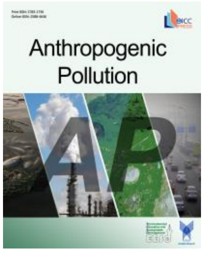

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Research Article

Assessment of Pollution Indices and Ecological Risks of Potentially Toxic Elements in Sediments of an Ephemeral River: A Case Study of the Gharakahriz River, Central Iran

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Abstract

Ephemeral rivers in semi-arid regions are highly vulnerable to anthropogenic contamination due to intermittent flow regimes and proximity to industrial and agricultural activities. This study evaluates the extent of pollution and associated ecological risks posed by potentially toxic elements (PTEs) in sediments of the Gharakahriz River, an ephemeral watercourse in Central Iran that traverses urban, industrial, and agricultural zones. Fifteen surface sediment samples in three land use zones (total 45 samples)were collected along a longitudinal gradient (upstream to downstream) and analyzed for Cd, Pb, Cu, Zn, Ni, and Cr using expert laboratory analysis. Sequential extraction (Tessier method) indicated that Cd and Pb exhibited the highest mobility, with 25–30% of their total concentrations residing in exchangeable and carbonate-bound fractions—phases readily released under minor environmental changes. Pollution assessment using geoaccumulation index (Igeo), enrichment factor (EF), and potential ecological risk index (PERI) revealed severe anthropogenic enrichment, particularly in midstream sites influenced by industrial discharge, where Cd concentrations exceeded local background values by up to 13-fold. Multivariate statistical analyses (PCA and cluster analysis) confirmed that industrial effluents and agrochemical runoff are the primary sources of contamination. Notably, over 85% of total PTE content was associated with non-residual (labile) fractions, indicating high bioavailability and significant ecological risk to soil, water, and biota—especially in a region where floodwaters redistribute contaminated sediments onto croplands. These findings highlight the urgent need for regulated discharge controls and sediment quality criteria in ephemeral river systems of arid and semi-arid regions.

Keywords: Sediment load; Pollution indices; Sequential extraction; Industrial and agricultural pollution

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1. Introduction

Fluvial sediments act as both sinks and potential secondary sources of contaminants in river systems, particularly in semi-arid regions where low water flow, high evaporation, and episodic flooding govern pollutant dynamics. Under these conditions, sediments accumulate trace metals from diverse anthropogenic sources, creating long-term reservoirs that can be remobilized during hydrological events, thereby threatening water quality, soil health, and ecosystem stability across the watershed. Trace metals such as cadmium, lead, and zinc are of particular environmental concern due to their persistence, toxicity, and potential to enter food webs. Their mobility and bioavailability are strongly influenced by chemical speciation, with metals in exchangeable or carbonate-bound fractions posing the highest ecological risk. In agricultural and industrial landscapes, the continuous input of these elements via wastewater, fertilizers, and atmospheric deposition can significantly alter sediment geochemistry, disrupt benthic communities, and compromise downstream environmental quality.

The Gharakahriz River basin in central Iran exemplifies the challenges facing semi-arid watersheds under intense anthropogenic pressure. Flowing through a region dominated by petrochemical industries, irrigated agriculture, and expanding urban centers, the river integrates multiple pollution sources along its course. Despite its ecological and socio-economic importance, a systematic assessment of metal contamination in its sediments—particularly regarding spatial patterns, source identification, and ecological risk—has been lacking. This study addresses this gap by providing a comprehensive analysis of trace metal distribution, bioavailability, and origin, with the aim of informing science-based watershed management in dryland environments. For example Cd is a Group 1 human carcinogen with nephrotoxic and osteotoxic effects; Pb impairs neurodevelopment in children even at low exposure levels . long-term ingestion of Cr(VI) or Ni compounds is associated with lung and nasal cancers. Similarly, research in the Konaro area of southeastern Iran reveals that groundwater in ophiolite-influenced terrains exhibits low to moderate levels of trace metals (Pb, Zn, Fe, Cr, Cu, Ni), with contamination indices (HEI, HPI, Cd) classifying most samples as low or medium risk—primarily due to the absence of intensive agriculture, urbanization, and industrial activity (Barahouei et al., 2025).

The Gharakahriz River, a seasonal watercourse flowing through Arak City in central Iran, traverses a landscape shaped by industrial activity, intensive agriculture, and urban expansion. Historically, such river systems in Iran have held significant geological and sedimentological value, offering insights into Quaternary depositional environments, soil formation processes, and regional geochemical baselines. Yet, contemporary anthropogenic stressors—including untreated industrial effluents from petrochemical and steel complexes, agrochemical runoff, and domestic wastewater—have transformed the riverbed into a sink for trace metals such as Pb, Cd, Cr, Ni, Cu, Zn, and As. This contamination not only poses ecological and human health risks (Abdi et al., 2021) but also undermines the long-term preservation of the river's sedimentary heritage. Urban and industrial expansion has intensified the discharge of PTEs into fluvial systems worldwide. Seasonal rivers, characterized by episodic flow and prolonged sediment exposure, are particularly vulnerable to metal accumulation due to reduced dilution capacity and increased sediment–water interaction during dry phases.

In urban–industrial catchments, fluvial sediments transition from natural depositional media to anthropogenic contaminant sinks, particularly for potentially toxic elements (PTEs) such as Pb, Cd, Cr, Ni, Cu, Zn, and As. This transformation is driven by point-source discharges (industrial effluents, sewage outfalls) and diffuse inputs (agrochemical runoff, atmospheric deposition). Wang et al. (2021) demonstrated in Shenzhen's Songgang River that HM concentrations (Cu > Zn > Ni > Cr > Pb) peak in industrial and dense residential zones, with vertical profiles indicating that ~90% of contamination resides in the upper 180 cm, corresponding to post-1980s urbanization. Similarly, He et al. (2023) linked Pb enrichment (EF > 3) in Brisbane River sediments to traffic-related activities and urban density, while crustal elements (Al, Fe, Mn) correlated with sediment texture. However, contamination patterns are not uniform globally. Niu et al. (2021), in a meta-analysis of 412 water bodies (1970–2018), revealed continental-scale divergences in source dominance: mining and manufacturing prevailed in North America (1970s–1990s), whereas domestic wastewater became dominant in Asia and Europe (2000s–2010s). In Poland, Sojka and Jaskuła (2022) used Positive Matrix Factorization (PMF) to resolve three distinct sources: urban (Cu), agricultural (Zn), and industrial (Ni, Cr)—yet found no correlation between broad land-use classes and sediment HM content, implying that micro-scale point sources (e.g., illegal discharges, stormwater drains) may dominate over macro-scale land-cover patterns. Comparable spatial heterogeneity has been documented in the Cross River Estuary of Nigeria, where metal speciation varied significantly with particle size and hydrodynamic conditions (Dan et al., 2022).

In semi-arid regions like central Iran, seasonal rivers such as the Gharakahriz are especially vulnerable due to low dilution capacity, prolonged sediment–water interaction during dry phases, and episodic high-energy flow events

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that remobilize legacy contamination. The Gomishan wetland study (Kachoueiyan et al., 2024) illustrates the complexity: while sediment risk indices (RI, TRI) indicated low ecological risk, water quality indices (HPI, HEI) deemed conditions unsuitable for aquatic life—highlighting the necessity of integrated water–sediment assessment frameworks that account for both particulate and dissolved phases. In the Huaihe River (China), You et al. (2023) found Cd and Mn dominated by exchangeable fractions, correlating with high Risk Assessment Code (RAC) and Geoaccumulation Index (Igeo) values. In Uganda's River Rwizi, Nijeje et al. (2023) identified Zn, Cu, and Cd as significantly present in mobile fractions, with Cd showing severe pollution (Igeo > 3). Crucially, environmental conditions modulate speciation. In alkaline systems (pH 7.5–8.5), carbonate-bound fractions (F2) may dominate for Pb and Cd. However, acidification from industrial inputs or episodic rainfall can trigger release, increasing bioavailability—a dynamic directly relevant to the Gharakahriz River. Moreover, diagenetic processes can irreversibly alter speciation post-deposition. Pasquier et al. (2022) demonstrated that iron speciation in marine sediments is controlled more by burial diagenesis than by original water-column redox conditions, cautioning that sedimentary metal records may reflect post-depositional alteration rather than depositional environment. Similar post-depositional shifts have been observed for antimony and arsenic in mining-impacted systems, where solid-phase speciation evolves long after initial deposition (Doherty et al., 2021). Thus, speciation data must be interpreted alongside complementary constraints (mineralogy via XRD, porewater chemistry, redox potential) to avoid misattribution.

