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Heavy Metal Contamination and Ecological Risk Assessment of River Birim under Illegal Artisanal Mining in Ghana

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Abstract

Illegal artisanal gold mining has emerged as a major environmental challenge in Ghana, with significant consequences for water resources. This study assessed contamination risks posed by heavy metals in water and sediments of the River Birim, a river system severely impacted by unregulated mining. A total of 60 samples, comprising 30 water samples and 30 sediment samples, were collected from five different sites along the river using appropriate standard procedures. The samples were then analysed for metals, including iron (Fe), manganese (Mn), nickel (Ni), cadmium (Cd), zinc (Zn), chromium (Cr), lead (Pb), and mercury (Hg), using atomic absorption spectrophotometry. Risk indices, such as the Potential Ecological Risk Index (PERI) and human health indices, including the hazard quotient (HQ), hazard index (HI), and TCGLR, were also employed. Sediment concentrations (mg/kg) followed the order Fe (8986.33) > Mn (425.90) > Ni (24.68) > Cd (17.67) > Zn (11.23) > Cr (2.50) > Pb (1.33) > Hg (0.50), while water concentrations (mg/L) ranked as Fe (5.36) > Cd (0.23) > Ni (0.08) > Zn = Hg (0.04) > Cr = Mn (0.03) > Pb (0.02). Concentrations of Cd, Fe, Pb, Hg, and Ni in water exceeded World Health Organisation (WHO) limits for potable water. Sediment quality indices indicated moderate to severe contamination by Hg and Cd, with cadmium alone contributing approximately 98% of the total ecological risk (PERI = 10,827.3). Non-carcinogenic risks were below the threshold of concern (HI < 1). However, carcinogenic risk assessments revealed that ingestion of Cd- and Ni-contaminated water and Cd-rich sediments exceeded permissible limits, suggesting potential long-term health implications. These findings highlight the urgent need for stricter environmental regulation, sustainable mining practices, and continuous monitoring to protect communities reliant on the River Birim.

Keyword: River Birim, Heavy metals, Galamsey, Ecological risk, River pollution, Sediment contamination, Ghana

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Introduction

Heavy metal contamination in freshwater systems is a global environmental and public health issue. Heavy metals are toxic, persistent, and capable of bio-accumulating in aquatic organisms, making them highly dangerous for ecosystems and humans alike. Once released, they persist for decades, travel across ecosystems, and magnify through food chains, thereby threatening biodiversity and human health (Meng et al., 2016). Exposure to heavy metals such as lead (Pb), cadmium (Cd), and mercury (Hg) has been associated with carcinogenicity, neurological disorders, kidney damage, and multi-organ toxicity in humans, as well as bioaccumulation in aquatic organisms that disrupts ecological balance (Sati et al., 2026; Gavrilescu et al., 2021). In aquatic ecosystems, these contaminants reduce species diversity, impair reproduction in fish and invertebrates, and alter trophic interactions, thereby degrading ecosystem functioning over time (Gadd & Griffiths, 1977; Gadd, 2023). This directly undermines access to safe, clean water, a core target of SDG 6. Due to their environmental persistence and tendency to bioaccumulate, heavy metals can produce significant cumulative ecological and health impacts even at low levels of contamination.

Globally, heavy metals originate from both natural and anthropogenic sources, including volcanic activity, rock weathering, industrial effluents, and mining operations (Kumar et al., 2017). In aquatic systems, sediments serve as both sinks and secondary sources of contaminants; changes in pH or hydrodynamics can remobilise trapped metals into the water column, increasing bioavailability and ecological risk (Sun et al., 2018). To mitigate these risks, a range of remediation technologies has been developed, including physicochemical approaches such as chemical precipitation, adsorption, ion exchange, membrane filtration, and dredging; however, these methods are often costly, energy-intensive, and may generate secondary pollutants (Ali et al., 2020; Foulquier et al., 2013). Emerging approaches in tropical river basins increasingly emphasise nature-based solutions such as phytoremediation and bioremediation, which use plants and microbial processes to remove, immobilise, or detoxify heavy metals in water and sediments (Yadav et al., 2025; Ayilara & Babalola, 2023). Such processes compromise water quality and safety, posing challenges to achieving universal access to clean water as outlined in SDG 6. In sub-Saharan Africa, and Ghana in particular, artisanal and small-scale illegal artisanal gold mining (ASGM)—commonly called *galamsey*—has become a dominant source of contamination. While prior research has reported mining impacts on water quality (Ansah-Asare & Asante, 2000; Amuah et al., 2022; Kazapoe et al., 2023), few studies have quantitatively assessed heavy metal accumulation in both sediments and water while integrating ecological and health risk indices. This constitutes a major gap in the literature.

The River Birim, located in Ghana's Eastern Region, exemplifies this challenge. It is an essential freshwater resource for domestic use, agriculture, and livelihoods, yet it is significantly degraded by illegal artisanal mining. In comparable tropical river systems, remediation strategies such as constructed wetlands, aquatic macrophyte deployment, and riparian buffer restoration have demonstrated effectiveness in removing heavy metals through processes such as phytoextraction, *rhizofiltration,* and phytostabilisation (Amrita & Dwiharto, 2026). Constructed wetlands, in particular, act as natural filtration systems that treat mining-impacted water while simultaneously enhancing biodiversity and ecosystem services, making them suitable for resource-limited settings (Vymazal, 2011; recent wetland reviews). Its deterioration threatens sustainable water supply and sanitation efforts, which are central to SDG 6. Its role in supporting local communities, coupled with its vulnerability to contamination from *galamsey,* makes it a critical site for this study. By assessing contamination levels in this river, the study aims to provide crucial data to inform policy interventions and sustainable management strategies for both the river ecosystem and the surrounding communities.

The River Birim is a crucial freshwater resource for domestic use, agriculture, and livelihoods, yet it faces significant degradation from illegal artisanal mining. These mining operations introduce mercury for gold amalgamation, along with cadmium and lead from industrial waste, and nickel and iron from both geogenic and anthropogenic sources (Obasi & Akudinobi, 2020). While previous studies (Asare-Donkor et al., 2018; Afum & Owusu, 2016) have highlighted general declines in water quality, systematic assessments of heavy-metal risks to both ecosystems and human populations remain limited. In tropical environments, remediation effectiveness is influenced by hydrological variability, sediment dynamics, and biological interactions, necessitating integrated approaches that combine biological, chemical, and engineered solutions for sustainable outcomes (de Lima et al., 2022; Li et al., 2025). This gap constrains efforts to ensure water quality monitoring, pollution reduction, and safe water access, which are key targets under SDG 6. This lack of integrated ecological and human health risk evaluations has hindered the development of effective policy interventions.

