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Contamination, ecological, and human health risks of heavy metals in water from a Pb–Zn–F mining area, North Eastern Nigeria

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ABSTRACT

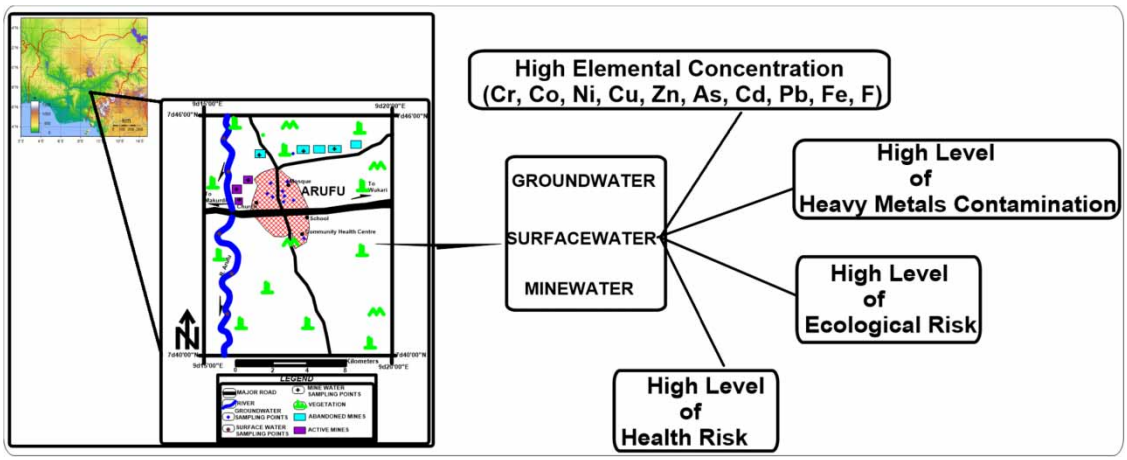
In Nigeria, artisanal mining has become a serious issue. In the Nigerian mining region of Arufu Pb–Zn–F, this study assessed the level of pollution, ecological hazards, and health risks related to the presence of metals in the water. In the dry and rainy seasons, 36 water samples (20 from the ground, 10 from the surface, and six from the mine) were gathered. Samples were examined for the presence of heavy metals such as Cr, Co, Ni, Cu, Zn, As, Cd, and Pb. Other than Cu, Zn, As, Cd, Sb, and Cd (surface water, dry season), which were below the acceptable norm, all water samples had metals over the suggested limits. Heavy metals from nearby mining activities polluted the water, according to contamination evaluations utilizing the contamination factor (CF). Metals in the water may pose very significant ecological dangers, according to ecological risk assessments. The evaluation of human health risks revealed that both adults and children in the region are susceptible to carcinogenic and non-carcinogenic health hazards since the hazard index (HI) values for both indices were above 1×10^{-5} and above 1, respectively. This report emphasizes the need for monitoring mining operations in the nation to safeguard public health.

Key words: artisanal mining, Arufu, ecological risk assessment, human health risk assessment, Pb–Zn–F deposits, water

HIGHLIGHTS

- Metal pollution of Nigeria's water is severe owing to mining activity.
- The major contributors are toxic metals, including Cr, Co, Ni, Cu, Zn, As, Cd, Pb, and Fe.
- Metals in the water pose high ecological risks in the area.
- The total HQ and HI values of metals for both oral and dermal intake were greater than 1.
- Results indicate that residents of this area, including children and adults, are susceptible to both carcinogenic and non-carcinogenic health issues.

GRAPHICAL ABSTRACT



INTRODUCTION

The survival of people, animals, and aquatic life depends on water, which is a crucial element of sustainable development (Silver 2019). Water quality is so crucial to the ecosystem. Climate change, human activity, and natural processes all have an impact on water quality. An important concern that has an impact on ecosystem health, economic growth, and human health is water quality (Adewumi & Laniyan 2021). Poor water quality can cause a number of health issues, such as skin rashes, gastrointestinal issues, and waterborne illnesses in both children and adults (Ngole-Jeme & Fantke 2017). Additionally, it may have an impact on the availability of freshwater resources, which may have an effect on residential consumption, industrial output, and agriculture. Additionally, low water quality can lead to ecological imbalances, endangering aquatic species' existence and upsetting the food chain (Belle *et al.* 2021).

A collection of substances known as heavy metals (HMs) are often found in modest amounts but are harmful to the environment. These metals include Cr, Co, Ni, As, Cd, Pb, Cu, Zn, and Mn as examples. The ecosystem and human health have been said to be negatively impacted by HMs in water. Studies conducted in developing nations, including Ghana (Hadzi *et al.* 2018), India (Bhardwaj *et al.* 2017), Cameroon (Rakotondrabe *et al.* 2018), South Africa (Dzwairo & Mujuru 2017), Bangladesh (Ahmad *et al.* 2018), and Nigeria (Adewumi & Laniyan 2021), revealed that metal contamination in water can have an impact on the health of the local population.

Mining is an important economic activity that supplies vital raw materials for advancements in industry and technology. However, mining operations have the potential to significantly degrade water quality, contaminate, and deplete freshwater supplies (Adewumi & Laniyan 2021). The impact of mining on water quality is caused by the emission of several contaminants from mining sites, including HMs, minerals, and chemicals (Abiya *et al.* 2019). Drilling, blasting, mining, ore processing, and other operations that might affect water quality are all part of the mining sector (Hadzi *et al.* 2018). These activities often include the use of water that is polluted with sediments, chemicals, and other pollutants that have the potential to affect ecosystems, human health, and aquatic life (Wang *et al.* 2015).

One of the various methods created to evaluate the effects of HMs on the environment is ecological risk assessment. It is a methodical assessment of the possible harmful impacts that pollutants might have on the environment (USEPA 2016). Several aspects need to be taken into account in order to evaluate the ecological danger of metals in water. These include the bioavailability of the metals present, the length of exposure, the frequency of exposure, and the organism's sensitivity (USEPA 2016). The most important issue is the metal content in the water since it affects how poisonous the metal could be to organisms. While low amounts may have little to no effect, metal concentrations beyond the acceptable limits can have negative consequences (USEPA 2016).

Metals in water can not only cause ecological harm but also pose a health risk to those who consume the water or use it for other purposes (Ngole-Jeme & Fantke 2017). Developmental and neurological disorders, cancer, and cardiovascular disease are just a few of the health concerns that metals like lead, arsenic, and mercury may bring on (Rakotondrabe *et al.* 2018). Determining the possible human exposure to the metals and evaluating the likelihood and seriousness of adverse health consequences are part of the health risk assessment of metals in water (USEPA 2016). Hazard identification, exposure assessment, dose-response assessment, and risk characterization are the four phases of the procedure (USEPA 2016). Finding out if a certain metal is detrimental to human health and what kind of harm it could cause entails hazard identification (Muhammad *et al.* 2011).

Artisanal mining is the most popular form of mining practice utilized in Nigeria to access precious mineral resources. In several regions of the country, anthropogenic activities have considerably contributed to the pollution of soils, stream sediments, and water. Arufu is a significant region in Nigeria's Benue Trough that has a significant deposit of lead, zinc, and fluorite, and artisanal mining of these ores is done there every day. The level of heavy metal pollution in water and the potential risks to the environment and public health have not yet been the subject of any studies. To achieve this, groundwater, surface water, and mine water samples were collected during the dry and wet seasons. All samples were examined for the presence of HMs, and the level of pollution, ecological danger, and human health risk were determined using methods that were acceptable.

