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# ASSESSMENT OF THE COPPER AVAILABILITY BY EXTRACTION OF RIVERBED SEDIMENTS FROM EASTERN SERBIA WITH 0.5 M HCl

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**Abstract**

*This study assessed copper contamination and availability in riverbed sediments from 181 locations in Eastern Serbia. The highest total Cu concentrations (up to 26,400 mg/kg) with HCl-extractable fractions up to 80% were recorded downstream of the confluence of Bela and Timok Rivers, where secondary, highly labile copper phases dominated. In contrast, 145 of 181 samples contained <50% 0.5 M HCl-extracted Cu, indicating limited mobility. The findings highlight the need to assess both metal concentrations and speciation to evaluate ecological risk and guide site-specific management.*

***Keywords**: Copper, Riverbed sediments, Bioavailability, Extraction*

## 1. INTRODUCTION

Mining and metallurgical activities in the Bor region have significantly polluted river water and sediments in Eastern Serbia with potentially toxic elements (PTEs). Repeated discharges of flotation tailings into local rivers have led to their accumulation on riverbeds and floodplains along the Bor, Krivelj, Bela, and Timok Rivers. These tailings are still visibly present even at the confluence of the Timok and Danube Rivers. Approximately 2,000 hectares of fertile floodplain land along the Timok River have been contaminated by these deposits. In addition to the direct deposition of tailings, metal precipitation from polluted river water has further contributed to sediment contamination throughout the river system [1,2].

Although total PTE concentrations in sediments are elevated, the bioavailability of these elements to plants remains uncertain. Sequential extraction methods, such as the BCR procedure, are commonly employed to evaluate the partitioning of PTEs among different geochemical fractions [3]. However, these procedures involve multiple steps, making them labor-intensive and less practical for routine assessments. As an alternative, single extraction using diluted HCl has been proposed as a simplified and effective approach for estimating the concentrations of labile PTE forms in sediments [4-7].

In this study, the total digestion and 0.5 M HCl extraction was performed on riverbed sediment samples from Eastern Serbia, collected from areas impacted by copper mining and processing. The main objective was to assess the availability of copper and to evaluate the spatial distribution of both total and 0.5 M HCl-extracted copper concentrations.

## 2. EXPERIMENTAL

Riverbed sediment samples were collected at 181 locations in Eastern Serbia during the 2015 and 2016 sampling campaigns using a scoop sampling method. An average sampling density of approximately one sample per 46 km² was achieved. The samples were transported to the laboratory in labeled plastic bags, air-dried at room temperature, and subsequently sieved. The fraction smaller than 180 µm was retained for chemical analysis and extraction.

The total concentration of copper in the sediment samples was determined by Actlabs (Canada) following total digestion and analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). To estimate the available fraction of copper, 0.5 g of each sediment sample was subjected to extraction with 10 mL of 0.5 M hydrochloric acid [4]. The suspensions were agitated on a mechanical shaker for 1 hour, then centrifuged at 3,000 rpm for 20 minutes to separate the extract from the solid residue. The supernatants were filtered through 0.45 µm cellulose acetate syringe filters to remove any particulate matter. The filtered extracts were analyzed for copper concentrations using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), model SPECTRO CIROS VISION, at the Mining and Metallurgy Institute Bor. The percentages (%) of extracted Cu, were calculated based on the total and HCl-extracted Cu concentrations.

## 3. RESULTS AND DISCUSSION

Table 1 summarizes the statistical parameters for total copper concentrations, 0.5 M HCl-extractable copper, and the percentage of extractable copper in riverbed sediments from Eastern Serbia. The total copper concentrations ranged from 3.1 mg/kg to 26,400 mg/kg, with a median of 49.8 mg/kg and an average of 990 mg/kg, indicating a strong spatial variability influenced by mining and metallurgy-related inputs.

*Table 1. Descriptive statistics data based on the total and 0.5 M HCl-extracted Cu concentrations*

| Parameter | Unit | Minimum | Median | Average | Maximum |
|---|---|---|---|---|---|
| Total conc. of Cu | mg/kg | 3.1 | 49.8 | 990 | 26,400 |
| HCL extracted Cu | mg/kg | 1.2 | 16.8 | 404 | 20,660 |
| HCL extracted Cu | % of total Cu | 4.7 | 35.4 | 37 | 99.4 |

Figure 1 shows the geochemical maps of total copper concentration (mg/kg) and the percentage of 0.5 M HCl-extracted copper concentrations relative to the total copper content in river bed sediments. The highest total copper concentrations were recorded in sediments from the Bor and Bela Rivers, as well as in the Timok River downstream from its confluence with the Bela River. Elevated concentrations were also observed in the middle and lower reaches of the Timok River, as well as in the Krivelj and Pek Rivers.