This study aims to address this gap by analysing water and sediment samples from the River Birim to (i) quantify heavy metal concentrations, (ii) evaluate sediment pollution indices, (iii) assess ecological risks using the Potential Ecological Risk Index (PERI), and (iv) conduct non-carcinogenic and carcinogenic risk assessments for human health. By integrating insights from remediation technologies and documented health impacts, the study not only quantifies contamination but also provides a scientific basis for targeted mitigation strategies in tropical river systems (Ali et al., 2020; Dagdag et al., 2023). By generating evidence to support water quality management and pollution control, the study contributes to achieving SDG 6 targets to improve water quality and reduce contamination. By combining ecological and public health perspectives, the study provides comprehensive evidence of the extent of heavy metal contamination. This paper presents the methods, results, and implications of these findings, and concludes with recommendations for sustainable mining governance and watershed management.

Materials and Methods

Study Area

The Birim River is a major freshwater system located in the Eastern Region of Ghana. Rising from the Atewa Range, it flows approximately 181 km before joining the Pra River. Along its course, the river supports several settlements, including Anyinam, Kibi, Oda, Akwatia, and Kade, which together host a population of about 57,000 residents (Adranyi et al., 2024).

The Birim River basin, located in the Eastern Region of Ghana, is a socio-ecological hotspot, with surrounding communities relying on the river for drinking water, agriculture, fishing, and small-scale industry (Aboah et al., 2026). However, widespread artisanal and illegal artisanal gold mining (*galamsey*) has placed the river under severe environmental stress. Mining activities in the catchment include dredging, open-pit extraction, and panning, often accompanied by mercury amalgamation for gold recovery (Donkor et al., 2024). Additional land uses include subsistence farming, palm oil production, and small-scale commercial agriculture.

Geologically, the basin is underlain by Birimian basement rocks and Voltaian metamorphic sediments, comprising schists, granites, and phyllites, overlain by quartz arenites and carbonate formations. The riverbed itself contains mud, limestone, gravel, and sand. Still, sediment loads are significantly increased by artisanal mining, which accelerates erosion and mobilises heavy metals from soils and rocks into the aquatic system.

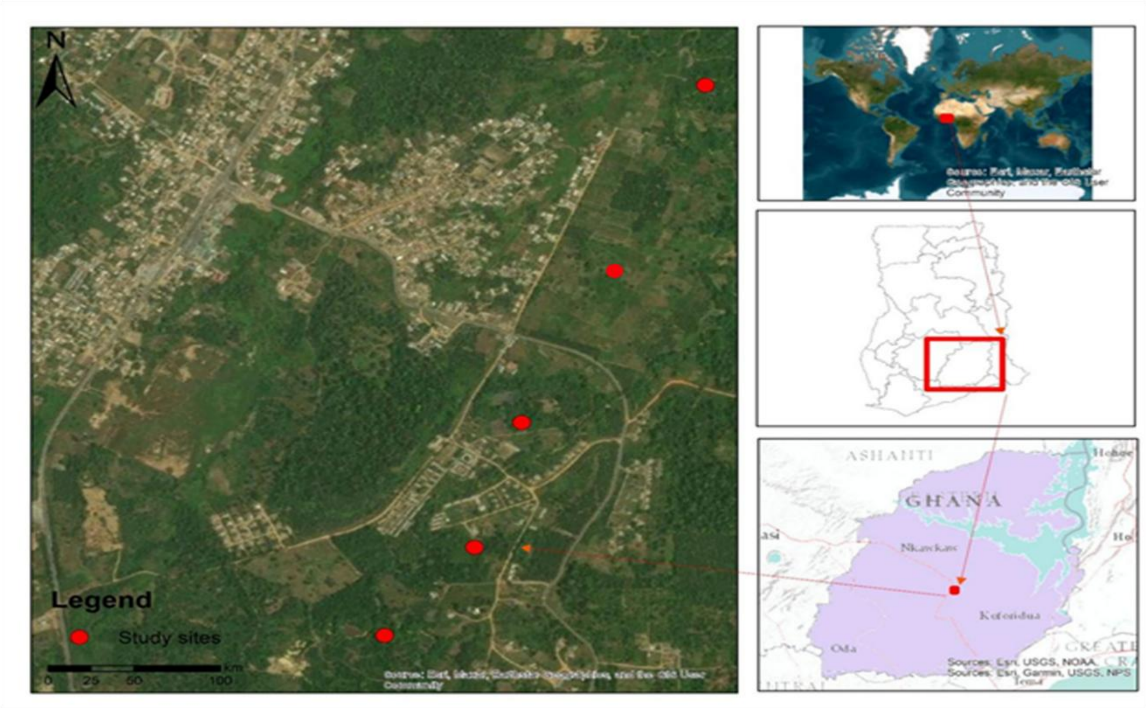

Figure 1: Map of the study area

Sampling Strategy

Water and sediment samples were collected from five purposively selected sites along the River Birim. The sites represented upstream, midstream, and downstream sections of the river, with an emphasis on areas visibly affected by illegal artisanal gold mining.

Sampling was conducted during the dry season, from January to March 2023, to reduce the influence of rainfall, surface runoff, and stormwater dilution on metal concentrations. Samples were collected twice monthly throughout the study period. Water samples were collected using Van Dorn polycarbonate bottles at depths greater than 20 cm below the surface. At each site, three 250 mL replicate samples were taken during each sampling visit. The samples were immediately filtered through 0.45 µm filters and acidified with 1.0 mL of concentrated nitric acid (HNO_3) to prevent precipitation of metal hydroxides and preserve the stability of dissolved metals prior to laboratory analysis.

Sediment samples were collected within a 2 m radius using an Ekman grab sampler. Three sediment replicates were collected at each site during each sampling visit and composited to form a single representative sediment sample per site. Similarly, the three water replicates collected at each site were composited to produce one representative water sample per site for each sampling event.

In total, the study generated 30 composite water samples and 30 composite sediment samples for laboratory analysis. The compositing approach was adopted to minimise small-scale spatial variability and improve site-level representativeness. GPS coordinates were recorded at each sampling site to support spatial accuracy and future monitoring.

Sample Preparation and Analysis

Water samples: In the laboratory, 150 mL of each water sample was re-filtered using a 0.45 µm Whatman filter. The filtrate was acidified with 65% nitric acid and digested at 105 °C for 2 hours, reducing the volume to ~40 mL. The digested solutions were diluted to a final volume of 120 mL with deionised water and stored in pre-cleaned vials for metal analysis.

Sediment samples: Sediments were air-dried, pulverised in an agate mortar, and sieved (<0.15 mm). Five grams of each sediment sample was digested with aqua regia (HNO_3: HCl, 1:3) at 105 °C to extract acid-soluble metal fractions, rather than to achieve complete dissolution of silicate minerals. The resulting digest was diluted to a final volume of 10 mL with ultrapure water before metal analysis.

Metal concentrations (Fe, Mn, Ni, Cd, Zn, Cr, Pb, Hg) were determined using atomic absorption spectrophotometry (AAS). Results were expressed as mg/L (water) and mg/kg (sediment).

