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Ecotoxicological and Human Health Risk Assessment of Heavy Metals in Surface Water from the Upper Genale Dawa River Basin, Ethiopia

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Abstract

Due to their toxicity, non-biodegradability, bioaccumulation, environmental stability, and persistence in nature, heavy metals (HMs) have currently become pollutants of global concern. Either acutely or chronically exposed aquatic life and human beings can result in severe damage to the structure and function of vital organs such as the kidney, liver, and brain. Water quality is negatively affected by HMs released into river ecosystems. This study, therefore, investigates the levels of HMs in surface water of the Upper Genale Dawa River Basin to assess water quality and associated ecotoxicological health risks at the study site. The mean levels of HMs (mg/L) in surface water followed the pattern: Hg (0.029) > Mn (0.028) > Cu (0.022) > Pb (0.022) > Ni (0.021) > As (0.021) > Co (0.019) > Cd (0.017) > Fe (0.017) > Zn (0.016) > Cr (0.016) > Se (0.014). Primarily, areas close to significant pollution sources exhibited higher concentrations of HMs. Water quality index (WQI) values for drinking water [Heavy Metal Pollution Index (HPI) = 1958.40 and Heavy Metal Evaluation Index (HEI) = 35.10] indicated the quality of water was compromised. The HI values of the HMs for both children and adults via ingestion of drinking water were 7.24 and 3.98, respectively; and their values via dermal exposure in both children and adults were found to be 1.87 and 0.99, indicating intolerable noncarcinogenic health risks to the community as HI > 1 poses noncarcinogenic risks to exposed populations. The ecotoxicological risk indices that account for the synergistic impacts of multiple metals [Ecological Risk Index (ERI) = 492.59; Degree of Contamination (CD) = 34.85; modified Degree of Contamination (mCD) = 2.90; and Pollution Load Index (PLI) = 0.34] indicated the overall contamination of the river water by HMs considered in this study. The CR values of the HMs for both children and adults via ingestion of drinking water were 1.39×10^{-2} and 7.61×10^{-3}, respectively; and their value *via dermal exposure in both children and adults were found to be* 1.83×10^{-5} *and* 9.70×10^{-6}*, implying potential carcinogenic health risks to the community as* $CR > 1\times10^{-4}$ *poses carcinogenic risks to HM-exposed groups. This research highlights the urgent need for monitoring and intervention strategies to mitigate HM pollution at the Genale Dawa River Basin to protect community health and the safety of the riverine ecosystem.*

Keywords: Carcinogenic; Ecotoxicological Health Risk; Heavy Metals; Noncarcinogenic, Pollution; Toxicity; Upper Genale Dawa River Basin.

1. Introduction

Water is a primary resource to the existence of life on earth due to its importance for maintaining the overall biological functioning of living organisms (Khan *et al*., 2023; Zamora-Ledezma *et al*., 2021). It also serves as the socioeconomic development to people (Yildiz, 2017). Although more than 70% of the earth's surface is covered by water, only 2.5% of which is fresh that plants and animals require for survival (Kipsang *et al*., 2024). As a vital resources of fresh water (Anderson *et al*., 2019; Abiy *et al*., 2024; Berego*et al*., 2024), rivers play a critical role in supporting socioeconomic development and human well-being in providing water resources for drinking, industrial, and agricultural purposes, domestic uses, and recreational activities (AlAfify and AbdelSatar, 2022; Li *et al*., 2020). However, pollution of river ecosystems has emerged as a prominent concern in recent decades. Because, the river water ecosystems are serving as sinks and endpoints of various pollutants that pose potential risks to the aquatic biota and human health (Ahamad *et al*., 2024; Khan *et al*., 2023; Mokarram*et al*., 2022).

Among the pollutants entering the riverine ecosystems, heavy metals are recently becoming the primary contaminants of global concern due to their toxicity, persistence, non-biodegradability, abundance, bioaccumulation, and biomagnification through the food chain (Khan *et al*., 2023; Alahabadi and Malvandi, 2018). Heavy metals are produced either from natural processes (weathering and erosion of rocks) and anthropogenic activities (agricultural runoff, mining and industrial effluents) and finally enter aquatic ecosystems (Alahabadi and Malvandi, 2018, Abdipour et al,2025). While some heavy metals including Zn, Mn, Fe, Cu, Ni, and Co are essential for living organisms in trace amounts, they become toxic to living organisms at higher exposure levels (Pham *et al*., 2023). On the other hand, other heavy metals such as Pb, Hg, As, Cr, and Cd are known to cause adverse effects, even at low levels of exposure and with the potential to pose acute and chronic toxicities in humans and other biota (Norvivor *et al*., 2024; Pham *et al*., 2023; Khan *et al*., 2023; Zhang *et al*., 2023). The deleterious effects of such toxic heavy metals to the riverine environment and human health would be more alarming in underdeveloped and developing countries like Ethiopia with almost no monitoring and enforcement of environmental regulations (Sultana *et al*., 2022).

Of the United Nations Sustainable Development Goals to be achieved in 2030 (SDGs 2030), SDG-3 (good health and well-being), SDG-6 (clean water and sanitation), and SDG-14 (life below water) underpin the idea of environmental justice in which the accumulation of toxic pollutants such as HMs in the natural ecosystems and their impacts on biological community (Habineza *et al*., 2023, Jafari, et al., 2019). However, African countries including Ethiopia are still grappling with heavy metal pollution in water bodies due to rapid population growth, industrialization, inadequate environmental regulations, and poor waste management practices across the continent (Gelaye, 2024). This situation is against the aforementioned SDGs that everyone has access to clean water and sanitation as well as ensuring good health and well-being. Moreover, life below water should be prevented from heavy metal contaminations. Therefore, river water quality monitoring from toxic heavy metal contaminants in vulnerable countries like Ethiopia is essential to help achieve the sustainable development goals (Zhang *et al.*, 2024; Giri and Singh, 2013; Meybeck, 2013) and safeguarding the riverine ecosystem and human health.

Although Ethiopia is rich in river water resources, only few studies have been reported regarding the heavy metal contamination levels of river basins (Asefa *et al*., 2024; Hailu *et al*., 2024; Assegide *et al*., 2022; Kassegne *et al*. 2018; Dirbaba *et al*., 2018; Aschale *et al*., 2016; Awoke *et al*., 2016; Mekonnen *et al*., 2015; Mekonnen *et al*., 2012). Genale-Dawa River Basin is one of the largest and most drought prone regions in Ethiopia and serving as an important alternative water source for the communities living near its catchment (Kassahun and Mohamed, 2018). However; to the best of our knowledge, the concentrations of HMs and their potential ecotoxicological health risk assessments at this study site have not been conducted yet. Therefore, the present study was aimed to estimate the levels of heavy metals and their potential ecological and health risk assessments at the Upper Genale-Dawa River Basin of Ethiopia.

2. Materials and Methods

The study employed a combination of field sampling and laboratory analysis to assess the levels of heavy metals in water, collected from the Upper Genale-Dawa River Basin. A total of 14 sampling sites were purposely selected in the river basin, with a focus on areas with known wet coffee industrial and gold mining activities that may be contributing to heavy metal pollution (Figure 1). Water samples were collected using a grab sampler. The river water is used for domestic use.

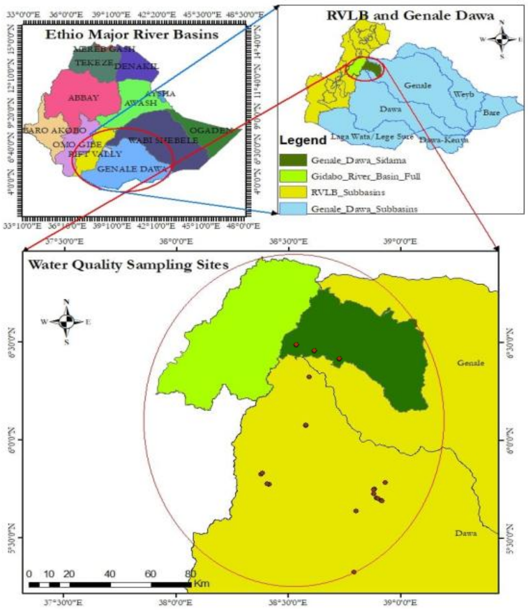

Figure 1. Sampling Sites (Source: https://www.ethiogis-mapserver.org/)

2.1. Sample Collection and Preparation

Sampling was done between November 12 to December 24, 2024, along Upper Genale-Dawa River Basin. A total of fourteen grabbed water samples were collected at a depth of 30 cm from fourteen stations purposely selected in the river basin, with a focus on areas with known wet coffee industrial and gold mining activities that may be contributing to heavy metal pollution .To collect the water samples, 0.5 L plastic bottles which had been pre-cleaned with distilled water and 20% HNO_3 (APHA,2005) were used. A portable GPS was used to record the longitudes and latitudes of the sampling points. Without infiltration, the collected water samples were digested with 5 ml of nitric acid to $pH < 2$. The acid was added to acidify and preserve the water samples.

