

## Quantitative health risk assessment and multivariate source identification of heavy metals in a river-treatment Plant continuum

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### Abstract

**Background:** This study investigated the continuum of surface water contamination and treatment by quantitatively assessing human health risks and identifying sources of heavy metal pollution (Pb, Cd, Cu, and Zn) in the Ziarat River and the Naharkhoran Drinking Water Treatment Plant.

**Methods:** In this analytical study, 61 water samples were collected along the river course and from the inlet and outlet of the treatment plant. Heavy metal concentrations were determined using a 797 Metrohm polarograph. Human health risks for children and adults were evaluated using chronic daily intake (CDI), hazard quotient (HQ), hazard index (HI), and lifetime cancer risk (LCR). Multivariate statistical techniques, including correlation analysis and source apportionment, were applied to identify potential pollution sources.

**Results:** Heavy metal concentrations showed substantial spatial variability throughout the river-treatment system. The mean concentrations of lead and zinc at the treatment plant inlet were 0.170 and 0.65 mg/L, respectively, with high coefficients of variation (231% for Pb and 115% for Zn). Reductions in Pb, Cd, and Zn concentrations at the plant outlet were limited and statistically insignificant ( $p > 0.05$ ). Copper exhibited the greatest variability along the river continuum, indicating heterogeneous upstream inputs. Several samples exceeded WHO guideline values for lead by more than two orders of magnitude. The mean Hazard Index for children at the inlet ( $HI = 2.56$ ) exceeded the acceptable threshold, with lead accounting for 97.7% of the total non-carcinogenic risk. Cadmium-related lifetime cancer risks remained within acceptable limits. Overall, the treatment plant reduced health risk indices by approximately 80%. Multivariate analysis revealed a strong correlation between zinc and copper ( $r = 0.87$ ,  $p < 0.01$ ), suggesting common pollution hotspots and shared anthropogenic sources.

**Conclusion:** Despite partial risk mitigation by the treatment plant, persistent lead contamination along the river-treatment continuum poses significant non-carcinogenic health risks to children. Effective source-control strategies and continuous water quality monitoring are essential to protect vulnerable populations and ensure the safety of treated drinking water.

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### Highlights

#### What is current knowledge?

Heavy metal contamination in water resources is a global concern, primarily arising from anthropogenic sources. Pb and Cd are priority toxic metals because of their persistence and associated health risks. Risk assessment models (HI, LCR) and multivariate analyses are established tools. However, previous studies have mostly investigated rivers and WTPs separately, lacking an integrated continuum approach.

#### What is new here?

This study uniquely integrates a river-WTP continuum assessment. Key novelties include: (i) Pb exceeded WHO limits by  $>100\times$ , with insignificant removal by the WTP; (ii) children were at the highest risk ( $HI = 2.56$ , with Pb contributing 97.7%); (iii) a strong Zn-Cu correlation ( $r = 0.87$ ) indicated common sources; (iv) overall health risk was reduced by  $\sim 80\%$  despite poor metal removal; and (v) four-month sampling captured seasonal variability.

### Introduction

Water is essential for life. However, freshwater accounts for only 3% of the Earth's total water resources, and only 0.01% of this amount is readily accessible for human consumption (1). This limited freshwater

reserve is under considerable pressure from mining activities and anthropogenic factors, including rapid population growth, urbanization, mining operations, vehicle-related greenhouse gas emissions, and unsustainable agricultural and industrial practices (2). Consequently, toxic heavy metals enter aquatic systems through multiple pathways, including atmospheric deposition, weathering of different bedrock types, agricultural and urban runoff, industrial wastewater, and drainage waters (3). Once introduced, elevated concentrations of heavy metals contaminate both surface water and groundwater, thereby degrading water quality and adversely affecting aquatic biological systems as well as human health and well-being (4). Therefore, the impacts of these water pollutants must be systematically assessed, followed by appropriate measures to remediate contaminated waters. Metals occur naturally in the Earth's crust, and their compounds vary across geographical regions, resulting in spatial variations in background concentrations (5). Heavy metals are unique environmental contaminants because they cannot be transformed into non-toxic forms (6). Surface water pollution caused by groundwater discharge and surface runoff has long been recognized as a global concern (6). Heavy metals released into the environment enter the human body through three main routes: inhalation, ingestion, and dermal absorption. These exposures occur through contaminated air, water, and food, as well as through numerous synthetic chemicals and manufactured products (7). When heavy metal concentrations exceed permissible limits, they can induce toxicity (8). Heavy metals are non-biodegradable and may bioaccumulate in ecosystems to levels that threaten human health (9).

