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ASSESSMENT OF THE POLLUTION LEVEL AND DETERMINATION OF THE GEO-ACCUMULATION INDEX OF HEAVY METALS IN THE SOIL FROM THE OLD FUNICULAR DUMP AREA – URICANI

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Abstract: *As a result of the mining activities carried out in the Jiu Valley, tailings dumps resulted. Currently, some of these tailing dumps are greened, some are inactive, and some of them are still active within operational exploitation perimeters. In order to capture the negative effects of these deposits, in this work an assessment of the degree of contamination will be carried out and the level of geo-accumulation of heavy metals will be determined in the soil in the area of the Old Funicular dump, an inactive one for about 12 years. The dump was formed following the deposition of tailings resulting from coal mining in the Uricani mine. The main purpose is to identify the types and concentrations of heavy metals present in the soil and determine the level of accumulation of these metals in a certain area. The study involved the collection of soil samples from 17 sampling points, followed by detailed chemical analyses to determine the concentrations of heavy metals present in the soil at the tailings dump. The results indicated variable levels of heavy metal contamination, with concentrations exceeding the normal value of these heavy metals in soil in certain areas. The geo-accumulation index (I_{geo}) was calculated to assess the degree of accumulation of each heavy metal in soil. The I_{geo} values obtained varied from slightly polluted to moderately polluted, suggesting a significant influence of mining activities on the soil in this area. The conclusions of the study emphasize the need to implement phytoremediation measures and continuous monitoring to prevent ecological and human health risks.*
Keywords: *contamination, heavy metals, mining, Old Funicular, soil, tailings dump*

1. Introduction

At the European level, numerous organizations and governments have implemented strict regulations to control and reduce soil contamination caused by closed mining activities. These regulations include the Basel Convention, which deals with the transboundary transport of hazardous waste and its disposal; the Minamata Convention, which focuses on reducing mercury emissions globally; and the European Union Directives, respectively, the Waste Framework Directive and the Industrial Emissions Directive, which impose strict standards for mining waste management and pollution control [1, 2, 3, 4].

During approximately two centuries of mining activity in the Jiu Valley, there have been significant consequences for the environment and the economy, manifested by extensive pollution and the exclusion of considerable areas of land from the economic circuit [5].

Soil pollution with heavy metals is a major environmental problem with significant implications for human health and ecosystems. Heavy metals such as lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), and nickel (Ni) are known for their toxicity and ability to accumulate in living organisms. These can come from various sources, such as industrial activities, household and agricultural waste, vehicles, and emissions from fossil fuel combustion [6].

The effects of heavy metal exposure on human health include neurological problems, impaired kidney

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function, cardiovascular disease, and other imbalances. For example, lead and mercury can cause learning and behavioral disorders in children, and arsenic and nickel can affect the central nervous system, causing tremors, insomnia, and personality changes [7, 8].

In terms of ecosystems, heavy metals can reduce biodiversity by affecting organisms at the bottom of the food chain, such as soil microorganisms, plants, and small animals. Soil contamination can lead to a decrease in its fertility, thus affecting agricultural productivity and, implicitly, food security.

Tailings dump from mining activity are important sources of heavy metals in soil [9]. This study focuses on determining the concentration of heavy metals in the soil, evaluating the level of pollution by comparing the determined concentrations with reference values, and determining the geo-accumulation index (I_{geo}) of heavy metals in the soil in the area of the Old Funicular tailings dump.

The main purpose is to identify the types and concentrations of heavy metals present in the soil and determine the level of accumulation of these metals in a certain area.

The tailings dump Old Funicular was formed following the deposition of the tailings resulting from the mining of coal in the Uricani mine. The Uricani mine is located in the western part of the Jiu Valley coal basin, and the tailings dump is located in the southern part of the mine, at a distance of approximately 1000 m from it, occupying an area of 5.17 ha and a volume of 31,169 thousand m^3. The existence of a body of water or a human settlement was not detected near this tailings dump.

The Old Funicular tailings dump has been an inactive dump for about 12 years. This tailings dump was not included in the greening process after the disposal of waste material on it was stopped. So, over time, herbaceous vegetation naturally settled on the surface of the two branches of the tailings dump, except for the plateau area, such as mulberry, rose hip, hornbeam, hawthorn, and medicinal plants horsetail, dandelion, and others. This process of natural vegetation colonization contributed to soil stabilization and reduced erosion. On the slopes of the tailings dump, tree species such as birch and acacia were identified, along with other native species. Figure 1 shows the Old Funicular tailings dump as well as its location in the area of the Jiu Valley coal basin [10] (Fig. 1.)

