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Original Research

Assessment of Pollution and Distribution of Heavy Metals in the Soil Near the Flotation Tailings Gornje Polje

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Abstract

This paper refers to the distribution of heavy metals in soil located near the Gornje Polje flotation tailings in Zvečan, in North Kosovo. Physical and chemical properties, determination of total metal concentration by acid digestion and sequential extraction scheme according to BCR (Community Bureau reference) were applied to soil samples. X-Ray diffractometry and inductively coupled plasma-optical emission spectrometry (ICP-OES) was used to analyze soil samples. The obtained results showed that the flotation tailings Gornje Polje still contain quite significant amounts of solid waste, which can release heavy metals into a potential source of pollution. The ratio between the mean concentrations of the tested metals was determined in the order: Pb (3862 mg/kg)>Zn (950.45 mg/kg)>Cu (386.75 mg/kg)> As (365.47 mg/kg)>Ni (220.87 mg/kg)>Cd (23.63 mg/kg). Pb, Zn and Cd showed the highest concentrations in mobile fractions in soil, compared to other metals. According to the calculated index of potential environmental risk, it was confirmed that the mobility of Cd has a great impact on the environment. The order of potential environmental risk is Cd>As>Pb for all samples of the analyzed soil, and the most polluted places are near the tailings.

Keywords: BCR sequential extraction, heavy metals, soil, ecological risk index

Introduction

Mining and related activities have a negative impact on the environment, both during mining operations and in the years after mine closure [1]. One of the main problems are tailings, i.e. mining waste that is generally toxic [2]. Environmental problems associated with tailings lie in their chemical composition, because ore extraction generates heterogeneous waste of potentially toxic elements [3].

Heavy metals are an important class of pollutants [4]. It is known that the activities of Pb/Zn smelters lead to significant soil contamination in the environment. Soils represent a direct receptor for pollution emitted by smelters into the atmosphere, as well as for solid waste and slag disposed of in the environment [5]. However, soil is not just a passive acceptor, contaminated soil becomes a source of contamination

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for other environmental components [6]. Heavy metals cannot decompose, they tend to accumulate and remain in the soil [7]. The complex diversity of processes in the environment affects the distribution and efficient isolation of heavy metals, which causes their release or transformation into different types that can be more or less bio-available and toxic [8]. Toxicity and bio-availability do not depend only on the total concentration, but also on their shape, so they can be divided amongst different phases, i.e. associated with carbonates, Fe-Mn oxides, organic complexes and residual fraction [9]. In addition to pollution in the northern part of Kosovo and Metohija, the presence of heavy metals is a good indicator of the impact of production processes and existing passive and active landfills for mining waste [10]. The release of wind-borne particles and pollutants in the form of gases from metallurgical plants into the atmosphere during ore processing and tailings are the main source of soil pollution. The complexity of the tailings waste deposit Gornje Polje was presented in detail in the previous study [11]. The tailings waste characterization presented chemical, mineralogical and granulometric composition of the tailings waste that influence the environmental impact, too.

Identification and quantification of different types or forms in which heavy metals occur is very important for determining their bio-availability in the environment [6]. In cases of soil contamination with heavy metals, visible and hidden forms of metals can be identified using the method of sequential extraction, based on the use of a series of selective reagents selected for successive solubilization of different mineral fractions [12]. There are numerous methods of sequential extraction. The difference is in the reagents and conditions in which the experiment is performed, as well as in the number of steps involved, and the most commonly applied are Tessier et al. 1979; Gibson and Farmer 1986; Dold 2003, G. Rauret et al. 1999 [13-16]. Also, the application of methodological approaches, such as contamination factor (C_f), potential ecological risk factor (E_i) and potential ecological risk (R_i), enables a better understanding of the potential ecological risk of toxic elements. Hackson (1980) [17] developed an index of potential environmental risk by calculating the pollution index, which is still used today to assess pollution of the ecological system.