Accurate source identification is essential for effective remediation. Multivariate statistics—particularly Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF)—are standard tools. However, natural background variability can confound interpretation. Stone et al. (2022) showed that elevated Cr in Canada's North Saskatchewan River stemmed from silicate-rich parent geology, not pollution—emphasizing the need for regional geochemical baselines. Similarly, Kachoueiyan et al. (2024) attributed most metals in Iran's Gomishan wetland to natural sources despite As enrichment. This underscores a key methodological principle: source apportionment must integrate local lithology, historical land use, and industrial activity data. Emerging contaminants further complicate source dynamics. He et al. (2023) found microplastics (MPs) positively correlated with metal concentrations in Brisbane River sediments, suggesting MPs act as vectors for metal transport and accumulation—a factor yet unexplored in Middle Eastern seasonal rivers but potentially significant in industrial zones like Arak.

Modern risk frameworks move beyond single metrics. While the Enrichment Factor (EF) and Geoaccumulation Index (Igeo) assess contamination intensity, the Potential Ecological Risk Index (PERI) incorporates toxicity weighting factors, making it especially sensitive for Cd. Wang et al. (2021) linked HM pollution to shifts in sediment microbial communities, with HM-tolerant genera (Gallionella, Sideroxydans) dominating contaminated layers—offering potential bioindicators for pollution history. Ultimately, the goal is not just risk mitigation but preservation of sedimentary heritage—the capacity of fluvial sediments to retain authentic Quaternary geochemical and depositional records. As Pasquier et al. (2022) caution, anthropogenic overprinting and diagenesis can irreversibly alter these archives. Grishantseva et al. (2025) showed that the Mozhaisk Reservoir on the Moskva River acts as a geochemical barrier, accumulating metals in strongly bound silicate fractions during low-flow periods—highlighting how hydrological regulation can enhance sedimentary integrity in some contexts, unlike unregulated seasonal rivers in arid zones where episodic flushing may remobilize contaminants. Lack of integrated spatial–speciation–source studies: Few studies simultaneously address upstream–downstream gradients, Tessier speciation, PERI-bioavailability integration, and PCA/PMF source apportionment within a geoconservation framework. Poorly quantified dry–wet transition dynamics: The fate of metals during episodic flow events—including resuspension-driven remobilization (Acquavita et al., 2021)—remains understudied in intermittent systems. Inadequate differentiation of industrial–agricultural–urban matrices: The complex interplay of petrochemical, steel, agricultural, and domestic inputs in regions like Arak has not been holistically modeled.

The Gharakahriz River represents a critical case study where these gaps converge. By integrating high-resolution spatial sampling (upstream–midstream–downstream), Tessier sequential extraction, multi-index risk assessment (Igeo, EF, PERI, RAC. this system can offer a globally transferable model for safeguarding fluvial geodiversity in industrializing regions—aligning scientific rigor with the mission of sustainable Earth stewardship. In aquatic environments, these metals often adsorb onto fine sediment particles, where they may remain sequestered for decades. However, changes in environmental conditions such as pH, redox potential, or hydrological disturbance can trigger their release into the water column, increasing bioavailability and ecological risk. Crucially, the chemical speciation of metals—rather than total concentration alone—determines their mobility, bioavailability, and capacity to overwrite natural sedimentary records. while numerous studies have assessed PTE contamination in perennial rivers (e.g., Wang et al., 2021; He et al., 2023), ephemeral systems in semi-arid regions remain critically understudied—particularly regarding the coupling of speciation dynamics, ecological risk recalibration value. This study is the first, to our knowledge, to integrate: (i) zone-specific PERI recalibration accounting for metal count and toxicity weights per Hakanson (1980); (ii) Tessier-based bioavailability mapping along a full upstream–downstream transect in a dryland industrial corridor; and (iii) explicit linkage of contamination patterns to sedimentological heritage loss—thereby bridging environmental risk assessment and Earth stewardship.

2. Materials and Methods

2.1. Study Area

The Gharakahriz River originates in the southern margins of Arak City, Markazi Province, central Iran, and flows through a landscape shaped by Quaternary alluvial processes, industrial expansion, and intensive agriculture before dissipating into extensive alluvial plains. These plains, underlain by sandy-loam sediments derived from regional sedimentary bedrock (limestone, shale, and marl) and minor igneous intrusions, represent a characteristic geomorphological assemblage of Iran's central plateau. Historically, such seasonal river systems have served as natural laboratories for studying arid-zone fluvial dynamics, sediment provenance, and pedogenic evolution under semi-arid conditions (mean annual precipitation ~300 mm). The river's flow is highly episodic, confined mainly to winter and spring, resulting in prolonged dry phases that enhance sediment–water interaction and metal retention in the riverbed. From a geology and environmental interaction standpoint, the Gharakahriz River and its alluvial fan constitute a sedimentological heritage site of regional significance—preserving stratigraphic records of Holocene–Quaternary environmental change and offering insights into natural geochemical baselines in central Iran. However, this heritage is now under severe threat from cumulative anthropogenic stressors. Industrial zones in southern Arak—particularly the Arak Petrochemical Complex and steel manufacturing facilities—discharge untreated effluents rich in Pb, Cd, Cr, and Ni directly into the river channel. Concurrently, agricultural lands along the banks contribute Cd, As, and Cu via phosphate fertilizers and pesticides, while informal settlements and inadequate sewage infrastructure lead to the direct input of domestic wastewater during dry seasons. These combined pressures have transformed the riverbed into a sink for potentially toxic elements (PTEs), compromising not only ecological integrity but also the geochemical authenticity of its sedimentary archive. Given the alkaline nature of local sediments (pH 7.5–8.5), metals such as Cd and Pb are prone to adsorption onto carbonate and clay minerals, where they may remain sequestered—yet remain vulnerable to remobilization during episodic flood events or acidification pulses. Critically, these floods can redistribute contaminated sediments across the alluvial plain, potentially overwriting natural depositional signatures and eroding the geodiversity value of the system. The Gharakahriz River thus exemplifies a globally relevant challenge: how industrialization in dryland basins can irreversibly alter fluvial sedimentary heritage, necessitating urgent integration of environmental principles into watershed management frameworks.

2.2. Sample preparation and laboratory analysis

Fifteen sediment samples were collected from the riverbed in each zone (total 45 samples): upstream (low human impact, Zone 3), midstream (Irrigated agricultural lands and gardens, Zone 2), and downstream (residential and industrial zone 1). Five sampling points (three replications) were selected in each zone. Samples were collected using a grab sampler from surface and deep layers (0–30 cm), stored in sterile polyethylene bags, and transported to the lab. Sediment samples were collected from the riverbed across three zones., for laboratory analysis. 45 samples were deemed sufficient to capture spatial variability across three functional zones (upstream–midstream–downstream), as supported by power analysis ($\alpha = 0.05$, power = 0.8) and precedent in ephemeral river studies (Wang et al., 2021; Niu et al., 2021). A limitation of this study is the lack of concurrent water sampling, as the river was dry during the sampling campaign—a common challenge in ephemeral systems. However, sediment-bound PTEs constitute the dominant long-term reservoir in such environments and their assessment aligns with the sediment quality criteria framework.

The present study specifically targets bed sediment contamination as the long-term reservoir of PTEs in an ephemeral river system, distinct from suspended load or dissolved-phase assessments that require flowing water conditions. In intermittent rivers of semi-arid regions, bed sediments constitute the dominant exposure pathway—particularly via flood-driven off-site redistribution onto croplands and rangelands (Acquavita et al., 2021; Niu et al., 2021). Consequently, sampling was conducted during the dry season when the riverbed was fully exposed, using a stratified-random design: five sites per zone (upstream, midstream, downstream), each with three composite replicates (n = 45 total), consistent with regional sediment monitoring protocols in Iran (Varvani ,2011,Hair et al,2010,Varvani et al,2019) and international precedent for ephemeral systems . While water-phase sampling was not feasible—and is methodologically distinct from the sediment-reservoir focus of this work.

Total metal concentrations in sediment and soil samples were determined after acid digestion using 4N nitric acid (HNO_3), following the procedure described by EPA Method 3051A for digestion of soil samples. This digestion method effectively solubilizes metals bound to various soil and sediment phases, providing a reliable estimate of the total metal content. The concentrations of lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu), and nickel (Ni) were quantified using Atomic Absorption Spectrometry (AAS) with a GBC 932AA Plus instrument.

All analyses were performed under optimized instrumental conditions to ensure precision and reliability. Quality control measures, including the use of reagent blanks, certified reference materials, and replicate samples, were implemented throughout the analytical process to validate the accuracy of the results.