Water samples were analysed at Bless Agri Food Laboratory Services PLC. Water samples were digested following the nitric acid digestion method adapted from Standard Methods 3030 E and EPA Method 3005/3010 . A 50 mL aliquot of each acidified, well-mixed water sample was transferred into a 125 mL digestion beaker. To the beaker, 5 mL of concentrated nitric acid (HNO_3, ≥69%, trace metal grade) was added, along with a few clean boiling chips to promote even boiling and prevent bumping.

The beaker was placed on a temperature-controlled hot plate and heated gradually to 95–105°C, bringing the sample to a slow boil. The sample was evaporated until the volume was reduced to approximately 15–20 mL, taking care to avoid complete dryness or precipitation of salts. After cooling slightly, an additional 3 mL of concentrated HNO_3 was added, and the heating process was repeated. In cases where the digestate remained colored or turbid, a second 5 mL aliquot of HNO_3 was added, and heating continued until the solution became clear, light-colored, and brown fumes (nitrogen oxides) were no longer evolved, indicating complete digestion.

The digested sample was allowed to cool to room temperature. The solution was then filtered through acid-washed Whatman No. 42 filter paper (0.45 µm pore size) into a 50 mL volumetric flask to remove any particulate matter. The beaker and filter paper were rinsed with 5–10 mL of ultrapure deionized water (18.2 MΩ·cm), and the rinsate was combined with the filtrate. The volumetric flask was then brought to volume with ultrapure water. For quality control, a method blank (ultrapure water processed identically to samples) and a certified reference material (CRM) were prepared alongside each batch of samples . All digested samples were stored in pre-cleaned polypropylene tubes at 4°C until ICP-MS analysis, which was completed within 30 days of digestion . To check the accuracy and precision of analyses, a triplicate sample was taken after taking for every sample, resulting in a total of 42 samples were analyzed for QA/QC.

Water samples were analysed for heavy metals such as arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), iron (Fe), zinc (Zn), manganese (Mn), and selenium (Se) using a standard methodThe samples were then being transported to the laboratory for further analysis using inductively coupled plasma mass spectrometry (ICP-MS Made USA) to determine the concentrations of heavy metals.

2.2. The Heavy Metal Pollution Index (HPI)

Heavy Metal Pollution Index (HPI) is an essential parameter that indicate an overall water quality regarding its heavy metal content (Mohan *et al.*, 1996; Alma *et a*l., 2022). Diverse amounts of heavy metals in water and their collective influence on quality of water were carefully assessed using HPI value **(**Taygi*et al.*, 2013**)** and is estimated by the following equation (Mohan *et al*., 1996; Ahmed *et al*., 2023)

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi} \qquad \text{Equ… 1}$$

$$\mathrm{W_i} = \frac{K}{Si} \qquad \text{Equ… 2}$$

$$\mathrm{K} = \frac{\mathbf{1}}{\Sigma(\frac{\mathbf{1}}{\mathbf{Vstandard}})} \qquad \text{Equ… 3}$$

$$\mathrm{Q_i} = \frac{Mi - Ii}{(Si - Ii)} \times 100 \qquad \text{Equ… 4}$$

Where, HPI indicates metal pollution index (Equations 1); Wi, unit weighting of the i^{th} heavy metal(Equation2); K, proportionality constant and inversely proportional to the maximum allowable value (S_i) of the heavy metals for drinking, livestock and irrigation use that is calculated as presented in Equation 3; and Q_i, sub-index of i^{th} heavy metal and calculated using Equations 4. M_i and I_i are the monitored and ideal values of the i^{th} parameter, respectively for heavy metals expressed in µg/L. An HPI < 100 indicates low pollution due to heavy metals; HPI = 100 is the threshold value at which harmful health consequences are probable; and HPI > 100 represents the water is unsuitable for consumption (Mohan *et al.*, 1996; Elsiddig *et al*., 2020; Tala *et al*., 2023).

2.3. The Metal Index (MI)

MI is a very important indicator of water quality and it is used to assess the overall status of contamination resulting from the concentrations of heavy metals compared to their corresponding Maximum Allowable Concentrations (MACs). It is used to evaluate the quality of water for various purposes (Josephine et al., 2021). According to the metal index, water samples can be categorized into three groups: potable (MI<1), on the threshold of risk of drinking (MI = 1) and non-potable (MI> 1) as indicated in Table 1 below and calculated according to the equation 5(Jafarabadi*et al*., 2017; Goher*et al*., 2020; Ahmad *et al*., 2023).

$$\mathrm{MI} = \sum_{\mathbf{i=1}}^{\mathbf{n}} \frac{\mathbf{C_i}}{\mathbf{MAC}} \qquad \text{Equ… 5}$$

Where, MI represents metal index, C_i, mean concentration of each heavy metal, and MAC is the maximum permissible concentration for each heavy metal in the water sample. An MI < 1 implies the water is suitable for use; and while an MI >1 implies the water is not suitable for domestic purpose (Edet and Offiong, 2002; Alma *et al.*, 2022) and further classification is presented in Table 1 below (Caerio*et al*., 2005).

Table 1. Water Quality Classification using metal index (MI) values

MI	Description
< 0.3	Very pure
0.3 - 1	Pure
1 - 2.2	Slightly affected
2 - 4	Moderately affected
4 - 6	Strongly affected
> 6	Seriously affected

2.4. The Heavy Metal Evaluation Index (HEI)

Heavy metal evaluation is an important parameter to provide relevant information of the overall quality of water regarding to metals. The HEI is estimated by using equation 6 as follows (Zakir*et al*., 2020; Edet and Offiong, 2002).

$$\text{HEI} = \sum H_C / H_{mac} \qquad \text{Equ… 6}$$

Where, H_c represents monitored concentration of the heavy metals; and H_{mac}, maximum permissible concentrations (MAC) of the heavy metals (Sobhanardakani, 2016; Zakir*et al*., 2020). Regarding interpretations, an HEI < 1.0 is considered as “Fit”; and while HEI >1.0, the water is “Unfit “for domestic purposes (Singh *et al*., 2017; Zakir*et al*., 2020). Based on the findings by Edet and Offiong (2002), the quality of water with regard to the value of HEI is further categorized as an HEI < 10 for low pollution; 10 < HEI < 20 for moderate pollution; and HEI > 20 for high pollution.

2.5. The Human Health Risk Assessment

Human health risks of heavy metal contamination can be attributed from direct oral ingestion of water and dermal absorption through the skin; and hence, the common exposure pathways to water used to determine human health risks are mainly contributed from dermal absorption and oral ingestion of drinking of heavy metal contaminated water (Rofhiwa*et al*., 2021).

2.6. Exposure Assessment

Human health risks from heavy metals in water through oral ingestion and dermal absorption were determined by using the United States Environmental Protection Agency (USEPA) risk assessment guidelines (USEPA, 2004). To evaluate the noncancer and cancer risks to humans (children and adults), the chronic daily intake (CDI) of HMs, which represents the lifetime average daily dose (LADD) of exposure to a contaminant was used (USEPA, 2004; Bamuwuwamye *et al*., 2017). The CDI of the HMs in water via oral ingestion and dermal absorption was calculated by using the following equation (Govind *et al*., 20222; Ugwu *et al*., 2022):

$$CDI_{\text{ingestion}} = \frac{(\text{C x IR x EF x ED})}{(\text{BW x AT})} \quad \text{Equ… 7}$$

$$CDI_{\text{dermal}} = \frac{(\text{C x EF x ED x ET x SA x KP x CF })}{(\text{BW x AT})} \quad \text{Equ… 8}$$

Where, CDI = chronic daily intake (mg/kg/day); C = mean concentration of heavy metal in water (mg/L); IR = ingestion rate per day (1 L/day for a child and 2.2 L/day for adult) (Bamuwuwamye *et al.*, 2017; Ugwu *et al.*, 2022); ED = exposure duration (6 years for a child and 30 years for an adult) (WHO, 2015; Ahmad *et al.*, 2023); EF = exposure frequency (365 days/year); ET = exposure time (0.58 h/day for adults; 1 h/day for children (UNEPA, 2004); BW = average body weight (15 kg for a child and 60 kg for adult) (WHO, 2012) over the exposure period; AT = average time representing the period over which exposure is averaged [(for carcinogens, AT=65×365=23,725 days for both children and adults in Ethiopia; for non-carcinogens AT=ED × 365 which equals 2190 days and 10950 days for children and adults, respectively) (Seifu *et al.*, 2024)]; SA = exposed skin area available for contact (18000 cm^2 for adults; 6600 cm^2 for children) (USEPA, 2004); KP = dermal permeability coefficient of heavy metal in water(cm/h) [Pb (0.004), Ni (0.001), As (0.001), Hg (0.001), Cd (0.001), Co (0.001), Cu (0.001), Zn (0.006), Mn (0.001), Se (0.001)), (Fe (0.001), and Cr (0.001)]; CF = unit conversion factor (0.001L/cm^3) (UNEPA, 2004;Bamuwuwamye *et al.*, 2017; Govind *et al.*, 20222).