In addition to conventional water sources, water packaging materials have recently become major sources of contamination in bottled and bagged waters (8). Heavy metal contamination in drinking water and its associated health risks are critical considerations in the evaluation of drinking water quality (10,11). The entry of heavy metals into the human body through the aforementioned pathways can pose both carcinogenic and non-carcinogenic health risks (12). The chemical form of each metal plays a decisive role in its toxicity and bioaccumulation in humans. For example, the absorption rate of lead (Pb) through ingestion is approximately 15% for inorganic species, whereas it reaches up to 80% for organic species (13). Lead is highly toxic and may cause long-term health risks, including headaches, loss of appetite, congenital defects, intellectual disability, hypertension, lung cancer, and kidney damage (11). Cadmium (Cd) is a recognized human carcinogen. Because of its preferential distribution to the kidneys and bones, cadmium can significantly impair the function of these organs (14).

Copper (Cu) and zinc (Zn) are essential trace elements for normal physiological functions in the human body. However, either deficiency or excess beyond the optimal level can cause substantial adverse health effects (14). Excessive copper intake can lead to nausea, vomiting, abdominal pain, and liver damage. In severe cases, copper may accumulate in the liver and brain, leading to cirrhosis and neurological disorders (15). Excessive zinc intake is associated with nausea, vomiting, and loss of appetite, and it interferes with copper absorption. Long-term, high-dose zinc consumption causes secondary copper deficiency and impairs immune system function (15,16). The potential health consequences of exposure to multiple pollutants in an ecosystem can be estimated by assessing their associated potential risks (17). Accordingly, numerous studies have used this approach to evaluate the potential health hazards of human exposure to contaminated water sources (17,18). Health risk assessment is recognized as an effective tool for quantifying the relationship between environmental quality and human health because it expresses risk levels quantitatively (18). Based on this established methodology, the present study evaluated the health risks associated with exposure to heavy metals, specifically lead (Pb) and cadmium (Cd), through drinking water sourced from the Ziarat River and the Nahar Khoran Water Treatment Plant in Gorgan, Iran.

## Methods

### Study Area and Sampling

In this study, 61 water samples were collected, including 37 samples from the Ziarat River and 24 samples from the inlet and outlet of the Naharkhoran water treatment plant in Gorgan. Sampling from the Ziarat River was conducted at four main stations: (1) 200 meters upstream of Naharkhoran Square, (2) within the Naharkhoran Square area, (3) the urban district, and (4) the Estarabadi area. Sampling was performed during four selected months, namely Bahman, Esfand, Ordibehesht, and Khordad, corresponding to the winter (January-March) and spring (April-June) seasons.

Samples were collected in sterile polyethylene containers that had been pre-washed with a 10% nitric acid solution before sampling.

Following acid digestion, during which 1 mL of concentrated nitric acid was added to 5 mL of each water sample and mixed thoroughly, heavy metal concentrations were measured using a Metrohm model 797 polarograph (Metrohm, Switzerland). Acid digestion was performed to remove organic impurities and prevent interference during the heavy metal measurement process.

### Statistical Analysis

Statistical analyses were performed using SPSS software (Version 20.0). Since the heavy metal concentrations exhibited a non-normal distribution, the associations between metal concentrations and the calculated indices were evaluated using Spearman's rank correlation coefficient (*r*). Correlation coefficients from -1 to +1, where values approaching ±1 indicate strong positive or negative associations and values near zero suggest the absence of a significant relationship. Absolute correlation coefficients (*|r|*) > 0.70 were interpreted as strong, whereas values between 0.50 and 0.70 were considered moderate. Subsequently, Principal Component Analysis (PCA) was applied to reduce data dimensionality, multivariate relationships among heavy

metals, and identify potential contamination sources by extracting orthogonal components that account for the majority of the dataset's variance.

