

## Article

# Characterization of Sterile Mining Dumps by the ICP-OES Analytical Method: A Case Study from Baia Mare Mining Area (Maramures, Romania)

Ioana Andreea Petrean <sup>1,\*</sup>, Valer Micle <sup>1</sup> , Ioana Monica Sur <sup>1,\*</sup>  and Marin Şenilă <sup>2</sup> 

<sup>1</sup> Department of Environment Engineering and Entrepreneurship of Sustainable Development, Faculty of Materials and Environmental Engineering, Technical University of Cluj-Napoca, 400114 Cluj-Napoca, Romania

<sup>2</sup> Research Institute for Analytical Instrumentation, 400293 Cluj-Napoca, Romania

\* Correspondence: ioana.petrean@imadd.utcluj.ro (I.A.P.); ioana.sur@imadd.utcluj.ro (I.M.S.)

**Abstract:** This paper describes a former sterile dump site that is the result of mining and ore processing. A large site located in the Baia Mare mining area (Romania) with a significant amount of Suior-type mining concentrate deposits was selected for this research. The method of analysis used in this study is inductively coupled plasma optical emission spectrometry (ICP-OES). To characterize the contaminated area, a total of 27 sterile samples and one soil sample were collected from the studied site, which was affected by the mining activity. The samples were mineralized by a mix of hydrochloric acid and nitric acid. The disaggregation of the samples took place on a sand bath, and the concentrations of nine heavy metals were determined using an inductively coupled plasma optical emission spectrometer. The investigations provided the information for a detailed analysis allowing the assessment of trace element concentrations to establish whether the area requires remediation. This paper aims to highlight the importance of obtaining quantitative analysis data when characterizing heavy metal contaminated areas that need to undergo the remediation processes, utilizing accurate and fast systems such as modern multispectral analytical devices. The objective of this paper consists of the characterization of an area in the Baia Mare municipality, Romania, affected by high heavy metal concentrations due to sterile mining material being deposited on its surface in order to determine if the area requires remediation.

**Keywords:** optical emission spectrometry; trace elements; contamination; health risks; Baia Mare; Romania



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## 1. Introduction

Over time and particularly in recent decades, water and soil have been drastically affected by pollution as a result of rapid industrialization, urbanization, agricultural practices, the improper use of chemicals and pesticides, non-qualitative irrigation water, mining, and increased quantities of waste [1]. Mining wastes pose physical risks due to the construction of their supporting infrastructure, the increased erosion rates, the suspended materials in the surface water systems, and increased instability of soil and rocks also involve chemical risks due to the dispersion of the extracted materials or chemical agents used in mining or ore processing [2,3].

Anthropogenic and natural activities have led to the contamination of soil and water [4–6]. Heavy metal pollution from mining sites causes the immediate and long-term contamination of soil, water, and air, affecting the flora, the animals, and the nearby human population [7,8]. The sources of heavy metal pollution in soils are industrial emissions, effluents, and solid discharges [9]. Heavy metal toxicity and its potential to enter the food chain are major environmental problems [10–12].

Changes in the quality of soil, water, and atmosphere caused by the presence of heavy metals due to human activities cause changes in the structure of living organisms and

pose an exposure risk to people living and working in mining areas [13,14]. Mercury, lead, arsenic, and cadmium are non-essential metals for the human organism, but they are lethal [13,15–18]. Heavy metals are absorbed into the body through mechanisms such as skin contact, soil diet, inhalation, and oral intake; they cannot be degraded and can cause damage to vital human organs, leading to mutagenesis and carcinogenesis [19]. Increased heavy metal concentrations can be ingested by air, sediments, water, or food contamination [20,21], causing autoimmune illnesses, allergies, and interference with the function of the corpus luteum of the ovary, which prepares the mucous membrane of the uterus for the implantation of a fertilized egg [22], cardiovascular disorders, lung cancer mortality, and overall mortality [23–25].

