

Original Research

HEAVY METAL DISTRIBUTION AND CHEMICAL SPECIATION IN SOILS NEAR THE GORNJE POLJE FLOTATION TAILINGS

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Abstract

A modified BCR (Bureau of Community Reference) sequential extraction procedure and the potential ecological risk index method were applied to assess the ecological behavior and potential risks of metals in soil. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for sample analysis. The mean concentrations of the analyzed metals followed the order: Pb > Cu > As > Ni > Cd. The highest proportions in the mobile fractions were observed for Pb and Cd compared to the other metals. Based on the calculated potential ecological risk index, Cd was identified as having a pronounced impact on the environment due to its high mobility. The order of potential ecological risk was: Cd > As > Pb across all analyzed soil samples, with the highest levels of contamination detected in the immediate vicinity of the tailings dump. The obtained results indicate that the flotation tailings at the Gornje Polje site still contain significant amounts of material that may act as a potential source of heavy metal release into the environment.

Keywords: BCR sequential extraction, heavy metals, bioavailability, potential ecological risk.

INTRODUCTION

The growing demand for metals during industrial development has led to the exploitation of sulfide ores using flotation, a process that separates sulfide minerals from the surrounding material [1]. After the flotation process, material that does not contain economically valuable components is considered tailings and classified as mining waste [2]. The mineralogy of sulfide tailings is highly heterogeneous and specific, and upon exposure to an oxidative environment, it becomes chemically unstable which can lead to the release of harmful metals and environmental contamination if not properly managed [3].

Soil contamination by heavy metals in the vicinity of mining tailings represents a critical environmental challenge [4]. Mining tailings are rich in persistent and potentially toxic elements and are characterized by the presence of organic matter and low pH values, which favor metal mobility [5]. The total metal content is not an adequate indicator of

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ecotoxicological risk; their behavior in the environment depends not only on total concentration but also on the chemical forms in which they occur [6].

The sequential extraction procedure is widely applied to a large number of potentially toxic elements in various types of samples and represents an important tool for understanding their environmental behavior [4,7]. It primarily defines the distribution of metals within solid matrices, as well as their speciation, mobility, and adsorption capacity [8].

The analytical procedure of sequential chemical extraction was originally developed based on the work of Tessier, Bison, and Campbell in 1979 [6]. In that study, a method for the fractionation of trace metals into five fractions was proposed: exchangeable, carbonate-bound, Fe–Mn oxide-bound, organic matter-bound, and residual. Today, this method is applied to various types of materials, including soils [9], river, lake, and marine sediments [10], atmospheric particles [11], and mining waste [12].

This study investigates the ecological behavior and potential ecological risks of metals in soil located near a flotation tailings pond that is not subject to regular monitoring. For this purpose, a modified BCR sequential extraction procedure was applied, and the potential environmental risk associated with the deposited tailings waste was assessed.

MATERIALS AND METHODS

Sampling, BCR Extraction, and Potential Ecological Risk of Metals

The collected soil samples were air-dried in a closed space at room temperature for one week. After drying to constant weight, the samples were homogenized and sieved to a particle size of < 2 mm. The prepared soil samples (1 g of each sample) were subjected to a BCR sequential extraction procedure, as well as to the determination of pseudototal heavy metal concentrations. For the determination of pseudototal metal content, the ground soil samples were digested with aqua regia (15 mL of 37% HCl and 5 mL of 65% HNO₃) at 80 °C in a water bath for 5–6 hours. Pseudototal concentrations of metals (As, Cd, Cu, Pb, and Ni) in the soil samples were determined using inductively coupled plasma optical emission spectrometry (ICP-OES). The BCR extraction course was as follows:

- Step 1 (exchangeable, water, acid-soluble fraction): 1 g of sample was treated with 0.11 mol/dm³ CH₃COOH and shaken for 16 h to obtain F1;
- Step 2 (reducible fraction): F1 was treated with 0.5 mol/dm³ NH₂OH·HCl (adjusted to pH 1.5) and shaken for 16 h to obtain F2;
- Step 3 (oxidizable fraction): F2 was treated with 8.8 mol/dm³ H₂O₂ and 1 mol/dm³ CH₃COONH₂ (adjusted to pH 2) and shaken for 16 h to obtain F3;
- Step 4 (residual fraction): F3 was digested with aqua regia (15 mL of 37% HCl and 5 mL of 65% HNO₃) at 80 °C for 5–6 h to obtain F4.

