Revista Minelor – Mining Revue
ISSN-L 1220-2053 / ISSN 2247-8590
vol. 30, issue 3 / 2024, pp. 22-29

# CORRELATION ANALYSIS OF HEAVY METAL CONCENTRATIONS IN THE TAILING DUMPS BRANCH 1 AND 2 LUPENI USING PEARSON COEFFICIENT MATRIX

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DOI: 10.2478/minrv-2024-0023

**Abstract:** *In the context of growing concerns related to the impact of mining activities on the environment, the present study focuses on the analysis of the correlations between the concentrations of heavy metals in Branch 1 and 2 tailing dumps in Lupeni, using Pearson correlation coefficient matrix. Tailing dumps from mining activity can be significant sources of soil contamination with heavy metals. In this work, the waste dumps Branch 1 and 2 were taken as a case study. This dump has been inactive for about 7 years and is the result of the exploitation of the waste from Lupeni mine located in the Jiu Valley. In this study, soil samples from the two branches of the tailing dump were collected and analyzed to determine heavy metal concentrations. Using Pearson correlation coefficient, statistical relationships between the concentrations of these heavy metals were calculated, providing a detailed matrix of correlations between them. This statistical analysis can help develop more effective remediation and management strategies, lessening the long-term impact of mining activities on the environment and human health.*
**Keywords:** *contamination, heavy metals, tailings dump, concentrations, statistical analysis, correlation coefficient*

## 1. Introduction

Coal mining is a major source of energy worldwide, but this activity generates substantial amounts of waste stored in the form of tailings dumps, which can have harmful effects on the environment. Branch 1 and 2 tailing dumps resulting from Lupeni mining operations in the Jiu Valley is a representative example of the long-term impact of this activity. In particular, the accumulation of heavy metals in these tailings can lead to soil contamination with potentially severe consequences for ecosystems and human health. Therefore, monitoring and analysis of these contaminants is essential for assessing ecological risks and developing effective remedial strategies.

Heavy metals such as lead, copper, cadmium, chromium, nickel, and mercury are toxic substances that can persist in the environment for long periods of time. These metals have the potential to bio-accumulate in living organisms and may have adverse health effects. In tailings dumps, concentrations of these heavy metals can vary significantly, and interactions between different metals can influence their distribution and mobility in the environment. [1]

Being a current topic, over time research has been carried out in different parts of the world, in mining areas with potential soil contamination with heavy metals. A notable example is the study by Singh et al. (2020), who used inductively coupled plasma and mass spectrometry (ICP-M) to analyze soils around a tailings dump in India, providing a detailed picture of heavy metal distribution and potential sources of contamination. [2] Research by Moore et al. (2017) highlighted the adverse effects of mercury contamination on aquatic communities near mines, demonstrating long-term impacts on biodiversity and ecosystem health. [3] Another notable study is the one conducted by Li et al. (2019) in mines in Henan Province, China. They used the Pearson correlation coefficient to identify relationships between these metals, concluding that certain heavy metals tend to associate due to common contamination sources and similar geochemical

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processes. [4] In their research, Johnson et al. (2018) used the Pearson coefficient matrix to analyze correlations among heavy metals in soils from an industrial region, finding significant interdependencies that suggested common sources of pollution. [5]

The aim of this study is to analyze the correlations between the concentrations of heavy metals in the Branch 1 and 2 tailing dumps in Lupeni using the Pearson correlation coefficient matrix. This statistical approach allows the evaluation of linear relationships between different heavy metals, facilitating the identification of interdependencies and possible sources of contamination. By elucidating these relationships, the study will provide valuable information on contamination dynamics and contribute to the development of more effective remediation strategies. In addition, the obtained results can guide a waste dump management policy and the implementation of environmental protection measures, thus ensuring a reduced impact on ecosystems and local communities.

## 2. Description of the study area

From Lupeni mining operations located in the Jiu Valley, coal was extracted for the first time in 1866. As a result of mining activities on this perimeter, deposits of waste material resulted.

The Branch 1 and 2 tailings dump resulted as a by-product of the coal preparation process within Lupeni Preparation Plant. The dump is located in the northern part of the mining operation, at a distance of 1000 m. The sterile material, in the form of solid waste resulting from the separation of coal from impurities, was systematically transported and stored in Boncii Valley. The waste material was transported by means of a funicular, which allowed the waste to be efficiently moved from the factory to the storage site. Once at its destination, the material was leveled using bulldozers, ensuring the even distribution and structural stability of the dump.