Heavy metals accumulate in the adipose tissues as well as in the liver, kidneys, and brain, influencing biochemical and hormonal processes such as metabolism, cell proliferation, and fertility [22]. The accumulation of Pb, Se, Hg, As, and Cr in high concentrations can cause toxic effects in the body and lead to death [18,26–29]. Pb and Cd are nephrotoxic elements [30], especially in the renal cortex. Pb exposure in children has an irreversible effect to neurological functions, whereas chronic exposure in adults causes high blood pressure, damage to the cardiovascular system, neurotoxicity, and cancer development [31–33]. As is well known for being toxic to living organisms [34–36]. In humans, the adverse effects on As ingestion are nausea, stomach pain, bloating, diarrhea, and problems related to the kidneys, liver, skin, and prostate cancer [37,38]. Cd, more than other heavy metals, is toxic at very low concentrations to plants, humans, and animal health. It causes serious diseases in humans if ingested through the food chain [39–41], such as high blood pressure and constant pain caused by cancer disease [40,42–44]. Chronic Cd exposure can cause the deterioration of the kidneys, liver, skeletal, and cardiovascular system, as well as vision and hearing loss and the development of malignancies of the lungs, breasts, prostate, pancreas, urinary bladder, and nasopharynx [45–49]. Heavy metals alter the Zn metabolism, resulting in Zn insufficiency, which can disturb the function of the pituitary, thyroid, adrenal glands, ovaries, and testicles, reducing fertility [22]. Removing heavy metals from the soil, including Cd [50], can be carried out through physical, chemical, and physiochemical remediation technologies to increase the soil's pH [51].

Soil contamination with heavy metals has become a globally major environmental concern due to the increase in industrialization and agriculture [16,52]. Globally, over 20 million hectares of soil are contaminated with As, Cd, Cr, Hg, Pb, Co, Cu, Ni, Zn, and Se, with concentrations above the regulatory levels [19]. Industrial processes such as mining and metallurgy are the main causes of heavy metal enrichment [19]. Over 100 billion tons of mining wastes are generated globally per year [53]; the main waste stream is tailings, a mixture of non-economical crushed rock and processing fluids generated from a mill, washery, or concentrator during mineral processing that often contain potentially hazardous contaminants [54,55]. Land contamination with heavy metals has become a major environmental problem worldwide [12,56–59], and there are serious issues regarding soil pollution in Romania. There were 108 tailing ponds and 1101 sterile dumps inventoried in Romania, of which 180 sterile dumps are situated in Maramures County [60].

Maramures County (Romania) has a long history of exploiting non-ferrous minerals; mining has been an important source of income for the county's inhabitants for centuries. After the Union of 1918, the metal mines in the Baia Mare region dealt in gold and silver, lead, copper, zinc, and pyrite mining [61–63]. The materials extracted from the mines were subjected to a mineral concentration process in treatment plants. Pre-concentration was an important factor in the mining industry and was applied in mines around the world [64]. The flotation method caused the accumulations of wastes that were generated in tailing ponds and dams [65]. The mining waste deposits and mines closed down their activity one at a time due to a failure to adhere to the environmental commitments assumed by Romania through the Treaty of Accession to the Union European Parliament on 1 January 2007. The polymetallic sulfide ores extracted in underground mining works were processed without environmental concerns, and the generated waste rocks and tailings

were simply deposited in the vicinity of the exploitation areas [66–68]. Plenty of these mining sites were abandoned for many years under the action of erosive agents, leading to the spread of trace elements and the contamination of soils, waters, and sediments with heavy metals [69]. Some of these mining sites have undergone rehabilitation actions, mostly using constructive techniques such as coastal fences beyond which the saplings were planted, but no additional maintenance works were carried out [70]. Many sterile waste dumps were left in Maramures and the surrounding area of Baia Mare, posing a serious threat to the environment due to a failure to seal their contents and prevent the mobilization of heavy metal, and revegetate the abandoned sites [54,70–72].

One of the critical areas in Maramures County, determined by the historical pollution resulting from mining and metallurgical activities, is situated in the Baia Mare municipality and is represented by arsenic pyrite deposits located near the former Central Flotation [63,73–75]. Detailed knowledge of the characteristics of the accumulated wastes is required to carry out the remediation of the contaminated sites [65]. Therefore, it is necessary to evaluate the trace element concentration levels of the contaminated sites. The analysis of this study has been carried out using a promising tool for the quantitative detection of elements [76]: inductively coupled plasma optical emission spectrometry (ICP-OES). This technique stands out due to its versatility and detection capacity [77].

The contaminated sites must be treated with the best available techniques to recover the ecosystem's functions. The efficiency of the remediation of a contaminated site depends on the characteristics of the site, such as the degraded physical structure and poor nutritional status, a high concentration of trace elements and low pH, contaminant type as a consequence of the pyrite oxidation, and acid drainage, physicochemical interactions among the contaminants that might create new and unexpected problems and site-specific conditions, such as soil type and the depth of groundwater table from the surface, costs, and the final destination use of the soil [7,78].

