

RESEARCH ON THE PHYTOREMEDIATION OF SOIL CONTAMINATED WITH HEAVY METALS FROM MINING ACTIVITY: CASE STUDY BALOMIR-URICANI TAILINGS DUMP

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Received: September, 12, 2024

Accepted: December, 10, 2024

Abstract: This study evaluates the ability of various plant species to adapt and grow in heavy metal-contaminated soils, using the Balomir-Uricani tailings dump as a case study. Soil samples were collected from 17 points and analyzed for heavy metal content using atomic absorption spectrometry. In the lab, two phytoremediation methods-phytostabilization and phytoextraction-were tested using three types of plants: hyperaccumulators, phytostabilizers, and phytoextractors. The results highlight the importance of selecting the suitable species for phytoremediation, as those thriving at the Balomir-Uricani site show promise for rehabilitating soils contaminated by mining activities.

Keywords: *contaminated soil, heavy metals, hyperaccumulation, phytoextraction, phytostabilization, tailings dump*

INTRODUCTION

Soil contamination with heavy metals is a major environmental problem in areas where mining activities have taken place. In the United States, soils contaminated with heavy metals from mining and metallurgical activities have been phytoremediated using the plants mountain cress (*Thlaspi caerulescens*) and gooseberry (*Arabidopsis halleri*) [1, 2]. These plants have been used to extract zinc and cadmium from contaminated soils. In some industrial areas of China where mining activities have taken place, soil contaminated with heavy metals has been phytoremediated with vetiver grass (*Chrysopogon zizanioides*). And in areas of southern China, willow (*Salix spp.*) has been used for phytoremediation of soils contaminated with lead, copper, and zinc [3, 4]. In India, fern (*Pteris vittata*) has been used for phytoremediation of arsenic-contaminated soils [5, 6]. In France, sunflower (*Helianthus annuus*) and rapeseed (*Brassica napus*) have been used for phytoremediation of soils contaminated with heavy metals, cadmium and zinc, in industrial regions [7]. In Germany, poplar (*Populus spp.*) and willow (*Salix spp.*) were planted for phytoextraction and phytoevapotranspiration in soils contaminated with heavy metals such as lead, cadmium, lead, and zinc from industrial and mining activities [8]. In Australia, native plants such as eucalyptus (*Eucalyptus spp.*) and tea tree (*Melaleuca spp.*) have been used to stabilize soils contaminated with heavy metals such as lead, zinc, and cadmium in mining and industrial areas [9]. Heavy metals present in the soil, such as lead, cadmium, mercury, cobalt, chromium, and nickel, are mobile and toxic, which negatively affects both ecosystems and human health. Although there are environmental standards and laws globally that provide for solutions for on-site management of mine waste, mine closure, and contaminated land remediation, they are not fully implemented [10 – 19]. Phytoremediation, using the ability of plants to accumulate, stabilize, or degrade pollutants, offers a sustainable solution to these problems. The Balomir tailings dump, located in the western part of Jiu Valley, serves as a case study to investigate the effectiveness of phytoremediation in improving soils contaminated with heavy metals following the deposition of tailings resulting from Uricani mining. This paper details the plant selection methodology, remediation mechanisms, and results obtained, contributing to the development of effective management strategies for contaminated sites.

MATERIALS AND METHODS

Localization of the mining site

The Jiului Valley, located in Romania's Carpathian Mountains, was a region rich in mineral resources, especially coal. Throughout history, there have been several mining operations in this area for the extraction of coal, an activity that had a significant impact on the economic and social development of the region. The mining activity practiced in the Jiu Valley area for over 200 years has led to pollution and the removal of large areas of land from the economic circuit [20].

Tailings dumps are deposits of residues resulting from mining activities. They contain significant amounts of heavy metals, which can contaminate soil and groundwater.

Ecological effects include deterioration of soil quality, loss of biodiversity, and risks to human health through bioaccumulation in food chains.

Figure 1 shows the location of the Balomir tailings dump in the Jiului Valley mining area.