Quality Assurance and Quality Control

To ensure analytical accuracy, precision, and reproducibility, comprehensive quality assurance and quality control procedures were implemented throughout the study. Certified reference materials, specifically CRM 320 for water and IAEA-405 for sediment, were employed to validate methodological performance. Calibration curves were generated from 1000 ppm stock standards (Sigma-Aldrich, Switzerland) and diluted to working solutions appropriate for each analyte. All glassware underwent acid washing with 10% nitric acid and subsequent oven-drying to eliminate potential contamination. Instrumental detection limits, method detection limits, and limits of quantification for the heavy metals in water and sediment samples are shown in **Table 1.**

Table 1: Instrumental Detection Limits, Method Detection Limits, and Limits of Quantification for Heavy Metals in Water and Sediment Samples

Metal	IDL (mg/L)	LOD (mg/L)	LOQ (mg/L)
Fe	0.001	0.003	0.010
Mn	0.0003	0.001	0.003
Ni	0.0007	0.002	0.007
Cd	0.0002	0.0005	0.0015
Zn	0.0003	0.001	0.003
Cr	0.0007	0.002	0.007
Pb	0.001	0.003	0.010
Hg	0.0001	0.0002	0.0007

Recovery tests demonstrated acceptable analytical performance, with water sample recoveries ranging from 84% to 109% and sediment recoveries from 90% to 103%. Relative standard deviations for replicate measurements were consistently below 5%, confirming the precision of the atomic absorption spectrophotometric analyses. Multi-point calibrations were verified prior to sample analysis, with correlation coefficients exceeding 0.995 for all metals. Method and reagent blanks were processed alongside each analytical batch to confirm the absence of contamination, and any detected blank values were subtracted or triggered re-analysis.

Duplicate and replicate analyses were routinely conducted to assess intra-sample precision, while continuing calibration verification standards were analysed intermittently during instrument runs to monitor stability. Observed concentrations of check standards remained within ±10% of expected values, ensuring instrument reliability throughout the analytical sequence. Non-detects below the method detection limit (LOD) were reported as <LOD, and concentrations between the LOD and the limit of quantification (LOQ) were interpreted with caution, reflecting the analytical constraints inherent to low-level metal detection.

Collectively, these QA/QC measures—including use of certified reference materials, calibration verification, procedural blanks, replicate analyses, and stringent contamination control—provided robust assurance of data validity and reliability, supporting the integrity of subsequent risk assessment calculations for both ecological and human health endpoints.

Sediment Pollution Assessment

Three indices were applied to evaluate sediment quality:

Geo-accumulation Index (Igeo): calculated following (Chen et al., 1991), comparing current metal concentrations against geochemical background levels (global shale values).

$$I_{geo} = \log 2\left(\frac{C_i}{1.5GB_i}\right) \qquad (1)$$

where Ci represents the concentration of the ith metal in the sediment sample, and GBi denotes its corresponding geochemical baseline value. The constant 1.5 is a background correction factor used to account for natural variations in the sediment matrix due to lithological differences. Based on Igeo values, contamination was classified into seven categories: ≤0 (practically uncontaminated), 0–1 (uncontaminated to moderately contaminated), 1–2 (moderately contaminated), 2–3 (moderately to heavily contaminated), 3–4 (heavily contaminated), 4–5 (heavily to extremely contaminated), and >5 (extremely contaminated). For this study, background concentrations were based on global average shale values (mg/kg): Fe = 47,200; Pb = 20; Mn = 850; Cd = 0.05; Ni = 68; Hg = 0.09; Zn = 95; and Cr = 90. Furthermore, the severity of sediment pollution due to heavy metal accumulation was evaluated using the pollutant load index (PLI). The PLI is calculated as the nth root of the product of the metal contamination factor (CF).

Contamination Factor (CF): determined as the ratio of measured concentration to baseline value.

$$CF_{metal} = {C_{metal}}/{C_{background}} \qquad (2)$$

where CF is the ratio of each metal's concentration in sediment to its baseline value (Derived from the average shale value); the PLI provides an assessment of the sample's overall toxicity status. As a result, a PLI value of 0 denotes perfection, a value of 1 denotes the presence of only threshold amounts of contaminants, and values greater than 1 imply continual deterioration in the site's quality. According to Udo et al. (2026), there are four levels of contamination factor (CF) for monitoring the occurrence of an individual metal over time: (1 ≤ CF < 3) moderate degree, (CF < 1) low degree, (CF ≥ 6) very high degree and (3 ≤ CF < 6) high considerable degree.

Pollution Load Index (PLI): calculated as the nth root of the product of CF values for all metals, providing a composite measure of overall sediment quality (Islam et al., 2015).

$$PLI = (CF_1 \times CF_2 \times CF_3 \ldots\ldots CF_n)^{\frac{1}{n}} \quad (3)$$

Potential Ecological Risk Index (PERI)

The PERI method (Hankanson, 1980) was employed to evaluate the ecological sensitivity of metals by integrating CF values with toxicity response factors (Trf). Metals assessed included Cr (2), Ni (5), Cd (30), Pb (5), Zn (1), Fe = Mn (1), and Hg (40).

The following formula was used to determine E_i:

$$E_i = Trf \times CF_i \qquad (4)$$

The Potential Ecological Risk Index (PERI) is calculated by adding the ecological risk index (E_i) for each of the metals. To calculate PERI, the following formula was used:

$$PERI = \sum_{i}^{n} E_i \qquad (5)$$

Where Trf is the toxicity response factor of the ith metal, and CF is the contamination factor of the ith metal. The ecological risk is classified into 5 classes: $E_i \geq 320$ (very high risk); $40 \leq E_i < 80$ (moderate risk); $E_i < 40$ (low risk); $160 \leq E_i < 320$ (high risk) and $80 \leq E_i < 160$ (considerable risk). However, Hankanson (1980) categorised PERI as follows: 40 ≤ PERI < 80 (moderate risk), PERI < 40 (low risk), PERI ≥ 320 (very high risk), 160 ≤ PERI < 320 (high risk), and 80 ≤ PERI < 160 (considerable risk).

Human Health Risk Assessment

Health risk assessment considered two categories:

Non-carcinogenic risks were estimated using Chronic Daily Intake (CDI), Hazard Quotient (HQ), and Hazard Index (HI). Exposure pathways included ingestion and dermal contact for water, and ingestion, dermal contact, and inhalation for sediments (USEPA 2015). The CDI of heavy metals in sediments and water via the ingestion and dermal pathways was estimated using equations 9 and 10, and equations 6 and 7, respectively, in Appendix 1. By dividing each metal's estimated chronic daily intake by its corresponding reference oral dose (RfD), the estimated HQ for each pollutant was determined. The HQ was established using equation 8 as seen in Supplementary 1. Accordingly, the vulnerable population is considered unsafe when HQ ≥1 and safe when HQ < 1. The total risk to humans from exposure to a specific group of pollutants in water and sediments in an area was calculated using the HI estimated from equation 12 (Supplementary 1). Exposure to heavy metals with an HI level above 1 is deemed harmful to human health. All calculations and evaluations were conducted using adult exposure scenarios, reflecting the higher likelihood of prolonged environmental exposure among adults, as detailed in the Supplementary **Table (S_1).**

Children were not modelled as a separate exposure group because the study did not collect age-specific behavioural and anthropometric data for children in the sampled communities, including child-specific water ingestion rates, sediment ingestion rates, dermal exposure frequency, and body weight. The adult scenario was therefore retained as the primary screening assessment to avoid introducing unverified assumptions into the risk model. However, because children generally have higher exposure per unit of body weight and greater physiological vulnerability to Cd, Pb, Hg, and Ni, the absence of a child-specific scenario is acknowledged as an important limitation that may lead to an underestimation of risk among younger residents. Future work should conduct parallel child-risk calculations using age-appropriate USEPA exposure parameters and locally validated child exposure patterns.