Removing heavy metals from contaminated environments can be carried out through different treatment methods such as acid leaching, soil washing, physical or chemical separation of the contaminants, electrochemical treatment, electrokinetics, chemical treatment, thermal or pyrometallurgical separation, biochemical processes [79–83], treatments by activated carbon adsorption, microbes' usage, air stripping [84,85] and the biosorption treatment [80]. Most techniques used to remediate the sites contaminated with heavy metals are effective, but they require high costs [79], are laborious and complicated [85], have limited applicability to soil remediation [4,86], do not allow the natural recovery of soil and are time-consuming [87,88].

The aim of this paper is to characterize the studied area by the determination of heavy metal concentrations from the affected site in order to determine if it requires remediation.

## 2. Materials and Methods

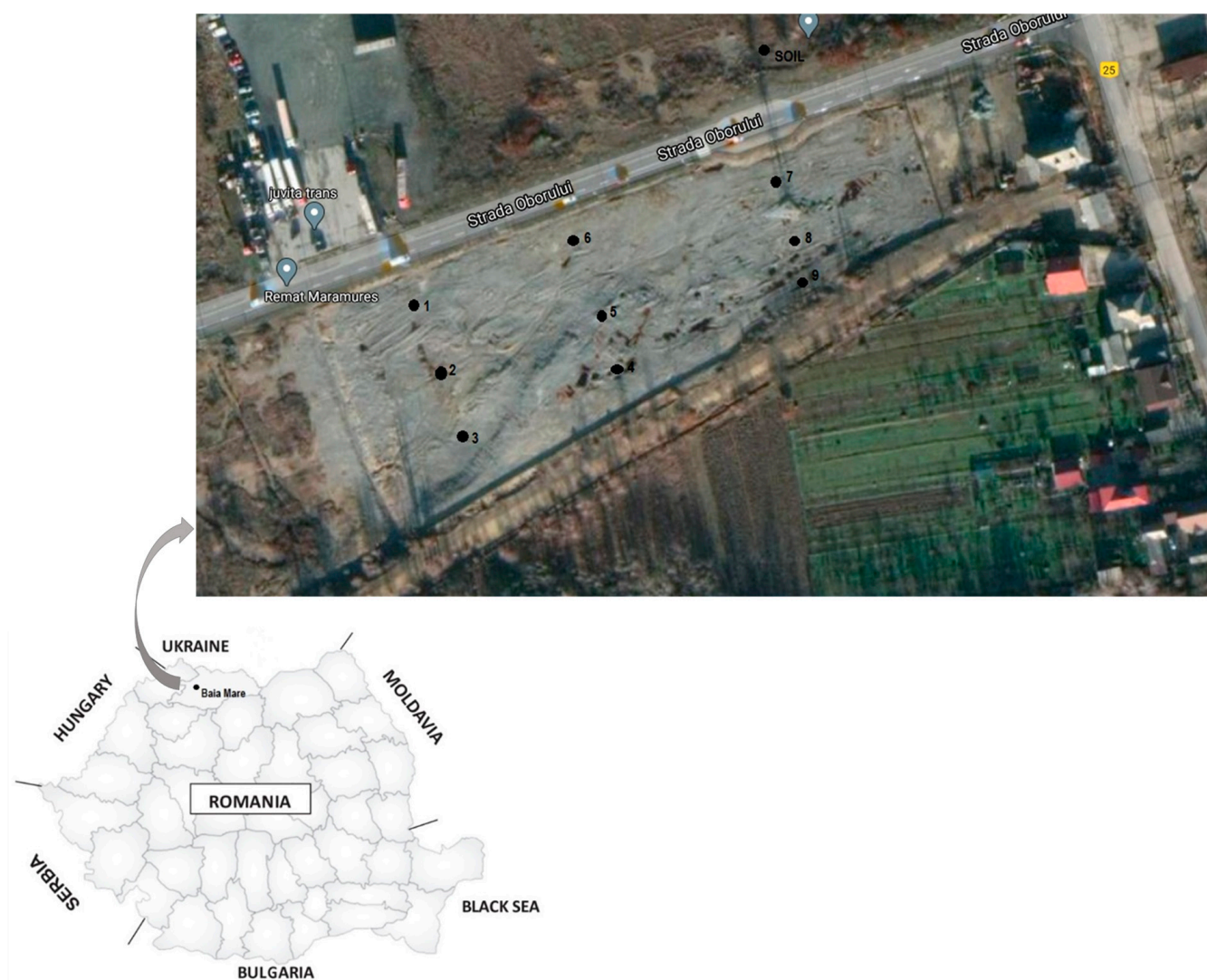
### 2.1. Baia Mare Area

The studied site is located in the Baia Mare area in Romania, Maramures County. The types of soils present in the South-Eastern part of the Baia Mare area affected by the metallurgical industry are eutricambosol, typical luvisol, stagnic, gleyic luvisol, and aluviosols [89,90].

