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ASSESSMENT OF SEASONAL DIFFERENCES AND As–Cu RELATIONSHIP IN SOILS OF THE BOR MINING AREA

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Abstract

Seasonal differences and As–Cu relationships were evaluated at ten mining-affected soil sites in the Bor mining area. The same locations were sampled in four campaigns from summer 2025 to spring 2026, resulting in a total of 40 samples analyzed by ICP-MS. Friedman tests showed no significant differences among campaigns for Cu ($p = 0.077$) or As ($p = 0.896$). The strongest Pearson correlation occurred in autumn ($r = 0.946$, $p < 0.001$), when both elements reached their maxima at S6, whereas Spearman correlations were moderate and non-significant. Neither systematic seasonal differences nor a stable As–Cu relationship were confirmed.

Keywords: *arsenic, copper, seasonal differences, correlation analysis, repeated-site sampling*

1. INTRODUCTION

Mining and metallurgical activities are important anthropogenic sources of potentially toxic elements in soil. Metal-bearing particles released during ore extraction, processing, tailings disposal and smelting may be deposited in surrounding areas and contribute to elevated concentrations of As and Cu. Their presence in soil may affect ecosystem quality and contribute to human exposure through transfer into plants and the food chain [1,2].

The Bor mining area in Eastern Serbia has been exposed to intensive copper mining and metallurgical activities for more than a century. Previous studies have identified arsenic (As) and copper (Cu) as major soil contaminants in this area, with elevated concentrations reported near the metallurgical complex, flotation tailings ponds and locations affected by prevailing winds [3,4]. However, repeated measurements at fixed sites are also needed to determine whether campaign-to-campaign fluctuations represent a systematic seasonal effect and whether the relationship between As and Cu remains stable over time.

Accordingly, this study tested whether As and Cu concentrations at ten repeatedly sampled soil sites differed significantly among four seasonal campaigns. It also evaluated Pearson and Spearman correlations separately for each campaign to determine whether the As–Cu relationship was stable throughout the monitoring period. Comparisons with Serbian soil limit values were retained only as supporting screening information.

2. EXPERIMENTAL

2.1. Study area and sampling

Ten soil sampling locations (S1–S10) were selected near major mining-related sources: S1, S4 and S5 in the vicinity of the Čukaru Peki processing plant; S2 near the Old Flotation tailings pond; S3 near the Zagrađe lime mine and processing facility; S6 in the vicinity of the Čukaru Peki and Jama underground mines; S7 near Field 2 of the Veliki Krivelj flotation tailings pond; S8 near the Veliki Krivelj open pit mine and S9 and S10 in the vicinity of the Cerovo open pit mine (Figure 1). Together, these locations cover areas influenced by different mining and processing facilities. The same sites were sampled during four campaigns (summer and autumn 2025 and winter and spring 2026), resulting in 40 composite samples for evaluating seasonal differences and As–Cu relationships.

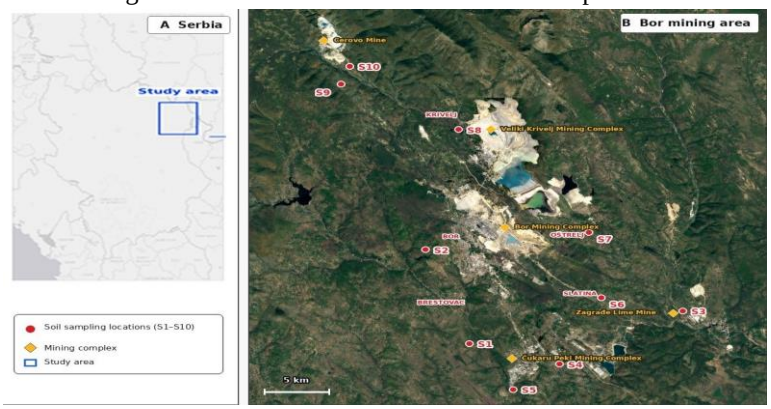


Figure 1. *Sampling locations in the Bor mining area*

At each site, soil was collected from a depth of 0–30 cm. Five subsamples were taken within the sampling area and combined to form one composite sample representative of the selected location. Approximately 1 kg of soil was collected per site. The samples were placed in labelled polyethylene bags and transported to the laboratory for preparation and analysis.

2.2. Sample preparation and analysis

The samples were air-dried at approximately 25 °C, homogenized and passed through a 2 mm sieve. Visible plant residues, stones and other coarse materials were removed before analysis. A representative portion of approximately 0.25 g was microwave-digested with a mixture of nitric acid (HNO_3) and hydrochloric acid (HCl) in an ETHOS UP system (Milestone, Italy), according to EPA 3051A:2007. After digestion, the obtained solutions were quantitatively transferred and diluted to a final volume of 25 mL.

As and Cu concentrations were determined using an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS) in accordance with EPA Method 6020A:2007. The results were expressed as mg kg^{-1} of dry soil.

