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*Original Research*

# Assessment of Contamination with Heavy Metals in Environment: Water, STERILE, Sludge and Soil around Kishnica Landfill, Kosovo

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### Abstract

This research paper represents the results of concentrations of heavy metals in; soil, water, waste after floatation and sludge at the landfill Kishnica mines in Kosovo. The waste material; after the flotation process and water after technological processes are directly discharged through the pipe into the surface of the soil, near the agricultural lands in this zone. This industrial discharge, with high concentration of heavy metals, has caused the land around this area to be highly contaminated by the waste of the junk materials being discharged from the Pb-Zn industry in Kishnica. The sampling was performed in June 2018, while the measurements were done using atomic absorption spectroscopy (AAS).

In our results, we have found that the concentration of heavy metals in this analyzed zone around this area, has not exceeded the maximum amount allowed compared to EU-WHO standards, for contamination, and Dutch list for soils and Interventions.

**Keywords**: heavy metals, soil, water, sludge, Kishnica Complex

## Introduction

Studies showed that anthropogenic activities are the main source of metal contamination in the environment. Environment can get polluted or contaminated by different organic, inorganic and heavy metals substances. Heavy metal toxicity disrupts natural ecosystems and affects the food chain and different living organisms leading to different health problems. Once metals are introduced into the environment, they undergo several biological and chemical processes that lead to their distribution in environmental compartments such soils, sediments, water etc, [1-2].

The Kishnica mines are part of the industrial complex of Trepça, located in the northeastern part of Kosovo, in the Graçanica municipality area, just a couple of kilometers away from capital city, Prishtina. These mines, with their production capacities, discharge large amounts of waste into the environment because ore is only a small fraction of the total volume of processed material, around 30% for Pb residuals, and 50 % for residual waste Zn, which is the remnant of the mineralization process at the Kishnica flotation. The Kishnica mineral mines are considered as one of the most important Pb-Zn deposits in the mining area in Kosovo.

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The need to do this study is that heavy metals are not biodegradable in the environment, and are involved in the biogeochemical cycles through which they are concentrated in the sediment, and in the living organisms. Therefore, this research is very important since these elements can easily end up in the food chain. In order to evaluate the environmental pollution in water, soil and sludge we measured heavy metals (Pb, Zn, Cu, Cd, Ni and Fe) using AAS technique.

## Materials and Methods

### Study Area

The scheme below shows sampling points for water, soil, waste after floatation and sludge near Kishnica mines. The samples were taken around Graçanka River, as shown in the Fig. 1.

### Sample Collection of Waste after Floatation

For the sampling we chose different spots that represent water, soil, wastes and sludge. The waste material after floatation was taken in amount of around 1-2 kg from four different locations. The first sample was collected in the northern part of the landfill, the second in front of the flotation plant in Kishnica, the third sample in the southern part of the mine and the last one in the middle of the landfill. From the collected samples, we prepared the representative sample for chemical analysis. Initially we mixed and homogenized the samples, and then divided them into four equal parts, about 900g, then the we mixed and crushed it and then we used the sample as a mat, for further chemical analysis.

### Sample Collection of Soil

In order to have representative data, we focused on four different locations to take the soil samples, in an area with lower impact of the material waste at the landfill, close to the playground field of the Kishnica Club, near the waste of the landfill material and the garbage of Graçanica town; and the fourth one in an agricultural land-2.5 km from the town of Graçanica. All the samples were dried in 105ºC, until they were brought to constant weight.