The Metallogenetic district of Baia Mare is spatially and genetically associated with the volcanoes of the Gutâi Mountains due to their predominantly polymetallic character [91,92]. The southern side of Gutâi and Tibleş Neogene eruptive is composed of volcanic rocks with gold ores and non-ferrous metals [93–95] such as lead, zinc, copper, etc. The characteristic activities of the mining industry that were taking place in Baia Mare caused historic pollution with a significant impact on the quality of the environment, affecting long-term environmental factors through the presence of heavy metals [96–98]. So, there is a pressing need for sample analysis of the lands contaminated with heavy metals in order to determine the boundaries of polluted areas, control pollution, and remediate the areas affected by heavy metals [99].

## 2.2. Site Location and Sample Collection

The sampling site ( $47^{\circ}65'15.4''$  N,  $23^{\circ}61'66.5''$  E) is the emplacement of a former sterile dump located in the industrial area of the Baia Mare municipality, very close to the Central Flotation of Baia Mare. In order to characterize the material from the studied emplacement, a total of 27 sterile samples (Figure 1) and 1 soil sample was collected. The collection of the sterile material samples was performed from 9 sampling points noted from 1 to 9 and from a total depth of 0 to 60 cm (A: 0–15 cm, B: 15–30 cm, and C: 30–60 cm). Because the sterile site is plated with limestone, taking samples deeper than 60 cm is not possible; these points were located after numerous excavations, where perforations were found in the limestone.



**Figure 1.** Sampling points on the studied site in Baia Mare, Romania.

The sampling was carried out according to the methodological norms stipulated in STAS 7184/1-75 [100].

The sterile material that was situated in the dump (Figures 2 and 3) consisted of gold pyrite mining concentrate that could not be exploited in Romania due to the lack of technology, folded with European environmental requirements. This concentrate was sold abroad between the years 2013 and 2016, where the non-ferrous precious metals were extracted by cyanide or frying.





**Figure 2.** The sterile dump in Baia Mare, Romania (<https://www.google.ro/maps> (accessed on 23 March 2021)).



**Figure 3.** The site of the sterile dump in Baia Mare, Romania (photo: I.A.P.).

### 2.3. Sample Preparation and Analysis

Prior to the determination of the physico-chemical parameters, the samples were dried at room temperature for about 2 weeks in the laboratory of Procedures and Remediation Equipment for Soil at the Technical University of Cluj Napoca (Romania).

The texture of the samples was determined by the experimental separation of the granulometric fractions using the sieving method, which consists of separating the granules according to their size (in granular fractions) by sieving with screeners and sieves of the non-cohesive soils. The methods for determining the granulometry are standardized in Romanian legislation according to STAS 1913/5-85 [101]. For each sample, the granulometry was determined using a Retsch AS 200 sieving machine with 5 sieves (250  $\mu\text{m}$ , 500  $\mu\text{m}$ , 1 mm, 2 mm, 4 mm).

The pH of the samples was determined using a multiparameter, Multiline IDS-3430, an aqueous solution of sterile, and the respective soil, with a mass:soil to water ratio of 1:10. The pH was determined according to STAS 7184/13-88 [102] and ISO 10390:2021 [103,104]. Thus, the following methodology was used for the pH determination of the samples: 10 g from each sample was weighed on the balance to the accuracy of 0.1 g and placed in 100 mL glasses, to which 100 mL of distilled water was added. After this, the suspensions were homogenized by stirring for 5 min; then, they were left to equilibrate with  $\text{CO}_2$  in the atmosphere for approximately 2 h. After each measurement, the electrode was washed with distilled water.

The structure of the samples was determined using the Sekera method, which refers to the determination of the hydrostability of the soil macrostructure. The aggregates condition was examined and compared by providing marks from 1 to 6 according to a support board using the Sekera method [105]. The assessment of the stability of soil aggregates subject to water action was standardized at an international level in ISO 10930:2012 [106].

