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An Experimental Investigation of the Environmental Risk of a Metallurgical Waste Deposit

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Abstract: The aim of this study is to investigate the environmental risk of long-term metallurgical waste disposal. The investigated site was used for the open storage of lead and zinc waste materials originating from a lead smelter and refinery. Even after remediation was performed, the soil in the close vicinity of the metallurgical waste deposit was heavily loaded with heavy metals and arsenic. The pollutants were bound in various compounds in the form of sulfides, oxides, and chlorides, as well as complex minerals, impacting the pH values of the investigated soil, such that they varied between 2.8 for sample 6 and 7.34 for sample 8. In order to assess the environmental risk, some eight soil samples were analyzed by determining the total metal concentration by acid digestion and chemical fractionation of heavy metals using the BCR sequential extraction method. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine six elements (As, Cd, Cu, Pb, Zn, and Ni). Total concentrations of the elements in the tested soil samples were in the range of 3870.4–52,306.18 mg/kg for As, 2.19–49.84 mg/kg for Cd, 268.03–986.66 mg/kg for Cu, 7.34–114.67 mg/kg for Ni, 1223.13–30,339.74 mg/kg for Pb, and 58.21–8212.99 mg/kg for Zn. The ratio between the mean concentrations of the tested metals was determined in this order: As > Pb > Zn > Cu > Ni > Cd. The BCR results showed that Pb (50.7%), Zn (49.2%), and Cd (34.7%) had the highest concentrations in mobile fractions in the soil compared to the other metals. The contamination factor was very high for Pb (0.09–33.54), As (0.004–195.8), and Zn (0.14–16.06). According to the calculated index of potential environmental risk, it was confirmed that the mobility of Pb and As have a great impact on the environment.

Keywords: lead production waste; remedy; environmental risk; BCR sequential extraction

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1. Introduction

Mining and metallurgy waste deposits represent a risk to the environment. However, even after the remediation of the waste deposit site was performed, there was an impact of long-term heavy-metal pollution that had penetrated into the soil and nearby water flow. The metallurgical waste deposit was situated in the open space, between the tailing waste deposit of Žitkovac and the flow of the Ibar River. Primary lead and zinc metallurgy production generate lead-containing waste from lead smelters and refineries, including pyrite roasting residue, lead ash, lead slag, lead-containing dust from the refinery, lead anode slime, and lead sludge during the zinc electrowinning process, [1–3]. The authors focused on the possibilities for Pb stabilization in sludge at lower temperatures in pyrometallurgical processes by using sulfur compounds, as well as SiO_2, CaO, TiO_2, and Al_2O_3 [4]. The leaching of heavy metals, especially lead and arsenic, was investigated in secondary alkaline lead slag as form of hazardous waste due to its solubility and mobility along the depth column [5]. The authors proposed a process for As removal and Pb immobilization.

The use of different leaching methods was investigated as a valuable method for extracting Pb and Zn from the fly ash [6]. Several authors have also investigated the revalorization of lead from lead scrap and lead paste from spent lead-acid batteries [7,8]. Lead production waste presents a large negative impact to the ecosystems and human health if not adequately managed [9,10]. On the other hand, lead-containing waste usually contains valuable metals [11], and primary lead production is decreasing. The most commonly used process for primary lead production is the pyrometallurgy process. Industrial waste is generated by primary lead production in the pyrometallurgical process, starting from lead sulfide roasting and lead oxide reduction in the shaft furnace. The raw lead is then refined by segregating the impurities as residual mixtures from the refining process. For many decades, this industrial waste was stored in an open field. Even after remediative action was taken, there remained a significant amount of heavy metal content in the upper soil level, which had penetrated from the waste storage and was polluting the environment.

The specific nature of the metallurgical waste was a source of the unusual behavior of heavy metals and arsenic on the soil surface and along the depth column in the base of the industrial landfill. The tailings were formed during different processes, including the use of different agents for oxidizing and refining the raw lead. The smelting of lead involves several elements that are required to reduce the various forms of lead (mainly lead oxide and lead sulfates) into metallic lead, such as neutralizing agents like caustic soda, soda ash, or lime, and fluxing agents, which are used to capture sulfur and improve lead recovery. The removal of impurities and other metals from the crude lead (S, Cu, Ni, As, Sb, Bi, Ag, Au, etc.) requires elementary sulfur for copper removal; tin (Sn) is next removed by either chlorine (Cl_2) or ammonium chloride (NH_4 Cl) oxidation, producing tin chloride ($SnCl_2$) skims. Arsenic (As) and antimony (Sb) are selectively removed by oxidation with a mixture of sodium nitrate ($NaNO_3$) and sodium hydroxide (NaOH). Those skims are a mixture of oxides (25% Sb, 10% As, and 65% Pb). Silver (Ag) comes next, and its removal is carried out via the Parkes process, by which the excess zinc is removed from the de-silvered lead by vacuum distillation and then by sodium hydroxide (NaOH). The industrial waste originating from this procedure was deposed as produced, randomly, and the pollutants' penetration and distribution in the soil, after the cleaning process, was investigated here. Heavy metals and arsenic were bonded into sulfides, oxides, chlorides, carbonates, and complex compounds, and the investigations were aimed at determining heavy metal and arsenic behavior in the soil column based on mineral composition.

