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Original Research

Evaluating the Presence of Heavy Metals in the Vicinity of an Industrial Complex

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Abstract

Heavy metals occur naturally in the earth's crust, but anthropogenic activities such as mining can release them in large quantities into the environment.

Mines are important industrial complexes for economic development, but may have major environmental consequences if the relevant standards are not met. In the Mitrovica region of Kosovo there is a Pb and Zn mine known as Trepça. This mine was built decades ago, and is a major source of environmental pollution, with a considerable amount of sterile material that remains after the mine's flotation. This results in the contamination of water, soil and sludge.

This research focuses on the pollution containing heavy metal waste that comes from the Trepça mine generated from lead and zinc mining activities. In order to evaluate the environmental pollution in water, soil and sludge, we measured heavy metals (Pb, Zn, Cu, Cd, Ni and Fe) using inductively coupled plasma optical emission spectrometry (ICP AES). Our results indicate that the presence of metal contamination in the study area is strongly influenced by mining activities. The results presented here can serve national agencies in taking measures to implement monitoring programs for heavy metals in areas surrounding the Trepça mining complex.

Keywords: pollution, heavy metals, mining, Pb-Zn

Introduction

Heavy metal pollution, in particular from metalores, represents a major concern for general public health. Mining activities impact natural and regional water systems and the environment in general, and their effects may become obvious only after mining. Pollution from mining also is influenced by the method of mining, ore processing, waste disposal techniques, mine type, environmental factors, etc. El Alaoui [1] stated that mining is associated with high risk of contaminating surrounding soils. Furthermore, the ability of heavy metals to diffuse into surface and underground waters, subsequently enter the food chain, and bio accumulate is also evident. [2-3].

The Trepça mine is one of the largest sources of Pb/Zn ore in Europe and extends over 80 km in northern Kosovo, which is naturally rich in lead and zinc deposits. The mine is located less than 10 km from Mitrovica city in Kosovo. Although the complex has been inactive for years, the consequences of mining-related pollution are still evident. The environmental pollution from this complex has caused considerable disruption to the ecosystem because Trepça, with its

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activity, starting from ore exploitation and enriching with the flotation process, had a significant impact in environmental pollution, in the territory of the town of Mitrovica and beyond. As the Trepça complex produces sterile material that contains these heavy metals, it poses a potential risk to the surrounding ecosystems and communities [3-4]. Primary products are ore and concentrates of lead and zinc, with a significant content of silver and gold.

Materials and Methods

Sample Collection

Field sampling was conducted within the period of September 2017 in five different areas of study. Sterile samples were taken in so-called landfills, known by the locals as IPM (Industrial Park of Mitrovica) as well as in the Kelmend landfill sterile layer. Also, in the vicinity of these zones, the soil samples were taken for analysis. The water and sludge samples were taken in the Sitnica, Trepça and Iber rivers.

The analyzed samples were: sterile, water, sludge, and soil. Water samples were taken in 1L plastic containers, while sterile, sludge and soil samples were collected in plastic containers [5]. The samples were initially dried, then ground and milled prior to treatment.

Sample Digestion

Treatment of Water Sample

First, water samples were filtered before being placed by a 50 ml aliquot into Teflon vessels. Samples were then treated with 1 mLofHCl and 5 mL of HNO_3 and digested in a BERGHOF-Speed Wave microwave [5].

Treatment of Soil, Sterile and Sludge Samples

A 3.5 gram of solid sample (soil, sludge and sterile) was weighed and placed in Teflon vessels. Samples were then treated with 10 ml of aqua regia and digested in the microwave. After the microwave digestion was finished, samples were filtered and diluted to 100 ml using distilled water.

Instrumentation and Statistical Analyses

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to measure the concentrations of heavy metals. For each group of analytical samples, two spiked blanks and two method blanks were simultaneously processed.

Calculation and presentation of statistical charts was done using the Minitab 19 software program and are shown separately for each element individually.

Results and Discussion

The focus of this study is to evaluate the presence of Pb, Zn, Cu, Cd, Ni and Fe in water, soil, sludge and sterile material sampled in the vicinity of the Trepça industrial complex as a possible pollution site. Moreover, a tentative link between their distribution from sterile material of the factory into water, sludge and soil is also given [6-7].

Lead

Lead is an element that can be found naturally in earth, but anthropogenic activities, including mines, can contribute to high concentrations of this metal. This element is a toxicant that affects several organs in the body: kidneys, liver, central nervous system, etc. [8].

