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Mining liabilities as a source of toxic metals and physicochemical contaminants in tropical rivers

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ABSTRACT

Global mining activities have led to widespread river pollution, jeopardizing aquatic ecosystems and human well-being by releasing harmful contaminants. The mining liabilities left by a company after ending its activity in 1990 have resulted in the environmental release of metals in surrounding rivers in Líbano de Tilarán, Guanacaste, northern Costa Rica. We examined whether the metal concentrations in water and sediment affected by these mining liabilities are exposure sources for benthic macroinvertebrates in the San José and Cañas rivers. The metal concentrations in these organisms were related to the spatial distribution of exposure concentrations. We also assessed spatial changes in the physicochemical water characteristics due to the direct influence of mining liabilities. Arsenic, cadmium and lead concentrations in water were below the limits of quantification (2–4 μg/L), but in sediments high concentrations were found which were related to seasonal variations in river discharge. The high concentrations of arsenic and lead in the sediments of the San José River explained the low number of macroinvertebrate families, with smaller individuals (<0.4 mg dry weight) of the *Leptohyphidae* family showing higher average concentrations of arsenic (10.6 μg/g), cadmium (1.25 μg/g) and lead (1.30 μg/g) than larger individuals (>0.4 mg, dry weight) of the same family. The enrichment of sediments with metals, together with their heterogeneous spatial distribution, makes the benthic macroinvertebrates more exposed especially to arsenic, which may reduce their abundance, survival, and growth. The strong correlation between the spatial distribution of metal concentrations in sediments and their accumulation in benthic organisms, alongside changes in water quality, demonstrates the impact of mining liabilities on the San José and Cañas rivers.

1. Introduction

The global increase in population and the intensification of industrial activities have contributed to the expansion of mining operations worldwide. Although mining provides important economic benefits, it also poses serious risks to public health and the environment due to metal pollution (Azimi et al., 2017). A significant portion of this pollution arises from the use of toxic substances, such as cyanide and mercury, during metal extraction processes, as well as from the abandonment of waste materials that contain over 99 % of the extracted mineral content. These waste materials ultimately remain in the environment, becoming mining liabilities (Fashola et al., 2016). Over time, these waste materials release significant loads of metals that are easily accumulated and may cause toxic effects (Maharjan et al., 2021). Gold mining in Costa Rica was a significant industrial activity for many decades, supported by both government initiatives and private enterprises (Arauz, 2014; Alvarado and Quesada-Román, 2024). Although gold mining was officially banned by law in 2010, it left behind extensive mining liabilities with high concentrations of metals in acidic environments. One of the most critical sites is the mining district of Líbano de Tilarán, in Guanacaste, where approximately 106,000 tons of abandoned mining waste have remained exposed to the environment for over

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30 years. These residues contain an estimated 20, 0.4 and 38 tons of arsenic, cadmium and lead, respectively (Rojas-Conejo et al., 2022). Exposure to rainfall triggers erosion and oxidation processes that mobilize these contaminants, particularly during high rainfall periods and floods, which enhance surface runoff and infiltration. This results in the transport of contaminated materials from mining liabilities into nearby rivers, altering their physicochemical properties and contributing to metal enrichment in both dissolved and particulate forms (Picado and Bengtson, 2012). The dissolved fraction is transported downstream, while the particulate fraction accumulates in sediments or is suspended and redistributed by river flow. This sedimentary enrichment increases the risk of metal bioaccumulation in aquatic organisms, particularly benthic macroinvertebrates, even when metal concentrations in surface waters are low (Dadar et al., 2016). Despite the common decline of metal concentrations after mine closure—often dependent on flood frequency and magnitude (Ciszewski, 2019)—the case of Líbano de Tilarán demonstrates the prolonged release of toxic metals, posing persistent threats to river ecosystems and nearby human populations.

Tropical rivers are among the most biodiverse ecosystems on Earth, providing critical ecosystem services such as water purification, nutrient cycling, and habitat for aquatic species. However, these ecosystems are particularly vulnerable to metal pollution due to their dynamic hydrological conditions and the bioaccumulation potential of toxic substances in food webs. Understanding the impact of mining-related contamination in tropical rivers is essential for preserving their ecological integrity and mitigating risks to human well-being (Timoner et al., 2020; Marle et al., 2021; Rojas-Conejo et al., 2022). One important component of tropical river ecosystems is the benthic macroinvertebrate community. Benthic macroinvertebrates play a crucial role in aquatic food webs, serving as key intermediaries in energy transfer (Vannote et al., 1980; Rosi-Marshall and Wallace, 2002). Closely associated with the benthic substrate, they facilitate material exchange between sediments and the water column (Hussain and Pandit, 2012). Due to their sensitivity to contaminants, these organisms are widely used to assess the ecological impacts of metal pollution in aquatic environments (Cairns and Pratt, 1993; Bere and Nyamupingidza, 2014). Metals present in water or sediments can be absorbed directly through gill surfaces and external body structures (Clements et al., 1988), while ingestion of contaminated food further contributes to bioaccumulation (Merritt et al., 2017). The benthic macroinvertebrate community represents an important component of secondary production within an aquatic ecosystem (Li et al., 2013). Its structure may vary in response to the magnitude of contaminant exposure (Caro-Borrero et al., 2016), generating an impact on the aquatic ecosystem and potential risks of disruption within the food chain (Timoner et al., 2020; Marle et al., 2021). Therefore, understanding the response to this phenomenon will enable the evaluation of the effect of elevated concentrations of metals (arsenic, cadmium, and lead) in water and sediments on the families of benthic macroinvertebrates inhabiting the San José and Cañas rivers in Guanacaste, Costa Rica.

This study examined the presence of metals such as arsenic (As), cadmium (Cd) and lead (Pb) in the San José and Cañas rivers, focusing on their concentrations in water and sediments influenced by leachates from mining liabilities. Our aim was to examine whether these waters and sediments serve as exposure sources of metals for the benthic organisms inhabiting these rivers and whether the metal concentrations in these organisms are related to the spatial distribution of the metal concentrations in sediments and water, which could suggest possible effects on their communities. Additionally, our study also reveals spatial changes in the physicochemical characteristics of the water due to the direct influence of leachates from the abandoned mining sites. These findings may shed light on the environmental risks posed by mining liabilities, which remain underrecognized as significant stressors in tropical aquatic ecosystems.

2. Methodology

2.1. Study area

The main channel of the Cañas River (CR) catchment is a fourth-order stream, with 96 tributaries and a total length of 35.66 km. During rainfall events, particularly in September and October, when the average annual precipitation reaches 1805 mm, runoff is greater in the upper part of the catchment (maximum elevation of 1540 m above sea level (masl), average temperatures around 17 °C), resulting in elevated water levels in the lower part (minimum elevation of 140 masl). The elongated shape of the catchment contributes to increased sedimentation in the CR. Approximately 65 % of the catchment lies above 400 masl, an area characterized by steep slopes and low stability, which increases the risk of flooding near the Cañas municipality.

Seven sites within the CR catchment were sampled (Fig. 1). Sampling began at a reference site (Site 1, located upstream of the mining waste mound, representing undisturbed water) on the San José River (SJ) in Líbano. A second site was located adjacent to the mining waste, followed by five additional sites downstream in the middle section of the CR sub-basin. The CR catchment covers an area of approximately 144.15 km^2 and is part of the Tempisque-Bebedero watershed, located in the Guanacaste province, North Pacific Region of Costa Rica.

2.2. Sample collection and field measurements

Water and sediment sampling was conducted twice: during the rainy season (October 2015, Sites 1–6) and the dry season (February 2016, Sites 2–7) (Fig. 1). Field parameters including pH, electrical conductivity (EC), temperature, salinity, total dissolved solids (TDS), and dissolved oxygen (DO) were measured in situ using a multiparameter probe (OAKTON 600 Series). Oxidation–reduction potential (ORP) was determined with a calibrated meter (Thermo Scientific Redox, series H00862). Cross-sectional profiles and river flow were measured with a graduated rope and a calibrated digital current meter (AA, USGS, ±0.1 m/s) to estimate discharge.

For water sampling, three subsamples of 1 L were collected by hand at 30 cm depth in plastic bottles at each site, combined into a composite sample, and preserved with 2 mL of concentrated HNO_3. An additional sample was filtered through a 0.45 μm nitrocellulose filter.

Sediment sampling involved collecting six surface subsamples (~15 cm depth) within a 50 m radius using a Van Veen grab sampler. Subsamples were homogenized in groups of three, yielding two composite samples (~50 g each).

Benthic macroinvertebrates were collected at all sites during the transition from dry to rainy season (March–April 2016) using a D-frame net in slow-flowing vegetated areas and manual brushing of cobblestones. Larger organisms were picked.