2.7. The Noncarcinogenic Risk Assessment (HQ and HI)

Noncancer risks of HMs in water were determined by using the hazard quotient (HQ) and hazard index (HI) values according to equations 9 to 11, respectively.

$$HQ_{Ingestion} = \frac{CDI_{Ingestion}}{RfD_{Ingestion}} \quad \text{Equ… 9}$$

$$HQ_{Dermal} = \frac{CDI_{Dermal}}{RfD_{Dermal}} \quad \text{Equ… 10}$$

$$\text{HI} = \sum \text{HQ} \quad \text{Equ… 11}$$

Where, HI = overall potential for noncarcinogenic effects posed by more than one pollutant via ingestion and dermal path ways; while HQ = non-cancer hazard quotient; CDI = chronic daily intake (mg/kg/day) (USEPA, 2002; USEPA, 2005; USEPA, 1995; Akaninyen *et al.*, 2022). The potential risk to human health posed by exposure to multiple HMs was measured by the hazard index (HI), which is the sum of all HQs calculated for each heavy metal. A value of HQ or HI < 1 indicates no significant non-cancer risk; a value > 1 indicates significant non-cancer risk; whose risk generally increases with increasing HQ or HI (Govind*et al.*, 2022; Ugwu*et al.*, 2022).

2.8. Carcinogenic Risk Assessment (CR)

Cancer risk was calculated as the quotient of the CDI (mg/kg/day) and cancer slope factor (CSF) measured in (mg/kg/day). In the present study, the CR was assessed for elements that are considered to be toxic to humans such as Hg, As, Cr, Pb, Cd, and Ni.

The carcinogenic risks (CR) associated with the ingestion pathway can be estimated using the following formula:

$$CR_{ingestion} = CDI_{ingestion} \times CSF_{ingestion} \qquad \text{Equ… 12}$$

$$CR_{dermal} = CDI_{dermal} \times CS_{dermal} \qquad \text{Equ… 13}$$

Where CR $_{ingestion}$ = carcinogenic risk (CR) associated with ingestion; CDI = chronic daily intake (mg/kg/BW/day); and CSF$_{ingestion}$ = the oral carcinogenic slope factor (mg/kg/day), which is 0.0085 for Pb, 0.5 for Cr, 1.7 for Ni ,6.1 for Cd,1.5 for As and 1.00 for Hg. The total cancer risk as a result of exposure to multiple contaminants due to consumption of a particular type of water was assumed to be the sum of each metal cancer risk (∑CR). The United States Environmental Protection Agency (USEPA) suggested that a CR $<10^{-6}$ indicates no carcinogenic risk to human health; and while a CR $> 1 \times 10^{-4}$ indicates a high risk of developing cancer; and a risk ranging from 1×10^{-6} to 1×10^{-4} represents an acceptable risk to human health' (Seifu *et al*., 2024).

2.9. Ecotoxicological Risk Assessment

In this study, the ecotoxicological risks of heavy metals from surface water samples of the Upper Genale Dawa River Basin was assessed using four multi-element risk indices (Liu *et al*., 2020; Samuel *et al*., 2020; Tytła *et al*., 2023; Sridhar *et al*., 2024). These parameters include Degree of Contamination (CD), modified Degree of Contamination (mCD), potential Ecological Risk Index (ERI), and Pollution Load Index (PLI) (Yap *et al*., 2021; Agho et al., 2021). According to Vu *et al*. (2017), since heavy metals are more likely to have synergistic effects in the environment, and hence, the multi-element indices that consider the synergistic effects of different heavy metals could provide sufficient information in their assessment of the potential ecotoxicological risks of such pollutants at study sites.

2.9.1. Potential Ecological Risk Index (ERI)

This parameter is one of the most commonly used assessment method of heavy metal contamination levels of study sites. It assesses the overall potential ecological hazards and toxicity posed by heavy metals in of riverine ecosystem using river water; while utilizing the method proposed by Håkanson (1980). In other words, ERI is the sum of all of the ecological risk factors for the heavy metals in the investigated (Samuel *et al.*, 2020; Thongyuan *et al.*, 2020) as described in equation (14) below.

$$ERI = Er_1 + Er_2 + Er_3 + \ldots + Er_n \qquad \text{Equ… 14}$$

Where, n represents the number of investigated heavy metals; ERI is the potential ecological risk index which is defined as the sum of all single heavy metal ecological risk factors. The ERI is classified as ERI ≤ 150 = low ecological risk; 150 < ERI ≤ 300 = moderate ecological risk; 300 < ERI ≤ 600 = considerable ecological risk; and ERI > 600 = very high ecological risk (Agho *et al*., 2021).

2.9.2. Degree of Contamination (CD)

The CD value estimates the total degree of overall contamination of the riverine ecosystem of the study site based on the calculation of CF for each HM toxicant. Thus, it is defined as the sum of the contamination factors (Samuel *et al*., 2020; Agho *et al*., 2021) by the following equation (Eq. 15):

$$CD = CF_1 + CF_2 + CF_3 + \ldots + CF_n \qquad \text{Equ… 15}$$

Where, n represents the number of investigated HMs; and CF denotes the contamination factor. Based on Håkanson (1980), the CD is categorized as $CD < 6$ = low degree of contamination; $6 \leq CD < 12$ = moderate degree of contamination; $12 \leq CD < 24$ = considerable degree of contamination; and $CD \geq 24$ = very high degree of contamination.

2.9.3. Modified Degree of Contamination (mCD)

This parameter was introduced to estimate the overall degree of contamination at a given site (Samuel *et al.*, 2020). It is defined as the sum of CF values divided by the number of investigated heavy metals and estimated according to equation (16) below.

$$mCD = (CF_1 + CF_2 + CD_3 + \ldots CF_n)/n \qquad \text{Equ… 16}$$

Where, n is the number of investigated heavy metals, CF is the degree of contamination, and mCD is the modified degree of contamination which is described according to Håkanson (1980) as follows: $mCD < 1.5$ =Very low degree of contamination; $1.5 < mCD < 2$ = low degree of contamination; $2 < mCD < 4$ = Moderate degree of contamination; $4 < mCD < 8$ = High degree of contamination; $8 < mCD < 16$ = Very high degree of contamination; $16 < mCD < 32$ = Extremely high degree of contamination; $mCD > 32$ = Ultra - high degree of contamination.

2.9.4. Pollution Load Index (PLI)

This parameter provides the means for evaluating the overall level of heavy metal contamination. Each sampling site can be evaluated for the extent of the heavy metal contamination by employing the method proposed by by Thongyuan *et al*. (2020) and can be expressed by the following equation (17) below.

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots CF_n)^{1/n} \qquad \text{Equ… 17}$$

Where, CF denotes the contamination factor; n represents the number of analyzed heavy metals; and CF_n denotes the contamination factor for the nth element. Using the methods by Thongyuan *et al*. (2020) and Samuel *et al*. (2020), the $PLI < 1$ implies no indication of pollution; and while $PLI > 1$ indicates significant heavy metal pollution.

3. Results and Discussions

3.1. Concentration of Heavy Metals at the Upper Genale Dawa River Basin Surface Water

The mean concentration of heavy metals in the Genale Dawa River Basin water samples are shown in Table 2; the average levels followed the decreasing order: Hg (0.029 mg/L) > Mn (0.028 mg/L) > Cu (0.022 mg/L) > Pb (0.022 mg/L) > Ni (0.021 mg/L) > As (0.021 mg/L) > Co (0.019 mg/L) > Cd (0.017 mg/L) > Fe (0.017 mg/L) > Zn (0.016 mg/L) > Cr (0.016 mg/L) > Se (0.014 mg/L). Cd, As, and Zn were not detected in sample site 12 indicating the absence of Zn, As, and Cd-containing pollution sources in the neighbouring catchment area that drain into the river water surrounding this particular sampling site. The maximum concentrations of heavy metals detected in the studied river water samples was recorded for Mn (0.165 mg/L) at a sampling site 4; and while the minimum recorded value at this particular site was for Se (0.062mg/L). The sampling site 4 was the area where the concentrations of most of the heavy metals are getting higher indicating the likely presence of heavy metal pollution sources in the proximity of the river catchment in this study site.

In this particular study, manganese (Mn) levels in water samples ranged from <0.01 to 0.165 mg/L, with the mean level of0.028mg/L. The mean concentrations of Mn in the present study (0.028 mg/L) was larger than the finding from Sosian River (Emily *et al*. 2023) in Kenya. When compared to the previous research findings, the mean level of Mn in this study was lower than the previous studies in Malaysia (0.497mg/L) (Tengku *et al*., 2020), and in Turkey (6.48mg/L) from Akcay River (Yasemin and Fusun, 2021). Remarkably, the mean concentration of Mn in the present study was lower than the WHO permissible limits for manganese in drinking water, i.e., 0.4 mg/L (WHO, 2017). Even with lower average concentrations, manganese (Mn) and mercury (Hg) can exceed water quality thresholds due to several factors. These include variations in concentration across different locations and times, the presence of localized pollution sources, and the potential for bioaccumulation in the food chain.