Fig. 1. Location tailings dump Old Funicular (Source: GoogleEarth)

2. Research methods and techniques

2.1 Taking soil samples

In order to take soil samples in the initial stage, the mapping of the Old Funicular tailings dump was carried out. 17 soil sampling points were established, according to Ministerial Order No. 184/1997, for the approval of the Environmental Assessment Procedure. (Fig. 2.)

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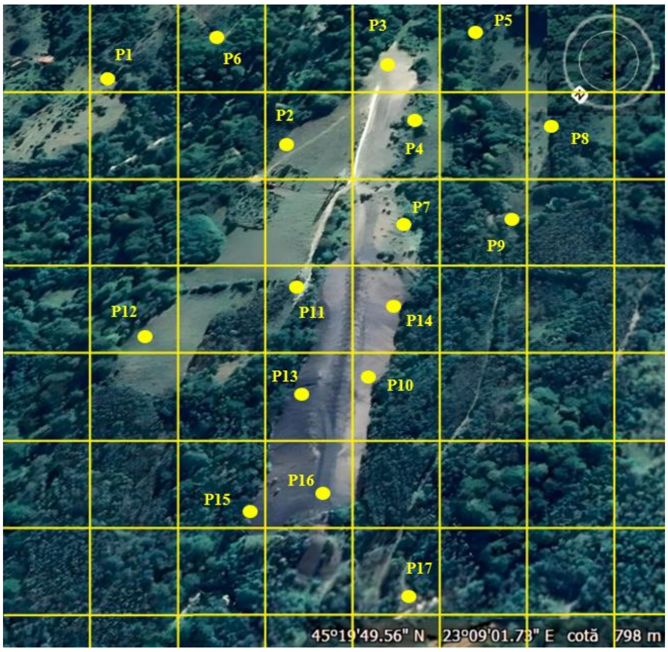

Fig. 2. Mapping of the Old Funicular tailings dump with the 17 sampling points

The actual collection of the samples was carried out at two depths of 0–20 and 20–40 cm, respectively, with the help of a shovel (Fig. 3). Before sampling, the soil was cleaned to remove organic remains (plants, roots, leaves, etc.). A container of approximately 100–200 ml was used, which I filled to the brim with shredded soil, according to the state standard (STAS) 7184/1:1984: Soil quality/collection of samples for pedological and agrochemical studies [11].

Fig. 3. Sampling and labeling of soil collected from the Old Funicular tailings dump

The soil sampled in this way was placed in 500-gram plastic bags labeled with the place of sampling, the depth, and the date on which the collection was carried out.

In order to better understand the properties and qualities of the soil in the study area, a soil sample unaffected by the mining activity was taken. This soil sample was taken from agricultural land in the yard of a local in the city of Uricani.

The soil samples were transported to the Environmental Laboratory of the University of Petrosani to undergo chemical analysis.

2.2 Determination of heavy metals

2.2.1 The utensils and equipment used

- grinding mill, which grinds all types of soil to sizes smaller than 150 µm without producing contamination with elements to be determined;
- sieve with a mesh size of 0.150 mm;
- desiccator with a nominal volume of 2 l;
- a reaction vessel with a nominal volume of 250 ml;

- refrigerant with ground glass conical coupling;
- absorption vessel without return;
- unpolished glass balls with a diameter between 2 and 3 mm;
- a temperature-controlled heating device capable of heating the contents of the reaction vessel to the reflux temperature;
-funnel, with a diameter of approximately 110 mm;
- rated flask with a nominal capacity of 100 ml;
- quantitative filter paper, without calcination residue, based on cellulose, with an average pore size of approximately 8 µm and a diameter of 150 mm.

Reagents used: They must meet the purity conditions for further analysis. The purity of these reagents was verified by analyzing the blank sample taken.

- the water used must correspond to the quality according to ISO 3696.
- hydrochloric acid c (HCl) = 12.0 M, ρ = 1.19 g/ml;
- nitric acid c (HNO_3) = 16.3 M, ρ = 1.42 g/ml;
- nitric acid c (HNO_3) = 0.5 M dilute 32 ml of nitric acid (ρ = 1.42 g/ml) with water to 1.