The physical and chemical properties of the samples were determined in the laboratory of Procedures and Remediation Equipment for Soil at the Technical University of Cluj Napoca from Romania. The heavy metal concentrations contents were determined in the laboratory of the Institute of Research for Analytical Instrumentation in Cluj Napoca (Romania), using the ICP-OES technology. Each analyzed sample was prepared according to the SR ISO 11464:2006 standard [107] regarding soil extractions of trace elements in aqua regia, as follows: the fraction of less than 2 mm was subsampled by quartering, grounded, and passed through a 150  $\mu\text{m}$  sieve. Then, 3 g of each sample was weighed to the accuracy of 0.001 g and placed in 100 mL Berzelius glasses and moistened with 0.5 to 1.0 mL of distilled water. A total of 21 mL of concentrated hydrochloric acid (HCl) were then added with stirring and then by dripping 7 mL of concentrated nitric acid ( $\text{HNO}_3$ ). The glasses were covered with a watch glass and left in the niche for mineralization. After the disaggregation on the sand bath, the samples were cooled and passed through filter paper into 100 mL volumetric flasks, washing the filter paper until homogenized.

The concentrations of nine heavy metals were determined in the samples using an inductively coupled plasma optical emission spectrometer (ICP-OES) according to ISO 22036:2008 standards [108]. Each sample was measured 3 times, and the paper shows the average data of these measurements.

### 3. Results and Discussions

#### 3.1. Physical and Chemical Properties of Samples

Depending on the size of the particles, the granularity of a material can be determined using direct measurements, sieving, sedimentation, or a combined method (sieving and sedimentation) [109]. The experimental granulometry determinations using the particle separation by sieving showed that the texture of the sterile samples was mostly made of sand (80.73%) mixed with dust (19.27%), and the soil sample was made of 95.53% sand mixed with 4.47% dust. The results in the sterile samples are presented as the arithmetic means for the coarse sand (>0.2 mm) and fine sand (0.2–0.02 mm) in each of the sampling points from the total depth of 0 to 60 cm (Figure 4).

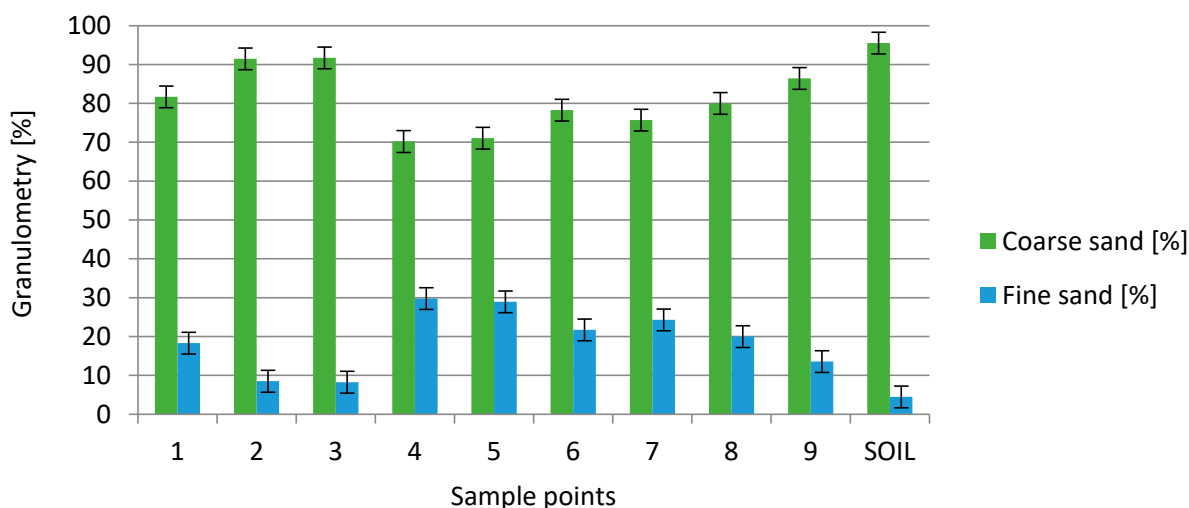
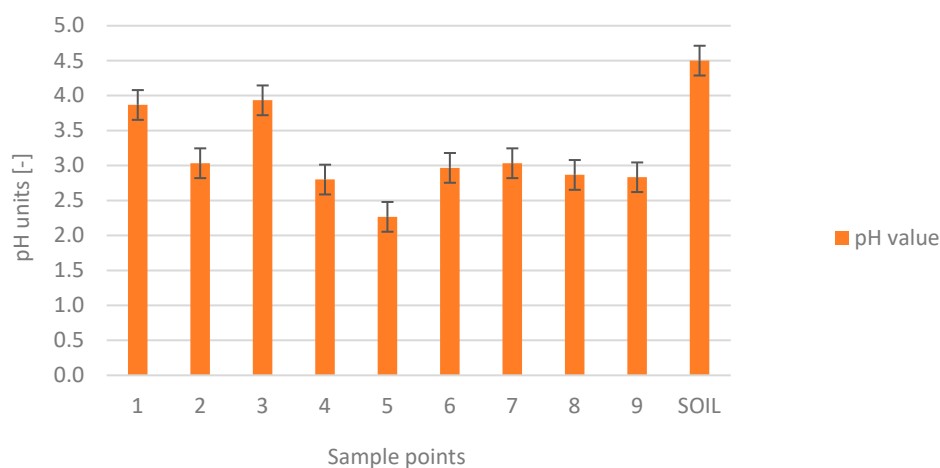


