Levels of Heavy Metals and Associated Human Health Risk Assessment at the Upper Genale-Dawa River Basin of Ethiopia

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Abstract

This study investigates the concentration of heavy metals in the Upper Genale Dawa River Basin to assess water quality and potential health risks. The primary objective was to quantify the levels of heavy metals, and to evaluate the associated risks to human health, particularly concerning non-carcinogenic and carcinogenic effects. Water samples were purposely collected from 24 sites in the River Basin. Analytical techniques were utilized to measure the heavy metal concentrations, revealing the average concentrations of heavy metals followed the order of 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). Notably, areas near significant pollution sources exhibited higher concentrations, especially Mn, which peaked at 0.165 mg/L. Pollution indices (HPI, HEI, MI) indicated that water quality was compromised for both drinking and irrigation uses. Risk assessment revealed non-carcinogenic hazards (HQ and HI) primarily linked to arsenic and cadmium, presenting intolerable risks, especially for children. Carcinogenic risk evaluations indicated a high risk for developing cancer based on oral intake, while dermal exposure remained within acceptable limits. This research highlights the urgent need for monitoring and intervention strategies to mitigate heavy metal pollution in the Genale Dawa River Basin, ensuring community health and environmental safety.

Keywords: *Heavy metals, carcinogenic, Genale Dawa, Pollution, Water Quality Index (WQI), Health Risk*

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) and the socioeconomic development to people (Yildiz, 2017).Surprisingly, over 70% of the earth's surface is covered by water and only 2.5% of which is fresh that plants and animals require for survival; hence, fresh water resources such as rivers, lakes, and wetlands (Kipsang *et al*., 2024) are vital and critical resources to all forms of life on land (Anderson *et al*., 2019; Abiy *et al*., 2024; Berego*et al*., 2024). As major and extremely important freshwater resources, rivers play a critical role in supporting socioeconomic development and human well-being in providing water resources for drinking, industrial, agricultural, domestic uses, and recreational activities (AlAfify and AbdelSatar, 2022; Li *et al*., 2020). However, the issue of pollution in aquatic environment has emerged as a prominent concern in recent decades as water ecosystems act as sinks and endpoints of various pollutants from both point and non-point sources and particularly, any form of river contamination poses potential risks to human health (Ahamad *et al*., 2024; Khan *et al*., 2023; Mokarram*et al*., 2022).

River receive various toxic hazards from different sources; and primarily the issue of heavy metal pollution in river ecosystems is a global concern due to their persistence, bioaccumulation, biomagnification, and toxicity in the food chain(Khan *et al*., 2023).The heavy metals, such as Mercury (Hg), Arsenic (As), Cadmium (Cd), Lead (Pb) and Chromium (Cr) rank among the priority metals that are of great public health significance and their presence in riverswhich are significant resources as water sources for nearby communities (Khan *et al*., 2023) are known to cause kidney damage, liver failure, gastric and skin cancer, mental disorders, and harmful effects on the reproductive system of humans (Jaiswal*et al*., 2022; Zhang *et al*., 2023). Temesgen and Shewamolto (2022) also described heavy metals as a major class of pollutants in our world arising principally from natural (soil erosion, volcanic activity, precipitation) and anthropogenic (smelting, factory discharges, mineral processing, domestic wastes, agricultural practices) sources. A good understanding of heavy metal sources in the rivers play a significant role in environmental forensics in tracing the sources of chemicals to their origins and helping the investigators track down guilty parties, assess civil claims for damages; and identify strategies to mitigate long-term harm (ACS, 2017).

Protecting water resources for sustainable provision of clean, safe and secure water to humans is a critical developmental issue and has long been a goal of national and international policy worldwide (Chathuranika *et al*., 2023; Attua *et al*., 2014). Access to safe and clean water is the United Nations-backed agenda and among the 17 United Nations Sustainable Development Goal (SDG) targets to be achieved by 2030; of these the SDG-6 target is attributed to ensuring safe and accessible water and sanitation for all and related targets SDG-3 and SDG-15 are targeted to ensure health and well-being for all and safety of freshwater ecosystems, respectively (Asefa *et al*.,2024; Bhaduri *et al*.,2016). However, African nations including Ethiopia are still grappling with heavy metal pollution in water bodies due to rapid industrialization and inadequate environmental regulations, artisanal and small-scale mining activities, worsened by unplanned and informal settlements lacking proper sanitation and waste management across the continent, disproportionately affecting vulnerable populations living in poverty (Gelaye, 2024).

