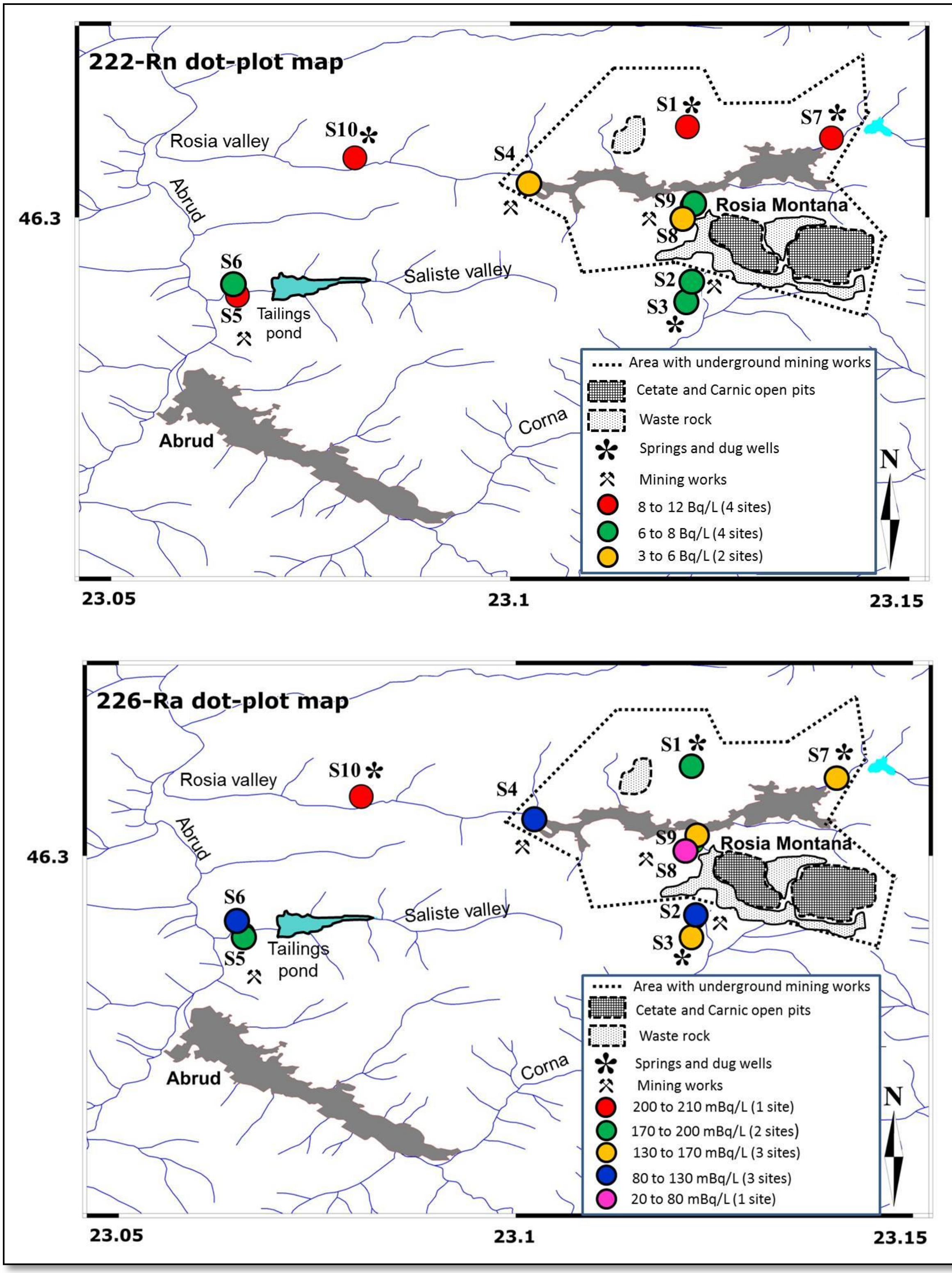

Figure 12. Map of concentrations of Rn^{222} and Ra^{226} in the study area (Cozma et al., 2016).