For complete physicochemical characterization, surface water samples were also collected at three reference sites: upstream of mine liabilities (FQ-1), downstream of mine liabilities (FQ-2), and in the CR (FQ-3) (Fig. 1).

2.3. Laboratory analysis

2.3.1. Physicochemical analysis in water

Physicochemical analyses of water were performed at the Geochemistry Laboratory, CSRG-ICE, following *Standard Methods for the Examination of Water and Wastewater* (Clesceri, 1998). Duplicate analyses, blanks, and quality control samples were used, with calibration curves prepared from ≥4 NIST-traceable standards.

2.3.2. Metal analysis in water

Samples from the **Rainy season** were analyzed at LASEQ-UNA using graphite furnace atomic absorption spectrophotometry (AAS; Perkin Elmer AAnalyst 800) with Zeeman background correction. Samples from

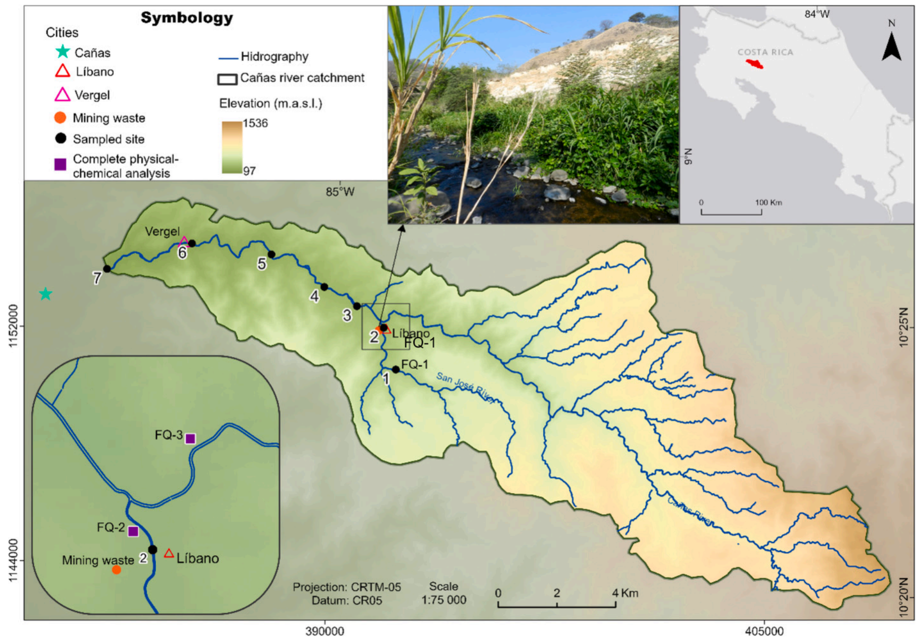

Fig. 1. Cañas river (CR) catchment in Guanacaste, Costa Rica. The map figure indicates the elevation changes (meters above sea level, masl) in the catchment, the main towns (Cañas, Vergel and Líbano) and the study sites. The small photograph shows an old mine in a hillslope nearby the river reach, the insert the river catchment in the Costa Rican geographical context. In both figures, the locations of the points for full physicochemical analysis sampling (FQ-1, FQ-2, and FQ-3) are shown.

the **Dry season** were analyzed at LAA-UNA using graphite furnace AAS (Perkin Elmer AAnalyst 700). In both cases, calibration curves were prepared with 6–8 standards (PMA 036 Metals, modified from APHA 3113B, APHA, 2012). Recovery tests using fortified samples achieved 90–110 %.

2.3.3. *Sediment analysis*

Sediment pH was determined following AOAC Official Method 994.16 (AOAC International, 1997) and SW-846 Method 9045D (U.S. Environmental Protection Agency [US EPA], 2004), using a 1:1 slurry of 20 g dry sediment and 20 mL distilled water. Measurements were conducted with a Thermo Scientific Orion 4-Star pH meter, duly calibrated with NIST-traceable buffer standards.

For metals analysis, dried and sieved (<250 μm) samples (~1.5 g) were digested with concentrated HNO_3 and HCl (1:3) in a water bath at 80 °C for 1 h, and the extracts were analyzed by graphite furnace atomic absorption spectrometry (AAS) using a Perkin Elmer AAnalyst 700. All analyses were performed by LASEQ, and calibration curves were prepared with 6 to 8 standards (PMA 036 Metals, modified method based on 3113 B, Clesceri, 1998).

2.3.4. *Macroinvertebrate analysis*

Taxonomic identification was performed under a stereoscope (Olympus Tokyo) using Springer (2010) keys. For metal determination, larger organisms were digested with HCl and HNO_3 (1:3), while smaller organisms were digested with HNO_3 and $HClO_4$ (7:1) at controlled heating rates until complete digestion. Analyses were performed using flame or graphite furnace AAS (Perkin Elmer PinAAcle 900Z). Detection limits were 0.18–0.34 μg/L (As), 0.18–0.20 μg/L (Cd), and 0.51 μg/L (Pb). Recoveries from the DOLT-4 reference material ($n = 2$) were 93 ± 6.0 % (As), 17 ± 9.3 % (Cd), and 66 ± 45 % (Pb); data were not recovery-corrected due to concentration differences between reference and environmental samples. The structure of the biological community was analyzed using descriptive statistics and a series of diversity indices. Species richness was quantified using the Margalef index (Mulya et al., 2021), and the degree of dominance within the community was assessed using the Berger-Parker index (Quanz et al., 2021).

3. Results

3.1. *Physical-chemical properties of the San José and Cañas river waters*

The number of samples was limited, so the results are presented descriptively. Both the San José (SJ) and Cañas rivers exhibited a calcic bicarbonate-type hydrochemistry, characterized by high concentrations of bicarbonate and calcium (Table 1). A slight increase in most physicochemical parameters at site FQ-2 (located downstream of the mining liabilities), compared to site FQ-1 (upstream reference site), suggests a possible contribution of ions from mining liabilities to the SJ river water. This pattern was observed during the rainy season but not during the dry season (Table 1).

Although no statistical analyses could be conducted due to the limited number of observations, a rough comparison of key parameters such as pH, electrical conductivity (EC), and sulfate concentration (Table 1) allows for speculation regarding seasonal changes in water quality. The shift in pH values between seasons may reflect the influence of leachates from mining liabilities, whose mobilization into the river is enhanced by rainfall. These slight pH changes, together with variations in EC, could affect overall water quality and potentially limit the solubility and mobility of metals in the water column.

During the rainy season, there was greater transport of ions from the basin, which is reflected in the higher electrical conductivity (EC) at FQ-1 and FQ-2 than at FQ-3. A decline in EC values during the dry season (Table 1) indicates a reduction in the concentration of dissolved ions in the river. However, levels of certain ions, such as bicarbonate, sodium, potassium, and calcium, remained relatively stable across both seasons (Table 1), suggesting that these components are less affected by seasonal variation.

Iron and NH_4-Nitrogen concentrations were consistently low or below the limit of quantification (LQ) in both seasons, indicating a minimal contribution of these elements to water chemistry. At sites FQ-1 and FQ-2, chloride and sulfate concentrations decreased by less than 35 % and 52 %, respectively, during the dry season (Table 1), further highlighting the influence of seasonal changes on ion concentrations.

Table 1
Concentrations (mg/L) and physicochemical properties of the water of the San José and Cañas rivers, Guanacaste province, Costa Rica, measured in the rainy season of 2015 and the dry season of 2016 at three sites, FQ-1, FQ-2 and FQ-3, see Fig. 1.

Parameter	Rainy Season 2015			Dry Season 2016			Limit of Quantification (mg/L)
	FQ-1	FQ-2	FQ-3	FQ-1	FQ-2	FQ-3	
pH	8.01	7.96	8.00	8.52	8.60	8.70	*
Electrical Conductivity (EC) (μS/cm)	212	227	132	189	185	123	*
Sodium (mg/L)	8.71	11.6	6.15	8.70	8.90	6.40	1.00
Potassium (mg/L)	3.28	3.33	1.06	3.10	3.10	1.50	1.00
Calcium (mg/L)	17.9	18.5	11.1	18.2	18.5	13.0	0.50
Magnesium (mg/L)	6.7	7.2	3.9	6.4	6.6	4.0	0.05
Iron (mg/L)	0.26	0.23	<LQ	<LQ	<LQ	<LQ	0.07
Chloride (mg/L)	4.63	4.80	3.65	3.05	3.57	3.98	0.10
Sulfate (mg/L)	14.4	16.6	5.99	6.90	7.80	4.53	0.10
Bicarbonate (mg/L)	115	119	76.0	117	118	78.0	0.70
NH_4- Nitrogen (mg/L)	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	0.50
Ratio Ca^{2+}/Na^{+}	2.05	1.59	1.80	2.09	2.08	2.03	*
Ratio Ca^{2+}/Mg^{2+}	2.67	2.57	2.84	2.84	2.80	3.25	*
Ratio SO_4^{2-}/Cl^{-}	3.11	3.46	1.64	2.26	2.18	1.14	*
Ratio HCO_3^{-}/SO_4^{2-}	7.95	7.17	12.7	16.9	15.1	17.2	*
Ratio HCO_3^{-}/Cl^{-}	24.7	24.8	20.8	38.2	32.9	19.6	*

"< LQ": below the limit of quantification; *: no data is reported or doesn't apply.