Among the locations with the highest total copper concentrations, the sites along the Timok River after its confluence with the Bela River exhibited the highest percentage of 0.5 M HCl-extracted copper. The source of labile copper is likely the precipitated material in the sediment that was formed by the neutralization of acidic waters from the Bela River by the alkaline waters of the Timok River [2]. Precipitated copper(II) species – such as copper(II) hydroxide ($Cu(OH)_2$), copper(II) carbonate ($CuCO_3$), and copper ions adsorbed onto iron(III) oxyhydroxides – are known to be readily soluble in acidic conditions, such as those provided by the 0.5 M HCl extraction. As a result, copper in these sediments is considered labile and may be readily mobilized under changing environmental conditions, increasing its potential bioavailability to aquatic organisms and plants.

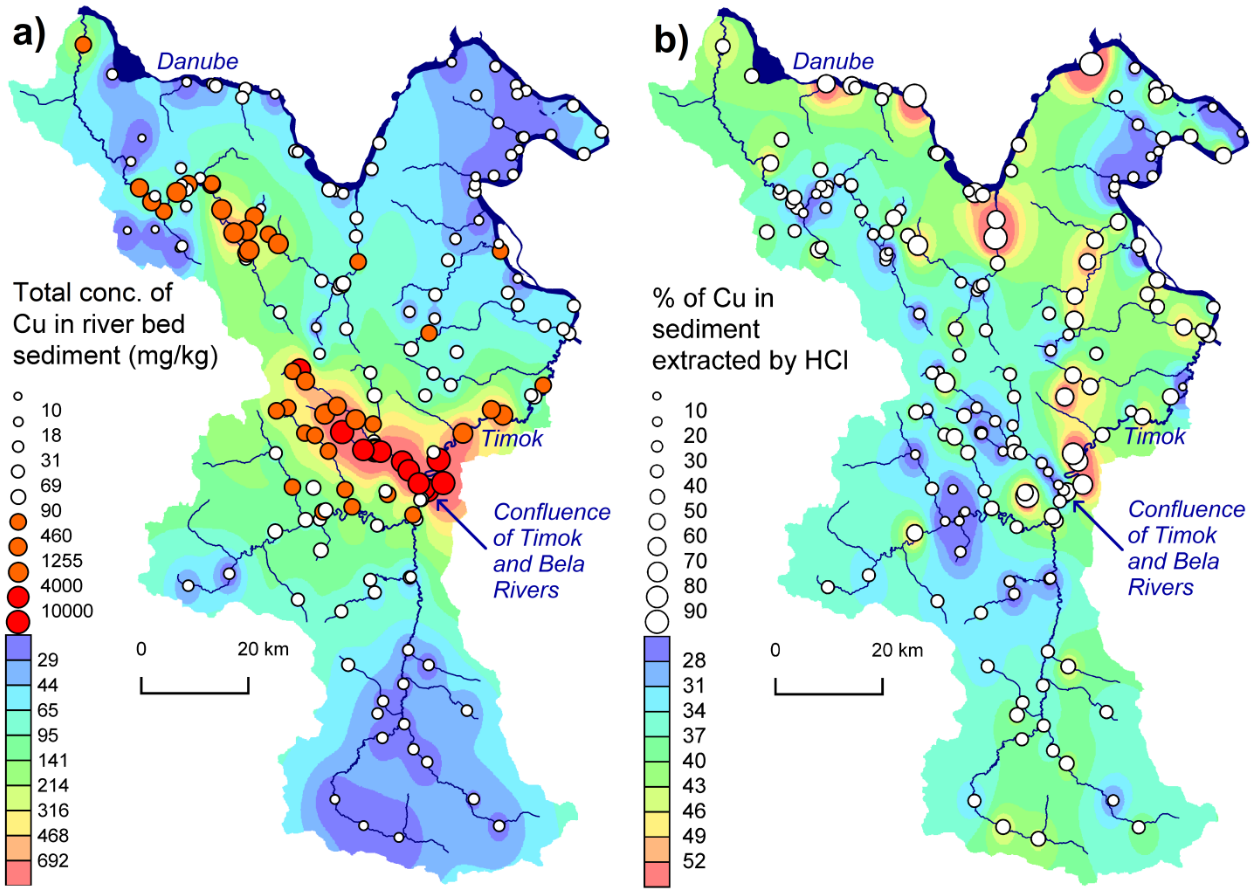


*Figure 1. Geochemical maps of (a) total copper concentrations (mg/kg) and (b) the percentages of HCl-extracted copper relative to the total copper contents in river bed sediments*

Figure 2 illustrates the relationship between total copper concentrations in riverbed sediments (blue bars, right y-axis) and the percentage of copper extracted using 0.5 M HCl (red line, left y-axis) for 181 sediment samples collected across Eastern Serbia. The samples are arranged in ascending order based on the percentage of 0.5 M HCl-extracted copper, enabling a direct comparison between the total copper content and its potentially available fraction.