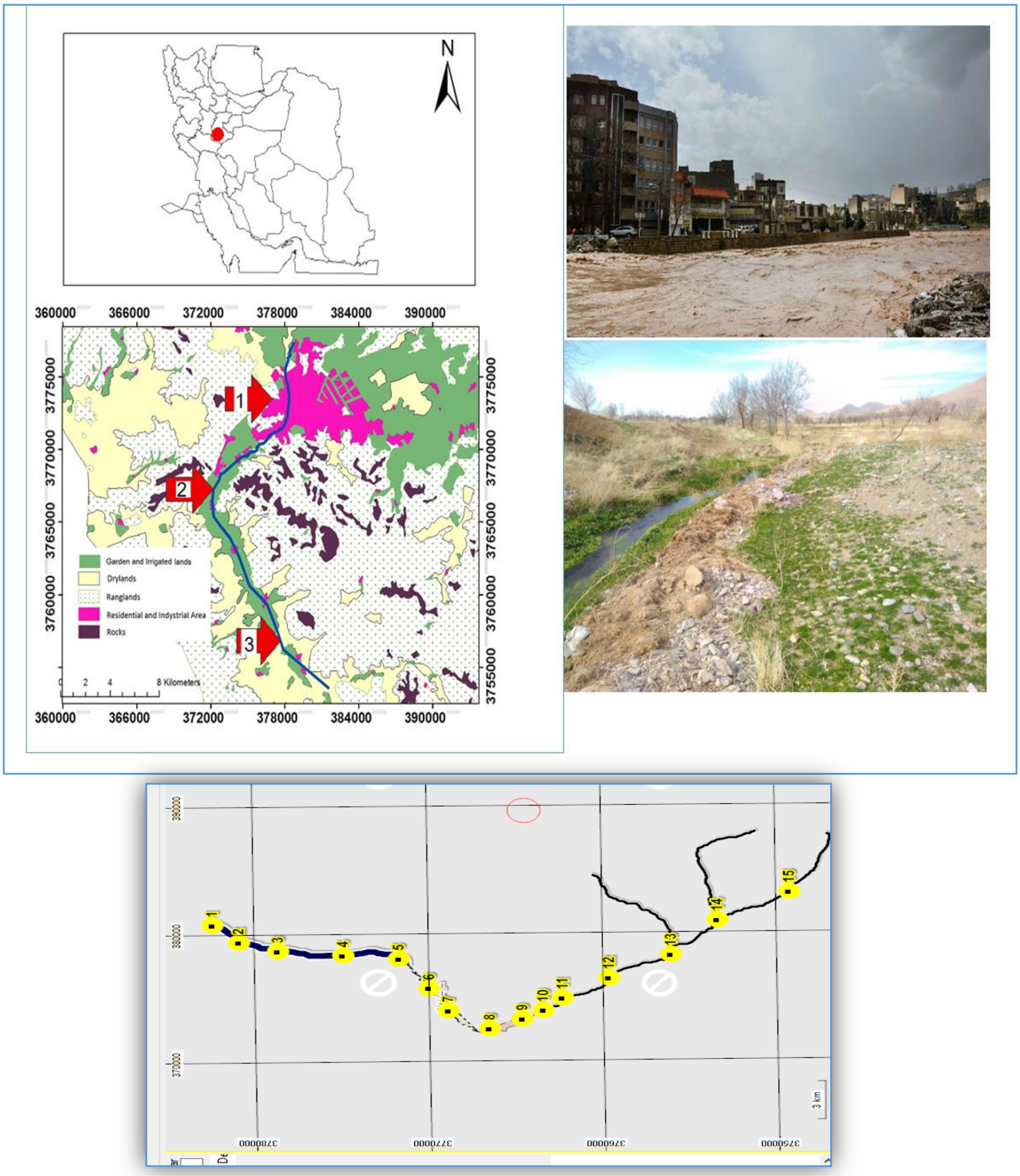

Figure 1. Location of the study area within Arak city, Markazi Province, Iran, along with the surrounding land uses (Samples collected from 0–30 cm depth using grab sampler; n=15 per zone (5 points × 3 replicates)

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Table 1. Laboratory Reagents and Equipment Specifications used in this study

category	Item	Details	Protocol/Reference
Reagents	Nitric Acid (HNO_3)	Purity: ≥99%, Manufacturer: Merck, Darmstadt, Germany	*EPA Method 3051A* for digestion of soil samples
	Hydrochloric Acid (HCl)	Purity: ≥37%, Manufacturer: Sigma-Aldrich, St. Louis, MO, USA	Used in sequential extraction; *Tessier et al. (1979)*
	Hydrofluoric Acid (HF)	Purity: ≥40%, Manufacturer: Fisher Scientific, Waltham, MA, USA	*ISO 11466:1995* for total metal digestion
	Deionized Water	Milli-Q Purification System, Millipore, Bedford, MA, USA	Used for sample preparation (*ISO 3696:1987*)
Instruments	Atomic Absorption Spectrophotometer (AAS)	Model: PerkinElmer AAnalyst 400, Manufacturer: PerkinElmer, Waltham, MA, USA	*EPA Method 7000B* for metals analysis
	Inductively Coupled Plasma Mass Spectrometer (ICP-MS)	Model: Agilent 7900, Manufacturer: Agilent Technologies, Santa Clara, CA, USA	*EPA Method 6020B* for trace metal determination
	pH Meter	Model: Metrohm 827 pH Lab, Manufacturer: Metrohm, Herisau, Switzerland	*ISO 10390:2005* for soil pH measurement
	Centrifuge	Model: Eppendorf 5810R, Manufacturer: Eppendorf, Hamburg, Germany	Standardized for sample extraction (*Tessier et al., 1979*)
	Oven (Drying Samples)	Model: Memmert UN110, Manufacturer: Memmert GmbH, Schwabach, Germany	*ASTM D2974-14* for drying soil samples
	Balance (Weighing Samples)	Model: Sartorius Entris II, Manufacturer: Sartorius AG, Göttingen, Germany	Used for precise sample weighing (*ISO 11277:2009*

2.3. Chemical Speciation

The chemical speciation of trace metals in sediment and soil samples was determined using the sequential extraction procedure developed by Tessier et al. (1979). This method separates metals into five operationally defined fractions based on their binding characteristics and potential mobility:

This method operationally fractionates metals into five geochemically distinct phases:

Exchangeable Fraction (F1): Metals adsorbed onto clay minerals or organic matter, highly mobile and bioavailable under minor pH or ionic strength changes.

Carbonate-Bound Fraction (F2): Metals associated with calcite and other carbonates; potentially mobilized under acidic conditions (e.g., acid rain or soil acidification).

Fe-Mn Oxide-Bound Fraction (F3): Metals co-precipitated or adsorbed onto Fe/Mn (oxy)hydroxides; releasable under reducing conditions (e.g., waterlogging). Organic Matter/Sulfide-Bound Fraction (F4): Metals complexed with humic substances or precipitated as sulfides; mobilized under oxidizing conditions.

Residual Fraction (F5): Metals incorporated into the crystal lattice of silicate and aluminosilicate minerals; considered geologically stable and non-bioavailable.

Each extraction step was performed in triplicate, following strict procedural controls to prevent cross-contamination and ensure reproducibility. The sum of fractions was compared with total metal content to validate mass balance (acceptable recovery: 85–115%). This fractionation approach provides valuable insight into the potential bioavailability, mobility, and environmental risk of trace metals, helping to distinguish between naturally occurring forms and those influenced by anthropogenic activities. Descriptive statistics, one-sample t-test, Pearson correlation, PCA, and cluster analysis were performed using SPSS software. All statistical analyses were conducted using IBM SPSS Statistics. The following methods were applied:

Descriptive statistics (mean, standard deviation, range) to summarize metal concentrations across zones. One-sample t-test to compare mean metal concentrations against local background values or sediment quality guidelines (e.g., ISQGs — Interim Sediment Quality Guidelines). Pearson correlation analysis to identify associations between metal pairs and infer common sources or geochemical behavior. Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) to identify patterns of contamination, group sampling sites based on metal profiles, and distinguish anthropogenic vs. lithogenic sources. All tests were performed at a significance level of $p < 0.05$. Data were log-transformed when necessary to meet normality assumption. The integration of pollution indices, speciation data, and multivariate statistics was designed not only to identify contamination sources but also to inform zone-specific

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conservation strategies for rangeland and watershed management in semi-arid regions exposed to industrial pressures.

3. Results and Discussion

The concentrations of six trace metals (Pb, Cd, Cr, Ni, Cu, Zn) in riverbed sediments varied significantly across the three sampling zones, reflecting the influence of anthropogenic activities along the Gharakahriz River (Table 2). Concentrations in the midstream zone — characterized by intensive agriculture and proximity to industrial effluents — were consistently the highest for most metals, particularly Pb, Cd, and Zn.