3.2. Metal concentrations in the San José and Cañas river waters

According to the Canadian Water Quality Guidelines for the Protection of Aquatic Life (Canadian Council of Ministers of the Environment (CCME), 2014), the limits for surface waters are: Pb = 0.001–0.0007 mg/L (1987), As = 0.005 mg/L (1997), and Cd = 0.000017 mg/L (1996). The analytical quantification limits of the laboratories used in this study were higher than these thresholds. For the rainy season samples (2015), analyzed at the LASEQ laboratory, the limits of quantification were < 0.008 mg/L Pb and < 0.006 mg/L As (Cd was not reported). For the dry season samples, analyzed at the LAA laboratory, the limits of quantification were < 0.004 mg/L Pb, <0.003 mg/L As, and < 0.002 mg/L Cd. Therefore, the reported values reflect methodological quantification limits rather than actual concentrations and do not allow us to confirm whether concentrations were below ecotoxicological thresholds.

The EC, pH, S, ORP, T, TDS, and DO parameters of the river water did not show a significant seasonal change (Fig. 2). During the dry season, pH levels ranged from 7.84 to 8.36, with Site 2 in closer proximity to the mine having the lowest pH. EC values ranged from 145 to 203 μS/cm. DO remained relatively consistent, ranging from 7.89 to 8.63 mg/L. Site-specific differences in temperature, oxygen saturation, salinity, TSS, and redox potential were also evident.

During the rainy season, the water pH ranged from 7.75 to 8.10, with Site 5 exhibiting the lowest pH. EC ranged from 140 μS/cm to 223 μS/cm, indicating potential fluctuations in dissolved ion concentrations. Site 2 had the highest EC, suggesting an impact from both natural and anthropogenic factors, possibly associated with the historical mining activities. DO concentrations during the rainy season ranged from 7.97 to 8.40 mg/L, being highest at Site 6. The variations T, DO, S, TDS, and oxidation-reduction potential (ORP) were also apparent across the sites. Site-specific differences in these parameters highlight the dynamic nature of water quality during the rainy season, potentially influenced by increased precipitation and runoff.

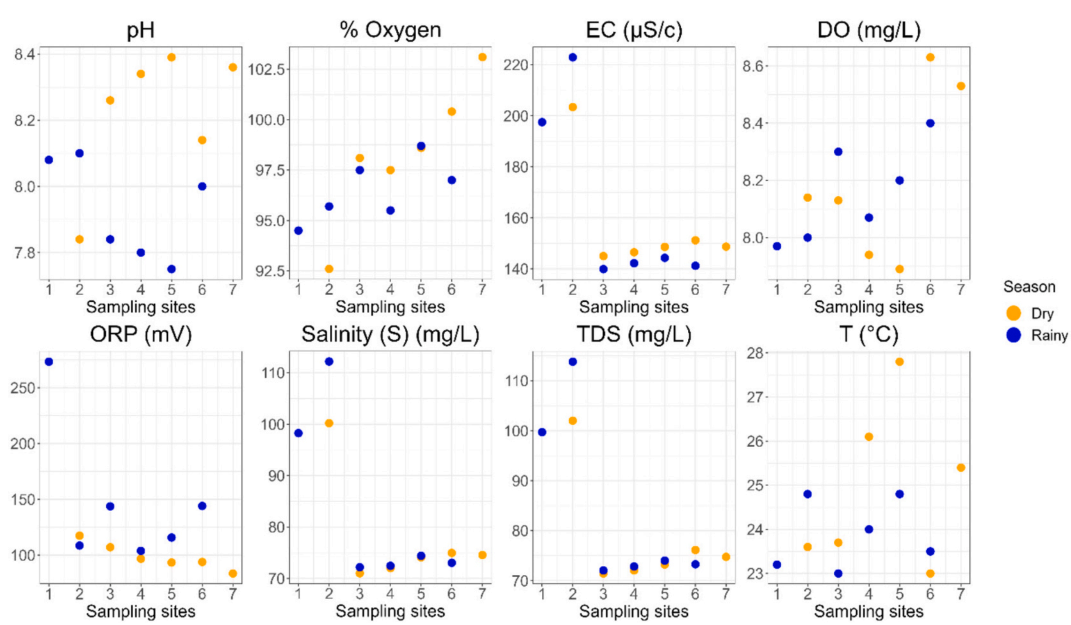

Fig. 2. Physicochemical properties of the water of the San José and Cañas rivers in Costa Rica, measured in the field during the rainy season of 2015 and the dry season of 2016. EC: Electrical Conductivity; DO: Dissolved Oxygen; T: Temperature; TDS: Total Dissolved Solids; ORP: redox potential.

3.3. Metal concentrations in the sediments of the San José and Caña Rivers

The highest metal concentrations in the sediments were observed at site 2 (Fig. 3). The highest concentration (85.1 mg/kg) belonged to As and was observed in the dry season in the sediment of the site 2 where the Pb concentration was half of this value, and the Cd concentration two orders of magnitude lower (0.16 mg/kg). Sites 3, 4, 5, and 6 had comparatively lower concentrations of these elements. The concentrations of As and Pb were below detection limits in sediments at site 1, while site 7 showed detectable but relatively lower concentrations of these metals. These observations suggest that the dispersion of metals could response to factors such as precipitation, dilution, and to the dynamic of the geochemical processes.

Sediment pH was not measured at Site 7 during the rainy season of 2015, and at Site 1 (reference site) during the dry season of 2016. In the wet season, sediment pH was slightly acidic at Site 1 and Site 6, but near neutral at the Sites 2–5, ranging from 6.23 and 7.46, with Site 5 displaying the highest pH and Site 6 the lowest (Fig. 3). In the dry season, there was less variation in sediment pH with all values ranging between 6.70 and 7.10, with Site 2 exhibiting the highest pH and Site 5 the lowest.

Fig. 4 (a and b) shows the correlation between metal concentrations in sediments and the flow, velocity, and depth of water in the San José and Cañas rivers. In places where the water currents were smaller, the physical, chemical, and biological conditions showed greater stability, allowing metals to precipitate in the sediment, while at the places of the river where the currents had a higher velocity, there was a greater removal of the metals from Site 2. During the rainy season, arsenic, cadmium and lead concentrations correlated positively, indicating similar behavior in terms of flow, and negatively with flow, meaning that the greater the flow, the lower the concentration in the sediment.

During the rainy season, arsenic, lead, and cadmium concentrations were positively correlated with each other (>0.97) (Fig. 4), suggesting a common origin and similar environmental behavior. Metal concentrations were negatively correlated with river discharge and water depth relative to the sediments (−0.91 to −0.85), indicating that higher water flow results in lower metal accumulation. Similarly, metal concentrations were also negatively correlated with water velocity (−0.64 to −0.69), suggesting that increased flow reduces contaminant retention in sediments.

Metal concentrations were correlated with sediment pH but negatively correlated with %Oxygen (Fig. 4a), indicating that lower metal accumulation was associated with higher oxygen levels. Additionally, redox potential (ORP) showed a negative correlation with discharge, suggesting that deeper waters had more reducing conditions.

During the dry season, arsenic and cadmium concentrations showed a strong positive correlation (0.85) (Fig. 4b), suggesting a common origin and similar behavior within the aquatic ecosystem. In contrast, lead concentrations showed a very weak correlation with arsenic (0.09) and cadmium (0.05) concentrations, indicating that its distribution may be influenced by different sources or processes. Additionally, the concentrations of these elements were negatively correlated with river discharge and water depth (−0.51 to −0.56 for arsenic and − 0.45 to −0.85 for cadmium), suggesting that areas with greater flow and depth accumulated less contaminants. Similarly, arsenic concentrations negatively correlated with water velocity (−0.78), indicating that higher flow reduced its retention in sediments.

Metal concentrations showed a moderate positive correlation with sediment pH (0.41 with arsenic, 0.40 with lead, and 0.33 with cadmium) (Fig. 4b), suggesting that more alkaline conditions may favor their presence in sediments. Arsenic and cadmium concentrations were negatively correlated with %Oxygen (−0.64 for arsenic, −0.61 for cadmium), indicating that areas with higher oxygen content accumulated less contaminants.

