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Water-sediment interactions, pollution indices, and ecological risk assessment of potentially toxic metals in the Mirusha waterfall, Kosovo

Jeton Halili[1], Shkurtesa Krasniqi[1], Skender Demaku[1*]

[1] Department of Chemistry, Faculty of Natural Science and Mathematics, University of Prishtina "Hasan Prishtina", 31 George Bush Str., Prishtina 10000, Kosovo
* Corresponding author's e-mail: skender.demaku@uni-pr.edu

ABSTRACT

Growing urbanization and land-use changes increase the vulnerability of small freshwater ecosystems to contamination by potentially toxic metals (PTMs). This study presents an integrated assessment of PTMs in water and surface sediments of the Mirusha waterfall, Kosovo, combining chemical analysis, pollution indices, ecological risk evaluation, and multivariate statistical analysis. Water and sediment samples were collected from six stations (June–July 2024) and analyzed using ICP-OES. In water, copper concentrations ranged from 0.00284 to 0.00287 mg L^{-1}, manganese from 0.67 to 0.79 mg L^{-1}, zinc from 0.95 to 2.36 mg L^{-1}, iron from 0.33 to 0.35 mg L^{-1}, chromium from 0.068 to 0.078 mg L^{-1}, and lead from 0.027 to 0.031 mg L^{-1}. Manganese concentrations exceeded the USEPA guideline value (0.5 mg L^{-1}) at all sampling sites, while iron and lead exceeded selected international guideline thresholds. Sediment metal concentrations were uniformly low (e.g., Cu: 3.85–3.98 mg kg^{-1}; Zn: 1.59–2.41 mg kg^{-1}; Cr: 0.69–0.96 mg kg^{-1}), remaining well below international sediment quality guidelines. Pollution load index (PLI) values ranged from 0.0119 to 0.0139, indicating absence of sediment contamination. The ecological risk index (RI = 1.22–1.61) classified all sites as low ecological risk. Principal component analysis explained 86.7% of total variance (PC1 = 69.4%, PC2 = 17.3%), indicating that metal distributions are predominantly governed by natural geochemical background and hydro sedimentary processes, with limited evidence of strong point-source anthropogenic inputs. Although sediment quality remains good, exceedance of selected guideline values in water highlights the importance of periodic monitoring to ensure long-term ecological protection of this protected freshwater ecosystem.

Keywords: Mirusha waterfall, potentially toxic metals, ecological risk assessment, water, sediment, ICP-OES method.

INTRODUCTION

The rapid growth of the global population, together with urbanization and increasing human activities, has resulted in the continuous release of hazardous pollutants into aquatic ecosystems, among which potentially toxic metals (PTMs) are of particular concern. These elements are persistent in the environment due to their non-biodegradable nature, tendency to accumulate in biota, and potential to cause adverse effects on ecosystems and human health (Islam et al., 2015; Ndhlovu et al., 2023).

Sediments play a dual role in aquatic systems, acting both as carriers and as potential secondary sources of PTMs in rivers, lakes, and waterfall environments (Pejman et al., 2015). For this reason, sediment analysis provides valuable information on long-term contamination trends. Although trace metals such as Fe, Mn, Zn, and Cu are essential for biological functions, elevated concentrations may disturb aquatic ecosystems and pose risks to organisms through bioaccumulation and food-chain transfer (Botle et al., 2024; Chang et al., 2024).

The environmental behavior of potentially toxic metals in freshwater systems is strongly controlled by physicochemical conditions and hydro sedimentary processes. Metal partitioning between the dissolved phase and sediments depends on pH, redox potential, ionic strength, and the presence of carbonate minerals, which influence metal speciation, adsorption, and precipitation reactions.

In carbonate-dominated geological settings, such as the Mirusha waterfall region, metal mobility may be affected by complexation with carbonate species and by co-precipitation with iron and manganese oxides. Furthermore, the hydrodynamic characteristics of waterfall systems including turbulence, sediment resuspension, and variable flow velocity can modify metal distribution patterns by influencing particle transport and deposition processes.

Therefore, understanding water–sediment interactions under site-specific geochemical and hydrological conditions is essential for accurate interpretation of metal concentrations and ecological risk.

Heavy metal inputs to freshwater systems originate from a range of anthropogenic activities, including industrial discharges, wastewater effluents, urban runoff, agricultural practices, and traffic-related sources (Ali et al., 2016; Kosovo Agency of Statistics, 2024). The Mirusha waterfall, located in Malisheva, Kosovo, represents an ecologically and recreationally important natural site that is increasingly exposed to such pressures due to nearby residential areas, small-scale commercial activities, agricultural land use, and the presence of a wastewater treatment facility in the catchment area.

Despite the environmental importance of this area, no comprehensive assessment of potentially toxic metals has previously been conducted for the Mirusha waterfall system. Although several studies have investigated metal contamination in rivers and artificial lakes across Kosovo, this protected waterfall ecosystem has not been systematically evaluated with respect to combined water–sediment metal distribution and ecological risk. In particular, integrated application of pollution indices (CF, Igeo, PLI), ecological risk assessment (ER and RI), and multivariate statistical analysis has not been reported for this site.

Given that sediments may function both as sinks and secondary sources of metals under changing physicochemical conditions, a simultaneous assessment of water and sediment compartments is essential for reliable ecological evaluation. Therefore, the present study provides the first integrated investigation of selected potentially toxic metals in water and surface sediments of the Mirusha waterfall.

By establishing baseline concentration levels and evaluating ecological risk using multiple complementary indices, this work contributes essential reference data for future monitoring and environmental management of this freshwater system.