The contamination factor (C_f^i) for individual metals in sediments was calculated according to the method proposed by Min *et al.* [13]. The contamination factor (C_f^i) for the analyzed sediment samples was determined using the following expression:

$$C_f^i = C_{\text{simple}}^i / C_{\text{reference}}^i \quad (1)$$

where C_f^i represents the contamination factor for a specific heavy metal, C_{simple}^i denotes the measured concentration of the metal in the analyzed soil sample, and $C_{\text{reference}}^i$ represents the reference value used as the basis for the calculation.

The potential ecological risk factor (E_f^i), as defined by Håkanson [14], was used to assess the toxicity of heavy metals and the sensitivity of the environment to their presence. Within this approach, each metal is assigned a specific toxicity coefficient, as follows: Cd = 30, As = 10, Cu = Pb = Ni = 5, and Zn = 1. The potential ecological risk factor for an individual heavy metal was calculated using the following formula:

$$E_f^i = C_f^i \cdot T_f^i \quad (2)$$

where T_f^i represents the toxicity factor for an individual heavy metal. The overall potential ecological risk index (R) for a set of heavy metals is expressed as the sum of the individual risk factors:

$$R = \sum E_f^i \quad (3)$$

Accordingly, the potential ecological risk factor (E_f^i) and the overall potential ecological risk index (R) are used to assess the overall environmental impact of heavy metals (Table 1).

Table 1 Relationship between the potential toxicity index (R), the potential ecological risk index (E_f^i), and pollution level

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
$40 \leq E_f^i < 80$	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		

RESULTS AND DISCUSSION

Pseudo-total concentrations of heavy metals (Cd, Cu, Pb, Ni, and As) in the studied soil samples indicate a clear enrichment of potentially toxic elements in the investigated area. The observed distribution pattern suggests a significant influence of anthropogenic activities, particularly mining and flotation tailings disposal, on metal accumulation in the soil.

The total concentrations of the analyzed elements in the soil samples ranged from 45 to 263 mg/kg for As, 2.03 to 18.38 mg/kg for Cd, 43.5 to 215.5 mg/kg for Cu, 8.66 to 195.58 mg/kg for Ni, and 611 to 4135 mg/kg for Pb. The concentrations of the examined metals, compared with the maximum allowable concentrations (MAC) prescribed by the national regulation [15], exceeded the permissible limits in almost all samples.

Although pseudo-total concentrations do not directly reflect the mobility or bioavailability of metals, they provide an essential initial indicator of the extent of soil contamination. In this

study, the elevated concentrations suggest that soils near tailings sites are significantly impacted and may pose a potential environmental risk

Table 2 Chemical composition of soil samples

Element (mg/kg)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Current limit value*
Cd	10.27	2.03	12.38	18.38	5.58	3
Cu	106.7	43.5	78.6	215.5	73.7	100
Ni	8.66	91.55	64.25	115.86	195.58	50
Pb	4135	611	733	3038	1345	100
As	70.0	45.0	184.0	263.0	124.0	25

*Official Gazette RS 23/94.

The results of the BCR sequential extraction are presented in Figure 1, which shows the distribution of Cd, As, Cu, Ni, and Pb, i.e., their mobility and bioavailability in soils from the investigated area. The distribution between stable and mobile fractions is clearly defined, allowing a more realistic assessment of environmental risk.