To assess the mobility and bioavailability of the toxic elements, their chemical and mineralogical composition is needed. The assessment includes several extraction steps [8,12]. In the literature data, there are two most-commonly used procedures, one developed by Tessier et al. [13], and the other, which has been set by the Community Bureau of Reference (BCR) [14]. Many researchers have investigated this problem, and there are different methods used to assess the potential ecological risk and pollution indices [15]. In the case of heterogeneous material, the indices of each pollutant are used to evaluate the combined environmental risks [16,17]. The sequential extraction procedure was recently used for the identification of metals in heavily polluted soils [18,19]. Min et al. [20] performed an environmental risk assessment on zinc leaching residue using the modified Community Bureau of Reference (BCR) three-stage extraction procedure. Yang et al. [21] investigated the potential extraction of As, Pb, and Zn from tailing waste deposits using acidic and alkaline solutions. The original BCR procedure uses acetic acid for ion exchangeable fraction (BCR 1), hydroxylamine hydrochloride ($NH_2\,OH \cdot HCl$) for reduction (BCR 2), and hydrogen peroxide ($H_2\,O_2$) for oxidation (BCR 3) [11]. The modified BCR procedure provided evidence on how the metals are associated with the different compounds that affect their availability in soil and sediments. The metals' availability decreases with every extraction step of the BCR procedure, as reported by several authors [12,14,22–24], and at the same time, there are studies reporting that the bioavailability increases [12,16,19–21,23]. The term "bioavailability" has not yet been defined precisely [2,25]. So, bioavailability is seen as a dynamic process, depending on the ecosystem, exposure paths, metals, and soil properties [26–28]. This study was performed in order to understand the pollutant behavior in the investigated land, considering its previous purpose as a metallurgy waste deposit, for its huge range of pH values and variations in the mineralogical compositions of the pollutants.

2. Materials and Methods

2.1. Study Area

The Gater Landfill is located in the alluvium along the Ibar River, north of the central part of Zvečan (Figure 1). It is irregular and very elongated in shape, measuring about 480 m long at the longest part, and ranging from 80 m wide at the narrowest part to approximately 160 m at the widest part. It is bounded on the south by the Zvečan–Raška Road, on the west by the embankment and the Zvečan–Zubin Potok Road, on the north by the road and the tailings field of Flotation Tailings (which has been partially rehabilitated and recultivated as a part of the process in RMHK "Trepča"), and on the east by the Kosovo Polje–Beograd railway. The altitude (absolute) is between 490 and 500 m, and in relation to the surrounding terrain, it is almost flat, with certain deviations, which range from 0.5 to 2.5 m. In addition, the part towards the West is a hill that is barely elevated, while in the extreme part on the north side, there is a large excavation, about 2–2.5 m deep, which was created during the last cleaning of the landfill.

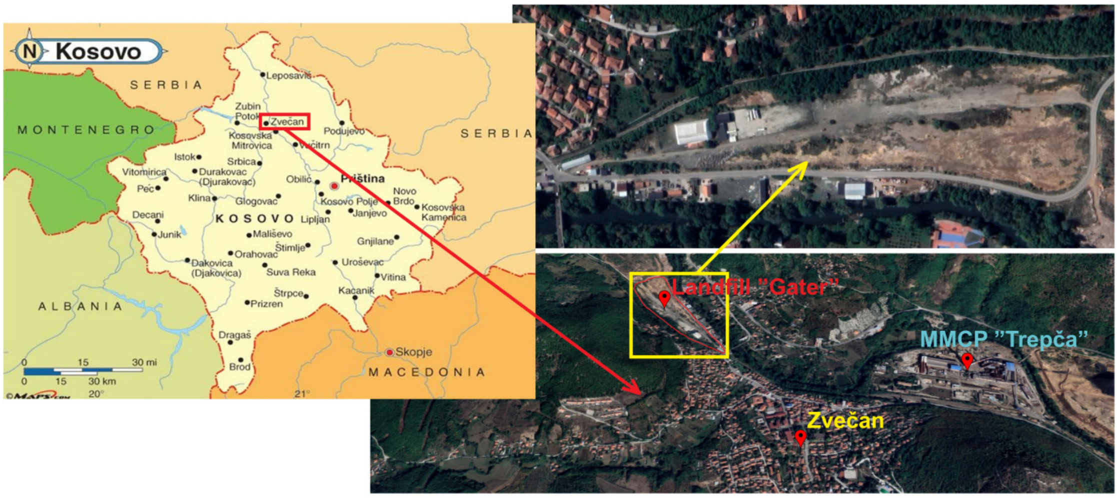

Figure 1. Location of the Gater Landfill in relation to settlements and industrial facilities.

The surface of the landfill is mostly composed of hardened tailings, partly fine and very fine granulation, almost sandy in appearance, reddish-brown to dark-brown in color, and white in places where lead chloride is present.

There is a minimal number of plant species at the landfill. Fauna is not present; there are no nests, resident birds, or migrants, and no settlements of any species of mammals or reptiles have been observed.

The proximity of the Ibar River, which is only 20–30 m from the landfill, indicates that the penetration of toxic substances is possible due to the deposited material and alluvium, especially in a high-water regime when groundwater levels rise.

2.2. Soil Sampling

The samples were taken from locations which were determined based on several impacts: review of the reports of the Trepca Company on the deposited waste on the site, which was covering the investigated soil for 30 years; visual inspection of the site; and comparisons of the relief at the site with maps provided by the company for selected locations (Figure 2). The samples were collected in July 2021. The whole area was divided into eight sectors, with each being covered by a different waste composition, such that the samples could be considered as representative. The eight analyzed soil samples were taken from the surface at a depth of 50 cm, using a shorter probe of 1 m long of a type refered to as "meia–cana". The collected soil samples were air-dried indoors at room temperature for a week. After drying to constant weight, the soil samples were homogenized and then ground to a grain size <2 mm to determine soil properties and heavy metal concentrations. The prepared soil samples (1 g from each sample) were subjected to BCR sequential extraction procedures and pseudo-total concentrations of the heavy metals in the study area were determined.

Figure 2. Picture of the tailings with the sampling locations marked.

In the area that was not analyzed, there were changes on the surface of the tailings zone, so sampling was not possible. The material from that surface was deposited in the zone of sample No. 6. and was processed as decribed below.

The exact definitions of the sampling areas, with altitudes as well as with northern (N) and eastern (E) geographical coordinates, are given in Table 1.

Table 1. Altitude with northern (N) and eastern (E) geographical location.

