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SPATIOTEMPORAL PATTERNS OF POTENTIALLY TOXIC ELEMENTS IN SOILS OF THE BOR AND MAJDANPEK MINING AREAS

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Abstract

This study evaluated spatial patterns and multi-season persistence of Cd, Cu, Ni, Pb, Zn and As at 14 soil locations in the Bor and Majdanpek mining areas, including 12 mining-affected and two reference sites. Fifty-six samples collected from summer 2025 to spring 2026 were assessed using descriptive statistics and screening indices based on uncorrected base values specified by Serbian legislation. Cu showed the most frequent exceedances (50/56), followed by As (16/56). Mean PLI values were highest at S6 and S2, whereas reference sites showed lower values. The results identify persistent Cu enrichment and priority locations for continued monitoring.

Keywords: *soil, mining, potentially toxic elements, spatial patterns, screening index*

1. INTRODUCTION

Mining and ore-processing activities introduce potentially toxic elements (PTEs) into surrounding soils through atmospheric deposition, particulate transport, runoff and redistribution of mine waste. Unlike river water, which responds rapidly to hydrological conditions, soil can retain contaminants and integrate inputs over longer periods. Consequently, repeated soil sampling can distinguish isolated high values from spatially persistent enrichment and identify locations requiring priority monitoring [1,2].

Eastern Serbia contains major copper-mining and mineral-processing areas, with agricultural and forest soils located at varying distances from open pits, flotation tailings ponds and processing plants. Previous research in the municipality of Bor identified Cu and As as the principal contaminants, demonstrated uneven spatial distributions and highlighted selected locations as monitoring priorities [2,3,4]. However, the persistence of PTE enrichment at fixed soil locations across consecutive seasons remains insufficiently described.

The objective of this study was to evaluate spatial patterns and multi-season persistence of Cd, Cu, Ni, Pb, Zn and As at 14 soil locations using descriptive statistics and concentration-based screening indices. Comparisons with Serbian limit values were used only for preliminary screening.

2. EXPERIMENTAL

Field reconnaissance was conducted before sampling to select 14 locations in the Bor and Majdanpek mining areas. S1–S12 represented agricultural or forest soils located near active mining, mineral-processing or tailings facilities, whereas S13 (Mosna) and S14 (Kobišnica), outside the direct influence of mining activities, served as reference sites (Figure 1). The same locations were sampled in summer and autumn 2025 and winter and spring 2026, resulting in a total of 56 samples. At each location, soil was collected from a depth of 0–30 cm using a soil-sampling probe, and approximately 1 kg of composite soil was obtained by combining five subsamples collected within the same site. The samples were labelled, placed in polyethylene zip-lock bags, and transported to the laboratory for further preparation and analysis.

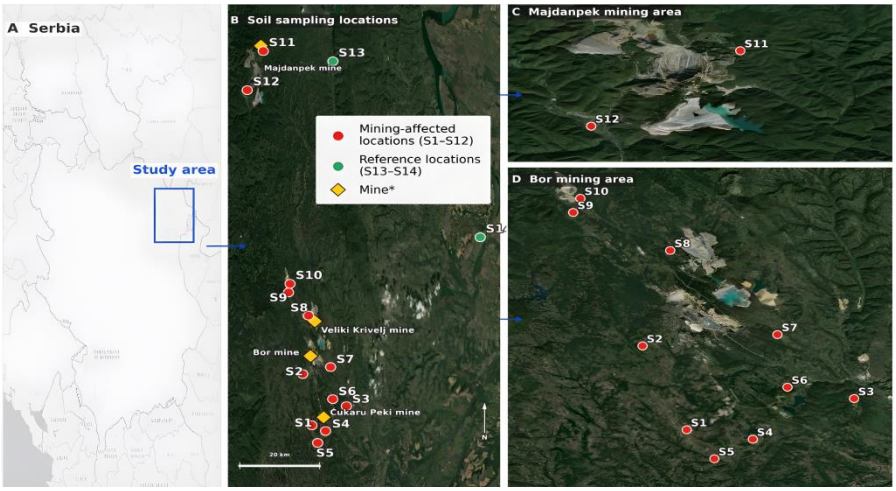


Figure 1. *Location of soil sampling sites in the study area, including mining-affected and reference sites*

In the laboratory, soil samples were air-dried at 25 °C, after which stones, plant residues and other visible debris were removed. The samples were crushed, homogenized and passed through a 2 mm sieve. Approximately 0.25 g of sample was microwave-digested with a mixture of nitric acid (HNO_3) and hydrochloric acid (HCl) using an ETHOS UP microwave system (Milestone, Italy), according to EPA 3051A:2007. The digest was quantitatively transferred and diluted to 25 mL with ultrapure water. Cd, Cu, Ni, Pb, Zn and As were determined using an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS), according to EPA 6020A:2007.