The mean concentration of iron (Fe) in water sample ranged from not-detected (ND) to 0.089 mg/L; and with the mean level of 0.017mg/L which is within permissible limit set by WHO (2017), with no significant pollution detected, suggesting a stable ecosystem. This finding was in comparable with study at Nyl River, South Africa which reported Fe levels within natural ranges (Greenfield *et al*., 2012). Moreover, the level of Fe in this study was lower as compared to the previous studies from various rivers in Ethiopia. For instance, 0.30 mg/L in Togona River of Goba Town, Oromia Region (*Get al*., 2015); 8.926 mg/L in Lower Omo River (Abiy *et al*., 2024). Similarly, Fe was identified as a primary water quality issue in GilgelAbay River, although specific mean concentrations were not detailed (Wondim *et al*., 2015).

Likewise, the Fe level in this study was much lower than a study at Kou River, Tanzaniawhich reported Fe levels ranged from 4.1 to 5.38 mg/L, exceeding irrigation and aquatic life standards, indicating significant pollution (Gebreyohannes *et al., 2022*). Moreover, in West African Rivers, moderate levels of Fe concentrations were reported with higher levels during dry and flood seasons, influenced by local contamination (Ouattara *et al*., 2018). In Manyame River of Zimbabwe, elevated Fe levels were reported; particularly in areas affected by industrial pollution (Nhiwatiwa *et al*., 2011). The mean concentrations of Fe in water samples from various rivers show significant variability, reflecting both natural and anthropogenic influences. Notably, various studies indicated that Fe concentrations can exceed acceptable limits, posing risks to both aquatic life and human health (Viana *et al*., 2021).

In the present study, the concentrations of nickel (Ni) ranged from < 0.011 to 0.125 mg/L, with mean concentration of 0.021mg/L. The result was in line with the previous study at Ogunpa River that reported 0.27 mg/L (Peter *et al*.,2019) and river water in Cameron which was found to be 0.04 mg/L, with higher concentrations observed in spring water (0.06 mg/L) and industrial waste (0.05 mg/L) (Nga, 2023). However, this finding was higher than the previous study reported in Ethiopia at Lower Omo River that notably reported as low as 0.007 mg/L (Abiy *et al*., 2024). Additionally, the Little Akaki River reported a mean Ni concentration of 6.66 µg/L, which is approximately 0.007 mg/L (Aschale *et al*., 2014). In contrast to this, the present finding was lower than a study at the Bamo River ranging from 2.93 to 3.58 mg/L (Mz, 2022); River Nigerfrom0.78 ± 0.12 mg/L (Olatunji and Osibanjo, 2012). These differences in concentrations of Ni suggest that rivers are not equally affected by industrial contamination (Nhiwatiwa *et al*., 2011).

The concentrations of cobalt (Co) in this study ranged from < 0.013 to 0.101 mg/L with its mean concentration of0.019 mg/L. The finding of the present study was comparable with the recent study done in lower Omo river which reported 0.06 mg/L (Abiy *et al*., 2024). On the other study; however, a lower mean concentration of Co (0.003 mg/L) was reported at little Akaki River (Aschale *et al*., 2014). Remarkably, its mean concentration in the present study was above the WHO (2017) permissible limits for drinking water quality indicating the probable risk of this water resource for drinking purpose to the community.

The concentration of copper (Cu) in this study ranged from < 0.013 to 0.113 mg/L; with the mean level of 0.022 mg/L. The finding of the present study was in-line with the previous study by Qiang *et al*. (2021) from Buerhatong River (0.013 mg/L) in China and Adem *et al*. (2023) from Borkena River (0.03 mg/L) in Ethiopia. However, the result from this study was lower than the finding from Togona river (0.20mg/L) in Ethiopia (Fisseha*et al*.,2015); from Megech River ranged from 0.11 to 0.17 mg/L (Engdaw *et al*., 2022); Omo river (0.318 mg/L) in Ethiopia (Abiy *et al*.,2024) as well as in Awash River during the dry season (0.12 mg /L) and the wet season (0.15 mg/L) (Eliku and Leta,2018). Notably, its mean concentration in the present study was below the WHO (2017) permissible limit for drinking water quality and the FAO (1985) for livestock.

The zinc (Zn) level in this study ranged from ND to 0.08 mg/L with mean value of 0.016 mg/L. The mean concentration of Zn in the present study was comparable with the previous study by Azlini *et al*., (2018) from highland River of Malaysia (0.033 mg/L). However, the Zn level of the river water in the present study was lower than that in the previous study by Engdaw *et al*., (2022) from Megech River (0.13 mg/L) in Ethiopia. On the other studies, the mean concentrations of Zn were reported ranging from 0.274 to 0.330 mg/L (Haile, 2022) in the Bamo River; 0.1 mg/L in Omo river, Ethiopia (Abiy *et al*., 2024); and 176 mg/L from Muchawka River in Poland (Mariusz and Joanna, 2023). Its mean concentration in the present study was below the WHO (2011) permissible limits for drinking and the FAO (1985) for livestock.

Particular to this study, the cadmium (Cd) level ranged from ND to 0.085 mg/L with the mean concentration of 0.017 mg/L. The finding from the present study was in comparable with a study conducted in South Africa that reported the Cd level in Umtata River from trace level to 0.007 mg/L, which was below the South African water quality guidelines (Fatoki *et al*., 2004). However, this finding was higher than previous study done in Ethiopia; for instance, the mean concentration of Cd in the Little Akaki River was reported as below 0.001 mg/L (Aschale *et al*., 2014), and in Omo river not detected (ND) (Abiy *et al*.,2024); and was significantly below the permissible limits for drinking water. The concentration of Cd in the present study was above the WHO (2017) permissible limits for drinking (0.003 mg/L).

The level of Mercury (Hg) in this study ranged from 0.001 to 0.108 mg/L; with mean level of 0.029 mg/L. The result from the present study was higher than the mean Hg concentrations reported below 0.001 mg/L from both little Akaki River (Aschale *et al*., 2014), and Bug River (Jabłońska and Kluska, 2020). However, the finding from the present study was comparable with a study from areas near gold mining at Banyuwangi exhibited levels of Hg ranging from 0.031 to 0.033 mg/L (Qomariyah *et al*., 2022) that implies that in the present study the level of mercury was exceeding the safe threshold value. The Possible sources of Hg in this study may be due to the natural process (weathering of mineralized rocks) and/or traditional artisanal gold mining or extraction through amalgamation process using Hg as a raw material.

The lead (Pb) level in this study ranged from ND to 0.101 mg/L; with the mean concentration being 0.022mg/L. The mean concentrations of Pb in the present study was comparable with the previous study by Kubra *et al*. (2023) which was found to be 0.029mg/L in Rupsha River, Bangladesh. Similarly, this finding was in line with the previous study by Engdaw *et al*. (2021) which was found to be 0.040 mg/L and by Ibukun *et al*. (2018), reported at the level of0.019 mg/L from Nigeria. On the other hand, the mean concentration of Pb in the present study was lower than the previous studies by Abiy *et al*. (2024) which was 0.318 mg/L from Ethiopia; Emily *et al*. (2023), 0.105 mg/L from Kenya; Hellar-Kihampa and Mihale (2023), widely varied from 0.7 to 24.0 mg/Lin Urban Rivers, Dar es Salaam, Tanzania;and Mariusz and Joanna (2023), 9.3mg/L. However, the result from the present study was higher than the previous studies by Alma *et al*. (2022),0.0021mg/L from Albania and Sirait *et al*. (2024),0.003 mg/L from Bah Bolon River, Indonesia. The mean concentrations of Pb in the present study was above the permissible limits for drinking water quality (WHO,2017) and below the permissible limit for livestock set by (FAO, 1985).

In this study, the level of Arsenic(As) ranged from ND to 0.143mg/L;with the mean concentration of 0.021 mg/L. This finding was in comparable with the studies by Mohammad and Tempel (2019) at Humboldt River which revealed As concentrations ranged from 0.012 to 0.06 mg/L and by Liu *et al*. (2023) at Zijiang River (0.001-0.01 mg/L). On the other hand, different levels of Arsenic were detected at various points from TukadBadung River (Sari & Kartika, 2023) with concentrations 0.769 mg/L and 0.081 mg/L. The mean concentration of Arsenic in the present study was higher than the permissible limit for drinking water according to WHO (2017) and USEPA (2011).