Undeniably, river water quality monitoring is essential, specially where the water serves as drinking water source and threatened by heavy metals as such activities form an important part of managing water resources within a particular river catchment (Giri and Singh, 2013; Meybeck, 2013). Well managed water resources of river basins play a crucial role in supporting livelihoods of residents and safeguarding human health and achieving the sustainable development goals, particularly in arid and semi-arid regions (Zhang *et al*., 2024).

Despite Ethiopia is known to have abundant river water resources, only few studies have been published regarding the heavy metal contamination levels of river basins (Jin *et al*., 2023; Assegide *et al*., 2022; Hailu *et al*., 2024; Awoke *et al*., 2016). 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 community proximity to its catchment (Kassahun and Mohamed, 2018). However; as far as our knowledge is concerned, the contamination status of heavy metals and human health risk assessments have not been conducted yet. Thus, the objective of this study is to evaluate the level of heavy metals at Genale-Dawa River Basin of Sidama Regional State and Gedio Zone of Southern Ethiopia and also assess the human health risks. This study serves as a valuable source of toxicological information regarding heavy metal contamination to regulatory bodies and various stakeholders working in public health and environmental issues at the study site. Furthermore, the research findings will also help as the baseline data to conduct further researches on heavy metal pollution status of rivers and safeguard the health of the community.

Materials and Methods

The study employed a combination of field sampling and laboratory analysis to assess the levels of heavy metals in water and sediment, 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.

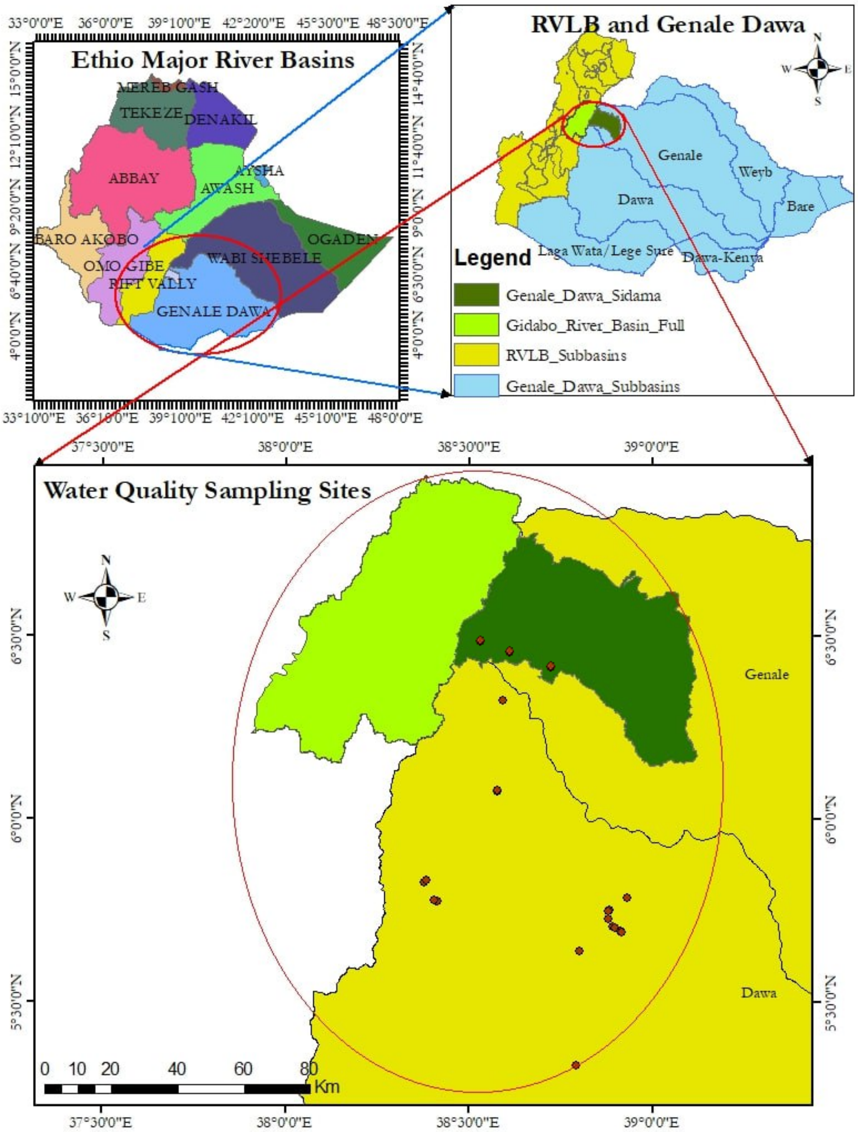

Figure 1: Sampling Sites

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 method.