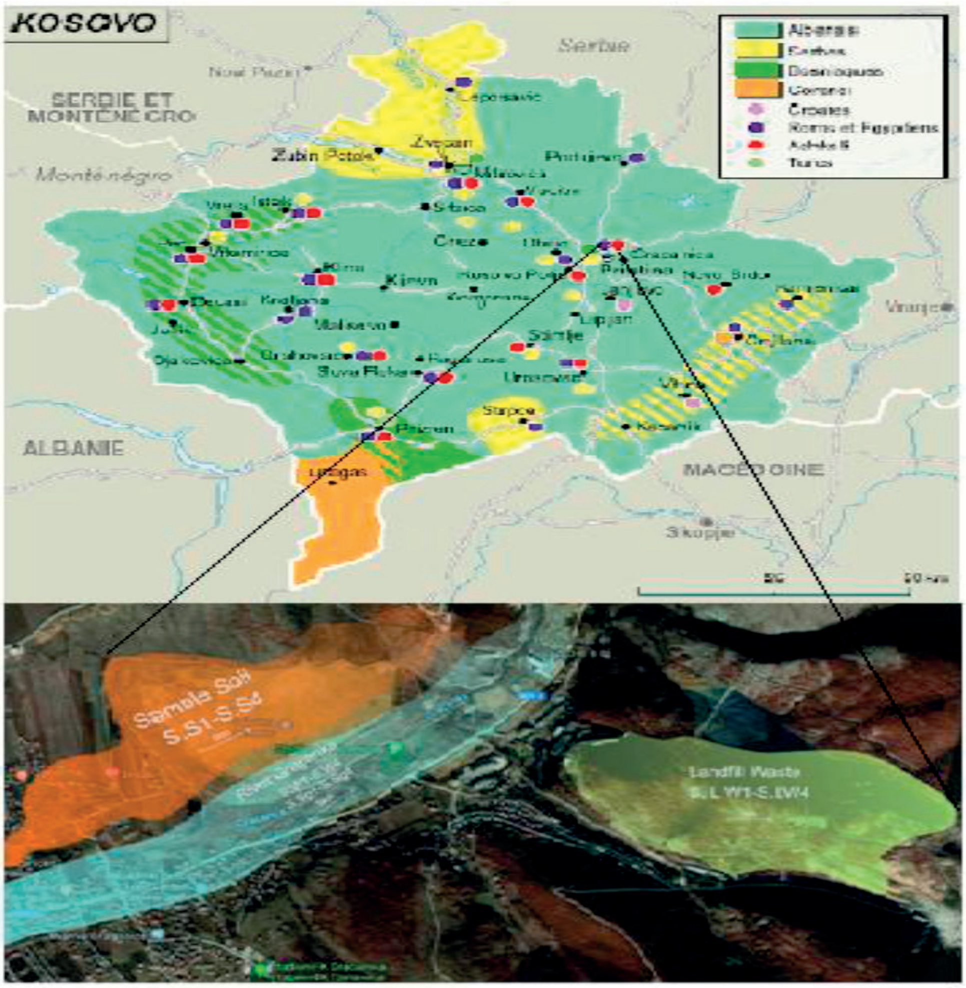


Fig. 1. Study area near Kishnica, around Graçanka River.

### Water Collection and Digestion

Water samples were taken around Graçanica River. The samples were taken near Badovc Lake; waste water discharge pipe; directly to the pipe and the last one in Graçanica River in town of Graçanica. First, water samples were filtered, before placing a 50 ml aliquot into Teflon vessels. Samples were then treated with 1mL of HCl and 5 mL of $HNO_3$ and digested in a BERGHOF-Speed Wave microwave.

### Sludge Chemical Analysis

In order to determine the heavy metals contents in sludge, for the digestion of chemical elements in the sludge we used acid mixtures; perchloric acid and nitric acid (ratio 1: 4). For chemical analysis, we got around-0.25 g of dried matter of sludge initially at- 105ºC then to we cooled them to room temperature. We dissolved samples in the mixture of 10 ml of perchloric acid and nitric acid digested the sample into the homogenization. After the process was done, we filtered, leveled the sample to 100 ml with distillated water. We measured the heavy metals using atomic absorption spectroscopy (AAS).

