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Quality assessment indicators of surface waters and soils in the vicinity of the former sulfur mine in the Călimani Mountains

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Abstract

A native sulfur mineralization was quarried out intensively for a period of almost 30 years in Călimani Mountains, the Eastern Carpathians. The waste resulted from this exploitation activity was stored in four waste dumps, while the residues resulted from the processing were disposed in a settlement pond. Although mining operations closed in 1997, the remains of the former sulfur mining are listed among the major pollutants in Romania.
The present paper intends to present a preliminary analysis and the current state of the impact of pollution of the former mining exploitation on different environmental factors, by assessing some quality indicators of surface waters and soils. Water and soil samples from different areas situated in the proximity of the former mine were collected and analyzed, performing pH, conductometric, turbidity, chemical and microbiological determinations.
The results of this study demonstrate that the pollutant potential of the former sulfur mining from the Călimani Mountains is still very high, a fact proved by the acidic pH of the surface waters and soil, high turbidity and conductivity of the water respectively by the high number of impurities detectable through a simple preliminary chemical analysis.

Keywords: *sulfur mining, the Călimani Mountains, pollution, pH, turbidity, chemical analysis, microbiological analysis, quality assessment*

Rezumat. Indicatori de evaluare a calității apelor de suprafață și solurilor în proximitatea fostei exploatări de sulf din Munții Călimani

Zăcământul natural de sulf din Munţii Călimani, Carpaţii Orientali, a fost exploatat intensiv de-a lungul unei perioade de aproape 30 de ani. Sterilul rezultat din activitatea de exploatare s-a depozitat în patru halde de steril, în timp ce reziduurile rezultate din procesarea minereului s-au evacuat într-un iaz de decantare. Deşi operaţiunile miniere au fost sistate în anul 1997, rămăşiţele fostei exploatări de sulf sunt clasificate printre principalii factori poluanţi din România.
Lucrarea de faţă are ca scop prezentarea unei analize preliminare şi a stadiului actual al impactului poluării fostei exploatări miniere asupra factorilor de mediu, prin evaluarea unor indicatori ai calităţii apelor de suprafaţă şi a solurilor. Probe de apă şi sol au fost colectate din diferite regiuni aflate în proximitatea fostei mine şi au fost analizate, efectuând determinări de pH, conductometrice, turbidimetrice, chimice şi microbiologice.
Rezultatele obţinute demonstrează faptul că potenţialul ca şi agent poluant al fostei mine de sulf din Munţii Călimani este în continuare foarte ridicat, fapt reliefat de pH-ul acid al apelor de suprafaţă şi a solului, conductivitatea şi turbiditatea ridicată a apei respective prin numărul ridicat de impurităţi detectabile printr-o simplă analiza chimică preliminară.

Cuvinte-cheie: *exploatarea sulfului, Munţii Călimani, poluare, pH, turbiditate, analiză chimică, analiză microbiologică, evaluarea calităţii*

Introduction

The Călimani Mountains are the largest mountain unit of the Oriental Carpathians, with a total area of about 2000 km^2, being considered as the highest and the most spectacular volcanic mountain in Romania. But not everything linked with Călimani Mountains can be described in idyllic colors; thus few know of the existence of more than 300 hectares of bare mountain without any trace of green vegetation. This is the present picture of the Negoiu Românesc peak, or rather the picture of its remains. The former sulfur mine exploitation, opened during the communist regime is responsible for the destruction of wildlife and vegetation, right in the middle of the protected Călimani National Park is.

The sulfur deposit from the northern part of Călimani Mountains is located, from the administrative point of view, on the territory of Şarul Dornei village. The first written attestation of the presence of sulfur ore in the region of Negoiu peak, appeared in the second half of the 19th century, but the exploitation activities began only in 1969, as the seventies were a economic period in which chemistry was considered an engine for the national economy, requiring high amounts of sulfur containing substances. As market demands were high, the sulfur was highly sought after; consequently the damages caused to the environment have been neglected, excelling only the

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economic interest. The mine was closed by government decision in 1997, the primary motivation being that sulfur exploitation cost three more time than its production value; according to these conclusions the mine lasted for almost 30 years due to the reported false production figures, and was never profitable (Georgescu et al. 2005; Ştumbea, 2010; Teodor, 2010).

From a valuable source of sulfur supply for the Romanian steel industry, nowadays the sulfur mine became a headache for environmentalists. Today, the remains of the former sulfur exploitation seem a "bad joke" thrown in the middle of the Călimani National Park area.