### Human Health Risk Assessment

Health risk assessment was categorized into carcinogenic and non-carcinogenic hazards, both defined according to the probability of adverse effects of each pollutant over a lifetime. This assessment estimates potential health risks from exposure by calculating the likelihood of adverse effects on the human body (19).

### Exposure Assessment

To evaluate non-carcinogenic and carcinogenic risks for children and adults, chronic daily intake (CDI), representing the lifetime average daily dose (LADD) of a contaminant, was calculated (20). CDI via oral ingestion was computed using Equation [1]:

$$CDI = \frac{C \cdot IR \cdot EF \cdot ED}{BW \cdot AT} \quad [1]$$

where:

- CDI = chronic daily intake (mg/kg/day)
- C = contaminant concentration in water sample (mg/L)
- IR = ingestion rate (1 L/day for children, 2.2 L/day for adults) (20)
- EF = exposure frequency (365 days/year)
- ED = exposure duration (6 years for children, 30 years for adults)
- BW = body weight (15 kg for children, 70 kg for adults)
- AT = averaging time (For carcinogens: 70 years × 365 days = 25550 days; for non-carcinogens: ED × 365 days; i.e., 2190 days for children and 10950 days for adults) (20).

The other variables used to estimate human health risk through various pathways are summarized in Table 1.

**Table 1.** Parameters used to estimate exposure to heavy metals in drinking water (20,21)

| Parameter                  | Reference Value            | Unit                     |
|----------------------------|----------------------------|--------------------------|
| C (Metal Concentration)    | -                          | mg/L                     |
| IR (Ingestion Rate)        | Children = 1; Adults = 2.2 | L/day                    |
| EF (Exposure Frequency)    | 365                        | days/year                |
| ED (Exposure Duration)     | Children: 6; Adults: 30    | years                    |
| BW (Body Weight)           | Children: 15; Adults: 70   | kg                       |
| AT (Averaging Time, Adult) | 10950                      | days                     |
| AT (Averaging Time, Child) | 2190                       | days                     |
| Oral Reference Dose (Cd)   | 0.0005                     | mg/kg/day                |
| Oral Reference Dose (Pb)   | 0.0003                     | mg/kg/day                |
| Cancer Slope Factor (Pb)   | 0.0085                     | (mg/kg/day) <sup>1</sup> |
| Cancer Slope Factor (Cd)   | 6.3                        | (mg/kg/day) <sup>1</sup> |

### Non-Carcinogenic Risks

Non-carcinogenic risks from heavy metals in drinking water were calculated using the hazard quotient (HQ), based on Equation [2]:

$$HQ = \frac{CDI}{RfD} \quad [2]$$

where:

- HQ = Non-Cancer Hazard Quotient
- CDI = Chronic Daily Intake (mg/kg/day)
- RfD = Chronic Oral Reference Dose, defined as an estimate of a daily exposure level unlikely to cause adverse effects, even in sensitive subgroups (22).

The cumulative potential health risk from exposure to multiple heavy metals was expressed as the hazard index (HI), calculated by summing all individual HQ values (20). HQ or HI values less than 1 indicate no significant non-carcinogenic risk, whereas values equal to or greater than 1 suggest a significant risk that increases as the value rises (23).

### Carcinogenic Risk

Cancer risk is defined as the probability of developing cancer over a 70-year lifetime from continuous exposure to a carcinogenic contaminant at an average daily dose of 1 mg/kg body weight. Lifetime incremental cancer risk (ILCR) quantifies this risk as the increased likelihood of cancer due to continuous exposure (24). Carcinogenic risk was calculated by multiplying CDI by the cancer slope factor (CSF) (mg/kg/day)<sup>-1</sup>, as shown in Equation [3]:

$$\text{ILCR} = \text{CDI} \times \text{CSF} \quad [3]$$

where:

- ILCR = incremental lifetime cancer risk
- CDI = chronic daily intake (mg/kg/day)
- CSF = cancer slope factor (mg/kg/day)<sup>-1</sup>.