2.4. Applicability of natural tracers and quality of water bodies

2.4.1. Surface water quality

High concentrations of Ni, Cu, Zn, Cd, Pb, sulphate, ammonium, magnesium and calcium were measured at point S2 (Downstream confluence Roşia with Abrud), S4 (Downstream Rosia valley), S6 (Downstream Adit 714), S28 (Abruzel valley) (**Tables 2** and **3**). In these points the values exceed the limit for the third class and are included in the fourth class of quality, according to Order 161/2006. Also the pH is very low at these points, below 6.5.

At the same time, for the Corna Valley, there are exceedances of the allowable values, being classified in the fourth class of quality. The least affected are the upstream points of the mining objectives. In the case of lakes, there are exceedances of NO_2 and NH_4 caused by organic pollution.

Due to the poor quality of surface water, diatom species are affected, in areas highly contaminated by mining activity, diatom communities have disappeared almost everywhere (Baciu et al., 2018).

2.4.2. Springs and wells quality

According to the law 458/2002 the springs and wells show concentrations above the limit in the case of nitrates and lead. Sulphate concentrations are excessive at point S24 (C120), in the other 3 sources of drinking water falling within normal limits (**Tables 2** and **3**).

2.4.3. Mine water quality

The mine waters discharge high concentrations of contaminants in streams, above the limit imposed by HG 352/2005, thus exceeding the limits imposed for wastewater in the case of Cd, Ni, Cu, Zn, Pb, nitrates, sulphates, magnesium, calcium and ammonium (**Tables 2** and **3**).

The high concentrations of sulphates, nitrates and metals in mine waters, together with the low pH, are an essential problem for the environment in Roşia Montană area. These mine waters flow directly into the surface waters with very strong effects in the Roșia valley and more moderate in the Corna valley and Săliște valley. All these valleys have their flow in the river Abrud, which suffers a significant contamination.

The concentration of nitrates in the waters can be a consequence of the use of fertilizers or of the work done during the operation of the mine.

Tabel 2. The average concentrations of the analysed heavy metals and exceedances of the admissible values are established by the regulations (HG188 / 2002 modified HG 352/2005), (Law 458 / 2002), (Order 161/2006).