The sulfur exploitation from the Călimani Mountains remains one of the biggest ecological disasters in Romania and in the range of the Carpathians. The intensive mining activities led to the physical destruction of a mountain (Negoiul Românesc), 300 hectares of highly damaged land, heavily polluted water and soil and ultimately became a major threat for the health of exploitation workers and locals from the region.

The mineralization contained sulfur associated with pyrite and iron oxides; the sulfur occurred as diffused impregnations, nests and thin layers within the structure of ore bodies containing pyrite, aluminous limestone, silica, clay minerals and iron oxides. The sulfur was being extracted from rocks in a specially designed grinding plant and the sterile material was laid nearby as waste dump. The waste resulted from the exploitation, were stored in four waste dumps (Dumitrelu, Ilva, Pinu, Puturosu) while the waste resulted from ore processing using floatation and subsequent treatments were disposed in a settlement pond (Dumitrelu pond) (Georgescu et al. 2005; Teodor, 2010, Surdeanu et al, 2011).

The degraded soils, the waste dumps are often very unstable and become sources of pollution; the direct effects are related to the loss of forest or grazing land while the indirect effects include air, soil and water pollution (Rojanschi et al. 1997).

The ecological restoration of the land started, stopped and then started again in the last years. The workers' town was demolished and just one or two abandoned buildings are left testimony for the daily presence of thousands of people at the exploitation during its golden years of existence. However, it will take many years and huge financial efforts to alleviate the environmental disaster.

Surprisingly, there are only a few published articles regarding the impact of the pollution generated by the former mining exploitation, and the data on pollution levels and ecologization efforts can be considered controversial (Ditoiu and Ciobanu, 2002; Georgescu et al. 2005; Ştumbea, 2010; Stoica et al. 2011; Surdeanu et al. 2011).

The large majority of the published studies approach the relationship between the geomorphic processes such as landslides, debris-flow or hyperconcentrated flows and vegetation colonization processes, focusing on the development of natural rehabilitation strategies (Ditoiu and Ciobanu, 2002; Pop et al. 2009; Surdeanu et al. 2011).

The paper aims at presenting a preliminary analysis of water and soil samples collected from different areas in the vicinity of the former mining area, as a conclusive evidence of the effects of long term human intervention over the environment in its reckless pursuit of rapid exploitation of natural resources.

Methods

1. Sampling

Solid soil samples (S1-S4) from the quarry, waste dumps and water samples (W1-W4) from the seasonal puddles developed onto the plateaus of the quarry, waste deposits and from Neagra Şarului stream were collected and analyzed. The samples were collected from representative areas, thus to cover a distance of about 5 km around the mining operation region. Samples were collected from the epicenter of the mining area (S1, W1), from the plateau of the Puturosu waste deposit (S2, W2), from the stream crossing the mining area (S3, W3) and from the stream at the entrance of Neagra Şarului village (S4, W4) (Fig. 1). All the samples were collected from the designated areas in June 2013.

Neagra Şarului stream gathers its waters of the northern side of the Călimani Mountains inside the volcanic crater, being by far the most affected creek by the mining activities. Neagra Şarului village is the nearest settlement to the mine and it stretches near the confluence of the Hăita and Neagra Şarului streams.

For sampling we used plastic (polyethylene) sterile containers; two samples were taken from each designated area (sample and counter-sample), the samples were kept in a cooler (2-5 C) during transport.

Organoleptic analysis pH, turbidity and conductometric determinations were performed 24 hours after sampling. Microbiological and chemical purity analyses were performed 48 hours after sampling.

Samples collected on the field were processed according to the type of determination. In order to carry out pH, conductometric and chemical determinations from soil, the solid samples were immersed in distilled water in a 3:1 ratio (3 parts distilled water: 1 part solid sample), centrifuged at 3500 rpm for 5 minutes, and left for sedimentation for 30 minutes before every determination, as the measurement were made from the supernatant.

