Contamination Levels, Source Apportionments, and Health Risks Evaluation of Heavy Metals from the Surface Water of the Riruwai Mining Area, North-Western Nigeria

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Article Info	ABSTRACT
	Mining is one of the most environmentally damaging human activities, having long-term health effects on humans. In this research, the levels of contamination, source distribution, and health risks of heavy metals to residents from drinking surface water near Riruwai mining sites were investigated. The findings of the study indicated that the heavy metal levels ranged from As (0.00–0.04 mg/L), Cd (0.00–0.04 mg/L), Cr (0.02–0.06 mg/L), Mn (0.02–0.07 mg/L), and Pb (0.00–0.05 mg/L), with mean levels of 0.02, 0.013, 0.03, 0.02, and 0.04 mg/L, respectively. The concentrations of all metals, with the exception of Mn and Cr, are higher than acceptable limits. The values of the heavy metal pollution index (*HPI*) for all the metals, with the exception of Mn, exceed the threshold limit of 100, indicating serious pollution of the surface water. This was confirmed by the results of Nemerow's pollution index (*NPI*). Multivariable analysis revealed anthropogenic and natural sources as the main sources of heavy metal contamination, with Cd, As, Cr, and Pb originating from mining activities and Mn possibly coming from parent materials. The total hazard index (*HI*) and non-cancer risk (*HQ*) values in children and adults are within acceptable limits. However, the total life cancer risks (*TLCR*) of As and Cd were higher than the tolerable limit of 1.00E-06. Therefore, heavy metals in surface water, particularly As, Cd, and Pb, should be properly monitored and a treatment program implemented to safeguard the health of local residents, especially children.

INTRODUCTION

Water is indispensable for life and is fundamental for human health and prosperity (Varol and Ekerci, 2018; Ajala et al., 2020; Sur et al., 2022). However, human activity has deteriorated its quality (Eletta, 2012; Ighalo and Adeniyi, 2020). Urbanization, industrialization, and rapid population growth have made a significant contribution to water resource pollution in recent decades, leading to serious human health issues around the world, particularly in developing nations (Adeniyi and Ighalo, 2019; Arulbalaji et al., 2019; Ghahraman et al., 2020). Heavy metal pollution of the surface water recently gained international concern because of its non-biodegradability, toxicity, and persistence (Yuan et al., 2011; Giri and Singh, 2015; Reis et al.,

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2019; Tolche, 2021). The accumulation of heavy metals can degrade water quality and pose serious health concerns for the public (Hasan et al., 2016; Nafeesa et al., 2022). Contamination of heavy metals in the surface water could be caused by both natural processes, which include weathering of minerals, volcanic eruptions, and soil leaching, and anthropogenic activities like effluent discharge from household and industry, urban storms, water runoff, landfill leachate, mining operations, atmospheric sources, and so on (Rezaei et al., 2019; Gao et al., 2020). Mining constitutes one of the most important anthropogenic sources of heavy metal pollution in surface water (Giri and Singh, 2015; Ewusi et al., 2022). Despite its importance for the economic growth of many countries, mining is one of the most environmentally damaging human activities, having long-term health effects on humans (Baeten et al., 2018; Santana et al., 2020). During mining operations, significant quantities of dangerous heavy metals are released to the environment, which could pose serious environmental and health risks (Fashola et al., 2016; Tay et al., 2019). Heavy metals may enter the human body through different routes, including direct drinking, breathing, and skin contact with contaminated media (Chowdhury et al., 2016; He et al., 2018). Heavy metal exposure, both short-term and long-term, has been linked to a number of health issues in humans, including issues with the skin, lungs, heart, kidneys, hematology, liver, and immune system (Chowdhury et al., 2016; Hu et al., 2019). For instance, extensive links between Pb and distorted pregnancy, pulmonary disease, premature membrane rupture, sexual dysfunction, and renal diseases have been well established (United States Agency for Toxic Substances and Diseases Registry, USATSDR, 1999). Cd has been linked to renal failure, and it may biochemically replace Zn in human bodies, causing high blood pressure (Rajappa et al., 2010). The problem of heavy metal contamination of surface water due to mining activities is particularly severe in developing countries like Nigeria, where environmental laws are not effectively implemented, surface water resources are not properly monitored, and illegal mining is widespread (Kenneth et al., 2017). Therefore, appropriate heavy metal monitoring and assessment approaches, particularly in the surface water near mining areas, are necessary.

The Nemerow's pollution index (*NPI*) and heavy metal pollution index (*HPI*) are two major indexing approaches for assessing the quality and heavy metal contamination levels of surface water (Sheykhi and Moore, 2012; Zakhem and Hafez, 2015; Su et al., 2022).

To efficiently and systematically control heavy metal pollution in surface water, it is necessary to identify their origins and distributions (Yuanan et al., 2020). Multivariate analysis techniques like correlation analysis, principal components analysis (*PCA*), and hierarchical cluster analysis (*HCA*) are frequently used to assess the trends in water quality and possible heavy metal contamination distributions and sources in the surface water (Boruvka et al., 2005; Pan et al., 2020). These powerful statistical techniques enabled us to differentiate between anthropogenic and geogenic heavy metal contamination sources (Wang et al., 2019; Zeng et al., 2020).

Human risk assessment is a method of estimating the likelihood of incident occurrences and the amount of potentially negative outcomes for humans from exposure to risks such as heavy metal pollution over a given time period (United States Environmental Protection Agency [USEPA], 2004; Wu et al., 2009; Wongsasuluk et al., 2014). It is an efficient technique for evaluating the association between the health of humans and the environment, which can be measured based on the levels of danger (Muhammad et al., 2011; Ma et al., 2016). Health risk assessment includes exposure assessment and cancer and non-cancer risk assessments, which correlate heavy metal levels with the likelihood of toxic effects on humans (Jiang et al., 2017; Ghahramani et al., 2020).

Riruwai is a mining community in Kano State, Northwestern Nigeria. Large scale mining began in 1979, when nearly nine hundred tons of tin and zinc ores were produced every day. The mining operations were stopped after 5 years of continuous activity (Abdullahi, 2017).