## Results and Discussions

The aim of this study is to evaluate the presence of Pb, Zn, Cu, Cd, Ni and Fe in water, soil, sludge and waste material after floatation sampled in the vicinity of industrial complex "Kishnica" as a possible pollution site. The results are presented in mg/kg of a dry mass for elements and divided into four groups:

### Determination of Pollutants in Wastes after Flotation Processes

Different studies have shown that environmental pollution can come from mining [4-6]. Various research also concluded that open-pit mining produces around ten times as much waste as underground mines because a greater amount of topsoil, overburden and barren or waste rock has to be removed. Gold mining in South Africa over the centuries has resulted in the accumulation of thousands of voluminous tailings dumps which are scattered all over the country with lots of potentially negative impact on the environments [7].

Fig. 2 shows the similarity distribution of Pb, Zn, Cu, Cd, Ni and Fe in waste measured samples. The results are presented in mg/kg.

The dendogram presented above, represent the similarity percentage of lead, zinc, cadmium, iron, copper and nickel in waste samples. From the results obtained, the similarity between Cd in Fe is the highest, almost 99.99%. The similarity between zinc and the group of cadmium and iron is also very high, with almost 95%. It is shown that the high percentage is

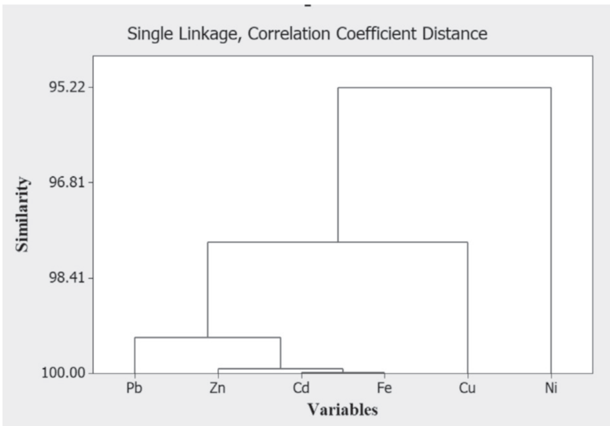


Fig. 2. Distribution dendogram of Pb, Zn, Cd, Fe, Cu and Ni in analyzed samples of waste.

between the lead and zinc and that we can conclude that the source of contamination with this metal comes from Kishnica mines.

The Fig. 3 represents the histogram of normal distribution of these elements (Pb, Zn, Cd, Fe, Cu and Ni) in mg/kg.

### Determination of Water Pollution from Kishnica Mines

Heavy metal pollution is caused when different toxic metals contained in excavated rock or exposed in an underground mine come in contact with water. Metals can end up in water during the process of water washes over the rock surface. Metals can become mobile in neutral pH conditions, leaching are particularly accelerated in the low pH conditions. Contaminations of surface and ground water have particularly been experienced in mining communities [8]. Mining has played a significant role in the socioeconomic life of the world for the past hundreds of years [9].

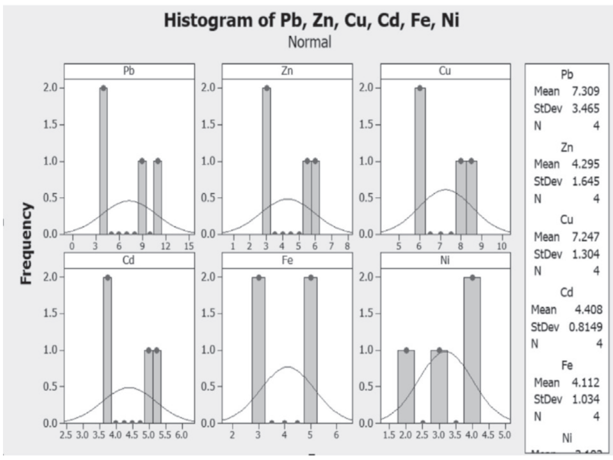


Fig. 3. Distribution of elements in waste analyzed samples (mg/kg).