The total carcinogenic risk from multiple pollutants in a single water source was equal to the sum of all individual ILCRs ( $\Sigma\text{ILCR}$ ). The United States Environmental Protection Agency (USEPA) considers the acceptable cancer risk range for regulatory goals to be between  $1 \times 10^{-6}$  and  $1 \times 10^{-4}$  (20).

### Results

Table 2 presents the descriptive statistics of four heavy metals, namely cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn), in water samples from the Ziarat River and the Naharkhoran water treatment plant. The highest concentrations followed the order  $\text{Zn} < \text{Cu} < \text{Pb} < \text{Cd}$ . According to the calculated coefficients of variation (CV), metal concentrations in the water showed low variability. The largest standard deviations were observed for Zn and Cu, whereas Cd showed the lowest standard deviation. Notably, the maximum Pb concentration in some Ziarat River water samples greatly exceeded the World Health Organization guideline limit of 0.01 mg/L, which is concerning. Although the mean Cd concentration was below the permissible limit (0.003 mg/L), certain samples, such as one from the treatment plant inlet, exceeded the limit, reaching 0.0037 mg/L (25).

A CV greater than 30% indicates high data dispersion, and a CV above 100% reflects very high variability in metal concentrations. The highest variability was observed for Cu in river samples (CV = 283.6%), and the elevated variability for Pb in treatment plant samples (CV ≈ 232%) highlights considerable spatial and temporal fluctuations in these metals' concentrations.

Spearman correlation analysis (Table 3) was used to assess relationships among heavy metal concentrations. The results showed a highly significant positive correlation between Zn and Cu ( $r = 0.87$ ,  $p < 0.01$ ), significant negative correlations between Zn and Pb ( $r = -0.42$ ,  $p < 0.05$ ) and between Cu and Pb ( $r = -0.35$ ,  $p < 0.05$ ), and no significant correlations between Cd and the other metals.

**Table 3.** Spearman's rank correlation matrix of heavy metal concentrations

| Parameter | Zn     | Cd   | Pb     | Cu   |
|-----------|--------|------|--------|------|
| Zn        | 1.00   | -    | -      | -    |
| Cd        | 0.15   | 1.00 | -      | -    |
| Pb        | -0.42* | 0.08 | 1.00   | -    |
| Cu        | 0.87** | 0.22 | -0.35* | 1.00 |

\*Significant at  $p < 0.05$ ; \*\*Significant at  $p < 0.01$

Principal component analysis (PCA) was applied to characterize the data structure and identify potential pollution sources. Table 4 presents the PCA results for heavy metals in the study samples. Component 1 explained 55.25% of the total variance and was strongly correlated with Zn (0.94) and Cu (0.91). Component 2 explained 29.5% of the total variance and was significantly associated with Cd (0.89) and Pb (0.86).

**Table 4.** Principal Component Analysis (PCA) results for heavy metals

| Index                   | Component 1 | Component 2 | Component 3 |
|-------------------------|-------------|-------------|-------------|
| Eigenvalue              | 2.21        | 1.18        | 0.48        |
| Variance (%)            | 55.25       | 29.50       | 12.00       |
| Cumulative Variance (%) | 55.25       | 84.75       | 96.75       |
| Factor Loadings         |             |             |             |
| Zn                      | 0.94        | -0.18       | 0.12        |
| Cd                      | 0.28        | 0.89        | 0.23        |
| Pb                      | -0.35       | 0.86        | -0.29       |
| Cu                      | 0.91        | 0.24        | 0.18        |

Non-carcinogenic risk assessment results for adults and children, including chronic daily intake (CDI), hazard quotient (HQ), and hazard index (HI), are shown in Tables 5 and 6. The data clearly indicate that children are at considerable risk.

Human health risk quantification for exposure to heavy metals in water sources followed the USEPA protocol. CDI values represent the estimated average daily intake (mg/kg body weight) of contaminants over the exposure period. The highest CDI was observed for Pb in children from treatment plant inlet samples (0.009 mg/kg-day), warranting heightened public health attention.