Artisanal and small-scale mining and processing of tin, columbite, lead, and other solid minerals are still going on in the area (Lambu, 2019). Several mining sites are located close to settlements and farmland where people are engaged in farming and other activities. The mining has resulted in the accumulation of various tailings heaps that have been randomly dispersed over large areas. These tailings are reprocessed and used as building materials, and the land is being used by locals for farming (Ismaila et al., 2022). Residents of the nearby communities are constantly at risk of coming into contact with toxic heavy metals through direct contact, drinking contaminated water, or eating crops that have been contaminated. Previous research conducted around the world has shown that people who live near mining areas are at an extremely high risk of being exposed to heavy metal pollution (Li et al., 2014; Irzon et al., 2018). Thus, it is essential to evaluate heavy metal pollution levels and potential health risks in surface water from the Riruwai in order to understand the extent of heavy metal contamination and protect the health of the local inhabitants. To our knowledge, no scientific study has ever been performed to investigate the levels of heavy metal pollution and their source distributions in the surface water (from the dam) of the research area. Additionally, there was no information on any potential health risks to humans from heavy metals linked to surface water consumption. The information reported in this study would be valuable in regulating and controlling the impacts of mining on surface water, and would help in educating local miners and people living near the mining area about the potential dangers of heavy metal exposure. This study will give researchers and policymakers baseline information for comparison when monitoring the environment in the area and other similar places.

MATERIALS AND METHODS

Riruwai, situated between latitudes 10°43'97" and 10°45'01" N and longitudes 8°43'3" and 8°47'39" E (Fig. 1), has a total area of 129 km² and is also called the foot slope of Jos, Plateau State (Alhaji et al., 2017; Lambu, 2019). The climate was classified as tropical savanna by the
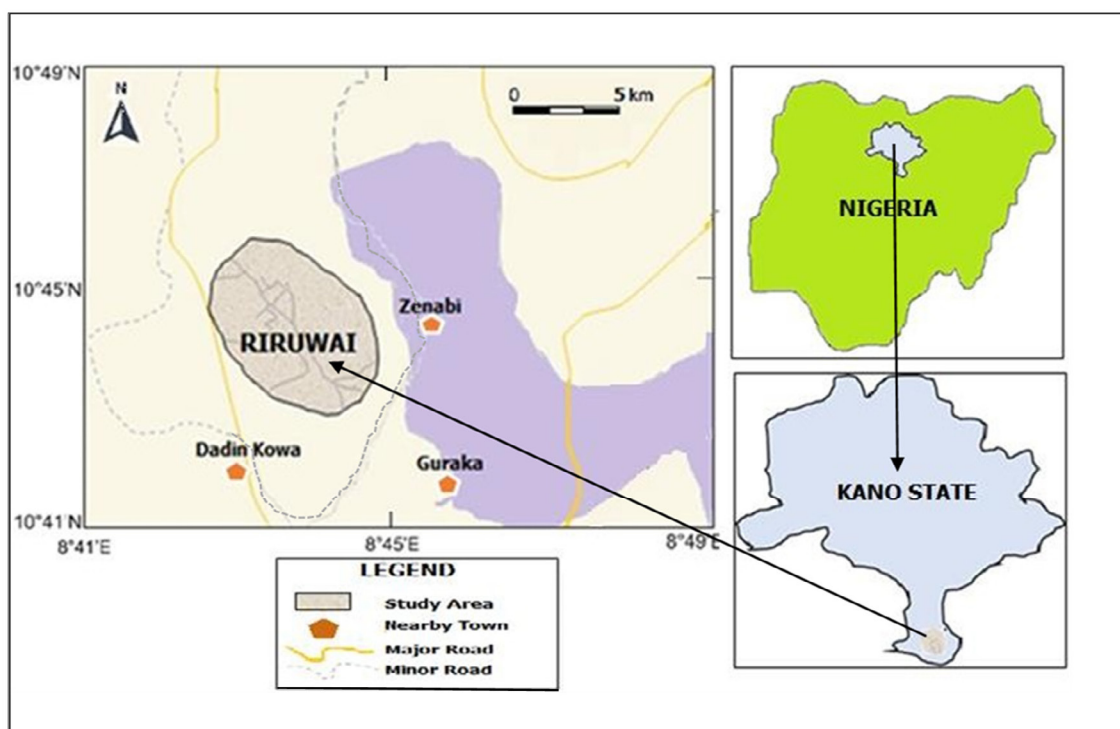

Fig. 1. Geographic map of the research area

Köppen climatic classification system. The mean annual rainfall varied between 400 and 1,200 mm each year, with a minimum temperature of 14.02 °C and a maximum temperature of 32.03 °C (Yakubu, 2016; Badamasi et al., 2021). In terms of geology, Riruwai is one of Nigeria's more recent granite complexes. The complex is an excellent example of decayed alkaline volcano roots that formed in the early Jurassic as part of a sequence of anorogenic centers that formed sequentially over time (Martin and Bowden, 1981). It is surrounded by a collection of calc-alkaline meta-igneous and metamorphic rocks that have undergone metamorphism and a Cambrian age modification (Olasehinde et al., 2012).

Surface water sampling was carried out during the rainy season (May to September, 2020). The reason for choosing the rainy season for sample collection was that previous studies had shown that heavy metal pollution is typically found to be at its highest during the rainy season as run-off water from mines leaches out a significant amount of metal from the ores, overloads surface water, and then leaches into surface water (Naz et al., 2016; Dhakate et al., 2008). A total of 21 (RSW1–RSW21) surface water samples were obtained from the dam in the vicinity of the mining area. The dam (shown in supplementary material 1) is the primary drinking water source for the people of the study area. In order to ensure the accuracy of the sampling locations, a GPS receiver (Garmin 64s, USA) was employed to record the geographical coordinates of each sampling station. Each sample was collected in duplicate at a depth of 20 cm below the surface water by dipping the polyethylene bottles into the water with an open-end facing to allow the water to flow in for each sample. Each sample was collected in a new 1000 cm^3 bottle that had been previously washed with 10 % nitric acid (HNO$_3$) and deionized water. Two bottles were used during the sampling process. In the first bottle, a few small drops of HNO$_3$ (65 %) were added to bring the pH of the samples below 2. The HNO$_3$ was added to prevent metals from adhering to container walls (American Public Health Association [APHA], 1998; Abdu et al., 2011). The first bottle's samples were used to determine heavy metals, while the second bottle's samples (without HNO$_3$) were used to measure conductivity (EC), pH, and total dissolved solids (TDS). The TDS, pH, and EC were recorded in the field using the Deluxe Water and Soil Analysis Kit (Model No. 1024 G). The surface water samples were labeled, sealed, stored in ice box cooler, and moved to the Bayero University Center for Dryland Agriculture laboratory in Kano, Nigeria, for heavy metals analysis.