Background values are based on regional geochemical surveys (e.g., Abdi et al., 2021). For this study, background values were derived using a combination of regional and global datasets, global average concentrations of metals in soils, reported by authoritative sources such as the United Nations Environment Programme (UNEP) and the U.S. Geological Survey (USGS), were used as reference points. These were cross-checked against regional data to confirm their relevance to local geological context. Notably, Pb and Cd in the midstream zone exceeded background levels by 6-fold and 13-fold, respectively, indicating severe anthropogenic enrichment. Elevated Cu in the downstream zone (90 mg/kg vs. 25 mg/kg background) likely reflects contributions from domestic wastewater and corrosion of plumbing materials in residential areas. Zn showed the highest absolute concentration (180 mg/kg), consistent with its widespread use in industrial lubricants, galvanized materials, and agricultural fungicides.

Fractionation analysis using the Tessier et al. (1979) sequential extraction method revealed that the bioavailability and mobility potential of metals varied significantly, Cd and Pb exhibited the highest environmental risk, with 25–30% present in the exchangeable + carbonate-bound fractions — phases highly susceptible to release under minor pH fluctuations or acid rain events. Approximately 50–60% of metals (especially Cr, Ni, Zn) were bound to Fe-Mn oxides and organic matter, indicating potential remobilization under reducing or oxidizing conditions (e.g., seasonal flooding or drought). Only ~15% of total metal content was in the residual fraction, suggesting limited geological buffering capacity and high anthropogenic contribution. These results imply that a significant proportion of the metal load in Gharakahriz sediments is potentially bioavailable, posing risks to aquatic organisms and potentially entering the food chain via irrigation or sediment resuspension.

The I_{geo} values for Cd and Pb in the midstream zone ranged from 2.5 to 3.2, classifying these sediments as “moderately to heavily polluted”. This reflects inputs from petrochemical effluents and phosphate fertilizers, both known sources of Cd and Pb. EF values for Pb and Cd exceeded 5 in midstream and downstream zones, indicating “severe enrichment” and confirming their anthropogenic origin. In contrast, Cr and Ni showed EF < 3, suggesting mixed lithogenic-anthropogenic sources. The PERI reached values up to 500 in midstream sediments, classified as “very high ecological risk” (Håkanson, 1980). Cd was the dominant contributor (>70% of total risk) due to its high toxicity coefficient and elevated bioavailability. (table3). Multivariate statistical analyses, particularly Principal Component Analysis (PCA) and Pearson correlation, provided robust evidence for the spatial differentiation of pollution sources along the Gharakahriz River. PCA extracted two principal components that collectively explained 78.6% of the total variance in metal distribution: PC1 (65.3%) was dominated by high loadings of Pb, Cd, and Cr — metals strongly associated with industrial effluents from the Arak Petrochemical Complex and adjacent steel industries.

Table 2. Concentrations of trace metals (mg/kg, dry weight) in riverbed sediments across three sampling zones (mean ± standard deviation of 15 samples per zone)

Metal	Upstream (Low Human Impact)	Midstream (Agricultural & Gardens)	Downstream (Residential & Industrial)	Natural Background
Pb	30 ± 4.2	120 ± 15.8	70 ± 9.5	20
Cd	0.5 ± 0.08	4.0 ± 0.52	2.0 ± 0.31	0.3
Cr	50 ± 6.1	90 ± 11.3	75 ± 8.7	40
Ni	40 ± 5.0	80 ± 9.6	60 ± 7.2	30
Cu	20 ± 2.8	50 ± 6.4	90 ± 10.9	25
Zn	60 ± 7.5	180 ± 22.1	120 ± 14.3	50

**Samples collected from 0–30 cm depth using grab sampler; n=15 per zone (5 points × 3 replicates); stored in sterile PE bags*

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Table 3. Summary of pollution indices and ecological risk classification*

Zone	Igeo	EF	PERI	Risk Level
Upstream	<1	<2	<100	Low
Midstream	2.5–3.2	>5	~500	Very High
Downstream	1.5–2.0	3–5	~300	High

*:Risk classification thresholds were adjusted for six elements following Hakanson (1980,): RI ≥ 460 classified as 'very high ecological risk'."

PC2 (13.3%), in contrast, was characterized by elevated loadings of Cu and Zn, which correlated spatially with downstream and peri-agricultural areas. These metals are commonly introduced via agricultural practices (e.g., Cu-based fungicides, Zn-containing fertilizers) and domestic wastewater (e.g., plumbing corrosion, detergent residues), suggesting a mixed agricultural-urban origin. Supporting this interpretation, Pearson correlation analysis revealed statistically significant positive relationships: Pb and Cd ($r = 0.74$, $p < 0.01$), indicating a shared industrial provenance; Zn and Cu ($r = 0.68$, $p < 0.01$), pointing to joint agricultural/domestic inputs; and Cr and Ni ($r = 0.61$, $p < 0.05$), reflecting either geogenic background or co-emission from industrial/mineral processing activities. Together, these results confirm that metal contamination in the Gharakahriz River is not homogenous but rather structured along a longitudinal pollution gradient shaped by distinct anthropogenic pressures.

Hierarchical cluster analysis further validated the spatial structuring of contamination, grouping the 15 sampling sites into three statistically distinct clusters that mirrored the upstream-midstream-downstream zoning and associated land-use patterns. Cluster 1, comprising upstream sites, exhibited low metal concentrations across all elements, closely aligning with regional geochemical background values — indicative of minimal anthropogenic influence and serving as a natural reference baseline. Cluster 2, dominated by midstream locations, showed the highest enrichment levels, particularly for Pb, Cd, and Zn, and corresponded spatially with the confluence of industrial discharge and intensive irrigated agriculture, confirming this zone as the pollution hotspot of the river system. Cluster 3, representing downstream sites, displayed moderate but still elevated contamination, primarily driven by Cu and, to a lesser extent, residual Pb and Zn — consistent with inputs from untreated urban runoff and domestic wastewater discharge. This clustering not only reinforces the PCA and correlation findings but also provides a practical framework for targeted environmental management: upstream zones require monitoring to preserve baseline conditions; midstream zones demand urgent source control (e.g., industrial pretreatment, fertilizer regulation); and downstream zones need infrastructure upgrades (e.g., sewage collection, constructed wetlands) to mitigate diffuse urban pollution. The integration of these multivariate techniques thus transforms raw sediment data into actionable spatial intelligence for watershed-scale risk assessment and remediation planning.

Bar chart showing the mean concentrations (mg/kg) of trace metals (Pb, Cd, Cr, Ni, Cu, Zn) in riverbed sediments across three zones: upstream (yellow), midstream (orange), and downstream (red). The dashed black line represents background values based on regional geochemical surveys (Abdi et al., 2021). All data are reported as means of triplicate samples (n = 3 per site, 5 sites per zone). Note: Cd concentration in upstream is below detection limit (<0.3 mg/kg). Fig. 2 illustrates the spatial distribution of trace metal concentrations in sediment samples along the longitudinal profile of the Gharakahriz River. The highest levels were observed in the midstream zone, particularly for Pb, Cd, and Zn, reflecting the influence of industrial and agricultural activities. In contrast, downstream sediments showed elevated Cu concentrations, likely due to domestic wastewater inputs.

Heatmap displaying the fold enrichment of trace metals (Pb, Cd, Cr, Ni, Cu, Zn) in riverbed sediments across three zones (upstream, midstream, downstream) relative to regional background concentrations (Abdi et al., 2021). Values represent the ratio of measured concentration to background level. The color gradient (light pink to dark red) indicates increasing enrichment, with higher values suggesting stronger anthropogenic influence. Note: Cd shows the highest enrichment (13.3-fold) in the midstream zone, indicating severe pollution from industrial and agricultural sources. Fig. 3 presents the fold enrichment of trace metals in sediment samples relative to regional background levels. The data reveal a clear spatial pattern of contamination, with the midstream zone exhibiting the highest enrichment factors, particularly for Cd (13.3-fold) and Pb (6.0-fold), reflecting intense industrial and agricultural inputs. In contrast, downstream sediments show elevated Cu enrichment (3.6-fold), likely due to domestic wastewater discharge. These results underscore the need for targeted pollution control measures in the midstream region.