Serial Number	Altitude, m	N, °	E, °
1.	499	42.91833	20.83206
2.	495	42.91859	20.83264
3.	494	42.91868	20.83312
4.	495	42.91808	20.83332
5.	495	42.91792	20.83377
6.	495	42.91790	20.83382
7.	498	42.91686	20.83277
8.	498	42.01671	20.83284

Devices with an accuracy of 0.5 m to a maximum of 2.8 m, based on the position of not less than 7 satellites, were used to determine the position of characteristic points, as well as to determine the altitude (absolute).

2.3. Sample Analyses

As part of the sampling procedure, numerous soil samples were collected from the surface (0–50 cm), and the paper presents 8 samples with high concentrations of heavy metals (Figure 1). The collected soil samples were air-dried indoors at room temperature for a week. After drying to constant weight, soil samples were homogenized and ground to a grain size <2 mm to determine soil properties and heavy metal concentrations. Standard methods were used for soil characterization. The pH and electrical conductivity (EC) were measured for the suspension of soil in distilled water (1 to 2.5 ratio). pH value was measured using a WTW inoLab ph/Cond 720, Knibbelweg 18C, NL-2761 JE Zevenhuizen (ZH), The Netherlands instrument (ISO 10309, 2005; ISO 11265, 1994). A multi-element stock solution containing 1.000 g/L of the elements (Ca, Mg, Na, and K) was used to prepare standard solutions for the inductively coupled plasma optical emission spectrometer (ICP-OES) measurements (iCAP 6500 Duo; Thermo Scientific, Loughborough, UK).

To determine the pseudo-total metal concentrations, 0.5 g of the unmilled sample was digested with aqua regia (15 mL 37% HCl and 5 mL 65% HNO_3) at 80 °C for 5 h. The digest was filtered through a filter paper and finally diluted to 50 mL with distilled water. 1-g metal concentrations were analyzed using an ICP-OES instrument (iCAP 6500 Duo; Thermo Scientific, Loughborough, UK) connected to a computer equipped with iTEVA software, 2009 Thermo Fisher Scientific, Cambridge CB5 8BZ.United Kingdom). Instrument operating parameters were as follows: radio frequency power, 1.150 kV; plasma gas, 12.0 L/min; auxiliary gas, 0.50 L/min; carrier gas, 0.50 L/min; and direction of view: axial. The selected wavelengths (in nanometers) were as follows: As (189.0); Cd (214.4); Cr (267.7); Cu (224.7); Ni (231.6); Pb (220.3); and Zn (202.5).

2.4. BCR Sequential Extraction

A modified BCR three-step sequential extraction procedure was used to analyze the fractionation of heavy metals in the soil samples. This method was described in detail by Rouret et al. [14]. In addition, there is the fourth step, performed by dissolving the final residue by the dysthenic process in the aqua medium (ISO, 11466, 1995). Table 2 gives a detailed overview of the reagents used and the analytical procedure. Each sample was analyzed in two copies, and each analysis consisted of three replicates. The sample was weighted at 1 g of soil. A shaking procedure of 16 h overnight at 20 ± 2 °C was used to obtain the extract. The extract was separated from the solid phase by centrifuge at 3000 rpm for 15 min, then filtrated through Whatman no. 42 filter paper. After each extraction step, each extract was filled up to 5 mL with 2% HNO_3 solution, and the residue was washed with 20 mL of deionized water without losing the solid residue.

Table 2. Modified BCR three-step sequential extraction procedure [29].

Extraction Step	Solid Phase	Extraction Procedure
BCR 1	Exchangeable, water, acid-soluble fraction	1 g of a soil sample, 40 mL of 0.11 mol/L CH_3COOH, shake 16 h at room temperature.
BCR 2	Reducible fraction	40 mL of 0.5 mol/L $NH_2OH{\cdot}HCl$ (pH = 1.5, 2 mol HNO_3), shake 16 h at room temperature.
BCR 3	Oxidizing fraction	5 mL of 8.8 mol/L H_2O_2 (pH 2), shake for 2 h at 85 °C, cool, then 25 mL of 1 mol/L CH_3COONH_4 (pH = 2, HNO_3 conc.), shake 16 h, room temperature.
Residual	Residual fraction	The pseudo-total minus the three fractions. The pseudo-total: digestion of 1 g sample in aqua regia (3 mL HCl + 1 mL HNO_3), shake for 16 h.

2.5. Quality Assurance of Data

In order to check the accuracy of the applied method for determining the pseudo-total metal concentrations in the examined soil samples, the certified reference soil material (GBV 07410) was analyzed using a Milestone ETHOS One Advanced Microwave Digestion

System with temperature control and according to ISO 11466 method, certified reference material GBV 07410 was digested in the aqua region, and the obtained results are shown in Table 3. The measured element concentrations showed good agreement with reference sample values. The obtained data were statistically compared with a two-pair *t*-test with the significance level of $p = 0.05$. The calculated t-value of 0.463 was lower than the critical value of 2.259.

Table 3. Results of pseudo-total metal content (mean ± standard deviation) for certified reference material GBW 07410 after digestion in aqua regia.

Element	Certified Value mg/kg ± σ (mg/kg)	Measured Value mg/kg ± σ (mg/kg)
Cd	0.09 ± 0.03	0.09 ± 0.05
Cu	23.2 ± 2.2	22.2 ± 0.5
Pb	29.2 ± 3.2	29.3 ± 1.8
Ni	27.6 ± 2.8	28.1 ± 1.1
Zn	72.8 ± 4.5	70.9 ± 1.3
As		

σ: standard deviation.

The efficacy of BCR three-step SEP was assessed by the analysis of BCR®-701 certified reference material of the European Commission Institute for Reference Materials and Measurements (Geel, Belgium). The results of determining the elements in the reference material BCR®-701 are presented in Table 4. Agreement between the declared and the measured concentrations of elements was observed, i.e., statistical comparison with a two-pair *t*-test with a significance level of $p = 0.05$, showed a calculated t-value of 1445, which is lower than critical (2107). Residual measurements also confirmed a satisfactory correlation with the declared indicative values (t-value 1886, t-critical 2570, $p = 0.05$).