A clear distinction is observed between samples in which copper is predominantly bound within stable mineral phases and those where it occurs in more labile, readily soluble forms. In 145 of 181 samples (~80% of samples), the percentage of 0.5 M HCl-extractable copper was below 50%, indicating that copper in the majority of samples was predominantly retained within relatively immobile mineral matrices. In contrast, two samples with the highest total copper concentrations (26,400 mg/kg and 16,300 mg/kg) also exhibited some of the highest percentages of 0.5 M HCl-extractable copper (78.3% and 79.3%, respectively). As discussed earlier, these locations are situated within 15 km downstream of the confluence of the Timok and Bela Rivers.

Some samples with relatively high total copper concentrations (5,000–15,000 mg/kg) but low extractable fractions (10–20%) still contain considerable amounts of labile copper (500–3,000 mg/kg), which may represent a potential ecological concern. The majority of these sediments were exposed to the acidic waters of the Bor and Bela Rivers, where the most mobile copper was likely already leached out. Conversely, 126 samples contained low total copper concentrations (<100 mg/kg), and although some of them exhibited relatively high percentages of mobile copper (up to 99.4%), the overall low copper content suggests that these locations are less likely to pose significant environmental risk despite the elevated copper availability.

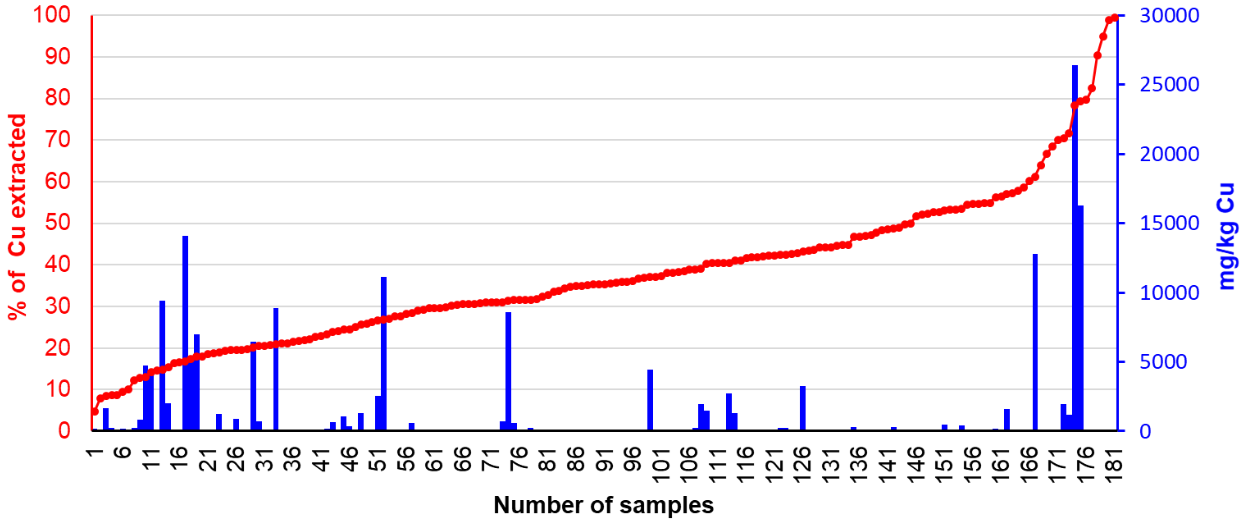

*Figure 2. Total copper concentrations (blue bars) and percentages of HCl-extractable copper (red line)*

## 4. CONCLUSION

This study demonstrates significant spatial variability in copper contamination and mobility within riverbed sediments of Eastern Serbia. While about 80% of samples contained less than 50% of 0.5 M HCl-extracted copper, indicating limited mobility, several pollution hotspots along the Timok River downstream of its confluence with the Bela River, exhibited extremely high total Cu concentrations (up to 26,400 mg/kg) combined with high extractable fractions (~80%). These locations were dominated by secondary, highly labile copper phases that can be readily mobilized under changing environmental conditions. The findings emphasize the need to assess both total metal concentrations and their chemical speciation when evaluating ecological risk and highlight the importance of site-specific management strategies.

## ACKNOWLEDGEMENTS

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