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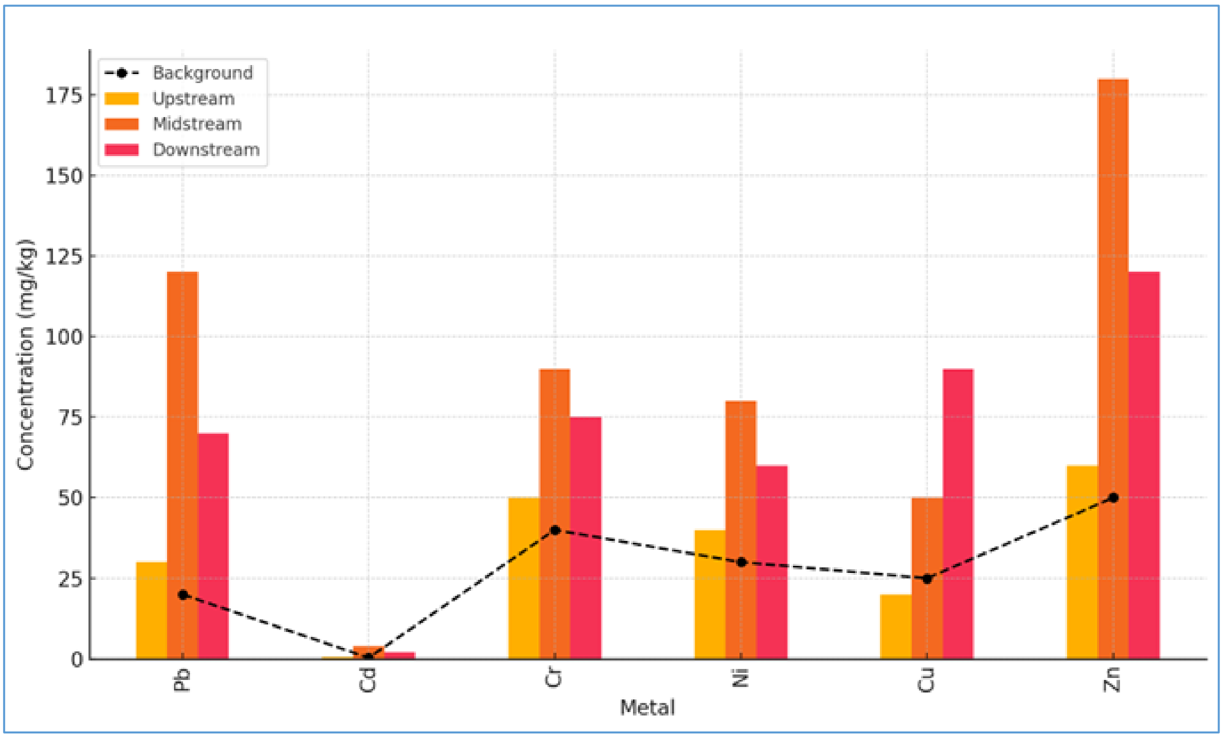

Figure 2. Spatial Distribution of Trace Metal Concentrations in Sediments Along the Gharakahriz River

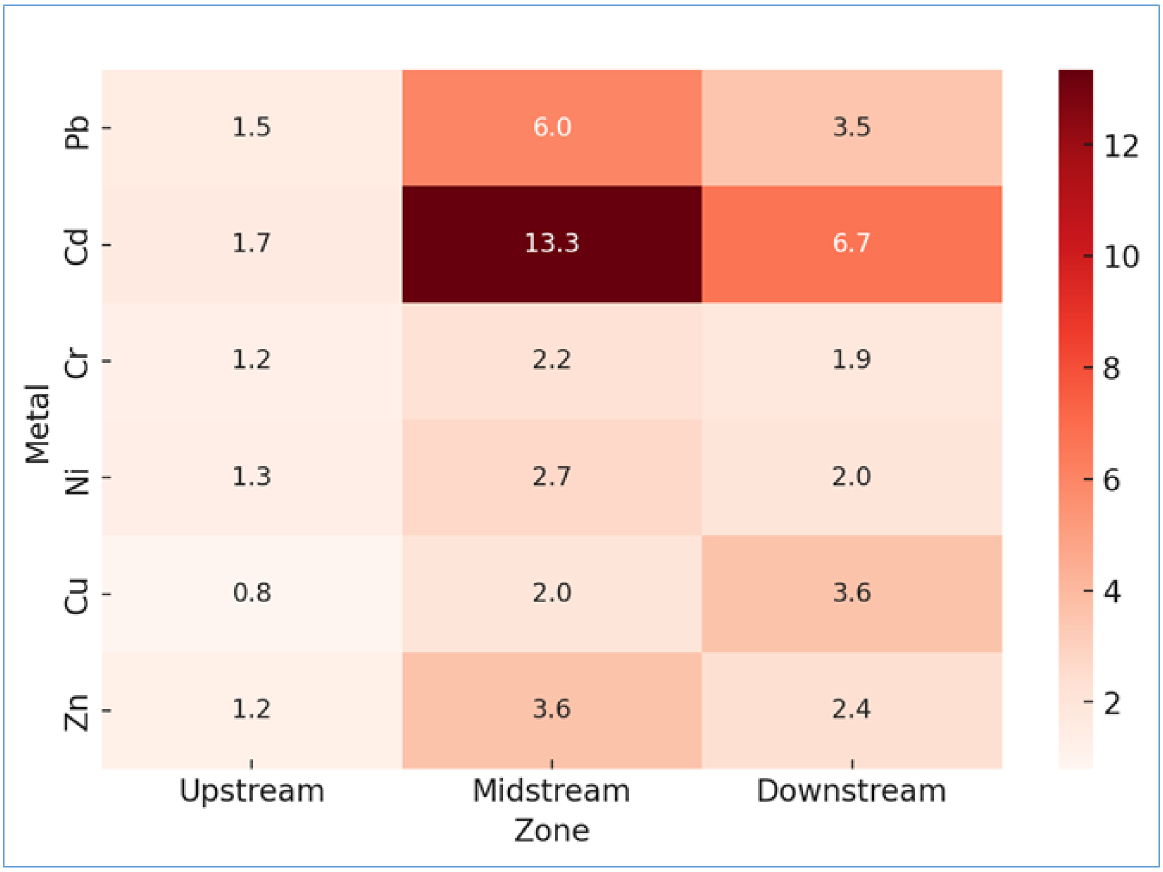

Figure 3. Fold Enrichment of Trace Metals in Sediments Relative to Regional Background Levels

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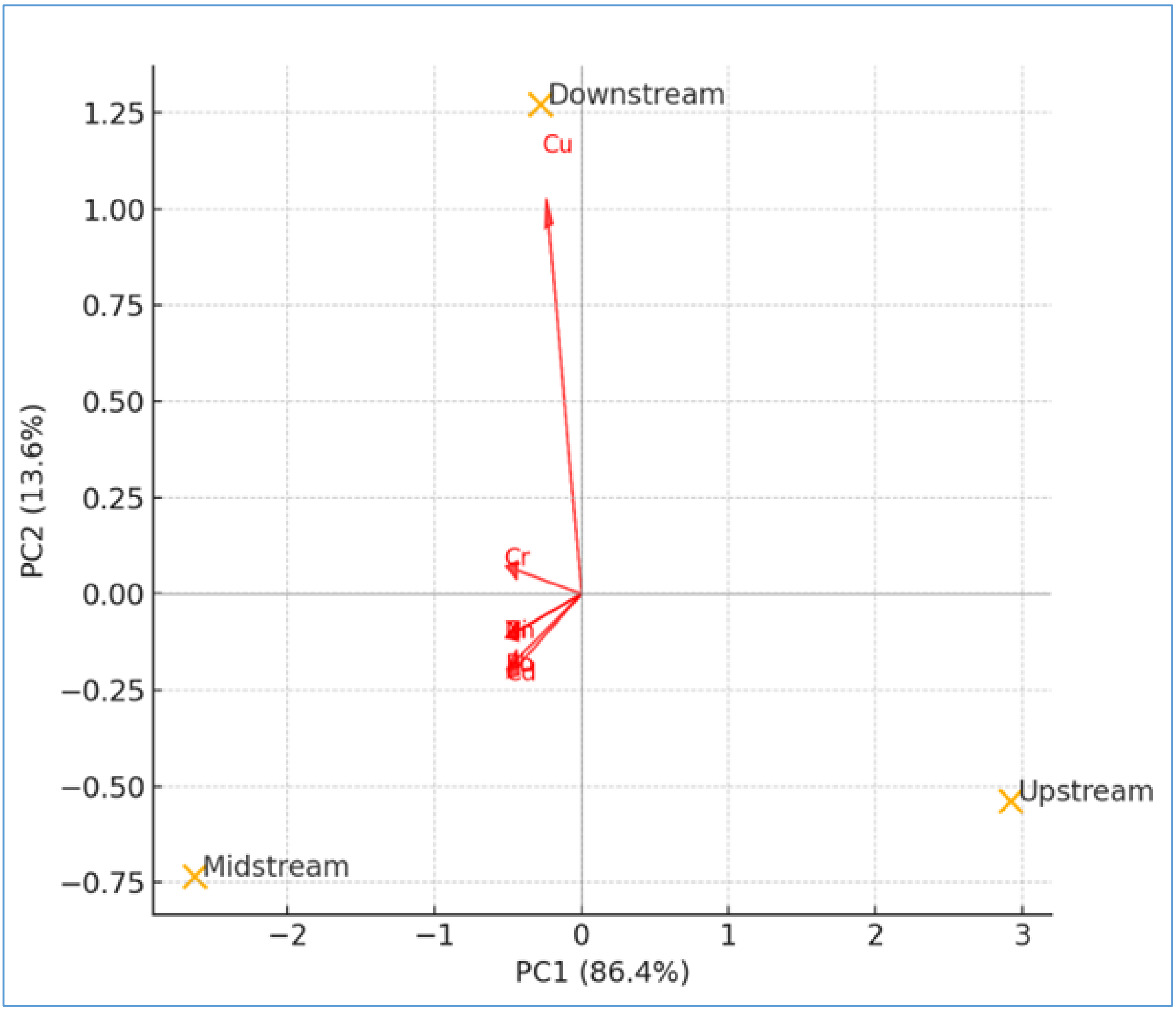