Table 4. Quality control of sequential extraction data using the certified reference material, BCR®-701.

Extraction Step	Element	Certified Value (mg/kg) (Mean ± *U*)	Measured Value (mg/kg) (Mean ± *U*)
BCR 1	Cd	7.3 ± 0.4	8.44 ± 0.03
	Cr	2.26 ± 0.16	2.37 ± 0.06
	Cu	49.3 ± 1.7	63.0 ± 1.1
	Ni	15.4 ± 0.9	16.9 ± 0.1
	Pb	3.18 ± 0.21	3.54 ± 0.03
	Zn	205 ± 6	217 ± 4
BCR 2	Cd	3.77 ± 0.28	3.87 ± 0.06
	Cr	45.7 ± 2	44.8 ± 0.3
	Cu	124 ± 3	122 ± 2
	Ni	26.6 ± 1.3	27.1 ± 0.2
	Pb	126 ± 3	121 ± 2.5
	Zn	114 ± 5	108 ± 0.9
BCR 3	Cd	0.27 ± 0.06	0.28 ± 0.03
	Cr	143 ± 7	161 ± 3
	Cu	55 ± 4	53 ± 1.1
	Ni	15.3 ± 0.9	14.81 ± 0.07
	Pb	9.3 ± 2	8.61 ± 0.4
	Zn	46 ± 4	43 ± 2
INDICATIVE	Cd	0.13 ± 0.08	0.12 ± 0.2
	Cr	63 ± 8	50 ± 10
	Cu	39 ± 12	36 ± 4
	Ni	41 ± 4	38 ± 2
	Pb	11 ± 6	9 ± 4.5
	Zn	95 ± 13	94 ± 6

U: uncertainty (half-width of the 95% confidence interval).

2.6. Potential Ecological Risk of Metals

To assess soil contamination, many studies have confirmed the use of magnitude contamination factors C_f^i , representing the relationship between the concentration of heavy metals in the soil and pre-industrial reference levels, allowing for the assessment of soil pollution by heavy metals and arsenic [20]. The formula used to calculate the contamination factor of a single heavy metal in the soil is:

$$C_f^i \; = C^i{}_{simple} / C^i{}_{reference} \tag{1}$$

where C_f^i —is the pollution coefficient for a particular heavy metal, $C^i{}_{simple}$—is the measured concentrations of heavy metals in the analyzed soil samples, and $C^i{}_{reference}$—is a parameter to calculate. The values of the upper limits of heavy metals in the soil are based on the guidelines of the European Union [30]. The potential environmental risk factor (E_f^i) proposed by Hackanson [15] was used as a criterion for assessing the levels of heavy metal toxicity and ecological susceptibility to heavy metal pollution. The corresponding coefficients based on its toxicity were: Hg = 40, Cd = 30, Cu = Pb = Ni = 5, Cr = 2, Zn = 1, and metalloid As = 10 [31]. The formula for calculating the potential environmental risk factor for individual heavy metal pollution is:

$$E_f^i = \mathrm{C}_f^i \times \mathrm{T}_f^i \tag{2}$$

where T_f^i is the toxicity factor of a single heavy metal. The formula for the index of potential toxicity reaction for various heavy metals is:

$$R \; = \; \Sigma\, E_f^i \tag{3}$$

Standards for assessing the potential environmental risk of heavy metals are listed in Table 5.

Table 5. Relationship between potential toxicity index I, potential ecological risk index (E_f^i), and pollution level [29].

Scope of Potential Ecological Risk Index (E_f^i)	Ecological Risk of Single-Factor Pollution	Scope of Potential Toxicity Index I	General Level of Potential Ecological Risk
$E_f^i < 40$	Low	$R < 150$	Low grade
$40 \leq E_f^i < 80$	Moderate	$150 \leq R < 300$	Moderate
$80 \leq E_f^i < 160$	Higher	$300 \leq R < 600$	Severe
$160 \leq E_f^i < 320$	High	$600 \leq R$	Serious
$320 \leq E_f^i$	Serious		

3. Results and Discussion

3.1. Physical and Chemical Analysis

Analytical values of the studied chemical properties for soil samples in the study area are shown in Table 6. According to the pH value, soil samples taken from layers from a depth of 0–50 cm are acidic to moderately alkaline chemical reactions. The pH value of the soil varies from acidic (2.80–5.23) to slightly alkaline (6.43–7.34), but the majority of the soil samples were found to be acidic (mean 5.34). For samples 5 and 6, the pH value of 2.80 pH units was determined, while samples 2 and 8 were moderately alkaline reactions and contained the highest values of free calcium. The specific electrical conductivity ranged from 61.5 to 2630 mS/cm, with a mean value of 978.47 mS/cm. pH value is the most important property of soil, whose values are a function of organic matter, clay, and dominant cations (Na^+, NH^{4+}, Ca^{2+}, and Mg^{2+}) in the soil. Values range from 3 to 8, and the solubility and availability of nutrients to the plant world depend on it. The best accessibility of the elements Pb, Fe, Mn, B, and Zn occurs when pH values are within the range of 6 to 8. It was determined that the alkalinity of the soil was influenced by the cations Na^+, NH^{4+}, Ca^{2+}, and Mg^{2+}. However, when the values exceed 8.5, the cations Ca^{2+} and Mg^{2+} become inaccessible, i.e., they are deposited in the form of carbonates. In contrast, when the pH value decreases, i.e., in the acidic zone, the concentrations of Al and Mn are released to toxic values. Soils can be “salinized”, and salinity occurs as a result of increased concentrations of sodium salts. In this case, the EC is determined for saline soils. The higher concentrations of these salts in the soil, the higher the EC values. At a neutral pH, the EC values are minimal.

