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SEDIMENT TRAPPING AND TRACE METAL ENRICHMENT IN FLUVIAL SCULPTED FORMS OF A BEDROCK RIVER (MIÑO RIVER, OURENSE, NW IBERIAN PENINSULA)

APRISIONAMENTO DE SEDIMENTOS E ENRIQUECIMENTO EM METAIS VESTIGIAIS EM FORMAS FLUVIAIS ESCULPIDAS DE UM RIO DE LEITO ROCHOSO (RIO MINHO, OURENSE, NOROESTE DA PENÍNSULA IBÉRICA)

ATRAPAMIENTO DE SEDIMENTOS Y ENRIQUECIMIENTO EN METALES TRAZA EN LAS FORMAS FLUVIALES ESCULPIDAS DE UN RÍO DE LECHO ROCOSO (RÍO MINHO, OURENSE, NOROESTE DE LA PENÍNSULA IBÉRICA)

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Abstract

This study focuses on sediment composition and trace metal accumulation in the Miño/Minho River, with an emphasis on bedrock rivers. The research employs robust non-parametric statistics to analyze sediment composition in three distinct deposition microenvironments: (i) surface sediments trapped in rock cavities, (ii) permanent sediment trapped in a pothole, and (iii) untrapped river sediment. Robust regression is used for reference level estimation. Enrichment assessment through local enrichment factors reveals Cu and Pb accumulation in rock cavities, potentially linked to post-depositional processes influenced by seasonal water dynamics. The study highlights the effectiveness of robust statistics for sediment data analysis and identifies rock cavities as significant traps for trace elements, possibly of anthropogenic origin, in urban river settings. However, the study acknowledges the necessity of further research to comprehensively understand the intricate processes shaping sediment composition in bedrock rivers, considering the multifaceted physical, chemical, and biological factors at play.

Keywords: Bedrock river. Trace elements. Sedimentation microenvironments. Miño River. Urban river.

Resumo

Este estudo foca na acumulação de metais traço nos sedimentos do rio Miño/Minho, referindo-se aos rios sobre rocha. Este trabalho utiliza estatísticas robustas para analisar a composição do sedimento em três microambientes de deposição diferentes: (i) sedimentos superficiais aprisionados em cavidades rochosas, (ii) sedimentos permanentes aprisionados numa marmita de erosão e (iii) sedimentos fluviais não aprisionados. A regressão robusta é utilizada para a estimativa do nível de referência. A avaliação do enriquecimento através do fator de enriquecimento local revela uma acumulação de Cu e Pb em cavidades rochosas, possivelmente ligada a processos pós-deposicionais influenciados pela dinâmica sazonal da água. O estudo destaca a eficácia das estatísticas robustas para a análise de dados sedimentares e identifica as cavidades rochosas como armadilhas significativas para elementos traço que poderiam ter uma origem antropogénica em ambientes urbanos fluviais. No entanto, é necessário reconhecer a necessidade de mais investigação para compreender de forma abrangente os intrincados processos que moldam a composição dos sedimentos em rios sobre rocha, considerando os diversos fatores físicos, químicos e biológicos em jogo.

Palavra-chave: Rio de leito rochoso. Elementos traço. Microambientes de sedimentação. Rio Minho. Rio urbano.

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Resumen

Este estudio se centra en la acumulación de metales traza en sedimentos del río Miño/Minho, referenciando los ríos sobre roca. Este trabajo utiliza estadísticos robustos para analizar la composición del sedimento en tres microambientes de deposición diferentes: (i) sedimentos superficiales atrapados en cavidades rocosas, (ii) sedimentos permanentes atrapados en una marmita de erosión, y (iii) sedimentos fluviales no atrapados. Se utiliza la regresión robusta para la estimación del nivel de referencia. La evaluación del enriquecimiento a través del factor de enriquecimiento local revela una acumulación de Cu y Pb en cavidades rocosas, posiblemente vinculada a procesos post-deposicionales influenciados por la dinámica estacional del agua. El estudio destaca la eficacia de los estadísticos robustos para el análisis de datos sedimentarios e identifica las cavidades rocosas como trampas significativas para elementos traza que pudieran tener un origen antropogénico en entornos urbanos fluviales. Sin embargo, se debe reconocer la necesidad de más investigación para comprender de manera integral los intrincados procesos que dan forma a la composición de los sedimentos en ríos sobre roca, considerando los diversos factores físicos, químicos y biológicos en juego.