Figure 4. PCA Biplot of Trace Metal Concentrations and Sampling Zones in the Gharakahriz River

Principal Component Analysis (PCA) biplot showing the relationship between sampling zones (upstream, midstream, downstream) and trace metal concentrations (Pb, Cd, Cr, Ni, Cu, Zn). The plot is based on zone mean values and explains 86.4% of total variance along PC1 and 13.6% along PC2. Arrows represent the loading vectors of metals; their direction and length indicate correlation strength and contribution to principal components. The positions of sampling zones reflect their metal composition profile. Note: Midstream samples are strongly associated with Pb, Cd, and Cr, while downstream is dominated by Cu. Fig. 4 presents a PCA biplot illustrating the spatial distribution of trace metal contamination across the Gharakahriz River. The first principal component (PC1, 86.4%) separates upstream from midstream sites, with the latter strongly associated with industrial pollutants such as Pb, Cd, and Cr. The second component (PC2, 13.6%) distinguishes downstream sediments, which are enriched in Cu, likely due to domestic wastewater inputs. This multivariate analysis confirms that pollution sources are spatially distinct, with industrial activity dominating the midstream zone and urban runoff influencing the downstream reach.

Dendrogram illustrating the hierarchical clustering of sampling zones (upstream, midstream, downstream) based on trace metal concentrations. The vertical axis represents the distance (Euclidean) between clusters, with higher values indicating greater dissimilarity. The dendrogram reveals three distinct clusters: upstream forms a separate cluster, while midstream and downstream merge at a lower distance threshold, suggesting shared pollution characteristics despite differing dominant sources. Fig. 5 presents the hierarchical clustering dendrogram of the three sampling zones based on their trace metal profiles. The upstream zone forms a distinct cluster, reflecting its low contamination levels and natural background conditions. In contrast, midstream and downstream zones cluster together at a moderate linkage distance, indicating shared pollution signatures despite different primary sources. This result supports the PCA findings and underscores the need for

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integrated management strategies in the middle-to-lower reaches of the river.

Fig. 6 illustrates the ecological risk contribution of individual trace metals across the three zones. The midstream zone exhibits the highest PERI value (500), classified as "very high ecological risk," with cadmium (Cd) contributing over 80% of the total risk due to its high toxicity and elevated concentration. In contrast, the upstream zone shows minimal risk (PERI = 100), while the downstream zone remains at a moderate-to-high risk level (PERI = 300), primarily driven by Cd and Pb. These findings highlight the critical role of Cd in shaping the environmental hazard profile of the Gharakahriz River system.

In Fig. 7 stacked bar chart showing the percentage distribution of trace metals across three operationally defined fractions: exchangeable + carbonate (light blue), Fe-Mn oxide/organic (orange), and residual (brown). Data represent mean values from midstream sediments (highest contamination zone). The exchangeable + carbonate fraction accounts for 25–30% of Cd and Pb, indicating high bioavailability and environmental mobility. In contrast, Cr and Ni are predominantly bound to Fe-Mn oxides and organic matter, suggesting moderate risk under changing redox conditions. The residual fraction is minor (<15%) for all metals, confirming anthropogenic origin and limited natural buffering capacity.

The spatial distribution of trace metal concentrations along the Gharakahriz River reveals clear longitudinal differentiation driven primarily by anthropogenic pressures. Midstream sediments, located downstream of the Arak petrochemical complex and intensively cultivated fields, exhibited the highest enrichment of Pb, Cd, and Zn, with concentrations exceeding background levels by factors of 6, 13, and 3.6, respectively. In contrast, upstream sediments closely matched natural background levels, confirming minimal anthropogenic input. This distinction between anthropogenically impacted and near-pristine zones echoes findings from the Konaro area in southeastern Iran, where the absence of urbanization and intensive agriculture resulted in groundwater trace metal concentrations well below permissible limits and classified as low-to-moderate pollution (Ghiasi et al., 2025). The downstream zone showed moderate but still elevated contamination, notably with Cu, consistent with contributions from domestic wastewater and plumbing material corrosion. When compared with regional and international baseline values (Abdi et al., 2021)UNEP; USGS), the degree of contamination in the midstream zone is severe.

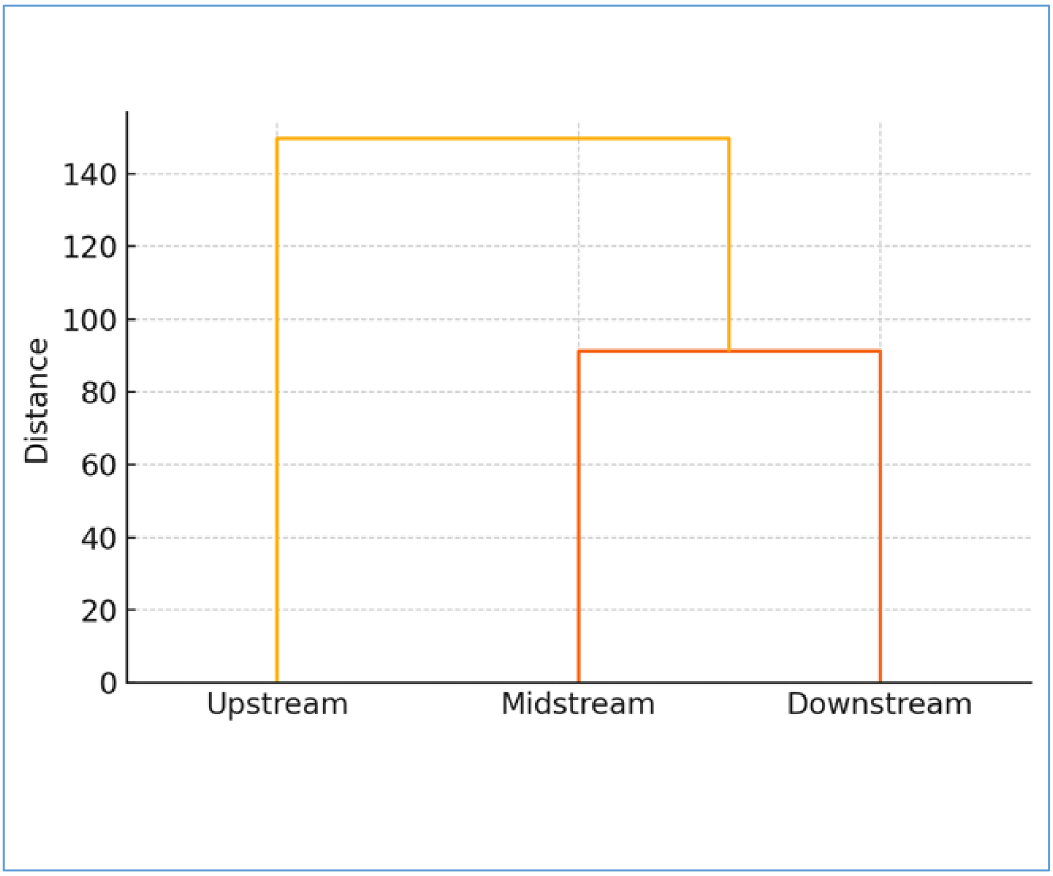

Figure 5. Hierarchical Clustering Dendrogram of Sampling Zones Based on Trace Metal Concentrations