Figure 4. Variation of coarse and fine sand in the samples [%].

In the east of Baia Mare, where the sterile from the Central Flotation plant was stored, the pH in the groundwater samples near the pond ranged between 4.0 and 7.9 [110]. Our experimental analyses showed that the average pH in the sterile samples from each point of the total depth of 0 to 60 cm (A: 0–15 cm, B: 15–30 cm, and C: 30–60 cm) (Figure 5) was predominantly extremely acidic ( $\leq 3.5$ ) and the soil pH was strongly acidic (4.5).



**Figure 5.** Values of pH in the collected samples.

The analysis of the structural condition of the aggregates using the Sekera method showed that the samples collected from the site of the former sterile dump were poorly structured and the soil sample was well structured.

### 3.2. Trace Elements

The values of the concentrations for the elements analyzed with ICP-OES in the sterile samples are presented in Table 1.

**Table 1.** The results of the ICP-OES determinations of the heavy metal concentrations from samples collected from the Baia Mare mining area.

Sample	Metal Concentration [mg kg <sup>-1</sup> ]								
	Cd	Cr	Zn	Cu	Mn	Pb	Fe	Ni	Co
1A	274	14.2	733	1126	53.0	492	7710	12.0	9.93
1B	339	12.4	743	1241	50.2	942	7887	36.6	11.6
1C	327	11.0	1273	1913	179	305	7593	17.7	15.9
2A	144	6.67	759	849	51.5	1073	7327	8.73	9.10
2B	128	16.7	615	543	95.7	1364	7067	10.8	6.13
2C	5.77	17.3	735	64.5	212	109	6733	14.3	13.5
3A	95.8	11.5	617	463	87.3	280	7637	9.70	7.23
3B	7.77	24.5	489	211	168	165	6483	12.9	5.07
3C	7.00	20.4	251	48.1	262	165	6837	10.4	5.70
4A	130	2.07	587	444.7	28.6	268	8090	9.77	10.9
4B	349	7.27	593	1036	37.5	200	7720	11.3	11.2
4C	353	12.7	973	1973	120	331	7650	16.1	16.2
5A	166	1.70	426	242	14.0	243	79,167	10.2	13.5
5B	429	19.6	572	335	21.2	267	76,307	17.2	11.9
5C	568	8.23	614	535	30.0	266	79,907	12.4	13.4
6A	165	18.1	644	479	43.2	185	78,407	11.9	8.07
6B	270	20.0	934	2228	178	275	74,700	13.4	12.1
6C	183	21.6	1365	2537	483	211	7406	17.5	14.8
7A	495	92.2	962	4203	38.5	362	7650	20.4	12.6
7B	438	51.8	846	4576	32.8	453	7740	18.1	12.6
7C	323	23.1	1106	4217	141	368	7907	18.9	14.9
8A	277	122.2	953	4683	51.8	95.5	7790	35.4	12.7
8B	465	139.3	1281	5067	63.7	76.4	7670	26.1	13.8
8C	146	49.7	1035	8883	148	2068	7076	27.7	11.7
9A	285	126.1	923	4540	53.5	586	7943	29.3	8.57
9B	309	154.4	1203	6883	81.8	269	7673	38.2	15.2
9C	86.8	79.1	1033	6700	233	1818	7393	29.2	10.4
SOIL	2.13	25.6	269	301	74.5	393	6437	10.2	3.40

According to Order 756/1997 [111], the concentrations of the heavy metals in the samples presented in Table 1 exceed the normal value for Cr, Ni, and Co; the normal value and the alert threshold are exceeded for Zn; the normal value, the alert, and the intervention thresholds are exceeded for Cd, Cu, and Pb.