The level of chromium (Cr)in the studied water samples ranged from 0.001 to 0.073mg/L; with the mean concentration of 0.016 mg/L. The concentration of Cr in this study was lower than the previous studies by Yasemin and Fusun (2021) from Ackay River (8.296 mg/L) in Turkey; by (Ardian, 2023) in the Opak River found to be 0.124 mg/L.However, the finding from the present study was higher than the studies by (Qiang *et al*., 2021) from Buerhatong River (0.00456mg/L) in China and (Tengku *et al*., 2020) from Tropical River (0.005mg/L) in Malaysia. On the other hand, the level of Cr in this study was in line with the studies by Ibukun *et al*. (2018) from Southwest Nigeria (0.059 mg/L); by (Singh and Sharma, 2018) in the Hindon River (0.096 mg/L). Notably, the mean concentrations of Cr in the present study was below the permissible limits for drinking water quality (USEPA, 2011; WHO, 2017) and the FAO permissible limits for livestock (FAO,1985).

In this study, the selenium (Se) concentrations ranged from 0.001 to 0.062mg/L with the mean concentration of 0.014 mg/L. The present fining was higher than the previous studies in South African river water samples near coal-fired power plants that reported the Se concentrations ranging from 0.00263 to 0.00820 mg/L (Shiri *et al*., 2023) and the lower Arkansas River Valley which reported the Se concentrations in river waters ranging from 0.0042 to 0.00230 mg/L (Herting and Gates, 2005). Conversely, in Japan river water sanples the Se levels were reported much lower, ranging from 0.000033 to 0.000094 mg/L, with a weighted average of 0.000057 mg/L(Suzuki *et al*., 1981) and in Wanshan, China, the total aqueous Se concentrations were highly variable, averaging 0.0038 µg/L(Zhang *et al*., 2013).Moreover, research findings in Croatia revealed low mean levels of Se contents in river waters, ranging from 0.021 to 0.187 µg/L (Maronić *et al*., 2024).This discrepancy in the levels of Se might be due to the variations in flooding and drought conditions affecting its distribution at the corresponding river waters.

3.2. Water Quality Indices (WQI)

Water Quality Indices (WQI) are the methods by which water quality data is monitored and summarized for reporting to the public in a consistent manner. These values are of the most effective tools to communicate information on the quality of water to the concerned citizens and policy makers (Sivaranjani*et al*., 2015; Seifu *et al*., 2024). In this study, thus, the indices of water quality were computed after estimating the levels of heavy metals. In that context, the heavy metal pollution index (HPI), heavy metal evaluation index (HEI), and metal index (MI) values were calculated to evaluate the quality of the Genale Dawa River water regarding the heavy metal levels for each sampling sites (Table 3).

3.3. Heavy Metal Pollution Index (HPI):

It indicates an overall quality of water regarding to heavy metals. Heavy metal pollution index values of river water for heavy metal concentrations to each sampling sites is depicted in Table 3 above and the HPI value of the Genale-Dawa River water ranges from 288.771 to 9614.433 with a mean value of 1958.404 (Table 3) for drinking water; while the HPI values for irrigation water ranges from 5783.822 to 12733.11 with a mean value of 7471.117. The HPI value shows that all sampling sites were heavily polluted as it exceeded the threshold value of the pollution index (HPI = 100) indicating that the water is unsafe for drinking and irrigation purpose. However, the mean value of HPI in the present study for drinking water, i.e. 1958.404 is lower than the value reported by Josephine *et al*. (2021) at the Mgoua water (1990.64) of South-western Cameroon. On the other hand, the mean HPI value reported in this study exceeds those reported by Ghaderpoori *et al* (2018) (HPI = 48.58) and Seifu *et al*. (2024) (HPI = 720) in drinking water from Khorramabad city in Iran and Lower Omo River in Ethiopia, respectively.

Table 2. Mean concentrations of heavy metals (mg/L) from surface water of the Upper Genale Dawa River Basin

No	**Mn**	**Fe**	**Ni**	**Co**	**Cu**	**Zn**	**Cd**	**Hg**	**Pb**	**As**	**Cr**	**Se**
1	0.0125±0.001	0.0091±0.001	0.0112±0.001	0.0132±0.001	0.0128±0.001	0.0093±0.001	0.0118±0.001	0.0289±0.04	0.0156±0.001	0.0106±0.001	0.0192±0.001	0.0084±0.001
2	0.0190±0.003	0.0336±0.002	0.0208±0.002	0.0187±0.002	0.0329±0.004	0.0228±0.002	0.0216±0.004	0.0479±0.02	0.0289±0.004	0.0234±0.001	0.0135±0.004	0.0220±0.001
3	0.0001±0.001	0.0001±0.0001	0.0005±0.0005	0.0005±0.003	0.0007±0.003	0.0001±0.001	0.0011±0.001	0.0116±0.001	0.0013±0.001	0.0001±0.001	0.0001±0.001	0.0003±0.001
4	0.1654±0.003	0.0892±0.001	0.1253±0.003	0.1014±0.001	0.0810±0.003	0.0852±0.003	0.0853±0.03	0.1076	0.1013±0.001	0.1426±0.02	0.0733±0.001	0.0619±0.04
5	0.0061±0.001	0.0030±0.001	0.0060±0.002	0.0064±0.002	0.0045±0.003	0.0020±0.001	0.0040±0.001	0.0103±0.001	0.0093±0.001	0.0062±0.001	0.0037±0.001	0.0039±0.001
6	0.0460±0.002	0.0422±0.002	0.0501±0.001	0.0331±0.003	0.0581±0.003	0.0439±0.004	0.0444±0.03	0.0757±0.02	0.0567±0.001	0.0457±0.001	0.0478±0.03	0.0380±0.001
7	0.1267±0.03	0.0556±0.001	0.0765±0.001	0.0878±0.002	0.1126±0.002	0.0607±0.03	0.0655±0.05	0.0885±0.03	0.0761±0.001	0.0526±0.001	0.0604±0.004	0.0577±0.001
8	0.0013±0.001	0.0006±0.003	0.0017±0.001	0.0016±0.003	0.0037±0.003	0.0011±0.001	0.0010±0.001	0.0065±0.001	0.0055±0.001	0.0030±0.001	0.0012±0.001	0.0013±0.001

9	0.0020 ±0.001	0.0002±0.001	0.0013±0.001	0.0008±0.002	0.0003±0.0001	0.0001±0.001	0.0010 ±0.001	0.0172 ±0.001	0.0081 ±0.001	0.0021 ±0.001	0.0003±0.001	0.0032±0.001
10	0.0001 ±0.001	0.0002±0.002	0.0008±0.0003	0.0002±0.002	0.0030±0.001	0.0002±0.001	0.0002 ±0.001	0.0019 ±0.001	0.0006 ±0.001	0.0007 ±0.001	0.0010±0.001	0.0003±0.001
11	0.0076 ±0.001	0.0013±0.002	0.0013±0.001	0.0019±0.002	0.0024±0.002	0.0054±0.001	0.0014 ±0.001	0.0023 ±0.001	0.0024 ±0.001	0.0011 ±0.001	0.0002±0.001	0.0005±0.001
12	0.0002 ±0.001	0.0001±0.0001	0.0002±0.001	0.0002±0.004	0.0006±0.002	0.0001±0.001	0.0001 ±0.001	0.0001 ±0.001	0.0010 ±0.001	0.0001 ±0.001	0.0004±0.001	0.0001±0.001
13	0.0001 ±0.001	0.0001±0.0001	0.0002±0.0001	0.0001±0.003	0.0002±0.003	0.0001±0.001	0.0002 ±0.001	0.0017 ±0.001	0.0001 ±0.001	0.0001 ±0.001	0.0002±0.001	0.0002±0.001
14	0.0001 ±0.0001	0.0001±0.0001	0.0018±0.001	0.0002±0.003	0.0007±0.002	0.0002±0.001	0.0003 ±0.001	0.0018 ±0.001	0.0011 ±0.001	0.0003 ±0.001	0.0002±0.001	0.0001±0.001
Av	0.0277	0.0168	0.0213	0.0190	0.0224	0.0165	0.0170	0.0287	0.0220	0.0206	0.0158	0.0141
mx	0.1654	0.0892	0.1253	0.1014	0.1126	0.0852	0.0853	0.1076	0.1013	0.1426	0.0733	0.0619
mn	0.0001	0.0000	0.0002	0.0001	0.0002	0.0000	0.0000	0.0001	0.0000	0.0000	0.0001	0.0001

The bold value indicates that it exceeds the WHO, 2011 standard value for drinking.