2.3. Statistical analysis

For each element and sampling campaign, the mean, median, standard deviation, minimum, maximum and range were calculated. The uncorrected soil limit values (LVs)

prescribed by Serbian legislation were 29 mg kg^{-1} for As and 36 mg kg^{-1} for Cu [5]. Because clay and organic matter contents were unavailable, site-specific corrected LVs could not be calculated.

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

Because the same ten locations were sampled repeatedly, differences among the four seasonal campaigns were assessed using the non-parametric Friedman test at a significance level of $\alpha = 0.05$. Pearson correlation coefficients were calculated to examine linear relationships between As and Cu concentrations. Spearman rank correlation coefficients were additionally used to evaluate whether their relationship remained consistent when the influence of extreme concentrations and deviations from linearity was reduced. The correlations were calculated separately for each campaign.

3. RESULTS AND DISCUSSION

3.1. Seasonal descriptive statistics

Descriptive statistics for Cu and As across the four campaigns are summarized in Table 1, with LV exceedances included as screening background (formal seasonal testing is provided in Section 3.2).

Table 1. *Seasonal Cu and As concentrations (mg kg ⁻¹ dry mass) and numbers of sites exceeding the uncorrected LVs*

Element	Season	Mean	Median	SD	Range	No. of sites >LV
Cu	Summer	162.7	130.9	104.0	65.9–398.6	10
Cu	Autumn	417.9	248.5	575.6	40.7–2024.0	10
Cu	Winter	233.0	265.5	98.9	73.5–373.4	10
Cu	Spring	319.2	324.5	169.7	109.0–632.0	10
As	Summer	24.1	19.6	12.3	10.8–47.6	2
As	Autumn	32.1	24.8	30.6	7.2–111.6	3
As	Winter	28.5	30.8	11.4	8.3–40.1	5
As	Spring	29.0	28.2	17.5	7.1–61.8	5

Seasonal mean Cu concentrations ranged from 162.7 mg kg^{-1} in summer to 417.9 mg kg^{-1} in autumn (Table 1, Figure 2a). The difference between the autumn mean and median indicates that the seasonal mean was strongly affected by a limited number of high observations. All measured Cu concentrations exceeded the uncorrected LV of 36 mg kg^{-1}; therefore, exceedance counts did not distinguish among campaigns.

Mean As concentrations ranged from 24.1 mg kg^{-1} in summer to 32.1 mg kg^{-1} in autumn (Table 1, Figure 2b). The uncorrected LV was exceeded at two sites in summer, three in autumn and five in winter and spring. In autumn, both Cu and As reached their highest concentrations at S6 (2024 and 111.6 mg kg^{-1}, respectively), which affected the seasonal means and the Pearson correlation for that campaign.

3.2. Seasonal differences

The Friedman test did not confirm significant differences among the four campaigns for Cu ($\chi^2 = 6.84$, $p = 0.077$) or As ($\chi^2 = 0.60$, $p = 0.896$). Thus, changes in seasonal means and medians were insufficient to demonstrate a systematic effect of sampling season.

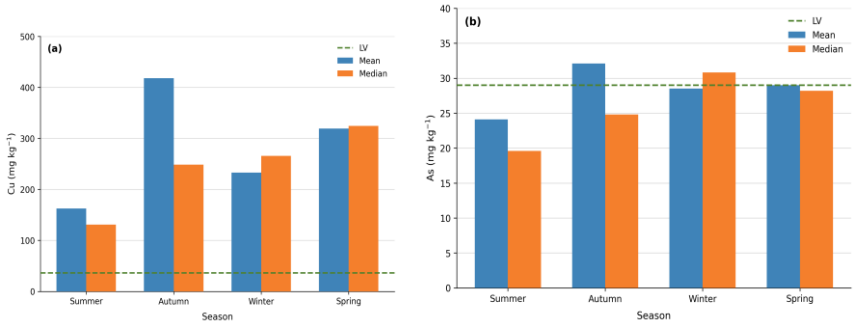


Figure 2. *Seasonal mean and median concentrations of (a) Cu and (b) As. Dashed lines indicate the applied uncorrected LVs.*

3.3. Relationship between As and Cu

Autumn showed the strongest Pearson As–Cu correlation ($r = 0.946$, $p < 0.001$), coinciding with the concentration maxima recorded at S6. Spearman correlations were moderate and non-significant ($\rho = 0.455–0.588$). The contrast between the two correlation measures suggests that the strong autumn linear relationship may have been influenced by these concentration maxima, while a stable As–Cu association across campaigns was not confirmed.

4. CONCLUSION

No significant seasonal differences in As or Cu were confirmed at the ten repeatedly sampled sites. The strong autumn Pearson correlation coincided with concentration maxima at S6, while the Spearman results did not support a stable As–Cu association across campaigns. The findings demonstrate the value of repeated-site sampling and complementary correlation methods for evaluating apparent seasonal changes.

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