During the dry season, arsenic and cadmium accumulation was influenced by river discharge and water velocity, with lower concentrations in areas of higher flow.

3.4. Metals bioaccumulation and effects on benthic macroinvertebrate families

The values of the biological indices applied to macroinvertebrates showed variations between the different sampling points (Fig. 5). The Margalef diversity index ranged from 1.90 to 3.25, with the lowest value at site 7 and the highest at site 5, while the Berger–Parker dominance index varied between 0.24 (site 1) and 0.77 (site 7). Site 2 presented the second lowest diversity value (2.81), a relatively low dominance (0.34),

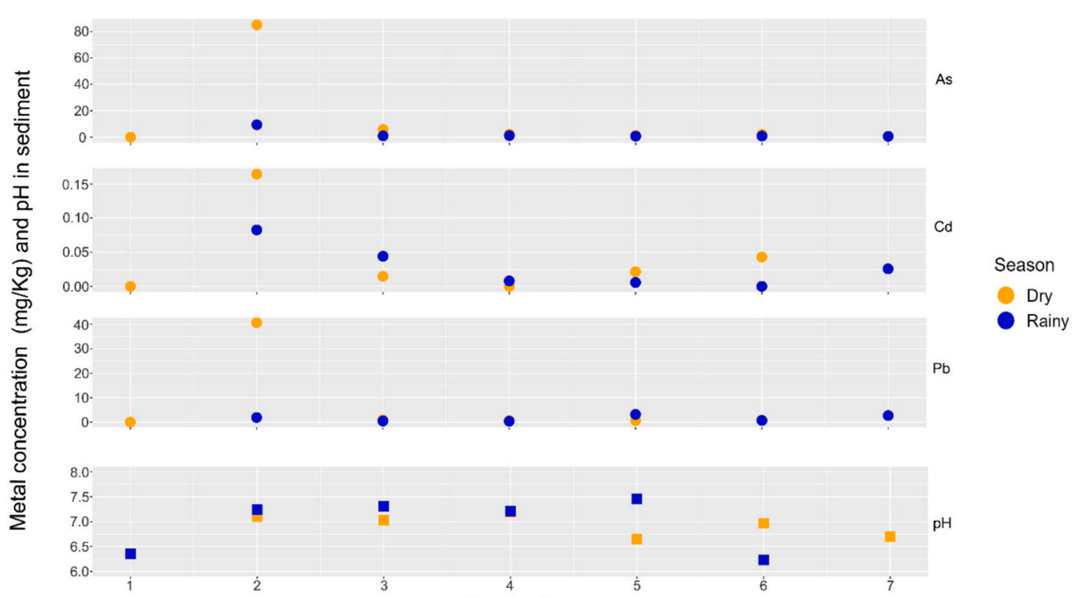

Fig. 3. Spatial distribution of pH and average concentrations of arsenic (As), cadmium (Cd), and lead (Pb) (mg/kg dry weight) in sediments from the San José and Cañas rivers. Samples from the rainy season of 2015 were collected at Sites 1–6, and from the dry season of 2016 at Sites 2–7. Note: Site 1 was not included in the dry season campaign due to budget constraints, while Site 7 was incorporated as a downstream site closer to the city.

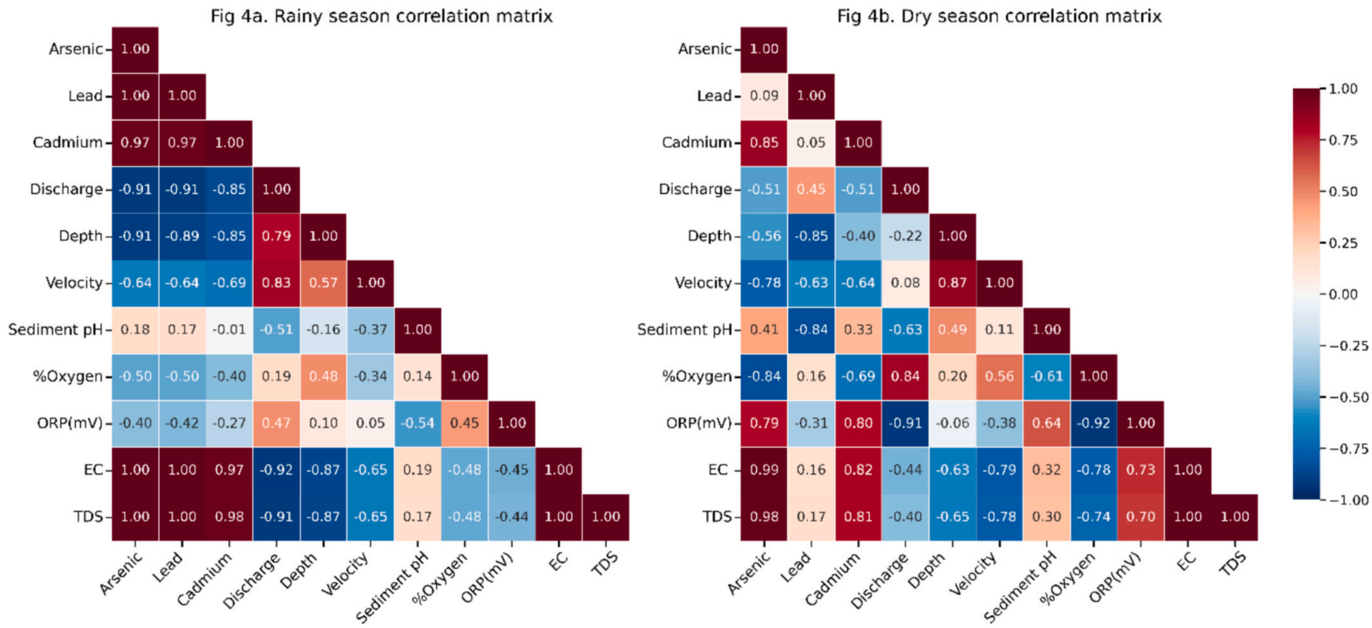

Fig. 4. a. Correlation (R) of arsenic, cadmium and lead concentrations in sediments, sediment pH, depth, velocity, discharge, %Oxygen, ORP, EC and TDS of the San José and Cañas rivers in Costa Rica, measured during the rainy season of 2015.
b. Correlation (R) of arsenic, cadmium and lead concentrations in sediments, sediment pH, depth, velocity, discharge, %Oxygen, ORP, EC and TDS of the San José and Cañas rivers in Costa Rica, measured during the dry season of 2016.

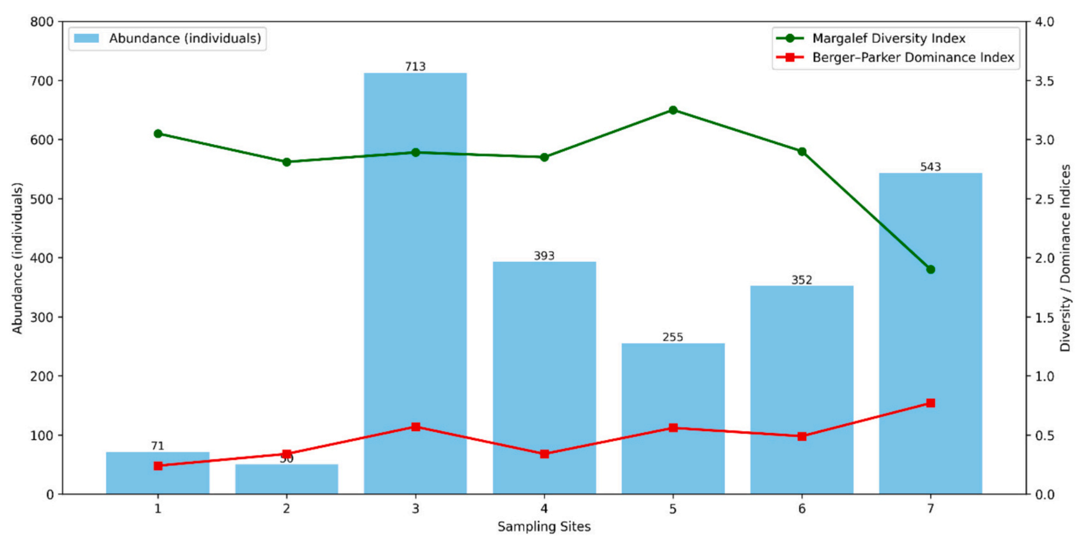

Fig. 5. Abundance of individuals and their correspondence with Margalef diversity index and Berger–Parker dominance index, normalized on sacle from 0 to 1, at each sampling site.

and the lowest total abundance (50 individuals), although five representative families were identified (Leptohyphidae, Hydropsychidae, Corydalidae, Chironomidae and Gomphidae). At site 3, an intermediate diversity value (2.89) coincided with high dominance (0.57), whereas site 5 combined the highest diversity (3.25) with a dominance of 0.56. Site 6 showed intermediate values for both indices (diversity: 2.90; dominance: 0.49). Overall, site 7 stood out for presenting the lowest diversity together with the highest dominance, reflecting a marked reduction in the equitable distribution of taxa.