Table 3. Drinking and irrigation water quality indices for heavy metals

Sites	Drinking Water					Irrigation water			
	∑WiQi	∑Wi	HPI	HEI	MI	∑WiQi	∑Wi	HPI	HEI
1	2247.825	1.776	1265.820	25.518	25.518	1036.466	0.143	7235.368	3.341
2	3649.332	1.776	2055.052	40.598	40.598	1228.251	0.143	8574.178	5.730
3	581.181	1.776	327.281	2.958	2.958	828.532	0.143	5783.822	1.189
4	17073.173	1.776	9614.433	179.380	179.380	1824.018	0.143	12733.110	14.036
5	997.642	1.776	561.803	11.346	11.346	830.179	0.143	5795.316	11.346
6	6731.455	1.776	3790.691	74.128	74.128	1437.058	0.143	10031.818	9.376
7	13437.781	1.776	7567.231	142.824	142.824	1580.421	0.143	11032.607	11.545
8	512.795	1.776	288.771	3.967	3.967	849.974	0.143	5933.501	3.967
9	639.446	1.776	360.092	5.150	5.150	890.650	0.143	6217.452	1.810
10	548.3670	1.776	308.804	0.755	0.755	891.875	0.143	6226.004	0.203
11	572.302	1.776	322.281	3.237	3.237	890.936	0.143	6219.452	0.273
12	569.194	1.776	320.531	0.333	0.333	908.918	0.143	6344.981	0.013
13	562.349	1.776	316.676	0.473	0.473	893.442	0.143	6236.942	0.178
14	565.0420	1.776	318.192	0.774	0.774	892.603	0.143	6231.086	0.190
Mean	3477.706	1.776	1958.404	35.103	35.103	1070.238	0.143	7471.117	4.5142

3.4. The Metal Index (MI) and the Heavy Metal Evaluation Index (HEI)

In this study, HEI values to water for drinking purpose ranged from 0.333 to 179.38 with a mean value of 35.103; and while the values of water for irrigation use ranged from 0.013 to 14.036 with a mean value of 4.5142. The mean values of HEI for both drinking and irrigation waters are greater than 1 indicate that the water is ‘unfit’ for domestic usage. According to the classification proposed by Edet and Offiong (2002), 5 sampling sites (1, 2, 4, 6 and 7) were categorized as high polluted (HEI > 20); sampling site 5 (10 < HEI < 20) was classified as moderately polluted; and the remaining 8 sampling sites (3, 8, 9, 10,11,12, 13 and 14) were categorized as less polluted for drinking water. Regarding the MI values, the maximum value in the investigated water was 179.38and 14.036for drinking and irrigation water, respectively. Nevertheless, the minimum MI values of water for drinking use was 0.333 and that of water irrigation was 0.013. The mean index values for both drinking and irrigation waters was 35.103 and 4.7 respectively. According to classifications proposed by Edet and Offiong (2002), all the sampling stations except 10, 12, 13 and 14 are polluted for drinking purpose.

3.5. The Human Health Risk Assessment

3.5.1. Noncarcinogenic Risks (HQ and HI)

The values for Chronic Daily Intake (CDI) and Hazard Quotient (HQ) of heavy metals (Mn, Fe, Ni, Co, Cu, Zn, Cd, Hg, Pb, As, Cr, and Se) for both children and adults through oral and dermal routes from Genale-Dawa River water are presented in Table 4. The HQs through oral ingestion for both children and adults were in the order: As > Cd > Mn > Cr > Hg > Se > Ni > Co > Cu > Zn > Fe, while the HQ values via the dermal route for both age groups followed the order: Cd > Hg > Mn > Pb > As > Cr > Ni > Se > Cu > Zn > Co > Fe. From the results of the present study, HQ > 1 was observed for arsenic and cadmium in children and arsenic in adults through oral ingestion. The HI values of the heavy metals for both children and adults via the ingestion route were 7.24 and 3.98, respectively. Similarly, the HI values of the heavy metals via the dermal route of exposure in both children and adults were found to be 1.87 and 0.99, indicating intolerable noncarcinogenic health risks to the public for children (HI > 1). (Table 4).

According to the finding of this study, As and Cd mainly contributed to the noncancer risks via ingestion route of exposure in children and adults. From this study, the HI values in children were higher than those for adults indicating that children would absorb more toxic chemicals like heavy metals than adults and experience more noncancer risks. The HQ values in children via ingestion for Arsenic and Cd in the present study was greater than that in the study by Maleki and Jari (2021) which was 0.78 for Arsenic and 0.016 for Cd from rural drinking water resources in Kurdistan, Iran. Moreover, the HQ value in children through ingestion for Arsenic in the present study was also greater than that in the study by Bamuwamye et al (2017) from drinking Water in Kampala, Uganda which was found to be 2.222. However, the HQ values via ingestion of Cd in children and adult of the present study was much lower than that in the study by Emanuel et al. (2022) for Cd in children (96.80) and adult (20.74) from drinking water source at south senatorial district of Anambra State, Nigeria. Emmanuel et al. (2022) also reported greater HI values for the three common toxic heavy metals: Pb, Hg and Cd at the same study area in children (236.62) and in adult (51.13) than the present study.

3.5.2. Carcinogenic Health Risks (CR):

The cancer risks were expressed in terms of incremental lifetime cancer risk (ILCR), which can be defined as the possibility that an individual may develop cancer over a 60-year lifetime due to 24-hour exposure to a potential carcinogen. In this particular study, the cancer risks (CRs) were assessed for Cd, Hg, As, Pb, Cr, and Ni, which are considered carcinogenic to humans, and the results are presented in Table 5. The CR values for heavy metals for both children and adults in this study followed the order: Cr > Cd > Pb > Ni > As > Hg through ingestion and Cr > Pb > Cd > As > Ni > Hg via dermal exposure. According to the findings of this study, the total CR values for children and adults via oral intake of water were 1.39×10^{-2} and 7.61×10^{-3}, respectively. The dermal exposure CR values for children and adults were 1.83×10^{-5} and 9.70×10^{-6}, respectively. Since the total CR via ingestion exceeds 1×10^{-4} for both age groups, there is a high risk of developing cancer in the exposed population (Table 5).

Table 4. Chronic daily intake and noncancer hazard quotients for children and adults

HM	**Conc. (mg/L)**	**CDI Ingestion (mg/kg/day)**	**CDI Dermal (mg/kg/day)**	**HQ Ingestion**		**HQ Dermal**		**Average**	
		Child	**Adult**	**Child**	**Adult**	**Child**	**Adult**	**Child**	**Adult**
Mn	0.028	0.00187	0.00103	1.23×10^{-5}	6.52×10^{-6}	0.1336	0.0735	0.246	0.1304
Fe	0.017	0.00113	0.00062	7.46×10^{-6}	3.95×10^{-6}	0.0016	0.0009	5.33×10^{-5}	2.82×10^{-5}
Ni	0.021	0.0014	0.00077	9.23×10^{-6}	4.89×10^{-6}	0.07	0.0385	0.00171	0.00091
Co	0.019	0.00127	0.0007	8.36×10^{-6}	4.43×10^{-6}	0.0423	0.0233	0.00052	0.00028
Cu	0.022	0.00147	0.00081	9.68×10^{-6}	5.13×10^{-6}	0.0368	0.0203	0.00081	0.00043
Zn	0.016	0.00107	0.00059	7.04×10^{-6}	3.73×10^{-6}	0.0036	0.002	0.00012	0.00006
Cd	0.017	0.00113	0.00062	7.46×10^{-6}	3.95×10^{-6}	1.13	0.62	0.746	0.395
Hg	0.029	0.00193	0.00106	1.27×10^{-5}	6.73×10^{-6}	0.193	0.106	0.635	0.3365
Pb	0.022	0.00147	0.00081	9.68×10^{-6}	5.13×10^{-6}	0.42	0.231	0.0739	0.0391
As	0.021	0.0014	0.00077	9.23×10^{-6}	4.89×10^{-6}	4.6667	2.5667	0.0738	0.0391
Cr	0.016	0.00107	0.00059	7.04×10^{-6}	3.73×10^{-6}	0.3567	0.1967	0.0939	0.0497
Se	0.014	0.00093	0.00051	6.16×10^{-6}	3.26×10^{-6}	0.186	0.102	0.00123	0.00065
HI = ΣHQ						**7.2413**	**3.9829**	**1.8725**	**0.9921**

Note: HI > 1 indicates significant noncarcinogenic risk. Children are more vulnerable than adults

Table 5. Incremental lifetime cancer risks for the children and adult through ingestion

HM	**Conc.** **(mg/L)**	**CDI Ingestion (mg/kg/day)**	**CDI Dermal (mg/kg/day)**	**CSF Ingestion**	**CSF Dermal**	**CR Ingestion**		**CR Dermal**		**Average**	
		Child	**Adult**	**Child**	**Adult**	**$(mg/kg/day)^{-1}$**	**$(mg/kg/day)^{-1}$**	**Child**	**Adult**	**Child**	**Adult**
Ni	0.021	0.00140	0.00077	9.23×10^{-6}	4.89×10^{-6}	1.7	0.34	0.00238	0.00131	3.14×10^{-6}	1.66×10^{-6}
Cd	0.017	0.00113	0.00062	7.46×10^{-6}	3.95×10^{-6}	6.1	1.22	0.00689	0.00378	9.10×10^{-6}	4.82×10^{-6}
Hg	0.029	0.00193	0.00106	1.27×10^{-5}	6.73×10^{-6}	1.0	0.20	0.00193	0.00106	2.54×10^{-6}	1.35×10^{-6}
Pb	0.022	0.00147	0.00081	9.68×10^{-6}	5.13×10^{-6}	0.0085	0.0017	1.25×10^{-5}	6.89×10^{-6}	1.65×10^{-8}	8.72×10^{-9}
As	0.021	0.00140	0.00077	9.23×10^{-6}	4.89×10^{-6}	1.5	0.30	0.00210	0.00116	2.77×10^{-6}	1.47×10^{-6}
Cr	0.016	0.00107	0.00059	7.04×10^{-6}	3.73×10^{-6}	0.5	0.10	0.000535	0.000295	7.04×10^{-7}	3.73×10^{-7}
ΣCR								**0.01385**	**0.00761**	**1.83×10^{-5}**	**9.70×10^{-6}**