Palabras clave: Río sobre roca. Elementos traza. Microambientes de sedimentación. Río Miño. Río urbano.

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1 Introduction

Bedrock rivers differ from alluvial rivers based on the extent of sediment cover. A bedrock river has little to no alluvium covering the bedrock over which it flows (WHIPPLE et al., 2013), Although most bedrock rivers are not in their pure form and are a combination of a bedrock channel and an alluvial channel, the distinction between the two types of rivers is primarily based on the extent of sediment coverage (TUROWSKI et al., 2008). The sediments in bedrock rivers are intermediate products of the weathering and erosion processes, and they can contain a variety of materials, including the imprint of human impact on natural systems. It is critical to correctly separate the natural and anthropogenic loads when trying to decipher human signals in sediments, particularly when trace metals like Cu, Ni, Pb, or Zn are used as indicators (BIRCH and OLMOS, 2008).

As trace metals are naturally present in sediments, the correct estimation of a baseline is crucial before determining the human load in sediment composition (MATYS GRYGAR et al., 2013). Among the many techniques used (BIRCH, 2017), normalization by a lithogenic element (reference element, hereinafter RE) and regression between the RE and the target element (TE) have shown to be highly useful (GRYGAR and POPELKA, 2016).

The compositional data analysis of sediments is commonly performed using parametric statistics assuming a normal distribution of the data, as evidenced by the extended use of the mean and the standard deviation to characterize populations. However, this approach requires a previous normality assessment and/or separation of different populations (ÁLVAREZ-VÁZQUEZ et al., 2018; FARINANGO et al., 2023), as sediment composition often responds to polymodal distributions caused by the participation of different lithologies or the presence of human alterations (GRYGAR and POPELKA, 2016; ÁLVAREZ-VÁZQUEZ et al., 2020). Non-parametric robust statistical techniques, like robust regression (RR) (GRYGAR et al., 2020), have been scarcely studied although they could make the analysis easier and more rapid.

The sediments in bedrock rivers are scarce, including sediment patches along the bed and materials trapped in potholes and other rock cavities. Previous investigations have suggested differential trace metal accumulation patterns depending on depositional environments (ÁLVAREZ-VÁZQUEZ et al., 2021: MILLER et al., 2021; ÁLVAREZ-VÁZQUEZ et al., 2023), hypothesizing that post-depositional dynamics and processes increase trace metal enrichment in sediments, particularly those trapped by rock cavities.

Consequently, the aim of this work is twofold. On the one hand, it performs a comparison between sediment composition and the accumulation of trace metals in different depositional microenvironments. On the other hand, this work relies only on robust non-parametric statistics, avoiding the assumption of normal distribution of the population composition.

2 Material and Methods

The Miño River (Minho in Portugal) is a 340-kilometer-long waterway originating in the Serra de Meira (Spain). Known as the region's longest and most iconic aquatic waterway, the Miño weaves through landscapes and historic towns, like the City of Ourense (Spain), which hosts slightly more than 100,000 inhabitants. As it nears the Atlantic Ocean, the river transforms into a lush estuary, fostering diverse flora and fauna. Serving as a cultural and environmental bridge between Spain and Portugal, the Miño forms a shared border for over 70 kilometers. Designated as a Natura 2000 site, the Miño River plays a key role in biodiversity conservation and sustainable development.

The surveyed area is a 5-kilometer urban stretch of the Miño River (Fig. 1) as it courses through the urban fabric of the city of Ourense. The area is highly modified by anthropogenic factors such as dams, roads, promenades, bridges, urban and industrial facilities, households, etc. This stretch can be considered a bedrock river, as the water flow traverses exposed granitic substrates with an abundance of sculpted forms, including areas with accumulated boulders, pebbles, and sandbars.

This work is an expansion of a previous study where 24 samples of sediments trapped by fluvial sculpted forms in the granitic substrate (potholes, furrows, and other rock cavities) were analyzed to compare composition similarities and differences related to particle size distribution (ÁLVAREZ-VÁZQUEZ et al., 2023). To complete the database, this work also includes data from 7 additional samples of untrapped sediments from patches along the riverbed margins.