The samples were then being transported to the laboratory for further analysis using inductively coupled plasma mass spectrometry (ICP-MS) to determine the concentrations of heavy metals.

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)

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi} \qquad (1)$$

$$W_i = \frac{K}{Si} \qquad (2)$$

$$K = \frac{1}{\sum(\frac{1}{\mathrm{Vstandard}})} \qquad (3)$$

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

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).

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).

$$MI = \sum_{i=1}^{n} \frac{C_i}{MAC} \quad (5)$$

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

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).

$$HEI = \sum H_C / H_{mac} \quad (6)$$

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.

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).

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):

$$CDI_{ingestion} = (C \times IR \times EF \times ED) / (BW \times AT) \quad (7)$$

$$CDI_{dermal} = (C \times EF \times ED \times ET \times SA \times KP \times CF) / (BW \times AT) \quad (8)$$

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 ($0.001 L/cm^3$) (UNEPA, 2004;Bamuwuwamye *et al.*, 2017; Govind *et al.*, 20222).

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.

$$HQ_{ingestion} = {CDI_{ingestion}}/{RfD_{ingestion}} \quad (9)$$

$$HQ_{dermal} = {CDI_{dermal}}/{RfD_{dermal}} \quad (10)$$

$$HI = \sum HQ \quad (11)$$

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); and RfD = chronic oral reference dose which is probably without a significant risk of harmful effects throughout the lifetime (Bamuwamye *et al.*, 2015). The oral reference doses ($RfD_{ingestion}$) of Pb, Ni, Co, Cu, Zn, Mn, Fe, and Cr are 0.0035, 0.02,0.03, 0.04, 0.3,0.014, 0.7, and 0.003 mg/kg/day (USEPA, 2004; USEPA, 2005; USEPA, 2016). The dermal reference doses (RfD_{dermal}) of Pb, Ni, Cu, Zn, Co, Mn, Fe, and Cr are 0.000525, 0.0054, 0.012, 0.06, 0.016, 0.00005, 0.14 and 0.000075) mg/kg/day, respectively (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).

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:

$$CR_{ingestion} = CDI_{ingestion} \times CSF_{ingestion} \quad (12)$$

$$CR_{dermal} = CDI_{dermal} \times CS_{dermal} \quad (13)$$

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).

Results and Discussions

Concentration of heavy metals in the Genale Dawa River Basin

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 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).

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 (Fissseha*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).

Table 2: Mean concentration of heavy metals (HMs) values for sampled water from the River

No	Mn	Fe	Ni	Co	Cu	Zn	Cd	Hg	Pb	As	Cr	Se
1	0.0125	0.0091	0.0112	0.0132	0.0128	0.0093	0.0118	0.0289	0.0156	0.0106	0.0192	0.0084
2	0.0190	0.0336	0.0208	0.0187	0.0329	0.0228	0.0216	0.0479	0.0289	0.0234	0.0135	0.0220
3	0.0001	0.0001	0.0005	0.0005	0.0007	0.0001	0.0011	0.0116	0.0013	0.0001	0.0001	0.0003
4	**0.1654**	0.0892	0.1253	0.1014	0.0810	0.0852	**0.0853**	**0.1076**	**0.1013**	**0.1426**	0.0733	0.0619
5	0.0061	0.0030	0.0060	0.0064	0.0045	0.0020	0.0040	0.0103	0.0093	0.0062	0.0037	0.0039
6	0.0460	0.0422	0.0501	0.0331	0.0581	0.0439	**0.0444**	0.0757	0.0567	0.0457	0.0478	0.0380
7	0.1267	0.0556	0.0765	0.0878	0.1126	0.0607	**0.0655**	0.0885	0.0761	0.0526	0.0604	0.0577
8	0.0013	0.0006	0.0017	0.0016	0.0037	0.0011	0.0010	0.0065	0.0055	0.0030	0.0012	0.0013
9	0.0020	0.0002	0.0013	0.0008	0.0003	0.0001	0.0010	0.0172	0.0081	0.0021	0.0003	0.0032
10	0.0001	0.0002	0.0008	0.0002	0.0030	0.0002	0.0002	0.0019	0.0006	0.0007	0.0010	0.0003
11	0.0076	0.0013	0.0013	0.0019	0.0024	0.0054	0.0014	0.0023	0.0024	0.0011	0.0002	0.0005
12	0.0002	0.0001	0.0002	0.0002	0.0006	0.0000	0.0000	0.0001	0.0010	0.0000	0.0004	0.0001
13	0.0001	0.0000	0.0002	0.0001	0.0002	0.0000	0.0002	0.0017	0.0000	0.0001	0.0002	0.0002
14	0.0001	0.0000	0.0018	0.0002	0.0007	0.0002	0.0003	0.0018	0.0011	0.0003	0.0002	0.0001
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 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.

