# Remediation of contaminated mining sites to halt the loss of biodiversity and ecosystem services

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#### Abstract

Mining has always had a dual role in industrial development, both in scope of scientific and technical innovations as well as a supplier of raw materials needed to develop industries and transport, being a decisive factor in developing of geographical areas.

In Suceava County, the North -West Region, there are significant deposits of copper ore, manganese, salt, uranium ore, baritone, sulfur, natural gas, construction rocks, peat and mineral waters. Of great importance after the First World War was the exploitation and valorization of manganese. At present only the Ulm deposits (Dorna Arini) are exploited.

The main activity in the Ulm Mining Perimeter is the exploitation of manganese ore by surface-toquarrying works been located in the northern central part of the Bistrita Mountains, at the source of the Ursaria creek. The relief of the region is mountainous, ranging from 1250 m to 800 m. The two tailings are located near two Natura 2000 sites: the Special Protection Area (SPA) Rarău-Giumalău Mountains and the Special Area of Conservation (SAC) Rarău-Giumalău Mountains.

There is a need for cost-effective, low energy technologies that can be applied at these sites. Applied properly, soil amendments reduce exposure by limiting many of the exposure pathways and immobilizing contaminants to limit their bioavailability and enables site remediation, revegetation and revitalization, and reuse.

The EU Biodiversity Strategy aims to halt the loss of biodiversity and ecosystem services in the EU and help stop global biodiversity loss by 2020. The remediation, revitalization of contaminated mining sites using organic soil amendments and phytoremediation are in the line with EU Biodiversity Strategy.

Keywords: contaminated site, remediation, phytoextraction, Biodiversity Strategy.

## 1. Introduction

Mining has always had a dual role in industrial development, both in scope of scientific and technical innovations as well as a supplier of raw materials needed to develop industries and transport, being a decisive factor in developing of geographical areas.

The 2016 national inventory identified 984 potentially contaminated sites spread across economic sectors in which 156 potentially contaminated sites in mining and metallurgy industry. The largest area is in the Romanian regions West (23.2%), Northeast (20.5%), North West (19.7%), Central (12.3%) and South West Oltenia (12.2%).

In Suceava County, the North -West Region, the industrial activities are diversified, represented mainly by the wood exploitation and processing industry, the extractive industry, the food industry, the textile industry and the footwear. The distribution of production waste by extractive industry, as reported by the economic operators in the annual statistical questionnaires for 2011-2015, is shown in Table 1.

*Table 1. Generation of non-hazardous production waste from extractive industry in Suceava County, 2011-2015* (Source: Annual Statistical Survey on Waste Generation and Management, LEPA Suceava)

Foonamia activity	Quantity (tonnes)					
Economic activity	2011	2012	2013	2014	2015	
Extractive industry	24720,28	146966,23	138848,57	232504,94	556283,68	

The quantitative differences in non-hazardous waste generated in the extractive industry in the period 2011-2015 are due both to the fluctuations in the number of economic operators reported and to the variations in

their production activity. Thus, in 2015 there is an increase in the activity in the extractive industry in Suceava County, as compared to the previous year.

In Suceava County, there are significant deposits of copper ore, manganese, salt, uranium ore, baritone, sulfur, natural gas, construction rocks, peat and mineral waters. Of great importance after the First World War was the exploitation and valorization of manganese. At present only the Ulm deposits (Dorna Arini) are exploited.

Ŷ	2011	2012	2013	2014	2015
Non - hazardous industrial waste deposits, of which:	7	7	7	7	8
- comply	6	6	6	6	8

Table 2. Situation of non-hazardous industrial deposits in Suceava County

During the period 2011-2014 there were 7 non-hazardous landfills: 3 tailings storage depots at CNU Cross, 1 waste disposal site at SC SINAROM MINING GROUP SRL, 1 waste disposal site at SC MANGAN MINEST SRL, warehouse of slag and ash of SC TERMICA SA Suceava, 1 ecological cell at SC AMBRO SA Suceava and a new landfill in 2015.