Source	***Water type***	***pH***	***Heavy metals (µg/L)***					
			Ni	**Cu**	**Zn**	**Cr**	**Cd**	**Pb**
S1	**Water course**	**7.71**	**33.18**	**16.06**	**27.34**	**9.70**	**40.57**	**31.65**
S2	**Water course**	**6.23**	**73.36**	**40.09**	**1052.30**	**9.53**	**40.37**	**37.87**
S4	**Water course**	**3.15**	**296.97**	**444.44**	**24154.90**	**27.99**	**80.24**	**85.00**
S6	**Water course**	**3.25**	**262.11**	**559.95**	**23034.80**	**24.53**	**69.81**	**83.46**
S12	**Water course**	**7.60**	**29.39**	**17.45**	**25.27**	**8.56**	**41.76**	**22.47**
S16	**Water course**	**7.13**	**28.15**	**13.65**	**65.96**	**9.27**	**7.89**	**26.56**
S17	**Water course**	**7.62**	**24.12**	**19.26**	**61.85**	**5.15**	**12.31**	**31.45**
S18	**Water course**	**6.64**	**46.82**	**36.41**	**143.13**	**12.75**	**56.73**	**51.54**
S19	**Water course**	**7.68**	**29.49**	**15.07**	**30.00**	**12.07**	**48.04**	**32.05**
S22	**Water course**	**7.87**	**31.48**	**29.75**	**26.61**	**8.39**	**38.45**	**40.64**
S23	**Water course**	**6.88**	**158.33**	**46.18**	**704.88**	**21.31**	**42.54**	**78.60**
S28	**Water course**	**4.48**	**86.13**	**906.55**	**1059.16**	**14.31**	**33.87**	**52.59**
S3	**Spring**	**7.25**	**20.26**	**28.72**	**26.68**	**7.31**		**32.59**
S11	**Dug well**	**6.61**	**22.41**	**21.31**	**25.47**	**9.59**		**28.73**
S14	**Spring**	**7.36**	**24.07**	**22.69**	**28.92**	**10.39**		**28.73**
S24	**Dug well**	**6.54**	**32.73**	**21.51**	**24.38**	**12.45**		**40.30**
S13	**Artifical lake**	**7.44**	**33.44**	**37.10**	**34.80**	**41.98**		**21.70**
S15	**Artifical lake**	**7.82**	**27.73**	**24.02**	**25.80**	**9.14**		**33.32**
S27	**Artifical lake**	**7.61**	**42.67**	**22.35**	**37.42**	**8.47**		**34.01**
S26	**Artifical lake**	**7.37**	**31.23**	**19.62**	**37.10**	**11.62**		**29.35**
S21	**Artifical lake**	**7.21**	**31.03**	**23.93**	**91.04**	**7.51**		**34.78**
S5	**Mine water**	**2.82**	**868.06**	**1535.21**	**52227.90**	**62.98**	**217.42**	**178.08**
S7	**Mine water**	**4.71**	**83.36**	**63.97**	**414.79**	**16.56**	**42.73**	**60.00**
S8	**Mine water**	**3.05**	**375.01**	**806.18**	**46665.20**	**44.76**	**236.67**	**97.15**
S9	**Mine water**	**2.54**	**1730.29**	**2294.48**	**75516.70**	**103.00**	**649.06**	**207.00**
S10	**Mine water**	**2.65**	**565.93**	**2514.48**	**18161.90**	**62.22**	**42.63**	**102.72**
S20	**Mine water**	**4.35**	**180.27**	**40.51**	**1284.08**	**38.98**	**50.46**	**156.52**
S25	**Mine water**	**3.51**	**606.80**	**169.20**	**18564.90**	**36.46**	**56.18**	**163.38**

HG 188/2002 modified 352/2005 for waste water

Law 458/2002 for drinking water

Order 161/2006 for the third class of surface water quality

Tabel 3. The average concentrations of the analysed major ions and exceedances of the admissible values are established by the regulations (HG188 / 2002 modified HG 352/2005), (Law 458 / 2002), (Order 161/2006).