Published studies on the Gornje Polje tailings ponds have analyzed the impact of this mining waste on the environment, analyzing surface soil, water, and air [10, 18, 19]. However, the forms in which heavy metals are stable at this location are not known. The aim of this study has been to assess the environmental activities and potential environmental risks of metals in the soil in the vicinity of the flotation tailings. For this purpose, the BCR sequential extraction method was applied to examine the metal fraction in the soil and to assess the amounts of potential toxic elements, as well as the potential environmental risk from lead ore processing residua in Trepča.

Study Area

The area of research was conducted in the northern part of Kosovo and Metohija, characterized by intensive mining activities. Mining, metallurgical, and chemical combine "Trepca" was one of the largest producers of lead, zinc, silver, and gold in Europe in the period from 1965 to 1985. Today, most Trepca's Combine factories are closed, there is a limited exploitation of minerals, and previous activities have left significant amounts of toxic waste. Waste acids, emission of dust particles, inadequate locations, poorly maintained and unstable tailings pose a daily danger to the environment [18].

Fig. 1. Map of soil samples near the flotation tailings Gornje Polje.

The analyzed soil samples were collected in the vicinity of the Gornje Polje flotation tailings pond, in the area between Kosovska Mitrovica and Zvečan. The disposed mine waste, generated in the Pb/Zn ore processing plants in Trepča, contains approximately 12,000,000 t of tailings [19], cover an area of approximately 500,000 m^2 and represents residua from the first metal extraction process completed by flotation. The distribution and behavior of different chemical species in surface geochemical spheres have resulted in high contamination in the study area [10].

Materials and Methods

Several tests were carried out in order to investigate the physical and chemical features the soil samples. As part of the sampling procedure, numerous soil samples were collected from the surface (0-10 cm), and the paper presents eleven samples characterized by high concentrations of detected heavy metals, (Fig. 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 then ground to a grain size <2 mm to determine soil properties and heavy metal concentrations.

The pH-value, conductivity, and elementary analysis of the samples were simultaneously measured after shaking 1 g of each sample with 100 mL distilled water at 100 rpm for 1 h. Soil pH and specific electrical conductivity were measured in 1:5 soil-water suspensions using a WTW inoLab ph/Cond 720 instrument (ISO 10309, 2005; ISO 11265, 1994). The carbon, hydrogen and nitrogen contents were measured using CHN analyzer 1000 LECO, in accordance with the ASTM D 5373 standard.

XRD (X-Ray Diffractometry) analysis was used for mineralogical investigation. Samples were investigated using diffractometer Philips PW 1710 under the following conditions: radiation from copper anticathode with CuK α = 1.54178 Å and graphite monochromator, working voltage U = 40 kV, current strength I = 30 mA. Samples were investigated in the range of 5 – 70o 2θ (with step of 0.02° and time 0.5 s).

Soil samples were digested in the aqua region (3 mL HCl + 1 mL HNO_3) to determine the pseudo-total metal contents (ISO, 11466, 1995). The procedure was applied to 1-gramme soil samples in three samples; metal concentrations were analyzed using an ICP-OES instrument (iCAP 6500 Duo; Thermo Scientific, Loughborough, UK) connected to a computer equipped with iTEVA software. Instrument operating parameters: 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 (189,0); Cd (214.4); Cr (267,7); Cu (224,7); Ni (231,6); Pb (220,3); i Zn (202,5).

Sequential Extraction Procedure

A modified BCR three-step SEP sequential extraction procedure was used to assess the fractionation of heavy metals in soil samples. This method was described in detail by Rouret et al. [16], and consists of three extraction steps. Furthermore, the addition is the fourth step, which consists of dissolving the final residua by the dysthenia process in the aqua region (ISO, 11466, 1995). Each sample was analyzed in duplicate, and each analysis consisted of three repetitions. For the analysis, it was necessary to weigh 1 g of soil, and the extraction course was as follows:

- Step 1 (exchangeable, water, acid-soluble fraction) 1 g of sample with 0.11 mol/dm^3 CH_3COOH and 16 h of sample shaking, F1;
- Step 2 (reducible fraction) precipitate from F1 with 0.5 mol/dm^3 $NH_2OH \cdot HCl$ adjusted to pH 1.5 and shaking again for 16 h, F2;
- Step 3 (oxidizable fraction) precipitate from F2 with 8.8 mol/dm^3 H_2O_2 and 1 mol/dm^3 CH_3COONH_2 adjusted to pH 2 and shaking from 16 h, F3, and
- Step 4 (residual fraction) precipitate from F3 with aqua regia, 15 ml of 37% HCl and 5 ml of 65% HNO_3, at 80ºC for 5-6 h, F4.