Table 6. Physical and chemical properties of soil.

Sample	pH	EC	K	Na	Ca	Mg
	H_2O	(μS/cm)	mg/kg		mg/100 g	
1	5.23	318.	1229.44	418.05	287.41	262.53
2	7.15	236.	1383.30	1578.65	2637.24	525.49
3	6.67	1075.	808.21	5537.64	1798.97	178.50
4	4.27	1273.	1472.32	176.51	402.51	328.41
5	2.86	2630.	1283.85	8.21	307.50	325.99
6	2.80	2110.	595.76	116.93	513.47	149.12
7	6.43	61.5	599.42	2808.69	1014.11	235.71
8	7.34	124.3	655.90	3458.07	2476.89	277.22

In addition, Table 6 shows the concentrations of macronutrients that played an important role in determining the effective mobility of metals in the investigated soil. Heavy metals adsorbed on clay minerals can leach out when they become cations (Na^+, K^+, $NH_4{}^+$, and Ca^{2+} I Mg^{2+}).

The values obtained for K show a significant presence in the soil, and its original source is minerals containing K. Potassium was not evenly distributed in the soil; it accumulated mostly in places where feldspars and mica predominated. Detected values for K were in the interval from 595.76 to 1472.32 mg/kg.

Sodium released during the decomposition of primary silicates is poorly bound by clay minerals, so this element is easily washed away from the soil. The soil was poor primarily in Na, but elevated concentrations of Na ions adversely affected the physical and chemical properties of the soil. In our work, the values detected for Na were in the interval from 8.21 to 5537.64 mg/kg.

The Ca content in the examined soil was in the interval from 287.41 to 2637.24 mg/100 g. Calcium is usually the most dominant cation available in the environment, and its values in soil can range from <25 mg/kg to more than 5000 mg/kg. The most important primary sources are aluminum silicate minerals containing Ca, such as feldspar, Ca phosphates, and Ca carbonates. The presence of Ca depends on the pH value of the soil, so based on Table 1, lower values of Ca can be observed in an acidic environment.

The content of Mg in the tested soil ranged from 149.12 to 525.49 mg/100 g, while according to research, its concentrations in the soil may be higher [32]. It can have irreplaceable, replaceable, and water-soluble forms in the soil, primarily depending on the pH value. Mg is most often present in the soil in secondary clay minerals, in the form of $MgCO_3$ or $MgSO_4$, and larger amounts are more often found in the deeper layers, similar to Ca, than they are in the upper parts of the soil profile [32].

3.2. Pseudototal

The level of contamination and migration in the soil was estimated using pseudo-total concentrations of heavy metals and arsenic in the surface layer (0–50 cm). Digestion of the aqua medium was performed to determine the pseudo-total content of six elements:

Cd, Cu, Pb, Ni, Zn, and As (Table 7). Total concentrations of elements in the tested soil samples were in the range of 3870.4–52,306.18 mg/kg for As, 2.19–49.84 mg/kg for Cd, 268.03–986.66 mg/kg for Cu, 7.34–114.67 mg/kg for Ni, 1223.1330339.74 mg/kg for Pb, and 58.21–8212.99 mg/kg for Zn.

Table 7. Chemical composition of soil samples.

Sample	Cd	Cu	Ni	Zn	As	Pb
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
1	5.40	714.98	40.27	633.96	3870.40	25,036.82
2	10.57	986.66	68.48	8212.99	5237.38	30,339.74
3	49.84	700.16	114.67	2584.52	39,102.38	10,079.91
4	17.77	268.03	57.31	2428.09	8583.59	7273.48
5	17.27	828.31	8.21	1142.29	50,966.14	5719.74
6	27.25	922.07	10.45	1513.39	52,306.18	2348.43
7	2.19	0.00	7.34	58.21	3986.73	1223.13
8	2.98	0.00	11.06	90.90	7586.22	1648.01

The distribution of heavy metals indicated small variations through the soil profile as shown in Table 7. Concentrations of tested metals, as compared to the MRL according to the Ordinance (Official Gazette of RS 23/94) [33], were far above the MRL in almost all samples. The obtained results show that the investigated area is loaded with heavy metals and arsenic caused by mining and metallurgical activities in RHMK “Trepča”. Significant differences in the minimum and maximum values indicate that the concentrations of the elements differ depending on the sampling site and the type of metallurgical waste.

3.3. Sequential Extraction Results

The chemical specification of metals (Pb, Zn, Cu, Cd, and Ni) and metalloid As in the soil samples at the sites of the former Gater metallurgical waste dump provided data on the level of pollution in the Zvečan area. Lead metallurgy waste has caused irreversible changes in the environment, so applying the method of sequential extraction shows the distribution of metals in the soil, which control both pollution and the geochemical characteristics of the soil. The different chemical fractions of metals in soil profiles are shown in Figure 3.

The first step of the sequential extraction process is the acid-soluble fraction consisting of exchangeable metals and carbonate-bound metals. Compared to other fractions, it is characterized as the most mobile and bioavailable to the living world [34]. The second step of sequential extraction, BCR 2, indicates metals associated with Fe and Mn oxy/hydroxides, making them thermodynamically very unstable and, therefore, easily released and available to the living world [35]. The third step of sequential extraction indicates metals associated with organic matter and sulfides. In the residual fraction, the metals are associated with aluminosilicate minerals, making them inaccessible to the environment.

