The 56th International October Conference on Mining and Metallurgy
22-25 October 2025, Bor Lake, Bor, Serbia
www.ioc.tfbor.bg.ac.rs

DOI: 10.5937/IOC25669S
Original scientific paper

ASSESSMENT OF HEAVY METAL CONTAMINATION OF SOIL AND THE ECOLOGICAL RISK BASED ON NATIONAL LIMIT VALUES AND QUANTITATIVE INDICES

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Abstract

Heavy metals were examined in arable land in the vicinity of the Zijin Copper mine, Serbia in Veliki Krivelj, Oštrelj, Brezonik and Zlot. Soil samples were analyzed by ICP-MS. In order to identify the degree of soil contamination with heavy metals and assess the potential ecological risk, a combination of quantitative indices was applied: descriptive statistics (including coefficient of variation - CV), geoaccumulation index (Igeo), enrichment factor (EF), contamination factor (CF) and site pollution index (PLI). These indices enable a multi-layered analysis — from the identification of variability and anthropogenic impact to an integrated risk classification by location. Limit values defined by the national regulations of the Republic of Serbia were used for the reference values, which ensures the regulatory relevance and practical applicability of the results in the agroecological context.

Keywords: *soil contamination, heavy metals, descriptive statistics, ecological indices*

1. INTRODUCTION

The intensification of the mining activities of the Zijin Copper company in eastern Serbia has caused increased attention of the population, but also of the professional public due to the potential impact on the quality of arable land [1]. In light of environmental challenges and increasingly frequent demands for sustainable resource management, the assessment of soil contamination with heavy metals becomes crucial for the preservation of agroecological functionality and the health of the local community. Many researchers have used pollution factors and indices in the study of soil pollution [2,3,4]. In this research, a combination of quantitative indices — including coefficient of variation (CV), geoaccumulation index (Igeo), enrichment factor (EF), contamination factor (CF) and site pollution index (PLI) — was applied to enable multi-level analysis of contamination levels and identification of anthropogenic impact. These indices have proven to be reliable tools in modern studies of land degradation in the mining zones of Serbia [5,6].

2. EXPERIMENTAL PART AND METHODOLOGY

In order to assess the ecological risk of soil contamination with heavy metals, a combination of quantitative indices and statistical methods was applied, which enable a multi-level analysis of the degree of pollution and the identification of potential anthropogenic sources. Soil samples were collected from Veliki Krivelj, Oštrelj, Brezonik and Zlot locations in the immediate vicinity of mining activities, in accordance with the standards for environmental monitoring. Analyzes of metal concentrations (Cr, Cu, Zn, Cd, Co, Mn, Ni, Pb) were performed using the ICP-MS method (Inductively Coupled Plasma Mass Spectrometry). Instead of the metal reference value (C_b), limit values from the "Official Gazette of the RS" [7] were used, which ensured the regulatory relevance of the results.

The following indices were used to assess the degree of pollution:

- Coefficient of variation (CV), is the standard deviation (SD) divided by the mean, multiplied by 100%, equation (1):

$$CV=(SD/Mean)\times 100 \tag{1}$$

CV was used as an indicator of spatial heterogeneity of metal concentrations. For CV < 20% variability is low. CV in the range of 20–50% shows moderate variability, while CV > 50% confirms high variability.

- Geoaccumulation index (Igeo), was used to determine the degree of soil contamination with a certain element, is calculated according to equation (2):

$$Igeo = log_2(C_i/1.5\times C_{ib}) \tag{2}$$

Where C_i is the measured concentration of the i-th metal, and C_{ib} is the geochemical background concentration of the i-th metal. The formula incorporates a constant factor 1.5 to account for variations in background data as a result of natural processes [8,9]. Geoaacumulation index (I_{geo}) values were interpreted as $I_{geo} \leq 0$ – practically uncontaminated; $0 < I_{geo} \leq 1$ – uncontaminated to moderately contaminated; $1 < I_{geo} \leq 2$ – moderately contaminated; $2 < I_{geo} \leq 3$ moderately to heavily contaminated; $3 < I_{geo} \leq 4$ – heavily contaminated; $4 < I_{geo} \leq 5$ – heavily to extremely contaminated; and $5 < I_{geo}$ – extremely contaminated [10].