To check the stability and accuracy of the procedures in all samples, a reference material (BCR-701) for the same process was used. Data quality assurance for reference material, certified by Refs (BCR-146R) and BCR-701, was performed by Kerolli-Mustafa et al. [20]. According to the procedure above-mentioned, the measured concentrations of the elements showed a very good agreement with the confirmed values of the reference sample.

Potential Ecological Risk of Metals

To assess soil contamination, many studies have confirmed the application of magnitude of contamination factor (C^i_f), which represents the relationship between heavy metal concentrations in the soil and pre-industrial reference levels, and allows the assessment of soil contamination by heavy metals [21]. The formula used to calculate the contamination factor of a single heavy metal in the soil is:

$$C^i_f = C^i_{simple} / C^i_{reference} \quad (1)$$

Where C^i_f - pollution coefficient for a certain heavy metal, C^i_{simple} - measured concentrations of heavy metals in the analyzed soil samples, $C^i_{reference}$ - a parameter for calculation. As for the criterion for assessing the levels of toxicity of heavy metals and ecological susceptibility to heavy metal pollution, the potential environmental risk factor (E^i_f) proposed by Hackanson was used [17]. The corresponding coefficients based on its toxicity were: Cd = 30, As = 10, Cu = Pb = Ni = 5, Zn = 1. The formula for calculating the potential environmental risk factor for individual heavy metal pollution is:

Table 1. Relationship between potential toxicity index (*R*), potential ecological risk index (E_f^i) and pollution level [1].

Scope of potential ecological risk index (E_f^i)	Ecological risk of single-factor pollution	Scope of potential toxicity index (*R*)	General level of potential ecological risk
$E_f^i<40$	Low	$R<150$	Low grade
$40\le E_f^i<80$	Moderate	$150\le R<300$	Moderate
$80\le E_f^i<160$	Higher	$300\le R<600$	Severe
$160\le E_f^i<320$	High	$600\le R$	Serious
$320\le E_f^i$	Serious		

$$E^i_f = C^i_f * T^i_f \tag{2}$$

Where T^i_f – toxicity factor of a single heavy metal. The formula for the index of potential toxicity reaction for different heavy metals is:

$$R = \Sigma E^i_f \tag{3}$$

Accordingly, the potential toxicity risk index (R) and the potential environmental risk index (E^i_f) are used to assess the potential environmental risk of heavy metals.

Results and Discussion

Physico-Chemical and Mineralogical Characterization

The physical and chemical properties of eleven soil samples are shown in Table 2. Soil pH varied from neutral to slightly alkaline (range 6.82-8.00), but most soil samples were found to be slightly alkaline (mean 7.37). Previous studies have attributed this alkalinity to the presence of carbonates [22]. Specific electrical conductivity ranged from 277 to 483 µS cm^{-1}, with a mean value of 354 µS cm^{-1}. Since the pH values are neutral to slightly alkaline, hence the lower values of electrical conductivity of ions in the examined soil samples. Concentrations of nitrogen, carbon, sulfur, and hydrogen in the soil are also shown in Table 2. Determination of the elemental composition of the soil showed that the nitrogen content is approximately the same in all samples, while the contents of sulfur and hydrogen differ. The sulfur and hydrogen contents were the highest in sample 1, where pH 7.32 and EC 317 µS cm^{-1} were measured. Carbon showed the highest content in sample 5.