Risk Classification: $CR < 1 \times 10^{-6}$ = No carcinogenic risk; $CR = 1 \times 10^{-6}$ to 1×10^{-4} = Acceptable risk; $CR > 1 \times 10^{-4}$ = High carcinogenic risk

3.6. Ecotoxicological Risk Assessment of Heavy Metals in water

3.6.1. Potential Ecological Risk Index (ERI)

The calculated ERI value for all the studied heavy metals in this study area was found to be 492.59 (Table 6). Based on the methodology by Agho *et al*. (2021) and Samuel *et al*. (2020), the ERI values are categorized as ERI ≤ 150 = low ecological risk; 150 < ERI ≤ 300 = moderate ecological risk; 300 < ERI ≤ 600 = considerable ecological risk; and ERI > 600 = very high ecological risk, indicating the potential of severe ecological risks mainly attributed from various human activities. Therefore, the heavy metals from surface water samples of the Upper Genale Dawa River Basin catchment areas have a potential to pose considerable ecological risks. Similar finding was reported in Ethiopia by Seifu et al (2024) from lower Omo River water. The findings of the present study clearly indicate that the investigated heavy metals can cause serious health hazards to the exposed aquatic organisms and human beings; hence, immediate remediation strategies should be made to safeguard the riverine biota and human health at this study site.

3.6.2. Degree of Contamination (CD)

The calculated value of CD for the investigated heavy metals in this study area is presented in Table 6 and it was found to be 34.85. According to Håkanson (1980), the CD values are classified as CD < 6 = low degree of contamination; 6 ≤ CD < 12 = moderate degree of contamination; 12 ≤ CD < 24 = considerable degree of contamination; and CD ≥ 24 = very high degree of contamination. Therefore, the findings from the present study indicates that the water samples of the Upper Genale Dawa River Basin catchment areas are highly contaminated with the studied heavy metals such as Cd, Hg, Pb, As, Cr, Mn, Fe, Ni, Co, Se, Cu, and Zn. The sources of heavy metals in this study could be primarily from different human activities such as traditional (artisanal) mining, commercial mines, uncontrolled use of phosphate fertilizer and pesticides to their agricultural activities, effluents coffee processing coupled with rapid population growth and also from natural sources such as weathering of rocks. The result indicated the likely intoxication of aquatic organisms due to the synergistic effects of multiple heavy metals and hence, appropriate measures should be undertaken to reduce the levels of heavy metals below the recommended national and international regulatory guidelines.

3.6.3. Modified Degree of Contamination (mCD)

As an overall indicator of river water contamination by multiple metals, the calculated value of mCD in this study was 2.90 and portrayed in Table 6. Based on Håkanson (1980) and Acharjee *et al*. (2022), mCD values are classified as follows: mCD < 1.5 = Very low degree of contamination; 1.5 < mCD < 2 = low degree of contamination; 2 < mCD < 4 = Moderate degree of contamination; 4 < mCD < 8 = High degree of contamination; 8 < mCD < 16 = Very high degree of contamination; 16 < mCD < 32 = Extremely high degree of contamination; mCD > 32 = Ultra - high degree of contamination of the sediments, indicating severe pollution due to anthropogenic activities. Based on the above classification of mCD values, the surface water from the Upper Genale Dawa River Basin catchment areas were in moderate degree of contamination with the investigated heavy metals requiring to take immediate actions to remediate this study site and safeguard the health of marine lives and human health.

3.6.4. Pollution Load Index (PLI)

The PLI value for the studied heavy metals in the present study was found to be 0.34 as presented in Table 6. Based on the methods by Thongyuan *et al*. (2020) and Ali *et al*. (2021), the PLI < 1 implies no indication of pollution; and while PLI > 1 indicates significant heavy metal pollution. Since the value of PLI < 1, the surface water in this study area would not show any indication of significant pollution. On the other hand, the PLI values below 1 (0.012) was interpreted as low metal contamination (Seifu *et al*., 2024). Thus, the PLI value for this study (0.34) could imply that the surface water in this particular study was less contaminated with the investigated heavy metals based on this index value.

Table 6. CD, mCD, ERI, and PLI values of the heavy metals in surface water

Index	**Abbreviation**	**Calculated Value**	**Classification**	**Interpretation**
Degree of Contamination	CD	34.85	≥ 24 = Very high	Very high degree of contamination
Modified Degree of Contamination	mCD	2.90	2 < mCD < 4 = Moderate	Moderate degree of contamination
Potential Ecological Risk Index	ERI	492.59	300 < ERI ≤ 600 = Considerable	Considerable ecological risk
Pollution Load Index	PLI	0.34	< 1 = No pollution	No significant pollution

3.7. Combined Ecotoxicological Risk of Multiple Heavy Metals for Aquatic Life

While single-metal risk assessments provide valuable baseline information, aquatic organisms in natural ecosystems are almost never exposed to individual contaminants in isolation. Instead, they face complex mixtures of heavy metals that can interact in synergistic, antagonistic, or additive manners. The multi-element indices calculated in this study—Degree of Contamination (CD = 34.85), modified Degree of Contamination (mCD = 2.90), Potential Ecological Risk Index (ERI = 492.59), and Pollution Load Index (PLI = 0.34)—collectively describe the holistic toxicological burden on the riverine ecosystem of the Upper Genale Dawa River Basin. Each index offers a distinct lens through which the combined risk to aquatic life can be interpreted.

3.7.1. Interpretation of the Combined Toxic Burden

The Degree of Contamination (CD = 34.85) falls into the "very high degree of contamination" category (CD ≥ 24 according to Håkanson, 1980). This value indicates that the cumulative contamination factor from all twelve investigated heavy metals is substantially elevated above background levels. For aquatic organisms, a very high CD value implies chronic, multi-metal stress that can overwhelm physiological detoxification mechanisms. Fish, macroinvertebrates, and phytoplankton inhabiting this river system are likely experiencing simultaneous challenges to osmoregulation, enzyme function, and oxidative stress defense systems due to the combined presence of toxic metals such as Cd, Hg, Pb, and As alongside elevated concentrations of essential but potentially toxic trace metals like Mn, Cu, and Zn.

The modified Degree of Contamination (mCD = 2.90) falls into the "moderate degree of contamination" category (2 < mCD < 4). This index normalizes the total contamination by the number of metals analyzed, providing a more conservative estimate of average contamination per metal. A moderate mCD value suggests that while no single metal dominates the contamination profile to an extreme degree, the additive effects of multiple metals present at moderately elevated concentrations collectively pose a significant threat. This is particularly relevant for aquatic life because different metals target different organ systems. For example, Cd and Hg primarily affect renal and neural tissues, while Pb and As target hematological and hepatic systems. The simultaneous assault on multiple physiological pathways reduces the likelihood of compensatory survival responses in exposed biota.

The Potential Ecological Risk Index (ERI = 492.59) falls into the "considerable ecological risk" category (300 < ERI ≤ 600). This index incorporates both the concentration and the toxicological potency (through toxic response factors) of each heavy metal. The fact that the ERI approaches the "very high ecological risk" threshold (ERI > 600) is particularly alarming. Among the twelve metals analyzed, Hg, Cd, As, and Pb—all of which possess high toxic response factors—are the primary contributors to this elevated ERI value. For aquatic life, considerable ecological risk translates into observable adverse effects at the population and community levels, including reduced species diversity, shifts in community composition toward more tolerant taxa, and impairment of critical ecosystem functions such as nutrient cycling and primary production.

The Pollution Load Index (PLI = 0.34) is the only index that falls below the pollution threshold (PLI < 1 indicates no significant pollution). This apparent contradiction with the other three indices requires careful interpretation. The PLI is a multiplicative index that tends to be heavily influenced by the lowest contamination factors among the analyzed metals. In this study, several metals (e.g., Fe, Zn, Cr, Se) had concentrations near or below background levels at many sampling sites, which, when multiplied across all twelve metals, reduced the geometric mean substantially. However, the PLI's insensitivity to high contamination in a subset of metals is a known limitation. For aquatic life, the PLI should not be interpreted as indicating safety. Even if the geometric mean of contamination factors suggests no pollution, the presence of even a few highly toxic metals at elevated concentrations can cause severe ecological harm. The other three indices (CD, mCD, and ERI) are more reliable indicators of the actual risk posed to aquatic organisms in this study system.