For each season and element, the mean, median, minimum, maximum, sample standard deviation and coefficient of variation were calculated. The single-element pollution index (PI) was calculated as follows:

$$PI_i = \frac{C_i}{GMV_i} \quad (1)$$

where C_i is the measured concentration of element i and GMV_i is the corresponding uncorrected base maximum limit value. The integrated pollution load index (PLI) was calculated as follows:

$$\mathrm{PLI} = (PI_{\mathrm{Cd}} \times PI_{\mathrm{Cu}} \times PI_{\mathrm{Ni}} \times PI_{\mathrm{Pb}} \times PI_{\mathrm{Zn}} \times PI_{\mathrm{As}})^{1/6} \quad (2)$$

The PLI was calculated as the geometric mean of the six PI values. The uncorrected base maximum limit values (GMVs) specified by Serbian legislation were 0.8, 36, 35, 85, 140 and 29 mg kg^{-1} for Cd, Cu, Ni, Pb, Zn and As, respectively [7]. Because clay and organic matter contents were unavailable, corrected GMVs could not be calculated.

Consequently, exceedance counts and PI/PLI values were interpreted as preliminary screening indicators rather than as the basis for a formal compliance assessment.

3. RESULTS AND DISCUSSION

3.1. Spatial distribution and priority locations

The distribution of screening indices was strongly location-dependent. S6 and S2 had the highest mean PLI values, 1.240 and 1.201, respectively. Table 1 summarizes the five highest-ranked mining-affected locations. S2 showed the greatest persistence, with PLI values above 1 in all four seasons; the ranking of S6 was influenced by a pronounced autumn maximum.

Table 1. *Spatial screening priorities based on mean PLI and multi-season persistence*

Rank	Location	Mean PLI	Seasons with PLI > 1	Principal driver	Max. PI
1	S6	1.240	2	Cu (Autumn)	56.22
2	S2	1.201	4	Cu (Autumn)	12.97
3	S11	0.989	2	Cu (Spring)	12.36
4	S4	0.967	1	Cu (Spring)	17.56
5	S1	0.937	2	Cu (Spring)	14.39

The highest individual concentration was Cu at S6 in autumn (2024 mg kg^{-1}; PI = 56.22). This extreme value increased the maximum seasonal PLI at S6 to 2.441. The reference locations S13 and S14 had substantially lower mean PLI values (0.416 and 0.286, respectively), although S14 contained an isolated autumn Ni concentration of 184.5 mg kg^{-1}. This finding demonstrates why integrated indices should be interpreted together with individual element concentrations.

3.2. Multi-season persistence

Figure 2 shows that integrated enrichment was spatially concentrated rather than uniformly seasonal. S2 and S6 remained among the most elevated locations across multiple campaigns, whereas most other sites had PLI values below 1. A recent study of Bor soils also reported uneven spatial distributions and Cu-dominated contamination; however, its PLI values used geochemical background concentrations and are not directly comparable with the regulatory-value-based indices used here [3]. The principal result is therefore the persistence of specific hotspots, rather than a common seasonal increase across the monitoring network.

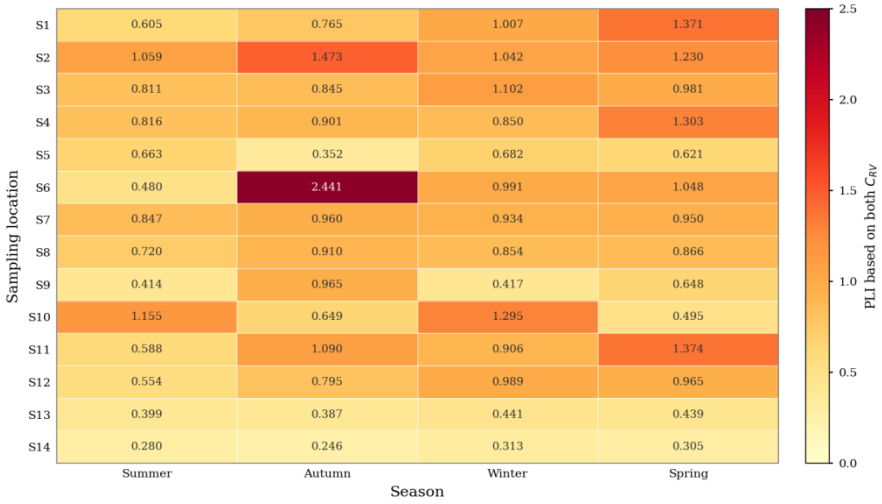


Figure 2. *Integrated PLI values by location and season; the blue line separates the reference sites*

3.3. Element-specific screening results

Across all 56 samples, exceedances of the uncorrected base GMVs occurred most frequently for Cu (50), followed by As (16), Zn (9), Cd (7), Ni (5) and Pb (1). Here, an exceedance denotes a measured concentration above the corresponding uncorrected base GMV. The predominance of Cu and the relevance of As agree with previous findings for soils influenced by mining and metallurgical copper production in the Bor area [2,3,4]. However, acid-extractable (pseudo-total) concentrations do not directly describe mobility or bioavailability, and geochemical fractionation can substantially alter environmental interpretation [1]. Therefore, the PI and PLI values identify screening priorities rather than ecological or human-health risks.

4. CONCLUSION

The study identified clear spatial contrasts and multi-season persistence of PTE enrichment in soils from eastern Serbia. S6 and S2 were the principal priority locations, while the two reference sites showed lower integrated values. Cu was the dominant screening concern, exceeding the uncorrected base GMV in 50 of 56 samples, followed by As. The results support location-focused monitoring and confirm that repeated sampling is useful for distinguishing persistent hotspots from isolated high values. Because clay and organic matter contents were unavailable, all regulatory comparisons and derived indices represent preliminary screening indicators and do not constitute a formal compliance assessment.

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