The extent of contamination and migration in the surrounding soil was estimated using pseudo-total concentrations of heavy metals in the surface layer of the soil (0-10 cm). Digestion of the aqua region was performed to determine the pseudo-total content of six elements: Cd, Cr, Cu, Pb, Ni, Zn and As, (Table 3). Total concentrations of elements in the tested soil samples were in the range of 25.8-2183.76 mg/kg for As, 7.58-115.35 mg/kg for Cd, 50-2050 mg/kg for Cu, 20.71-1095.92 mg/kg for Ni, 1162-11178 mg/kg for Pb, and 311-4257 mg/kg for Zn. Concentrations of tested metals in comparison with the values determined according to the Ordinance (Official Gazette of RS 23/94) [23] were far above the permitted concentrations in almost all samples. The maximum values of the heavy metals have been observed at the 8th station, located in the immediate area of the Gornje Polje

Table 2. Physical and chemical properties of soil, %.

Stations	pH (H_2O)	EC µS cm^{-1}	C (%)	H (%)	N (%)	S (%)
1	7.32	317	1.091	6.394	0.143	1.092
2	7.61	309	1.248	3.367	0.153	0.229
3	7.16	431	2.422	2.422	0.265	0.172
4	7.57	355	2.063	2.063	0.194	0.095
5	7.06	416	2.563	2.563	0.265	0.288
6	7.67	372	1.016	1.016	0.133	0.092
7	7.40	363	2.047	2.047	0.224	0.087
8	7.52	277	1.684	1.684	0.173	0.071
9	7.01	483	1.679	1.679	0.173	0.143
10	6.82	286	1.977	1.977	0.212	0.372
11	8.00	292	0.713	0.713	0.111	0.013

Table 3. Chemical composition of soil samples.

Stations	As mg/kg	Cd mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
1	101.03	10.39	126.5	20.71	5120	744
2	25.80	8.78	50.9	21.89	1230	420
3	93.09	7.58	62.7	100.15	1727	406
4	218.06	16.74	126.2	74.02	3932	571
5	123.46	18.56	87.0	107.38	1162	1244
6	327.32	22.31	115.1	257.46	3549	537
7	300.70	20.76	134.9	118.92	7000	503
8	2183.76	115.35	1157.2	1095.92	11178	4257
9	378.37	19.44	250.7	151.47	3511	804
10	139.71	9.34	2050.0	252.97	2512	658
11	128.93	10.66	93.1	228.71	1561	311
Mean±SD	365.47±613.08	23.63±30.88	386.75±636.02	220.87±301.99	3862±3017.82	950.45±1125.65
Min-Max	25.8-2183.76	7.58-115.35	50-2050	20.71-1095.92	1162-11178	311-4257
Current limit values[a]	25	3	100	50	100	300

[a] Official Gazette of the Republic of Serbia, No. 23/94.

flotation tailings. A noteworthy exception was Cu, as maximum values of concentration for Cu have been determined at the 10th station. The obtained results show that, unfortunately, the area of Zvečan and K. Mitrovica has been rich with heavy metals produced by mining activities at MMCC "Trepča". Input flows from mining waste to the surrounding land have been created by the transport of fine tailings by wind and runoff, as well as, mine drainage [24]. Significant differences in minimum and maximum values indicate that the concentrations of the elements differ depending on the sampling site and the distance from the mining waste. Maximum concentrations have been found in the immediate vicinity of the source (site 8), and the values decreased with an increase in distance from the area of Zvečan and Kosovska Mitrovica. Our findings are in agreement with previous investigations which have shown that the polluted area generally occupies a space ranging from one to several kilometres surrounding the source [18, 19]. The differences observed might be subjected to the wind direction, local topography, and distance from the source. The greatest contamination is associated with the immediate surroundings of the flotation tailings, with the contamination aureole sprawling along a predominant wind direction. It is important to emphasize that many research studies have confirmed the contamination of land with waste dust originated from Pb/Zn ore processing plants and tailings piles [25-27].