2.2.2 Mode of Work

According to the Romanian standard SR ISO 11047/1999, the microelement content was determined [12].

Thus, approximately 3 g of soil was weighed to the nearest 0.001 g in a 250-ml reaction vessel. Then the soil was moistened with about 0.5-1 ml of water, and with stirring, 21 ml of hydrochloric acid was added, followed by 7 ml of nitric acid. The absorption vessel and refrigerant were attached to the reaction vessel, and the mixture was left for 16 hours at room temperature to allow the organic matter in the soil to slowly oxidize.

The temperature of the reaction mixture was slowly raised until reflux conditions were reached, and this temperature was maintained for 2 hours, making sure that the condensation zone did not exceed 1/3 of the height of the refrigerant. After this interval, the mixture was allowed to cool.

The contents of the absorption vessel were added to the reaction vessel through the refrigerant, flushing both the absorption vessel and the refrigerant with an additional 10 ml of nitric acid. The insoluble residue in the reaction vessel was allowed to settle, and the decanted supernatant, relatively free of sediment, was passed through filter paper, thus collecting the filtrate in a 100-ml volumetric flask. The entire initial extract from the reaction vessel was passed through the filter paper, and then the insoluble residue on the filter paper was washed with a minimal amount of nitric acid, collecting this last filtrate together with the first.

2.3 Calculation of the geo-accumulation index of heavy metals in the soil

The geo-accumulation index (Igeo) was used to evaluate the level of soil contamination with heavy metals. Originally developed by Müller in 1969, this method allows us to evaluate the level of heavy metal pollution in the soil and determine the level of accumulation of these metals in a certain area. When calculating this index, the concentrations of heavy metals determined in the soil samples taken were taken into account, and the values obtained were compared with the values of the natural background [13, 14]. The geo-accumulation index was calculated using the formula:

$$I_{geo} = log_2\left(\frac{C_n}{1{,}5 \ x\, B_n}\right) \quad (1)$$

where:

- C_n is the concentration of the metal in the analyzed sample (mg/kg su);
- B_n represents the reference (background) concentration of the metal in the soil (mg/kg su);
- 1.5 represents the correction factor due to lithogen* (*is a sedimentary rock that is predominantly composed of particles resulting from the process of erosion, transport and sedimentation of other rocks or organic materials. These particles can include rock fragments, sand, clay, as well as organic materials such as shells and plant debris).

After all this processing, the analysis and interpretation of the results obtained following the determination of the heavy metal content of the soil samples taken from the Old Funicular tailings dump and the calculation of their geo-accumulation index were carried out.

3. Data analysis and interpretation

By analyzing and interpreting data, it contributes to the development of critical and analytical skills needed in the scientific field.

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In order to identify the presence of heavy metals in the soil taken from the Old Funicular tailings dump, the reference values for traces of chemical elements in the soil were taken into account, according to Order 756/1997 [15] (Table 1).

Table 1. Reference values for trace chemical elements in soil (mg/kg d.s)

Trace elements	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	200	150	500

Following the chemical analyses, it was found that, in the soil samples taken from the Old Funicular tailings dump at some sampling points, the determined value for **Cr (total)** was exceeded by **1.12 times** compared to its normal value in the soil. The presence of **Cu** was **2.83 times** higher compared to the normal value, and the determined value of **Ni** exceeded **4.12 times** its normal value in the soil (Table 2 and Fig. 4.)

Table 2. Determined values of soil samples from the Old Funicular tailings dump (mg/kg d.s)

Sampling points	Analyzed indicators		
	Cr (Total)	**Cu**	**Ni**
P1	20.53	46.39	56.49
P2	32,32	49,48	67.95
P3	40.84	56.95	99.22
P4	31.00	54.90	70.39
P5	27.58	53.81	71.28
P6	22.01	51,51	55.79
P7	43.31	55.33	104.42
P8	22.17	50.35	55.99
P9	44.81	54.87	72.57
P10	46.34	71.27	100.05
P11	32.12	47.78	79.64
P12	30.02	72.53	86.48
P13	33.17	70.18	101.82
P14	45.78	55.74	106.18
P15	32.02	60.03	87.60
P16	38.69	57.12	105.66
P17	30.11	54.91	79.37