MATERIALS AND METHODS

Location of the sampling area

Northeastern Nigeria's Taraba state includes the hamlet of Arufu in Wukari local government area. Its coordinates are: latitude 11°51′19.10″N, 12°15′27.05″N, longitude 5°51′27.01″E, 6°02′58.97″E. To the north of the area lies the river Benue; to

the south is Gboko, which is a significant town in Benue State; to the east is Wukari; and to the west is Akwana (Figure 1). To the west, the settlement serves as a border town, dividing Taraba State from Benue State. Between 200 and 300 meters above sea level, the area has an undulating surface. The drainage in the area is controlled by several tiny seasonal streams, including the rivers Pii and Kutaji, which originate from the River Benue. The area is characterized by a tropical wet-dry climate, and the streams are structurally controlled and typically join to form a dendritic drainage pattern.

Sample collection and preparation

Between July 2016 and January 2017, 36 water samples totaled 20 groundwater, 10 surface water, and six mine water samples. These samples were taken in July 2016 during the rainy season and January 2017 during the dry season. Control samples were collected in areas about 5 km from the study location where fewer human activities were observed. Each sample was taken and placed into clean 500-mL plastic bottles. The materials were brought into the laboratory after being preserved with HNO_3. The samples were stored in a refrigerator in the laboratory. The water was filtered using 0.45 μm filter paper before being subjected to chemical analysis. After that, analytical-grade HCl was used to lower the pH to 3.5. This method was used to reduce the number of microscopic organisms that may influence the quantity of heavy metals (HMs) in the samples.

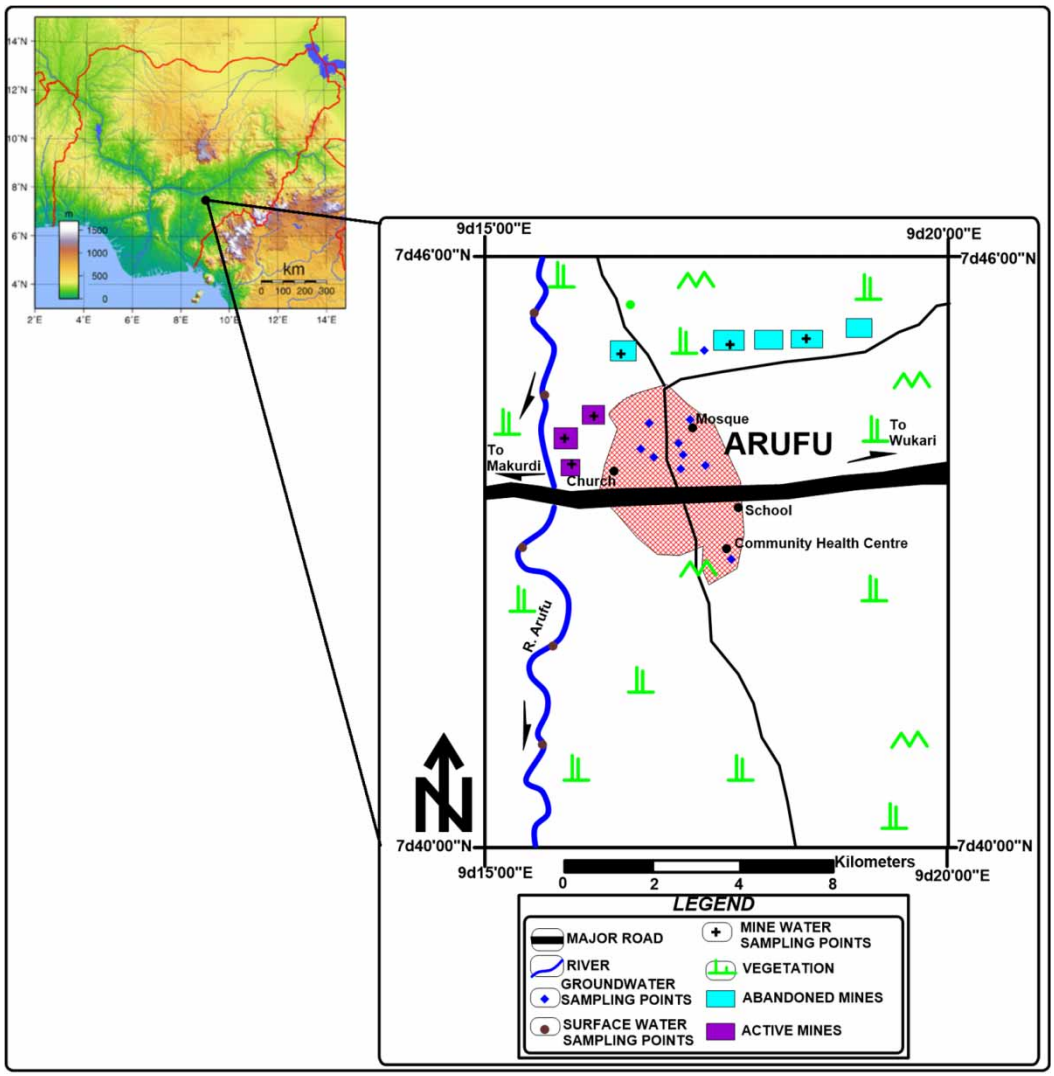


Figure 1 | Location of the sampling area.

Sample analysis

The State Key Laboratory of Environmental Geochemistry (SKLEG), Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China, used Agilent 7700 series high-performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) to measure the quantities of HMs (Fe, Cr, Co, Ni, Cu, Zn, As, Cd, Sb, Ba, and Pb) in the waters. These metals were analyzed because they are usually associated with and detected in geological formations in the area. In order to unravel the degree of mineral speciation in the different water types, according to Aqion 8.1.3, a software used to speciate minerals in water based on their physicochemical contents was employed in this area. MS Excel and SPSS were used to conduct the statistical analysis.

Quality control

For every 10 samples, an internal standard was evaluated, coupled with a calibration standard to assess the performance and effectiveness of the analytical device and a blank to continuously check for contamination. Using quality control standards, calibration curves were updated at each stage of the sample reading process. All glassware was properly cleaned with distilled water after spending the night soaking in 10% HNO_3, and it was then dried in an oven at 50–60 °C. The glassware was oven-dried first, then dried for roughly 20 min in a desiccator before use. By employing duplicates, reagent blanks, and internal standards in quality assurance and quality control methods, the analytical precision was greater than 10%.

Contamination assessment

To evaluate the degree of metal contamination in the area's water, the Geo-accumulation Index (Igeo), Contamination Factor (CF), Contamination Degree (CD), and Pollution Load Index (PLI) were utilized. Using Equation (1), the geo-accumulation index, a measure suggested by Muller (1969), was derived. Muller (1969) classified Igeo into five categories: Igeo < 0 (unpolluted); $0 \leq$ Igeo < 1 (unpolluted to moderately polluted); $1 \leq$ Igeo < 2 (moderately polluted); $2 \leq$ Igeo < 3 (moderately to heavily polluted); $3 \leq$ Igeo < 4 (heavily polluted); $4 \leq$ Igeo < 5 (heavily to extremely polluted); and Igeo < 5 (extremely polluted):

$$\text{Igeo} = \log_2 \frac{C_n}{1.5 \times B_n} \tag{1}$$

B_n is the metal concentration in the background sample, and C_n is the metal concentration in the sample. The constant 1.5 is used to reduce the impact of any background value fluctuations that can be caused by lithologic changes in the water.