Source	*Water type*	*Anions (mg/L)*					*Cations (mg/L)*				
		Fl^-	Cl^-	NO_2^-	NO_3^-	SO_4^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+
S1	**Water course**	0.09	10.94	2.51	3.12	22.77	7.32	18.2	10.39	49.97	19.24
S2	**Water course**	2.19	25.25	2.5	4.13	269.52	11.17	34.51	12.15	75.15	38.63
S4	**Water course**	1.76	12.07	SLD	14.99	2227.31	20.95	31.95	55.49	235.06	240.57
S6	**Water course**	1.92	19.17	SLD	81.62	2097.97	15.39	32.02	48.94	229.62	SLD
S12	**Water course**	0.06	3.67	1.13	3.4	116.32	6.09	5.16	4.58	30.52	23.41
S16	**Water course**	0.18	12.67	2.65	3.88	130.14	10.23	12.89	8.93	63.18	88.14
S17	**Water course**	0.3	15.88	2.78	22.83	105.77	10.37	8.81	7.33	57.47	SLD
S18	**Water course**	SLD	5.56	3.76	6.09	898.34	7.78	23.6	26.46	109.95	63.83
S19	**Water course**	0.61	4.24	3.05	2.26	56.8	5.18	7.86	8.7	50.27	63.86
S22	**Water course**	0.13	4.3	1.85	1.49	15.31	3.87	7.12	6.11	36.37	35.15
S23	**Water course**	0.14	17.62	15.96	16.74	2250.5	20.69	38.05	126.55	403.22	440.65
S28	**Water course**	1.71	7.81	SLD	7.76	1182.45	8.61	19.62	40.88	110.15	81.68
S3	**Spring**	0.15	3.49	3.35	1.86	27.53	9.35	7.89	7.28	54.11	39.03
S11	**Dug well**	0.07	4.85	1.06	1.75	15.47	9.72	13.26	3.82	29.58	43.98
S14	**Spring**	0.05	1.74	0.92	1.12	10.21	5.09	4.45	2.97	22.35	8.35
S24	**Dug well**	SLD	4.4	4.57	7.19	405.2	11.26	13.04	25.78	118.54	59.41
S13	**Artificial lake**	0.06	2.55	0.99	1.19	18.25	5.19	5.03	2.17	13.81	13.45
S15	**Artificial lake**	0.06	4.3	1.18	1.84	28.8	4.87	4	3.12	23.68	14.9
S27	**Artificial lake**	0.09	4.02	1.98	2.21	66.91	6.31	8.06	4.9	37.22	55.07
S26	**Artificial lake**	0.1	7.4	0.92	1.36	26.66	1.58	11.85	1.61	19.14	17.28
S21	**Artificial lake**	0.12	2.3	1.82	1.19	41.88	2.78	5.95	4.59	28.62	3.64
S5	**Mine water**	9.59	17.33	SLD	62.27	11085	38.67	59.25	222.11	659.72	764.92
S7	**Mine water**	0.36	5.6	SLD	14.08	934.21	5.1	17.95	20.78	229.97	2190.97
S8	**Mine water**	2.02	15.06	SLD	33.43	4024.77	16.14	34.97	80.84	351.51	364.97
S9	**Mine water**	6.91	42.47	SLD	98.23	31051.9	32.47	68.23	359.99	841.04	2697.97
S10	**Mine water**	2.81	18.26	SLD	24.83	5960.22	22.44	48.06	175.12	452.8	798.52
S20	**Mine water**	SLD	11.6	SLD	243.62	9773.13	24.34	90.94	311.54	874.41	4397.91
S25	**Mine water**	4.74	141.72	SLD	46.4	5535.73	19.55	49.97	164.35	685.24	563.91

HG 188/2002 modified 352/2005 for waste water
Law 458/2002 for drinking water
Order 161/2006 for the third class of surface water quality

CONCLUSIONS

Roşia Montană mining area is located in the southern Apuseni Mountains (western part of Romania) and belongs to the Golden Quadrilateral, hosting one of the most important gold and silver deposits in Europe (Manske et al., 2006). ***The relief*** is strongly influenced by the hydrographic network, the most important courses being Roșia, Corna, Sălişte and Abruzel, which have shaped the existing massifs in the area.

For the present study, the sample points were selected on the Roşia, Corna, Sălişte, Abruzel and Abrud water courses. Acidic waters from mining work have a significant contribution to the total cumulative flow of waters running. A special place between the surface waters is occupied by the artificial lakes in the area. From a total number of artificial lakes, four were chosen for monitoring, in order to establish correlations with the valleys on which they are located.

The climate in Roşia Montană is a temperate continental one, with some exceptions in the higher altitude areas, where the mountain microclimate dominates with cold winters and significant solid rainfall, with an interval between 4 and 6 months (RMGC, 2006). The average annual temperature is 7.38 ° C, with a monthly average of 18.6 ° C recorded in the warm season, in August, and with a minimum monthly average of -2.4 °C during the winter, recorded in January (Roşia Montană Weather Station).

The southern part of the Apuseni Mountains, including the area of the present study, represents the result of the operation of major Tethysian sutures, which probably began before Jurassic and lasted until the end of the Cretaceous. It is well-known the Golden Quadrilateral, which define a particularly rich metallogenetical district, known for over two millennia, especially for its precious metal resources. The ore in the area is represented by Au-Ag type (e.g. Roșia Montană), Au-Cu type (e.g. Rovina) and porphyry copper type (e.g. Roșia Poieni), to which are added deposits with common non-ferrous metals (lead, zinc). Roșia Montană is a ***maar-diatreme structure***, emplaced in a mass of Cretaceous sediments, dominated by black shale. As types of rocks, dominate the freatomagmatic type, volcanoclastic rocks, and intercalated subvolcanic porphyric dacite, dacitic dykes and late freatomagmatic breccias. The ***mineralization of interest*** in Roșia Montană area is interpreted as an epitermal system of moderate to low depth (Tămaş, 2007).