To determine the heavy metal concentrations in the surface water, the samples were concentrated and digested. This was accomplished by adding 10 cm^3 of concentrated nitric acid (HNO$_3$) at 80 °C and gradually heating the samples on a hot plate until a clear solution was produced. After cooling, the digested sample was filtered using Whatman filter paper number 42 and transferred to a 100 cm^3 volumetric flask, where deionized water was added to bring the solution up to the mark (APHA, 1998). A reagent blank was prepared using a similar procedure, and concentrations of As, Cd, Cr, Mn, and Pb were measured at the wavelengths of 245.732 nm, 298.702 nm, 415.273 nm, 401.086 nm, and 407.582 nm, respectively, using a Microwave Plasma Atomic Emission Spectrometer (Model No. 4200, Agilent USA). For each metal, the limit of detection was 0.0004 mg/L for As, 0.0003 mg/L for Cd, 0.0002 mg/L for Cr, 0.0004 mg/L for Mn, and 0.0004 mg/L for Pb. The limit of detection was computed as three times the standard deviation of blank measurements.

To guarantee analytical quality control and assurance, analytical-grade chemicals were used throughout the research with no additional purification. All glassware and plastic bottles were washed three times with distilled water, immersed in a 10 % HNO$_3$ solution overnight, and oven dried. They were carefully placed on a clean surface to avoid contamination. All surface water samples were analyzed three times, and the standards purchased from Sigma-Aldrich (Missouri, USA) were sequentially diluted to produce the standard solution for each metal. After every ten samples, the standard solutions and reagent blanks were analyzed to check for instrumental performance and correct its readings. A linear calibration curve for each heavy metal was generated with regression coefficient (R^2) values of 0.9995, 0.9998, 0.9993, and 0.996 for As,

Cd, Cr, Mn, and Pb, respectively. The RSD (relative standard deviation) of each measurement was less than 10 percent. Moreover, to verify the accuracy of the analytical procedures and instrumental methods, a certified reference standard (SRM-1640a) from the National Institute of Standards and Technology (NIST, USA) was employed, and the recovery rates ranged from 94 to 106 %, which indicates good agreements between measured and certified concentrations.

To evaluate contamination levels, heavy metal pollution index (*HPI*) and Nemerow's pollution index (*NPI*) were computed. The *HPI* is an effective tool for evaluation the heavy metal contamination levels and the total quality of surface water (Singh et al., 2015; Dey et al., 2021). *HPI* was calculated using Eq. (1):

$$HPI = \frac{\sum_{i=1}^{n} W_i \times Q_i}{\sum_{i=1}^{n} W_i} \tag{1}$$

The unit weightage, or W_i, is the inverse of S_i. S_i is the WHO (2011) recommended allowable value for drinking water for the ith parameter of heavy metal (Mohan et al., 1996; Kumar et al., 2019; Uugwanga and Kgabi, 2021).

$$W_i = \frac{1}{S_i} \tag{2}$$

Q_i represents the ith parameter sub-index and is computed using Eq. (3) (Biswas et al., 2017).

$$Q_i = \frac{V_i}{S_i} \times 100 \tag{3}$$

Where V_i is the observed heavy metal concentrations, μg/L. A surface water of *HPI* greater than 100 is regarded to be seriously contaminated (Sobhanardakani et al., 2017; Khan et al., 2020; Khelfaoui et al., 2022).

The *NPI* is a powerful tool that is employed to comprehensively evaluate the contamination levels of the surface water. The tool may provide a clear understanding of the pollution level in water (Su et al., 2022). The *NPI* was computed using Eq. (4):

$$NPI = \sqrt{\frac{\left(P_1\right)^2 + P_{i\,max}^2}{2}} \tag{4}$$

P_i is the single-factor pollution index, which is employed to appraise the contamination level of only one heavy metal in the surface water samples. It is calculated using Eq. (5):

$$P_i = \frac{C_i}{S_i} \tag{5}$$

C_i denotes the measured heavy metals concentration, and S_i denotes the heavy metals permissible standard (WHO, 2011). P_i max represents the maximum single-factor pollution index. P_1 is the mean single-factor pollution index value and is computed by Eq. (6):

$$P_1 = \frac{1}{n} \sum_{i=1}^{n} P_i \tag{6}$$

The *NPI* of less than 0.59 indicates no contamination; the *NPI* between 0.59 and 0.74 indicates slight contamination; the *NPI* between 0.74 and 1 signifies light contamination; the *NPI* between 1 and 3.5 indicates moderate contamination; and the *NPI* greater than or equal to 3.5 signifies serious contamination (Duncan, 2020; Su et al., 2022).

The evaluation of human health risks (cancer and non-cancer risks) was carried out using the model recommended by the USEPA in this study. It connects the presence of contaminants in the environment with the likelihood of toxic effects on humans. Cd, As, Cr, Mn, and Pb were selected for the health risk assessment due to their potentially toxic effects on humans (Chon et al., 2011). Two pathways linked to human exposure routes are commonly used in estimating the human risks of heavy metals in surface water (Ghahramani et al., 2020). Average daily intakes for the oral (ADI_{oral}) and dermal contact (ADI_{dermal}) of surface water were calculated using Eqs. (7) and (8) described by USEPA (2004):

$$ADI_{oral} = \frac{C \times IR \times EF \times ED}{BW \times AT} \tag{7}$$

$$ADI_{dermal} = \frac{C \times SA \times K_p \times ABS \times EF \times ED \times CF}{BW \times AT} \tag{8}$$

Where, C is the experimental concentration of heavy metals. The definitions of the other parameters in equations 1 and 2 are depicted in Table 1. The K_p for Cd, As, Cr, Pb, and Mn are 0.002, 0.001, 0.0001, and 0.003, respectively (Ghahramani et al., 2020; Yakovlev et al., 2022).

The hazard index (*HQ*) represents the non-cancer risk and is computed by dividing the average daily intake of heavy metals (*ADI*, mg/kg/day) by the reference dose (*RfD*, mg/kg/day). This is accomplished using the formula in Eq. (9). If the *HQ* value exceeds one, there is a likelihood of non-cancer risks to local populations, whereas less than one is considered an acceptable level (USEPA, 1989; Wu et al., 2009; Giri and Singh, 2015).

$$HQ = \frac{ADI}{RfD} \tag{9}$$

Table 1. Parameters used for assessing health risks via the oral and dermal routes (USEPA, 2004; Hadzi et al., 2015; Ghahramani et al., 2020)

Parameter	Unit	Symbol	Human Exposure	
			Child	Adult
Body weight	Kg	*BW*	16	70
Exposure frequency	days/years	*EF*	365	365
Exposure duration	years	*ED*	6	30
Ingestion rate	kg/day	*IR*	0.0001	0.0001
Exposed skin surface area	cm^2	*SA*	7422	18182
Soil to skin adherence factor	mg/cm^2	*AF*	0.07	0.2
Dermal absorption factor		*ABS*	0.001	0.001
Conversion factor	L/cm^3	*CF*	0.001	0.001
Exposure time	(Hour/event)	*ET*	0.54	0.71
Average time (for non-cancer risk)	days	*AT*	365 × ED	365 × ED
Average time (for cancer risk)	days	*AT*	365 × 70	365 × 70

The values of *RfD* for Cd, Cr, As, Pb, and Mn are 0.003, 0.003, 0.0003, 0.0035, and 0.033 mg/kg/day, respectively. To assess the combined non-cancer risks of multiple heavy metals, the hazard index (*HI*) is computed using Eq. (10):

$$HI = \sum_{i=1}^{n} HQ \tag{10}$$

When the *HI* value is below one, it is unlikely to have any severe health consequences. However, when the value of *HI* is greater than one, detrimental health repercussions may arise (Li et al., 2014).