About 20 % of the benthic macroinvertebrates identified in the samples collected from the San José and Cañas rivers belonged to the family Leptohyphidae, represented by the genera *Leptohyphes* sp., *Tricorythodes* sp., and *Vacupernius* sp. Due to their abundance and frequency of occurrence in all sampling sites, this family was chosen to determine the concentrations of As, Cd and Pb. Additionally, an organism from the family Gomphidae, genera *Herpetogomphus* sp., was also selected. Its presence was observed in sites 2 and 6, which were assumed to be the points where higher and lower concentrations of metals could be found, respectively. The other groups of macroinvertebrate families had a very dispersed representation. Fig. 6 shows the concentrations of arsenic, lead, and cadmium in organisms of the genera *Leptohyphes* sp., *Tricorythodes* sp., and *Vacupernius* sp.

Figs. 7 and 8 relate the internal metal concentrations with the size of the organisms, expressed as their dry weight. Higher metal concentrations were recorded in smaller organisms.

Predators of the genera *Herpetogomphus* sp., sampled in the dry season, had the highest arsenic and cadmium concentrations at Site 2 but did not bioaccumulate lead. At Site 2, *Herpetogomphus* sp. contained

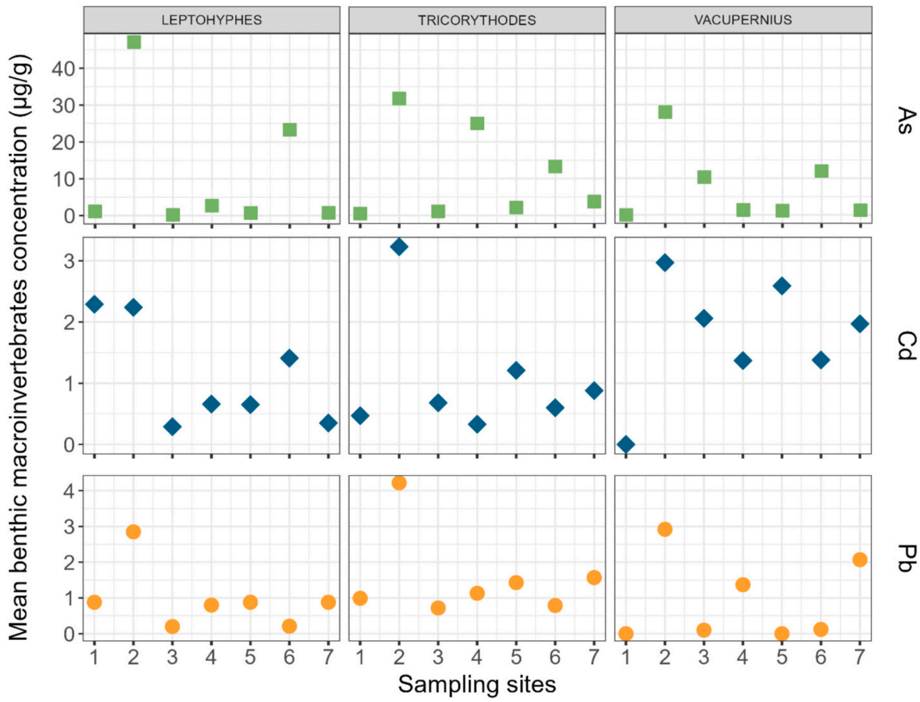

Fig. 6. Mean concentrations ($n = 2$ or 3) of arsenic, cadmium, and lead (µg/g dry weight) in the genera *Leptohyphes* sp., *Tricorythodes* sp., and *Vacupernius* sp., which are collector-scraper organisms from the family *Leptohyphidae*, sampled in the rivers San José and Cañas in Costa Rica in March and April 2016.

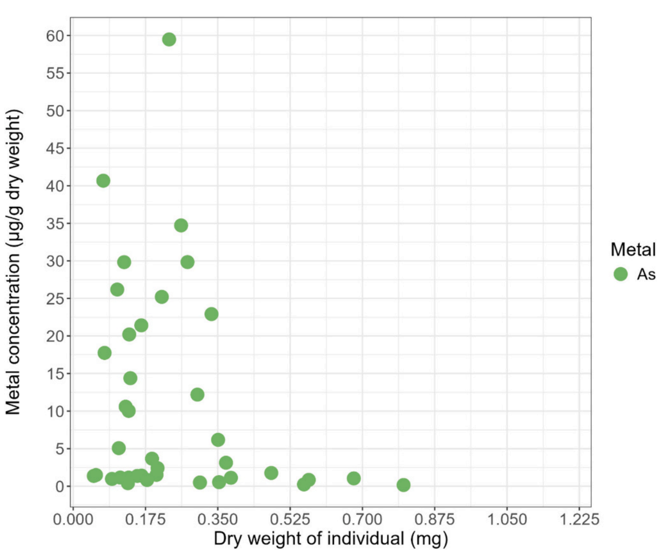

Fig. 7. Arsenic concentrations (µg/g dry weight) in benthic organisms of the genera *Leptohyphes* sp., *Tricorythodes* sp., and *Vacupernius* sp., from the San José and Cañas rivers in Costa Rica related to their dry weight. The animals were sampled in March and April 2016.

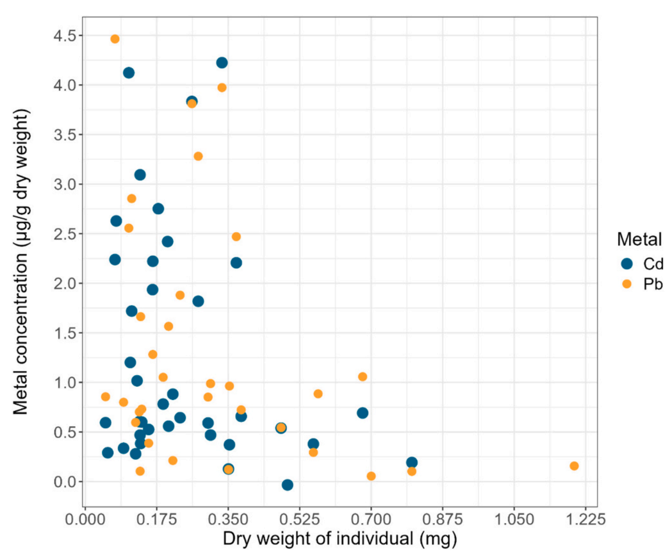

Fig. 8. Lead and cadmium concentrations (µg/g dry weight) in benthic organisms of the genera *Leptohyphes* sp., *Tricorythodes* sp., and *Vacupernius* sp., from the San José and Cañas rivers in Costa Rica related to their dry weight. The animals were sampled in March and April 2016.

18.8 µg As/g dry body weight and 0.50 µg Cd/g dry body weight, while at Site 6 markedly lower concentrations of 1.0 µg As/g dry body weight and 0.04 µg Cd/g dry body weight were recorded.

4. Discussion

This study showed a clear relationship between the spatial distribution of metal concentrations in sediments and their bioavailability to benthic macroinvertebrates, particularly during the rainy season when increased river discharge enhances sediment transport. This phenomenon highlights the dynamic nature of metal enrichment in sediments and its implications for aquatic organisms.

It should be noted that the number of samples collected in this study was limited, and for budget and practical reasons sampling in the wet and dry seasons also did not completely cover the same sampling points. Consequently, robust statistical analyses (e.g., ANOVA, correlation coefficients with p-values) could not be performed to evaluate seasonal or spatial trends in metal concentrations or physicochemical parameters. The results are therefore presented as descriptive comparisons, and this limitation should be considered when interpreting the findings.

Costa Rica's unique hydrological regime, marked by pronounced seasonality between dry and wet seasons and amplified by interannual climate phenomena such as El Niño and La Niña, profoundly influences contaminant transport and retention dynamics compared to other tropical systems. For example, in the hyper-arid Andean rivers such as Tambo and Camaná-Majes in Peru, 15 trace metals, including Co, Cu, Pb, and Mn, exhibited substantially higher concentrations during the wet season due to snowmelt and runoff, whereas others like As and B peaked in the dry season, reflecting contrasting hydrological controls (Ccanccapa-Cartagena et al., 2023). In the Western Ghats of India, monsoon rains lead to elevated levels of dissolved metals (e.g., Zn, Ni, Cu, Co), while dry seasons showed a changing dominance from groundwater and anthropogenic effluents (Nishitha et al., 2019). Similarly, in southern Chile's lakes fed by rivers such as Petrohué and Puelo, winter snowmelt and increased runoff significantly elevated the delivery of suspended metals into fjord systems (Muñoz-Fariña et al., 2025).