Fig. 1 shows the distribution dendogram of Pb in the measured samples. Fig. 2 shows the histogram of the normal distribution of Pb in sterile, water, sludge, and soil.

Lead can have high concentrations, and it is expected since this element could be found naturally in earth [9]. Also from soil, since Kosovo is very rich with this element, especially Trepça mine.

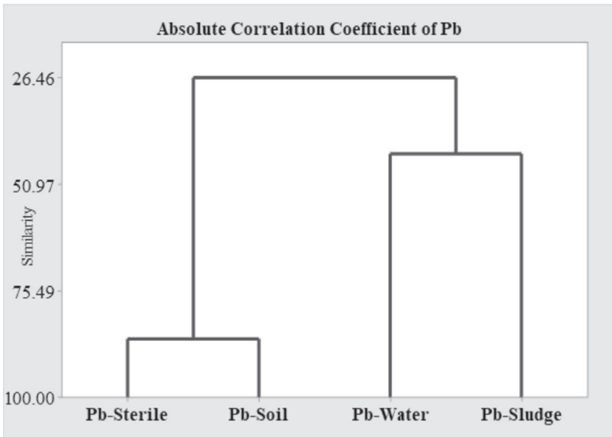

Fig. 1. Distribution dendogram of Pb in analyzed samples.

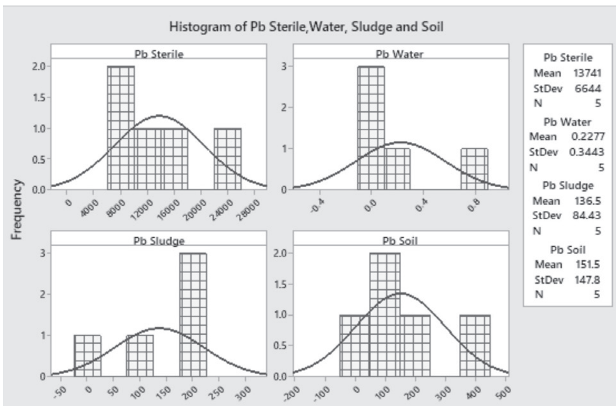

Fig. 2. Distribution of Pb in sterile, water, sludge and water.

The dendogram presented above represents the similar percentages of lead in sterile, water, sludge and soil samples. From the results obtained, the similarity between Pb in sterile and soil is around 87%, while the similarity between water and sludge is around 45%.

Given this high percentage of similarity between lead in sterile and soil samples, we can conclude that the source of contamination with this metal comes from the Trepça mine.

Cadmium

In 1950 in Japan itai-itai disease, caused by cadmium pollution, spread throughout the country [10]. Today it is a known fact that cadmium is a toxic heavy metal that can be accumulated in the human body and in the environment long-term.

Fig. 3 shows the distribution dendogram of Cd in the measured samples. Fig. 4 represents the histogram of the normal distribution of cadmium in analyzed samples.

The similarity of this element to the measured samples was found again in a higher percentage between soil samples and sterile ones at around 93%, while a very low percentage between the sludge and the water samples, with less than 6%.

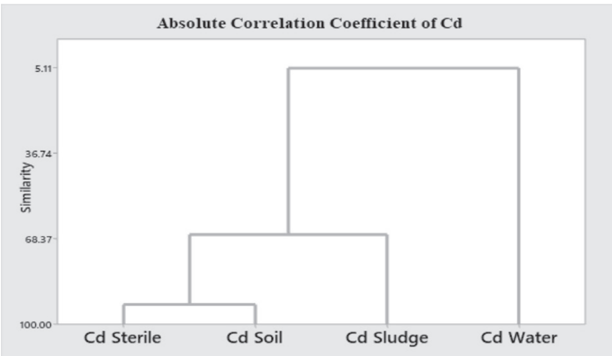

Fig. 3. Distribution dendogram of Cd in analyzed samples.