The assessment of water contamination was also carried out using the CF in Equation (2). The CF is the single element index, and all four classes are recognized (Hakanson 1980). The sub-classifications of CF are: CF < 1 (low contamination factor, indicating low contamination); $1 \leq$ CF < 3 (moderate contamination factor); $3 \leq$ CF < 6 (considerable contamination factor); and $6 \leq$ CF (very high contamination factor):

$$\text{Contamination factor} = \frac{\text{Metal concentration}}{\text{Concentration of elements in background sample}} \tag{2}$$

The total number of contamination factors for all the constituents under investigation indicates the environment's CD (Hakanson 1980). There are four groups assigned to the CD. Equation (3) provides the formula for calculating CD. CD is divided into four categories: CD < 8 (low contamination degree); $8 \leq$ CD < 16 (moderate contamination degree); $16 \leq$ CD < 32 (considerable contamination degree); and CD ≥ 32 (very high contamination degree):

$$\text{Contamination degree } (C_d) = \sum_{i=1}^{n} Cf \tag{3}$$

where C_d is the contamination degree and Cf is the contamination factor.

Additionally, Thomilson *et al.* (1980) created PLI (Equation (4)). This offers a straightforward but comparable method for evaluating the quality of a site, with a value of 0 indicating no pollution; 1 indicating none to medium pollution; 2 indicating moderate pollution; 3 indicating moderate to strong pollution; 4 indicating strong pollution; 5 indicating strong to very strong

pollution; and 6 indicate very strong pollution (Rai *et al.* 2019):

$$\text{Pollution load index (PLI)} = \sqrt{Cf_1 \times Cf_2 \times Cf_3 \times \cdots \times Cf_n}n \tag{4}$$

Ecological risk assessment

Ecological risk assessment is a scientific decision-making process that assesses risks based on the presence of a physical or biological agent, the amount of a chemical, a mixture of chemicals, or an emission discharged into a given environment, the exposure of an ecological receptor, and the inherent toxicity of the agent itself (Pedrazzani *et al.* 2019). The toxic-response factor (TRi) of Cu, Zn, Cd, Cr, Ni, and Pb is 5, 1, 30, 2, and 5 (μg/g), respectively, and is used to assess heavy metal contamination in water to link biological and environmental consequences with their toxicity (Hakanson 1980). Equation (5) represents ERI:

$$Er = Tr \times Cf \tag{5}$$

where Cf is the contamination of a single element factor and Tr is the toxic-response factor.

A semi-quantitative analysis of the amount of regional pollution is determined using the Potential Ecological Risk Index (PERI). Equation (6) may be used to represent it (Wang *et al.* 2015):

$$RI = \sum_{i=1}^{n} Er \tag{6}$$

where ER is the individual element's potential ecological risk (TR for Zn = 1, Cr = 2, Cu = 5, Pb = 5, Cd = 30).

Human health risk assessment

Chronic daily intake (CDI) from drinking water was estimated using Equation (7), modified by Muhammad *et al.* (2011). Metals enter the human body through a variety of channels, with oral consumption being the most concerning one:

$$\text{CDI}\left(\frac{\mu g}{\text{kg day}}\right) = \frac{C_{MW} \times I_R}{B_W} \tag{7}$$

where I_R and B_W stand for the daily water intake rate and body weights, respectively, and C_{MW} stands for the concentrations of HMs in water.

The annual exposure due to ingestion and dermal exposure was also calculated using Equations (8) and (9) (USEPA 2016):

$$\text{EXP}_{\text{ing}} = \frac{CM_o \times I_R \times E_F \times E_D}{B_w \times AT} \tag{8}$$

$$\text{EXP}_{\text{derm}} = \frac{CM_o \times I_R \times E_F \times E_D \times S_A \times P_c \times CF}{B_W} \tag{9}$$

Such that $A_T = E_F \times E_D$

where E_F is exposure frequency (days/year) (365 days for adults and children), and I_R is the water intake rate (L/day) (2.20 and 1.10 for adults and children, respectively). EA stands for exposed skin area (cm^2) (28,080 and 10,080 for adults and children, respectively), AT stands for average exposure time (h/day) (0.52 for both adults and children), E_D stands for exposure duration (years), B_W stands for average body weight (kg) (70 kg for adults and 15 kg for children), E_F stands for exposure time (days) (10,950 and 2,190 for adults and children, respectively), and CF stands for unit conversion factor (l/cm^3) (0.001 for both adults and children). EXP(ing) and EXP(derm) are the dosage rates of exposure (in grams per kilogram per day) by ingestion and the skin, respectively. P_c stands for permeability coefficient. The P_c (cm/h) for Pb, Cr, Cd, Fe, Mn, Cu, and Zn are 4×10^{-3}, 2×10^{-3}, 1×10^{-3}, 1×10^{-3}, 1×10^{-3}, 1×10^{-3} and 6×10^{-4}, respectively.

Estimates of the danger of non-carcinogens

The hazard quotient (HQ) was established for cutaneous and oral exposure routes for non-carcinogenic health risk assessment using Equations (10) and (11), which were, respectively, adapted from USEPA (2016):

$$\text{HQ (ing)} = \frac{\text{Exp (ing)}}{\text{RD (ing)}} \tag{10}$$

$$\text{HQ (derm)} = \frac{\text{Exp (derm)}}{\text{RD (derm)}} \tag{11}$$

where the hazard quotients by ingesting and dermal contact, respectively, are HQ(ing) (unit less) and HQ(derm) (unit less). In terms of (μg/kg/day), RD(ing) and RD(derm) are reference doses (RD) for cutaneous exposure and ingestion, respectively. The non-carcinogenic impacts were calculated as the total of all the HQ owing to individual metals, which results in the hazard index (HI) if the HQ is from n separate metals (USEPA 2016). Equations (12) and (13) for ingestion and dermal exposure were used to compute the HI:

$$\text{HI (ing)} = \sum_{i=1}^{n} \text{HQ(ing)}n = \sum_{i=1}^{n} \frac{\text{Exp(ing)}n}{\text{RD(ing)}n} \tag{12}$$

where HI(ing) is the HI (unitless) via ingestion of the different metals.

$$\text{HI (derm)} = \sum_{i=1}^{n} \text{HQ(derm)}n = \sum_{i=1}^{n} \frac{\text{Exp(derm)}n}{\text{RD(derm)}n} \tag{13}$$

The hazard index (unit less) from cutaneous contact with the n distinct metals is called HI(derm). The values are HI(derm), Exp(derm), and RD(derm) for each metal, which are presented in Table 1.