Cadmium in all the samples exceeded the normal value ( $1 \text{ mg kg}^{-1}$ ) and the alert threshold of Order 756/1997 ( $5 \text{ mg kg}^{-1}$ ), except for the soil sample. According to Order 756/1997, all samples also exceeded the intervention threshold ( $10 \text{ mg kg}^{-1}$ ), except for samples 2C, 3B, 3C, and the soil sample.

Chromium is below the alert threshold ( $300 \text{ mg kg}^{-1}$ ) and the intervention threshold ( $600 \text{ mg kg}^{-1}$ ), but it is also found in concentrations that exceed the normal value ( $30 \text{ mg kg}^{-1}$ ), in samples 7A, 7B, and in sampling points eight and nine (highest Cr concentrations).

Zinc concentrations exceed the normal value specified in Order 756/1997 ( $100 \text{ mg kg}^{-1}$ ) in all the samples and also the alert threshold ( $700 \text{ mg kg}^{-1}$ ), except for samples 2B, 4A, 4B, 6A, SOIL, and in sampling points three and five.

Copper was found in concentrations that exceeded the normal value ( $20 \text{ mg kg}^{-1}$ ) in all the samples and also the alert threshold ( $250 \text{ mg kg}^{-1}$ ), except for samples 3B, 3C, and 5A. The intervention threshold ( $500 \text{ mg kg}^{-1}$ ) was exceeded in all samples except for sampling point three and samples 2C, 4A, 5A, 5B, 6A, and SOIL.

Manganese concentrations in the samples were below the normal value ( $900 \text{ mg kg}^{-1}$ ). Lead had concentrations that exceeded the normal value ( $20 \text{ mg kg}^{-1}$ ) in all the samples. The alert threshold ( $250 \text{ mg kg}^{-1}$ ) was exceeded in sampling points one, seven, and nine and in samples 2A, 2B, 3A, 4A, 4C, 5B, 5C, 6B, 8C, and SOIL. The intervention threshold ( $1000 \text{ mg kg}^{-1}$ ) was exceeded in samples 2A, 2B, 8C, and 9C.

Nickel concentrations exceeded the normal value ( $20 \text{ mg kg}^{-1}$ ) in samples 1B, 7A, and point eight and nine. Cobalt was below the normal value ( $15 \text{ mg kg}^{-1}$ ), except for samples 1C, 4C, and 9A.

The results for the elements analyzed with ICP-OES in all sterile samples (mean, median, minimum, and maximum values) are presented in Table 2.

**Table 2.** Statistical ICP-OES data: mean, minimum, maximum, median, and standard deviation. Values of concentration are expressed in  $\text{mg kg}^{-1}$ .

Element	Mean	Minimum	Maximum	Median	Standard Deviation
Cd	250.65	5.77	568.33	274.10	154.31
Cr	40.13	1.70	154.37	19.57	46.04
Zn	824.76	250.90	1365	759.33	281.17
Cu	2445.32	48.07	8883.33	1241.00	2475.62
Mn	109.60	13.97	482.67	63.67	102.70
Pb	490.41	76.37	2067.67	275.17	516.98
Fe	7549.26	6483.33	8090.00	7650.00	401.21
Ni	13.78	8.73	38.20	16.07	8.94
Co	11.44	5.07	16.17	11.93	3.11

According to the Romanian legislation of the Ministry of Water, Forests, and Environmental Protection (Ord. 756/1997) [112] regarding the assessment of environmental pollution, the intervention thresholds for soils with less sensitive use are  $10 \text{ mg kg}^{-1}$  Cd,  $600 \text{ mg kg}^{-1}$  Cr,  $1500 \text{ mg kg}^{-1}$  Zn,  $500 \text{ mg kg}^{-1}$  Cu,  $4000 \text{ mg kg}^{-1}$  Mn,  $1000 \text{ mg kg}^{-1}$  Pb,  $500 \text{ mg kg}^{-1}$  Ni, and  $250 \text{ mg kg}^{-1}$  Co.

Thus, according to Order 756/1997, and by analyzing the mean concentrations in the samples, it is clear that the heavy metal means concentrations for Cd and Cu in the sterile samples were above the intervention thresholds for soils with less sensitive use, Zn and Pb were above the alert threshold, and Cr was above the normal value. In addition, the heavy metals concentrations varied from sample point to sample point and also with depth.