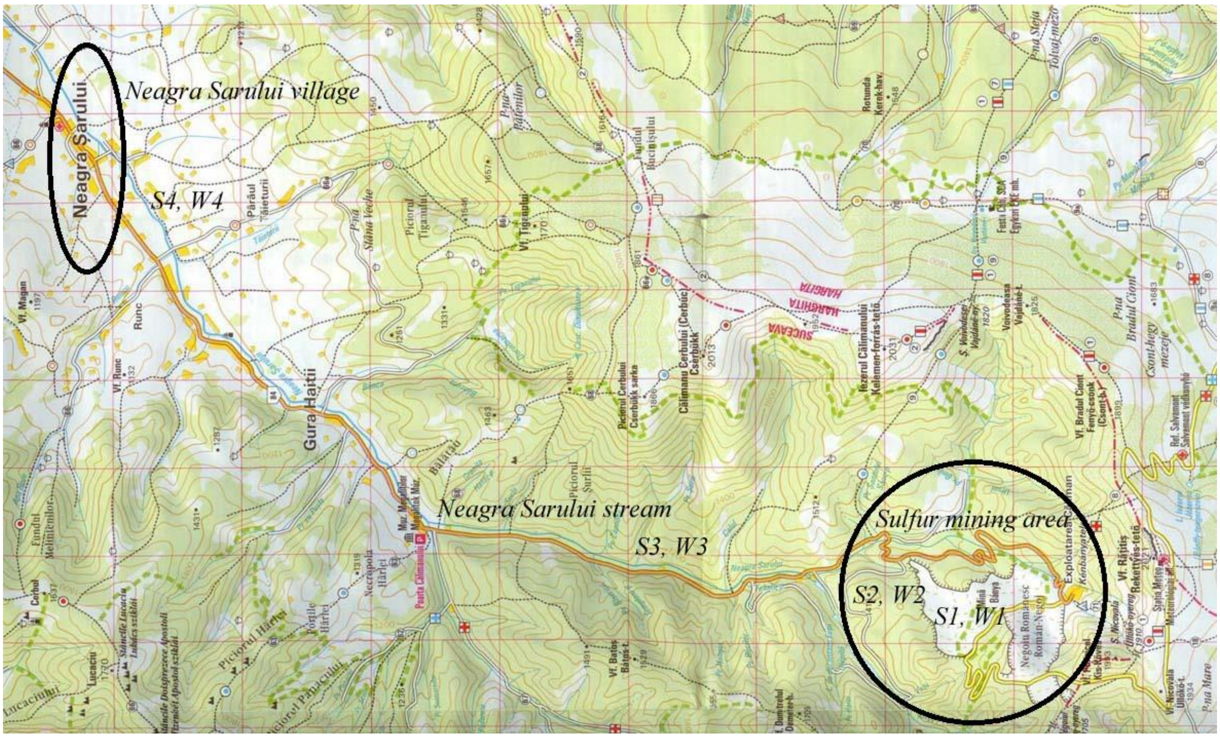

Fig. 1: Map of the former Călimani sulfur mining exploitation area and its vicinity

2. Apparatus

For the pH and conductometric determinations we used a multiparameter electrochemical potentiometer InoLab Multi 740 equipped with a glass electrode, and a calomel reference electrode immersed in a saturated solution of potassium chloride.

For the turbidity determination we used a Turb 555 turbidimeter, using a nephelometric measurement method.

The elemental chemical analysis was performed according to the stipulation of the Romanian (Farmacopeea Română, 10^{th} edition) and European (European Pharmacopoeia, 7^{th} edition) Pharmacopoeias.

The soil samples were centrifuged with a Centurion Scienatific Ltd centrifuge using 15 ml polypropylene conical centrifuge tube.

Results and Discussions

1. Field Research

An area covering more than two kilometers all around the former quarry operation is affected by the presence of sulfur. We could notice the lack of vegetation and the heavy sulfur smell the air. The water samples collected from the puddles developed onto the plateaus of the quarry and waste deposits were murky, yellowish and had a characteristic sulfur smell.

There were also noticed crashes and shifts of boulders and rocks on the bare slopes. The shaped forms of terraces testify for the influence of rainwater flows. The structure of altered, permeable and destabilized rocks caused the formation of drainage ditches. The frequency of landslides is high due to the existence of potential conditions: unstable and permeable rocks, steep slopes, destabilized material entrained by water rainfall or snowmelt and lack of vegetation.

Fig. 2: Image of the former mining exploitation from Călimani

2. Determinations of pH

The analysis of samples collected along the hydrographic network, draining the mining area, resulted in pH values between 2.40 and 4.40, while analysis of soil samples resulted in pH values between 3.20 and 6.80. Samples of water collected from puddles from the top of the quarry and waste deposits exhibited the most acidic pH values (table 1).

Due to the continuous impact of environmental factors, acidic waters are produced, migrate and contaminate surface and groundwater. The high acidic water confirms the intensive acidity of waste dumps, due to the reactivity of the contained sulfide in the presence of water and oxygen.