Calculations of the risk of cancer

The cancer slope factor (CSF) presented in Table 1 translates the anticipated exposure from metal consumption into an incremental risk of a person acquiring cancer over time and is used to express carcinogenic health concerns (USEPA 2016). Using Equation (14), the carcinogenic health hazards of the water from various sources were estimated:

$$\text{Risk (ing)} = \frac{\text{Exp (ing)}}{\text{CSF (ing)}} \tag{14}$$

Table 1 | Reference doses and carcinogenic slope factors (CSFs) for various metals

Elements	(RD)ing (μg/kg/day)	(RD)derm (μg/kg/day)	CSF (μg/kg/day)	Reference
Pb	1.4	0.42	8×10^{0}	USEPA (2004)
Cr	3	0.075	5×10^{-2}	USEPA (2004)
Cd	0.5	0.025	6×10^{-3}	USEPA (2004)
Fe	700	140	–	USEPA (2004)
Mn	24	0.96	–	USEPA (2004)
Cu	40	8	–	USEPA (2004)
Zn	30	60	–	USEPA (2004)

RESULTS AND DISCUSSION

Concentration of HMs in water

The mean concentrations of HMs in groundwater collected during the dry season in the Arufu area were above the WHO (2017) and NSDWQ (2007) recommended limits (Table 2). For groundwater samples collected during the wet season, HMs in all samples have concentrations above the recommended limits except Cr (0.05 mg/L), which is within the required standard. In all the surface water samples collected during the dry season, the amounts of HMs in them were above the recommended limits except for Zn (0.39 mg/L), As (0.03 mg/L), Cd (0.004 mg/L), and Sb (0.01 mg/L), which have concentrations lower than the standard limits. The amount of HMs in surface water collected during the wet season was above the acceptable limits except for Sb (0.01 mg/L), Cd (0.01 mg/L), and Zn (2.38 mg/L), which are below the recommended limit. This study further showed that in all mine water samples collected, all metals were above the recommended limits except for Cd (0.02 mg/L), which is below the recommended limits. Compared to similar studies, the amount of As in groundwater from both dry and wet seasons was higher than those reported in South Africa (Belle *et al.* 2021), Ghana (Hadzi *et al.* 2018), and Anka, Nigeria (Adewumi & Laniyan 2021), but lower than those observed in Abakaliki, Nigeria (Obasi & Akudinobi 2020). Manganese levels in groundwater collected in this area during the dry season were lower than those reported in Ghana (Hadzi *et al.* 2018) and Abakaliki (Obasi & Akudinobi 2020), while those collected during the wet season were higher than those in groundwater around mining areas in Ghana (Hadzi *et al.* 2018) but lower than those reported in water from Abakaliki (Obasi & Akudinobi 2020). This study also uncovered that the amount of Cr in groundwater in this area in both seasons was higher than those in Ghana (Hadzi *et al.* 2018), while it was lower than those in water around mining areas in Abakaliki (Obasi & Akudinobi 2020) and Anka (Adewumi & Laniyan 2021). The amounts of Co, Ni, and Zn in groundwater from this area were above those reported in Ghana (Hadzi *et al.* 2018), Abakaliki (Obasi & Akudinobi 2020), and Anka (Adewumi & Laniyan 2021). The concentrations of Cu in groundwater from this area were higher than those reported in those of South Africa (Belle *et al.* 2021), Ghana (Hadzi *et al.* 2018), Abakaliki (Obasi & Akudinobi 2020), and Anka (Adewumi & Laniyan 2021), respectively. Cadmium and Pb in the groundwater of this area were lower than those found in Abakaliki, while the metals were higher than those found in South Africa (Belle *et al.* 2021), Ghana (Hadzi *et al.* 2018), and Anka (Adewumi & Laniyan 2021). The concentration of Fe in groundwater in this area was higher than those reported in water around the mining area of Anka (Adewumi & Laniyan 2021), while it was lower than those found in South Africa (Belle *et al.* 2021) and Ghana (Hadzi *et al.* 2018).

Saturation indices for all water types studied are presented in Table 3. For groundwater sampled during the wet season, saturation indices for $Fe(OH)_3$, $Al(OH)_3$, Hydroyapatite ($CaS(PO_4)_3OH$), $Cu(OH)_2$, $Ni(OH)_2$, $Pb(OH)_2$, $MnHPO_4$, and $Cr(OH)_3$ were at equilibrium, while Goethite (FeOOH), Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Diaspore (AlOOH), Boehmite (AlOOH), Gibbsite $Al(OH)_3$, Cuprousferrite ($CuFeO_2$), Tenorite (CuO), Clpyromorphite ($Pb_5(PO_4)_3Cl$), and copper metal have SI values greater than 1 (Table 3). For groundwater collected during the dry season, saturation indices for $Fe(OH)_3$, Brucite ($Mg(OH)_2$), Pyrochroite ($Mg(OH)_2$), Hydroyapatite ($CaS(PO_4)_3OH$), $Cu(OH)_2$, $Ni(OH)_2$, $Pb(OH)_2$, $Zn(OH)_2$, and Fluorite (CaF_2) were at equilibrium, while Birnessite (MnO_2), Bixbyite (Mn_2O_3), Hausmannite (Mn_3O_4), Nsutite, Goethite (FeOOH), Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Pyrolusite (MnO_2), Boehmite (AlOOH), Gibbsite $Al(OH)_3$, Cuprousferrite ($CuFeO_2$), and Tenorite (CuO) have SI values greater than 1 (Table 3). For surface water sampled during the wet season, saturation indices for $Al(OH)_3$, Alunite ($KAl_3(SO_4)_2(OH)_6$), and $MnHPO_4$ were at equilibrium, while Goethite (FeOOH), Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Diaspore (AlOOH), Boehmite (AlOOH), Gibbsite $Al(OH)_3$, Cuprousferrite ($CuFeO_2$), Clpyromorphite ($Pb_5(PO_4)_3Cl$), and $FeCr_2O_4$) had SI values greater than 1 (Table 3). For surface water collected during the wet season, saturation indices for $Fe(OH)_3$, $Al(OH)_3$, $Cu(OH)_2$, $Ni(OH)_2$, $Pb(OH)_2$, $MnHPO_4$, $Cr(OH)_3$ were at equilibrium, while Goethite (FeOOH), Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Diaspore (AlOOH), Boehmite (AlOOH), Gibbsite $Al(OH)_3$, Cuprousferrite ($CuFeO_2$), $MgCr_2O_4$, $FeCr_2O_4$, and Cu metal have SI values greater than 1 (Table 3). For mine water collected during the wet season, saturation indices for $Al(OH)_3$, Alunite ($KAl_3(SO_4)_2(OH)_6$), and $MnHPO_4$ were at equilibrium, while Goethite (FeOOH), Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Diaspore (AlOOH), Boehmite (AlOOH), Gibbsite $Al(OH)_3$, Cuprousferrite ($CuFeO_2$), and Clpyromorphite ($Pb_5(PO_4)_3Cl$) had SI values greater than 1 (Table 3). The degree of saturation might have contributed to the release of Fe, Cu, Ni, Pb, Mn, Cr, Zn, and F in the groundwater, while it might have contributed to the release of Mn, Fe, Cu, Pb, Ni, and Cr in the surface water studied in both seasons. This process might have also contributed to the release of Mn, Fe, Cu, and Pb in the mine water during the wet season. The increased degree of saturation might have been mainly due to mining activities prominent in the area. Also, geogenic processes such as weathering and