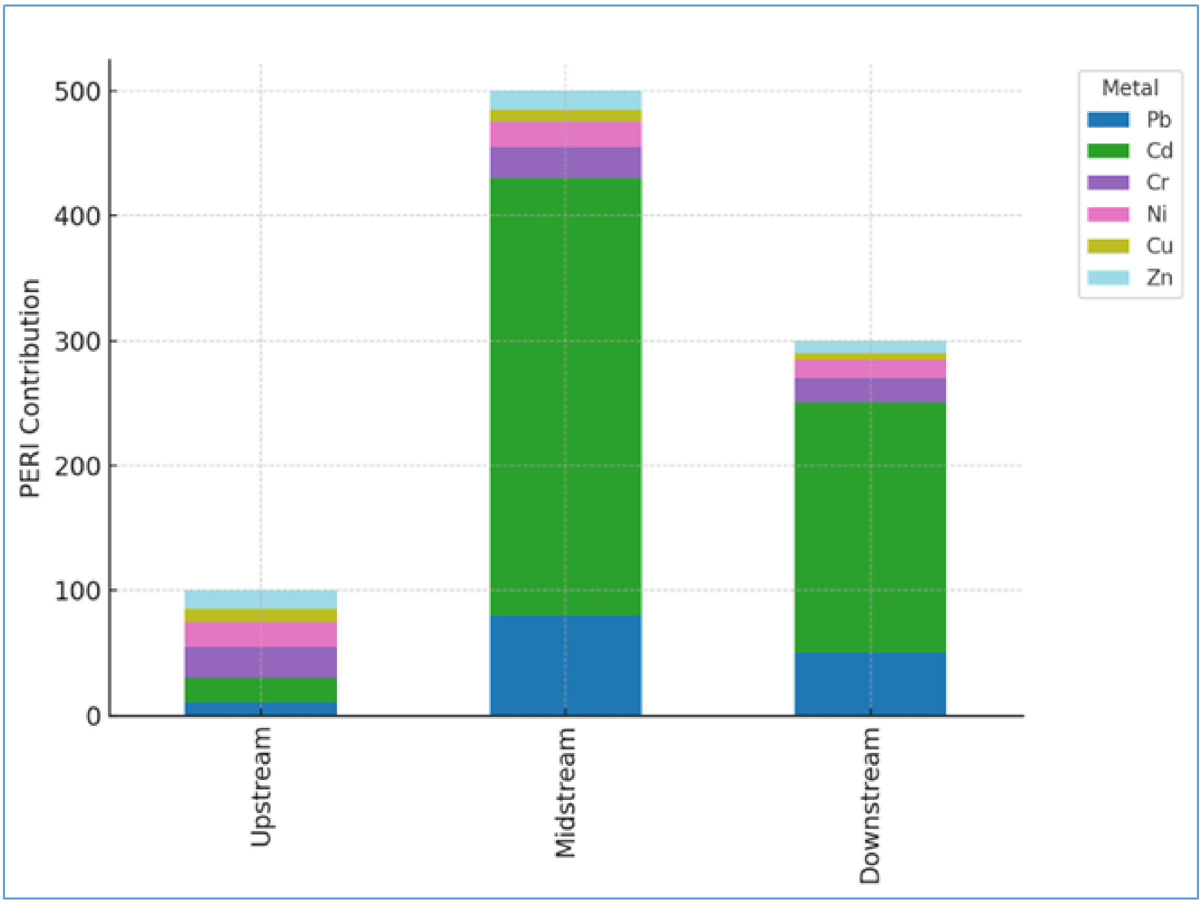

Figure 6. Ecological Risk Contribution of Trace Metals in Sediments Across Zones

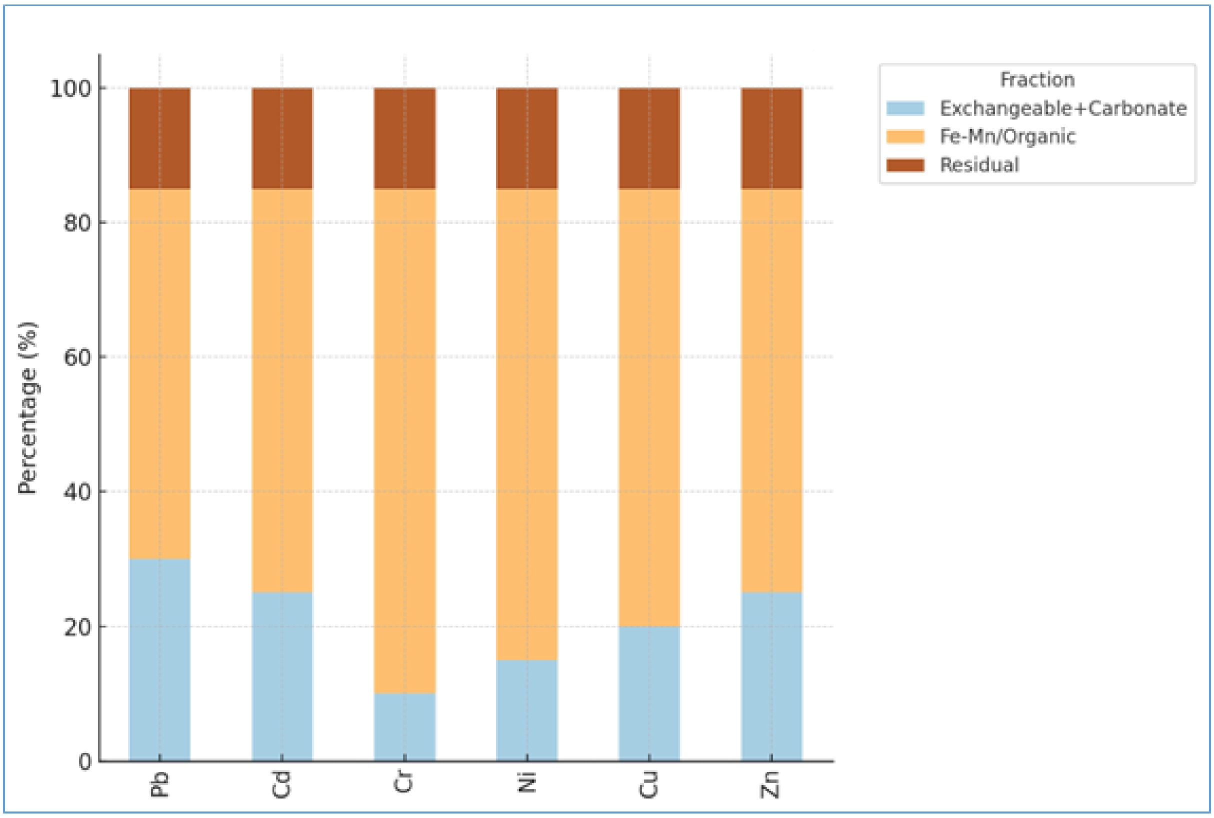

Figure 7. Chemical Fractionation of Trace Metals in Sediments and Implications for Bioavailability

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Cd concentrations in particular surpass sediment quality guidelines by more than an order of magnitude, positioning this metal as the most critical pollutant in the system. Such elevated Cd and Pb levels are characteristic of industrial discharge and phosphate fertilizer application, corroborating the land-use profile of the midstream reach.

The novelty of this study lies not in reporting high PTE levels—which are expected near industrial zones—but in revealing that ephemeral rivers in semi-arid basins generate a unique risk signature: extreme ecological risk (PERI > 460) driven primarily by labile-phase dominance (>85% non-residual), despite moderate total concentrations.

Fractionation results further underscore the ecological significance of this contamination. Approximately 25–30% of Cd and Pb occur in the exchangeable and carbonate fractions, phases that are highly labile and readily mobilized by minor pH fluctuations or acid deposition. Zn, Ni, and Cr are predominantly bound to Fe–Mn oxides and organic matter (50–60%), suggesting potential remobilization under reducing or oxidizing conditions, such as those arising from seasonal flooding or drought. Only ~15% of total metals are contained in the residual fraction, underscoring limited geological buffering capacity and highlighting anthropogenic dominance of the observed metal burden. This low residual fraction contrasts with natural polymetallic systems like Chah-Shaljami, where sulfide mineralization contributes to elevated but geogenic metal signatures—emphasizing that the Gharakahriz's metal burden is overwhelmingly anthropogenic rather than lithogenic (Ghiasi et al., 2025). Pollution indices reinforce these conclusions. Geoaccumulation index (Igeo) values for Cd and Pb in the midstream sediments fall between 2.5–3.2, classifying them as moderately to heavily polluted. Enrichment factors (EF) for these metals exceeded 5, further indicating severe anthropogenic enrichment. The potential ecological risk index (PERI) reached values approaching 500 in midstream sediments, placing this zone within the "very high ecological risk" category (Håkanson, 1980). More than 70% of this risk is attributable to Cd, reflecting both its high toxicity coefficient and elevated bioavailability. Downstream sediments show a lower but still concerning PERI (~300), driven by residual Pb, Zn, and particularly Cu inputs, whereas upstream sediments remain at low risk (PERI < 100).