MATERIALS AND METHODS

Description of sampling locations

The Mirusha waterfall is located in central Kosovo and extends across the municipalities of Klina, Malisheva, and Rahovec, covering a total protected area of approximately 598.4 ha. The area is designated as a natural monument and is predominantly composed of carbonate geological formations, mainly limestones characterized by fissure porosity, which results in limited and discontinuous groundwater flow (Kosovo Agency of Statistics, 2015–2024).

The hydrographic network of the region is relatively sparse. The Mirusha river represents the main watercourse and is supplemented by several smaller streams with permanent or seasonal flow regimes. These streams are primarily fed by atmospheric precipitation, including rainfall and snowmelt. Consequently, many tributaries do not maintain continuous flow throughout the year and typically contain water during spring and autumn, with reduced flow during winter and dry periods (Kosovo Agency of Statistics, 2015–2024).

Natural springs within the study area commonly originate at lithological contacts between permeable and less permeable rock units, including Paleozoic limestones and shale formations. Human activities within the catchment include small-scale fishing, vehicle and clothes washing, automobile repair, agricultural practices, local geoprocessing activities, and road traffic. These activities are concentrated near populated areas and along access routes close to the waterfall system, potentially contributing diffuse inputs to the aquatic environment (Kosovo Agency of Statistics, 2015–2024).

The catchment area of the Mirusha Waterfall is exposed to multiple potential sources of pollution, including domestic wastewater discharges, small industrial effluents, and inputs from a nearby sewage treatment facility. However, these sources are spatially dispersed and mainly associated with diffuse rather than point-source inputs.

During the sampling campaign (June–July 2024), no visible direct effluent discharge from the wastewater treatment facility was observed in the immediate vicinity of the selected sampling stations. Therefore, any potential influence is interpreted as indirect and spatially diffuse within the broader catchment area, rather than resulting from a clearly identifiable point-source discharge affecting the monitored sites.

Sample collection

Water and surface sediment samples were collected from six sampling stations to capture spatial variability along the waterfall system. Sampling sites M1 and M2 were located in the central section of the waterfall, M3 and M4 in the northeastern section, and M5 and M6 in the northwestern section. This spatial arrangement allowed for the assessment of potential changes in metal concentrations along the flow path of the river–waterfall system.

Samples were collected following standard procedures for environmental monitoring and were subsequently transported to the laboratory for chemical analysis of potentially toxic metals.

The geographic coordinates of the sampling stations were recorded using a GPS device and are presented in Table 1 (WGS84 coordinate system). Stations were distributed along the main hydrological axis of the waterfall system to capture spatial variability in metal concentrations. Inter-station distances were calculated from station coordinates (WGS84) using great-circle (Haversine) distances. The approximate straight-line distances between consecutive stations were: M1–M2 (0.477 km), M2–M3 (0.879 km), M3–M4 (0.741 km), M4–M5 (0.815 km), and M5–M6 (0.433 km).

Elevation (m above sea level) for each sampling station was extracted from a 30 m resolution digital elevation model (SRTM). Elevations ranged from 360 to 453 m a.s.l., reflecting the natural altitudinal gradient of the waterfall system.

Water samples were collected from the active flow zone at shallow depths, typically not exceeding approximately 0.5 m, depending on local hydro morphological conditions. The waterfall system is characterized by relatively shallow and fast-flowing sections, which allowed consistent sampling within the upper water column.

Sampling was conducted during the summer period (June–July 2024) under relatively stable hydrological conditions. The waterfall system exhibited moderate and continuous flow typical of the dry season, without evidence of extreme rainfall events or flood conditions during sampling.

Surface sediments were collected from the upper 0–5 cm layer of depositional zones along the active channel. Based on field observations, the sediments were predominantly coarse-grained, consisting mainly of sand and gravel fractions, with visible carbonate fragments typical of the local geological setting. No detailed granulometric analysis was performed in the present study.

Physicochemical parameters such as pH, dissolved oxygen (DO), electrical conductivity (EC), and redox potential (Eh) were not measured during the present sampling campaign. Therefore, mechanistic interpretation of metal mobility and partitioning processes is based on general geochemical principles for carbonate-dominated freshwater systems rather than site-specific in situ measurements. This represents a methodological limitation that should be addressed in future monitoring campaigns (Figure 1).

Water sample collection and preparation

Water samples were collected in pre-cleaned 2 L glass bottles and transferred to acid-washed Teflon containers. Samples were not filtered prior to acidification; therefore, the reported values represent total (acid-extractable) metal concentrations.

To preserve metals and ensure complete extraction of both dissolved and particle-associated

Table 1. Geographic coordinates and elevation of sampling stations (WGS84)

Station	Latitude	Longitude	Elevation (m a.s.l.)
M1	42.523903	20.600024	450
M2	42.523293	20.594268	453
M3	42.524065	20.583598	425
M4	42.524788	20.574614	360
M5	42.520474	20.566570	360
M6	42.523175	20.562768	361