Lupeni Branch 1 and 2 tailing dump occupies a total area of 1.14 ha and has an impressive volume of 775.64 thousand $m^3$. These substantial dimensions reflect the large amount of stored waste material resulting from the activity of the coal preparation plant extracted from Lupeni mine.

The construction of the tailings dump on Boncii Valley led to the formation of three lakes at its base. These lakes were formed following the process of dumping the sterile material, respectively, from the accumulation of groundwater and precipitation. These lakes represent important elements in the tailings dump landscape, having the potential to influence both local biodiversity and contaminant dynamics. [6]

Branch 1 and 2 Lupeni tailing dump has been an inactive dump for about 7 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 such as St. John's wort, mouse's tail, rosehips, murres, and the like naturally settled on the surface of the two branches of the dump. This process of natural vegetation colonization contributed to soil stabilization and reduced erosion. On the slopes of the dump, tree species such as birch and acacia were identified, along with other native species. Figure 1 shows the Branch 1 and 2 tailings dumps.


*Fig.1. Tailings dump Branch 1 and 2 Lupeni*
*(Source: Google Earth)*

## 3. Materials and methods

### *3.1. Taking soil samples*

Soil sampling is an essential step in assessing levels of heavy metal contamination. The sampling methodology must be rigorously planned and implemented to ensure the representativeness and accuracy of the data obtained. In this study, a systematic approach was adopted for taking soil samples from Branch 1 and 2 Lupeni tailing dumps. The soil samples were taken in accordance with the methodological norms provided in the STAS 7184/1:1984 standard. [7]

**Number of samples**

A total of 32 average soil samples were taken. This number was considered sufficient to provide a detailed and representative picture of the distribution of heavy metals over the entire surface of the tailings dump.

**Sampling depth**

Soil samples were taken from two distinct depths: 0–20 cm and 20–40 cm. This allowed the assessment of vertical variations in heavy metal concentrations and identified possible differences between the surface and sub-surface soil layers.

**Sampling locations**

17 sampling points were established; these points were strategically selected to uniformly cover the entire area of the dump. A zigzag sampling network was used, with sampling points located at approximately equal distances, to ensure a uniform distribution of the samples.

Aspects regarding the location of the soil sampling points on the tailings dump, Branches 1 and 2, Lupeni, are illustrated in figure 2.

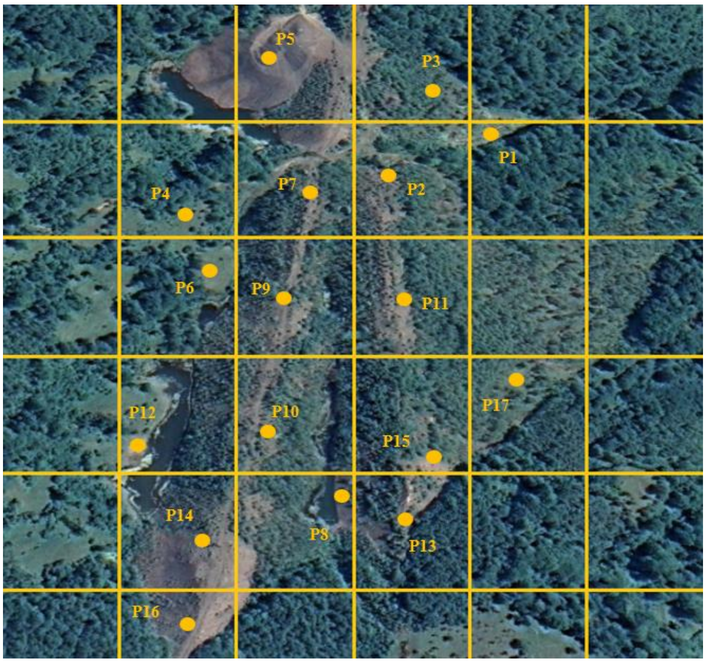


*Fig.2. Location of soil sampling points*

### *3.2. Instruments and equipment used for soil sampling*

**Manual soil sampler**

A manual soil sampler, also known as an auger, was used for sampling. This tool allowed the extraction of soil cylinders from different depths, keeping the soil structure intact for further analysis.