- Enrichment factor (EF), is a measure of the possible impact of antropogenic activity on the concentration of heavy metals in soil. EF is calculated by the following equation:

$$EF = \frac{(C_i/C_{ref})_{sample}}{(C_i/C_{ref})_{background}} \tag{3}$$

where: C_{ref} is the concentration of the selected reference element. Reference elements are characterized by the low variability of occurrence in the earth̓s crust, usually selected from the following group of metals: Fe, Al, Ca, Ti, Sc or Mn [10]. When EF > 2, soil enrichment is considered to be of anthropogenic origin. The EF has five classes: EF < 2, deficiency to minimal enrichment; 2 ≤ EF < 5, moderate enrichment; 5 ≤ EF < 20, significant enrichment; 20 ≤ EF ≤ 40, very high enrichment; EF > 40, extremely enrichment [9].

- Contamination factor (CF), is the ratio of the concentration of each heavy metal in the soil and the concentration of the respective heavy metal in the background (pre-industrial reference value for the same element). CF is calculated according to equation ():

$$CF = C_i/C_{ib} \tag{4}$$

The CF values indicate the following levels of contamination [9]: CF < 1, low contamination; 1 ≤ CF < 3, moderate contamination; 3 ≤ CF < 6, considerable contamination; CF ≥ 6, very high contamination.

- Pollution load index (PLI) was used for the total assessment of the degree of contamination in soil. It is defined as the n-th root of the multiplication of the CF of heavy metals involved. PLI for each location was calculated according to the following equation:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times ... \times CF_n)^{1/n} \tag{5}$$

Where CF_i is the contamination factor for the individual element, and n is the total number of pollution elements included in the study. PLI is usually classified as: PLI < 1 denotes no pollution, PLI =1 indicates only baseline levels of pollution and PLI >1 indicates deterioration of site quality [8,10].

3. RESULTS AND DISCUSSION

Descriptive statistics, shown in Table 1, indicate marked differences in the concentrations of heavy metals among the samples, both in terms of mean values and in terms of variability and the shape of the distribution. The coefficient of variation (CV) shows high heterogeneity for most metals. The highest variability has Cr (52.33%), Co (47.26%), and Mn (46.04%), which indicates uneven distribution and possible local sources of contamination. Zn (12.46%) shows the lowest variability, which may indicate a more uniform geogenic source or more stable mobility in the soil. The negative CV for Cd (-25.76%) is an artifact of the log-transformation and requires additional interpretation. Values were corrected due to detection limit.

Most metals exhibit negative kurtosis, indicating a flatter distribution with fewer extreme values than a normal distribution. Cd (skewness = 1.155) and Zn (1.052) show positive skewness, which may indicate the presence of samples with elevated concentrations — potentially relevant for identifying “hot spot” locations. Mn, Fe, Ni and Cu have skewness close to zero, suggesting an approximately symmetric distribution.

Fe has the highest mean concentration (39235 mg/kg), which is expected considering its natural abundance. Mn and Cu also show high values, while Ni, Co, and Cd are present in much lower concentrations. The ranges (min-max) indicate significant differences between locations, especially for Mn (482.7–1394.5 mg/kg) and Cu (192.7–605.5 mg/kg), which may indicate anthropogenic influence.

Table 1.Descriptive statistics applied to the presence of heavy metals in arable land at the locations: Veliki Krivelj, Oštrelj, Brezonik and Zlot

	mean	std	min	max	skewness	kurtosis	CV
Cr	32.9	17.3	15.9	49.2	-0.021	-1.938	52.33
Mn	973.1	447.9	482.7	1394.5	-0.104	-1.817	46.04
Fe	39235.0	10805.8	29982.4	52229.4	0.272	-1.641	27.54
Co	16.6	7.8	11.0	28	0.957	-0.845	47.26
Ni	14.9	5.6	9.9	21.7	0.294	-1.583	37.21
Cu	385.5	169.9	192.7	605.5	0.27	-1.016	44.09
Zn	79.5	9.9	72.9	94.1	1.052	-0.755	12.46
As	28.8	6.3	20.4	33.8	-0.544	-1.311	22.01
Cd	-0.132	0.034	-0.149	-0.081	1.155	-0.667	-25.76
Pb	36.8	10.8	28.8	52.6	0.962	-0.832	29.51

The highest variability, using formula (1), was shown by Cr (CV = 52.33%) and Co (CV = 47.26%), while Zn showed the lowest variability (CV = 12.46%), which indicates a more stable geogenic character. Cd was log-transformed, so the negative CV does not represent a physical value but a statistical one.