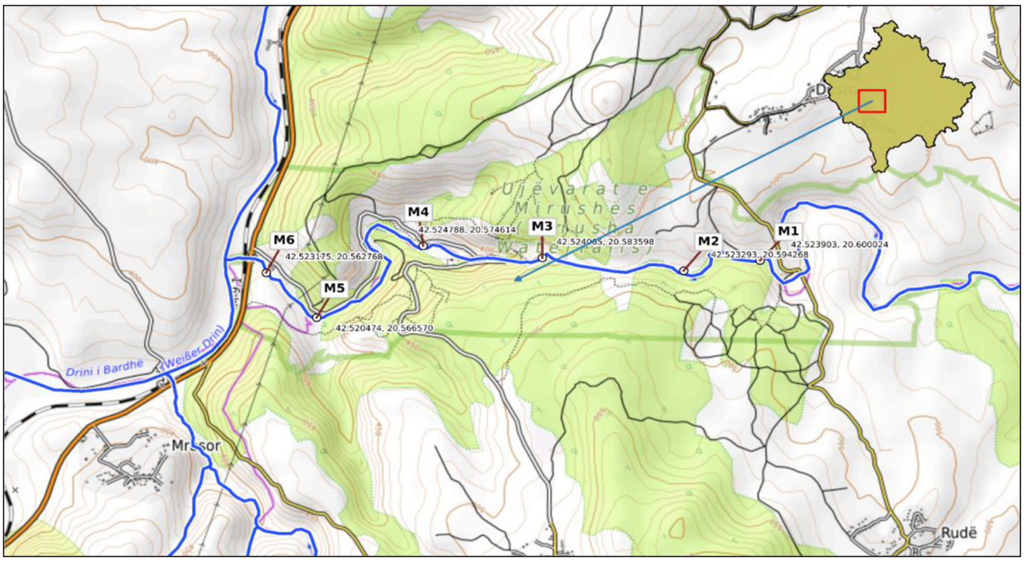


Figure 1. Location of the Mirusha waterfall in central Kosovo and spatial distribution of sampling stations (M1–M6). Geographic coordinates (WGS84) are indicated

fractions, samples were acidified with a mixed-acid system (HNO_3 + HCl) and subjected to microwave-assisted digestion prior to ICP-OES analysis.

High-purity standard solutions (99.98%) for all analysed elements were obtained from Merck (Germany) and used for instrument calibration and quality control (World Health Organization, 2015).

Sediment sample digestion and heavy metal analysis

For sediment analysis, approximately 0.5 g of air-dried and homogenized sediment was accurately weighed into a digestion flask. The samples were treated with 5 mL of nitric acid (HNO_3) followed by 1 mL of perchloric acid ($HClO_4$) and digested for about 2 h under controlled heating conditions. After cooling, 5 mL of diluted hydrochloric acid (1:1, v/v in deionized water) was added to the digest, following the procedure recommended by the US Environmental Protection Agency (US-EPA, 2017). The resulting solutions were diluted to a final volume of 100 mL with deionized water and filtered prior to instrumental analysis.

Sediment digestion using HNO_3 and HCl provided pseudo-total metal concentrations, as hydrofluoric acid (HF) was not applied. This approach targets the environmentally available and acid-extractable metal fraction rather than the total silicate-bound fraction.

Concentrations of potentially toxic metals, including As, Ni, Zn, Fe, Al, Cu, Cr, Pb, Mn, and Cd, were determined using inductively coupled plasma–optical emission spectrometry (ICP-OES, DW-2100), as described by Demaku et al. (2024).

Quality assurance and quality control

Instrument calibration was performed using multi-element standard solutions, and calibration curves were generated automatically by the ICP-OES software. The calibration linearity was assessed using the correlation coefficient (R^2), which was ≥ 0.997 for the analysed metals. All samples were analysed in triplicate, and the concentrations reported in Tables 1 and 3 represent the mean of three replicate measurements ($n = 3$). All reported concentrations were above the instrumental detection capability of the ICP-OES system. The analytical precision was evaluated through triplicate measurements, and the low variability between replicates confirmed the reliability of the reported values.

Instrumental detection limits provided by the ICP-OES manufacturer are in the low $\mu g\ L^{-1}$ range for the analyzed elements. All reported concentrations were above the instrumental detection capability of the instrument. Although the limits of detection (LOD) and limits of quantification (LOQ) were not formally determined during this study, the high calibration linearity ($R^2 \geq 0.997$) and consistent triplicate reproducibility support the analytical reliability of the dataset. Certified reference materials (CRM) and spike-recovery tests were not included in the present analytical campaign. This represents an analytical limitation; however, internal quality control was ensured through calibration verification and replicate measurements.

Statistical analysis and data visualization

Spatial visualization and graphical representations were generated using Python-based analytical workflows. The sampling location map (Figure 1) and all statistical figures (Figures 2–6), including concentration profiles, coefficient of variation plots, hierarchical cluster dendrogram, and principal component analysis (PCA) biplot, were produced using Python libraries (e.g., Pandas, NumPy, Matplotlib, and SciPy).

This approach ensured reproducibility of graphical outputs, consistent scaling, and standardized statistical visualization.

Contamination factor

The contamination factor (CF) was used to evaluate the level of metal contamination in sediments relative to background concentrations and to provide an indication of possible anthropogenic influence (Hakanson, 1980). The CF was calculated as:

$$CF = \frac{MC}{BC} \tag{1}$$

where: *MC* represents the concentration of a given heavy metal in the sediment sample, and *BC* denotes the corresponding background concentration.

Background values were adopted from the Upper Continental Crust data reported by Taylor and McLennan (1995) and Kumar et al. (2020).

Pollution load index

The pollution load index (PLI) was applied to assess the level of heavy metal contamination in sediments by integrating the contamination factors of individual metals. The PLI was calculated using the following equation:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times CF_4 \times \ldots\ldots CF_n)^{1/n} \tag{2}$$

where: *CF* represents the contamination factor of each metal and *n* is the number of metals analysed.

According to Ndhlovu et al. (2023), PLI values lower than 1 indicate the absence of pollution, whereas PLI values greater than 1 suggest sediment contamination.