On the basis of the presented results, the mineralogical analysis of the soil necessitated selection of three sites specific in terms of high concentrations of heavy metals (site 1 - Fig. 2a, site 4 - Fig. 2b, and site 8 - Fig. 2c). XRD mineralogical analysis confirmed the presence of major minerals such as quartz (SiO_2), anorthite (Ca ($Al_2Si_2O_8$)) and anglesite ($PbSO_4$), besides additional minerals such as pyrite, lanarkite, glossarite, and lauite. The connection of trace elements with clay minerals has been confirmed. The presence of arsenic oxide aggregates, containing concentrations of Fe, Mn, Ni and Zn, was detected, Fig. 2b) and 2c). There were also isolated pyrite crystals transformed into iron oxides (hematite and magnetite) that are not associated with trace elements. Some samples additionally contained calcite and oxides of individual elements, (Fig. 2).

Correlation Analysis

In order to define the relationship between the investigated heavy metals and the sources of soil pollution, a statistical correlation between the total concentrations of elements and physico-chemical characteristics was used. Pearson's correlation coefficients for the analysis of heavy metals, pH and EC were calculated, (Table 4). The obtained correlation values for pH and EC were not significantly related to the elementary data. Information on the sources and pathways of heavy metals reveals the relationships among the elements.

Positive correlations were observed between As, Cd, Ni, Pb and Zn, which may indicate a common origin or similar geochemical behavior. The matrix reflects the close relationship between several metal pairs such as As-Cd, As-Ni, As-Pb, As-Zn, Cd-Ni, Cd-Pb, Cd-Zn,

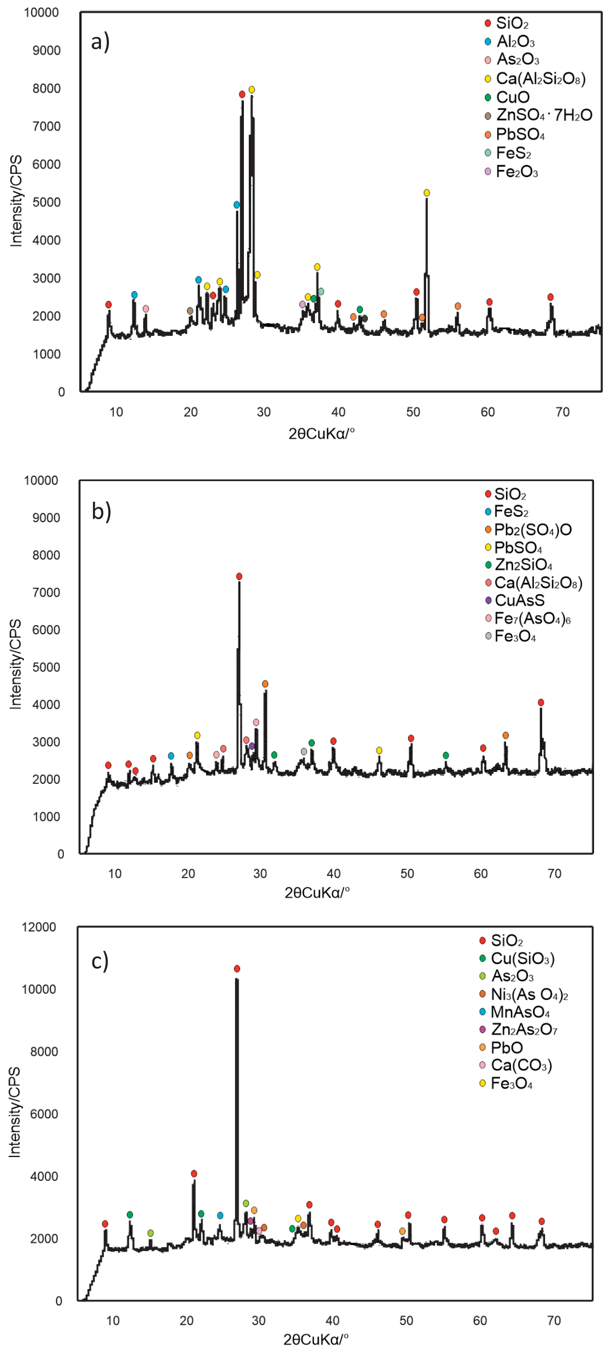

Fig. 2. XRD analysis of soil samples: a) sample 1 (site 1 - Rudare), b) sample 2 (site 4 -Zvečan) and c) sample 3 (site 8 - Kos. Mitrovica).

and Zn-Ni. The values of correlation coefficients (r) are in the range of 0.840-0.995, with a statistical significance of $p<0.01$. Considering that lead and zinc sulfide ore were exploited and processed in the investigated area, the correlations are in accordance with their geochemical affinities [28]. However, no statistical correlation was found amongst Cu and other elements. The source of Cu has been a combination of the presence of "parent" materials, as well as other human activities [29]. A similar type of correlation between elements indicating a common origin, especially sulfide ore processing, has been observed in other studies [30, 31].