Roșia Montană mining area is characterized by a ***long history of gold and silver extraction***, being an area of interest since the Roman Empire. Roșia Montană was documented for the first time in the year 131, under the Roman name of Alburnus Maior, this date being found on a waxed tablet in one of the mine galleries.

The underground network includes 140 km of galleries, extended in the area of Cârnic, Cetate and Orlea massifs. This network includes mining workings from all periods of operation, from the Roman era to the recent period.

In addition to the underground network, other mining objectives resulting from the operations are present, namely ***2 tailings ponds***, ***33 waste rock dumps*** and ***2 open pits***.

The influence of these mining works on the environment is obvious through the modification of lands, occupation of large fields and lands, visible degradation of its, the degrading of water quality, the change of the hydrodynamic system, the pollution of soils and negative effects on the biota.

In order to estimate the variability of the compositional parameters of the waters in the study area, a monitoring network was defined, which initially included 28 points, and was subsequently reconfigured to 24 points, considered representative for our purpose. The sampling was done monthly, approximately in the same period of each month, between August 2013 and August 2015. The water sources included in the study were classified into 5 types: 12 sampling points from water courses, 7 acid mine waters, 5 artificial lakes, 2 dug wells and 2 springs, in the initial configuration, and in the second phase 3 points from streams and 1 point corresponding to artificial lakes were eliminated.

For a better understanding of the genesis and dynamics of waters in Roşia Montană mining area, ***physico-chemical*** and ***chemical analyses*** (pH, electrical conductivity, turbidity, dissolved oxygen, redox potential, salinity, concentration of heavy metals and major ions) together with isotopic analyses were included. In order to draw the local meteoric line, two locations were selected for sample collection, the first being located at the ***Roşia Montană Weather Station***, at an altitude of about 1200 m, and the second station being located in ***Cluj Napoca*** at an altitude of 365 m. In both locations, precipitation collectors were installed with a system that prevents the evaporation of samples. The samples were collected with a monthly frequency, on the 1st of each month.

The following physico-chemical parameters were measured in the field:

Dissolved oxygen, pH, redox potential, turbidity, salinity, electrical conductivity and water temperature. The WTW 350I (Germany) multimeter and WTW Turb 430IR portable turbidimeter were used to measure the physico-chemical parameters.

Field samples were collected for laboratory analysis of heavy metals, major ions, isotopic analysis,and radionuclides.

Mine water and ***water courses*** have the most pronounced variations compared to other water categories. ***Most mine waters*** show a pH range of ***2 to 4***, while ***water courses*** have pH values between ***6 - 8***.

The hydrogeochemical facies of the water bodies from Roșia Montană is reflected in the Piper diagram (**Figure 6**). Mine waters (S20 – T.M.F. Săliște, S25 - Gallery C122, S5 - Gallery 714, S9 - Cetate gallery, S7 - Haldă Cetate 2, S8 - Gallery RO88) are placed in the field of the Piper diagram characterized as ***SO_4-Ca-Mg***. In the triangle of anions, the water courses are positioned on the ***SO_4-HCO_3 field, being predominantly SO_4*** those waters that were influenced by the mining works and ***predominantly HCO_3*** those which are non-affected by mining.

The Ficklin plot as well as the dendrogram constructed on the basis of the standardized average values of the investigated parameters, show three types of water from a qualitative point of view, present in the Roșia Montană mining area: ***1. waters strongly affected by the mining activity (mine waters), 2. contaminated water courses as a result of the discharges from the***

mine, 3. waters non affected by the mining activity (the areas upstream from the mining workings).