Geoaccumulation index

The geo-accumulation index (Igeo) was used to assess the degree of metal accumulation in sediments relative to background concentrations (Muller, 1979). The Igeo was calculated using the equation:

$$Igeo = log_2 \frac{(MC)}{1.5 \times BC} \tag{3}$$

where: *MC* and *BC* represent the measured and background concentrations of the metal, respectively. The constant 1.5 accounts for natural lithogenic variability.

Ecological risk assessment of potentially toxic metals in sediment

The potential ecological risk (ER) of individual potentially toxic metals (PTMs) was calculated using the equation:

$$ER = CF \times Tr \tag{4}$$

where: *CF* and *Tr* are the contamination factor and the toxicological response factor of the individual metal, respectively.

Tr values were obtained from Duodu et al. (2016) and Kumar et al. (2020) as follows: 5 for Cu and Pb, 1 for Zn, 2 for Cr, and 30 for Cd. The ecological risk index (RI) was then computed as the sum of ER values for all assessed metals according to:

$$RI = \sum_{i=1}^{n} ERi \tag{5}$$

The categorization of potential ecological risk factors follows Hakanson (1980) and Kumar et al. (2020). The classification of the ecological risk index is as follows: RI < 150 indicates low ecological risk, 150 ≤ RI < 300 moderate risk, 300 ≤ RI < 600 considerable risk, and RI ≥ 600 high ecological risk.

RESULTS AND DISCUSSION

PTMs composition in water

The measured concentrations of potentially toxic metals in the water of Mirusha waterfall are presented in Table 2. The concentration ranges of potentially toxic metals in the water across the sampling stations (M1 to M6) were as follows: Cu: 0.00284–0.00287 mg L^{-1}, Mn: 0.67–0.79 mg L^{-1}, Fe: 0.33–0.35 mg L^{-1}, Cr: 0.068–0.078 mg L^{-1}, and Pb: 0.027–0.031 mg L^{-1}. The concentrations of other elements were: Zn: 0.95–2.36 mg L^{-1}, Al: 0.10–0.11 mg L^{-1}, Ni: 0.02–0.022 mg L^{-1}, Cd: 0.001–0.002 mg L^{-1}, and As: 0.006–0.007 mg L^{-1}.

The highest concentrations among the analysed metals in water were observed for Zn (0.95–2.36 mg L^{-1}), Mn (0.67–0.79 mg L^{-1}), and Fe (0.33–0.35 mg L^{-1}), while Cu (0.00284–0.00287 mg L^{-1}) and Cd (0.001–0.002 mg L^{-1}) were present at comparatively lower concentrations.

This may be related to the fact that the Mirusha river (waterfall) flows through typical rural and urban areas, may be associated with diffuse anthropogenic inputs, including traffic and local activities. Additionally, various industries and agricultural activities in the surrounding area discharge effluents containing Mn, Cu, Fe, and Cr into the river (Oyeyiola et al., 2014).

Sources of potentially toxic metals in Mirusha waterfall are attributed to runoff from polluted and open sewer drainage systems, as well as leachates from solid waste dumps in the catchment area (Utete and Fregene, 2020).

In comparison with the maximum permitted values presented in Table 3 (WHO, 2017; USEPA, 2017), manganese concentrations exceeded the USEPA guideline value (0.5 mg L^{-1}) at all sampling sites, while iron slightly exceeded the USEPA threshold (0.3 mg L^{-1}) at several locations.

Lead concentrations (0.027–0.031 mg L^{-1}) exceeded the USEPA (0.015 mg L^{-1}) and EU/WHO (0.01 mg L^{-1}) limits, whereas chromium remained below the USEPA standard (0.1 mg L^{-1}) but above the more restrictive EU/WHO guideline value (0.05 mg L^{-1}). In contrast, copper, zinc, cadmium, arsenic, and nickel remained within their respective international regulatory limits.

PTMs contamination and ecological risk assessment in sediments

Table 4 presents the concentrations of potentially toxic metals measured in sediment samples collected from the Mirusha (M1–M6). The metal concentrations show limited spatial variability among sampling sites and remain well below the sediment quality guideline values recommended by USEPA and WHO, indicating generally low levels of contamination.

Sediment contamination was evaluated using the contamination factor, geo-accumulation index, pollution load index, and ecological risk indices, with background concentrations adopted from the upper continental crust (UCC). The calculated PLI values for all sampling sites ranged from 0.0119 to 0.0139, remaining well below unity, which clearly indicates the absence of heavy-metal pollution in the sediments of the Mirusha waterfall (Table 5). These low PLI values suggest that sediment quality is predominantly controlled by natural geochemical background conditions, with no evidence of significant anthropogenic contamination (Olagbemide, 2017).

Consistent with the PLI results, the geo-accumulation index (Igeo) classification indicates that sediments at all sampling locations fall within the "unpolluted" category. Although Cu, Fe, and Mn show slightly higher concentrations compared to other analysed elements, their corresponding Igeo classes remain within the unpolluted range.

Table 2. Concentration of potentially toxic metals (mg L^{-1}) in water samples from the Mirusha waterfall

Elements	Sampling locations					
	M1	M2	M3	M4	M5	M6
As	0.006	0.006	0.005	0.006	0.006	0.007
Ni	0.02	0.02	0.02	0.02	0.02	0.02
Zn	0.95	0.96	1.55	1.68	2.35	2.36
Fe	0.33	0.34	0.34	0.34	0.33	0.35
Al	0.10	0.10		0.10	0.11	0.11
Cu	0.00284	0.00285	0.00286	0.00285	0.00286	0.00287
Cd	0.001	0.001	0.002	0.001	0.001	0.002
Cr	0.068	0.069	0.069	0.073	0.075	0.078
Pb	0.027	0.028	0.029	0.030	0.030	0.031
Mn	0.67	0.69	0.71	0.74	0.77	0.79

Note: Values are mean of triplicate measurements (n = 3).