The total life cancer risk is usually measured by computing the lifelong cumulative risk of a person acquiring cancer after exposure to a possible human carcinogen (USEPA, 1989). It was calculated using Eq. (11).

$$TCR = ADI \times SF \tag{11}$$

Where, *SF*, mg/kg/day is the carcinogenicity slope factor. The *SF* values of heavy metals are: As (1.5), Cd (6.3), Cr (0.19), and Pb (0.008). Mn was included in the USEPA model, so it was not considered in the *TLCR* calculation (USEPA, 2011). The USEPA (2004) recommends tolerable levels of risk for carcinogens ranging from 10^{-4} (1 in 10,000) to 10^{-6} (1 in 1,000,000). Carcinogenic health risks greater than the tolerable range are considered significant and may pose significant health risks (Sultana et al., 2017).

All statistical analyses conducted using SPSS (version 23.0, USA) in this research. Origin (version 8.0, USA) was used in plotting graphs.

RESULTS AND DISCUSSION

The results of the statistical summary of the physicochemical parameters (pH, EC, and TDS) and heavy metal concentrations are presented in Table 2, and values for each sampling station are supplied in supplementary material 2. The pH varied from 6.51 to 8.01, with a slightly acidic average value of 6.99. The highest value was found at the RSW17 sampling station, while the lowest value was obtained at the RSW5. The pH levels in all of the samples are in

Table 2. Statistical summary of physico-chemical properties and heavy metal concentrations

Statistical Parameters	Parameters							
	As	Cd	Cr	Mn	Pb	pH	EC	TDS
Min.	BDL	BDL	0.01	0.02	BDL	6.51	230	145
Max.	0.04	0.04	0.06	0.07	0.05	8.01	950	520
Mean	0.02	0.013	0.03	0.04	0.02	6.99	614.33	376.52
Standard deviation	0.01	0.01	0.01	0.02	0.01	0.50	202.64	99.32
Coefficient of variation	0.74	0.90	0.41	0.37	0.83	0.07	0.33	0.264
WHO (2011)	0.01	0.003	0.05	0.4	0.01	6.5-8.5	1400	500
NSDWQ (2007)	0.01	0.003	0.05	0.2	0.01	6.6-8.5	1000	500

EC = Electrical conductivity, **TDS** = Total dissolved solids, **WHO** = World Health organization, **NSDWQ** = Nigerian Standard for Water Quality. **BDL** = Beyond the instrument detection limit. All the values are in mg/L with the exception of EC (μS/cm) and pH

the acceptable range of drinking water endorsed by the WHO (2011) and NSDWQ (2007). Comparative results were obtained by Khelfaoui et al. (2022) when they examined the pollution of surface water by heavy metals using pollution index and multivariate analysis near the Sidi Kamber abandoned mining area in Algeria. Our mean pH value is also closer to 6.8 ± 0.6 reported by Astuti et al. (2021) when they investigated the heavy metals risk in well water that surrounded the watershed area of Pangkajene, Indonesia. The slight acidity levels detected in the surface water could be caused by mine water discharges (Santana et al. 2020). The pH of water is an essential parameter for water quality, and measuring it is critical in determining water quality (Duncan et al., 2018). This is because pH controls the solubility and availability of some toxic metals in water, which could have serious consequences for aquatic organisms and the health humans (Silas et al., 2018). According to Nkansah et al. (2010), pH levels less than 6.5 are regarded as highly acidic for human consumption and might induce health concerns such as acidosis, which could harm the gastrointestinal and lymphatic systems of humans. Electrical conductivity (EC) is a measure of how well water conducts electricity and is directly related to its ionic content (Duncan, 2020), and higher EC signifies higher water pollution (Florescu et al., 2011). The values of EC varied from 230.00 to 950.00 µS/cm, with a mean value of 613.33 µS/cm. The highest value of EC was observed at RSW16, while the lowest was obtained at RSW17 stations. The values of EC in all the sampling locations are within the WHO (2011) and NSDWQ (2007) standards. Begum and Harikrishnarai (2008) reported that, the values of EC of less than 50.00 µS/cm are considered low, 50.00 to 600.00 µS/cm are considered moderate, while values more than 600.00 µS/cm are regarded as high. In the present study, 38% of sample stations had pollution levels exceeding 600.00 µS/cm, which is considered moderate. Total dissolved solids (TDS) are essential components of water quality and are mainly made up of inorganic salts dissolved in water (Mollo et al., 2022). The TDS varied from 145.00 to 520.00 mg/L. The mean value was 376.52 mg/L, which falls within the range of levels authorized by the WHO (2011) and the NSDWQ (2007) standards. Sampling points RSW8 and RSW17 recorded the highest and lowest values of TDS. According to WHO (2011) and NSDWQ (2007) recommendations, drinking water with a low TDS value (500 mg/L) is considered to be good for consumption (Astuti et al., 2021).