One of the major problems of the mining industry is the storage of residues from both extraction and ore preparation. The impact of this mining waste is the chemical and physical pollution of surface and underground waters, soil contamination with heavy metal ions, the occupation of large areas of agricultural land and / or forestry, the destruction of local ecosystems, changes in watercourses, the risk of landslides terrain, landscape destruction, air pollution, etc. Mining activities affect the fauna mainly due to the restriction of their natural habitat through infrastructure and specific mining activities, as well as due to environmental pollution.

Hard rock mining sites must move large amounts of non-mineralized rock (overburden) to get to and remove the ore. Tailings, created when the ore-rich rock is ground up and the economic mineral is extracted via flotation or screening, also can be present onsite or in adjacent tailing disposal facilities. Adjacent soil also may be contaminated from fluvial deposition or, in some instances, the use of historical irrigation practices. For most of these sites, overburden or waste rock, which often is acidic and has elevated contaminant concentrations, is the material left that needs to be revegetated.

On the territory of Suceava County there are 29 natural protected areas of national interest (botanical reserves, forest reserves, geological reserves, paleontological reserves, 1 scientific reserve, Călimani National Park with a total area of 24041 ha, of which 10700 ha in the territory Suceava County).

# 2. Materials and methods

# 2.1. Site description

The main activity in the Ulm Mining Perimeter is the exploitation of manganese ore by surface-to-quarrying works. Ulm mining perimeter is located in the northern central part of the Bistrita Mountains, at the source of the Ursaria creek. The relief of the region is mountainous, ranging from 1250 m to 800 m. The two tailings dumps occupy a land area which was a pasture on which the soil was removed and have a volume of 353.78 thousand  $m^3$  and the occupied area is 48.400  $m^2$ . The tailings dumps are located near two Natura 2000 sites: the Special Protection Area (SPA) Rarău-Giumalău Mountains and the Special Area of Conservation (SAC) Rarău-Giumalău Mountains.

No.	Name	Category	Surface (ha)
1	Calimani National Park	National Park	10.700
2	Rarău-Giumalău Mountains	SPA	2.157,3
3	Rarău – Giumalău	SCI	2.547

Table 3 . Protected natural areas in the vicinity



**Habitats.** Forests are the main habitats, consisting of Norway spruce, beech, and Arrola pine, while upper lands are covered with scrubs like dwarf pine, alpine rose, alpine blueberry and huckleberry.

According Council Directive 92/43/EEC of 21 May 1992 on the conservation of natural habitats and of wild fauna and flora the habitats from Calimani National Park are listed in the ANNEX I

- 3220 Herbaceous vegetation on the banks of mountain rivers;
- 4080 Scrubs with species sub artic of Salix;
- 4070 Scrubs with *Pinus mugo* and *Rhododendron myrtifollium*;
- 6230 Mountain meadows of Nardus;
- 9410 ; Acidophile forests of *Picea abies* in mountain region (*Vaccinio-Piceetea*)
- 9420; Forests of Larix decidua and/or Pinus cembra in mountain region.

Vulnerable plants: Angelica archangelica Viola dacica, Campanula Carpatica;

Endemic plants in the Carpathians: Centaurea phrygia, Dyanthus tenuifolius Hepatica transsilvanica.

#### 2.2. Sample collection and analytical methods

Data on chemical content of the ore, mineralogical composition, tailings composition, soil quality parameters, quality parameters of the Ursaria creek were collected in order to analyze the study area. Table 4 presents the chemical content of the ore.

No.	Chemical composition	%
1	SiO <sub>2</sub>	20,92
2	TiO <sub>2</sub>	0,63
3	Al <sub>2</sub> O <sub>3</sub>	5,07
4	$Fe_2O_3$ (totl	42,53
5	CaO	0,22
6	MgO	1,15
7	MnO	0,22
8	K <sub>2</sub> O	0,78
9	Na <sub>2</sub> O	0,21
10	P <sub>2</sub> O <sub>5</sub>	0,07
11	Combined Sulfur	29,86
12	SO <sub>3</sub>	0,95

Table 4. Chemical content of the ore

13	Cu	1,78
14	Pb	0,53
15	Zn	2,50

Table 5 shows the mineralogical composition of the ore.

#### Table 5. Mineral composition

No.	Mineral	%
1	Pyrites	70
2	Chalcopyrite	<1
3	Black-jack	1
4	Lithic	28

Table 6 shows the tailings composition in the tailings dumps.