Using the computed CDI values, the corresponding HQ and cumulative HI were calculated for each metal and for their combined effects. The results indicate that only children exposed at the treatment plant inlet exceeded the safety threshold, with an HI of 2.56 ( $>1$ ). Analysis of the contribution of each metal showed that Pb accounted for 97.9% of the non-carcinogenic risk in this group. The highest HQ was calculated for Pb in children (HQ = 2.5), indicating the potential for adverse health effects under prolonged exposure, as shown in Table 6.

Lifetime carcinogenic risk (LCR) for Cd, based on its carcinogenic slope factor, remained within the acceptable USEPA range ( $\text{LCR} < 10^{-4}$ ) across all groups. The highest LCR value was observed in children at the treatment plant inlet ( $1.8 \times 10^{-5}$ ). Evaluation of treatment plant efficiency revealed a significant 80% decrease in the total hazard index at the outlet compared with the inlet, primarily attributed to a 75% reduction in Pb concentration. However, some river samples contained concerning Pb levels (Maximum 1.09 mg/L), highlighting the need for upstream pollution control and continuous surface water quality monitoring, as shown in Table 7.

Cumulative heavy metal health risk assessments based on USEPA protocols confirmed Pb as the principal risk contributor across all populations. Specifically, Pb contributed 97.9% and 97.1% of the health risk for children and adults, respectively, in treatment plant inlet samples. Treatment processes substantially reduced overall health risk, with an 80.5% decrease in HI for children, mainly attributable to effective Pb removal at the treatment plant outlet.

**Table 2.** Descriptive statistics of heavy metal concentrations (mg/L) in different sampling locations

| Parameter | Sampling Location      | n  | Zn          | Cd              | Pb            | Cu          |
|-----------|------------------------|----|-------------|-----------------|---------------|-------------|
| Mean ± SD | Treatment Plant Inlet  | 12 | 0.65 ± 0.75 | 0.0006 ± 0.0013 | 0.170 ± 0.394 | 0.18 ± 0.16 |
| Mean ± SD | Treatment Plant Outlet | 12 | 0.36 ± 0.31 | 0.0005 ± 0.0009 | 0.043 ± 0.100 | 0.22 ± 0.27 |
| Mean ± SD | River                  | 37 | 0.96 ± 1.55 | 0.0003 ± 0.0006 | 0.159 ± 0.241 | 0.55 ± 1.56 |
| CV (%)    | Treatment Plant Inlet  | 12 | 115.4       | 216.7           | 231.8         | 88.9        |
| CV (%)    | Treatment Plant Outlet | 12 | 86.1        | 180.0           | 232.6         | 122.7       |
| CV (%)    | River                  | 37 | 161.5       | 200.0           | 151.6         | 283.6       |

**Table 5.** CDI values (mg/kg-day) for heavy metals

| Sample Group           | Population | Zn      | Cd      | Pb      | Cu      |
|------------------------|------------|---------|---------|---------|---------|
| Treatment Plant Inlet  | Adults     | 3.2E-04 | 4.1E-07 | 1.2E-03 | 1.7E-04 |
| Treatment Plant Inlet  | Children   | 2.4E-03 | 3.0E-06 | 9.0E-03 | 1.3E-03 |
| Treatment Plant Outlet | Adults     | 3.6E-04 | 2.8E-07 | 1.9E-04 | 5.8E-04 |
| Treatment Plant Outlet | Children   | 2.7E-03 | 2.1E-06 | 1.4E-03 | 4.3E-03 |
| River                  | Adults     | 8.2E-04 | 1.2E-07 | 2.5E-04 | 6.2E-04 |
| River                  | Children   | 6.1E-03 | 9.0E-07 | 1.9E-03 | 4.6E-03 |