**Sterile sample containers**

Soil samples were collected and stored in sterile, airtight sample containers to prevent cross-contamination and alteration of soil chemistry prior to analysis.

**Tagging and recording devices**

Each sample was clearly labeled with a unique identification code, the exact date, and the location of sampling. This information was recorded in a field log to ensure the traceability of the samples and the correctness of the data collected.

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**Portable GPS**

A portable GPS device was used to record the exact coordinates of each sampling location, ensuring the accurate location of sampling points and facilitating possible future replications or studies.

**Personal protective equipment (PPE)**

To ensure safety in the sampling process, appropriate personal protective equipment was used, including gloves, protective masks, and protective footwear.

### *3.3. Soil Sampling Procedure*

At each sampling point, the manual soil sampler was used to extract samples from the 0–20 cm and 20–40 cm layers. The samples thus taken were immediately placed in the sterile containers, labeled, and sealed.

The GPS coordinates of the sampling location were recorded and noted in the field log, along with relevant information about the sampling conditions (e.g., soil type, moisture, presence of vegetation). After all the samples were collected, they were transported to the laboratory for detailed chemical analysis.

## 4. Analysis of heavy metals

Atomic absorption spectroscopy (AAS) was used to determine the content of heavy metals in the soil samples taken from Branch 1 and 2 Lupeni tailing dumps. The principle of this determination consisted of the following steps: [8]

**Soil sample extraction**

Dry soil samples were treated with a mixture of nitric acid, according to the standardized procedure. The mixture of soil sample and nitric acid was kept at ambient temperature for 16 hours to allow complete extraction of heavy metals.

**Boiling under reflux**

After the extraction period at ambient temperature, the samples were subjected to boiling under reflux for 2 hours. This step ensures a complete digestion of the heavy metals in the soil.

**Filtering and volume adjustment**

The resulting extract was filtered to remove residual solid particles. The filtered solution was made up to volume with nitric acid to ensure adequate concentration for further analysis. [9]

**Determination of the content of trace elements:**

According to the SR ISO 11047/1999 standard, the content of trace elements was determined using atomic absorption spectroscopy (AAS). [10] This analytical technique allows the measurement of specific concentrations of heavy metals through the absorption of light radiation by atoms in the gaseous state.

## 5. Calculation of Pearson correlation coefficient

Pearson correlation coefficient matrix was used to determine if there was an association between heavy metal concentrations in various soil samples or in various areas of the tailings dump.

By using Pearson correlation matrix, it was possible to assess the degree and direction of the relationship between heavy metal concentrations. [11] A correlation coefficient close to 1 indicates a positive correlation, respectively (increasing concentrations of a heavy metal are associated with increasing concentrations of another heavy metal), while a correlation coefficient close to -1 indicates a negative correlation, respectively (increasing concentrations of one heavy metal are associated with decreasing concentrations of another heavy metal). [12] Using the correlation matrix, patterns or trends in the distribution of heavy metals in the tailings dump can be identified. This information is useful in making decisions regarding the remediation or monitoring of soil contamination with heavy metals. This data can also be used to estimate the extent of pollution and develop appropriate remediation strategies. [13]

Pearson correlation coefficient was calculated using the formula:

$$r = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sqrt{\sum(x_i - \bar{x})^2 \sum(y_i - \bar{y})^2}}}, \quad (1)$$

where:

- $x_i$ and $y_i$ are the individual values of the variables x and y;
- $\bar{x}$ and $\bar{y}$ are the arithmetic means of the variables x and y;
- $\Sigma$ represents the sum over the entire data set.

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## 6. Results and interpretations

### *6.1 Determinations of heavy metals*

In order to identify the presence of heavy metals in the soil taken from Branch 1 and 2 Lupeni tailing dumps, the reference values for traces of chemical elements in the soil, according to Order 756/1997, presented in Table 1, were considered. [14]

*Table 1. Reference values for heavy metals in soil (mg/kg su)*

| Heavy metal | 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 |
| Zinc (Zn) | 100 | 300 | 700 | 600 | 1500 |

Following the determination of the concentrations of heavy metals present in the soil samples using the atomic absorption spectroscopy (AAS) method, exceedance of the normal values in the soil was identified for total chromium (total Cr), copper (Cu), nickel (Ni), and zinc (Zn). The determined values of heavy metal concentrations that exceeded the normal value allowed in the soil are presented in Table 2, respectively Figure 3.