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)

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

	Drinking Water					Irrigation water			
Sites	∑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

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.

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.

The human health risk assessment

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 of drinking water from Genale-Dawa River water are presented in Table 4 below. Accordingly, the HQs through oral ingestion for both children and adults were in the order of As > Cd > Mn > Cr> Hg > Se > Mn > Ni > Co > Cu > Zn > Fe; while the values to HQ 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 result in the present study, HQ > 1 was observed for Arsenic and Cd in children and Arsenic in adults through oral ingestion. The hazard quotient (HQ) values for As (5.00034) and Cd (1.23795) in children via oral intake was nontolerable risk with HQ > 1. Similarly, the HQ value in adults for As (3.67983) was greater than 1 and results in unacceptable risk. Concerning the dermal route, none of the HQ values were greater than 1 for both children and adults, but their cumulative value, hazard index was greater than 1 (HI > 1) with a potential to cause intolerable risks to exposed population groups. The HI values of the heavy metals for both children and adults via ingestion route were 7.83124 and 5.76313, respectively. Similarly, the HI values of the heavy metals via dermal route of exposure in both children and adults were found to be 1.90889 and 1.01005 indicating intolerable noncarcinogenic health risks to public (Table 4).

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

HMs	**Concentration** (mg/L)	**CDI ingestion**		**CDI dermal**		**HQ ingestion**		**HQ dermal**	
		Child	Adult	Child	Adult	Child	Adult	Child	Adult
Mn	0.028	0.00202	0.00148	$1.33*10^{-5}$	$7.04*10^{-6}$	0.14408	0.10603	0.26626	0.14089
Fe	0.017	0.00122	0.00090	$8.07*10^{-6}$	$4.27*10^{-6}$	0.00175	0.00129	$5.77*10^{-5}$	$3.05*10^{-5}$
Ni	0.021	0.00155	0.00114	$1.02*10^{-5}$	$5.42*10^{-6}$	0.07755	0.05707	0.00190	0.00100
Co	0.019	0.00138	0.00102	$9.13*10^{-6}$	$4.83*10^{-6}$	0.06918	0.05091	0.00016	$8.39*10^{-5}$
Cu	0.022	0.00163	0.00120	$1.08*10^{-5}$	$5.70*10^{-6}$	0.04078	0.03001	0.00090	0.00047
Zn	0.016	0.00120	0.00088	$4.76*10^{-5}$	$2.52*10^{-5}$	0.00400	0.00295	0.00079	0.00042
Cd	0.017	0.00124	0.00091	$8.17*10^{-6}$	$4.32*10^{-6}$	**1.23795**	0.91102	0.81705	0.43232
Hg	0.029	0.00209	0.00154	$1.38*10^{-5}$	$7.30*10^{-6}$	0.20899	0.15380	0.65684	0.34755
Pb	0.022	0.00160	0.00118	$4.23*10^{-5}$	$2.24*10^{-5}$	0.45773	0.33685	0.08056	0.04263
As	0.021	0.00150	0.00110	$9.90*10^{-6}$	$5.24*10^{-6}$	**5.00034**	**3.67983**	0.08049	0.04259
Cr	0.016	0.00115	0.00085	$7.59*10^{-6}$	$4.02*10^{-6}$	0.38352	0.28224	0.00253	0.00134
Se	0.014	0.00103	0.00076	$6.78*10^{-6}$	$3.58*10^{-6}$	0.20535	0.15112	0.00136	0.00072
HI = ∑HQ						**7.83124**	**5.76313**	**1.90889**	**1.01005**

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.

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 a 24 h 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 for humans, and the results are presented in Table 5 below. The CR values for heavy metals to 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 of water for both children and adults. The CRs of Pb, Cr, and Ni through dermal exposure to the River water. According to the findings of this study the CR values of children and adults via oral intake of water were 6.44×10^{-2} and 4.74×10^{-2}, respectively. Similarly, the CR values of both children and adults via dermal exposure of the river water were 5.01×10^{-4} and 2.65×10^{-4}, respectively.