**Table 6.** Hazard quotient (HQ) values and final health risk indices\*

| Sample Group           | Population | HQ (Zn) | HQ (Cd) | HQ (Pb) | HQ (Cu) | HI   | LCR (Cd) |
|------------------------|------------|---------|---------|---------|---------|------|----------|
| Treatment Plant Inlet  | Adults     | 1.1E-03 | 8.2E-04 | 3.4E-01 | 4.3E-03 | 0.35 | 6.1E-06  |
| Treatment Plant Inlet  | Children   | 8.0E-03 | 6.0E-03 | 2.5E+00 | 3.2E-02 | 2.56 | 1.8E-05  |
| Treatment Plant Outlet | Adults     | 1.2E-03 | 5.6E-04 | 5.3E-02 | 1.5E-02 | 0.18 | 4.5E-06  |
| Treatment Plant Outlet | Children   | 9.0E-03 | 4.2E-03 | 3.9E-01 | 1.1E-01 | 0.50 | 1.3E-05  |
| River                  | Adults     | 2.7E-03 | 2.4E-04 | 6.9E-02 | 1.6E-02 | 0.10 | 2.0E-06  |
| River                  | Children   | 2.0E-02 | 1.8E-03 | 5.2E-01 | 1.2E-01 | 0.65 | 5.5E-06  |

\* HQ, HI, and LCR values represent the calculated health risk indices.

**Table 7.** Cumulative health risk indices in water samples

| Sample Group           | Population | HI   | LCR     | Pb Contribution to HI (%) | Risk Assessment | Treatment Efficiency (%) |
|------------------------|------------|------|---------|---------------------------|-----------------|--------------------------|
| Treatment Plant Inlet  | Adults     | 0.35 | 6.1E-06 | 97.1                      | Acceptable      | -                        |
| Treatment Plant Inlet  | Children   | 2.56 | 1.8E-05 | 97.7                      | Unacceptable    | -                        |
| Treatment Plant Outlet | Adults     | 0.18 | 4.5E-06 | 29.4                      | Acceptable      | 48.6                     |
| Treatment Plant Outlet | Children   | 0.50 | 1.3E-05 | 78.0                      | Acceptable      | 80.5                     |
| Ziarat River           | Adults     | 0.10 | 2.0E-06 | 69.0                      | Acceptable      | -                        |
| Ziarat River           | Children   | 0.65 | 5.5E-06 | 80.0                      | Acceptable      | -                        |

## Discussion

According to the results presented in Table 2, the mean concentrations of Zn and Cu in Ziarat River samples were significantly higher than those at the inlet and outlet points of the Naharkhoran treatment plant. This elevation is likely attributable to wastewater discharge, urban runoff, and erosion of geological formations. Similar patterns have been documented in comparable river studies; for instance, Islam et al. observed increased Zn and Cu concentrations at locations affected by anthropogenic activities (26). The high variability of these two metals in the river, reflected by elevated coefficients of variation (CV) (Cu = 283%, Zn = 161%), indicates unstable, point-source inputs, consistent with Varol's characterization of river systems under fluctuating pollutant pressures (27).

Cd concentrations were generally low and close to detection limits across all sites, although high CV values (Up to 216%) suggest that even low Cd levels may be influenced by diffuse or episodic inputs, a pattern confirmed in surface water by Ali et al. (28). Pb also exhibited very high CVs (152-233%) at all sampling points, indicating unstable behavior and event-dependent inputs such as wastewater discharges or industrial effluent infiltration (29). Overall, the differences between mean values and CVs across the three sampling sites indicate the dominant influence of anthropogenic pollution sources on the Ziarat River and the relative inefficiency of the treatment plant in removing certain metals, particularly Cu and Pb. These observations are consistent with global evidence regarding the variable behavior of heavy metals in fluvial environments.

Correlation analysis revealed a strong positive association between Zn and Cu ( $\rho = 0.87$ ), suggesting a common source and similar transport mechanisms in the Ziarat River environment, a phenomenon commonly reported in rivers affected by urban and industrial wastewater (27).

Conversely, the negative correlation of Pb with Zn and Cu ( $\rho \approx -0.4$ ) indicates different sources and point inputs of Pb, a pattern observed in many heavy metal-polluted rivers (30). Principal component analysis (PCA) results (Table 4) support these findings: the first component, accounting for 55.25% of the variance, loaded heavily on Zn (0.94) and Cu (0.91), indicating a shared dominant source, likely wastewater or contaminated surface runoff; the second component, explaining 29.5% of the variance, loaded strongly on Cd (0.89) and Pb (0.86), reflecting distinct sources and independent geochemical behaviors of these two metals (31). This behavioral segregation suggests that Pb and Cd are subject to different processes, such as sediment adsorption-desorption or heterogeneous anthropogenic inputs (31).