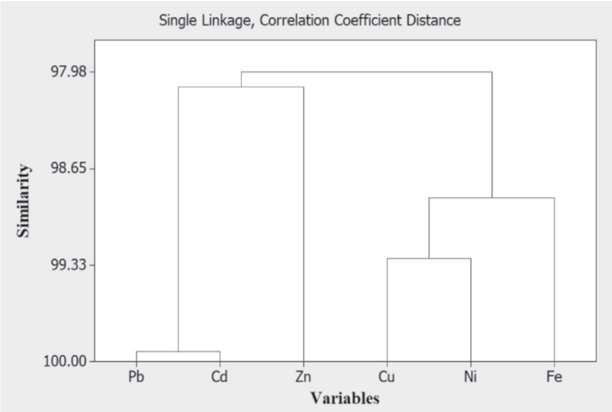


Fig. 4. Distribution dendogram of Pb, Zn, Cd, Fe, Cu and Ni in analyzed samples of water.

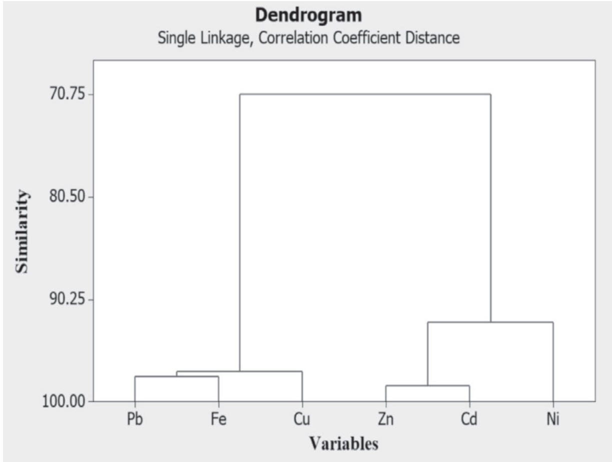


Fig. 6. Distribution dendogram of Pb, Zn, Cd, Fe, Cu and Ni in analyzed soil samples.

Fig. 4 represents the similarity distribution of Pb, Zn, Cu, Cd, Ni and Fe in water pollution measured samples. The results are presented in mg/kg. Fig. 5 shows the normal distribution of these elements in water samples measured, represented in mg/kg

The dendogram presented above, represent the similarity percentage of lead, zinc, cadmium, iron, copper and nickel in water samples. From the results obtained, the similarity between Cd and Pb is the highest, almost 100 %. The similarity between zinc and the group of cadmium and Pb in this case is around 96%. Also, it is shown that the high percentage is between the three other elements; copper and nickel around 98% while iron with this group has the similarity of 97%. From the results obtained we can conclude that the source of contamination with these elements comes from Kishnica mines.

Regarding the concentration of heavy metals in the river Graçanica, we can present the order of growth of these chemical elements, as follows; Pb> Cu> Fe> Cd> Zn and Ni. If we compare the results to EU standards, respectively directive 2008/105/EC [15], almost all chemical elements found in the river Graçanica exceed the limited under this Directive.

## Determination of Agricultural Soil Pollution from Kishnica Mines

Soil heavy metal pollution has become a severe problem in many parts of the world [10]. Different studies [11-12], stated that rapid social and economic development over the past several decades caused serious soil pollution with heavy metals in China. It is also stated that the pollution with these elements may occur naturally in soil and additional contributions come from anthropogenic activities such as agriculture, urbanization, industrialization, and mining.

Fig. 6 represents the similarity distribution of Pb, Zn, Cu, Cd, Ni, and Fe in soil pollution measured samples. The results are presented in mg/kg. Fig. 7 shows the normal distribution of these elements in mg/kg.