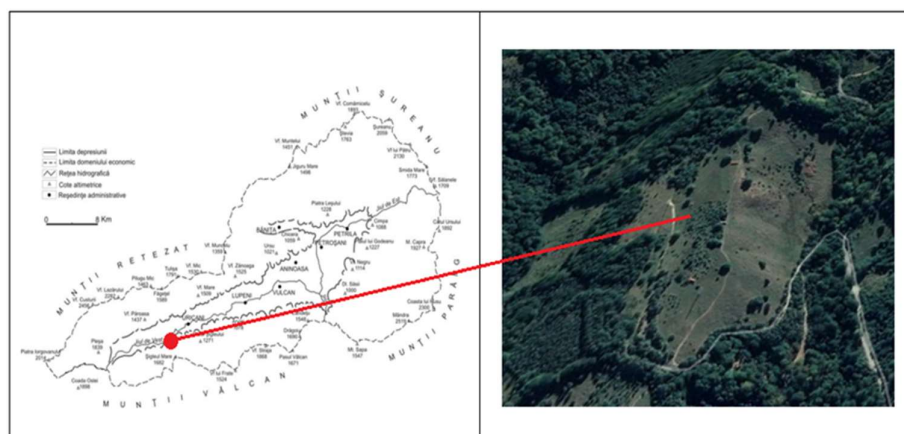


Figure 1. Location of the Balomir-Uricani tailings dump

In this area, facing both economic and ecological challenges, there is an urgent need to develop and implement sustainable and effective methods for remediation of contaminated sites. Phytoremediation presents itself as a promising solution due to its low costs and minimal ecological impact [21].

Collection of soil samples

In order to identify the value of the concentration of heavy metals in the Balomir waste dump, soil samples were collected from 17 sampling points. Figure 2 shows the sampling points established on the tailings dump.

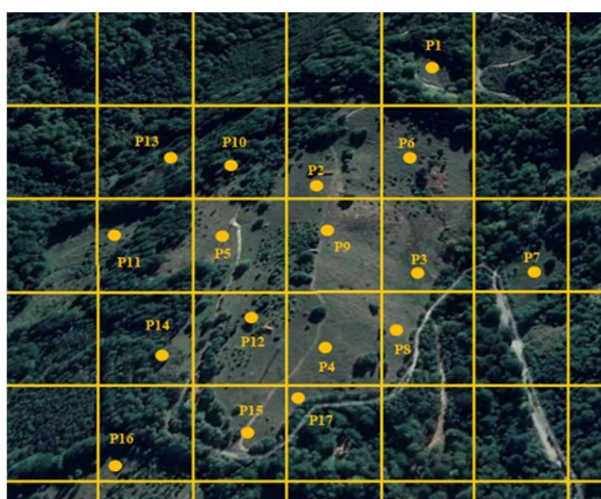


Figure 2. Mapping of the Balomir tailings dump

Soil samples were taken at two depths, respectively 0 - 20 cm and 20 - 40 cm, according to STAS 7184/1:1984, using a spade. The samples taken in this way were placed in plastic bags, labeled and transported to the laboratory to undergo chemical analysis [22].

Determination of heavy metals in soil

To determine the content of heavy metals in soil samples taken from the Balomir tailings dump, atomic absorption spectroscopy (AAS) was used- PerkinElmer PinAAcle 900F Atomic Absorption Spectrometer, manufactured by PerkinElmer in Shelton from the United States of America (USA).

The principle of this determination consisted of extracting the dry soil sample with a mixture of nitric acid and keeping it at ambient temperature for 16 hours. After that, for 2 hours, this sample was subjected to boiling under reflux. The resulting extract was clarified and brought to volume with nitric acid. According to the SR ISO 11047/1999 standard, the content of trace elements was determined [23, 24]. To identify the presence of heavy metals in the soil taken from the Balomir tailings dump, the reference values for traces of chemical elements in the soil, according to Order 756/1997, presented in Table 1, were taken into account [25].

Table 1. Reference values for trace chemical elements in soil ($\text{mg}\cdot\text{kg}^{-1}$ su)

Trace element	Normal values	Alert thresholds/types of use		Intervention thresholds/types of use	
		Sensitive	Less sensitive	Sensitive	Less sensitive
Total chromium (Cr)	30	100	300	300	600
Copper (Cu)	20	100	250	200	500
Nickel (Ni)	20	75	20	150	500

Determination of soil pH

Soil pH was determined by standardized laboratory methods using a digital laboratory pH meter. - WTW inoLab pH 7310, manufactured by WTW (a brand of Xylem Analytics) in Weilheim, Germany.