Regarding health risk analysis from ingestion of heavy metals in drinking water, the data in Table 5 show that chronic daily intake (CDI) levels for children at all sites were 8 to 10 times higher than those for adults. This disparity is attributable to children's higher consumption relative to body weight and greater sensitivity to metal absorption, consistent with population studies (20). Pb exhibited the highest CDI among metals at both the treatment plant inlet and river sampling sites, reflecting continuous and point-source pollution as well as the limited efficiency of traditional slow sand filtration in Pb removal. This pattern aligns with previous findings on Pb persistence and the limitations of conventional treatment methods (32).

The reduction in Cd CDI at the treatment plant outlet indicates relative removal, although increased Cu concentrations after treatment may result from one or a combination of the following mechanisms: (1) desorption or leaching from the sand filter media or oxide-carbonate coatings that release adsorbed metals over time; and (2) physicochemical changes inside the filter, such as dissolved organic carbon (DOC), pH shifts, and redox potential variations within the slow sand filtration system of the Naharkhoran plant (33).

Health hazard quotient (HQ) data (Table 6) indicate that non-carcinogenic metals posed minimal short-term risk to adults ( $HQ < 1$ ) in both inlet and outlet samples; however, children exhibited markedly higher HQ and hazard index (HI) values. Notably, children at the treatment plant inlet showed an HQ exceeding 2.5 for Pb, indicating a significant non-carcinogenic risk for sensitive groups (34). Our results are consistent with those of researchers such as Jaishankar et al., who identified Pb concentrations as the primary risk driver in many surface waters and the main contributor to HI (35). HQ values for Zn, Cd, and Cu were generally low, indicating lower toxicity at the measured concentrations, consistent with the findings of Jomova et al. (36).

Calculated carcinogenic risk (LCR) due to Cd for both age groups across all samples remained below  $10^{-4}$ , within internationally acceptable thresholds, mirroring similar surface water risk patterns reported globally (36). Comparisons among sampling points showed the highest HQ and HI values for children at the treatment plant inlet, suggesting increased pollutant concentrations along the river course toward the plant. The treatment process reduced pollutant concentrations downstream but did not achieve sufficient efficacy in removing heavy metals, especially Pb. This limitation confirms the restricted capacity of the Naharkhoran slow sand filtration system to remove heavy metals, echoing prior evaluations of treatment plant performance in Poland by Farhan et al. (37).

Quantitative health risk assessments of heavy metals in Ziarat River and treatment plant outlet water (Table 7) reveal clear vulnerability patterns in population dynamics and pollutant behavior. HI and lifetime carcinogenic risk (LCR) highlight significant age-related risk differences and underscore Pb's dominant contribution to overall risk. Children consistently demonstrated the highest risks, with a markedly elevated HI of 2.56 at the inlet, exceeding the safety threshold of 1 and falling within the “unacceptable” risk category, whereas adults' HI remained within “acceptable” limits at 0.35. This difference is attributable to established mechanisms, including proportionally higher water intake relative to body weight, increased metal absorption efficiency, and heightened neurological sensitivity during development (38). This finding aligns with global research showing children's increased susceptibility to heavy metal toxicity (39). Relative metal contributions indicate that Pb accounts for more than 97% of total HI at the treatment plant inlet. Given Pb's severe neurotoxicity and the absence of a safe exposure threshold for children, this finding represents a critical public health concern (40).

The decrease in Pb's contribution at the outlet (to 78%) and the 80.5% reduction in children's HI demonstrate that slow sand filtration, despite its low-pressure biological nature, can partially reduce heavy metal loads, likely through mechanisms such as surface adsorption to biofilms, trapping by filtration media, and turbidity reduction. However, Pb removal efficiency (~49% in adults) remains inferior to advanced treatments such as activated carbon adsorption or nanofiltration, consistent with previous studies on the limitations of slow sand filters (41). HI values for children in the Ziarat River remained elevated (0.65) compared with those for adults (0.10), although both were classified as “acceptable,” indicating that part of the Pb load at the treatment inlet likely originates from riverine sources and additional point and non-point upstream contamination.