Table 6. The tailings composition

No.	Tailings	% volume
1	chlorite - sericite shale	60
2	quartzite- sericite shale	7
3	acid riolytic metatuf rocks	30
4	rocks with poor mineralization	3

Poor mineralization rocks are Black-jack, Pyrites, Chalcopyrite, and Galena.

The presence of sulphides - the average: 30.72% in the polymetallic ore, 15.04% in the pyrite-copper-ore ore - includes the operating wastes in the category of the potentially acidifying waters, being non-waste according Article 1 (b) of COMMISSION DECISION of 30 April 2009 completing the technical requirements for waste characterization laid down by Directive 2006/21/EC of the European Parliament and of the Council on the management of waste from extractive industries.

Drainage that accumulates in the pit and drains the mineral tailings deposit may be contaminated as a result of chemical reactions with the rocks exposed to mining operations. This contamination - known as Acid Rocks Drainage (DAR) - usually involves the oxidation of metallic sulphides under acidic conditions.

When stored under natural conditions, oxidation of sulphides increases with temperature and oxidation is amplified by moisture, granulation, which makes it necessary to monitor the way of storage of the poor ore in the tailings pond - by mixing with the inert material - and ensuring the collecting of rainwater so as to limit the percolation of the deposit by them.

Soils, found in mining area suffer from a range of physical, chemical, and biological limitations. These include soil toxicity, too high or too low pH, lack of sufficient organic matter, reduced water-holding capacity, reduced microbial communities, and compaction.

Analyzes carried out for soil quality downstream of the tailings dumps show steady compliance with the parameters laid down by the existing legislation.

Table VII. Son quanty parameters downstream taiting aumps				
Sample depth	Parameter Name	Determined value	Quality requirements according to the law	
			Parameter	Value provided by
				law
0-5 cm	pН	7,81	Alert threshold	-
			value (PA)	
5-30 cm		8,0	Threshold	-
			intervention value	
			(PI)	
0-5 cm	Cu	21	Alert threshold	100
	(mg/kg ds)		value (PA)	
5-30 cm		20	Threshold	200
			intervention value	
			(PI)	
0-5 cm	Zn	9,9	Alert threshold	300

*Table VII. Soil quality parameters downstream tailing dumps* 

	(mg/kg ds)		value (PA)	
5-30 cm		11	Threshold	600
			intervention value	
			(PI)	
0-5 cm	Pb	22	Alert threshold	50
	(mg/kg ds)		value (PA)	
5-30 cm		23	Threshold	100
			intervention value	
			(PI)	

<u>Perimeter hydrogeology</u>. The mining perimeter is located in the Siret river catchment area. The waters within the basin are primarily fed by rainfall (60-75%) and secondary by groundwater.

Groundwater underground is mainly represented by accumulations in terraced deposits, near the minor bed, which are marked by many springs collected by the Bistrita River and its tributaries in the area. Ground morphology provides a rapid drainage of the meteoric waters that are drained by the watercourses that pass through the adjacent areas. The storage capacity of the metamorphic rocks in the perimeter is rather low due to their structure, texture and compactness, except for periods of heavy rainfall or snow melting, when it is growing somewhat. The circulation of water is of the pellicule type and the fissure. The infiltration of water from the slope deposits is done on the crystalline rock top ends and especially along the major slopes.

The analyzes of the samples taken did not reveal any exceedances of the concentration of the parameters foreseen in the legislation in force except for the  $Fe_{total}$  content. This is also due to the collection by the Ursaria creek of water from through the mineralized area.

Tuble VIII. Quality parameters of the Orsana creek				
Parameter Name	Determined value	Quality requirements according to		
		the law		
pH	6,5	6,5-8,5		
$Mn^{2+}$ (mg/l)	0,08	0,1		
$Zn^{2+}$ (µg/l)	6,7	200		
Fe <sub>total</sub> (mg/l)	0,78	0,5		
$Pb^{2+}(\mu g/l)$	-	10		
$Cu^{2+}(\mu g/l)$	18	30		
Sulfates (mg/l) (µg/l)	11,82	120		

Table VIII. Quality parameters of the Ursaria creek

### 3. Results and discussion

## 3.1 Pollution problems

There were identified the following pollution problems:

- drainage, including the collection and pumping of mine acid waters;
- leakage on the slopes that drives sediments (and sediment quality);
- effluents of waste water;
- soil contamination;
- solubilized pollutants in waste disposal areas;
- dust emissions from mining areas adjacent;
- Emissions of mine gases.