Carcinogenic risks were evaluated using the Cancer Gradational Lifetime Risk (CGLR) and Total Cancer Gradational Lifetime Risk (TCGLR), as defined in equations 13 and 14 in Supplementary 1, respectively, based on slope factors from the International Agency for Research on Cancer (IARC 2012). The CGLR calculates a person's risk of developing any of the cancers linked to daily or 24-hour exposure to a specific dose of a carcinogenic agent over a 70-year lifespan. The International Agency for Research on Cancer classified Cr, Cd, and Ni as group 1 carcinogens since they are believed to be the metals most likely responsible for causing cancer. Pb has also been associated with potential carcinogenic effects. Acceptable lifetime cancer risk thresholds were defined as ranging from 10^{-6} to 10^{-4}.

Exposure parameters (e.g., ingestion rate, exposure frequency, body weight) for Carcinogenic and non-carcinogenic exposures were adopted from USEPA guidelines and are summarised in Supplementary 1, Tables S1 and **S2.**

Statistical Analysis

Descriptive statistics (mean, standard deviation, range) were computed using SPSS version 18, and metal concentrations were compared against WHO standards.

Results and Discussion

Water quality parameters

The physico-chemical parameters of the River Birim are presented in **Table 2**. The mean river temperature was 28.2 °C, which falls within the typical range for tropical surface waters and the WHO-recommended range of 25–30 °C (WHO, 2011). The mean pH value was 6.45, indicating slightly acidic conditions and falling marginally below the WHO-recommended range of 6.5–8.5 for drinking water (WHO, 2011). The slightly acidic condition is important because lower pH can increase the solubility, mobility, and bioavailability of some metals in aquatic systems, thereby increasing their potential ecological and human health risks (Sun et al., 2018).

Dissolved oxygen recorded a mean value of 6.82 mg/L, which is above the minimum level of 5 mg/L generally required to support aquatic life (USEPA, 2011). This suggests that despite high suspended-sediment and mining pressures, the river still retains some capacity to support aerobic aquatic organisms. However, turbidity was extremely high, with a mean of 604.25 NTU, far exceeding the WHO/GEPA-recommended limit of 50 NTU. This high turbidity indicates substantial suspended solids in the water column, most likely associated with sediment disturbance, riverbank erosion, dredging, the washing of excavated materials, and the direct discharge of mining residues into the river, all of which are common features of mining-affected watersheds (Hilson, 2002; Kazapoe et al., 2023).

The mean conductivity, total dissolved solids and total hardness values were 255.7 µS/cm, 140.00 mg/L and 140.33 mg/L, respectively. These values were within acceptable limits, suggesting that the overall dissolved ionic load was not excessively high. Nevertheless, the high turbidity and slightly acidic pH provide important supporting evidence that mining-related disturbance may be influencing the mobility and transport of metals in the river (Sun et al., 2018).

Table 2: Water quality parameters of River Birim in Ghana

Parameters	**pH**	**DO (mg/L)**	**Conductivity (µS/cm)**	**Turbidity (mg/L)**	**TDS (mg/L)**	**TH (mg/L)**	**T/°C**
Mean	6.45	6.82	255.7	604.25	140.00	140.33	28.2
SD	0.52	1.12	35.2	25.42	15.45	40.40	8.5
Min.	6.02	5.32	95.7	104.52	84.00	50.00	21.5
Max.	7.10	8.11	488.5	889.35	192.28	246.00	30.4
WHO/GEPA	**6.5-8.5**	**5**	**1500**	**50**	**600**	**300**	

Heavy metals in water: exceedances and comparisons

The mean concentrations of heavy metals in the River Birim water (**Figure 2**) followed the order: Fe (5.36 mg/L) > Cd (0.23 mg/L) > Ni (0.08 mg/L) > Zn = Hg (0.04 mg/L) > Mn = Cr (0.03 mg/L) > Pb (0.02 mg/L). These results show that Fe was the most abundant metal in the water samples, while Pb recorded the lowest mean concentration among the metals analysed.

When compared with WHO guideline values for drinking water, Fe, Cd, Pb, Hg and Ni exceeded recommended limits (WHO, 2011). Fe recorded a mean concentration of 5.36 mg/L, nearly 18 times the WHO guideline value of 0.3 mg/L. This concentration is higher than values reported for Badagry Creek, Nigeria, and the Yautepec River in Mexico (Ndimele &

Kumolu-Johnson, 2012; Vargas-Solano et al., 2022). Cadmium was particularly elevated, with a mean of 0.23 mg/L, exceeding the WHO limit of 0.005 mg/L by approximately 46-fold. This level is comparable to findings from mining-affected communities in northern Ghana but higher than values reported in the Fenghe River Basin in China (Cobbina et al., 2015; Luo et al., 2021). Lead also exceeded the WHO guideline value of 0.01 mg/L, while Hg exceeded the 0.01 mg/L limit. Nickel was slightly above the WHO guideline value of 0.07 mg/L. In contrast, Cr, Mn and Zn were within acceptable guideline limits (ATSDR, 2007; WHO, 2011).
In addition to WHO standards, comparison with Ghanaian drinking water standards is important for interpreting local regulations. Based on Ghana Standards Authority guideline values, exceedances were also observed for Fe, Cd, Pb and Hg. For example, Fe exceeded the Ghanaian acceptable limit of 0.3 mg/L, Cd exceeded the national limit of 0.003 mg/L, Pb exceeded the 0.01 mg/L limit, and Hg exceeded the 0.006 mg/L limit (Ghana Standards Authority [GSA], 2013). The agreement between international and national standards indicates that the River Birim water is not suitable for direct domestic consumption without treatment. This is particularly important because surrounding communities depend on the river for domestic use, farming, fishing and livelihood activities (Adranyi et al., 2024).

The elevated concentrations of Fe, Cd, Hg, Pb and Ni can be explained by both geological and anthropogenic factors. Geologically, the River Birim basin is underlain by Birimian rock formations, which are associated with mineralisation and may naturally release iron-bearing minerals and other trace metals into the aquatic environment through weathering (Baki et al., 2018). Under acidic conditions, these naturally occurring metals may become more soluble and mobile (Sun et al., 2018). However, the magnitude of the recorded concentrations, particularly for Cd and Hg, suggests that natural weathering alone is unlikely to account for the observed contamination.