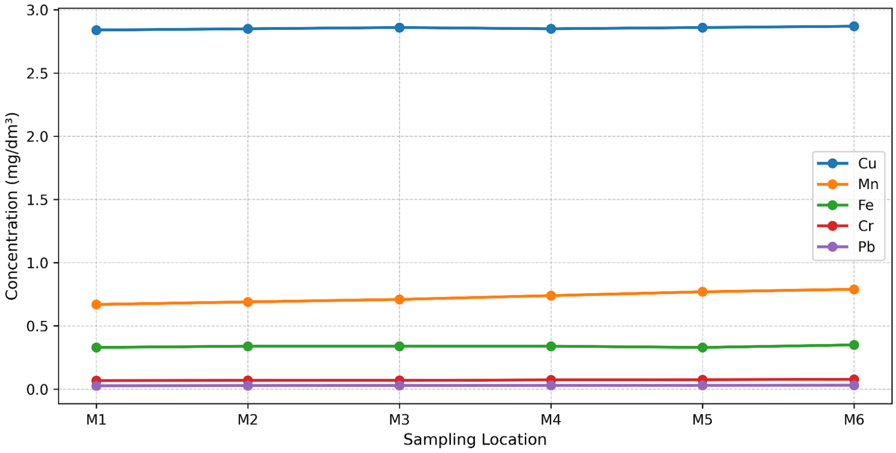


Figure 2. Concentration profiles of selected potentially toxic metals (Cu, Mn, Fe, Cr, Pb)

Table 3. Maximum permitted values of potentially toxic metals (mg/dm^3) in surface waters (2015–2022), according to various countries and international standards

Potentially toxic metals (PTMs)	USEPA standard	EU standard	WHO standard	China standard	Kenya standard	Indian standard
As	0.01	0.01	0.01	-	-	0.01–0.05
Cd	0.005	0.005	0.003	0.005	0.01	0.003
Cr	0.1	0.05	0.05	0.05	-	0.05
Cu	1.3	0.2	2.0	-	-	0.05–1.5
Pb	0.015	0.01	0.01	0.01	0.05	0.01
Hg	0.002	0.001	0.001	0.0001	0.02	0.001
Fe	0.3	0.2	0.2	-	-	0.3
Zn	5.0	-	3.0	-	-	5.0-15
Ni	0.02	0.02	0.02	0.03	-	-
Mn	0.5	0.05	0.5	-	-	-
Al	0.10–1.20	0.01–0.10	0.10	0.1	-	-

This pattern suggests minor variations related mainly to natural geochemical heterogeneity and sediment–water interaction processes along the waterfall system, rather than to substantial anthropogenic accumulation.

The observed discrepancy between moderately elevated Mn concentrations in water and low sediment contamination factors may be attributed to the dynamic hydrological regime of the waterfall system and the predominance of coarse-grained carbonate sediments. In high-energy lotic environments, limited fine-particle retention reduces long-term metal accumulation capacity.

Additionally, in well-oxygenated and high-energy lotic environments such as waterfall systems, manganese may remain relatively mobile due to continuous water turbulence and limited fine-particle retention, which reduce the opportunity for effective sedimentary accumulation.

Figure 3 illustrates the spatial distribution of selected major and minor metals (Cu, Fe, Mn, and Zn) in sediment samples collected from sites M1–M6. The observed variations are gradual and limited in magnitude, suggesting that metal distribution is primarily influenced by natural sediment transport processes and local lithological characteristics rather than by point-source contamination.

Lead (Pb) presented separately as a trace metal, shows consistently low concentrations and minimal spatial variability across the sampling sites.

This distribution pattern further supports the interpretation that sediment metal levels are largely governed by natural geochemical background conditions, with no clear indication of significant anthropogenic impact on sediment quality.

The assessment of potential ecological risk indicates that the individual ecological risk values

Table 4. Presentation of the concentration of potentially toxic metals (mg/kg) in the analyzed sediment samples of Mirusha waterfall

Elements	Sampling locations						USEPA standard
	M1	M2	M3	M4	M5	M6	
As	0.009	0.009	0.007	0.006	0.008	0.007	-
Ni	0.21	0.23	0.35	0.24	0.35	0.29	16
Zn	1.90	1.92	1.59	1.62	2.13	2.41	110
Fe	3.36	3.31	3.38	3.39	3.36	3.91	30
Al	0.10	0.11		0.10	0.11	0.11	-
Cu	3.85	3.91	3.96	3.85	3.95	3.98	16
Cd	0.001	0.002	0.001	0.002	0.002	0.001	0.6
Cr	0.84	0.81	0.96	0.85	0.69	0.92	25
Pb	0.39	0.31	0.43	0.38	0.46	0.49	40
Mn	2.69	2.72	2.79	2.81	2.78	2.97	30

Note: Values are mean of triplicate measurements (n = 3).