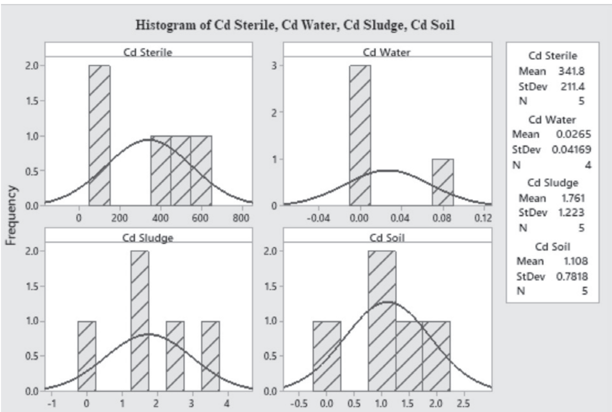

Fig. 4. Distribution of Cd in sterile, water, sludge and water.

Zinc

Zinc is an element that the World Health Organization considers as an essential metal and its deficiency can cause different diseases in the human body [11].

Figs 5 and 6 show the distribution dendogram of this element in the measured samples and the histogram of the normal distribution of zinc in analyzed samples.

As the part of the similarity of pollution distance between the measured samples sterile, water, sludge and soil, the results show that it is lower in the zinc case than the other elements compared so far. Here we have a comparison between the two groups: one group of soil and sludge samples, and the other group of water and sterile. The similarity between soil and sludge samples is about 74%, while the other group (water and sterile) is about 38%.

Copper

Copper is an essential metal, along with cobalt, iron, magnesium, manganese, molybdenum, nickel, selenium and zinc, required for various biochemical

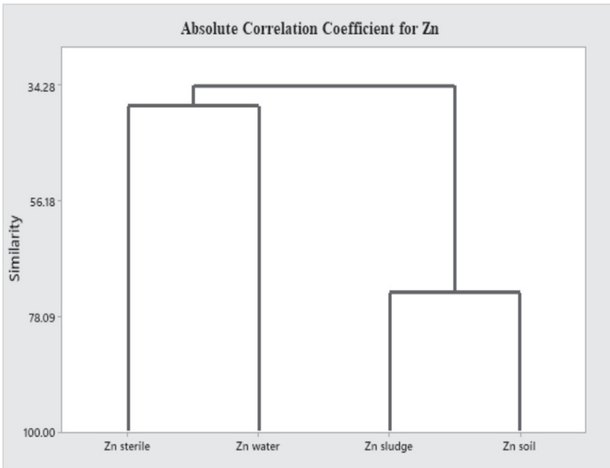

Fig. 5. Distribution dendogram of Zn in analyzed samples.

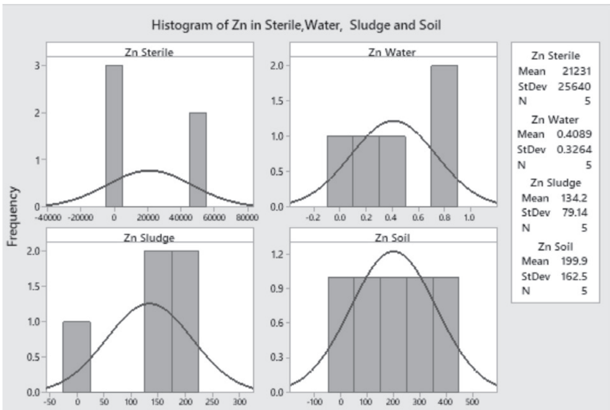

Fig. 6. Distribution of Zn in sterile, water, sludge and water.

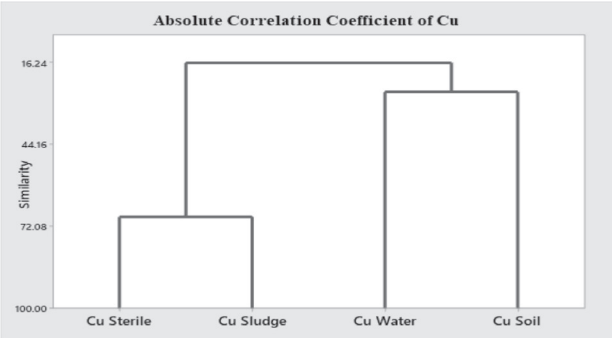

Fig. 7. Distribution dendogram of Cu in analyzed samples.