Thus, the final database includes (i) 12 surface sediment (5 cm depth) samples trapped in rock cavities (CAV code); (ii) 12 samples from a column of consolidated sediment trapped in a pothole-like cavity (COR code), sliced in 2 cm layers from the surface to the bottom (22 cm depth); and (iii) 7 river sediment samples untrapped by rock cavities (RIV code).

Samples were collected during low flow in the dry season (summer) directly from areas commonly flooded by the river water level. Sediments were withdrawn with a plastic spatula and stored in plastic zip bags.

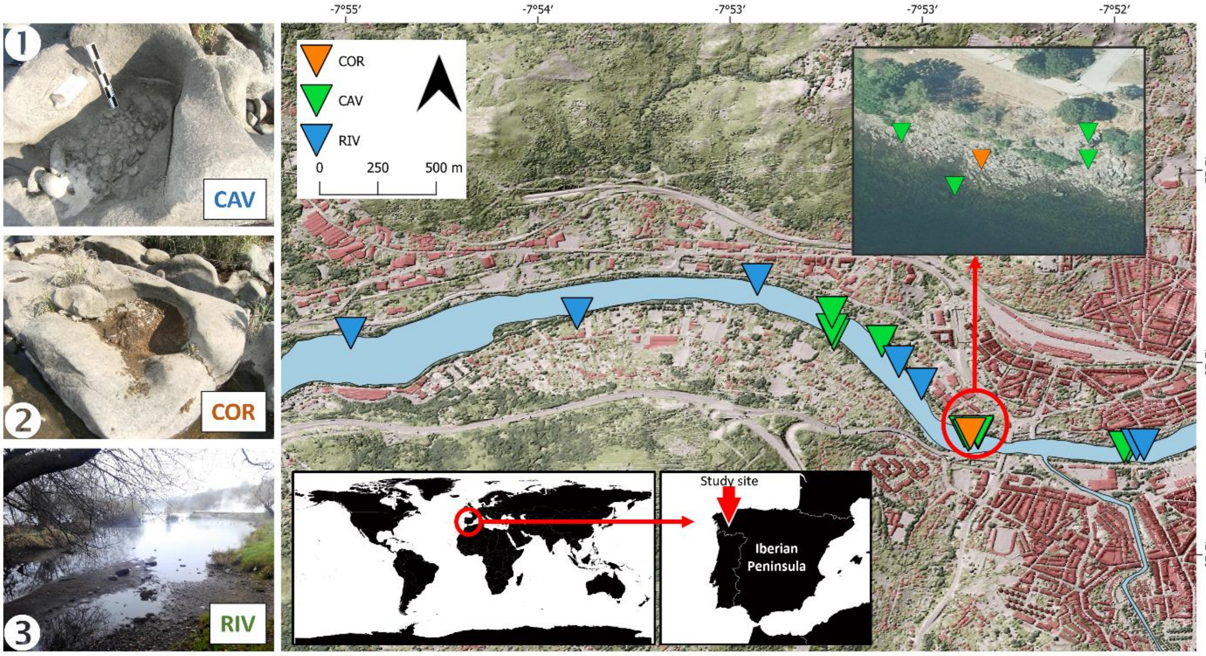

Figure 1. Location map of the study area and its urban context. Pictures represent the three sedimentation microenvironments under study: (1) surface sediments trapped in rock cavities, (2) permanent sediments trapped in a fluvial pothole, and (3) untrapped fluvial sediments. The map was elaborated using QGIS software, with basemaps sourced from PNOA and PNOA LiDAR (IGN, Spain).

Sediments were oven-dried at 45±5 °C until a constant weight was reached. A first normalization procedure was employed to minimize particle-size on sediment composition (LORING, 1991; HERUT and SANDLER, 2006). To achieve this, samples were sieved, and the fine fraction (particle size < 0.063 mm) was separated for further analysis. The composition of the fine fraction was determined by ICP-OES, after acid digestion, in the Center for Scientific-Technological Research Support (CACTI) of the University of Vigo. Five potential reference elements (i.e. Al, Ca, Mg, U, and Y) and four target elements (i.e. Cu, Ni, Pb, and Zn) were included in the working dataset.

The statistical data treatment was performed using the R software (R CORE TEAM, 2023). For code completion, code generation, debugging, and other specific tasks related to the coding process, ChatGPT 3.5, developed by OpenAI, was utilized (OPENAI, 2023). Only robust statistics were employed in the data analysis.