Table 1: pH values of water and soil samples

Water samples	pH	Soil samples	pH
W1	2.40	S1	3.20
W2	2.95	S2	3.90
W3	3.60	S3	4.80
W4	4.40	S4	6.80

After analyzing the results, we can state that the water and the soil samples collected near the mining area have a very acid pH, incompatible with the aquatic life. We also observed that, following the seasonal water level rise, the sensitive vegetation at the bank of the stream was heavily affected, especially the adjacent coniferous species (Fig. 3).

Fig. 3: Effects of water acid pH from Neagra Şarului stream on the vegetation surrounding the mining area

It is also worth mentioning and very alarming that in an inhabited village like Neagra Şarului, the pH of the water crossing the settlement is around 4.00. At the entrance of Neagra Şarului village, deposits of sediments from the mining area can be observed, due to the development of a natural dam (Fig. 4). Soil samples collected from the mining area had also disturbing acid pH values, which explains the lack of vegetation.

Fig. 4: Deposit of sediments near Neagra Şarului village

We also discovered signs of potential acid rains, as acid rains attack plants, first of all their leaves (by blocking the respiratory system and disrupting the processes of photosynthesis), but also the roots of trees (by neutralizing soil nutrients). The high concentrations of sulfur dioxide can cause acute injury to leaves as foliar necrosis, even after a relatively short exposure time (Fig. 5). The sulfur is discharged into the air as sulfur dioxide and sulfur trioxide; and these in combination with rainwater form sulphuros acid and sulphuric acid, respectively.

Fig. 5: Effects of acid rains over the leaf lamina

The release of acidic solutions from quarries and waste dumps depends on the presence of sulfides within the rock structure as well on their reactivity in the presence of water and oxygen. Drainage of acidic waters from different sources varies and depends on local prevailing environmental conditions. The release of mine waters can result in the contamination of both groundwater and surface waters, resulting in long-term environmental pollution (Ditoiu and Ciobanu, 2002; Ştumbea, 2010).

3. Conductometric determinations

Conductivity is the property of the solutions to allow electric current to pass them through. Conductivity changes when ions of different substances (salts, acids, bases) are in contact with the water; as a result, a high concentration of ions in the analyzed solution will generate high conductivities. Conductivity, in the case of aqueous solutions, is strongly influenced by the concentration of the present substances, being used as an indicator of the degree of mineralization of water (Naşcu and Jantschi, 2006).

Analysis of water samples collected along the hydrographic network resulted in conductivity values between 0.3750 and 0.0503 $\Omega^{-1}m^{-1}$, while analysis of soil samples indicated conductivity values between 0.0895 and 0.0096 $\Omega^{-1}m^{-1}$. Samples of water collected from puddles from the top of the quarry and waste deposits exhibited the highest conductivity values (table 2).

Table 2 Conductivity values of water and soil samples

Water samples	Conductivity / $\Omega^{-1}m^{-1}$	Soil samples	Conductivity / $\Omega^{-1}m^{-1}$
W1	0.3750	S1	0.0895
W2	0.3350	S2	0.0596
W3	0.1503	S3	0.0456
W4	0.0503	S4	0.0096

The standard value of the conductivity of drinking water is between 0.0005 and 0.05 Ω-1 m-1, previous studies indicating that high conductivity values can be an evidence of water contamination.

4. Turbidity determinations

The turbidity is an optical scattering of the luminous flux passing through a fluid medium containing particles in suspension or in colloidal state. Determination of turbidity is based on the Tyndall effect according to which murky water becomes bright when crossed by a light beam, because the suspended particles diffuses sideways some of the light rays (Naşcu and Jantschi, 2006).

Table 3: Turbidity values of water and soil samples

Water samples	Turbidity /FTU	Degree of turbidity
W1	317.70	40
W2	306.66	40
W3	253.84	33
W4	76.92	10

Maximum allowable turbidity value for drinking water is 5, higher values indicating contamination. All of our samples presented organic and inorganic particles in suspension, and some of them didn't form sediments in a period of 24 hours. The high turbidity of the samples (Table 3) demonstrates the presence of water contaminating elements, which may present even an epidemiological hazard because particles in suspension can be a support for pathogenic germs.

5. Chemical elemental analysis

The elemental analysis of water and soil samples was performed according to the stipulation of Romanian (Farmacopeea Română, 10th edition) and European Pharmacopoeia (European Pharmacopoeia, 7th edition), to which other specific analytical chemistry reactions were added in order to highlight the presence of potential elements (Săndulescu et al 2007).

The quantitative determination of the detected impurities requires further investigation and determinations, using modern instrumental techniques.

Numerous sulfur deposits were found on the rocks near different water flows and especially in the ford of Neagra Şarului stream (Fig. 6).