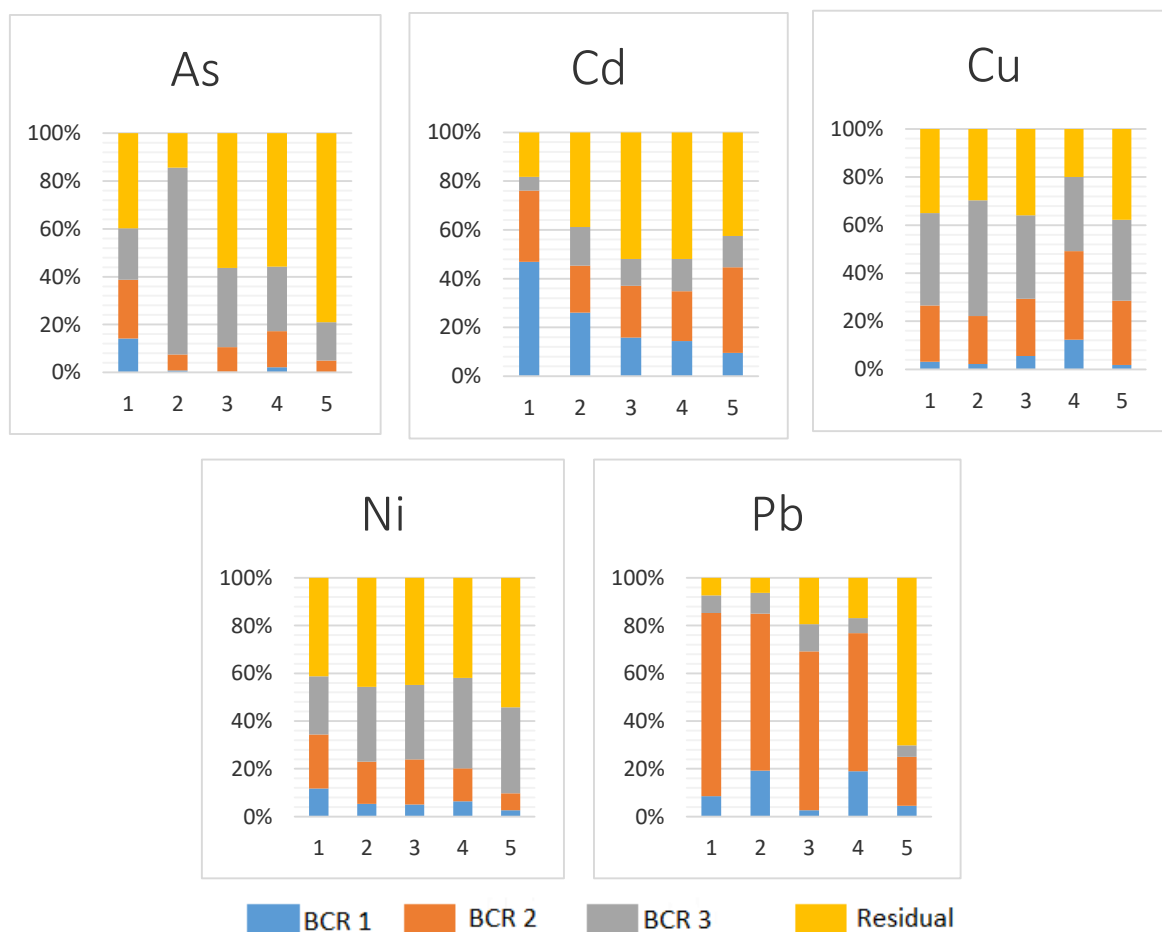


Figure 1 Distribution of metals in soil samples as determined by modified BCR sequential extraction procedure

The BCR 1 fraction is considered the most mobile and readily available, as metals in this phase are weakly bound to carbonates and exchangeable sites. Based on Figure 1, Cd appears

as the most mobile metal. Under low pH conditions, carbonates dissolve, leading to the release of Cd into the environment.

The BCR 2 fraction is particularly dominant for Pb and, to a lesser extent, for Cu and Cd, indicating that these metals are associated with Fe–Mn oxides through surface adsorption processes, which largely control their mobility and bioavailability. Under oxidative conditions, characteristic of mining tailings, Fe–Mn oxides and hydroxides play a significant role in the immobilization of metals such as Cd, Ni, As, Cu, and Pb through adsorption. However, the establishment of reducing conditions may destabilize these mineral phases, causing their dissolution and the subsequent release of bound metals into the environment [16].

The third step of the sequential extraction, BCR 3, corresponds to metals bound to organic matter and sulfides. Ni is predominantly associated with this fraction and may therefore be released under oxidizing conditions. Consequently, it shows low abundance in the most mobile fractions (Figure 1). As and Cu are also weakly associated with organic matter.