3 Results and Discussion

3.1. Assessment of trace metals contents

The measured contents of target trace elements in the samples under study are summarized in Figure 2 as box and whisker plots to show the dispersion of data distribution. These contents, expressed as the median, are similar to or higher than some references.

Compared with the contents of the average Earth crust composition (i.e., 50 mgCu kg^{-1}, 80 mgNi kg^{-1}, 14 mgPb kg^{-1}, and 75 mgZn kg^{-1}; EMSLEY, 2011), the Upper Continental Crust (i.e., 28 mgCu kg^{-1}, 47 mgNi kg^{-1}, 17 mgPb kg^{-1}, and 67 mgZn kg^{-1}; RUDNICK and GAO, 2003), the reference of floodplain sediments of the Geochemical Atlas of Spain (i.e., 27 mgCu kg^{-1}, 27 mgNi kg^{-1}, 37 mgPb kg^{-1}, and 91 mgZn kg^{-1}; LOCUTURA et al., 2012), and reference levels of Galician sedimentary soils (i.e., 12 mgCu kg^{-1}, 25 mgNi kg^{-1}, 20 mgPb kg^{-1}, and 44 mgZn kg^{-1}; MACÍAS VÁZQUEZ and CALVO DE ANTA, 2008). The comparison of contents of three microenvironments (i.e., CAV, COR, and RIV subsets, Fig. 2) reveals particularly high values in the COR samples for Cu (up to 303 mg kg^{-1}) and Pb (3031 mg kg^{-1}), both in the deeper layer (22 cm) of the core.

For statistical assessment of similarities and differences, a multiple sample comparison was conducted after the Kruskal-Wallis test to identify which pairs of groups differed significantly (alpha 0.5). This was done using the *kruskalmc* function from the *pgirmess* package (GIRAUDOUX et al., 2022). The results revealed how the COR contents significantly differentiate from the other depositional microenvironments for Cu and Pb, with the contents of Ni and Zn not significantly different between the CAV, COR, and RIV subsets. In other words, the depth-consolidated sediments trapped in a rock cavity (COR) tend to accumulate higher contents of Cu (2.6-3.3 times higher) and Pb (3.3-3.6). The other elements, Ni and Zn, showed similar median contents.

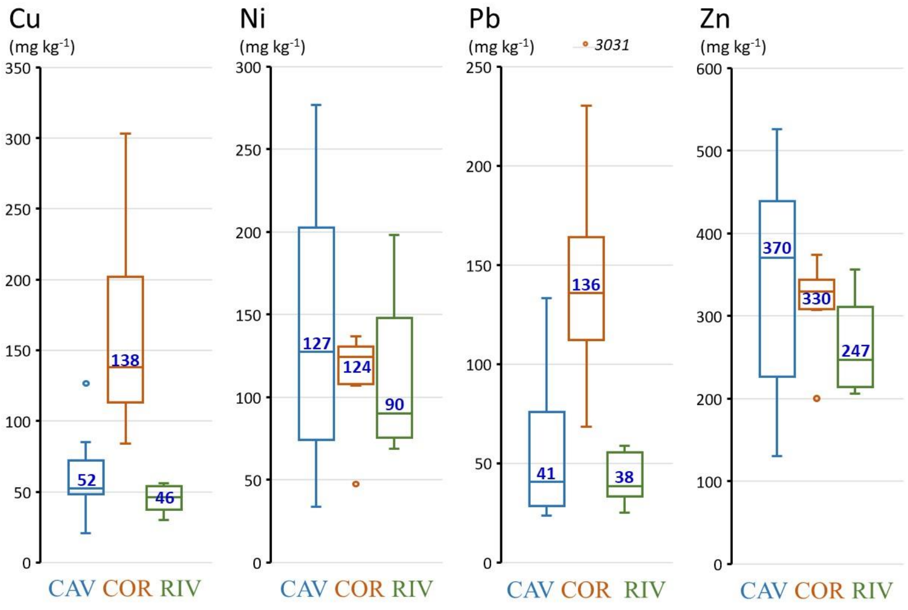

Figure 2. Box and whisker plots of the content data distribution for the four trace elements under study. Numbers inside the box indicate the median value.