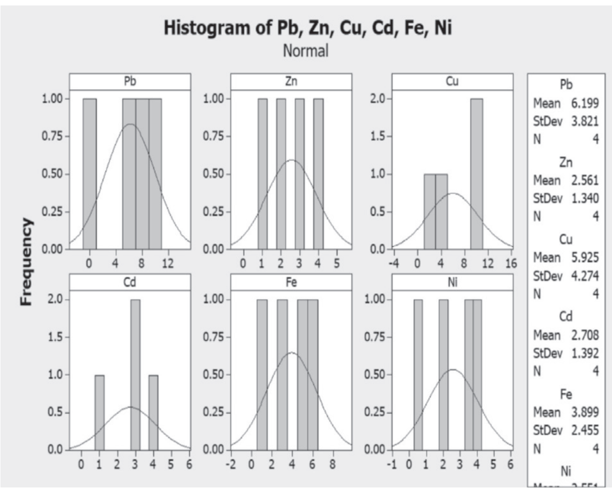


Fig. 5. Distribution of elements in waste analyzed samples (mg/kg).

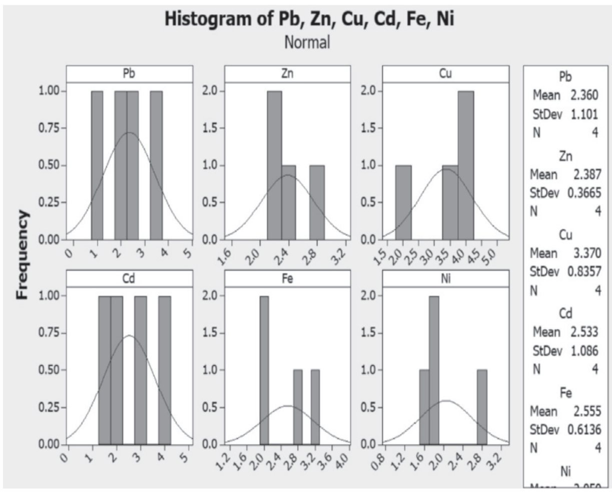


Fig. 7. Distribution of elements in analyzed soil samples (mg/kg).

In this element combination there is a lower scale of probability similarity than in the other groups; waste and water determination.

The highest concentration of the elements in this case is shown by Cu>Pb>Fe>Cd>Zn and Ni. If we compare them as a similarity of their distribution, we can say that they are divided into two bigger categories: Pb and Fe with 97 % of similarity and also the group of Zn and Cd, with around 92%.

Fig. 7 presents the histogram of heavy metals in agricultural soils around Kishnica in Gracanica, Kosovo.

## Determination of Sludge Pollution from Kishnica Mines

The production of sewage sludge increases every year that comes from population growth, industry growth etc. It is mentioned that the production of sludge in European Union (EU) is going to reach around 13,000,000 tons of dry matter. Sludge can contain different pollutions, inorganic and organic ones, including the toxic heavy metals, i.e., cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) etc. Our study represents the pollution of sludge with heavy metals from Kishnica mines in Kosovo. Fig. 8 represents the similarity distribution of Pb, Zn, Cu, Cd, Ni and Fe in sludge pollution measured samples. The results are presented in mg/kg. Fig. 9 shows the normal distribution of these elements in mg/kg.

In the case of distribution diagram of these elements in sludge, we have the results divided into two major groups: Pb, Zn and Cd in one and in the other hand between Cu, Fe and Ni. The first group of elements showed a similarity of about 99% and the second one where copper, iron and nickel are, showed the similarity of 98%.

To obtain more comparable results, we also extracted other tabular data that include various statistical variables. The following table (Table 1) is a summary of all results in the form of statistical analyzes

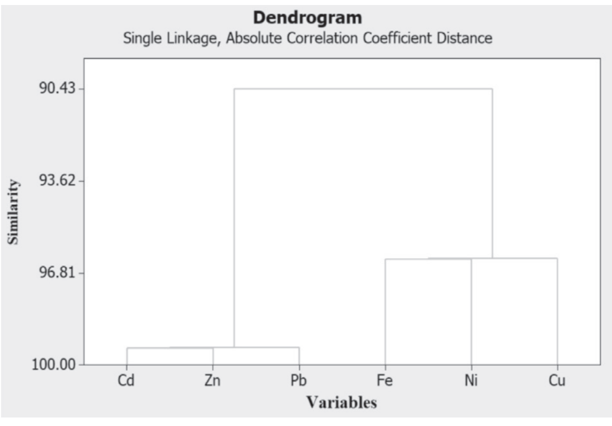


Fig. 8. Distribution of elements in analyzed soil samples (mg/kg).