The levels of heavy metals in the surface water fall in the ranges of As (BDL–0.04), Cd (BDL–0.04), Cr (0.01–0.06), Mn (0.02–0.07), and Pb (BDL–0.05), with mean values of 0.02, 0.013, 0.03, 0.04, and 0.02 mg/L, respectively (Table 2). The mean values of all metals are above the WHO (2011) and NSDWQ (2007) allowable limits except for Cr and Mn. As, Cd, Cr, Mn, and Pb concentrations exceed the WHO (2011) and NSDWQ (2007) guidelines in approximately 43 %, 71 %, 5 %, 0 %, and 52 % of the sample stations, respectively (Online Resource 2). A high concentration of heavy metals exceeding WHO (2011) and NSDWQ (2007) levels was discovered at the Gidan Saru Mining Site in Zamfara State, Nigeria (Ahmad et al., 2016). Higher heavy metal concentration levels were also found in the surface water (dam) of the Klein Aub abandoned mine in Namibia (Uugwanga and Kgabi, 2021). Furthermore, Rakotondrabe et al. (2018) reported a high level of heavy metals when they investigated water quality close to the gold mining area of Bétaré-Oya, Cameroon. The coefficients of variation (CV) for Cd, As, Cr, Pb, and Mn were 0.90, 0.74, 0.41, 0.83, and 0.37, respectively. Mn has the lowest CV value, whereas Cd has the highest. The CV is used to evaluate the spatial variation characteristics and degree of heavy metal apportionment in surface water (Fan and Wang, 2017; Meng et al., 2022). A CV value larger than 0.5 suggests that the pattern of distribution of heavy metals in the surface water is not homogeneous and that there may be point source contamination from anthropogenic sources (Dahmouni et al., 2019). In this study, As, Cd, and Pb have CV values greater than 0.5. The high CV values of As, Cd, and Pb show substantial variability and could be caused by human activities (mining operations). According to Guo et al. (2012), the values of CV impacted by anthropogenic activities are relatively high, but the
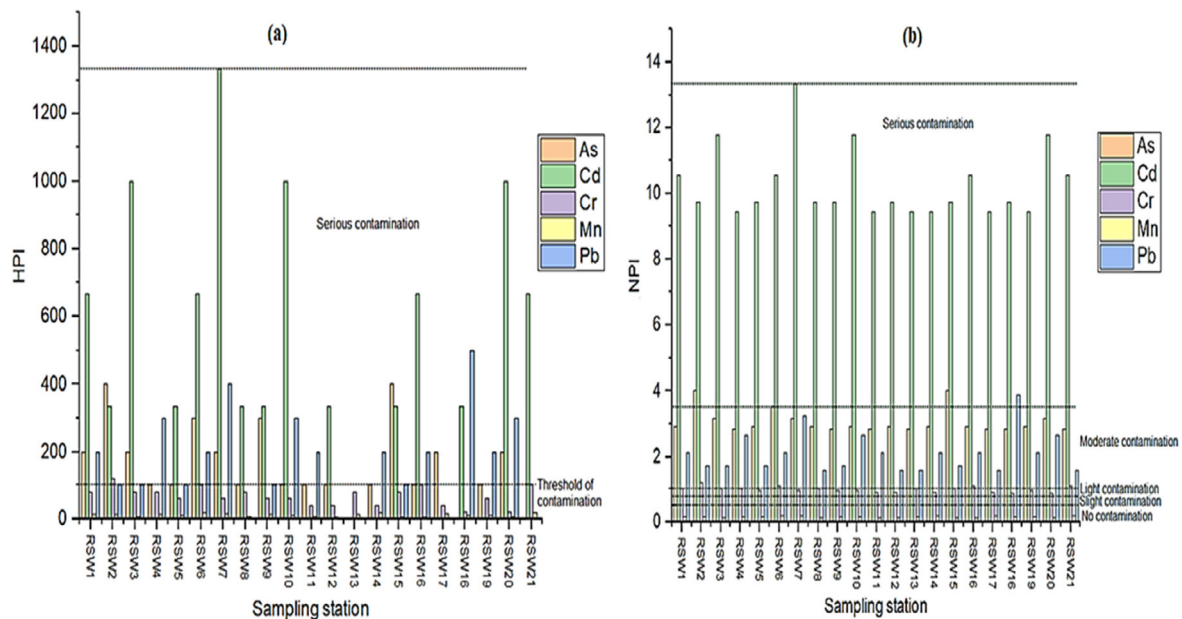
Fig. 2. Heavy pollution index, *HPI* (a) and Nemerow's pollution index, *NPI* (b) of heavy metals in the surface water

values dominated by natural sources are often low. Thus, Mn due to its low CV value might be originated from natural source.

The heavy metal pollution index (*HPI*) of heavy metals was computed to assess the degree of pollution and suitability of Riruwai surface water for drinking, and the results are shown in Figure 2. The *HPI* is a powerful tool for evaluating the overall heavy metal contamination levels of the surface water (Khan et al., 2020; Rima et al., 2022). The *HPI* values of As, Cd, Mn, and Pb ranged from 0.00 to 400.00, 0.00 to 1333.00, 20.00 to 120.00, 5.00 to 18.00, and 0.00 to 500.00, with a mean value of 119.05, 444.38, 166.67, 11.24, and 166.67, respectively (Fig. 2). With the exception of Mn, the mean *HPI* values demonstrate that all of the heavy metals examined had *HPI* values more than the threshold of 100. This indicates serious contamination of the surface water. *HPI* values greater than or equal to 100 are found in almost half of the sample locations. The specific contributions of heavy metals to high *HPI* values (*HPI* > 100) are As (86 %), Cd (71 %), Cr (19 %), Mn (0 %), and Pb (76 %). High *HPI* values (greater than 100) have been reported by Biswas et al. (2017) when they evaluated the *HPI* in the water samples from Barapukuria mine, Bangladesh. Khelfaoui et al. (2022) observed higher *HPI* values when they assessed the surface water pollution by hazardous metals in the vicinity of Sidi Kamber mine, North eastern Algeria. Piroozfar et al. (2021) also observed that the mean of the surface water they analyzed showed *HPI* values above the critical index value. High *HPI* values may be attributed to mining operations, which have directly impacted the quality of the surface water from the dam in the study area. Therefore, policymakers should seriously take into consideration such high *HPI* values because the environment and public health are in significant danger. The Nemerow's pollution index (*NPI*) of heavy metals ranged in the following order: As (2.83–4.00), Cd (9.43–13.33), Cr (0.86–1.20), Mn (0.13-0.18), and Pb (1.58–3.87). The average *NPI* values for Cd, As, Cr, Pb, and Mn are 10.26, 3.06, 0.98, 2.11 and 0.15, respectively (Fig. 2). The average *NPI* value of Cd in all the sampling stations were much higher than 3.5, indicating serious contamination. All 21 sampling points were seriously contaminated by copper. Only three of the 21 sampling points were seriously contaminated by As, and only one by Pb. No samples were contaminated with Cr or Mn. This demonstrates that heavy metals, particularly Cd, should be accorded specific consideration in this research area.

Table 3. Pearson's correlations between heavy metals and physicochemical parameters

	As	Cd	Cr	Mn	Pb	pH	EC	TDS
As	1.00							
Cd	0.36	1.00						
Cr	0.40	0.11	1.00					
Mn	-0.14	-0.04	0.17	1.00				
Pb	0.01	0.34	-0.36	0.04	1.00			
pH	-.448*	-0.23	-0.37	0.27	0.11	1.00		
EC	0.39	0.36	0.36	-0.37	0.09	-.817**	1.00	
TDS	0.31	0.13	0.33	-.468*	-0.16	-.905**	.795**	1.00

* Correlation is significant at the 0.05 level (2-tailed), ** Correlation is significant at the 0.01 level (2-tailed). The bolded numbers indicate significant values.