Table 2 | Physicochemical parameters in water

	Groundwater				Surface water				Mine water							
	Wet season		Dry season		Wet season		Dry season		Wet season							
Parameters	Range	Avg. (*p*-value)	Range	Avg. (*p*-value)	Range	Avg. (*p*-value)	Range	Avg. ± SD (*p*-value)	Range	Avg. (*p*-value)	WHO (2017)	NSDWQ (2007)	Control Sample	South Africa [1] GW	Ghana [2] SW	Abakaliki Nigeria [3]	Anka Nigeria [4] MW
pH	5.78–7.12	6.45 ($p < 0.01$)	5.87–7.10	6.31 ($p < 0.01$)	5.69–7.11	6.57 ($p < 0.01$)	5.62–7.24	6.54 ($p < 0.01$)	6.27–6.78	6.46 ($p < 0.01$)	6.50–8.50	6.50–8.50	6.84	-	-	-	-
EC (μS/cm)	639–1025	819.50 ($p < 0.01$)	543–718	641.80 ($p < 0.01$)	728–1125	901.33 ($p < 0.01$)	693–966	824.28 ($p < 0.01$)	527–1059	863 ($p < 0.01$)	1400	1000	597	-	-	-	-
Temp. (°C)	24.08–27.56	25.57 ($p < 0.01$)	24.58–29.05	27.03 ($p < 0.01$)	25.28–29.17	27.10 ($p < 0.01$)	25.87–29.11	27.00 ($p < 0.01$)	26.47–29.07	27.90 ($p < 0.01$)	-	-	28.08	-	-	-	-
TDS (mg/L)	365–1077	621.60 ($p < 0.01$)	556–773	631.90 ($p < 0.01$)	783–1107	958.67 ($p < 0.01$)	764–956	856.60 ($p < 0.01$)	634–986	819 ($p < 0.01$)	1000	500	749	-	-	-	-
F (mg/L)	1.93–5.35	**3.77** ($p < 0.01$)	1.36–4.63	**2.99** ($p < 0.01$)	1.71–4.16	**3.20** ($p < 0.01$)	1.98–4.89	2.60 ($p < 0.01$)	1.62–4.87	**2.69** ($p < 0.01$)	1.50	1.50	0.32	-	-	-	-
Cr (mg/L)	0.02–0.19	**0.08** ($p < 0.01$)	0.02–0.12	0.05 ($p < 0.01$)	0.01–0.27	**0.07** ($p < 0.01$)	0.03–0.06	**0.04** ($p < 0.01$)	0.02–0.05	**0.04** ($p < 0.01$)	0.05		0.001	-	0.003	0.29	0.41
Co (mg/L)	0.01–0.09	**0.16** ($p < 0.01$)	0.13–0.69	**0.33** ($p < 0.01$)	0.01–0.09	**0.06** ($p > 0.01$)	0.01–0.21	**0.10** ($p < 0.01$)	0.01–0.08	**0.04** ($p < 0.01$)	0.05	0.05	0.004	-	0.06	0.09	0.05
Ni (mg/L)	0.07–0.90	**0.43** ($p < 0.01$)	0.07–0.75	**0.53** ($p < 0.01$)	0.01–0.91	**0.40** ($p < 0.01$)	0.12–0.76	**0.51** ($p < 0.01$)	0.26–0.83	**0.53** ($p < 0.01$)	0.02	-	0.009	-	0.005	0.03	0.32
Cu (mg/L)	1.06–8.17	**4.53** ($p < 0.01$)	0.83–1.99	**1.46** ($p < 0.01$)	1.24–5.23	**3.74** ($p < 0.01$)	0.91–5.89	**2.73** ($p < 0.01$)	2.78–6.43	**4.74** ($p < 0.01$)	2.00	1.00	0.41	0.22	0.004	0.02	4.16
Zn (mg/L)	4.05–9.56	**5.84** ($p < 0.01$)	1.74–8.34	**4.77** ($p < 0.01$)	0.25–2.43	0.89 ($p < 0.01$)	0.45–3.51	2.38 ($p < 0.01$)	1.59–4.12	**3.79** ($p < 0.01$)	3.00	3.00	0.11	-	-	-	-
As (mg/L)	0.11–0.58	**0.31 ($p < 0.01$)**	0.15–0.99	**0.42** ($p < 0.01$)	0.01–0.08	0.03 ($p > 0.01$)	0.02–0.59	**0.17** ($p < 0.01$)	0.05–0.82	**0.57** ($p < 0.01$)	0.05	-	0.007	0.02	0.01	1.34	0.04
Cd (mg/L)	0.01–0.05	**0.05** ($p < 0.01$)	0.02–0.09	**0.06** ($p < 0.01$)	0.002–0.01	0.004 ($p > 0.01$)	0.01–0.02	0.01 ($p < 0.01$)	0.02–0.04	0.03 ($p < 0.01$)	0.03	0.03	0.001	-	-	0.63	0.04
Sb (mg/L)	0.01–0.07	**0.04** ($p < 0.01$)	0.05–0.06	**0.06** ($p < 0.01$)	0.01–0.02	0.01 ($p < 0.01$)	0.01–0.02	0.01 ($p < 0.01$)	0.001–0.06	**0.03** ($p < 0.01$)	0.02	-	0.0001	-	-	-	-
Ba (mg/L)	1.12–10.78	**4.28** ($p > 0.01$)	1.41–9.34	**4.33** ($p < 0.01$)	1.46–3.57	**2.41** ($p < 0.01$)	2.59–6.66	**4.21** ($p < 0.01$)	1.12–7.81	**6.06** ($p < 0.01$)	0.70	-	0.37	-	-	-	-
Pb (mg/L)	0.09–0.44	**0.44** ($p < 0.01$)	0.02–0.83	**0.46** ($p < 0.01$)	0.004–0.22	**0.07** ($p < 0.01$)	0.08–0.95	**0.30** ($p < 0.01$)	0.33–4.18	**1.84** ($p < 0.01$)	0.01	0.10	0.008	0.01	0.002	1.66	0.05
Fe (mg/L)	0.15–1.49	**0.59** ($p < 0.01$)	0.03–7.06	**2.22** ($p < 0.01$)	1.15–7.59	**2.86** ($p < 0.01$)	0.01–2.78	**0.99** ($p < 0.01$)	0.78–2.38	**1.51** ($p < 0.01$)	0.30	-	0.25	2.87	6.76	-	0.52
Mn (mg/L)	1.22–8.46	**4.21** ($p < 0.01$)	1.04–2.46	**1.61** ($p < 0.01$)	1.16–15.22	**7.43** ($p < 0.01$)	0.92–9.28	**3.67** ($p < 0.01$)	1.12–7.81	**4.13** ($p < 0.01$)	0.12	0.10	0.14	-	2.66	4.71	-

[1]: Belle *et al.* 2021; [2]: Hadzi *et al.* 2018; [3]: Obasi & Akudinshi, 2020; [4]: Adewumi & Laniyan, 2021]; GW: Groundwater; SW: Surfacewater; MW: Minewater.
Bold values indicate that the amount of elements are above the recommended limits approved by WHO (2017) and NSDWQ (2007)