3.7.2. Synergistic and Additive Toxicity Mechanisms

The combined risk of multiple heavy metals to aquatic life is not merely the sum of individual effects. Several interaction mechanisms can amplify toxicity in a synergistic manner, which may be occurring in the Upper Genale Dawa River Basin:

Metal–metal interference with detoxification, the presence of multiple metals can saturate metal-binding proteins such as metallothioneins. When Cd, Hg, Pb, and Cu are present simultaneously, the limited pool of metallothionein becomes preferentially bound to the metal with the highest affinity (typically Cu or Hg), leaving other metals unbound and free to exert toxicity. This mechanism effectively lowers the threshold concentration at which adverse effects appear for each individual metal.

Oxidative stress amplification: Many heavy metals induce oxidative stress through the generation of reactive oxygen species (ROS). When multiple metals are present, the cumulative ROS burden can exceed the antioxidant capacity of aquatic organisms more rapidly than any single metal alone. The resulting oxidative damage to lipids, proteins, and DNA can lead to cellular dysfunction, tissue necrosis, and organismal mortality even when each metal individually is present at sublethal concentrations.

Ionoregulatory disruption: Fish and aquatic invertebrates maintain ion homeostasis through specialized gill and epithelial transport proteins. Multiple metals—particularly Cu, Zn, Cd, and Pb—compete for binding sites on these transporters and inhibit their function. The combined effect is a severe disruption of sodium, calcium, and chloride balance, leading to ionoregulatory collapse. This mechanism is especially relevant in the soft, low-alkalinity waters typical of Ethiopian highland rivers, where ionoregulatory stress is already a challenge for native biota.

Behavioral and reproductive impairment: Sublethal concentrations of multiple heavy metals can impair feeding behavior, predator avoidance, swimming performance, and reproductive success. For example, simultaneous exposure to Pb and Hg has been shown to reduce spawning success in cyprinid fish at concentrations well below individual acute toxicity thresholds. In the Upper Genale Dawa River Basin, such behavioral effects may be reducing recruitment rates in native fish populations even if adult mortality remains low.

3.7.3. Predicted Effects on Trophic Levels

Based on the multi-index assessment (CD, mCD, and ERI all indicating moderate to very high contamination), the following effects on different trophic levels are predicted for the Upper Genale Dawa River Basin:

Phytoplankton and periphyton are these primary producers are typically the most sensitive to heavy metal mixtures. The combined contamination is likely reducing photosynthetic efficiency, chlorophyll content, and growth rates in algal communities. This may lead to decreased primary productivity, which cascades upward to reduce energy availability for higher trophic levels. Additionally, metal-induced shifts in algal community composition toward more tolerant (often less nutritious) species may alter food quality for grazers.

Macroinvertebrates such as Benthic macroinvertebrates such as mayflies (Ephemeroptera), stoneflies (Plecoptera), and caddisflies (Trichoptera)—which are typically metal-sensitive—are likely reduced in abundance or absent from the most contaminated sites (Sites 4 and 7 in particular). Their replacement by metal-tolerant taxa such as oligochaetes, chironomids, and gastropods represents a classic pollution-induced community shift. Such shifts reduce the food supply for fish that rely on sensitive insect taxa and impair ecosystem functions such as leaf litter breakdown and nutrient recycling.

The native fish fauna of the Genale Dawa River Basin, including species such as *Labeobarbus intermedius* and other cyprinids, are likely experiencing multiple sublethal effects. Histopathological alterations in gill, liver, and kidney tissues are probable given the elevated Cd, Hg, and Pb concentrations. Reduced growth rates, altered hematological parameters, and immunosuppression would increase susceptibility to disease and parasites. For piscivorous birds and mammals that prey on contaminated fish, the biomagnification of Hg and other metals through the food chain poses additional risks.

Amphibians and reptiles: If present in the study area, amphibians would be particularly vulnerable due to their permeable skin, which facilitates direct metal absorption from water. Even low concentrations of metal mixtures have been shown to cause developmental abnormalities, reduced hatching success, and behavioral impairments in amphibian larvae.

3.7.4. Comparison with Ecotoxicological Thresholds

When compared to established water quality criteria for the protection of aquatic life, the combined risk becomes even more apparent. The United States Environmental Protection Agency (USEPA) Criterion Continuous Concentration (CCC) for Cd, for example, is 0.00025 mg/L in waters of moderate hardness, while the mean Cd concentration in this study (0.017 mg/L) exceeds this threshold by a factor of 68. For Hg, the CCC is 0.000012 mg/L for the protection of chronic aquatic life exposure, while the mean concentration (0.029 mg/L) exceeds this by a factor of 2,417. The Canadian Council of Ministers of the Environment (CCME) Water Quality Guideline for the protection of aquatic life for Pb is 0.001 mg/L, and the mean Pb concentration in this study (0.022 mg/L) exceeds this by a factor of 22. These exceedances, when considered simultaneously, indicate that the combined metal mixture is highly likely to cause chronic toxicity to sensitive aquatic species.

3.7.5. Implications for Riverine Ecosystem Management

The combined ecotoxicological risk identified by the multi-element indices has several important implications for ecosystem management:

Immediate remediation priority: The "very high" CD and "considerable" ERI values indicate that the Upper Genale Dawa River Basin should be classified as a priority site for remediation. Passive management approaches (e.g., monitoring only) are insufficient given the magnitude of the combined risk.

Source identification and control: The spatial pattern of contamination—with Sites 4 and 7 showing the highest combined risk—suggests localized pollution sources (likely artisanal gold mining and wet coffee processing effluents). Targeted interventions at these source areas would be the most effective strategy for reducing the multi-metal burden on aquatic life.

Biological monitoring integration: The multi-index assessment should be complemented by biological monitoring using sentinel species. Biomarkers of metal exposure (e.g., metallothionein induction, oxidative stress enzymes, histopathology) in resident fish or transplanted caged organisms would provide direct evidence of biological effects and validate the risk indices.

Ecosystem recovery trajectory: Given the persistence of heavy metals in riverine sediments, even complete cessation of pollution inputs would result in a slow recovery trajectory. The mCD value of 2.90 (moderate) suggests that natural attenuation may eventually reduce contamination, but the CD value of 34.85 (very high) indicates that the total metal burden currently exceeds the assimilative capacity of the ecosystem. Active remediation (e.g., sediment dredging in hotspots, constructed wetlands for effluent treatment) may be necessary to accelerate recovery.

3.7.6. Summary of Combined Risk to Aquatic Life

In summary, the multi-element indices collectively demonstrate that the Upper Genale Dawa River Basin is experiencing a moderate to very high degree of combined heavy metal contamination that poses a considerable ecological risk to aquatic life. The CD (34.85) and ERI (492.59) indices are the most informative for ecological risk, both indicating conditions under which chronic toxicity, community structure alteration, and ecosystem function impairment are expected. The apparent contradiction with the PLI (0.34) highlights the importance of using multiple indices rather than relying on any single metric. For the protection of aquatic life in this river system, urgent interventions are required to reduce the input of toxic metals—particularly Hg, Cd, As, and Pb—from anthropogenic sources. Without such interventions, the long-term sustainability of the riverine ecosystem and the fisheries resources it supports remains severely compromised.

4. Conclusions

The current study presents clear evidence of significant heavy metal concentrations in the Upper Genale Dawa River Basin, revealing an alarming state of pollution. Mean concentrations for notable heavy metals included mercury (Hg) at 0.029 mg/L, manganese (Mn) at 0.028 mg/L, and lead (Pb) at 0.022 mg/L, with all sampling sites exceeding permissible limits for drinking and irrigation. As evidenced by the calculated Heavy Metal Pollution Index (HPI), which ranged from 288.77 to 9614.43, severe pollution was indicated across sampling sites, rendering the water unsuitable for both drinking and irrigation. Cadmium (Cd) and arsenic (As) posed the highest noncarcinogenic risks, particularly for children, with hazard quotient (HQ) values of 4.6667 for As and 1.1300 for Cd when ingested. The risk assessment for carcinogenic exposure indicated critical concerns, especially regarding chromium (Cr) and cadmium (Cd), with incremental lifetime cancer risk (ILCR) values illustrating a high risk for both children and adults through ingestion routes, quantified at 1.39×10^{-2} and 7.61×10^{-3}, respectively.

Moreover, as overall indicators of water pollution, the ecotoxicological risk indices that account for the synergistic impacts of multiple metals (ERI = 492.59; CD = 34.85; mCD = 2.90; PLI = 0.34) showed that the river water in this study was severely contaminated by the investigated HMs. This data underscores an urgent need for remediation efforts to mitigate exposure to these heavy metals, along with ongoing monitoring to protect community health. Mitigation measures include appropriate treatment of effluents and using phytoremediation techniques to alleviate heavy metal contaminants. As the findings align with global trends in environmental contamination, it is crucial for local authorities and policymakers to implement effective regulations and pollution control measures to ensure the safety and sustainability of water sources in the region. By doing so, the objectives of the Sustainable Development Goals would be addressed.

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