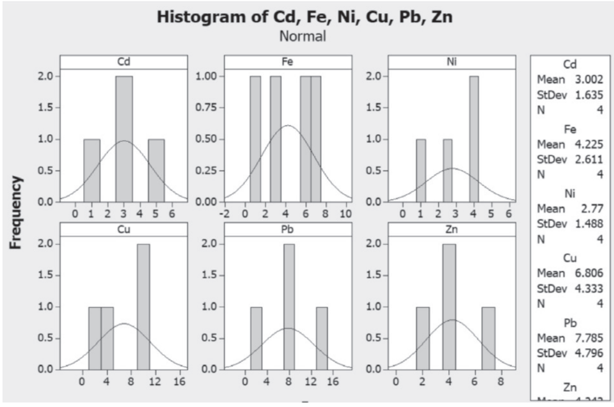


Fig. 9. Distribution of elements in analyzed soil samples (mg/kg).

of measurements made on waste after floatation, water, soil and sludge samples. The results are presented as mean, standard deviation, minimum, median and maximum. Results are presented in mg/kg.

Lead is a heavy metal present as a naturally found element on Earth, but also but anthropogenic activities, including mines ones can contribute to increase the concentrations of lead. It is a toxic metal that affects several organs in the body: kidneys, liver, central nervous system etc [13]. If we separate each element, we see that the concentration of lead decreased in order of the measured samples of: sludge, waste after floatation, water and soil samples, while the lowest concentration of this element was found in water (0.9 mg/kg), soils, sludge and in waste after floatation with the lowest concentration of 4.4 mg/kg.

World Health Organization classifies zinc as an element that is essential for living organisms, and its deficiency can cause different diseases in human body. Concentration of Zn in the water ranges from 0.978 as the lowest concentration to 4.136 mg/kg. The highest concentration was observed in the sludge samples starting from 1.88-6.77 mg/kg as the highest result.

Copper is considered an essential metal, along with different other elements including; iron, magnesium, selenium, calcium etc. This element plays an important role for different biochemical and physiological functions, and the deficiency of these elements can cause different diseases or syndromes. In our samples, copper concentrations ranged from 1.05 mg/kg as the lowest concentration found in water to 10.9 mg/kg found in sludge.

Decades ago, a disease “itai-itai” in Japan was spread, which was caused by the cadmium pollution [14]. Today it is known fact that cadmium is a toxic heavy metal which can be accumulated in the human body and in the environment long-term.

According to the results presented concentration of Cd in our soil samples ranged from 1.513 to 3.831 mg/kg, while the target value of this element in soils according to the Dutch standard list is 0.8 mg/kg

Table 1. Descriptive statistics of heavy metals in waste, water, soils and sludge (mg/kg).