Table 3 | Mineral speciation in different water types from the study area

Water type	SI = 0 (minerals equilibrium)	SI > 0 (Supersaturated)
Groundwater (Wet season)	$Fe(OH)_3$, $Al(OH)_3$, Hydroyapatite ($CaS(PO_4)_3OH$), $Cu(OH)_2$, $Ni(OH)_2$, $Pb(OH)_2$, $MnHPO_4$, $Cr(OH)_3$	Goethite (FeOOH), Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Diaspore (AlOOH), Boehmite (AlOOH), Gibbsite $Al(OH)_3$, Cuprousferrite ($CuFeO_2$), Tenorite (CuO), Clpyromorphite ($Pb_5(PO_4)_3Cl$), Cu metal (Cu)
Groundwater (Dry season)	$Fe(OH)_3$, Brucite ($Mg(OH)_2$), Pyrochroite ($Mg(OH)_2$), Hydroyapatite ($CaS(PO_4)_3OH$), $Cu(OH)_2$, $Ni(OH)_2$, $Pb(OH)_2$, $Zn(OH)_2$, Fluorite (CaF_2)	Birnessite (MnO_2), Bixbyite (Mn_2O_3), Hausmannite (Mn_3O_4), Nsutite, Goethite (FeOOH), Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Pyrolusite (MnO_2), Boehmite (AlOOH), Gibbsite $Al(OH)_3$, Cuprousferrite ($CuFeO_2$), Tenorite (CuO),
Surface water (Wet season)	$Al(OH)_3$, Alunite ($KAl_3(SO_4)_2(OH)_6$), $MnHPO_4$	Goethite (FeOOH), Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Diaspore (AlOOH), Boehmite (AlOOH), Gibbsite $Al(OH)_3$, Cuprousferrite ($CuFeO_2$), Clpyromorphite ($Pb_5(PO_4)_3Cl$), $FeCr_2O_4$
Surface water (Dry season)	$Fe(OH)_3$, $Al(OH)_3$, $Cu(OH)_2$, $Ni(OH)_2$, $Pb(OH)_2$, $MnHPO_4$, $Cr(OH)_3$	Goethite (FeOOH), Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Diaspore (AlOOH), Boehmite (AlOOH), Gibbsite $Al(OH)_3$, Cuprousferrite ($CuFeO_2$), $MgCr_2O_4$, $FeCr_2O_4$, Cu metal (Cu)
Mine water (Wet season)	$Al(OH)_3$, Alunite ($KAl_3(SO_4)_2(OH)_6$), $MnHPO_4$	Goethite (FeOOH), Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Diaspore (AlOOH), Boehmite (AlOOH), Gibbsite $Al(OH)_3$, Cuprousferrite ($CuFeO_2$), Clpyromorphite ($Pb_5(PO_4)_3Cl$)

mineral leaching may be contributing factors. According to Okereafor *et al.* (2020), mine tailings contribute a high amount of HMs to the water in mining areas. This is substantiated by Adewumi & Laniyan (2021) in their study carried out in the Anka Gold area of Nigeria. In Ghana, Hadzi (2022) affirmed that mining activities contributed significantly to the elevated concentration of HMs in groundwater. Rashid *et al.* (2023) also stressed that weathering and mineral dissolution of rocks play important roles in the presence of HMs in groundwater in the chromite mining area in Heroshah, Malakand, Pakistan.

Contamination assessment

In this study, Igeo, enrichment factor (EF), CF, CD, and PLI were employed to determine the extent of elemental contamination in water collected from the study area. The values for Igeo, EF, and CF are presented in Table 4. The range of Igeo of metals in groundwater collected during the wet season is between 0.23 (Fe) and 8.04 (Sb), respectively, while for the dry season, the range values are between 1.63 (Fe) and 7.48 (Sb) each. The groundwater assessed during the wet season was extremely contaminated by Cd, Co, and Fe. During the dry season, the groundwater was moderately to extremely contaminated by Co, while it was uncontaminated to strongly contaminated by Cu. Cadmium posed moderately-strongly to strongly-extremely high contamination, while Pb posed moderately-strongly to extremely high contamination. In this season, the samples were uncontaminated (strongly to extremely contaminated) by Fe. In both seasons, groundwater was moderately to strongly contaminated by F, while it was moderately to strongly contaminated by Mn, Ni, and Ba. They were strongly to extremely contaminated by Cr, Zn, and As, while extremely contaminated by Sb.

For surface water collected during the wet season, the range of Igeo was between 5.34 (Sb) and 0.33 (Fe), respectively, while for the dry season, it was between 1.79 (Cd) and 2.36 (F) each. Results uncovered that during the wet season, surface water was moderately to extremely contaminated by Co, Zn, Cr, Ni, Cu, As, Ba, and Pb, while during the dry season, it was uncontaminated to extremely contaminated by Cr, Co, Ni, Cu, Zn, As, Cd, Ba, and Pb each. During the dry and wet seasons, surface water was uncontaminated to extremely contaminated by F, Mn, Sb, and Fe, respectively.

For mine water, the Igeo values were between 1.58 (Fe) and 5.89 (Sb) and showed that they were moderately to strongly contaminated by F, Cu, and Fe, respectively. They were also moderately-strongly to extremely contaminated by Mn, As, and Sb, while they were strongly-extremely to extremely contaminated by Cr, Ni, and Pb, respectively. Furthermore, Igeo revealed that they were uncontaminated (moderately to strongly contaminated) by Co and Ba, while they were strongly to strongly-extremely contaminated by Zn and Cd, respectively.

Table 4 | Geo-accumulation index (Igeo), enrichment factor (EF), and contamination factor (CF) of heavy metals in water of the Arufu mining area

Index	Samples ID	Statistics	F	Mn	Cr	Co	Ni	Cu	Zn	As	Cd	Sb	Ba	Pb	Fe
Igeo	GWS	Min.	1.46	2.52	3.36	4.54	2.44	0.43	3.47	3.89	3.72	8.00	1.34	0.95	−1.27
		Max.	3.23	5.31	6.35	6.95	5.82	1.69	5.72	6.63	5.70	8.21	4.08	6.03	1.99
		Avg.	2.52	4.03	4.89	5.64	5.09	1.18	4.69	5.09	4.90	8.04	2.75	4.56	0.23
	GDS	Min.	1.97	2.28	3.28	1.24	2.42	0.79	4.69	33.41	2.56	5.58	1.00	2.78	−3.44
		Max.	3.44	3.53	6.94	6.45	6.09	3.73	5.92	5.85	5.92	8.55	4.28	6.48	4.26
		Avg.	2.86	2.84	5.39	3.91	4.53	2.58	5.16	4.69	4.59	7.48	2.66	4.69	1.63
	SWS	Min.	1.80	2.11	2.84	0.88	−0.32	1.02	0.64	0.34	0.28	4.72	1.40	−1.75	−4.73
		Max.	3.08	5.44	7.47	4.09	6.11	3.09	3.95	2.98	1.47	6.64	2.68	4.10	2.88
		Avg.	2.67	3.59	4.68	2.85	3.83	2.45	1.95	1.26	0.99	5.34	2.06	1.51	0.33
	SDS	Min.	2.00	2.44	4.07	1.18	3.14	0.57	1.51	0.70	0.31	4.72	2.22	2.65	1.61
		Max.	3.12	6.16	5.42	5.21	5.86	3.26	4.47	5.87	3.93	6.15	3.58	6.23	4.33
		Avg.	2.34	4.67	4.53	3.71	4.99	1.89	3.63	2.88	1.79	5.45	2.83	3.92	2.56
	MW	Min.	1.72	2.39	4.00	0.91	4.28	2.18	3.33	2.36	3.19	2.40	1.01	4.69	1.03
		Max.	3.31	5.19	5.15	3.83	5.98	3.39	4.71	6.37	4.47	8.27	3.81	8.37	2.65
		Avg.	2.29	3.93	2.59	2.59	5.24	2.89	4.07	5.36	3.89	5.89	3.17	6.17	1.58
CF	GWS	Min.	4.14	8.60	15.42	34.84	8.16	2.03	16.62	21.54	19.83	385.33	3.81	2.89	0.62
		Max.	14.10	59.50	122.49	185.37	84.81	4.87	79.25	144.02	78.26	444.69	25.31	98.13	5.94
		Avg.	9.14	29.62	53.53	88.24	60.11	3.57	45.32	60.25	48.31	394.60	11.68	54.70	2.32
	GDS	Min.	5.88	7.29	14.62	3.53	8.01	2.59	38.58	15.49	8.84	71.77	3.01	10.29	0.14
		Max.	16.31	17.34	184.54	130.89	102.51	19.93	90.95	84.01	90.97	560.75	29.06	134.77	28.05
		Avg.	11.50	11.35	75.64	41.72	48.91	11.05	55.55	45.18	44.63	335.19	11.55	51.99	8.81
	SWS	Min.	6.02	8.15	25.18	3.39	13.26	2.22	4.26	2.37	1.86	39.65	6.99	9.47	4.57
		Max.	13.09	107.13	64.29	55.63	87.64	14.39	33.34	85.23	22.78	106.62	17.95	112.84	30.18
		Avg.	7.94	52.25	37.37	27.32	57.57	6.65	22.54	24.99	7.88	68.87	11.36	36.32	11.37
	SDS	Min.	5.23	6.48	10.76	2.76	1.20	3.04	2.34	1.83	1.82	39.59	3.96	0.45	0.06
		Max.	12.69	65.32	265.46	25.65	103.52	12.16	23.11	11.42	4.16	149.83	9.64	25.79	11.05
		Avg.	9.74	25.86	74.45	15.69	45.39	9.13	8.50	4.27	3.09	67.98	6.49	8.08	3.97
	MW	Min.	4.93	7.86	24.00	2.82	29.31	6.79	15.09	7.44	13.79	7.92	3.01	38.74	3.08
		Max.	14.87	54.96	53.10	21.38	94.88	15.70	39.14	119.75	33.33	464.63	21.07	497.44	9.44
		Avg.	8.19	29.06	35.90	11.25	60.81	11.56	26.51	83.28	23.44	206.02	16.34	219.18	5.99