Selection of plants for phytoremediation of contaminated soils

The following native plant species that develop and grow near these tailings deposits have been selected, each with specific phytoremediation properties:

Hyperaccumulating plants: marigolds (*Calendula officinalis*), daisy (*Alyssum spp.*), and violet (*Viola calaminaris*). These are often adapted to soils with high levels of heavy metals but may be limited by acidic soils or the simultaneous presence of other pollutants. These species require careful soil management to optimize the uptake of heavy metals [26 – 28].

Phytostabilizing plants: clover (*Trifolium spp.*), millet (*Panicum miliacuum*), and wheat (*Triticum aestivum*) are selected for their ability to grow in soils with variable fertility and pH conditions while stabilizing heavy metals and preventing their dispersion. These species are relatively resistant to abiotic and biotic stress factors, making them ideal for use in various ecosystems [29].

Phytoextractive plants: lupine (*Lupinus spp.*), St. John's wort (*Hypericum perforatum*), and mustard (*Brassica spp.*) are effective in absorbing and accumulating heavy metals but may be sensitive to extreme environmental conditions. These species require well-aerated soil and a neutral to slightly acidic pH to maximize phytoextraction efficiency. They also require constant monitoring to ensure the proper harvesting and disposal of contaminated biomass [30].

The experiments were carried out under controlled laboratory conditions, using 18 pots of vegetation. Nine plant species were selected, each with specific phytoremedial properties. Two types of soil were used, namely contaminated soil taken from the Balomir tailings dump and commercial flower soil used as a control sample, as illustrated in Figure 3.



Figure 3. The soil in which the plants were sown

18 vegetation pots were prepared, of which 9 were filled with contaminated soil and 9 with flower soil. In each of the 9 pots with contaminated soil, three species of plants were planted (one from each category: hyperaccumulators, phytostabilizers and phytoextractors). The same procedure was followed for the 9 pots with flower soil.

The vegetation pots were maintained under controlled laboratory conditions, ensuring adequate lighting, constant temperature and regular irrigation. Plants were monitored for growth, health and development over a 6-month period. Plant germination, growth and survival rates in both soil types were observed and documented. Aspects such as plant height, number of leaves, general health and adaptability to contaminated soil were carefully analyzed and compared with the control sample.

RESULTS AND DISCUSSION

Afterwards, the analysis and interpretation of the results obtained following the determination of the content of heavy metals were carried out. Table 2 shows the values of heavy metal concentrations that exceeded the normal values allowed in the soil.

Table 2. Determined values of soil samples from the old Funicular dump ($\text{mg}\cdot\text{kg}^{-1}\text{dw}$)

Sampling points	Analyzed indicators		
	Cr (total)	Cu	Ni
P1	36.51	54.93	72.78
P2	35.91	56.46	101.42
P3	53.85	56.20	72.42
P4	48.55	72.40	107.55
P5	46.77	74.69	108.84
P6	32.40	47.59	70.93
P7	34.44	55.82	57.36
P8	33.43	61.50	90.62
P9	49.76	75.09	109.37
P10	31.31	56.20	89.00
P11	33.94	51.85	57.68
P12	34.46	48.98	81.74
P13	39.47	50.97	58.72
P14	31.00	53.18	81.49
P15	35.60	58.51	102.70
P16	33.40	56.12	72.22
P17	35.73	56.09	104.33
Standard deviation	7.10	8.30	18.65

In our research on the phytoremediation of soil contaminated with heavy metals at the Balomir tailings dump, an essential component was the determination of soil pH . Soil pH is an essential parameter that significantly influences the behavior and mobility of heavy metals, as well as the development and health of plants used in phytoremediation [31].

Determining pH allows us to better understand soil chemical conditions and how they can affect phytoremediation processes. In low pH soils, heavy metals tend to be more soluble and therefore more accessible for plant uptake. Conversely, a higher pH can reduce the mobility of heavy metals by forming insoluble compounds, thus limiting the ability of plants to accumulate these metals [32].

To assess the pH variability in the analyzed soils, we took samples from 17 distinct points on the tailings dump. The pH values in these samples ranged from 6.4 to 8.2, indicating a slightly acidic to alkaline soil. This variation in pH gives us insight into soil chemical diversity and the potential impact on phytoremediation [33].