3.2. Baseline estimation

Before estimating a reference content baseline, the potential reference elements were empirically checked to select the most appropriate one for each target element, as recommended by Grygar and Popelka (2016). Spearman's rank correlation coefficients were calculated using the *cor* function from the *stats* package (R CORE TEAM, 2023), a method used to assess the strength and direction of the monotonic relationship between two variables.

The analysis revealed good correlations between the following pairs of elements (RE-TE): Al-Cu (correlation coefficient = 0.67), Al-Pb (0.63), Mg-Ni (0.72), and Mg-Zn (0.78). Only the higher correlation coefficients are presented; more detailed results are in Table 1. Consequently, Al was selected as the reference element for Cu and Pb, while Mg was chosen for Ni and Zn.

Table 1. Spearman rank correlation coefficients between potential reference elements (columns) and target elements (rows).

	Al	Ca	Mg	U	Y
Cu	0.67	-0.00	0.33	0.29	0.37
Fe	0.79	-0.24	0.33	0.15	0.32
Ni	0.27	0.68	0.72	-0.27	0.70
Pb	0.63	0.07	0.25	0.30	0.30
Zn	0.26	0.62	0.78	-0.17	0.71

The reference baseline was estimated as background functions (BGf) by Robust regression (RR) with MM-estimator using the *lmrob* function from the *robustbase* package (MAECHLER et al., 2022). Background functions allow the estimation of the empirical background content of any target element ($[TE]_{BG}$) as a function of the measured content of a reference element ([RE]). In this case, a linear relationship was selected and the BGf takes the shape of a line, general formula $[TE]_{BG} = a[RE] + b$, where a stands for the slope and b for the intercept. The resulting background functions, graphically presented in Figure 3, were as follows:

$[Cu]_{BG} = 0.0119[Al] - 107.2$ R: 0.65

$[Ni]_{BG} = 0.0604[Mg] - 124.4$ R: 0.77

$[Pb]_{BG} = 0.0129[Al] - 122.8$ R: 0.60

$[Zn]_{BG} = 0.1244[Mg] - 181.3$ R: 0.82

To check the performance of RR, Table 2 presents a comparison of the estimated reference baseline in this study with the former work (ÁLVAREZ-VÁZQUEZ et al., 2023) where the BGfs were calculated by iterative least squares regression (iLSR). This last approach implies successive regressions, deleting unusual residuals in each step, while RR was performed directly in a single step.

The estimated contents presented in Table 2 are relatively similar, and no statistically significant difference was found between the pair of values for each target element.

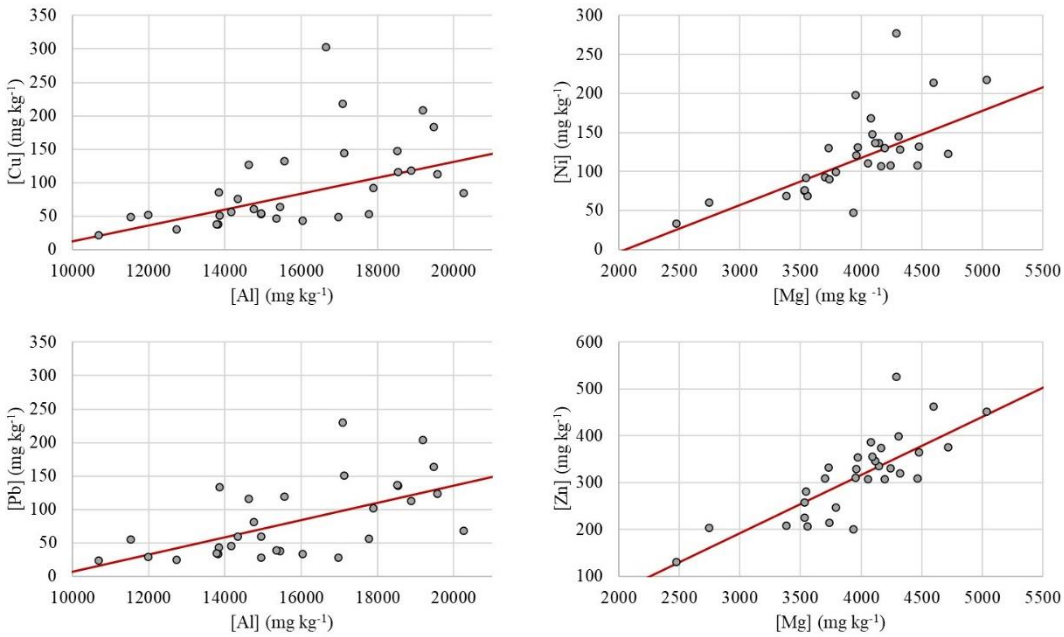

Figure 3. Graphical representation of the background functions from robust regression.