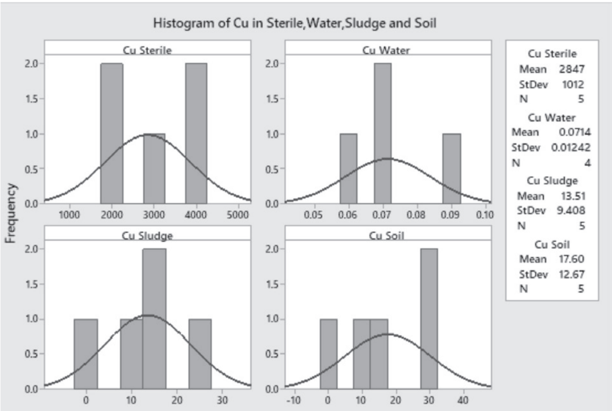

Fig. 8. Distribution of Cu in sterile, water, sludge and water.

and physiological functions, and the deficiency of these elements can cause different diseases or syndromes [11].

Fig. 7 shows the distribution dendogram of copper in the measured samples. Fig. 8 represents the histogram of the normal distribution of this element in analyzed samples.

In the case of copper, we have a more similar distribution between this element in sterile and in sludge form. The similarity of these two forms of distribution is about 69%, while lower percentages have been shown for soil and water samples of about 27%. These two groups have similarities in their distribution of about 16%.

Nickel

Nickel is an essential metal for living organisms and toxicity symptoms that can occur when the redundancy or deficiency of this element might happen. The quantity of nickel can vary; in earth's crust with around 1.2 mg/L, in soils 2.5 mg/L, in streams it is 1 μg/L and in groundwater it is <0.1 mg/L [12]. Nickel concentration increases also with anthropogenic activities; mining works, emission of smelters, burning of coal and oil, and sewage [13].

Fig. 9 shows the distribution dendogram of Niin the measured samples. Fig. 10 represents the histogram of the normal distribution of Ni in analyzed samples.

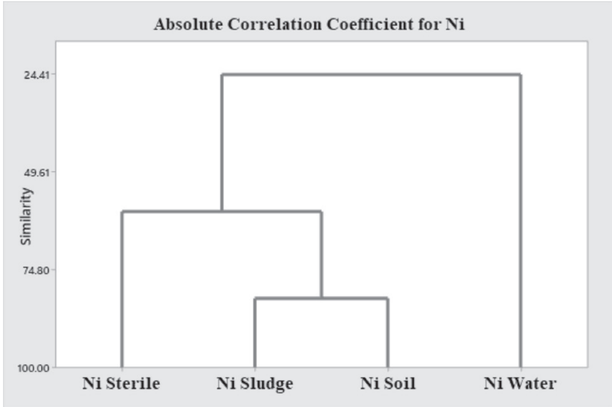

Fig. 9. Distribution dendogram of Ni in analyzed samples.

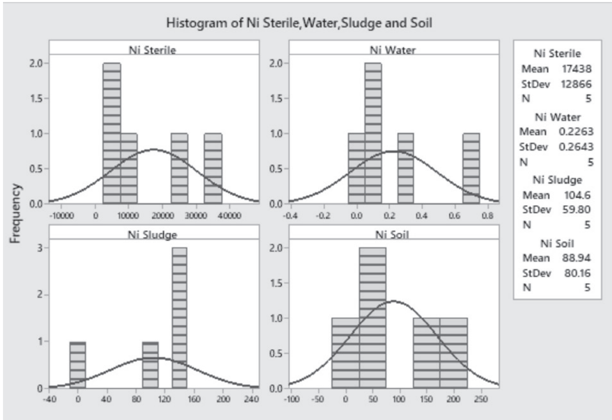

Fig. 10. Distribution of Ni in sterile, water, sludge and water.

The percentage of similarity from nickel samples show a higher percentage in sludge and soil samples (higher than 82%), while much less similarity has been shown with sterile and a still lower percentage of water samples with all other groups.

Iron

Iron is an essential element and the most abundant in the earth's crust, and it is present in the environment mainly as ions Fe^{2+} or Fe^{3+}. This heavy metal is generally present in surface waters as salts containing Fe(III) when the pH is above 7 [12].

Fig. 11 shows the distribution dendogram of iron in the measured samples. Fig. 12 represents the histogram of the normal distribution of this element in analyzed samples.

The group classification of iron in samples is divided into three separate sets: the one between the sterile and soil, then the similarity of sludge with the first group and water samples being as a separate set, with less similarity to the first two. We measured a greater similarity between sterile and soil with about 83%, while slightly more than 50% with sterile similarity the first group (soil and sterile).