To identify the sources and distribution of heavy metal in the surface water, multivariable analyses like correlation, principal component, and hierarchical cluster analyses are commonly used (Zhao et al., 2011; Piroozfar et al., 2021). Pearson's correlation analysis was employed to find the possible linear interrelationships between the various heavy metals and physicochemical parameters in surface water. It is valuable since it can identify the correlations between variables that demonstrate the cohesiveness of data and define the influencing variables that assist in determining the sources of various heavy metals (Rakotondrabe et al., 2018; Ayub and Ahmad, 2020). The correlation analysis's results are depicted in Table 3. Akoglu (2018) reported that a correlation coefficient between 0.01 and 0.29 signifies a weak correlation, 0.30 to 0.69 denotes a moderate correlation, and 0.70 to 1.00 indicates a significant correlation between the parameters. In this research, pH had moderately negative correlations with As and Cr, as well as a significant negative association with EC and TDS. The significant negative correlation of pH with EC and TDS implies that when pH values are increased, the EC and TDS values will be decreased, and vice versa. Similarly, the negative correlation between pH and As and Cr indicates that these metals are only available at lower pH levels (Panaskar et al., 2016; Ayub and Ahmad, 2020). This is true since the heavy metals (As and Cr) that are responsible for increased levels of EC and TDS are only available at lower pH values. Bondu et al. (2020) reported that chemical species in an aqueous environment depend on changes in pH and redox levels. Electrical conductivity (EC) has a moderately positive relationship with As, Cd, and Cr, as well as a moderate relationship with Mn. TDS, on the other hand, is found to be moderately positively correlated with As and Cr and negatively correlated with Mn. Negative correlations were observed between EC, TDS, and pH, and moderately negative associations between As and Cr. A positive correlation existed between Cd, Cr, EC, TDS, as well as a negative association with pH. While Cd had a positive relationship with Pb and EC, Cr has a moderate relationship with Pb, pH, EC, and TDS. Contrarily, Mn does not correlate with any metal and is unaffected by pH changes. The positive association among the heavy metals could be due to their common source, as evidenced by the fact that heavy metals with a high correlation coefficient may exhibit similar behavior under similar environmental conditions (Khanorangaa and Khalid, 2019). The lack of association of Mn with other metals indicates that it came from a different source. As such, Cr, Cd, and Pb may have originated from anthropogenic activity in the area (mainly mining activities), while they could be obtained through a natural process (parent materials). Many prior studies reported that Mn in water might be controlled by parent material (Yuan et al., 2016; Zeng et al., 2009). This can be confirmed by the low Mn contents in the surface water and its low spatial variability (low CV value), as reported earlier in Table 1.

Table 4. Principal component analysis, extraction, and component matrix of heavy metals and physicochemical parameters

	Component		
Heavy Metal	1	2	3
As	0.31	**0.59**	0.34
Cd	0.14	0.27	**0.80**
Cr	0.14	**0.88**	-0.17
Mn	-0.72	0.42	0.04
Pb	-0.08	-0.34	**0.81**
pH	-0.84	-0.39	-0.06
EC	**0.83**	0.30	0.26
TDS	**0.93**	0.23	-0.07
% Eigen values	3.41	1.49	1.30
% Variance	42.57	18.62	16.19
% Cumulative	42.57	61.19	77.38

The bolded numbers indicate significant values.

Principal components analysis (PCA) is used to assess the contribution of different heavy metal sources in the surface water and to identify the dominating component(s) contributing to pollution (Egbueri et al., 2020). In PCA, factor loadings are categorized as strong if they exceed 0.70, moderate if they fall between 0.50 and 0.70, and weak if they are below 0.50 (Elhadi et al., 2017). Before performing the analysis, a test to measure sampling sufficiency called the Kaiser-Meyer-Olkin (KMO) was carried out to find out whether our data was suitable for PCA. The KMO value was found to be more than 0.5, as shown in supplementary material 3, confirming adequate sampling. Additionally, Bartlett's sphericity test yields a high significant result (p = 4.750E-07), which confirms that the correlation matrix is a nonidentity matrix. The Kaiser criterion with an eigenvalue more than one was used to identify the number of major main components. Three major components with a total variance of nearly 61.19 % were extracted (Table 4). The first component accounted for 42.57 % of the overall variation and has high EC (0.83) and TDS (0.93) loadings, whereas the second component had high As (0.59) and Cr loadings (0.88). The third component contained strong loadings of Cd (0.80) and Pb (0.81). Mn is very weakly loaded on all components, indicating a different origin from the rest of the metals. Mn could be derived from natural sources, as confirmed from our previous discussion (Tables 2 and 3). The PCA results were in accordance with the correlation analysis.

The hierarchical Cluster Analysis (HCA) analyzes the link between two variables and divides them into several clusters to show the variables' diverse environmental sources (Gao et al., 2020). HCA with the average linkage method was used in the present study to identify relationships between the heavy metals and physico-chemical characteristics of the surface water (Fig. 5). From the results of the HCA analysis, three clusters were identified. The first cluster contains As, Cd, Pb, and Cr. The second cluster is composed of Mn and pH. Finally, the third cluster consists of EC and TDS. Heavy metals converging in a single cluster are said to have common sources, while those from separate clusters are said to have different sources (Piroozfar et al., 2021). Thus, it could be concluded that As, Cd, Pb, and Cr might have come from similar anthropogenic sources, which are mining activities, whereas Mn might have originated from a natural source. The findings of HCA agreed with PCA and correlation analysis.