According to the results, in the first and second extraction steps, in the fractions that are easily accessible, significantly large parts of Pb (50.7%), Zn (49.2%), and Cd (34.7%) were determined. Since these are fractions in which the metals Pb, Zn, and Cd can be easily released, these metals with high mobility are of great concern for the environment in the event of acid rain [36]. In soil samples with a high carbonate content, Pb could be associated with sulfur, and in the oxidation step, this fraction can be released [37]. The stability of Pb in non-residual fractions indicates that Pb is most often present in sulfide tailings as Galena, which is subject to the oxidation process and dissolves more easily than other sulfide minerals [38]. Based on the results presented in Figure 3, the highest percentage of Pb in all samples (40.8%) was contained in the reduction fraction, which indicates that it occurs in forms related to Fe/Mn oxides. This trend has been confirmed by other studies [39,40]. Additionally, a certain concentration of Pb (24.1%) formed a complex with organic forms [41]. Therefore, if Pb were bound to iron/manganese oxides, organic matter would be released when environmental conditions changed. These data suggest that Pb poses a certain environmental risk [42]. A large proportion of Cd (30%) proved to be very mobile in the first extraction phase due to its association with sulfide minerals in tailings. That is, at lower pH values such as 8, an increase in Cd bound to carbonates was observed, i.e., increased concentrations of Cd occurred due to the dissolution of the carbonate matrix [43]. In addition to the connection with carbonates, a low rate of Cd sorption (6.7%) on Fe/Mn oxides was observed [41], while in the fraction that is characterized by connection with organic forms, Cd participates only with 9%. Therefore, based on the results presented in Figure 3, it can be concluded that Cd is mainly bound to the first three fractions, i.e., to carbonates > organic matters > Fe/Mn oxides, and that it is the least associated with clay minerals [40]. The stability of Cd in the acid-soluble fraction indicates that, with a slight decrease in soil pH, a significant part of Cd would become bioavailable to the environment [40].