These data are essential for the correct interpretation of the efficiency of phytoremediation and for the development of strategies for the optimized management of tailings dumps. Table 3 shows the average pH value of the 17 soil samples taken from the Balomir tailings dump, as well as the pH of the reference soil (commercial flower soil).

Table 3. Average determined pH values

Soil pH tailings dump	pH blank sample (flower soil)
6.9	6.5

The study was designed to evaluate the suitability of the three types of plants (hyperaccumulators, phytostabilizers, and phytoextractors) in soils contaminated with heavy metals. In the selection of plants used for the phytoremediation of soil contaminated with heavy metals, a number of ecological and limiting factors were taken into account to ensure their adaptability and efficiency in various environmental conditions. These factors include soil type, pH, nutrient availability, climatic conditions, and the presence of other contaminants [34 – 36].

In Figures 4 - 6, the plants that had the best development are illustrated.



Uricani (contaminated soil) Control (flower soil)

Figure 4. Mustard (*Brassica* spp.)



Uricani (contaminated soil) Control (flower soil)

Figure 5. Wheat (*Triticum aestivum*)



Uricani (contaminated soil) Control (flower soil)

Figure 6. Calendula (*Calendula officinalis*)

Following the experiment, it was observed that the plants grown in pots with soil taken from the Balomir - Uricani tailings dump had a better development compared to those grown in the control sample soil. This suggests that contaminated soil from the tailings dump may provide favorable conditions for certain plant species used in phytoremediation.

Among the phytoextractor plants studied, mustard (*Brassica spp.*) stood out for its superior development, demonstrating considerable potential for use in the extraction of heavy metals from contaminated soils. In the category of phytostabilizing plants, wheat (*Triticum aestivum*) had an optimal development, indicating adaptability and capacity to effectively stabilize heavy metals in the soil. Regarding hyperaccumulating plants, marigolds (*Calendula officinalis*) showed good growth, highlighting their ability to accumulate heavy metals and develop in contaminated soils. In contrast, the other plant species germinated but failed to develop properly, indicating greater sensitivity to contaminated soil conditions. Millet (*Panicum miliacuum*), a plant with phytostabilizing capabilities, did not germinate in any of the pots, suggesting an incompatibility with the experimental conditions or a high sensitivity to soil contaminants, an aspect illustrated in Figure 7.



Uricani (contaminated soil) Control (flower soil)

Figure 7. Millet (*Panicum miliacuum*)

CONCLUSIONS

The field and laboratory study carried out in the area of the Balomir tailings dump, located on the perimeter of the Uricani mining operation, reveals a significant contamination of the soil with heavy metals, namely chromium (total Cr), copper (Cu), and nickel (Ni).

The normal values allowed in the soil for the analyzed heavy metals (total Cr, Cu and Ni) were exceeded in the studied area. In some sampling points, the normal value of Cr (total) was exceeded by 1.15 times, that of Cu by more than 2.90, and that of Ni exceeded by 4.20 times its normal value in the soil. This suggests a potential risk to the environment and, by implication, to human health.

The mining activity carried out in this area and the tailings storage have led to high concentrations of heavy metals in the soil, thus affecting the natural balance.

The mobility of these metals in soil is a critical factor, influenced by soil physico-chemical properties such as pH, texture, organic matter content, and cation exchange capacity.

In order to reduce the impact of pollution and restore soil quality, it is recommended to implement some phytoremediation measures.

Phytoremediation of the tailings dump in the Mining Basin of the Jiu Valley can be a cheap method depending on the period of their inactivity and in the absence of an ecological rehabilitation strategy after the cessation of activity, which would lead over time to a stabilization of these heavy metals and an elimination theirs from the environment.

The results of this study emphasize the importance of the appropriate selection of plant species for phytoremediation, depending on the specific conditions of the contaminated soil. The species that demonstrated optimal development in the soils of the Balomir - Uricani tailings dump can be considered optimal for use in remediation strategies for soils contaminated by heavy metal mining activities. For optimal results, the combined use of the three plant species with different phytoremedial capacities would be recommended. Future studies will address the long-term evaluation of the effectiveness of these herbs and the investigation of the physiological mechanisms underlying heavy metal tolerance and accumulation.

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