Due to insufficient data on the Romanian territory, especially in the Apuseni mountains area, we took the initiative to create two new LMWLs, Roșia Montană and Cluj-Napoca (Cozma et al., 2017), which will be references for other isotopic studies and were used in the present study for a better interpretation of the isotopic data obtained.

The isotopic composition of precipitations from Roșia Montană for δD has a range between -115.58 ‰ (February 2015) and -25.88 ‰ (August 2015), with an average of -65 ‰ ± 0.09 ‰. For $\delta^{18}O$ it varies between a minimum of -15.17 ‰ (December 2014) and -3.78 ‰ (August 2015), with an average of -9.47 ‰ ± 0.01 ‰. Therefore, the equation of the regression line for ***Roșia Montană*** is:

$$\delta D = 7.87^{18}O + 11.72‰$$

For Cluj-Napoca, the range of isotopic ratios for δD is -7.49 ‰ (December 2014) and -23.79 ‰ (July 2015), with an average of -63.32 ‰ ± 0.09 ‰. With regard to δ18O, there was a minimum of -14.89 ‰ (December 2014) and a maximum of -4.27 ‰ (July 2015), with an average of -9.29 ‰ ± 0.03 ‰. The regression line for ***Cluj-Napoca*** has the following equation:

$$\delta D = 8.03^{18}O + 11.29‰$$

Isotopic analyses confirm that all types of water in the study area have meteoric origin. All water bodies have a recharge from precipitation, with strong seasonal variations given by the isotopic characteristics, especially in the case of water courses, but without significant deviations from the LMWL. Most points are located between LMWL and GMWL.

Roșia Montană mining area has also been examined in terms of radioactive potential. The results of the study, which monitored 10 points over a period of 9 months, November 2013 to July 2014, reflect a ***low level of radioactivity in the area***. Radon and radium concentrations do not exceed the thresholds imposed by international regulations.

The underground workings are partially flooded as a result of the closure of the mines, which denotes the creation of favourable mixing conditions. Therefore, the seasonal variations of chemical and isotopic parameters in ***mine waters*** are small, with a few exceptions (***S8, S9*** and ***S25***). The residence time in these 3 galleries is short, the aquifer being shallow and closely related to the external factors that outline its geochemical characteristics.

Of all the 4 galleries positioned on the Cetate massif (S5, S8, S9 and S10) ***S5*** and S***10*** have a relatively homogeneous system and are supplied with water from the underground. Also, from the perspective of the similar behaviour of the two mentioned galleries S5 and S10, it can be assumed ***a water residence time in the order of years, up to decades***. S8 and S9 have a close connection with external factors, therefore they are highly influenced by the weather conditions.

FUTURE DIRECTIONS

In a complex hydrogeological system where the processes are multiple, it is very difficult to quantify flows, absolute residence time, or a clear water pathway. Natural tracers widely used in many areas of the world can elucidate these aspects in a fairly large proportion. In the present study there were limitations in the research, especially regarding the location of the mixing point of the different water sources within the underground works, their flow paths and in establishing the exact residence time of the waters.

A subsequent, more detailed study of the Roșia Montană water system could include:

- Taking samples from inside the underground works for a better representation;
- Use of artificial tracers to be able to track the flow paths and the residence time of the water;
- Daily sampling and immediate analysis. It really represents a challenge from several factors (effort, financial costs, etc.). Daily sampling would greatly reduce errors, as the measurements could be correlated with each precipitation event and thus we could quantify a more precise residence time of the waters.

At global scale, several methods have been established that have been used successfully. Namely infiltrometers, mini-piezometers, geophysical techniques (electrical resistivity), radioactive isotopes (cosmogenic S35), those used in the present study (stable isotopes, concentration of metals and main ions, radon), CFC (Chlorofluorocarbons) and SF6 (Hexafluoride), 3H (tritium), 3H / 3He (tritium / helium).

The coupling of methods, instruments and tracers is necessary for a better understanding of the processes that take place in an area, either natural or anthropogenic.

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