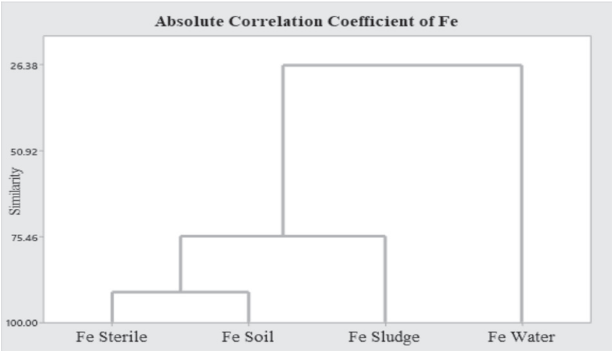

Fig. 11. Distribution of Fe in analyzed samples.

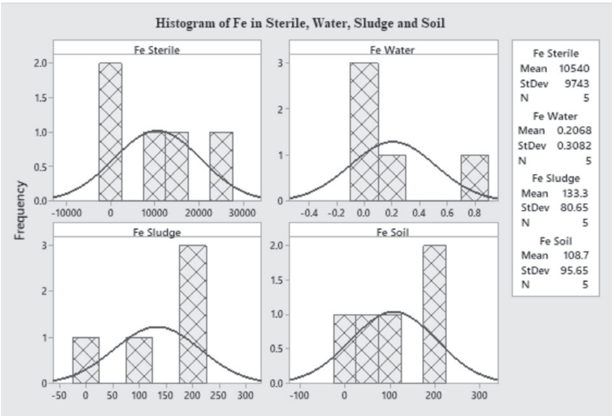

Fig. 12. Distribution of Fe in sterile, water, sludge and water.

The water appears alone, with a similarity of about 30% to sludge samples.

Table 1 is a summary of all results in the form of statistical analyses of measurements made on sterile, water, and sludge and soil samples. The results are presented as mean, standard deviation, variance, sum, minimum, maximum, Q1, Q3, median and range. Results are presented in mg/kg.

The obtained results show that that the concentrations of heavy metals are very high, and these values are directly correlated to Trepça activity [6, 14]. Statistical data show that the highest concentration of heavy metals (mg/kg) is presented in the sterile samples and the lowest concentration in the water samples (Table 1).

From the above results (Table 1) we see that the highest concentration was found in Zn> Ni>Pb> Fe> Cu>Cd. These results are expected due to the higher concentration of these elements (Pb, Zn) in the ore from Trepça. As for the lower concentrations, we found in water samples and are ranked due to decreased concentrations Zn>Ni>Fe>Pb>Cu>Cu. A similar study was also done by Sun et. al., 2018 [15].

Hassaan et. al. 2016 [16] classified elements based on their contamination of sediment. These values are presented for comparison.

In our samples, copper concentrations ranged from 0.74 to 26.88 mg/kg, and according to his study (Table 2), sediment tends to be moderately contaminated with this element. However, if we compare the heavy metals in the soil samples according to the Dutch standard [17], for soil we find that the concentration of this element in soil is 36 mg/kg, as a target value, while in our samples it is lower, ranging from 0.3 to 30.5 mg/kg.

Concentration of zinc the sludge ranged from 1.17 to 200.8 mg/kg, while according to Table 2 we can classify them as moderately contaminated. In soil samples, it ranged from 11.23 to 403.2 mg/kg, which by comparison with the Dutch standard for the values of this element in soils, it exceeded the maximum amount allowed (140 mg/kg) by nearly three-fold (Table 2).

For Ni, we observed higher concentrations in both soil and sediment samples. In soil samples the Ni concentration is more than 5 times higher than the Dutch standard for soils (35 mg/kg), while in sediment the concentration of this element ranged from 1.61 to 146.32 mg/kg. According to Table 2, it is classified in the heavily polluted group (>50 ppm).

According to the results, the presented concentration of Cd in our soil samples ranged from 0.06 to 2.11 mg/kg, while the target value of this element in soils is 0.8 mg/kg (Table 2). In either case, we do not have values of this element higher than 12 mg/kg, which is the Dutch standard for intervention.

In our analyzed soil samples, Pb concentration

Table 1. Descriptive statistics of heavy metals in sterile, water, sludge and soil in mg/kg.