Table 2. Geoaccumulation index (Igeo) of heavy metals in agricultural soil at the locations L1 (Veliki Krivelj), L2 (Oštrelj), L3 (Brezonik) and L4 (Zlot)

	Igeo_Cr	Igeo_Mn	Igeo_Fe	Igeo_Co	Igeo_Ni	Igeo_Cu	Igeo_Zn	Igeo_As	Igeo_Pb	Igeo_Cd
L1	-1.608	-2.221	-0.398	-0.089	-2.407	3.487	-1.447	-0.201	-1.277	-0.585
L2	-1.693	-1.672	-0.388	-0.055	-1.275	2.857	-1.507	-0.110	-1.861	-0.585
L3	-3.238	-0.782	-0.231	0.060	-2.268	2.708	-1.158	-0.112	-2.054	-0.481
L4	-2.878	-0.690	-0.157	0.317	-1.610	1.835	-1.526	-0.329	-2.146	-0.532

Positive Igeo values, Table 2, for Cu (up to 3.487 at L1) indicate heavy contamination and Co (at L3 and L4), indicate while all other elements showed negative Igeo values, suggesting an uncontaminated state in relation to the limit values.

The highest value of enrichment factor (EF), Table 3, for Cu (61.635 at L3) indicates a dominant anthropogenic contribution, probably related to mining exploitation. Cd and Mn also show significant enrichment, especially at sites L3 and L4. In this study Cr was selected as reference element.

Table 3. Enrichment Factor (EF) of heavy metals in agricultural soil at the locations: L1, L2, L3, L4

	EF_Cr	EF_Mn	EF_Ni	EF_Cu	EF_Zn	EF_Cd	EF_Pb
L1	1	0.654	0.575	34.186	1.118	2.033	1.258
L2	1	1.015	1.336	23.414	1.138	2.155	0.890
L3	1	5.488	1.959	61.635	4.227	6.761	2.272
L4	1	4.557	2.409	26.239	2.553	5.086	1.661

The highest value of pollution load index (PLI), Table 4, was recorded at L2 (0.850), indicating a slightly elevated level of total contamination. All sites have PLI<1, suggesting that the soil is not in the high risk zone, but local values of Cu and Cd require further attention.

Table 4. Contamination factor (CF) and Pollution load index (PLI) of heavy metals in agricultural soil at the locations: L1, L2, L3, L4

	CF_Cr	CF_Mn	CF_Ni	CF_Cu	EF_Ni	CF_Zn	CF_Cd	CF_Pb	PLI
L1	0.492	0.322	0.283	16.819	0.575	0.550	1.000	0.619	0.823
L2	0.464	0.471	0.620	10.864	1.336	0.528	1.000	0.413	0.850
L3	0.159	0.873	0.311	9.800	1.959	0.672	1.075	0.361	0.730
L4	0.204	0.930	0.491	5.353	2.409	0.521	1.038	0.339	0.710

The combined application of these indices enables a multi-level assessment of the ecological state of the soil and the identification of heavy metals that require further attention in the context of agro-ecological security.

4. CONCLUSION

The results of descriptive statistics indicate a pronounced variability of metal concentrations, especially Cr, Co, Cu and MnThe results of the geoaccumulation index indicate that the soil in the analyzed locations is mostly uncontaminated when it comes to heavy metals Cr, Mn, Fe, Ni, Zn, As, Cd and Pb. However, the presence of positive Igeo values for Cu at all locations and Co on L3 and L4, suggests the existence of anthropogenic influence, probably related to mining exploitation and metallurgical activities in the area. The Enrichment Factor (EF) further confirms this tendency, with extreme values for Cu and significant enrichment for Cd at sites L3 and L4. Contamination Factor (CF) and Pollution Load Index (PLI) indicate moderate overall contamination, with no site exceeding the high risk threshold (PLI > 1).

These findings confirm the need for further analysis of ecological indices and spatial characterization of contamination.

ACKNOWLEDGEMENTS

The research presented in this paper was done with financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, within the Conctract No. 451-03-136/2025-03/200052.

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