Table 4 The results impurity control limits of water and soil samples

Impurities	W1	W2	W3	W4	S1	S2	S3	S4
Acidity	+	+	+	+	+	+	+	+
Ammonium	+	+	-	-	+	-	-	-
Calcium	+	+	+	+	+	+	-	-
Chlorine	+	+	+	+	+	+	+	+
Iron	+	+	+	+	+	+	+	+
Heavy metals	+	+	+	+	+	+	+	+
Magnesium	+	+	-	-	-	-	-	-
Nitrate/Nitrite	+	+	+	+	+	+	+	+
Sulfates	+	+	+	+	+	+	+	+
Sulfides	+	+	+	+	+	+	+	+
Sulfites	+	+	+	+	+	+	+	+
Zinc	+	+	-	-	+	+	-	-

Fig. 6: Sulfur deposit on the rocks of the Neagra Şarului stream ford

The total water hardness was determined by a complexonometric method, using complexon III at a pH of 9-10 (ammonia buffer), and eriocrom T as indicator (Săndulescu et al 2007). The allowed hardness value for water is between 5 and 10 ° Ge. The hardness of the collected samples is situated between 10 – 140 ° Ge, demonstrating the presence of divalent metal ions (especially calcium and magnesium ions).

6. Microbiologic analysis

In order to study qualitatively the microbiological contamination of the samples we seeded the samples on solid culture mediums distributed in Petri dishes, the culture media were incubated in a bacteriological oven at a temperature of 37 ^{0}C for 48 hours, and after incubation the culture characters were studied and the possible biochemical characteristics of microbial cultures were evaluated.

In order to perform the seeding, the sampling process was conducted under aseptic conditions; for sampling we used a bacteriological loop, made of a platinum wire, and mounted on a support. For an easy identification of different groups of microorganisms, different specifics media cultures were used.

Samples were seeded on four different culture media: Sabourraud, blood agar, lactose agar and Chapman; and also twelve staining tests for Gram positive and Gram negative bacteria were made. The inseminated dishes were incubated and analyzed respecting the protocol for each microorganism groups.

Since the pH of collected mine waters and from local rivers was too acid, it has not allowed the development of pathogenic microorganisms, consequently all the results of seeding culture media were negative.

However, we cannot consider that the water samples are totally free of microorganisms, because mine waters with significantly high content of sulfur, nitrites, iron and heavy metals are a favorable environment for development of chemoautotrophic bacteria (Ulea and Lipşa, 2009).

A study analyzing the eventual presence of microorganism in mine tailings, detected the presence of some aerobic and anaerobic nitrogen-fixing bacteria (eg: *Azobacter chroococcum, Clostridium pasteurianum*), which are involved in nutrient cycles, creating the premises for an ecological reconstruction for degraded soils resulted from the mining activities (Ulea and Lipşa, 2009).

Conclusion

Our preliminary analysis demonstrates once more that the pollution potential in the Călimani Mountains former mining area is extremely high, even after a period of more than 15 years since the mine closed. Thus, the main objective should be to reduce acid mine drainage generation, which has severe impact on the quality of surface and groundwater, and thus on the whole environment.
The extent of the pollution impact on living natural structures is more than obvious even to the naked eye. Following the mining activity, the forest vegetation has been affected, both a direct impact through vegetation removal, and also an indirect one, materialized in the devastating effects on the forest situated near the slopes of the waste dumps, because of highly acidic waters, which wash the dumps.

It is a worrying situation that the water from Neagra Şarului stream, in which the waters washing the waste dumps flow, is characterized by a strong acidic pH (2-4), high mineral total load (high conductivity), increased turbidity, hardness, and high content of sulfates, sulfites, iron and heavy metals. The soil quality has also undergone significant changes in the mining area; demonstrated by its acidic pH, by the presence of numerous chemical impurities and also by the lack of vegetation in the proximity of the mine. We also noticed evidence of acidic rains, due to the high content of sulfur of the tailing storage, which after photochemical reactions is oxidized into sulfur dioxide, and subsequently in sulphuric acid aerosols; as evidenced on the effects on vegetation in the surroundings of the mining area.

No pathogenic microorganism could be detected in the analyzed samples, which can be correlated with the high acidity of the samples.

Happily, although late, the area of the Călimani Mountains became a national park, enjoying the legal protection of its precious nature. Although the former exploitation occupies a small part of its territory, its dramatic sight is a strong reminder of past mistakes that hopefully won't be done elsewhere in Romania.

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Enikő Barabás contributed at the microbiological analysis.

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