Sequential Extraction Results

The chemical specification of metals (Pb, Zn, As, Cu, Cd and Ni) in the soil sampled in the vicinity of the flotation tailings, generated by the processing of Pb/Zn ores, provided data on the level of pollution in the area of Zvečan and Kosovska Mitrovica. The test results show that heavy metals are mainly of anthropogenic origin, which confirms their concentrations in the first three steps of sequential extraction.

The first step of BCR1 sequential extraction involves poorly absorbed metals retained on the soil surface, which can be released by exchange processes or precipitated in the presence of carbonates [4]. Considering the high mobility and potential bio-availability of heavy metals, compared to other fractions, it is characterized as the most mobile and bio-available to the living world [32]. According to the results, Cd and Zn were detected as the most mobile elements in the BCR1 fraction. These outcomes suggest that Cd and Zn were more likely to be associated with carbonate minerals, since they have a very similar ionic radius as Ca. Therefore, they can easily replace Ca ion in calcium carbonate [33]. The fact that Zn, Pb, and Cd are partially associated with an exchangeable fraction suggests that their presence is the result of ion exchange in clay minerals or deposition as oxides on their surface [34]. Although with a low percentage of presence observed, toxic metals such as Ni, Cu and As may, when changing environmental conditions, change this scenario and pose a potential environmental risk.

The second step of sequential extraction, BCR 2, indicates metals that are commonly associated with Fe and Mn oxy/hydroxides. The metals extracted in this fraction are thermodynamically very unstable, and are therefore easily released and available to the living world [35]. The ability to adsorb on clay minerals has caused that a relatively high percentage of Pb has been associated with the reducing material [36]. Fe-Mn oxides play an important role in the fixation of metals, especially Zn, As and Cu, (Fig. 3). High affinity of Cu for these oxides has been previously studied [37, 38]. In these studies, Pb and Zn were elements that have been mainly extracted in the first and second steps of sequential extraction. Metals Ni and Cd also showed affinity for this fraction, but in lower concentrations, (Fig. 3). This confirms the fact that although present in small amounts, environmental risks cannot be eliminated.

The third step of sequential extraction, BCR 3, indicates metals that are bound to organic matter and sulfides. Ni and Cu are predominantly bound to organic matter and are consequently released under oxidative conditions into the environment. Hence, they were barely present in the most mobile fractions,