In contrast, Costa Rican rivers displayed sharp contaminant pulses tied to intense storm-driven runoff, with rapid mobilization and downstream transport of sediment and associated contaminants, as documented by high-resolution monitoring of rainfall-runoff-turbidity relationships (Waylen and Laporte, 1999; Ciszewski and Grygar, 2016; Solano-Rivera et al., 2019). This episodic and localized transport is further accentuated by the steep volcanic terrain, the highly dynamic response of surface flow pathways, and the short recovery time ($\sim$3 months) of sediment transport following extreme events (Solano-Rivera et al., 2019). These characteristics make temporal contamination patterns in Costa Rica distinct from tropical systems with more stable or glacier-fed hydrology, highlighting the need to consider local climate-driven variability when generalizing findings compared to other tropical environments.

4.1. Metal concentrations and physicochemical conditions of San José and Cañas Rivers

The hydrochemistry of the SJ and CR rivers waters is represented by the ratios of the ionic concentration in the water collected at sites without human activities, FQ-1 and FQ-3 (Table 1). The slight difference in the physicochemical composition of the water between the sites FQ-1 and FQ-2 (Table 1) indicates that the water at site FQ-2 is affected by the leachates and particulate material removed and mobilized from the mining liabilities at Líbano to the SJ river.

Metals and ions such as sodium, calcium, sulfate, and to a lesser extent bicarbonate are removed from the oxidized mining liabilities by rainfall and transported to nearby rivers. The removal by leaching from mining liabilities of As, Cd, and Pb, along with other ionic species (Rojas-Conejo et al., 2022), and transport via surface runoff are the predominant mechanisms promoting the contamination of the SJ and CR rivers. In leachates, metals can be associated with dissolved chemical species and colloidal particles, and when leachates combine with surface runoff containing eroded material, the load of metals transported to the rivers increases (Picado and Bengtson, 2012). Arsenic (As), cadmium (Cd), and lead (Pb) were not detected in the water of the SJ and CR rivers; reported values reflect the laboratories' quantification limits, which were higher than ecotoxicological thresholds.

An examination of the physicochemical composition of the water along the sampled sites revealed distinctive trends and variations. For instance, water pH decreased downstream from Site 2 (near the mining liabilities) to Site 5 (Fig. 2) in the rainy season. This clearly indicates that the leachates from the mining liabilities, promoted by precipitation, altered the natural conditions of the water. In contrast, the water pH in the dry season (Fig. 2) increased. Other parameters, such as EC and TDS, which correlated closely with each other regardless of the season ($R = 1$, $\alpha = 0.05$), corresponded with spatial changes in the concentrations of dissolved ions, contrasting with the presence of mining liabilities at Líbano. Notably, the values of all the parameters measured at Site 2 serve as a point of departure for the changes recorded in downstream water, highlighting the dynamics of water influenced by increased precipitation and runoff during rainy events. These findings underscore the spatial heterogeneity in water quality parameters, providing crucial insights into the potential impacts of historical mining activities on the local aquatic ecosystem.

Although surface water runoff is the main agent of transport and dispersion of significant loads of metals (Walker et al., 2006), the aqueous concentrations of metals in the affected rivers are not often quantifiable by the methods used in laboratories. Indeed, metal concentrations in river water from humid tropical countries affected by gold mining are commonly reported to be below the quantification limits (Rodríguez-Zapata and Ruiz-Agudelo, 2021; Marinho et al., 2022; Spiegel et al., 2018), and most of the reported concentrations are from metals in the sediments. These concentrations are generally from 1 to 5 orders of magnitude higher than in the water (Razo et al., 2004; Uugwanga and Kgabi, 2020).

Unfortunately, the partitioning between the sediments and water of As, Cd, and Pb in the San José and Cañas rivers remains unknown due to the scarcity of data. However, we estimated the expected concentrations of As, Cd, and Pb to be $\sim$0.1 μg/L by using the average values of the distribution coefficient (Log Kd; L/Kg) for As (2.5), Cd (3.6), and Pb (5.1) reported for other surface water bodies (Allison and Allison, 2005), and the observed respective concentrations in the sediments of the SJ and CR rivers (Fig. 3). The concentration of 0.1 μg/L is one order of magnitude lower than the limits of quantification (LQs) of the methods used in this study. Therefore, As, Cd, and Pb were not detected in the water, and consequently, the correlation between the concentrations and the physicochemical parameters (Fig. 2) is not shown.

The physicochemical conditions of river water and sediments, which are intrinsically related (Dalu et al., 2017; Marinho et al., 2022), influence metal partitioning in rivers. In addition to pH-driven precipitation and complexation processes (Trivedi and Axe, 2000; Zhang et al., 2014), redox-sensitive compounds such as iron and manganese oxides significantly affect Pb behavior (Ciszewski and Grygar, 2016; Copaja and Muñoz, 2018; Michalopoulou et al., 2024). In our study, Pb showed a weak negative correlation with %O_2 during the rainy season and a very weak positive correlation during the dry season (Fig. 4), suggesting that seasonal variations in oxygen levels influence its sorption–desorption dynamics. Notably, these patterns were observed even though pH values remained close to neutral, which indicates that redox-driven interactions with Fe/Mn oxides, rather than acid–base conditions, were the dominant factor controlling Pb mobility. This interpretation is consistent with previous studies reporting that Pb can be immobilized under reducing conditions through sulfide precipitation and organic matter complexation, and conversely stabilized under oxidizing conditions by Fe/Mn oxides (U.S. Geological Survey, 1995). Therefore, redox-driven processes represent a key control on Pb distribution and bioavailability in these tropical rivers.

Furthermore, changes in the physicochemical conditions of water, along with bioturbation by benthic organisms, can enhance the bioavailability of metals by releasing weakly bound or adsorbed species from sediments (Ciszewski and Grygar, 2016). This process facilitates the accumulation of metals such as As, Cd, and Pb in benthic macroinvertebrates, even in the absence of detectable aqueous concentrations (Allison and Allison, 2005). Although bioturbation was not measured directly in this study, the observed body concentrations in macroinvertebrates suggest that these metals were bioavailable and that sediments served as the primary source of exposure. Similar patterns of metal mobilization and bioaccumulation linked to sediment interactions have been reported in tropical river systems affected by mining activities (Eggleton and Thomas, 2004; Luoma and Rainbow, 2008).

4.2. Spatial distribution of metals in sediments of the San José and Cañas rivers

During the rainy season, the concentrations of metals in the sediments were differentially distributed downstream, initially accumulating in Site 2 in the San José River, where the mining waste is located and distributed from this site to the sediments of the Cañas river (Fig. 3). The concentrations of metals in the sediments of Site 2 were higher than at the other sampling points due to its proximity to mining liabilities, with 85.1 mg As/kg, 0.16 mg Cd/kg and 40.7 mg Pb/kg. Sites 3, 4, 5, and 6 displayed comparatively lower concentrations of these metals. Arsenic and lead concentrations were below detection limits in sediments at Site 1, while Site 7 showed detectable but relatively low concentrations of these metals.

The increasing flow of rivers leads to changes in the spatial distribution of sediments, as well as a decrease in the accumulation of metals along their channels (Ibisate et al., 2011; Lin et al., 2022). It is notable that the spatial distribution (Fig. 3) of these elements during the rainy season was characterized by decreasing concentrations and a positive correlation between the concentrations of the different metals (Fig. 4a). In contrast, only the Cd concentrations, which are distributed downstream in the sediments, were correlated with As concentrations in the dry season (Fig. 4b).

The observed spatial patterns of metal concentrations in the sediments are driven by a combination of hydrological/physical and geochemical/chemical processes. Hydrologically, rainfall events and increased river discharge promote the transport and downstream dispersion of sediment particles and associated metals, redistributing loads from mining liabilities to downstream sites. Geochemically, factors such as sediment pH, redox potential, adsorption/desorption dynamics, precipitation, and interactions with organic matter or carbonates regulate the retention and mobilization of metals within the sediment matrix. Together, these mechanistic drivers explain the seasonal differences in metal accumulation and the spatial heterogeneity observed across the sampled sites (Byrne et al., 2012; Luo et al., 2020; Qin et al., 2019; Zhang et al., 2014; Zhao et al., 2024).