STERILE										
Variable	Mean	StDev	Variance	Sum	Minimum	Q1	Median	Q3	Maximum	Range
Pb	13741	6644	44140815	68706	7951	8246	12076	20069	24139	16188
Zn	21231	25640	6.57E+08	106156	2239	2294	3059	49254	51656	49417
Cu	2847	1012	1023490	14235	1754	1825	2898	3844	3899	2145
Cd	341.8	211.4	44710.8	1708.9	113.2	124.8	383.9	537.7	591.7	478.5
Fe	10540	9743	94924405	52699	759	804	11974	19559	23120	22361
Ni	17438	12866	1.66E+08	87188	6975	7228	11871	30430	36948	29973

Table 1. Continued.

WATER										
Pb	0.228	0.344	0.119	1.139	0.007	0.051	0.097	0.47	0.84	0.833
Zn	0.264	0.287	0.083	1.318	0.039	0.039	0.144	0.548	0.711	0.672
Cu	0.0714	0.0124	0.00015	0.2856	0.059	0.0613	0.069	0.084	0.0886	0.0296
Cd	0.0265	0.0417	0.0017	0.106	0.004	0.0045	0.0065	0.0685	0.089	0.085
Fe	0.207	0.308	0.095	1.034	0.004	0.046	0.089	0.427	0.754	0.75
Ni	0.226	0.264	0.07	1.132	0.022	0.045	0.075	0.483	0.654	0.632
SLUDGE										
Pb	136.5	84.4	7128.9	682.6	1.1	54.5	178.7	197.5	206.2	205.1
Zn	134.2	79.1	6262.7	670.9	1.2	63.7	164.4	189.6	200.8	199.6
Cu	13.51	9.41	88.52	67.57	0.74	5.95	12.79	21.44	26.88	26.14
Cd	1.761	1.223	1.496	8.803	0.03	0.73	1.7	2.821	3.38	3.35
Fe	133.3	80.6	6504.4	666.6	1.1	56.4	175.4	189.2	194.7	193.5
Ni	104.6	59.8	3576.3	522.8	1.6	52.5	133.3	142.3	146.3	144.7
SOIL										
Pb	151.5	147.8	21846.1	757.3	6.5	34.2	96.5	296.2	378.1	371.6
Zn	199.9	162.5	26391.6	999.7	11.2	51.2	168.4	364.5	403.2	392
Cu	17.6	12.67	160.64	87.98	0.3	5.95	16.21	29.94	30.5	30.2
Cd	1.108	0.782	0.611	5.54	0.06	0.46	0.91	1.855	2.11	2.05
Fe	108.7	95.6	9148.8	543.4	3.4	21.3	84.3	208.3	219.2	215.8
Ni	88.9	80.2	6426.3	444.7	3	18.1	68.1	170.2	198.1	195.1

varied from 6.5-378.1 mg/kg. Compared to the Dutch standard for soils and interventions value, we find that this metal has exceeded the target value of 85 mg/kg in three soil samples, while its concentration in the sludge ranges from 1.1 to 206.2 mg/kg.

Table 2. Classification of heavy metals in sludge and in soils according to Dutch intervention values.

Elements in sludge	Non polluted (ppm)	Moderate polluted (ppm)	Heavily polluted (ppm)
Cu	>25	25-50	>50
Zn	>90	90-200	>200
Ni	>20	20-50	>50
Cd	-	-	-
Pb	-	-	-
Elements in soil	Target value (mg/kg)	Intervention value (mg/kg)	
Cu	36	190	
Zn	140	720	
Ni	35	210	
Cd	0.8	12	
Pb	85	530	

Conclusions

Ecological and environmental issues coming from Trepça mines have been aggravated over the last few decades, threatening environmental devastation not only in that region but throughout Kosovo. The specific risk associated with these heavy metals in the environment is bioaccumulation through the food chain and their persistence in nature.

In this study, several metals (Pb, Zn, Ni, Cd, Cu and Zn) were analyzed in four types of samples: water, soil, sludge and sterile material at five 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 Trepça.

The study confirms that the Trepça complex has a notable impact on the distribution of metals in the vicinity of the mine. To make matters worse, the mine is surrounded by residential areas, including a major city less than 10 km away. There is a very high risk for human exposure to metals contamination from the mine, but monitoring and surveillance of pollution is infrequent or nonexistent.

These results demonstrate that it is necessary to implement continuous monitoring in these zones. Due to the high levels of contamination reported here, proper disposal of mining waste should be done in order to decrease the risk of environmental disasters and to protect public health.

Conflict of Interest

The authors declare no conflict of interest.

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