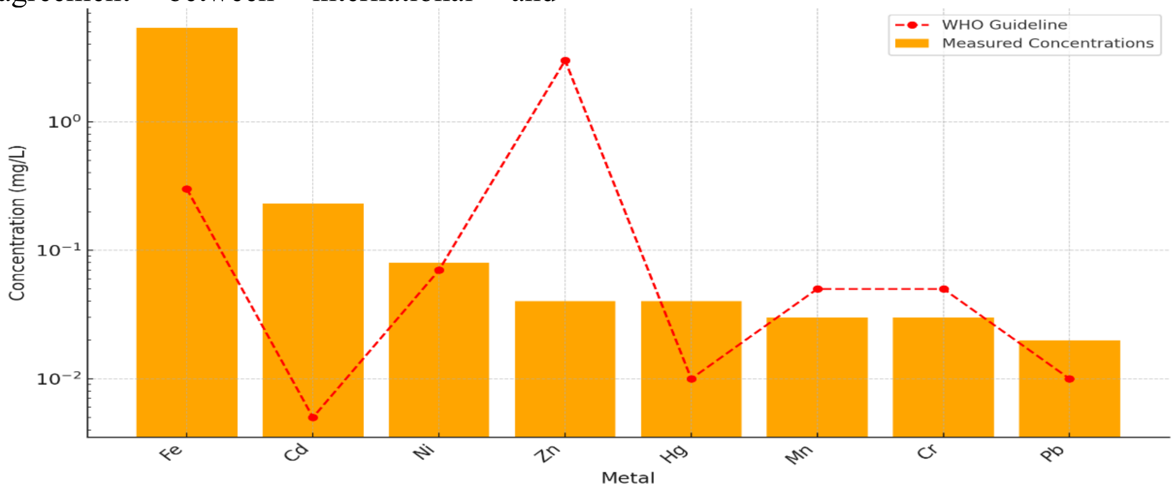

Figure 2: Heavy Metals Concentrations in River Birim compared with the WHO benchmark value.

Anthropogenic activities, especially illegal artisanal gold mining, appear to be a major contributor to the high metal concentrations. Galamsey activities disturb river sediments, expose mineralised soils and rocks, and increase the transport of metal-rich particles into the river (Hilson, 2002; Kazapoe et al., 2023). Ore washing, dredging, excavation, and tailings discharge can increase the concentrations of Fe, Cd, Pb, and Ni in surface water. Mercury contamination is particularly associated with gold amalgamation practices, in which Hg is used to recover gold and may be released directly into the aquatic environment (Asamoah-Boateng, 2009; Donkor et al., 2024). Reduced river flow during the dry season may also have increased metal concentrations by limiting dilution. Therefore, the high metal concentrations likely reflect the combined influence of local geology, acidic water conditions, dry-season concentration effects, and intensive illegal mining activities (Qin & Tao, 2022; Sun et al., 2018)

Heavy metals in sediments: exceedances and comparisons

The mean concentrations of heavy metals in sediments followed the order: Fe (8986.33 mg/kg) > Mn (425.90 mg/kg) > Ni (24.68 mg/kg) > Cd (17.67 mg/kg) > Zn (11.23 mg/kg) > Cr (2.50 mg/kg) > Pb (1.33 mg/kg) > Hg (0.50 mg/kg) in **Figure 3**. As expected, Fe and Mn occurred at relatively high concentrations, reflecting their natural abundance in geological materials. However, elevated Cd and Hg levels are of greater environmental concern due to their high toxicity, persistence, and potential for bioaccumulation (Ali et al., 2020; Tchounwou et al., 2012).

Compared with global background values, Cd and Hg were substantially enriched in the sediments. Cadmium, in particular, was far above its background concentration, suggesting strong anthropogenic influence. Mercury enrichment is also consistent with mining-related inputs, especially the use of Hg in gold extraction (Donkor et al., 2024). Sediments serve as both sinks and secondary sources of metals in aquatic systems. Metals deposited in sediments may remain stored for long periods but can be released back into the water column when environmental conditions change (Förstner & Wittmann, 2012; Sun et al., 2018). Dredging, flooding, changes in pH, sediment resuspension, and mining-related disturbance can remobilise sediment-bound metals, increasing their bioavailability to aquatic organisms (Varol, 2011).

The high sediment concentrations, therefore, indicate that contamination in the River Birim is not limited to the water column. Rather, the sediments represent a long-term reservoir of heavy metals. This is critical because even if direct discharge into the river is reduced, contaminated sediments may continue to release metals into the water column and aquatic food web over time (Förstner & Wittmann, 2012; Islam et al., 2015).

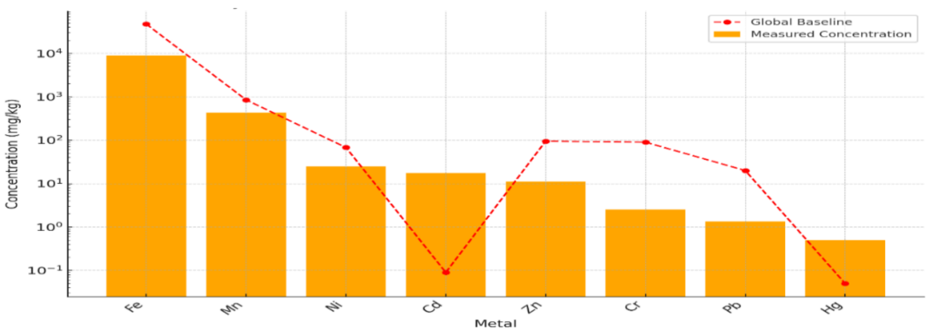

Figure 3: Heavy metal concentrations in River Birim sediments compared with global background values

Sediment pollution indices and ecological risk

The contamination factor values in **Table 3** showed that Cd was the most serious pollutant in the sediments, with a CF value of 353.4, indicating extreme contamination. Mercury recorded a CF value of 5.56, indicating considerable contamination, while the remaining metals had CF values below 1, suggesting low contamination relative to background levels. Similarly, the geo-accumulation index classified Cd as extremely polluted and Hg as moderately polluted. These classifications are consistent with the use of contamination factor and geo-accumulation index approaches in sediment pollution assessment (Chen et al., 1991; Islam et al., 2015).

The Pollution Load Index value of 0.594 suggested that the overall sediment pollution load was moderate when all metals were considered together. However, the Potential Ecological Risk Index gave a more serious indication of ecological threat. The PERI value of 10,827.318 classified the sediments as presenting very high ecological risk according to the Hakanson ecological risk classification (Hakanson, 1980). Cadmium alone accounted for approximately 98% of the total ecological risk, largely due to its high toxicity response factor and very high contamination factor. Similar Cd-dominated ecological risk patterns have been reported in mining-affected environments in Ghana and elsewhere (Jian-Min et al., 2007; Owusu-Prempeh et al., 2022).