The heterogeneous distribution of metals in the sediments may be influenced by factors such as sediment grain size, hydraulic sorting, and organic matter content. Although these parameters were not measured in this study, previous research has shown that organic matter and fine sediment fractions (silt + clay) play a critical role in metal retention and bioavailability, as metals tend to bind to these sediment components through adsorption, complexation, and incorporation into mineral matrices (Hu et al., 2013). More recent studies in mining-impacted rivers have confirmed that fine particles (<0.075 mm) and clay-rich fractions tend to accumulate higher concentrations of metals such as Cd, Pb, and As, with organic matter fixation and reducing mobility (Que et al., 2024). Sediments enriched in fine particles and organic matter not only retain greater metal loads but also affect their potential bioavailability to benthic organisms. Future work should include detailed sediment characterization and organic matter analysis, for example via loss-on-ignition, to better understand the mechanisms controlling metal distribution and to enable correlation analyses with metal concentrations.

Turbulent flows efficiently remove sediment particles and associated metals from riverbeds, affecting water quality and the bioavailability of metals (Byrne et al., 2012). In contrast, at very low water velocity, the physicochemical and biological conditions of the water can remain almost unaltered (Byrne et al., 2012), allowing metals to precipitate and temporarily accumulate in the sediments. Therefore, in the dry season, the metal content of the sediments was higher than in the rainy season as was observed at Site 2, where the concentrations of As, Cd, and Pb were higher in the dry season (Fig. 3). However, the concentrations in the downstream sediments, from Site 3 to Site 7, showed a similar distribution in both seasons. This could indicate that the increase in water velocity in the CR did not significantly alter the spatial distribution of As, Cd, and Pb in the sediments Fig. 3), yet the distribution may also depend on the chemical and biological processes occurring in the bed under conditions of water stability (Luo et al., 2020; Qin et al., 2019).

In sediment environments with slightly acidic to near-neutral pH (6.23–7.46, Fig. 3), metal mobility is generally limited. This is due to stronger adsorption onto sediment particles and precipitation of complexes formed such as hydroxides and carbonates, or through interactions with Fe-Mn oxides and organic matter (Sintorini et al., 2021; Zhao et al., 2024; Zhang et al., 2014). Elements such as Cd and Pb, which are often associated with carbonate fractions, can be particularly sensitive to pH changes: higher pH conditions tend to favor their precipitation, whereas lower pH can enhance their release into the water column (Korfali and Karaki, 2017; Ibrahim and Jurdi, 2010). Studies on lake sediments indicate that increasing pH shifts metals like Zn toward more stable residual forms while reducing their association with organic and sulfide-bound fractions, thereby decreasing their potential release (Zhao et al., 2024). Overall, systematic reviews show that elevated pH promotes the retention of metals in sediments, whereas a decrease in pH can increase their solubility and bioavailability, highlighting the importance of even small pH fluctuations for metal behavior in aquatic systems (Zhang et al., 2014).

Meanwhile, Li et al. (2013) have pointed out that alkaline conditions in sediments tend to promote the formation of less mobile phases, thereby reducing the availability and mobility of metals that are in solution or bound to carbonates. However, as seen in Fig. 4b, the negative correlation of Pb with sediment pH suggests that in environments with high pH, Pb tends to desorb and mobilize into the aqueous phase, especially when associated with labile fractions such as carbonates. A study in the Maipo River, Chile, showed that at higher pH, Pb adsorption decreases, facilitating its release into the water column (Copaja et al., 2020). The dissolution of carbonates in sediments increases the availability of Pb, forming soluble complexes that enhance its mobility (Liu et al., 2021). Furthermore, the increase in pH may lead to competition between cations like Ca^{2+} and Mg^{2+} with Pb^{2+}, which promotes the desorption of the metal (Kalakodio et al., 2017). If Pb is predominantly in non-residual forms, such as the carbonate or exchangeable fraction, it is more susceptible to changes in pH, as demonstrated by a study that found Pb had a greater affinity for adsorption sites in soils with lower pH (Onwudike et al., 2021).

The relationships between the physicochemical characteristics of the sediments and the anomalous concentrations of As, Cd, and Pb in the SJ and CR rivers have not been fully examined yet. However, we observed that the visible presence of organic matter in the sediments of the CR at Sites 5 and 7 coincided with the highest Pb concentrations in the sediments collected during the dry season. Fine sediments limit the water solubility and toxicity of metals because they contain an important fraction of organic matter that retains metals through complexation (Strom et al., 2011). Oxides and clay minerals also retain metals by forming complexes with inorganic ligands because these sediment components have variable surface charges, such that sorption-desorption becomes an important process in the exchange of metals in rivers (Copaja et al., 2020). We did not examine this interaction.

Changes in physicochemical water conditions, along with bioturbation, can enhance the bioavailability of metals in the aqueous phase by releasing weakly bound metals from sediments. This process facilitates the accumulation of metals in aquatic organisms, potentially leading to ecological alterations (Copaja and Muñoz, 2018). Although our study did not directly measure bioavailability, the concentration observed in benthic organisms indicated that As, Cd, and Pb were bioavailable, with sediments serving as the primary source of exposure.

The sediment pH range (6.23–7.46, Fig. 3) corresponds to slightly acidic to near-neutral conditions, under which metal mobility is generally reduced due to enhanced adsorption and precipitation as hydroxides, carbonates, or via binding to Fe-Mn oxides or organic matter (Zhao et al., 2024; Zhang et al., 2014). For instance, a recent study on lake sediments showed that increasing pH shifts Zn into more inert residual fractions while decreasing its presence in organic matter and sulfide-bound fractions, thus lowering its release risk (Zhao et al., 2024). Additionally, systematic reviews affirm that elevated pH enhances retention of metals in sediment matrices (Zhang et al., 2014). These observations align with the well-documented principle that declining pH fosters metal solubilization and bioavailability, highlighting the importance of even small pH shifts for metal fate in sediments.

4.3. Metals in benthic organisms

The decline in Margalef diversity and the increase in Berger-Parker dominance indices (Fig. 5) at sites with higher metal concentrations, particularly Site 2 (Margalef = 2.81; Berger–Parker = 0.34) and Site 7 (Margalef = 1.90; Berger–Parker = 0.77), indicate that heavy metal contamination exerts a strong structuring effect on macroinvertebrate assemblages. The lowest abundance observed at Site 2 (50 individuals), together with intermediate richness, coincided with elevated As (18.8 μg/g) and Cd (0.50 μg/g) concentrations in *Herpetogomphus* sp., suggesting that bioaccumulation surpassed the tolerance thresholds of sensitive taxa (e.g. Leptohyphidae). This agrees with previous studies highlighting Ephemeroptera, Plecoptera, and Trichoptera as among the most vulnerable groups to chemical stressors, whereas tolerant taxa such as Chironomidae and Oligochaeta persist and dominate under adverse conditions (Mmako et al., 2021; Akamagwuna et al., 2021; Tampo et al., 2021).

Beyond the direct toxic effects, the results suggest that habitat degradation exacerbates community shifts by reducing functional diversity and trophic stability, consistent with the findings of Zelnik and Muc (2020). The significant proportion of assemblage variation explained by metals (24–58 %), particularly Cd, further supports the role of these contaminants as primary ecological drivers, while habitat alteration exerts independent and synergistic effects (Sun et al., 2019; Rico-Sánchez et al., 2022). Bioavailable metals in sediments, due to their high mobility, likely reduce substrate suitability for colonization and increase exposure risks along the food web (Chen et al., 2023; Lipi et al., 2024). The strong dominance at Site 7 may therefore reflect concentrations of As, Cd, and Pb exceeding probable effect levels (PEL), thresholds previously linked to reductions in abundance, increased mortality, and behavioral impairment in benthic invertebrates (Canadian Council of Ministers of the Environment (CCME), 2014).

Elevated dissolved oxygen (DO) concentrations (Fig. 2) in the SJ and CR rivers indicate favorable respiratory conditions for aquatic biota. However, the co-occurrence of high metal concentrations in sediments presents a contrasting scenario, reflecting the potential for toxicological stress in benthic ecosystems (Islam et al., 2023).

Despite the limited dataset, the concurrence of elevated arsenic (As), cadmium (Cd), and lead (Pb) concentrations in both sediments (Fig. 3) and benthic macroinvertebrates (Fig. 6) at Site 2 suggests a strong influence of mining liabilities on biotic metal uptake in the SJ river. Spatial proximity to mining sources appears to be a critical determinant of metal bioavailability and trophic transfer within the aquatic food web. Encouragingly, a downstream attenuation of metal concentrations was observed from Site 3 to Site 7 in both matrices, potentially driven by differences in benthic community composition, species-specific uptake efficiencies, and local physicochemical conditions. These spatial dynamics highlight both the ecological disturbance and resilience of the system, modulated by water quality, habitat heterogeneity, and seasonal variability (Pandiyan et al., 2021).