The assessment of health risks is an efficient technique for evaluating the connection between human health and the environment (Ma et al., 2016). It entails determining the nature and
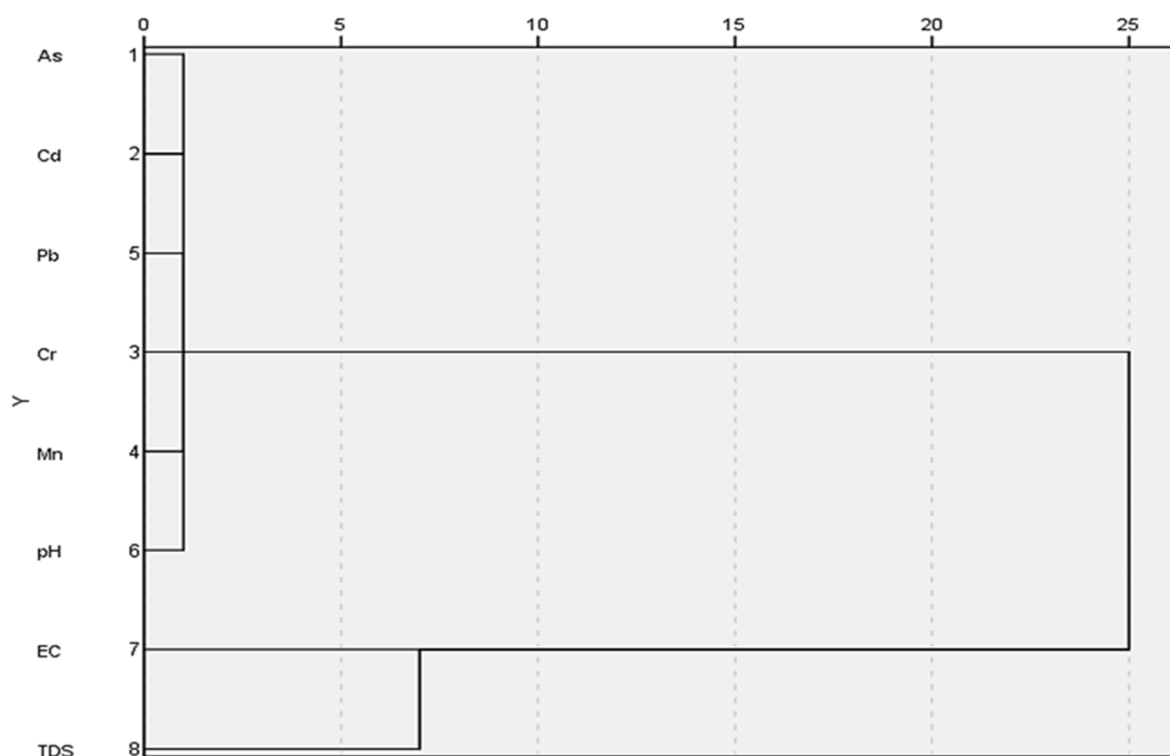
Fig. 3. Dendrogram showing clustering of heavy metals and some physicochemical parameters

severity of negative health consequences caused by hazardous substances such as heavy metals (Zakir et al., 2020). Heavy metal health risks in aquatic environments are typically assessed using two exposure pathways: direct ingestion (ADI_{ing}) and dermal contact (ADI_{dermal}) (Xie and Ren, 2022). Detailed results of the average daily exposure (ingestion and dermal) assessments used to compute cancer and non-cancer risks are given in supplementary material 4.

The non-cancer risk (*HQ*) values of heavy metals ranged as follows: As (0.00E+00 to 3.10E-02), Cd (0.00E+00 to 3.47E-03), Cr (1.21E-08 to 4.33E-03), Mn (2.25E-05 to 1.03E-03), and Pb (0.00E+00 to 3.71E-03) for children, with the mean values of 22.81E-03, 3.15E-04, 3.94E-04, 9.41E-05, and 3.37E-04, respectively. For adult population, the *HQ* values of ranged from As (0.00E+00 to 1.93E-02), Cd (0.00E+00 to 2.16E-03), Cr (0.00E+00 to 3.10E-03), Mn (1.40E-05 to 6.45E-04), and Pb (0.00E+00 to 2.31E-03), with mean values of 1.75E-03, 1.96E-04, 2.81E-04, 5.87E-05, and 2.10E-04, respectively (Figure 6). The *HQ* values in all the sampling stations are less than 1, indicating that the surface water does not cause significant non-cancer health risks to the residents of the study area. Wu et al. (2009) and Karim (2011) recorded similar observations. In both children and adults, As contributed the largest *HQ* value, representing approximately 71.1% and 70.1 % of the total risk, respectively. Mn, on the other hand, had the lowest values, corresponding to nearly 2.4 % of the total risk in adults and children, respectively. The *HQ* of heavy metals in all stations was significantly higher in children than in adults. Higher *HQ* values in children were correspondingly reported by Zhang et al. (2016); Hussain et al. (2019), and Ghahramani et al. (2020). This might be due to children's behavioral and physiological characteristics (Fan and Wang, 2017) and could be likely due to their high water consumption relative to their body weight (Ahmed et al., 2021).

To evaluate the accumulated non-cancer effects of multiple heavy metals, the Hazard Index (*HI*) was computed, and the results are presented in Figure 8. The *HI* ranged from 5.62E-05 to 5.73E-03 and 3.51E-05 to 3.39E-03 for children and adult groups, respectively. The mean *HI* values are 2.00E-03 for children and 1.40E-03 for the adult population. Children and adults

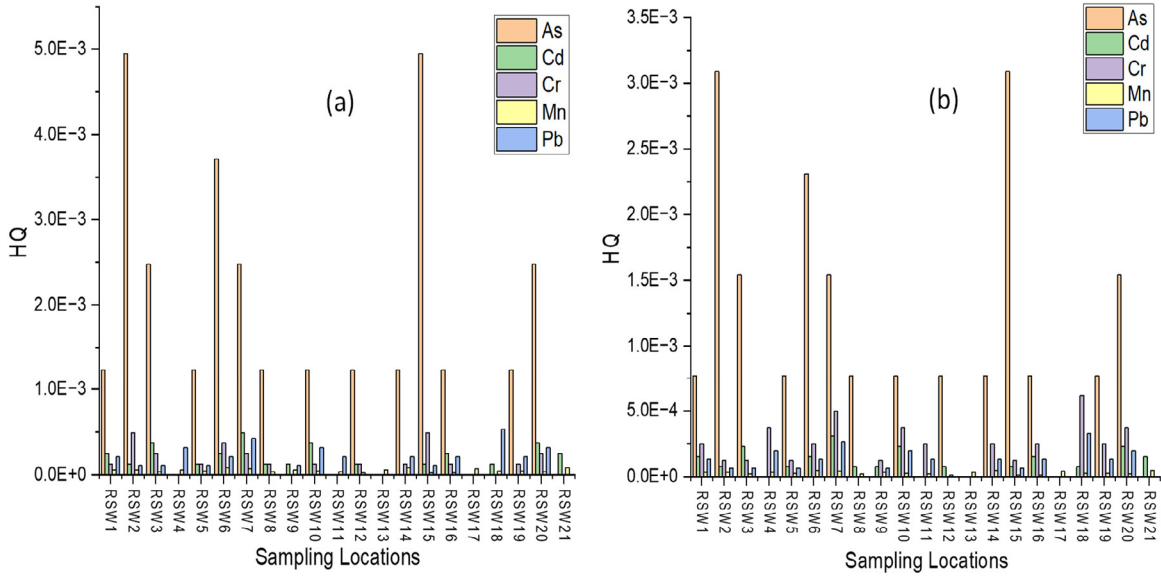**Fig. 4.** Total non-cancer risk (*HQ*) values of heavy metals for (a) children (b) adults in the surface water
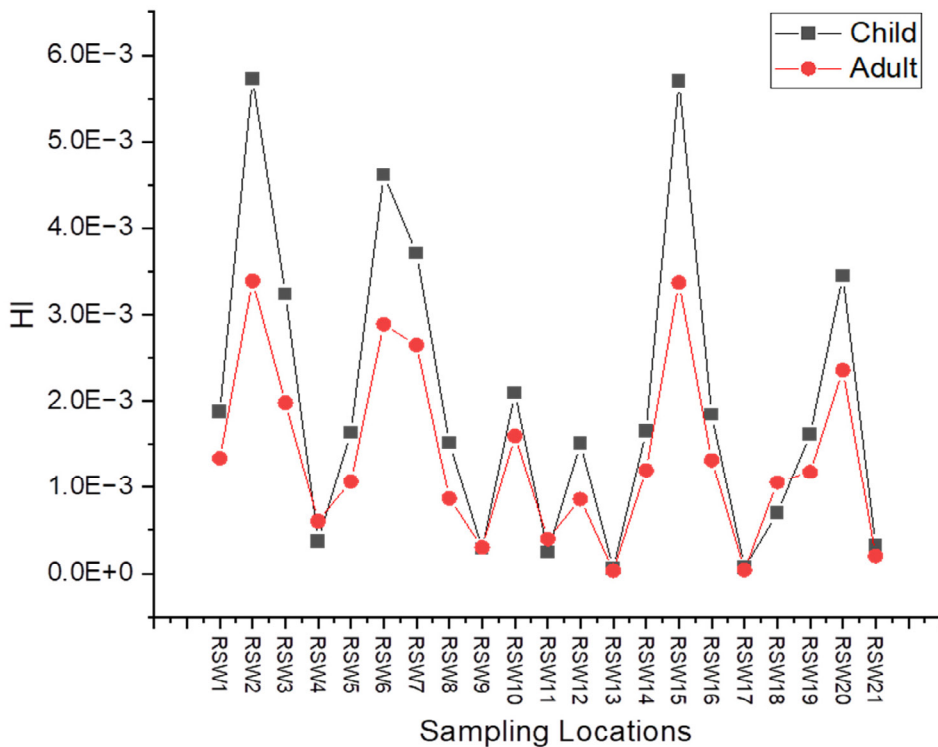