The residual (BCR IV) fraction represents the most stable form of metal binding, in which metals are associated with silicate minerals and are therefore considered largely unavailable to the environment and living organisms [17]. Based on Figure 1, it can be concluded that all analyzed metals occur in this fraction, with As and Ni showing the highest association with silicate-bound forms.

The main elements representing an environmental hazard are Cd, Pb, and As. The E_f^i values for Pb in samples S1 and S4 indicate a moderate potential ecological risk ($40 \leq E_f^i < 80$). Similar values were observed for As, although in different sampling locations compared to Pb. As exhibited a moderate potential ecological risk in samples S3, S4, and S5.

According to the results presented in Table 3, Cd shows the highest potential ecological risk values. In samples S1, S3, and S4, Cd indicates a higher potential ecological risk level ($80 \leq E_f^i < 160$), while sample S5 shows a moderate potential ecological risk.

The maximum R value was recorded in sample S4. According to the assessment criteria, samples S1, S3, and S5 exhibit a moderate level of ecological risk ($150 < R < 300$), whereas sample S4 indicates a severe level of ecological risk ($300 \leq R < 600$). Therefore, the soils in the investigated area show a significant potential ecological risk due to the presence of Cd, Pb, and As.

Table 3 Potential ecological risk assessment results of metals in soil samples

Sample	Element	C_{simple}^i ($\mu\text{g/g}$)	$C_{reference}^i$ ($\mu\text{g/g}$)	C_f^i	T_f^i	E_f^i	$R \sum E_f^i$
S1	Cd	10.27	3	3.42	30	102.6	199.2
	Cu	106.7	140	0.76	5	3.8	
	Ni	8.66	75	0.12	5	0.6	
	Pb	4135	300	13.78	5	68.9	
	As	70	30	2.33	10	23.3	
S2	Cd	2.03	3	0.67	30	20.1	52.9
	Cu	43.5	140	0.31	5	1.55	
	Ni	91.55	75	1.22	5	6.1	
	Pb	611	300	2.03	5	10.15	
	As	45	30	1.5	10	15	

Table 3 continued

S3	Cd	12.38	3	4.12	30	123.6	204.15
	Cu	78.6	140	0.56	5	2.8	
S4	Ni	64.25	75	0.85	5	4.25	337.65
	Pb	733	300	2.44	5	12.2	
	As	184	30	6.13	10	61.3	
	Cd	18.38	3	6.13	30	183.9	
	Cu	215.5	140	1.54	5	7.7	
S5	Ni	115.86	75	1.54	5	7.7	135.2
	Pb	3038	300	10.13	5	50.65	
	As	263	30	8.77	10	87.7	
	Cd	5.58	3	1.86	30	55.8	
	Cu	73.7	140	0.53	5	2.65	
S5	Ni	195.58	75	2.61	5	13.05	135.2
	Pb	1345	300	4.48	5	22.4	
	As	124	30	4.13	10	41.3	

CONCLUSION

The aim of this study was to investigate the influence of Gornje Polje flotation tailings on soil contamination with heavy metals. Based on the analysis of pseudo-total concentrations, the presence of As, Cd, Cu, Pb, and Ni was confirmed, with concentrations of the examined metals in most samples significantly exceeding the prescribed limit values.

The results of the sequential extraction indicate that heavy metals in soils adjacent to the flotation tailings are distributed among different geochemical fractions. It was observed that Cd is predominantly present in the mobile fraction, while Pb is mainly associated with the BCR 2 fraction, making it one of the most bioavailable metals after Cd. In contrast, Ni shows a stronger association with the oxidizable fraction, indicating its binding to organic matter and sulfide phases.

To assess the potential environmental risk, the individual ecological risk factor (E^i_r) and the overall risk index (R) were calculated. The results confirm that the mobility of Cd, Pb, and As has a significant influence on environmental risk, with the order of potential risk being $Cd > As > Pb$. The flotation tailings pond represents a long-term source of contamination, with the potential for metal remobilization under changing physicochemical environmental conditions.

Sequential extraction has proven to be an effective tool for environmental risk assessment and for understanding the behavior of heavy metals in contaminated soils.

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