In the study by Seifu *et al*. (2024) and Abedi *et al*. (2023), it was described that CR < 10^{-6} indicates no carcinogenic risk to human health; a CR > 1×10^{-4} indicates a high risk of developing cancer; and a CR ranging from 1×10^{-6} to 1×10^{-4} represents an acceptable risk to human health. According to this statement, the cumulative effect of the heavy metals for carcinogenic ($\sum$CR) for both children and adults via ingestion of water in this study (6.44×10^{-2} for children) and (4.74×10^{-2} for adults) have a high risk of developing cancer with regard to heavy metals as the CR values for both exposed age groups are greater than the threshold values (CR > 10^{-4}). Moreover, the dermal exposure of both children (CR $=5.01\times10^{-4}$) and adults (CR = 2.65×10^{-4}) to the river water in this study also exceeded the acceptable limit (CR = 1×10^{-4}) and with a high risk of developing cancer on the exposed population for the investigated heavy metals in this research work; and where corrective measures are required to safeguard the public health.

The CR values for both children and adults followed the order Cr > Cd > Pb > Ni > As > Hg**.** The CRs in adult was 3.47 $\times10^{-2}$ for Cr, 5.6$\times10^{-3}$ for Cd; 2.0$\times10^{-3}$ for Pb; 1.9$\times10^{-3}$ for Ni ;1.6 $\times10^{-3}$ for Arsenic and 1.5$\times10^{-3}$ for Hg. Similarly, the CRs in children were 4.72 $\times10^{-2}$ for Cr; 7.6$\times10^{-3}$ for Cd; 2.7$\times10^{-3}$ for Pb; 2.6$\times10^{-3}$ for Ni; 2.2 $\times10^{-3}$ for Arsenic; and 2.1 $\times10^{-3}$ for Hg (Table 5).

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

HMs	**Concen tration** (mg/L)	**CDI ingestion**		**CDI dermal**		**CR ingestion**		**CR dermal**	
		Child	Adult	Child	Adult	Child	Adult	Child	Adult
Ni	0.021	0.0016	0.0011	$1.02*10^{-5}$	$5.42*10^{-6}$	0.0026	0.0019	$1.74*10^{-5}$	$9.21*10^{-6}$
Cd	0.017	0.0012	0.0009	$8.17*10^{-6}$	$4.32*10^{-6}$	0.0076	0.0056	$4.98*10^{-5}$	$2.64*10^{-5}$
Hg	0.029	0.0021	0.0015	$1.38*10^{-5}$	$7.30*10^{-6}$	0.0021	0.0015	$1.38*10^{-5}$	$7.30*10^{-6}$
Pb	0.022	0.0016	0.0012	$4.23*10^{-5}$	$2.24*10^{-5}$	0.0027	0.0020	$7.19*10^{-5}$	$3.80*10^{-5}$
As	0.021	0.0015	0.0011	$9.90*10^{-6}$	$5.24*10^{-6}$	0.0022	0.0016	$3.62*10^{-5}$	$1.92*10^{-5}$
Cr	0.016	0.0012	0.0008	$7.59*10^{-6}$	$4.02*10^{-6}$	0.0472	0.0347	$3.11*10^{-4}$	$1.65*10^{-4}$
∑CR						$\mathbf{6.44*10^{-2}}$	$\mathbf{4.74*10^{-2}}$	$\mathbf{5.01*10^{-4}}$	$\mathbf{2.65*10^{-4}}$

Conclusions

The current study presents clear evidence of significant heavy metal concentrations in the 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 288.771 to 9614.433, suggested severe pollution across sampling sites, rendering the water unsuitable for both drinking and irrigation. Cadmium (Cd) and arsenic (As) posed the highest non-carcinogenic risks, particularly for children, with hazard quotient (HQ) values of 5.00034 for As and 1.23795 for Cd when ingested. Notably, the chronic daily intake and hazard index values also highlighted potential health threats, necessitating immediate intervention to address effluent discharge from local wet coffee processing industrial and gold mining activities. 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 6.44×10^{-2} and 4.74×10^{-2}, respectively. This data underscores an urgent need for remediation efforts to mitigate exposure to these heavy metals, along with ongoing monitoring to protect community health. 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.

Authors statement

Authors contributed to the work presented in the manuscript

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Data availability

All data generated or analyzed during this study are available from the corresponding author upon reasonable request.

Declarations

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

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