*Table 2. Determined values of heavy metal concentrations in soil samples (mg/kg su)*

| Soil sampling points | Analyzed indicators | | | |
|---|---|---|---|---|
| | Cr (Total) | With | us | Zn |
| P1 | 22.71 | 50.93 | 60,21 | 175.03 |
| P2 | 33.59 | 48.71 | 74.16 | 92.04 |
| P3 | 31.50 | 47,44 | 59.37 | 90.06 |
| P4 | 33.59 | 47.69 | 83.31 | 151.43 |
| P5 | 48.83 | 53.22 | 112.86 | 68.78 |
| P6 | 34.58 | 61.68 | 90.56 | 93.87 |
| P7 | 50.06 | 72.03 | 110.06 | 180.67 |
| P8 | 33.53 | 56,28 | 72.96 | 72.03 |
| P9 | 29.55 | 56.33 | 110.08 | 114.12 |
| P10 | 37,18 | 55.35 | 59.18 | 110.67 |
| P11 | 47.07 | 58,61 | 72.96 | 100.45 |
| P12 | 34.64 | 55.98 | 74.67 | 79.26 |
| P13 | 36.02 | 74.42 | 92.92 | 101.32 |
| P14 | 35.73 | 56.25 | 72,73 | 213.92 |
| P15 | 33,43 | 54.88 | 75.41 | 103.44 |
| P16 | 35.97 | 74.67 | 105.48 | 133.48 |
| P17 | 32,37 | 72.05 | 87.98 | 206.37 |

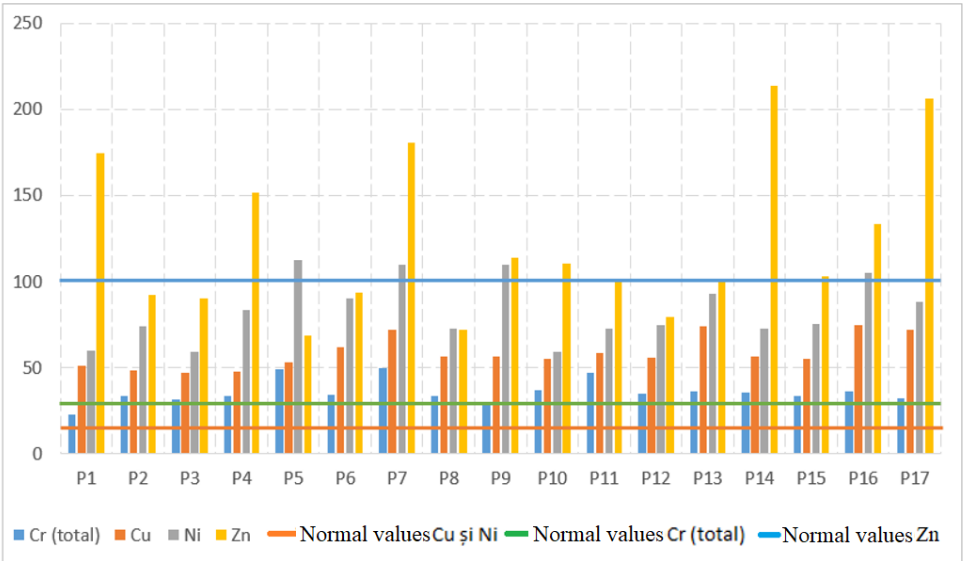


*Fig.3. Variation of heavy metal concentrations in soil samples*

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Table 2 shows that in almost all the sampling points, the determined values of heavy metal concentrations exceeded the normal values in the soil. It can be seen that the highest values of Cr (total) are at sampling points P5, P7, and P11; the highest values of Cu are at points P6, P7, P13, P16, and P17; the highest values of Ni were recorded at points P5, P7, P9, and P16; and the highest values of Zn were recorded at sampling points P1, P4, P7, P14, and P17.

Figure 3 shows that in some sampling points, the determined value of total chromium (total Cr) recorded values up to 1.65 times higher than normal, copper (Cu) showed concentrations 3.70 times higher than normal, and nickel (Ni) exceeded normal values more than 5.5 times. Also, zinc (Zn) was exceeded by up to 2 times compared to the normal value in the soil.