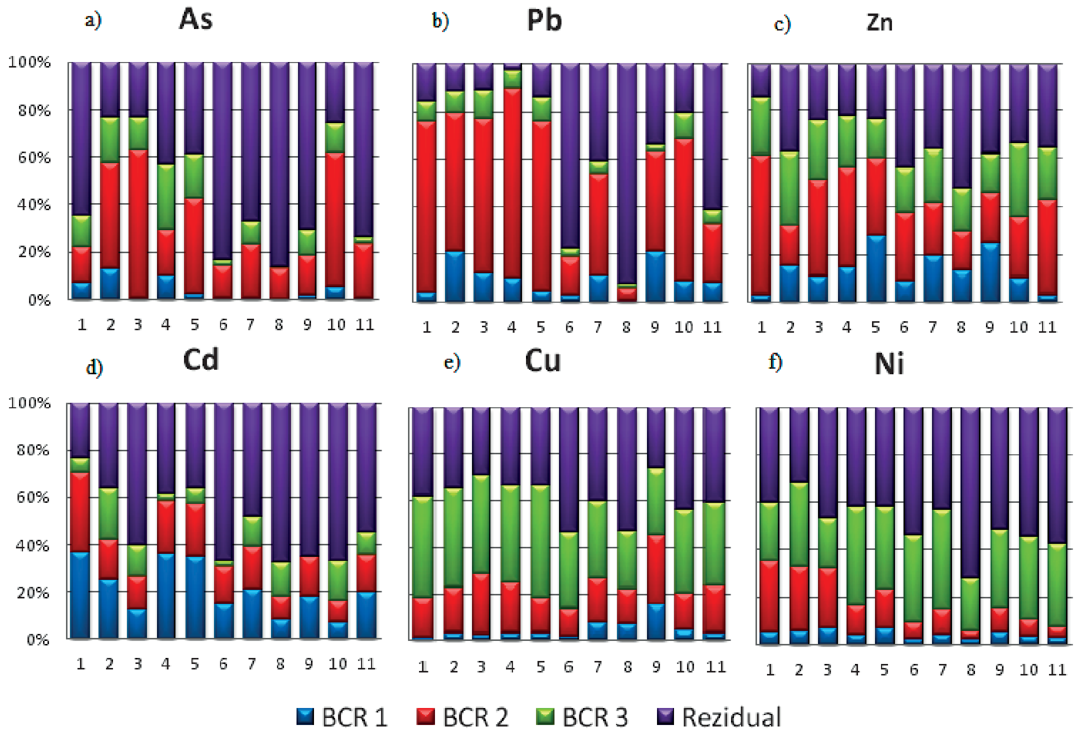

Fig. 3. Distribution of metals in soil samples as determined by modified BCR sequential extraction procedure.

(Fig. 3). According to Soltani et al. [25], Cu in the soil strongly retains in solid phases and due to its ionic properties, it is generally poorly soluble and not mobile. As and Zn were also weakly bound to organic matter. Due to the lower contribution of sulfides in the speciation of the heavy metals, it has been determined that the concentrations of the tested elements bound to this fraction were generally lower than those associated with Fe/Mn oxides, as it has been presented in Fig. 3.

In the residual fraction, the metals are bound to the aluminosilicate mineral, which makes them less mobile and accessible to the living world. The BCR results show that these metals have appropriate proportions of concentrations in the residual fractions, due to the presence of silicate minerals, which was confirmed by mineralogical analysis. The residual concentration of any heavy metal is considered a stationary fraction and is an important part that affects the nature of the mobility of heavy metals [34].

Environmental Implication

Contamination factor was used to estimate the load of soil pollution in relation to heavy metals. $\mathbf{C}^i_f$ values for heavy metals recorded at different sampling sites are presented in Table 5.

According to the classification described by Hackson [17], all samples collected in the vicinity of the flotation tailings pointed to highly polluted nature of the soil. The contamination factor was very high for As and Zn

Table 4. Pearson's correlation matrix between physic-chemical properties and the total concentrations of heavy metals in soil from 11 sampling sites.

	As	Cd	Cu	Ni	Pb	Zn	pH
Cd	0.995**						
Cu	0.385	0.353					
Ni	0.966**	0.958**	0.511				
Pb	0.851**	0.840**	0.284	0.753			
Zn	0.962**	0.974**	0.407	0.928**	0.775		
pH	0.125	0.143	-0.450	0.140	0.108	-0.000	
EC (μS cm-1)	-0.295	-0.304	-0.466	-0.394	-0.303	-0.290	-0.427

*Correlation is significant at the 0.05 level. ** Correlation is significant at the 0.01 level.

Table 5. Contamination factor values C^i_f of heavy metals in soil.

Stations	C^i_f					
	As	Cd	Cu	Ni	Pb	Zn
1	10.10	3.43	2.47	0.9	0.27	17.06
2	8.6	2.92	1.4	0.36	0.29	4.1
3	93.09	2.52	1.33	0.44	1.33	5.75
4	7.2	5.58	1.90	0.9	0.98	13.1
5	4.11	6.18	4.14	0.62	1.43	3.87
6	10.92	7.44	1.79	0.82	3.43	11.83
7	10.02	6.92	1.68	0.96	1.58	23.33
8	34.15	2.97	3.22	1.84	14.61	26.87
9	12.61	6.48	2.68	1.79	2.02	11.7
10	4.65	3.11	2.19	14.64	3.37	8.37
11	4.3	3.55	1.04	0.66	3.05	5.2

followed by Cd. Values for C^i_f were: Zn (3.87-26.87), As (4.11-93.09), Cd (2.52-7.44). According to the evaluation criteria, it can be confirmed that the measuring points are characterized by a high contamination factor. The calculated values for the elements Pb, Ni and Cu have significantly lower values, and are characterized by a low to moderate contamination factor.