LCR values ranged between  $10^{-5}$  and  $10^{-6}$ , falling within EPA's “acceptable” to “relatively acceptable” classifications, but they remain non-negligible from a public health perspective. An LCR of  $1.8 \times 10^{-6}$  for children corresponds to roughly 18 additional cancer cases per million individuals. Since Pb is classified as a probable human carcinogen (IARC group 2A), most LCR can be attributed to this metal (42). The spatial reduction in risk from inlet to outlet reflects the combined roles of natural attenuation processes, including sedimentation, dilution, and particulate adsorption, and the efficiency of slow sand filtration in reducing Pb pollution. Nevertheless, the presence of Pb in the riverine environment suggests that sediment beds act as active reservoirs recharged by upstream pollutant sources (5).

## Conclusion

This study provides compelling evidence that children are the most vulnerable group to Pb exposure in this setting and highlights the limited capacity of slow sand filtration to remove heavy metals. Given the intensification of pollution hotspots upstream and along the Ziarat River,

this treatment approach cannot serve as a long-term strategy for controlling heavy metal contamination, particularly Pb. Effective management requires source identification and control, enhanced treatment technologies, and continuous biomonitoring focused on sensitive groups, particularly children.

The integrated quantitative assessment provided in this study characterizes heavy metal pollution and its health implications in the Ziarat River, the main water source for the Naharkhoran plant, and evaluates plant performance. The key findings identify Pb as the primary pollutant, contributing more than 97% of the non-carcinogenic risk index at the intake. This dominant source reflects a concentrated pollution origin along the river, directing mitigation efforts toward reducing Pb load inputs. Children's vulnerability is quantitatively demonstrated by an HI of 2.56 at the primary pollution point, clearly exceeding safety thresholds and emphasizing the need to incorporate age-specific exposure factors into standard risk assessments.

Although downstream reductions in metal concentrations and risk indices suggest natural attenuation processes, these processes are inherently unpredictable and potentially reversible. Therefore, reliance on self-purification or the current treatment system cannot replace preventive and control strategies at the source. Although lifetime carcinogenic risk levels remain acceptable, they are significant at the population level and warrant a precautionary approach.

## Study Limitations and Future Directions

This risk assessment was based on total metal concentrations in water. Future studies should focus on bioavailability and chemical speciation, particularly for Pb, along with isotopic analysis to precisely trace and differentiate natural and anthropogenic sources. Comprehensive assessments should also consider complementary exposure pathways, including dust, soil, and food, as well as the cumulative effects of pollutant mixtures.

## Policy Implications

This study explicitly identifies the health risk in the Ziarat River as largely driven by a single contaminant (Pb) and a specific demographic group (children). Such analytical precision supports a targeted, cost-effective management strategy that concentrates monitoring and technological resources on reducing upstream Pb loads, combined with active biological monitoring of vulnerable children. This approach not only enhances efficiency but also exemplifies evidence-based water quality management prioritized by health impact, serving as a replicable model for other watersheds facing similar challenges.

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## Ethical Statement

The Institutional Review Board of Golestan University of Medical Sciences approved the study protocol (IR.GOUMS.REC.1403.161).

## Conflicts of Interest

The authors declare no conflict of interest.

## Author Contributions

A.Z.: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data Curation, Writing – Original Draft, Writing – Review & Editing, Visualization, Supervision, Project Administration. Y.S.: Conceptualization, Methodology, Formal analysis, Investigation, Data Curation, Writing – Review & Editing. All authors read and approved the final revised manuscript.

## Data Availability Statement

The data supporting the findings of the present study are available from the corresponding author upon reasonable request.

## Use of Artificial Intelligence

During the preparation of this work, the authors did not use any generative artificial intelligence (AI) or AI-assisted technologies for content generation, data analysis, or manuscript writing. All content, including text, tables, figures, and analyses, was prepared and compiled by the authors. The authors take full responsibility for the content of the manuscript and confirm the accuracy and originality of all its components.

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