Table 5. Summary of pollution load, geo-accumulation, and ecological risk indices for sediment samples collected at the Mirusha waterfall (M1–M6)

Station	PLI	PLI class	Igeo class	RI	RI class
M1	0.0119	No pollution	Unpolluted	1.22	Low
M2	0.0128	No pollution	Unpolluted	1.55	Low
M3	0.0125	No pollution	Unpolluted	1.27	Low
M4	0.0124	No pollution	Unpolluted	1.55	Low
M5	0.0139	No pollution	Unpolluted	1.61	Low
M6	0.0131	No pollution	Unpolluted	1.29	Low

for all investigated metals are low at every sampling site. The calculated ecological risk index, ranging from 1.22 to 1.61, remains far below the threshold associated with moderate ecological risk. This clearly suggests that the combined impact of potentially toxic metals in the sediments of the Mirusha waterfall currently poses a low ecological risk.

The ecological risk index applied in this study is based on the Hakanson model, originally developed for lake sediment environments characterized by relatively stable depositional conditions. In dynamic waterfall systems such as the Mirusha waterfall, sediment transport and hydrodynamic energy may influence metal redistribution and deposition patterns.

Therefore, while RI values provide a comparative assessment of potential ecological risk, their interpretation in lotic and high-energy environments should be considered with caution. Arsenic (As) and nickel (Ni) were not included in the ecological RI calculation, as toxic-response factors for these elements were not defined in the original Hakanson model. Therefore, RI values were calculated only for metals with established toxic-response coefficients.

Although Cu, Fe, and Mn contribute relatively more to the total RI compared to other elements, their absolute contributions are small and remain well within the low-risk category. These results indicate that, under present conditions, metal concentrations in the sediments are unlikely to cause harmful effects on benthic organisms or disrupt the functioning of the aquatic ecosystem.

From an ecological perspective, the low contamination and risk levels observed in the sediments suggest that adverse impacts on aquatic organisms and associated food webs are unlikely at this stage. However, it is well established that metals such as Cu, Mn, Fe, Cd, Ni, and As may become ecologically relevant at elevated concentrations (Olayinka et al., 2017; Jona and Ayodele-Olajire, 2022).

For this reason, regular monitoring of sediment quality is recommended to enable early detection

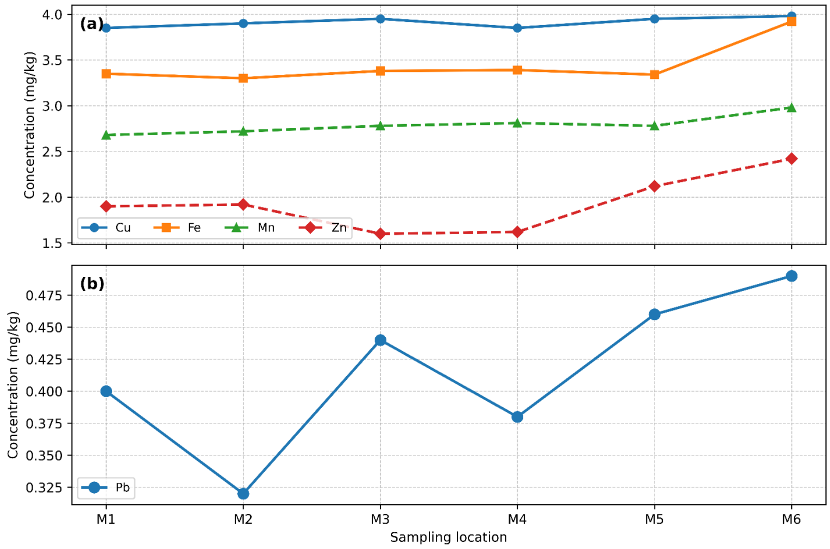


Figure 3. Contamination levels of PTMs (potentially toxic metals) in sediments: (a) spatial distribution of major and minor metals (Cu, Fe, Mn and Zn) in sediment samples collected along the Mirusha wAterfall (M1–M6), reflecting natural geochemical variability and sediment transport processes, (b) concentration profile of Pb in sediments, shown separately as a trace metal, indicating low levels and limited spatial variability along the sampling sites

of potential changes related to land-use practices, hydrological variability, or diffuse anthropogenic pressures within the catchment area (Figure 4).

The coefficient of variation (CV) was calculated to evaluate the relative dispersion of metal concentrations among sampling stations. Low CV values observed for most elements indicate limited spatial variability and a relatively homogeneous distribution of metals across the waterfall system.

This pattern suggests that metal concentrations are primarily controlled by natural geochemical background and hydro sedimentary processes rather than by localized point-source inputs.

Slightly higher variability observed for selected elements (e.g., Mn and Zn in water) reflects gradual spatial gradients along the flow path rather than abrupt contamination hotspots. Overall, the low dispersion metrics support the interpretation of stable environmental conditions and absence of significant anthropogenic accumulation in the sediment compartment.

According to USEPA and WHO sediment quality guidelines (Wang et al., 2023), elevated or high levels of sediment contamination are generally indicated when metal concentrations exceed the following reference values: Mn (30 mg/kg), Ni (16–20 mg/kg), Cr (25 mg/kg), Zn (110–123 mg/kg), Cu (16–25 mg/kg), Pb (40 mg/kg), Cd (0.6–6.0 mg/kg), and Fe (30 mg/kg), while no specific guideline value is defined for As.