Table 2. Estimated baseline comparison between results from iterative least squares regression (iLSR) and robust regression (RR). The iLRS estimation was performed with the CAV and COR samples (n = 24). The RR estimation also includes RIV samples (n = 31).

	iLSR	RR
$[Cu]_{BG}$	83.3±38.1	81.0±30.0
$[Ni]_{BG}$	102.3±27.3	115.0±31.6
$[Pb]_{BG}$	86.2±47.8	81.3±32.5
$[Zn]_{BG}$	331.7±59.5	311.8±65.1
Reference	Álvarez-Vázquez et al., 2023	This study

3.3. Enrichment assessment

After estimating the reference baseline, enrichment can be assessed. The enrichment factor (EF, COVELLI and FONTOLAN, 1997; BIRCH, 2023) measures the extent to which the content of a given target element ([TE]) deviates from its estimated baseline ($[TE]_{BG}$), calculated for each sample according to the background function. As it was estimated in a local context, it is referred to as the local enrichment factor (LEF, NOVÁKOVÁ et al., 2016) and its mathematical expression responds to the formula LEF = $[TE]/[TE]_{BG}$.

The calculation of the enrichment factor in function of a reference element is a way of chemical normalization (HERUT and SANDLER, 2006), which can reduce the effect of natural variability in sediment composition. Thus, LEFs seems to be a better magnitude to compare different datasets.

A summary of the LEF calculation for each sample and the distribution of the LEF values are presented in Figure 4. At first glance, by comparing ranges in the boxplots, the contents of Ni and Zn in the three microenvironments seem to belong to the same population, while for Cu and Pb, they seem to show a mixture between two populations, particularly in the CAV and COR samples. A multiple comparison test after Kruskal-Wallis (alpha 0.05) was again performed to check similarities and differences between the three subsets.

The results show that only Cu and Pb in the RIV samples (arrows in Fig. 4) are statistically different from the contents in the CAV and COR microenvironments.

These results show an increased accumulation of Cu and Pb not only in the COR but also in the CAV samples, suggesting any factor promoting the accumulation of these trace metals in sediments trapped into rock cavities. This enrichment is particularly intense in the bottommost sample of the COR (22 cm depth) where the LEFs for Cu and Pb reached the highest values, i.e., 3.33 (303 mgCu kg^{-1}) and 32.96 (3031 mgPb kg^{-1}), respectively. It is also noteworthy the absence of LEFs representative of significant enrichment (e.g., > 2) in the RIV samples.

	LEF Cu	LEF Ni	LEF Pb	LEF Zn
CAV01	0.87	1.21	2.38	1.01
CAV02	0.51	0.76	0.29	0.92
CAV03	1.18	2.06	0.96	1.49
CAV04	1.48	1.06	0.78	1.13
CAV05	0.83	1.39	0.50	1.18
CAV06	1.89	0.94	1.76	1.11
CAV07	1.61	1.45	2.12	1.27
CAV08	1.44	0.86	0.89	0.87
CAV09	1.05	1.33	1.56	1.03
CAV10	0.65	1.02	0.60	1.08
CAV11	0.75	0.90	0.41	0.97
CAV12	0.89	1.38	1.20	1.18
COR01	1.70	1.29	1.53	1.18
COR02	1.02	1.13	1.17	1.13
COR03	1.49	1.05	1.54	1.05
COR04	2.27	0.74	2.36	0.83
COR05	1.72	0.91	1.63	0.95
COR06	0.90	0.94	0.96	0.90
COR07	0.63	1.01	0.49	0.90
COR08	1.47	0.82	1.28	0.95
COR09	1.30	0.84	1.17	1.11
COR10	0.87	1.08	0.95	1.00
COR11	1.00	1.10	0.93	1.05
COR12	3.33	0.42	32.96	0.65
RIV01	0.50	0.85	0.52	0.87
RIV02	0.68	0.76	0.60	0.79
RIV03	0.91	0.95	0.76	0.85
RIV04	0.61	1.21	0.51	1.09
RIV05	0.51	1.73	0.40	1.00
RIV06	0.66	0.89	0.63	0.75
RIV07	0.76	0.85	0.84	1.00