GWS, groundwater wet season; GDS, groundwater dry season; SWS, surface water wet season; SDS, surface water dry season; MW, mine water.

For groundwater collected during the wet season, EF values range between 10.50 (Cu) and 1,160.81 (Sb), while during the dry season, the values are between 31.78 (Ba) and 625.39 (Sb). This showed that groundwater during the wet and dry seasons was moderately to extremely enriched by F, Mn, Zn, As, Ba, Pb, Cr, Ni, Cd, Co, Sb, and Cu (Table 3). For surface water collected during the wet season, EF is between 12.39 (Pb) and 827.75 (Sb), while during the dry season, it is between 4.12 (Cu) and 30.15 (Mn). Surface waters assessed during the wet season were depleted to extremely enriched by F, Co, Ni, As, Cd, Mn, Cr, Cu, Zn, Ba, Pb, and Sb, while those of the dry season were moderately to significantly enriched by these metals. In mine water, the EF values range between 5.45 (F) and 132.66 (Sb), which implied that they were moderately to significantly to very highly enriched by F, Cu, Ba, Mn, and Zn. Also, mine waters in this area were significantly to extremely enriched by Cr, Ni, Cd, Sb, and Pb, while they were moderately to very highly and moderately to extremely enriched by Co and As, respectively. This showed that the water in this area is highly enriched by HMs emanating from the exploitation and processing of the Pb–Zn–F deposit within this territory, although geogenic processes may also be a major contributing factor.

For groundwater collected during the wet season, average CF values range between 3.57 (Ni) and 394.60 (Sb), while during the dry season, they are between 11.05 (Cu) and 335.19 (Sb) each. This revealed that groundwater in this area during this period was considerably to very highly contaminated by F and Ba, while it was very highly contaminated by Mn, Cr, Co, Ni, Zn, As, Cd, and Sb (Table 3). Also, they were moderately to very highly contaminated by Cu, Pb, and Fe, respectively. During the dry season, groundwater was moderately to very highly contaminated by F, Co, Ba, Mn, Cr, Ni, Zn, As, Cd, Sb, Pb, and Cu. For surface water obtained during the wet season, CF is between 7.94 (F) and 68.87 (Sb), while for the dry season, it ranges between 8.08 (Pb) and 74.45 (Cr) each. This showed that the water was lowly to very highly contaminated by F, Mn, Cr, Ni, Sb, Ba, Pb, Co, Zn, Fe, Cu, As, Cd, and Fe. For mine water, the mean CF value is between 5.99 (Fe) and 219.18 (Ba), which shows that it was moderately to very highly contaminated by F, Ba, Fe, Mn, Cr, Ni, Cu, Zn, As, Cd, Sb, Co, and Pb.

The average values of CD and PLI for HMs in groundwater (wet and dry seasons), surface water (wet and dry seasons), and mine water for the study area are presented in Figure 2. The result showed that the average CD for groundwater (wet season),

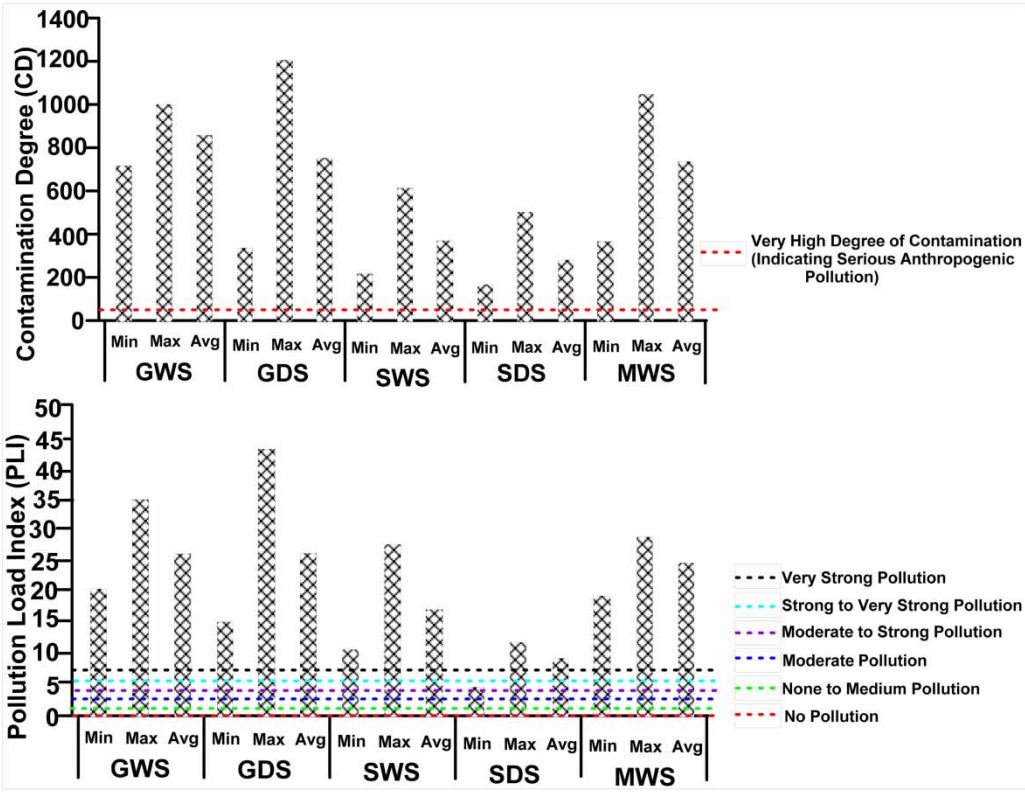


Figure 2 | Contamination degree (CD) and pollution load index (PLI) of metals in water.

groundwater (raining season), surface water (wet season), surface water (raining season), and mine water were 861.41, 753.08, 371.94, 282.63, and 737.56, respectively, while the mean PLI values were 26.41, 26.74, 17.61, 9.36, and 24.85, respectively. CD and PLI reflected that the waters in this area exhibited a very high degree of contamination and pollution caused by HMs that originated from mining activities.