This result shows that the ecological risk posed by the River Birim sediments is driven not simply by the total number of metals detected, but also by the toxicity and enrichment levels of specific metals, particularly Cd. Mercury also remains important because it can be transformed into methylmercury under suitable environmental conditions. Methylmercury is highly toxic, readily absorbed by aquatic organisms, and capable of biomagnifying through the food chain (Tchounwou et al., 2012).

Table 3: Heavy metal pollution indices found in sediments from the sampling sites

Metals	I_{geo}	CF	$Trf \times CF$
Zn	-3.665	0.118	0.118
Fe	-2.978	0.190	0.190
Mn	-1.582	0.501	0.501
Pb	-4.495	0.067	0.333
Ni	-1.982	0.380	1.898
Cr	-5.755	0.028	0.056
Cd	7.880	353.400	10602
Hg	1.889	5.556	222.222
		PLI = 0.594	**PERI = 10827.318**

I_{geo}-Geo-accumulation index, CF-contamination factor, PLI- pollution load index, PERI-potential ecological risk index

Human health risks

Non-carcinogenic risk: The hazard quotient and hazard index values for both water and sediment, as shown in **Tables 4 and 5,** were below 1, indicating no immediate non-carcinogenic risk under the exposure assumptions used in this study. This interpretation is consistent with USEPA risk assessment guidance, where HQ or HI values below 1 are generally considered to indicate no significant non-carcinogenic risk (USEPA, 2011, 2015). In water, ingestion was the dominant exposure pathway, with Cd recording the highest ingestion-related hazard quotient. Dermal exposure values were considerably lower than ingestion values, suggesting that direct consumption of untreated water is a more important route of exposure than skin contact.

For sediments, ingestion also contributed more to non-carcinogenic risk than dermal contact or inhalation. Although the hazard index values were below the threshold of concern, this should not be interpreted to mean that the river is safe for unrestricted use. Heavy metals such as Cd, Pb and Hg can accumulate in the body over time and may cause chronic health effects after prolonged exposure (Jaishankar et al., 2014; Tchounwou et al., 2012). Therefore, communities that depend on untreated river water may still face long-term health concerns, especially where exposure occurs through multiple routes, including drinking water, fish consumption, irrigation and contact with contaminated sediments (Wongsasuluk et al., 2014)

Carcinogenic risks. The estimated lifetime carcinogenic risk values for selected metals are presented in **Table 6**. In this study, cancer risk values were interpreted using the commonly applied risk range of 10^{-6} to 10^{-4}. Values below 10^{-6} were considered negligible, values between 10^{-6} and 10^{-4} were regarded as falling within a tolerable or potential concern range, while values above 10^{-4} were considered to indicate an unacceptable carcinogenic risk.

For water exposure, the carcinogenic risk through ingestion was highest for Cd, followed by Ni. The risk value for Cd ingestion in water was 4.14×10^{-5}, while that of Ni was 1.92×10^{-6}. These values exceeded the lower benchmark of 10^{-6} but remained below the upper threshold of 10^{-4}. This indicates that exposure to Cd and Ni through water ingestion may pose a long-term carcinogenic risk, particularly for populations with prolonged reliance on the River Birim as a water source. However, the values should not be interpreted as exceeding the upper unacceptable risk threshold.

For sediment exposure, Cd ingestion recorded a carcinogenic risk value of 4.48×10^{-6}, which also falls within the 10^{-6} to 10^{-4} tolerable risk range. The carcinogenic risks associated with Pb and Cr were at or below negligible levels across the assessed pathways. Across both water and sediment, ingestion contributed more substantially to carcinogenic risk than dermal contact or inhalation, indicating that oral exposure remains the dominant pathway of concern.

Although the total cancer risk values did not exceed the upper unacceptable threshold of 10^{-4}, the presence of Cd and Ni within the potential concern range suggests the need for precautionary management. Continuous exposure to untreated water, contact with sediment, or indirect food-chain transfer could increase long-term health risks, especially among vulnerable groups. Therefore, the findings support the need for regular monitoring, public health awareness, and provision of safer alternative water sources for communities dependent on the River Birim.

Uncertainty and conservative assumptions in cancer risk assessment: The cancer risk estimates should be interpreted within the assumptions of the USEPA-based exposure model. The assessment used adult exposure parameters, adopted reference doses and cancer slope factors from established literature, and assumed repeated exposure via ingestion and dermal contact. These assumptions provide a conservative screening-level estimate rather than a direct prediction of actual disease occurrence. The use of adult parameters may underestimate risk for children, who often have lower body weight and higher intake per unit body mass. In contrast, the use of default slope factors and exposure frequencies may either overestimate or underestimate risk, depending on local behaviour, water-use patterns, exposure duration, and metal bioavailability. In addition, risks based on total metal concentration may not fully reflect the fraction that is bioavailable or present in the most toxic chemical form.

Sensitivity of HI and TCGLR estimates: The non-carcinogenic and carcinogenic risk outputs are most strongly influenced by exposure parameters and toxicological constants. For HI, the dominant drivers are metal concentration, ingestion rate, exposure frequency, exposure duration, body weight, and the selected reference dose. For TCGLR, the most influential parameters are the chronic daily intake and the cancer slope factor, particularly for Cd and Ni, which contributed most to the calculated cancer risks. Because ingestion produced higher risk values than dermal contact, changes in daily water intake, incidental sediment ingestion, and exposure frequency would have the greatest effect on the final HI and TCGLR. This means that communities with higher consumption of untreated water, more frequent river contact, or greater dependence on river-derived fish and irrigated crops may face higher risks than the adult screening scenario suggests.

Table 4: Hazard indices and hazard quotients of heavy metals in water from the River Birim

Exposure pathways	Zn	Ni	Hg	Pb	Fe	Cr	Cd	Mn	HI
$HQ_{ingestion}$	3.81E-06	1.14E-04	3.81E-03	1.63E-04	2.19E-04	7.62E-04	6.57E-03	9.52E-04	**1.26E-02**
HQ_{Dermal}	3.58E-09	2.39E-09	5.97E-09	2.98E-10	7.99E-07	2.39E-08	3.43E-08	1.19E-08	**8.82E-07**

Table 5: Hazard indices and hazard quotients of heavy metals in sediment from River Birim

Exposure pathways	Zn	Fe	Mn	Pb	Ni	Cr	Cd	Hg	HI
$HQ_{Ingestion}$	5.13E-05	1.76E-02	2.43E-01	2.23E-04	7.24E-04	4.89E-04	1.03E-02	6.85E-03	**2.79E-01**
HQ_{Dermal}	1.02E-06	6.29E-05	2.42E-04	8.85E-06	1.07E-05	9.76E-05	4.14E-03	1.37E-05	**4.58E-03**
$HQ_{Inhalation}$	2.64E-08	9.05E-06	6.01E-03	1.14E-07	3.62E-07	2.64E-05	5.34E-06	1.1E-06	**6.05E-03**