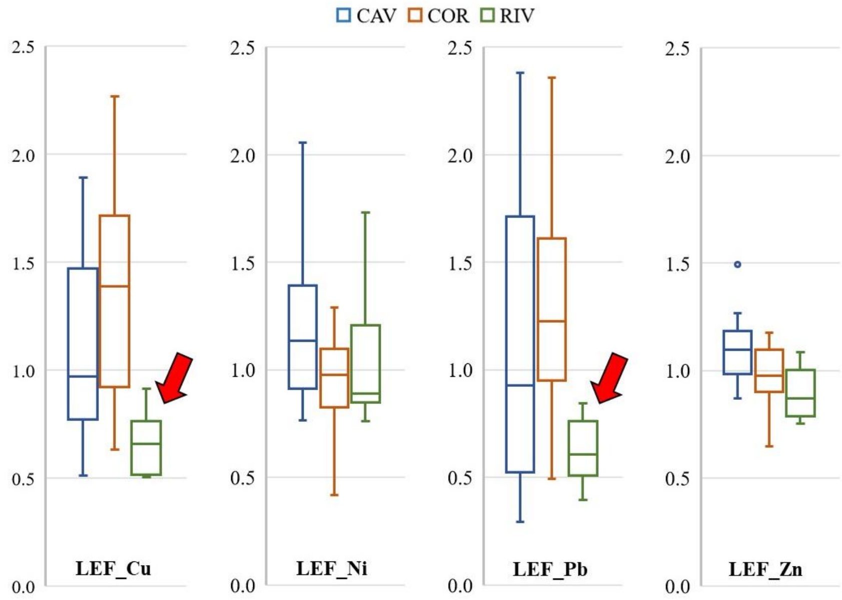

Figure 4. Results of the calculation of local enrichment factors (LEF) for each target element and their distribution in box and whisker plots. Arrows indicate those datasets statistically different from the others.

The reason for the enrichment of Cu and Pb in sediments trapped in rock cavities is not clear. Being an urban river reach, the enrichment can be related to human inputs since both elements are linked with urban effluents (EUROPEAN COMMUNITIES, 2001). Explaining the processes leading to a differential enrichment in rock cavities would require more research and a different experimental design.

However, it has been hypothesized that the dynamics of water in the cavities, flooded during most of the year and dried by evaporation during the dry season, could foster the precipitation of secondary authigenic minerals, such as the formation of Fe and Mn oxyhydroxides due to water oxygenation (MILLER et al., 2021).

Additionally, changes in water pH due to algal blooms within the cavities in summer (observed biofilms) could promote the precipitation of pH-dependent solutes (WALLACE and GOBLER, 2021).

4 Conclusions

In terms of methodology, the performance of robust statistics in this work demonstrated effectiveness. Robust regression proved to be at least as effective as least squares regression in estimating a reference baseline. Statistics not dependent on the normal distribution of the data can facilitate data analysis.

However, in this study, natural variability due to the lithology provenance of the sediments may be interpreted as not significant, given the reach scale's relatively homogeneous lithology. This approach needs to be tested in broader contexts. There is an enrichment of anthropogenic elements inside rock cavities, possibly related to post-depositional processes occurring within these semi-enclosed microenvironments. In this regard, the calculation of local enrichment factors proved to be more useful than a simple comparison of contents. Applying a double normalization, by selecting the fine fraction of sediments and calculating the local enrichment factors in function of a reference element, allowed for a better understanding of differences and similarities and the identification of rock cavities as sediment traps that accumulate Cu and Pb, two elements commonly associated with contaminants in urban environments.

This represents a significant contribution to previous works. However, further research is needed to understand the specific processes influencing sediment composition in bedrock rivers, particularly the physical, chemical, and biological complexities affecting the sediment contents of trace metals.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Conceptualization, M.A.A-V. Data curation, M.A.A-V and A.B. Formal analysis, M.A.A-V and A.B. Methodology, M.A.A-V. Writing, M.A.A-V and A.B. Proofreading, A.B.

DECLARATION OF INTEREST

The authors disclose that they have no known competing financial interests or personal relationships that could have appeared to influence the study reported in this manuscript.

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