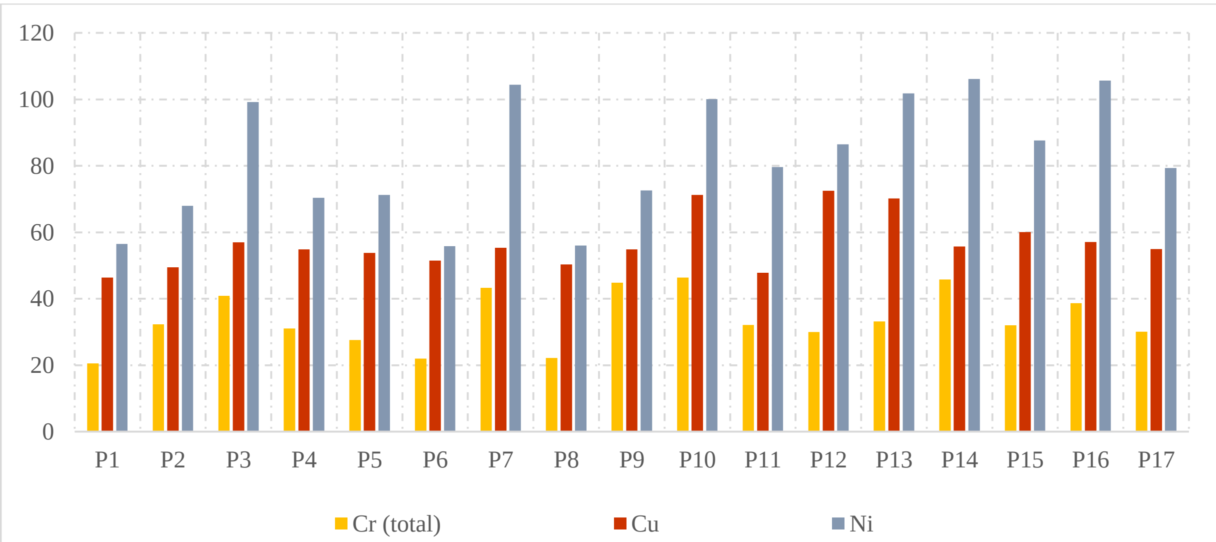

Fig. 4. The determined values of the soil samples

After determining the content of heavy metals in the control soil sample, taken from land not affected by mining activity, the following values resulted (Table 3):

Table 3. Determined values of the control sample (mg/kg d.s)

Analyzed indicators	Cr (Total)	Cu	Ni
Determined values	27.20	17.80	19.04

From Table 3, it can be seen that the heavy metals Cr (total), Cu, and Ni are also found in the control sample, but in lower concentrations than normal in the soil.

As a result of the calculations, the following values of I_{geo} emerged in the 17 sampling points of the soil collected from the Old Funicular tailings dump; they are presented in Table 4, respectively, in Figure 5.

Table 4. Determined values of the geo-accumulation index (I_{geo})

Sampling points	The values of the geo-accumulation index (I_{geo})		
	Cr (Total)	Cu	Ni
P1	0.13	0.46	0.56
P2	0.21	0.49	0.68
P3	0.27	0.56	0.99
P4	0.20	0.55	0.70
P5	0.18	0.53	0.71
P6	0.14	0.51	0.55
P7	0.28	0.55	1.04
P8	0.14	0.49	0.55
P9	0.29	0.54	0.72
P10	0.30	0.71	1.00
P11	0.21	0.47	0.79
P12	0.19	0.72	0.86
P13	0.21	0.70	1.02
P14	0.30	0.55	1.06
P15	0.21	0.60	0.87
P16	0.25	0.79	1.05
P17	0.19	0.55	0.79