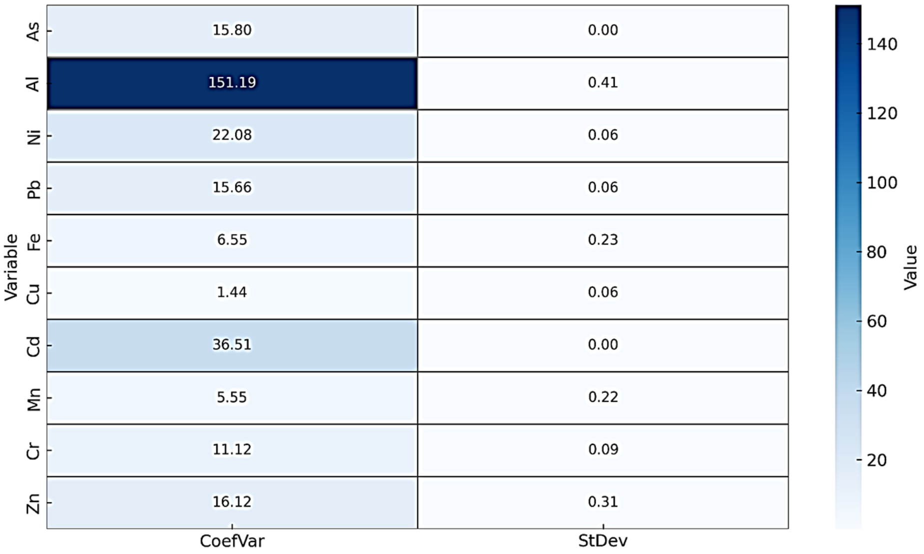
Based on the measured concentrations in the sediment samples collected from the Mirusha waterfall, none of the investigated metals exceeded these guideline thresholds. This further confirms that sediment quality at all sampling locations remains within acceptable limits according to USEPA and WHO criteria, supporting the classification of the study area as unpolluted with respect to heavy metal contamination (Wang et al., 2023).

The hierarchical cluster dendrogram groups the analyzed potentially toxic metals (PTMs) into three main clusters based on their similarity in concentration patterns across the sediment samples from the Mirusha waterfall (Figure 5). These groupings reflect differences in geochemical behavior rather than clear separation by contamination intensity.

The first cluster includes Fe, Mn, Pb, Zn, Cu, and Ni, which show similar distribution patterns across the sampling sites. This association likely reflects common controlling factors such as natural geochemical background, sediment composition, and hydro sedimentary processes, with possible minor contributions from diffuse anthropogenic activities within the catchment area.

However, the consistently low concentrations and pollution indices indicate that these elements are not significantly impacted by direct anthropogenic contamination.

The second cluster comprises As and Cd, which are present at very low concentrations and



Variable	CoefVar	StDev
As	15.80	0.00
Al	151.19	0.41
Ni	22.08	0.06
Pb	15.66	0.06
Fe	6.55	0.23
Cu	1.44	0.06
Cd	36.51	0.00
Mn	5.55	0.22
Cr	11.12	0.09
Zn	16.12	0.31

Figure 4. Coefficient of variation and standard deviation of potentially toxic metals

display limited variability among sampling locations. Their grouping suggests a predominantly natural origin, controlled by background geochemistry rather than external inputs.

The third cluster is represented by Cr, which forms a separate group, indicating distinct geochemical behavior compared to the other metals. This separation may be related to differences in mineral associations, mobility, or binding characteristics within the sediment matrix.

The cluster analysis supports the interpretation that metal distributions in the sediments of the Mirusha waterfall are mainly governed by natural geochemical controls, with no clear evidence of strong anthropogenic influence.

The first principal component (PC1) explained 69.4% of the total variance, while the second principal component (PC2) accounted for 17.3%, together explaining 86.7% of the overall dataset variability (Figure 6).

This high cumulative variance indicates that the dominant geochemical patterns of heavy metal distribution in the Mirusha waterfall are effectively represented within a reduced two-dimensional ordination space.

Metals displaying similar loading directions on the biplot are positively correlated, suggesting that they are influenced by comparable controlling factors. In particular, Cu, Mn, and Zn show relatively aligned loadings, indicating a

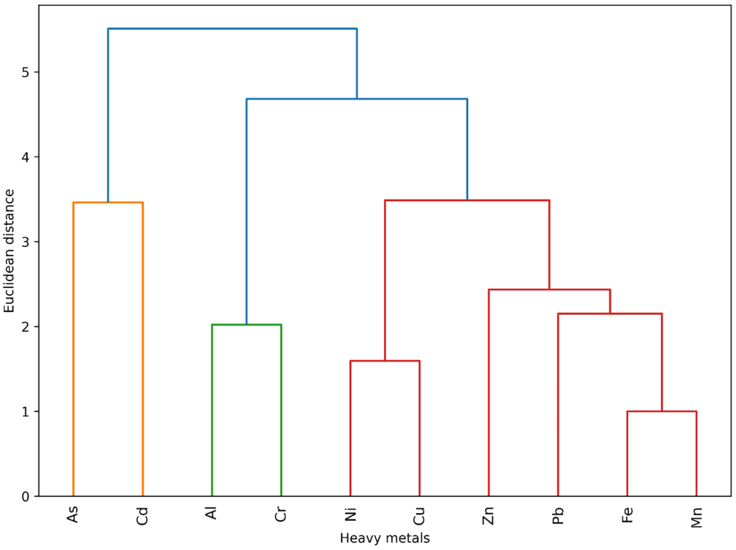


Figure 5. Cluster analysis dendrogram of potentially toxic metals in sediment samples