Table 6: Carcinogenic risks of heavy metals in sediment and water from the sampling area

	Pathways	Ni	Cd	Pb	Cr	TCGLR
Water	$CGLR_{ingestion}$	1.92E-06	4.14E-05	4.86E-09	4.29E-07	**4.38E-05**
	$CGLR_{Dermal}$	4.11E-09	5.91E-08	5.14E-09	1.54E-08	**8.38E-08**
sediment	$CGLR_{Ingestion}$	8.35E-07	4.48E-06	4.55E-10	5.03E-08	**5.37E-06**
	$CGLR_{Dermal}$	3.33E-09	1.79E-08	1.82E-12	2.01E-10	**2.14E-08**
	$CGLR_{Inhalation}$	4.29E-10	2.31E-09	2.35E-13	2.59E-11	**2.76E-09**

TCGLR-Total Cancer gradational Lifespan Risk, CGLR-Cancer gradational Lifespan Risk

Bioaccumulation and food chain implications

Heavy metals in aquatic systems do not remain confined to water and sediments but are taken up by aquatic organisms and biomagnify along the food chain. Metals such as mercury (in its methylated form), cadmium, and lead accumulate in fish tissues, with higher concentrations observed in predatory species (Burger & Gochfeld, 2005). Communities relying on fish from the River Birim are therefore at risk of dietary exposure. Chronic consumption of contaminated fish can lead to severe health outcomes, including neurological impairment from mercury, kidney damage from cadmium, and cognitive deficits from lead exposure (FAO/WHO, 2011; USEPA, 2018). Furthermore, the use of contaminated water for irrigation may introduce metals into crops, expanding exposure pathways beyond aquatic systems (Nagajyoti et al., 2010).

Expanded ecological implications beyond pollution indices: Although CF, Igeo, PLI, and PERI provide useful screening evidence of contamination, the ecological significance extends beyond numerical index classification. Elevated Cd and Hg concentrations in sediments can impair benthic invertebrates living in direct contact with contaminated sediment, reducing feeding activity, growth, emergence, reproduction, and survival. Such effects may alter benthic community composition and reduce prey availability for fish. Sediment-associated metals may also be transferred into organisms through direct sediment ingestion, gill uptake, and dietary exposure, creating the possibility of biota-sediment accumulation. Where biota-sediment accumulation factors exceed 1, this implies that organisms may accumulate metals at levels above sediment-normalised concentrations, thereby increasing exposure for predators and humans who consume fish. Although this study did not directly measure fish tissue or calculate site-specific biota-sediment accumulation factors, the elevated Cd and Hg burdens indicate a need for future biomonitoring of benthic macroinvertebrates and fish tissues to more precisely assess trophic transfer and food-chain risk.

Remediation and management implications

Mitigating heavy metal contamination in the River Birim requires integrated remediation strategies. Nature-based solutions such as phytoremediation and constructed wetlands have shown effectiveness in tropical river systems by removing or stabilising metals through plant uptake and microbial processes (Vymazal, 2011; Ali et al., 2013). In addition, physicochemical methods such as adsorption using activated carbon or biochar, ion exchange, and chemical precipitation can be applied for water treatment (Fu & Wang, 2011). However, these methods must be adapted to local socio-economic conditions.

At the source level, stricter enforcement of mining regulations, adoption of mercury-free gold extraction technologies, rehabilitation of degraded mining sites, and restoration of riparian vegetation are critical to reducing contamination inputs (Hilson & McQuilken, 2014). Public awareness and community-based monitoring programs are also essential to minimise human exposure and promote sustainable water use practices.

Policy and practical feasibility of interventions: The recommended interventions are most likely to succeed when they combine enforcement with technically feasible, socially acceptable alternatives for miners and riverine communities. Mercury-free gold recovery technologies, such as gravity concentration and improved processing methods, can reduce direct Hg discharge. However, adoption depends on miner training, access to equipment, financing, and sustained regulatory support. Community-based monitoring is also feasible in the Birim context because residents are direct users of the river and can support early reporting of turbidity changes, illegal dredging, fish kills, and visible discharge. Comparable mining-affected settings show that interventions are more sustainable when paired with alternative livelihoods, formalisation of artisanal mining, routine water-quality surveillance, and locally managed reporting systems, rather than enforcement alone (Hilson & McQuilken, 2014; Kazapoe et al., 2023). Practical implementation should therefore prioritise phased actions: immediate provision of safe water sources, short-term monitoring and public health education, medium-term miner training in mercury-free methods, and long-term rehabilitation of riparian buffers, abandoned pits, and contaminated sediment hotspots.

Synthesis with global evidence

The River Birim presents a contamination profile characteristic of ASGM hotspots: Fe dominance from geology, Cd and Hg enrichment from mining, and elevated Ni from mixed geogenic/anthropogenic origins. Compared with African, Asian, and Latin American mining rivers, Birim exhibits especially high Cd burdens in both water and sediments, making it a critical ecological and public health concern. Discrepancies with other studies reflect differences in geology, land use intensity, seasonality, and methodological baselines. Together, the findings indicate that the River Birim is highly impacted by cadmium-driven ecological risk and mercury pollution, with important implications for community health and watershed sustainability. Overall, the interaction between natural geological conditions and intensified anthropogenic activities has created a highly contaminated system where ecological integrity, water quality, and human health are at significant risk. Without urgent intervention, contamination levels may persist or worsen, undermining the long-term sustainability of the river system.

Conclusion

This study assessed heavy metal contamination in the water and sediments of the River Birim, a major freshwater resource in Ghana affected by illegal artisanal gold mining. The findings showed that concentrations of Fe, Cd, Ni, Pb and Hg in water exceeded recommended drinking water limits, indicating that the river is currently unsuitable for direct human consumption without appropriate treatment. Sediment analysis also revealed substantial enrichment of Cd and Hg, with cadmium contributing the largest proportion of the ecological risk. The Potential Ecological Risk Index classified the sediments as posing very high ecological risk, suggesting that the riverbed may serve as a long-term reservoir of contamination.

Human health risk assessment showed that non-carcinogenic risks were below the threshold of concern under the exposure assumptions used in this study. However, carcinogenic risk values for Cd and Ni via water ingestion, and for Cd via sediment ingestion, fell within the tolerable or potential concern range of 10^{-6} to 10^{-4}. Although these values did not exceed the upper unacceptable risk threshold of 10^{-4}, they indicate the need for precautionary public health action, especially for communities that have relied on the River Birim for prolonged periods for domestic, agricultural, and livelihood purposes.