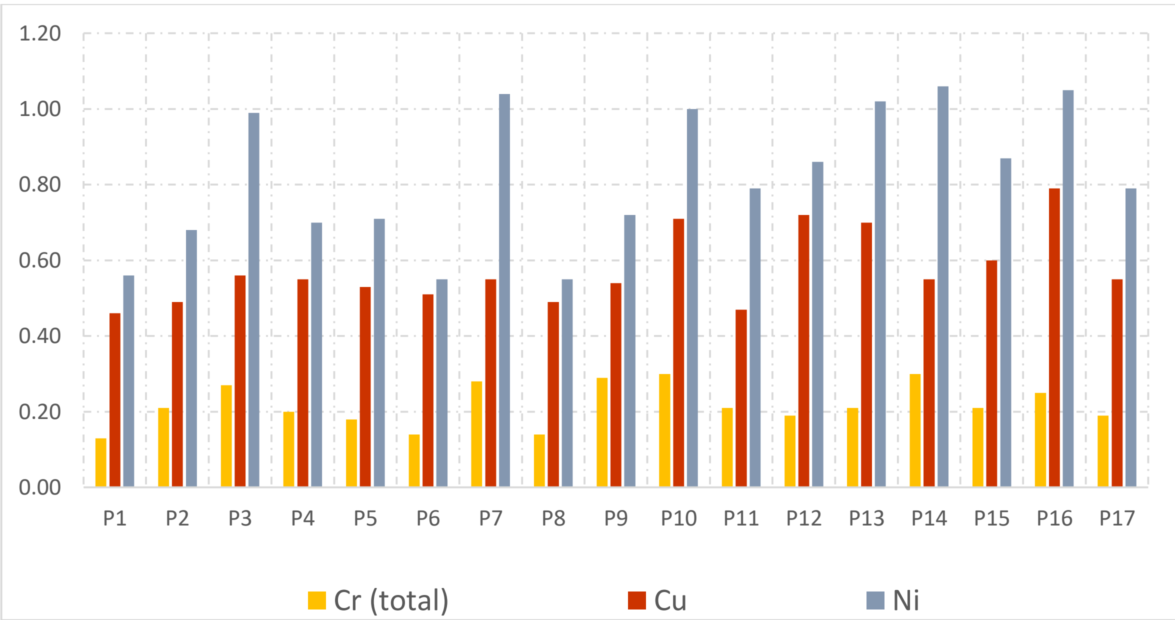

Fig. 5. Variation of the geo-accumulation Index (I_{geo})

To establish the rank of the geo-accumulation index of heavy metals present in the soil samples collected from the tailings dump, the following intervals were taken into account to identify the type of contamination present at the analyzed site (Table 5).

Table 5. Classification of the geo-accumulation index of heavy metals present in soil samples

Value I_{geo}	**Class vs. I_{geo}**	**Pollution level**
≤ 0	0	Unpolluted
0 - 1	1	Unpolluted to moderately polluted
1 - 2	2	Moderately polluted
2-3	3	Moderately to heavily polluted
3-4	4	Heavily polluted
4 - 5	5	Strong to very strong polluted
>6	6	Very heavily polluted

From the determination of the geo-accumulation index and based on its classification, it follows that the Old Funicular tailings dump falls into class 1 regarding the level of pollution with Cr (total) and Cu, which indicates a soil from unpolluted to moderately polluted, but in some sampling points from the dump, the geo-accumulation index of the heavy metal Ni falls into class 2, suggesting a moderately polluted soil with this metal. These aspects are directly proportional to the age of the dumped material, as the bio-geochemical reactions that take place in the dumps allow the release of the ions of these heavy metals.

4. Conclusions

The field and laboratory study carried out in the area of the Old Funicular 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 1.12 times, that of Cu by more than 2.83, and that of Ni exceeded by 4.12 times its normal value in the soil. This suggests a potential risk to the environment and, by implication, to human health.

Based on the I_{geo} index, the soil in this area is moderately polluted with nickel (I_{geo}=1.06), and the chromium (total Cr) and copper (Cu) contamination is classified as lightly contaminated, with I_{geo} values of 0.30 for Cr and 0.79 for Cu. This indicates a variability in the distribution of heavy metals in the soil, depending on the pollution sources and the physico-chemical properties of the soil.

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 and causing the I geo index values to increase. 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. This method, considered efficient and ecological, involves the use of plants with the ability to extract, stabilize, or degrade heavy metals from the soil. The application of phytoremediation on the Old Funicular tailings dump would significantly contribute to reducing heavy metal concentrations and improving the quality of the environment.

Proper management of tailings dump and continuous monitoring of soil quality are essential to protecting environmental quality and human health. The implementation of an active monitoring and remediation program is essential to maintaining an ecological balance in this area affected by mining activity.

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