| Elements in waste after floatation, presented in mg/kg. | | | | | |
|---|---|---|---|---|---|
| Variable | Mean | StDev | Minimum | Median | Maximum |
| Pb | 7.31 | 3.46 | 4.40 | 6.69 | 11.45 |
| Zn | 4.295 | 1.645 | 2.875 | 4.148 | 6.009 |
| Cu | 7.246 | 1.304 | 6.137 | 7.080 | 8.689 |
| Cd | 4.408 | 0.815 | 3.689 | 4.366 | 5.211 |
| Fe | 4.112 | 1.034 | 3.211 | 4.064 | 5.110 |
| Ni | 3.192 | 0.811 | 2.135 | 3.367 | 3.900 |
| Elements in water presented in mg/kg | | | | | |
| Pb | 6.20 | 3.82 | 0.90 | 6.95 | 10.00 |
| Zn | 2.561 | 1.340 | 0.978 | 2.564 | 4.136 |
| Cu | 5.93 | 4.27 | 1.05 | 6.34 | 9.97 |
| Cd | 2.708 | 1.392 | 0.822 | 2.918 | 4.174 |
| Fe | 3.90 | 2.46 | 0.90 | 4.15 | 6.39 |
| Ni | 2.551 | 1.482 | 0.650 | 2.888 | 3.779 |
| Elements presented in soils (mg/kg) | | | | | |
| Pb | 2.360 | 1.101 | 1.073 | 2.338 | 3.689 |
| Zn | 2.387 | 0.367 | 2.111 | 2.274 | 2.889 |
| Cu | 3.370 | 0.836 | 2.193 | 3.595 | 4.097 |
| Cd | 2.534 | 1.086 | 1.513 | 2.395 | 3.831 |
| Fe | 2.555 | 0.614 | 2.009 | 2.457 | 3.300 |
| Ni | 2.050 | 0.541 | 1.685 | 1.832 | 2.852 |
| Elements presented in sludge (mg/kg) | | | | | |
| Pb | 7.78 | 4.80 | 1.38 | 8.37 | 13.01 |
| Zn | 4.24 | 2.00 | 1.88 | 4.16 | 6.77 |
| Cu | 6.81 | 4.33 | 1.99 | 7.17 | 10.90 |
| Cd | 3.002 | 1.635 | 0.936 | 3.069 | 4.934 |
| Fe | 4.22 | 2.61 | 1.10 | 4.46 | 6.88 |
| Ni | 2.770 | 1.488 | 0.774 | 3.160 | 3.987 |

[16-17]. So, the results are a little higher than the target value, but none of the sample exceeded the amount of 12 mg/kg, value that is the Dutch standard for intervention. The lowest concentration was observed in water with the concentration of 0.822 mg/kg, while the highest concentration was recorded in waste products after floatation with concentration 5.211 mg/kg.

Nickel is an essential metal for living organisms and toxicity symptoms can occur when the redundancy or deficiency of this element might happen. For Ni, we observed higher concentrations in sludge>waste> water>soils, [16] in all of the samples not exceeding the concentration of more than 4 mg/kg. The lowest concentration of this element was presented in water<sludge<soils<waste products, not exceeding more than 2.135 mg/kg.

If we compare the whole results, we can conclude that we are dealing with low scale of pollution with heavy metals in this zone. This also can be justified due to the fact that activity of this mine has been shut down for a long time now, fortunately in this case making the pollution less in this zone.

## Conclusion

The environmental problems in Kosovo in general have been huge, especially in the last two decades, categorizing the environmental issues as a "luxury" and with less priority. Ecological and environmental issues coming from mines: Trepça, Kishnica, Ferronickel and so on, have aggravated over the last few decades, threatening environmental devastation not only in those regions, but also in a bigger scale. The specific risk associated with these heavy metals (Pb, Zn, Ni, Cd, Cu, and Fe) in the environment it is not only pollution, but also their ability and bioaccumulation through the food chain, and their persistence in nature.

In this study, several metals (Pb, Zn, Ni, Cd, Cu and Fe) were analyzed in four types of samples: water, soil, sludge and waste after the floatation in four different sampling positions. Results demonstrate that the presence of these metals in environmental samples has a common source: the concentrate type used in mining activities at Kishnica.

Since this ore is not active at the moment, we are dealing with low pollution in this zone. But, to keep it constant this zone and under control, to know the extent of contamination more accurately, it is preferable to continue with constant monitoring so that the zone does not exceed the maximum amount allowed with pollution in this zone.

## Acknowledgements

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## Conflict of Interest

The authors declare no conflict of interest.

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