Arsenic concentrations at Site 2 were particularly elevated, exceeding sediment quality guidelines, including the threshold effect level (5.9 mg/kg) and the probable effect level (17 mg/kg) (Canadian Council of Ministers of the Environment (CCME), 2014). This element exhibited bioaccumulation in *Tricorythodes* individuals at levels an order of magnitude higher than Cd and Pb. The persistence of *Leptohyphidae* (e.g., *Tricorythodes*) in arsenic-contaminated environments has been previously reported in Mexican and Brazilian river systems (Rico-Sánchez et al., 2022; Manoel and Uieda, 2021), suggesting adaptive tolerance mechanisms.

Elevated Pb concentrations in *Tricorythodes* nymphs at Sites 2, 5, and 7 correlated with seasonal peaks in sediment-associated Pb. This alignment suggests sediment as a dominant exposure pathway, facilitated by natural processes such as bioturbation, which modulate metal mobility and bioavailability (King et al., 2005). Lead concentrations displayed comparable trends across the genera *Leptohyphes*, *Tricorythodes*, and *Vacupernius*, with the latter also exhibiting the highest Cd accumulation across most sites. These metal burdens are plausibly linked to dietary exposure, particularly ingestion of fine particulate organic matter (FPOM), along with passive diffusion across permeable tissues—a mechanism corroborated by biomarker-based evidence in aquatic taxa (Kadim and Risjani, 2022).

A study conducted by Rodríguez et al. (2015), aimed at classifying Functional Feeding Groups (FFGs) within Ephemeroptera nymphs, identified *Leptohyphes*, *Tricorythodes*, and *Vacupernius* (all from the Leptohyphidae family) as collector-gatherers. This designation, grounded in gut content analysis and morphological features, indicates a trophic reliance on FPOM (<1 mm) accumulated in sediments. Such feeding behavior provides a mechanistic explanation for the presence of As, Cd, and Pb in these genera (Fig. 6), given the propensity of these metals to precipitate and accumulate in benthic substrates. Similar feeding ecology and contamination patterns were documented for *Leptohyphes* by Guzmán-Soto and Tamarís-Turizo (2014).

These genera spend the majority of their immature stages in the benthic zone of freshwater systems (Rivera-Pérez et al., 2023). As collector-gatherers and scrapers, they exploit detritus and periphyton adhering to submerged substrates (Jacobus et al., 2019), behaviors that heighten their exposure to sediment-bound pollutants. The demonstrated persistence of *Tricorythodes* and *Vacupernius* in metal-polluted habitats underscores their ecological plasticity and potential for tolerance. While *Tricorythodes* and *Vacupernius* generally occupy lentic or low-flow habitats with higher organic loads, *Leptohyphes* tends to be associated with more turbulent flows (Flowers and De la Rosa, 2010), potentially influencing both foraging strategies and contaminant exposure.

Owing to their sediment-dwelling habits, benthic macroinvertebrates are directly exposed to contaminants, rendering them especially susceptible to metal toxicity (Polar-Pérez, 2023). Uptake occurs via respiratory and digestive pathways, with preferential accumulation in metabolically active tissues such as gills, digestive glands, and the hepatopancreas (Erazo-Enríquez, 2022), generating alterations in cell structure, physiological damage, osmotic stress, genotoxic effects, and disrupted growth or reproduction (Pavé, 2012; Cardoso et al., 2023; Lu et al., 2018). Post-absorption, metals are transported via hemolymph, where they nonspecifically bind to proteins, altering their tertiary structure and impairing enzymatic function. This interaction is mediated by the high affinity of metals for sulfhydryl (-SH), carboxyl (-COOH), and amino ($-NH_2$) groups, mechanisms central to their toxicity (Erazo-Enríquez, 2022).

Biological traits such as size and developmental stage further influence metal bioaccumulation. Smaller individuals, by virtue of a higher surface-to-volume ratio, often exhibit elevated metal burdens under similar environmental conditions (Cardoso et al., 2023; Figs. 7 and 8). Moreover, the capacity for bioaccumulation and subsequent biomagnification through trophic interactions represents a tangible threat to ecosystem integrity and human health (Bonsignore et al., 2018).

The results obtained build upon this evidence, confirming that smaller macroinvertebrates often exhibit higher body burdens of As and Pb, which can be explained by size and metabolism, dependent bioaccumulation kinetics. In small-bodied taxa, higher mass-specific metabolic rates and feeding activity enhance uptake rates (ku), while reduced capacity for detoxification and storage leads to slower elimination (ke) (Rainbow, 2018; Zhang et al., 2022). This pattern has been observed across benthic insects, where early instars of Baetis and Leuctra accumulate greater metal concentrations than larger conspecifics, despite feeding on similar FPOM and biofilms (Arnold et al., 2021). Conversely, larger organisms may exhibit "biodilution" as rapid somatic growth outpaces metal uptake or regulate internal concentrations more efficiently through storage in granules and metallothionein-like proteins (Rainbow, 2018). Experimental kinetic studies further support this explanation: in *Chironomus riparius*, uptake constants for metals from water and diet decrease with larval size, consistent with metabolic scaling of assimilation (Silva et al., 2023). Therefore, both organism size and metabolism provide a mechanistic basis for the higher As/Pb burdens we observed in smaller macroinvertebrates, reinforcing the importance of considering allometric and physiological factors in biomonitoring interpretations.

The responses of macroinvertebrate assemblages demonstrate their value as effective bioindicators of both contaminant exposure and habitat degradation, integrating the additive and interactive effects of metal toxicity and ecological disturbance, and providing a mechanistic explanation for the reductions in diversity and abundance observed at the most impacted sites. When considered alongside sediment data, the marked contrast in metal concentrations between abiotic and biotic compartments highlights the urgent need for integrative environmental management strategies. The persistence of elevated As, Cd, and Pb burdens in sediments and their trophic transfer to benthic macroinvertebrates confirm that mining-derived pollutants remain a dominant ecological driver in tropical fluvial systems such as those in Líbano de Tilarán, Guanacaste, Costa Rica. Addressing these impacts requires ecosystem-specific interventions that account for the interplay of hydrology, biodiversity, and anthropogenic stressors, and that align with long-term conservation and public health goals.

5. Conclusions

The close relationship between the spatial distribution of arsenic, cadmium and lead concentrations in sediments and in benthic organisms, together with the observed spatial changes in the physicochemical water characteristics of water, demonstrate the impact of mining liabilities on the San Jose and Cañas rivers.

Proximity to mining liabilities has led to the environmental release of metals, including arsenic and lead, at potentially toxic levels that directly impact benthic macroinvertebrate communities. The significant correlation between the reduced abundance of sensitive families, such as Leptohyphidae, and metal concentrations in sediments underscores the cascading ecological consequences of sediment contamination. Moreover, the detection of bioaccumulated metals in predator organisms across multiple sites reveals the long-term ecological legacy of these pollutants.

The spatial and temporal dynamics of metal distribution, along with the frequency and intensity of post-closure flooding events, are key drivers of metal mobilization and deposition in riverine sediments. This emphasizes the dynamic nature of metal enrichment, especially during the rainy season when discharge increases sediment transport, thus intensifying exposure risks for aquatic organisms.

The results of this study not only provide valuable insights into understanding mining-related pollution but also provides a foundation for environmental conservation efforts and a call for the sustainable management of mining liabilities and protecting freshwater ecosystems in Costa Rica and beyond.

Based on these findings, we recommend implementing an environmental remediation plan focused on the mining liabilities of Líbano, Tilarán. This plan should incorporate experimental physicochemical, biological, and microbiological methodologies aimed at minimizing the toxicity and environmental risks posed by these mining wastes. Such interventions are essential to protect aquatic ecosystems and safeguard the health of local communities that rely on the Cañas River sub-basin for water resources.

CRediT authorship contribution statement

Johanna Rojas-Conejo: Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Francisco Picado-Pavón:** Writing – review & editing, Writing – original draft. **Cornelis A.M. van Gestel:** Writing – review & editing, Writing – original draft. **Andrea Suárez-Serrano:** Writing – review & editing, Writing – original draft. **Nicole Parra-Barrientos:** Writing – review & editing, Writing – original draft, Visualization. **Adolfo Quesada-Román:** Writing – review & editing, Writing – original draft, Visualization, Investigation. **Anny Guillén-Watson:** Writing – review & editing, Writing – original draft. **María López-Maietta:** Writing – review & editing, Writing – original draft.

Declaration of competing interest

We approve the final version of the submitted manuscript. We warrant that the article is the authors' original work, has not received prior publication and is not under consideration for publication elsewhere.

Data availability

Data will be made available on request.

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