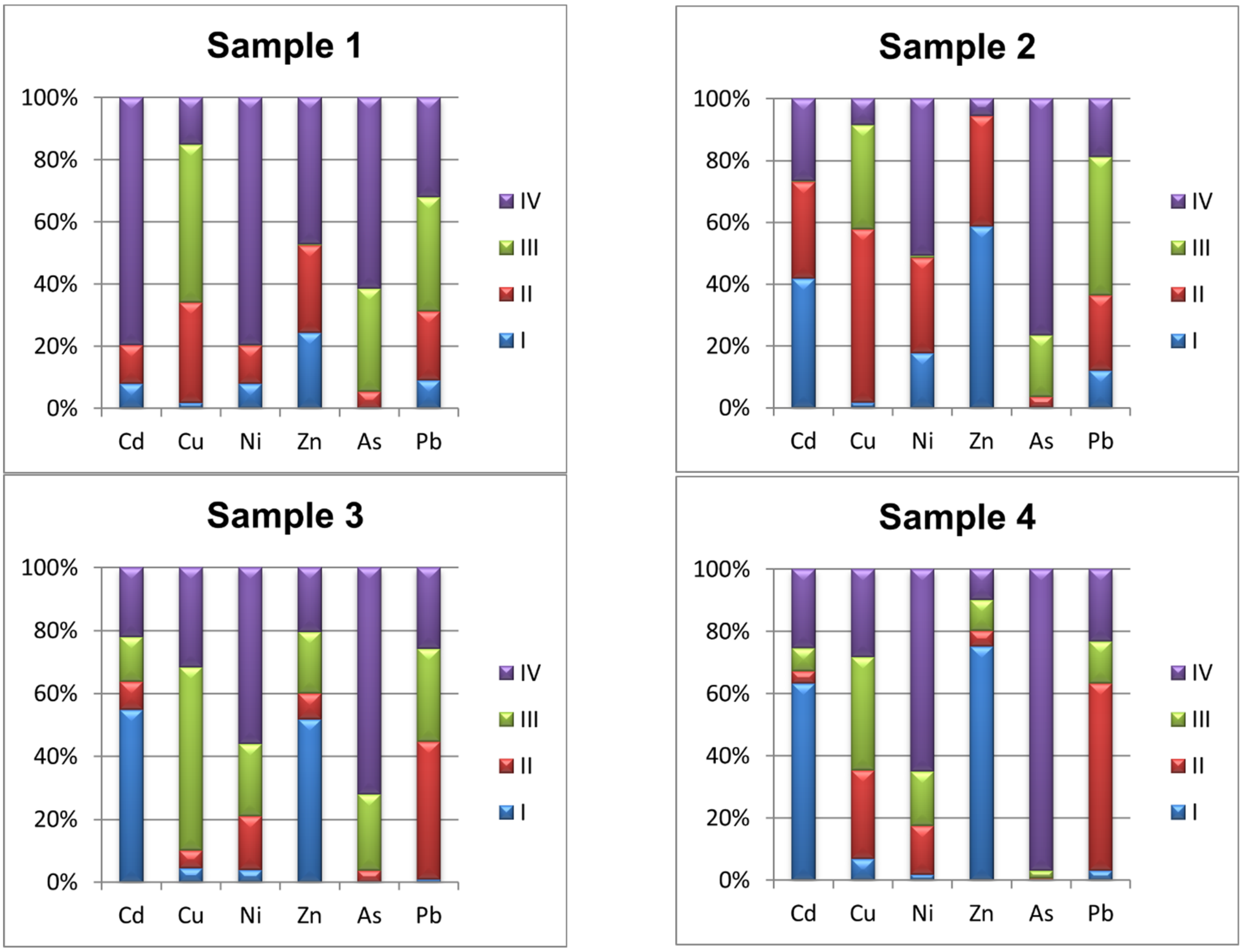

Figure 3. *Cont.*

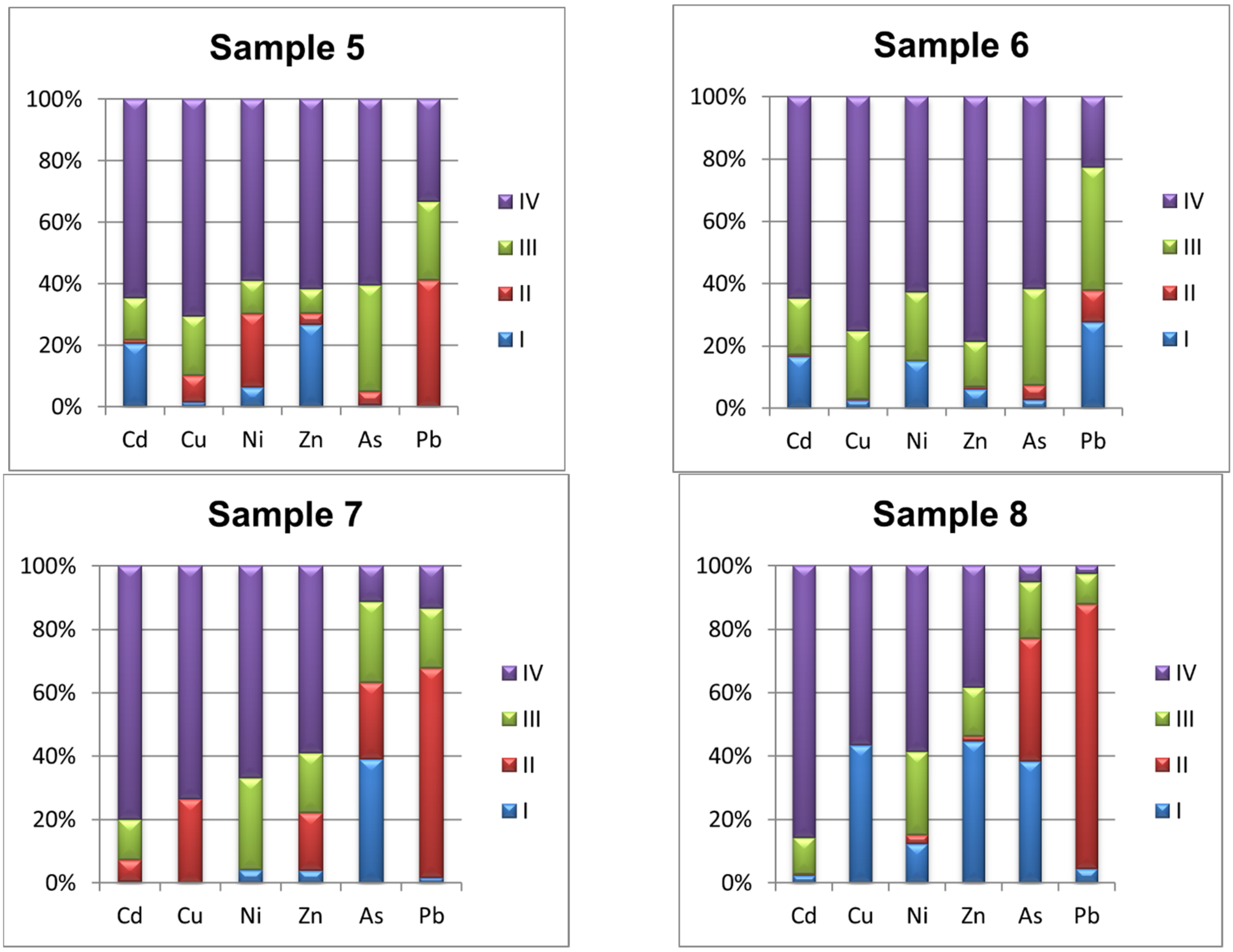

Figure 3. Distribution of metals in soil samples as determined by a modified BCR sequential extraction procedure. BCR 1 (blue)—mobile fraction, BCR 2 (red)—reducible fraction, BCR 3 (green)—oxidizable fraction, and BCR 4 (violet)—residual bound.

The distribution of Zn in the soil was determined in the following order: soluble phase > oxidizable phase > Fe/Mn oxides, i.e., 36.2 > 10.7 > 9.5%. Sorbents that control the distribution of Zn in the environment are Fe/Mn oxides that strongly affect its mobility; carbonate minerals that form complexes with Zn, clay minerals, and organic matter [44]. A large portion of zinc was found in the residual fraction (39.7%). The fact that Zn, Pb, and Cd are partially associated with the exchangeable fraction suggests that their presence is the result of ion exchange in clay minerals or deposition as oxides on their surface [45].

The dominant percentages of Cu are in the oxidizable fraction (25.6%). Studies have confirmed that Cu tends to accumulate in the organic fraction due to the high stability constant of organic Cu compounds [46,47]. The exceptions are a couple of samples in which Cu shows the presence in the reduction fraction (19%). Fe/Mn oxyhydroxides sorb Cu, initially in interchangeable forms, and then transform it into specially adsorbed forms; i.e., Cu in the soil occurs as an amorphous Mn oxide [48]. In addition, Cu showed a high presence in the residual fraction (47.1%).

The results show that metalloid As was mainly bound to clay minerals and organic sulfide fractions, as shown in Figure 3. This shows that As is less agile because oxidative (23.7%) and residual (55.2%) fractions dominated the fractionation. Exceptions were samples 7 and 8, in which As showed the concentration value in the first three steps of sequential extraction. Its presence in non-residual fractions resulted from the dissolution of the sulfide mineral arsenopyrite [49]. The key factors of As migration in the environment are pH value and redox potential [50]. According to other authors, As is mainly bound to iron hydroxides, and reducing conditions when dissolving Fe/Mn oxide increase its mobility [34,51,52].

Sequential extraction confirmed the highest concentrations of Ni in the residual fraction (62%), which indicates its low bioavailability and mobility. Based on the results presented in Figure 3, under appropriate conditions, Ni can be adsorbed on Fe/Mn oxides (12.2%) and organic matter (13.3%). The distribution of Ni takes place in the following order: residual phase > oxidizable phase > reduction phase > mobile phase. Limited mobility of Ni occurs due to the formation of Ni complexes with inorganic and organic ligands [36].

The presented results show that Zn had the highest extractivity in samples 3 and 4, while Pb dominated in sample 6. As shown in Figure 3, Cu, Cd, Ni, and metalloid As were present in the reduced and oxidizing fraction, while other metals like Zn and Pb were scattered among all fractions. In our case, BCR showed that the investigated heavy metals had significant concentrations in the residual fraction as well, and the rest of the concentrations were distributed among the other fractions. This confirms that sequential extraction is still a very useful method in assessing the mobility of trace elements.