# 3.2 Structural and functional features of the natural environment

Structural and functional features of the natural environment:

- the state of natural habitats;
- river flow and sedimentation regimes;
- groundwater regime and level;
- changes in the appearance of land.

Fragmentation of natural and semi-natural areas is an environmental indicator that provides information on the evolution of natural and semi-natural areas at pan-European level, calculating values derived from land cover maps. They come from satellite images with spectral properties. The Corine Land Cover database is based on 44 land cover classes, of which 26 are considered natural and semi-natural for the purpose of this indicator. These are grouped into forests, pastures, agricultural mosaics, semi-natural areas, inland waters and wetlands. From the point of view of biodiversity, the indicator is relevant as it indicates changes in the areas of natural and semi-natural areas for any ecosystem. If the area of the site decreases significantly, it will have a negative impact on habitat types and species dependent on these habitat types.

Removing land from the natural or economic circuit for landfills is a process that can be considered temporary, but which, in terms of the concept of 'sustainable development', extends over at least two generations if the periods of arrangement, exploitation, ecological recovery and post-monitoring are summing.

In terms of biodiversity, a landfill means removing 30-300 species / ha from the area affected by this use without considering the microbiological population of the soil.

Although the effects on flora and fauna are theoretically limited over time, during the exploitation of the deposit, the ecological reconstruction made after the release of the technological zone will not be able to restore the initial biological balance, the evolution of the biosystem being irreversibly modified.

#### 3.3 Monitoring

The tailing dumps are monitored by visual observations and topographic measurements. The occurrence of seepage from the body of the deposit is to be observed.

It monitors the water quality of the Ursaria creek at the exit of the undertraversing channel.

#### 4. Results

Remediation of the tailings dumps is done in situ. It is therefore necessary to undertake the following steps, after the clearance of the tailings dumps: reprofiling the tailings dumps, fences coast, laying of the cover layer of vegetal soil, sowing (erosion control), afforestation.

There is a need for cost-effective, low energy technologies that can be applied at these sites. Applied properly, soil amendments reduce exposure by limiting many of the exposure pathways and immobilizing contaminants to limit their bioavailability and enables site remediation, revegetation and revitalization, and reuse.

Appropriate soil amendments may be organic (e.g., composts). When specified and applied properly, these beneficial soil amendments limit many of the exposure pathways and reduce soil phytotoxicity. Soil amendments also can restore appropriate soil conditions for plant growth by balancing pH, adding organic matter, restoring soil microbial activity, increasing moisture retention, and reducing compaction and can reduce the bioavailability of a wide range of contaminants while simultaneously enhancing revegetation success and, thereby, protecting against offsite movement of contaminants by wind and water.

Revegetation should be ensured by sowing grass to obtain an immediate protection against erosion, and later woody vegetation can be planted to stabilize the dump. It is particularly important for revegetation to use grassy and arboreal species specific to the area, which have a high capacity for adaptation and for the integration of the new morphological form into the local landscape.

Active plant growth is an integral part of the soil amendment process; vegetation relocates water in the root zone and can transpire several hundred thousand gallons of water per acre during the greatly reducing surface water runoff and sediment loss to receiving streams. Plants stabilize the landscape from erosion, also reduce erosion caused by growing season.

The reestablishment of native species and plant communities should be emphasized where appropriate and if commensurate with post- revitalization land use. Native plant communities are best in providing the ecological diversity and long-term sustainability of the landscape. The objective of in situ treatment of contaminated lands using soil amendments is to establish a self-sustaining system that does not rely on artificial inputs and, ideally, is similar to and provides nearly equal ecological value as the undisturbed adjacent landscape.

In addition can be use phytoremediation technology Phytoextraction in order to remove contaminants by harvesting the plants uptake.

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