Despite the current level of contamination, the condition of the River Birim should not be regarded as irreversible. The river has potential for ecological recovery if further pollutant inputs are controlled and appropriate remediation measures are implemented. Reducing illegal mining activities, preventing direct tailings discharge, adopting mercury-free gold recovery technologies, restoring degraded riverbanks, and improving sediment management could gradually reduce contaminant loads and improve water quality. Nature-based approaches such as phytoremediation, bioremediation, constructed wetlands and riparian buffer restoration may also support long-term recovery by stabilising or removing metals from contaminated water and sediments.

This study has some limitations. Sampling was conducted only during the dry season and therefore may not fully represent seasonal variations in metal concentrations, particularly during periods of high rainfall, flooding, runoff and sediment resuspension. The study also focused on water and sediment samples and did not assess heavy metal accumulation in fish tissues, crops irrigated with river water, or human biological samples. In addition, the health risk assessment was based on standard exposure assumptions that may not fully capture local differences in water use, fish consumption, occupation, age, body weight, and exposure frequency among river-dependent communities. These limitations suggest that the findings should be interpreted with caution and supported by longer-term, site-specific monitoring.

Based on the findings, urgent remediation and management actions are recommended. Regulatory agencies should intensify monitoring and enforcement against illegal mining along the River Birim and its tributaries. Contaminated hotspots should be mapped and prioritised for sediment management, with dredging considered only where it can be safely conducted without resuspending pollutants downstream. Mercury-free mining technologies should be promoted, while degraded mining sites and riverbanks should be rehabilitated through reforestation and the establishment of riparian buffers. Communities depending on the river should be provided with safe alternative water sources, and public health education should be strengthened to reduce direct consumption of untreated river water. Future studies should include wet-season sampling, metal analysis in fish and food crops, and more localised human exposure assessments to guide effective remediation and protect both ecosystem and public health.

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Emmanuel Kaboja Magna: Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualisation. **Cecilia Asemah:** Writing – review & editing, Validation, Software, Methodology. **Elliot Haruna Alhassan**: Supervision. **Michael Dabi:** Visualisation, Supervision, Formal analysis. **William W. Anku:** Visualisation, Resources.

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Supplementary1

Non-carcinogenic Risk

Equations 6 and 7 below, formulated by the Environmental Protection Agency (Assessment 1998), were applied to calculate the pollutants' chronic daily intake (CDI) via ingestion and dermal contact.

$$CDI_{ingestion\ (Water)} = \frac{cw \times DI \times EF \times ED \times ABS}{AT \times BW} \quad (6)$$

$$CDI_{dermal\ (water)} = \frac{CW \times KP \times SA \times ET \times ABS \times EF \times CF \times ED}{AT \times BW} \quad (7)$$

Where:

ABS (unitless) is the dermal absorption factor; CW (mg/L) is the measured concentration of each metal in water; ED the duration of exposure;AT the mean time; BW, the body weight; EF (day/year) denotes the annual exposure frequency; KP (cm/hour) is the permeability coefficient; Contact-prone region of the skin (SA, in cm^2*); CF (*cm^3*) denotes the conversion factor; ET (h/event) is the exposure time; DI (L/day) is the daily mean consumption of water;*

Table S_1 lists the relevant standard values and additional requirements needed to calculate the chronic daily intake (CDI) by oral ingestion and superficial absorption.

$$HQ = \frac{CDI}{RFD} \quad (8)$$

Where:

HQ is the hazard index of the metal; RFD is the reference oral dose of the contaminant and CDI is the metal's estimated chronic daily intake

The CDI of toxic metals in sediments for various exposure pathways is given by the following formulas.

$$CDI_{ingestion\ (sediment)} = \frac{CS \times CF \times IRS \times ED \times EF}{AT \times BW} \quad (9)$$

$$CDI_{dermal\ (sediment)} = \frac{CS \times AF \times SA \times CF \times ABS \times ED \times EF}{AT \times BW} \quad (10)$$

$$CDI_{inhalation(sediment)} = \frac{CS \times ED \times EF \times ET}{PEF \times AT \times 24} \quad (11)$$

Where:

CS = contaminant exposure point level (mg/kg); ED (exposure duration) = 30 For adults, IRS is 100 mg/kg every day; EF = 350 d/year; CF (conversion factor)=0.000001 mg/kg; AT (average time) = 365 × ED; ET (exposure period) = 24 h per day; AF (adherence factor)= 0.7 mg/cm^2 *; BW (mean body weight)= 70 kg; AT (average time for carcinogens)= 365 × 70 d; ABS (dermal absorption fraction) = 0.0001; SA (Skin area susceptibility contact after exposure) =*$5700 cm^2$*; PEF (Particle emission factor) 1.36 ×* 10^9

Table S_1: Standard parameters for evaluating the health risk of contaminants in water

Parameters	Units	Dermal adsorption	Ingestion
CW	mg/L	-	-
DI	L/day	-	2
ET	Hr/event	0.58	-
SA	cm^2	18000	-
EF	Day/years	350	365
CF	L/cm^3	0.001	-
ED	Year	30	70
ABS	All	0.001	0.001

BW	kg	70	70
AT	Days	350×30	365×70

(Jolaosho et al., 2023)

$$HI = \sum_{i=1}^{k}[HQ(Pb) + HQ(Fe) + HQ(Mn) + HQ(Ni) + HQ(Zn) + HQ(Hg) + HQ(Cd) + HQ(Cr)] \quad (12)$$

Carcinogenic Risks

The cancer gradational lifespan risk (CGLR) was calculated using Equation 13 below:

$$Cancer\ gradational\ Lifespan\ risk\ (\ CGLR\ ) = CDI_k \times SF_k \quad (13)$$

Where:

Cancer gradational lifespan risk (CGLR); Chronic daily intake (mg/kg/day) of carcinogens (CDI) and the slope factor (mg/kg/day) of carcinogens (SF_k).

Equation 14 was used to determine the cumulative CGLR. Table 2 contains the reference dosage (RFD) values for ingestion, inhalation, and skin absorption.

$$TCGLR = \sum_{i=1}^{k}(CDI_k \times SF_k) \quad (14)$$

Table S_2: Cancer slope factors and Reference dose exposure limits of heavy metals

Heavy metals	**RFD_{ing} (mg/kg)**	**RFD_{inh} (mg/kg)**	**RFD_{dem} (mg/kg)**	**KP (mg/kg/d)**	**SF (mg/kg)**
Pb	0.0035	0.00352	0.0000525	0.001	0.0085
Fe	0.7	0.7	0.78	0.001	-
Mn	0.0024	0.00005	0.0096	0.001	-
Ni	0.02	0.0206	0.0054	0.0002	0.84
Zn	0.3	0.3	0.06	0.0006	-
Hg	0.001	0.0002	0.005	0.001	
Cd	0.001	0.001	0.00001	0.001	6.3
Cr	0.003	0.0000286	0.00006	0.002	0.5

KP-Dermal permeability coefficient; RFD_{ing}-RFD for ingestion, RFD_{inh}-RFD for inhalation; RFD_{dem} – RFD for dermal source: (Jolaosho et al., 2023)