### 6.2. Pearson correlation coefficient matrix analysis

Using Pearson correlation coefficient matrix to see if there are interactions between the heavy metals present in the soil samples taken from the 17 points located on Branch 1 and 2 Lupeni tailing dumps, the following aspects emerged, which are highlighted in Table 3 and Figure 4.

*Table 3. Matrix coefficient of Pearson correlation for heavy metals in soil*

| | *Cr (Total)* | *Cu* | *Ni* | *Zn* |
|---|---|---|---|---|
| Cr (Total) | 1 | | | |
| Cu | 0.293561 | 1 | | |
| Ni | 0.455444 | 0.545017 | 1 | |
| Zn | -0.13308 | 0.299998 | 0.030302 | 1 |

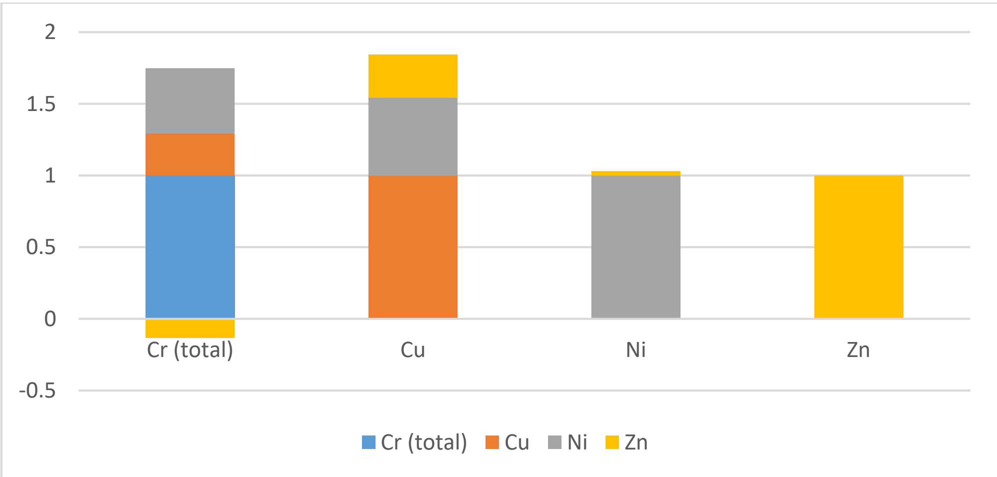


*Fig.4. Pearson correlation coefficient*

From Table 3 and Figure 4, respectively, we can see that when Cr is found in high concentrations in the waste material, the concentrations of the heavy metal Zn decrease. This indicates that there are interactions that can lead to the formation of insoluble compounds or their absorption on soil particles, an aspect that can reduce the availability of other elements, such as Zn.

### 7. Conclusions

Following the analysis of heavy metal concentrations in Branch 1 and 2 Lupeni tailing dumps using Pearson correlation coefficient matrix, significant exceeding levels of the normal values in the soil were identified for total chromium (total Cr), copper (Cu), nickel (Ni), and zinc (Zn). The study revealed that total Cr concentration values exceeded the normal limits in the soil by up to 1.65 times. In the case of copper (Cu), the concentrations at some sampling points were 3.70 times higher than the normal values in the soil. For nickel (Ni), exceeding values were even more significant, with values up to 5.5 times the normal limit. Zinc (Zn) showed exceeding values of more than 2 times the normal values at some points.

Pearson correlation coefficient matrix analysis revealed an inverse correlation between total Cr and Zn concentrations, indicating that increased chromium presence may reduce zinc availability in soil. This correlation suggests possible chemical interactions between heavy metals that can lead to the formation of insoluble compounds or their absorption on soil particles, thus limiting the mobility and availability of other elements, such as zinc. These findings are essential for understanding the behavior of heavy metals in contaminated environments and for developing effective remediation strategies for soils affected by mining activities.

The need to implement some phytoremediation techniques to remediate tailings dumps contaminated with heavy metals is essential. Phytoremediation, which involves the use of plants to extract, stabilize, and detoxify heavy metals from soil, can be used to reduce heavy metal concentrations and prevent their migration into the environment. The application of this method provides an environmentally friendly and sustainable way to address heavy metal contamination, helping to reduce environmental and human health risks while ensuring the effective recovery and rehabilitation of lands affected by mining activities.

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