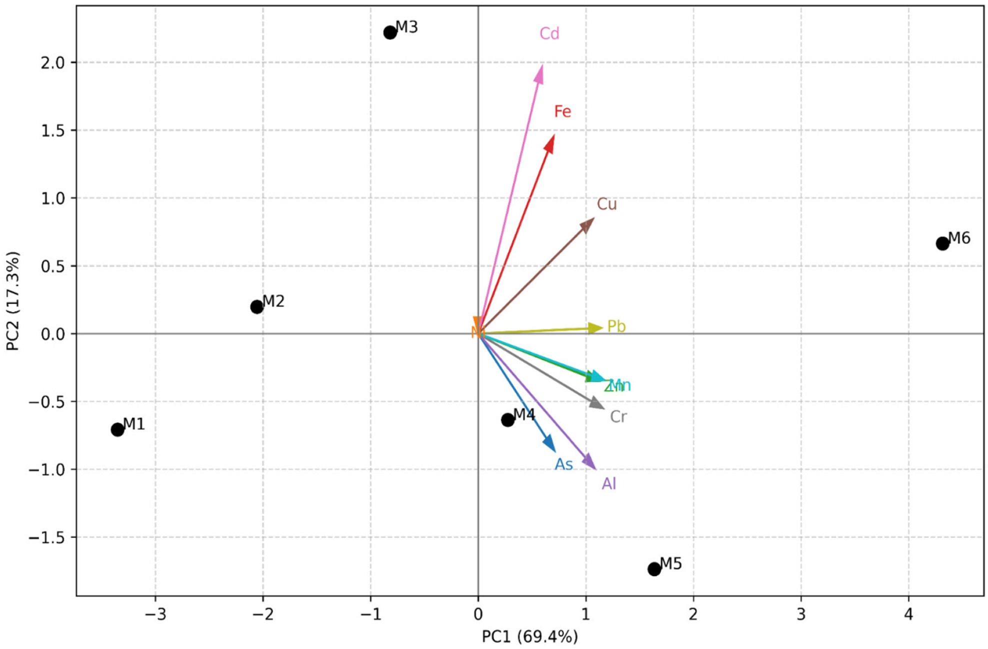


Figure 6. Principal component analysis biplot of standardized heavy metal concentrations in water samples from the Mirusha waterfall (M1–M6), showing the relationships between sampling sites and metal variables

shared geochemical behavior that is likely related to natural lithological characteristics and water–sediment interaction processes along the waterfall system.

In contrast, elements positioned in different quadrants of the biplot exhibit weaker associations, reflecting differences in geochemical mobility, mineral binding, or sedimentary affinity.

The distribution of sampling sites along the principal component axes shows a gradual separation among locations, which may reflect spatial variations along the waterfall rather than abrupt changes linked to point-source contamination. This pattern is consistent with the results obtained from hierarchical cluster analysis, further supporting the reliability of the multivariate grouping.

The PCA results complement the cluster analysis by clarifying inter-element relationships and the multivariate structure of the dataset.

Together, these analyses indicate that the observed distribution of potentially toxic metals in the sediments of the Mirusha waterfall is predominantly governed by natural geochemical variability and hydro sedimentary processes, with no clear evidence of strong localized anthropogenic influence under current conditions.

The results indicate that the distribution of PTMs in the study area is influenced by a combination of natural processes and diffuse human activities, rather than by dominant point-source pollution. Spatial variations in metal concentrations appear to reflect hydrological conditions, sediment transport dynamics, and local geochemical background, with possible minor contributions from urban and land-use-related activities within the catchment.

These findings highlight the dynamic interaction between water and sediment compartments and underline the importance of considering multiple environmental controls when interpreting metal behavior.

While human activities such as urban development, traffic, and small-scale commercial operations may contribute to localized inputs, their influence on sediment quality remains limited under current conditions. This interpretation is consistent with previous studies conducted in comparable freshwater environments (Zhuang et al., 2016; Wang et al., 2023).

Malisheva functions as an important regional center with developed infrastructure and transportation networks; however, the consistently low contamination levels observed in sediments suggest that any anthropogenic metal inputs are presently dispersed and do not result in measurable accumulation. This integrated assessment provides a balanced understanding of metal distribution patterns and supports the conclusion that natural geochemical controls play a dominant role in the study area.

CONCLUSIONS

The results indicate that although certain metals such as manganese, iron, and lead locally exceeded selected international guideline values in water, other analysed metals remained within regulatory thresholds.

Most analysed metals, including Cu, remained well below international regulatory thresholds. The observed variations are consistent with diffuse inputs and natural geochemical background rather than dominant point-source pollution.

In contrast, sediment samples exhibited consistently low concentrations of all investigated metals and remained well below international sediment quality guideline values. Pollution indices and ecological risk assessment clearly classified the sediments as unpolluted, with a low potential ecological risk across all sampling sites. These findings indicate that, under current conditions, metals are not significantly accumulating in the sediment compartment of the waterfall system.

Multivariate statistical analysis further suggests that the distribution of metals is primarily controlled by natural geochemical background, hydrological conditions, and sediment transport processes, while anthropogenic influence on sediment quality appears to be limited. The combined interpretation of water and sediment data highlights the dynamic interaction between these two environmental compartments and the importance of considering both in ecological assessments.

The Mirusha waterfall ecosystem currently shows good sediment quality and low ecological risk related to metal contamination. However, the presence of elevated metal concentrations in water emphasizes the need for regular monitoring and the implementation of preventive management measures. Such actions are essential to minimize future contamination, support sustainable use of the area, and protect the ecological and recreational value of this important freshwater system.

This study establishes the first integrated baseline dataset for potentially toxic metals in both water and sediments of the Mirusha waterfall system. The combined application of pollution indices, ecological risk assessment, and multivariate statistical analysis provides a comprehensive framework for evaluating metal dynamics in small protected freshwater environments.

Despite current low sediment-associated ecological risk, the exceedance of guideline values for manganese in water highlights the importance of continued surveillance. Future investigations incorporating seasonal sampling and in situ physicochemical measurements will further improve mechanistic understanding and long-term environmental management of the system.

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