Tailing particles sizes are mostly without gravel ( $<2 \text{ mm}$ ) and clay ( $<3.9 \mu\text{m}$ ), with sand ( $625 \mu\text{m}$  to  $2 \text{ mm}$ ) being more common than silt ( $3.9\text{--}625 \mu\text{m}$ ) and with a bulk density



of 1.8–1.9 t/m<sup>3</sup> [112]. The texture of the sterile dumps influences the permeability of the sterile material. A coarse texture allows heavy metals to migrate to greater depths than a fine texture, and it allows an intensive flow of substances from the soil via water, leading to the poor retention of the substances [71,72]. The sterile material collected from the site has a clay-like texture.

The consequence of mining sterile deposits originating from the Central Flotation plant of Baia Mare is the significant lead and copper pollution of the groundwater with contents higher than the intervention threshold [110]. The degradation of natural components and the high degree of the remnant landscape caused by anthropogenic intervention in the studied area has negative consequences on aesthetic evaluations [113]. Usually, in quantifying trace elements, high concentrations of As, Cu, Pb, and Zn are present in the tailings, and if Zn is high due to the chemical similarity, Cd is also analyzed [54]. The pollution status and probabilistic health risks of heavy metals in soils associated with Cu mining sites worldwide show that arsenic is the main contributor to non-carcinogenic risk, while Cu has the highest exceedance of carcinogenic risk [114].

The mean concentrations of heavy metals in the Baia Mare studied site is 1.9 times higher for Zn and 19.28 times higher for Cd than the highest concentration measured in samples collected from the sterile dump next to the closed Tarnița barite mine in Suceava, Romania [115]. The mean concentration for Cd determined in this study was 15 times higher than the highest concentration determined in the urban soils of Baia Mare [116]. Similar concentrations, determined by ICP-OES, were reported in the Aquisgrana (Spain) sludge dam, with values of 544 mg kg<sup>−1</sup> As, 987 mg kg<sup>−1</sup> Mn, 8065 mg kg<sup>−1</sup> Pb, and 5186 mg kg<sup>−1</sup> Zn [117]. The mean ICP-OES heavy metal concentrations in the samples collected from the studied site are 11.95 times higher for Cd, 33.56 times higher for Cu, and 25.26 times higher for Pb than the mean concentrations of heavy metals in the Wadi Jazan area of southwestern Saudi Arabia affected by agriculture and industries [118].

The storage of the sterile from the Central Flotation plant has a very important impact both on the environment and on human health, polluting the groundwater and surface waters intensively with heavy metals and affecting the flora and fauna [110]. In different countries, heavy metal pollution affects the quality of the water used for irrigation, livestock, and drinking [8]; human health through a very high cancer risk caused by the drinking of groundwater, vegetables, eggs, and meat consumption [119,120]; children are more likely to be affected with a substantially higher risk of epistaxis, colic chronic, dermatological changes, mood changes, the presence of white lines on the nails, and visual field loss [121,122].

#### 4. Conclusions

The issue of the remediation of the studied contaminated area caused by industrial and mining operations is highlighted since it presents a risk to human health, ecosystems, and environmental factors. The proactive isolation of tailings is a priority, as is the prevention of their entry into groundwater, rivers, lakes, and wind to avoid the contamination of food chains and drinking water. The texture of the studied site in the sterile samples is made of 80.73% sand with 19.27% dust, and in the soil, 95.53% sand is mixed with 4.47% dust. The pH in the sterile material is predominantly extremely acidic ( $\leq 3.5$ ), while the soil is also strongly acidic (4.5). The sterile dump is poorly structured, and the soil sample is well structured. Heavy metals are a danger to the soil, water, and humans. Heavy metal contamination has serious effects on human health and is harmful because of its toxicity, persistence, and bioaccumulation. The heavy metal determinations of the collected samples were performed using the inductively coupled plasma optical emission spectrometry technique (ICP-OES), which is versatile and accurate in heavy metal detection. The use of the ICP-OES analytical method allows the formation of an overall report of the characteristics of the studied location. The heavy metal concentration levels of the sterile dump in the Baia Mare area were analyzed and determined. The results of the heavy metals concentrations revealed that the sterile samples have high heavy metal

levels, with mean concentrations of  $250 \text{ mg kg}^{-1}$  Cd and  $2445.32 \text{ mg kg}^{-1}$  Cu and that most of the collected samples are severely contaminated and excessively polluted with heavy metals with negative effect potentials on plants and the environment. Low-cost and environmentally safe strategies are needed to remediate the affected area.

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