3.4. Environmental Implications

The contamination factor was used to estimate the load of soil pollution in relation to heavy metals. In this paper, the individual contamination factor was calculated based on the values of the concentrations obtained in the soluble fraction (BCR1). Many studies confirm that the soluble phase is a phase that directly pollutes the environment [13,16,18]. C_f^i values for heavy metals observed at different sampling sites are shown in Table 8. The contamination factors were very high for Pb, As, and Zn. Values for C_f^i were: As (0.004–195.8), Pb (0.09–33.54), and Zn (0.14–16.06). According to the evaluation criteria described by Hackason, it can be confirmed that the measuring points are characterized by a high contamination factor. The calculated values for the elements Cd, Ni, and Cu have significantly lower values and are characterized by a low contamination factor.

Table 8. Contamination factor values C_f^i of heavy metals in soil.

Sample	C_f^i					
	Cd	**Zn**	**Cu**	**Ni**	**Pb**	**As**
1	0.121	0.460	2.242	0.032	24.181	0.004
2	1.325	16.062	1.375	0.130	33.544	0.192
3	4.367	4.396	0.142	0.187	0.543	0.573
4	2.632	6.262	0.350	0.112	1.360	0.121
5	1.023	1.211	0.421	0.031	0.133	21.885
6	0.961	0.273	0.165	0.007	7.981	93.383
7	0.003	0.008	0.000	0.004	0.090	93.625
8	0.021	0.140	0.041	0.014	0.682	195.814

C_f^i* Contamination factor.

Table 9 shows the potential environmental risk indices Cd, Zn, Cu, Ni, Pb, and As for the measurement sites sampled in the study area. E_f^i values for Zn, Ni, and Cu in all samples were lower than 40, which was within the range of low or no potential environmental risk. In addition, Cd was within the range of low potential environmental risk in all samples except sample 3, where it showed values within the range of high potential environmental risk ($80 < E_f^i < 160$). The main elements that pose an environmental hazard are Pb and As. $E^i{}_f$ values for Pb showed higher potential environmental risk ($80 < E_f^i < 160$) in samples 1 and 2; in other samples, the values were within the range of low potential environmental risk. Sample 5, according to the $E^i{}_f$ values for As, showed a very high potential environmental risk ($160 \leq E^i_f \leq 320$), while samples 6, 7, and 8 were characterized as severe potential environmental risks ($320 < E^i_f$), Table 9.

Table 9. Potential ecological risk assessment results of metals in soil samples.

Sample	E^i_f						$R = \sum E^i_f$
	Cd	Zn	Cu	Ni	Pb	As	
1	3.62	0.46	11.28	0.15	120.91	0.04	136.15
2	39.10	16.06	6.85	0.54	167.73	1.91	232.01
3	130.82	4.39	0.73	0.93	2.74	5.75	144.47
4	78.02	6.26	1.75	0.55	6.85	1.00	94.36
5	30.61	1.21	2.14	0.15	0.55	218.87	253.36
6	28.83	0.27	0.83	0.035	39.90	933.81	1003.64
7	0.09	0.008	0.00	0.02	0.45	936.27	936.77
8	0.65	0.14	0.24	0.07	3.43	1958.06	1962.41

C^i_f pollution coefficient for a particular heavy metal,C_i—simple-measured concentrations of heavy metals in the analyzed soil samples, C_i reference—parameter to calculate, T^i_f—toxicity factor of a single heavy metal. The formula for the index of potential toxicity reaction for various heavy metals is: $R = \sum E^i_f$.

The total potential environmental risk index, R_i , is used to more closely define the degree of soil contamination by the analyzed elements. It represents the sum of individual environmental risk indices, and the calculated values compared with the potential environmental risk classes ([15] are given in Table 9. The overall potential environmental risk, R_i, ranged from 94.36 to 1962.41. The maximum value for R_i was found in sample number 8. According to the assessment standard, samples 1, 3, and 4 showed a low level of environmental risk ($R < 150$); samples 2 and 5 showed a moderate level of environmental risk ($150 < R < 300$); and a serious level of environmental risk ($600 < R$) was confirmed in samples 6, 7, and 8. Hence, the soil of this study area showed a serious potential environmental risk due to the presence of the metal Pb and metalloid As.

4. Conclusions

The study aimed to investigate long-term pollution caused by the storage of waste material with high concentrations of heavy metals. The accumulation of the toxic elements occurred via heavy metal and arsenic penetration into the topsoil. First, the presence of the major pollutants As, Cd, Cu, Pb, Zn, and Ni in the soil was determined based on the analysis of their pseudo-total concentrations. The results on the spatial distribution of heavy metals in the surface layer of the soil showed that the content of tested metals was far above the prescribed MDK values.

The BCR method of sequential extraction was applied to the analysis of heavy metals in order to obtain a pattern of distribution in the soil and investigate variations of metals in non-residual fractions. The extraction results showed that Pb, Zn, and Cd were associated with carbonates, making them mobile and accessible to the living world. In the reduction phase, significant concentrations were shown by almost all tested heavy metals and arsenic; i.e., their mobility is a function of pH value and redox potential. The exception was Ni, which showed a presence in the oxidative phase, as it was associated with sulfides. To show the retention of heavy metals in the soil samples, individual potential environmental risk indices were calculated, E^i_f as was the total potential environmental risk index, R_i. According to the assessment standard, samples 1, 3, and 4 showed a low level of environmental risk ($R < 150$), samples 2 and 5 showed a moderate level of environmental risk ($150 < R < 300$), and a serious level of environmental risk ($600 < R$) was confirmed in samples 6, 7, and 8. Hence, the soil of this study area shows a serious potential environmental risk due to the presence of Pb and As.

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