Fig. 5. Hazard Index (*HI*) of heavy metals in the surface water

had cumulative *HI* values of 4.23E-02 and 2.87E-02, respectively, accounting for 60 and 40 % of the total *HI*. The *HI* values were below the USEPA-recommended limit of 1 for all the age groups. This shows that the cumulative non-cancer effect of heavy metals is unlikely in the research area, and children are more susceptible to toxic contaminants than adults. A similar result was reported by Naz et al. (2016).
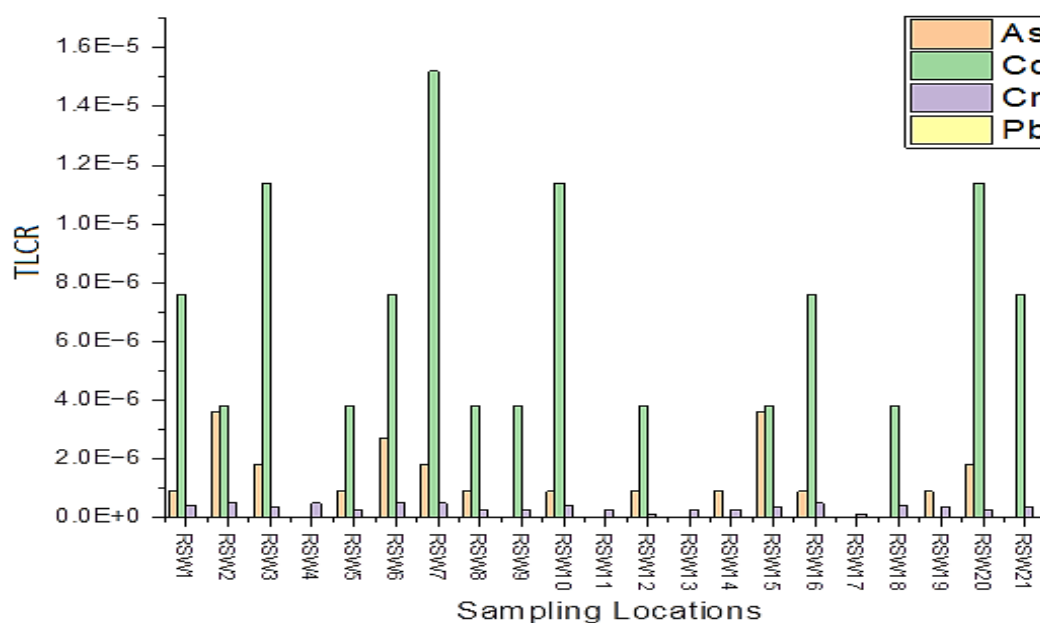
Fig. 6. Total life cancer risk values (*TLCR*) of heavy metals in the surface water

Figure 9 shows the total life cancer risk (*TLCR*) results of heavy metals in the study area. The average *TLCR* for As, Cd, Cr, and Pb, respectively, are 1.076E-06, 5.06E-06, 3.53E-07, and 8.53E-09. Cd recorded the highest risk, accounting for 77.9 % of the total risk, followed by As (16.5 %), Cr (5.4 %), and Pb (0.1 %). Selvam et al. (2022) recorded similar observations when they investigated the heavy metals risks in the surface water of the Punnakayal estuary, South India. This was also corroborated with the findings of Alidadi et al. (2019), who investigated the risks of exposure to heavy metals in the water from Mashhad, Iran. Cr and Pb had *TLCRs* that are within the tolerable range of 1.00E-04 to 1.00E-06, whereas As and Cd had *TLCR* values that are higher than the tolerable limit. As and Cd might thus be classified as probable carcinogens in the present study.

CONCLUSION

Contamination levels, sources distribution, and health risks evaluation of heavy metals in the surface water near the Riruwai mine were investigated. The findings this research reveal that, the average values of Cd, As, Pb are beyond the acceptable limits of WHO (2011) and NSDWQ (2007). The *HPI* values indicate that more than half of the sampling stations are severely contaminated by heavy metals (*HPI* > 100). This was supported by high *NPI* values. Multivariable analyses show a strong association between As, Cd, Cr, and Pb, implying a common source (mining activities). Mn, on the other hand, might have a natural origin. The *HQ* and *HI* values of all the heavy metals are below one, which indicates no potential non-cancer risk. However, the *TLCR* values of As and Cd were higher than the USEPA's tolerable limit of 1.00E-06. Therefore, it is recommended that heavy metals in surface water, particularly As, Cd, and Pb, be properly monitored and a treatment program established to safeguard the health of the local inhabitants, especially children. This research could be useful for reducing surface water pollution and establishing a baseline of data for future research in the area and other similar locations.

GRANT SUPPORT DETAILS

COMPETING OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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