Table 6 gives the calculation values that are compared with the classes of potential environmental risk. E^i_f values for Zn, Cu and Ni in all samples were lower than 40, which indicated a small potential environmental risk for these heavy metals. The main elements that pose an environmental hazard are Cd, Pb and As. The range of E^i_f values for Cd was in the range from 3.8 to 223, four measuring points showed higher ($80<E^i_f<160$) and five measuring points high potential environmental risk ($160<E^i_f<320$). As and Pb had slightly lower values in relation to Cd, ie at four measuring points they showed moderate potential environmental risk ($40<E^i_f<80$) and four measuring points higher potential risk ($80<E^i_f<160$). Measuring site S8, which is located in the immediate vicinity of the flotation waste landfill, according to the E^i_f values, is characterized by a serious potential environmental risk ($320<E^i_f$), (Table 6).

The maximum value for R of 11 measuring points was found at measuring point S8 and has a value of 610.57, and the minimum value of measuring point 3, ie 117.94. According to the assessment standard, measuring points S2 and S3 show a low level of

Table 6. Potential ecological risk assessment results of metals in soil samples.

Stations	E^i_f						$R = \Sigma E^i_f$
	As	Cd	Cu	Ni	Pb	Zn	
1	101.03	3.8	4.5	1.35	85.3	2.47	198.45
2	8.6	87.6	1.8	1.45	20.5	1.4	121.3
3	31.01	75.6	2.2	6.65	1.15	1.33	117.94
4	72	167.4	4.5	4.9	65.5	1.903	316.20
5	41.4	184.4	7.15	7.15	19.35	4.14	279.59
6	109.2	223.2	4.1	17.15	59.15	1.79	414.59
7	100.2	207.6	4.8	7.9	116.65	1.68	438.83
8	341.5	89.1	9.2	33.05	134.5	3.22	610.57
9	126.1	194.4	8.95	10.1	58.5	2.68	400.73
10	46.5	93.3	73.2	16.85	41.85	2.19	273.89
11	43	106.5	3.3	15.25	26	1.04	195.09

environmental risk (R<150), measuring points S1, S5, S10 and S11 moderate level of environmental risk (150<R<300), measuring points S4, S6, S7 and S9 severe level of ecological risk (300<R <600), while at the measuring point S8 a serious level of ecological risk (600<R) was confirmed. Hence, the soil of this study area shows a serious potential environmental risk due to the presence of the metals Cd, Pb and As.

Conclusions

The results obtained in this study add to our knowledge of elemental contents and their possible sources in soils of a Pb–Zn mining area. The application of modified methods of sequential extraction of BCR was used to assess the possible mobility of trace elements in the soil, which control both pollution and geochemical characteristics of the soil. By comparing the obtained results of the three fractions of the BCR fractions, we can conclude that the mobility of all trace elements is the greatest in the reduction and oxidation fractions. The extraction results show 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, except for Ni, which shows a significant presence in the oxidizable phase. Although the BCR sequential extraction procedure was applied to study the mobility of metals in the soil, the obtained metal concentrations were also used to calculate the potential environmental risk index. The potential environmental risk method is another important tool for assessing the risks associated with environmental pollution. The obtained results showed that Cd, Pb and As have a high potential index of ecological risk and that they require special attention in terms of potential ecological danger to the environment.

Based on the above, the application of BCR sequential extraction and the method of potential environmental risk open the possibility of insight into the current state of the endangered zone, as well as the choice of potential site remediation, which will be the subject of further work.

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Conflict of Interest

The authors declare no conflict of interest.

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