The multivariate statistical analyses provide robust evidence of pollution source differentiation. Principal component analysis (PCA) separated the dataset into two major components, explaining nearly 80% of variance. PC1 (65.3%) was dominated by Pb, Cd, and Cr, aligning with midstream sites and reflecting industrial inputs. PC2 (13.3%) was driven by Cu and Zn, which co-varied with downstream sites and point to mixed agricultural and domestic wastewater contributions. Pearson correlation analysis supported these associations, identifying statistically significant co-occurrence of Pb–Cd ($r = 0.74$, industrial), Zn–Cu ($r = 0.68$, agricultural/domestic), and Cr–Ni ($r = 0.61$, mixed lithogenic/industrial). However, the Cr–Ni association warrants caution: in tectonically active regions of Iran, such as the Arasbaran belt, Cr and Ni often originate from mafic–ultramafic volcanic rocks and associated mineral assemblages (e.g., hornblende, pyroxene), as documented in thermobarometric studies of Plio-Quaternary lavas (Ghiasi i et al., 2025). While our data suggest an anthropogenic signal dominates, a minor lithogenic contribution cannot be entirely ruled out without detailed mineralogical analysis. Hierarchical clustering further validated this structure, clearly grouping upstream, midstream, and downstream sites into three distinct clusters corresponding to their land-use and contamination profiles.

The integration of classical geochemical indices with advanced statistical analyses and fractionation data provides a coherent narrative: the Gharakahriz River is subject to a longitudinal pollution gradient dominated by industrial effluents in the midstream and agricultural/domestic inputs downstream. This pollution is not only elevated in magnitude but also characterized by high mobility and bioavailability, posing ecological and human health risks. Of particular concern is Cd, which combines high concentration, high bioavailability, and high toxicity, making it the primary target for management interventions.

From a management perspective, the findings suggest differentiated strategies are required along the river continuum. Upstream areas should be protected to preserve baseline conditions. Midstream sediments demand urgent interventions, including industrial pretreatment of effluents and regulation of phosphate fertilizer applications. Downstream areas, while less contaminated, require infrastructure upgrades such as improved sewage collection and the development of natural treatment systems (e.g., constructed wetlands), to mitigate diffuse urban and agricultural pollution. Without such measures, the bioavailable fraction of metals may enter aquatic food webs through irrigation and sediment resuspension, amplifying ecological risks. Overall, this study demonstrates the value of combining geochemical baselines, sequential extraction, pollution indices, and multivariate statistical analyses into a multi-layered risk assessment framework. The results not only diagnose the severity and sources of contamination but also translate into actionable recommendations for watershed-scale management. Future research should incorporate seasonal monitoring, sediment–water exchange dynamics, and

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ecotoxicological assessments of aquatic biota to further quantify the risks posed by trace metals in the Gharakahriz River.

From a geoconservation perspective, the Gharakahriz River basin represents a critically degraded fluvial system where anthropogenic contamination has compromised the geochemical integrity of its sedimentary heritage. Riverbed sediments—often overlooked as passive environmental media—are, in fact, dynamic archives of Earth's geodiversity, recording both natural processes and human impacts over time. In semi-arid regions like central Iran, seasonal rivers constitute unique geomorphological and sedimentological features that hold scientific, educational, and potential geotourism value. However, the severe enrichment of bioavailable Cd and Pb in midstream sediments not only poses ecological risks but also erodes the baseline geochemical character of this system, effectively diminishing its status as a natural heritage asset. The dominance of anthropogenic metal fractions (>85% in non-residual phases) indicates that the sedimentary record is being overwritten by industrial and agricultural signatures, masking its original geological narrative. This loss of geological authenticity directly contradicts the core principles of geoconservation, which emphasize the protection of Earth's abiotic heritage as a non-renewable scientific and educational resource. Protecting such fluvial systems requires reframing sediment management within a geoconservation framework—where preserving geochemical baseline conditions, preventing irreversible contamination, and maintaining sedimentological authenticity become explicit conservation goals alongside ecological and human health objectives.

Although sediment sampling was conducted within the active river channel, the high mobility of Cd and Pb—particularly their 25–30% presence in exchangeable and carbonate-bound fractions—implies a significant risk of off-site transfer to adjacent land surfaces during flood events or wind erosion. Given that the downstream plains of the Gharakahriz River support sparse but ecologically functional rangeland vegetation typical of Iran's central plateau, these bioavailable metals may infiltrate rangeland soils, alter soil microbial communities, reduce forage quality, and ultimately compromise rangeland productivity and resilience. This indirect linkage underscores the relevance of fluvial sediment quality to rangeland soil conservation in semi-arid watersheds.

The finding of very high ecological risk (PERI ≈ 500) dominated by Cd—despite the river's ephemeral nature—challenges the prevailing assumption that seasonal rivers inherently dilute or flush contaminants (Wang et al., 2021). In fact, our data demonstrate the opposite: prolonged dry phases in arid zones enhance sediment–water interaction, leading to disproportionate metal retention in labile phases. This aligns with Niu et al. (2021), who identified a global shift toward wastewater-driven metal enrichment in Asian dryland rivers post-2000, but critically extends it by showing that geochemical legacy—not just concentration—is being overwritten. Whereas Kachoueiyan et al. (2024) reported low ecological risk in Iran's Gomishan wetland due to dominant residual fractions, our study reveals >85% of PTEs in non-residual phases, signifying not merely contamination, but anthropogenic overprinting of the sedimentary archive—a concept central to contemporary geoconservation . The Gharakahriz case thus exemplifies a new risk paradigm: where the loss of geological authenticity becomes a measurable component of environmental degradation, demanding assessment frameworks that integrate ecotoxicity with geodiversity erosion

4. Conclusion

This study highlights that fluvial sediment contamination is not merely an aquatic issue but a critical threat to environmental soil health and sustainability in semi-arid basins, necessitating integrated environmental management approaches. This study provides a comprehensive assessment of trace metal contamination in riverbed sediments along the longitudinal profile of the Gharakahriz river, revealing a distinct spatial pollution gradient shaped by anthropogenic activities. The midstream zone — influenced by industrial discharges from the Arak Petrochemical Complex and intensive agricultural practices — emerged as the most severely contaminated segment, with Pb, Cd, and Zn concentrations exceeding regional background levels by up to 6-, 13-, and 3.6-fold, respectively. Cadmium, in particular, posed the greatest ecological threat, contributing over 70% of the total potential ecological risk (PERI ≈ 500) due to its high toxicity, elevated concentration, and significant bioavailability (25–30% in exchangeable + carbonate fractions). Downstream sediments, while moderately contaminated, exhibited elevated Cu levels, likely originating from domestic wastewater and corrosion of urban infrastructure, highlighting the growing impact of diffuse urban pollution. In contrast, upstream sediments closely mirrored natural geochemical baselines, confirming their role as a reference zone with minimal anthropogenic influence.

Multivariate statistical analyses robustly differentiated pollution sources: PC1 clearly associated Pb, Cd, and Cr with industrial inputs in the midstream, while PC2 linked Cu and Zn to agricultural and domestic sources downstream. Hierarchical clustering further validated this spatial structuring, grouping sampling sites into three distinct clusters aligned with land-use patterns. Critically,

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sequential extraction results revealed that the majority of metals (especially Cd and Pb) are bound in labile fractions, indicating high environmental mobility and potential for release under changing physicochemical conditions (e.g., pH shifts, redox fluctuations). With less than 15% of metals in the residual (geogenic) fraction, the anthropogenic origin of contamination is unequivocal — and its bioavailable nature poses tangible risks to aquatic ecosystems and potential entry into food chains via irrigation or sediment resuspension.

This study advances sediment risk assessment by demonstrating that ephemeral rivers in semi-arid industrial zones exhibit a distinct contamination regime: moderate total PTE concentrations coupled with exceptionally high ecological risk (RI up to 500), driven overwhelmingly by labile-phase dominance (>85% in non-residual fractions). This 'dryland risk signature' challenges the assumption that seasonal rivers inherently dilute contaminants, revealing instead that prolonged dry phases enhance metal retention in bioavailable forms. The convergence of EF, PCA, and PERI analyses robustly attributes contamination to anthropogenic sources — primarily industrial effluents and agrochemical runoff — with Cd emerging as the critical risk driver due to its disproportionate enrichment in exchangeable and carbonate fractions. Critically, this high-risk profile occurs without mining activity, positioning dryland industrial corridors as emerging hotspots comparable to legacy mining sites.

This study advances the field by demonstrating that sediment contamination in ephemeral rivers is not merely a pollution problem but a geoconservation crisis—where the loss of sedimentological authenticity constitutes an irreversible degradation of Earth's abiotic heritage. We provide the first evidence that industrial–agricultural interfaces in semi-arid basins generate a unique contamination signature: high Cd bioavailability coupled with low residual buffering, demanding recalibrated risk thresholds. More critically, we reframe watershed management as a dual mandate: ecological protection and geodiversity preservation. This paradigm shift offers a scalable template for dryland river basins globally facing industrial encroachment.

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Competing Interests

The authors declare that they have no competing interests.

Authors Contribution

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Maryam Sadeghi, Javad Varvani, Hamid Toranjzar, Abbas Ahmadi , Amir Hossein Baghaie. All authors read and approved the final manuscript.

Availability of data and materials

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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