Ecological risk

Results of the ecological risk assessment of HMs (Cr, Ni, Cu, Zn, Cd, and Pb) are presented in Table 5. The study showed that for the wet season, the range of Eri for Cr, Ni, Cu, Zn, Cd, and Pb in groundwater is 107.06, 300.57, 17.84, 45.32, 1,449.18, and 273.51, respectively, while during the dry season, the mean values are 151.28, 244.56, 55.25, 55.55, 1,338.76, and 259.99 each. For surface water, the average Eri for Cr, Ni, Cu, Zn, Cd, and Pb during the wet season are 74.75, 287.85, 33.27, 22.54, 236.37, and 176.59, respectively, while during the dry season, the average values are 13.92, 16.77, 6.04, 2.78, 23.80, and 25.79. For mine water, the mean Eri for Cr, Ni, Cu, Zn, Cd, and Pb are 71.80, 304.50, 57.81, 26.51, 703.28, and 1,095.89, respectively. The PERI for groundwater ranges between 1,477.57 and 2,895.25 for the wet season, while for the dry season, it is between 931.78 and 3,242.48, respectively. PERI for surface water in the wet season ranges between 519.74 and 1,630.26, while for the dry season, it is between 201.89 and 1,246.59. For mine water, PERI ranges between 1,436.49 and 3,366.84. The study showed that Cr in groundwater during the wet season poses a low to severe ecological risk, while Ni, Cu, Zn, Cd, and Pb pose moderate to very serious, low to moderate, very serious, and low to very serious ecological risks. During the dry season, Cr, Ni, Cu, Zn, Cd, and Pb pose low to very serious, moderate to very serious, low to considerable, severe to very serious, and low to very serious ecological risks, respectively. In surface water collected during the wet season, Cr, Ni, Cu, Zn, Cd, and Pb pose moderate to considerable, moderately to very serious, low to moderately low, moderately to very serious, and low to very serious ecological risks. For surface water collected during the dry season, Cr, Ni, Cu, Zn, Cd, and Pb pose low to very serious, low to very serious, low to moderate, low, moderate to considerable, and low to considerable ecological risks in the study area. For mine water, Cr, Ni, Cu, Zn, Cd, and Pb pose moderate to considerable, severe to very serious, low to considerable, low, very serious, and severe to very serious ecological risks in the area. PERI further revealed that HMs in groundwater and mine water pose very serious ecological risks, while those in surface water sampled during the wet and dry seasons pose very serious and severe to very serious ecological risks in the area.

Even at low levels of exposure, Cr can influence hatching, DNA damage, and survival in fish, as well as their liver and kidneys (Tumolo *et al.* 2020). Its negative effects on seed germination, photosynthetic rate decrease, suppression of key enzyme activities, and nutrient absorption eventually impede plant growth and development (Oliveira 2012; Stambulska *et al.* 2018). Nickel inhibits seed germination, root and shoot growth, biomass accumulation, and overall production. Furthermore, Ni poisoning in plants produces chlorosis and necrosis, as well as suppressing various physiological processes (photosynthesis, transpiration) and producing oxidative damage (Hassan *et al.* 2019). Cu, at hazardous levels in soil, inhibits water and mineral

Table 5 | Ecological risk assessment of metals

		Eri Cr	Eri Ni	Eri Cu	Eri Zn	Eri Cd	Eri Pb	PERI
Groundwater Wet season	Minimum	30.85	40.78	10.13	16.62	594.75	14.49	1,477.57
	Maximum	244.98	424.02	24.36	79.25	2,347.88	490.64	2,895.25
	Average	107.06	300.57	17.84	45.32	1,449.18	273.51	2,193.47
Groundwater Dry season	Minimum	29.25	40.03	12.98	38.58	265.05	51.43	931.78
	Maximum	369.08	512.59	99.66	90.95	2,729.20	673.85	3,242.48
	Average	151.28	244.56	55.25	55.55	1,338.76	259.99	2,105.40
Surface water Wet season	Minimum	50.36	66.27	11.10	4.26	55.67	47.33	519.74
	Maximum	128.59	438.19	71.94	33.34	683.69	564.17	1,630.26
	Average	74.75	287.85	33.27	22.54	236.37	176.59	831.37
Surface water Dry season	Minimum	21.51	6.02	15.17	2.34	54.58	2.23	201.89
	Maximum	530.92	517.60	63.79	23.11	124.79	128.99	1,246.59
	Average	13.92	16.77	6.04	2.78	23.80	25.79	89.10
Mine water	Minimum	48.00	146.53	33.98	15.09	413.63	193.69	1,436.49
	Maximum	106.20	474.38	78.50	39.14	999.90	2,487.22	3,366.84
	Average	71.80	304.05	57.81	26.51	703.28	1,095.89	2,259.35

nutrient absorption (Shabbir *et al.* 2020), induces oxidative stress (Nazir *et al.* 2019), and interferes with photosynthesis (Cambrollé *et al.* 2015), resulting in decreased growth (Marques *et al.* 2018) and plant output (Kumar *et al.* 2021). Reduced root development and suppression of different physiological processes such as transpiration, respiration, and photosynthesis are all symptoms of zinc toxicity in plants. Zinc poisoning is characterized by stunted development, leaf epinasty, and chlorosis in younger leaves (WHO 2001). Cd toxicity lowers nutrient and water absorption and translocation, increases oxidative damage, affects plant metabolism, and inhibits plant shape and physiology in agricultural plants (Haider *et al.* 2021). Lead contamination covers the leaf's surface, reducing the quantity of light that reaches it. This stunts or kills the plants by lowering the rate of photosynthesis, limiting respiration, increasing plant cell elongation, affecting root development, and causing premature aging (Zulfiqar *et al.* 2019).

Human health risk assessment

Daily intake of metals in water

The daily intake of HMs in water through oral ingestion and dermal contact for adults and children is presented in Figure 3. This study showed that for children, the total daily intake of HMs through oral ingestion in groundwater during the wet season is 1.49 mg/L, while during the dry season, it is 1.74 mg/L. For surface water during the wet season, the daily intake of metals via ingestion is 1.71 mg/L, while during the dry season, it is 1.14 mg/L. For mine water, the total daily intake of metals through oral ingestion for kids is 1.83 mg/L. For kids, the total daily intake of HMs through dermal contact with groundwater collected during the wet and dry seasons is 0.14 and 1.68 mg/L, while for surface water, the daily intake through skin contact during the dry and wet seasons is 0.17 and 0.11 mg/L, respectively. For mine water, the daily intake of metals for adults through dermal contact is 0.21 mg/L. For adults, daily consumption of metals through oral intake of metals from groundwater for wet and dry seasons is 0.63 and 0.75 mg/L, respectively, while for surface water, it is 0.73 and 0.49 mg/L, respectively. For mine water, the daily intake through ingestion by adults is 0.78 mg/L. The total intake of metals via dermal contact with groundwater for wet and dry seasons is 1.78 and 2.09 mg/L, while for surface water, it is 2.05 and 1.37 mg/L. For mine water, the total daily intake of metals through dermal contact is 2.05 mg/L. This assessment revealed that the ingestion of HMs in water samples from the study area revealed that the estimated daily chronic intake of Fe is below the recommended allowable daily intake (NIH 2022). In Nigeria, one-third of the inhabitants does not have access to clean water and consume contaminated water (UNICEF 2020). Although no published data was found to know the amount of water consumed daily by Nigerians, a report by Lagunay (2023) suggested that people living in tropical regions of the world are required to drink at least

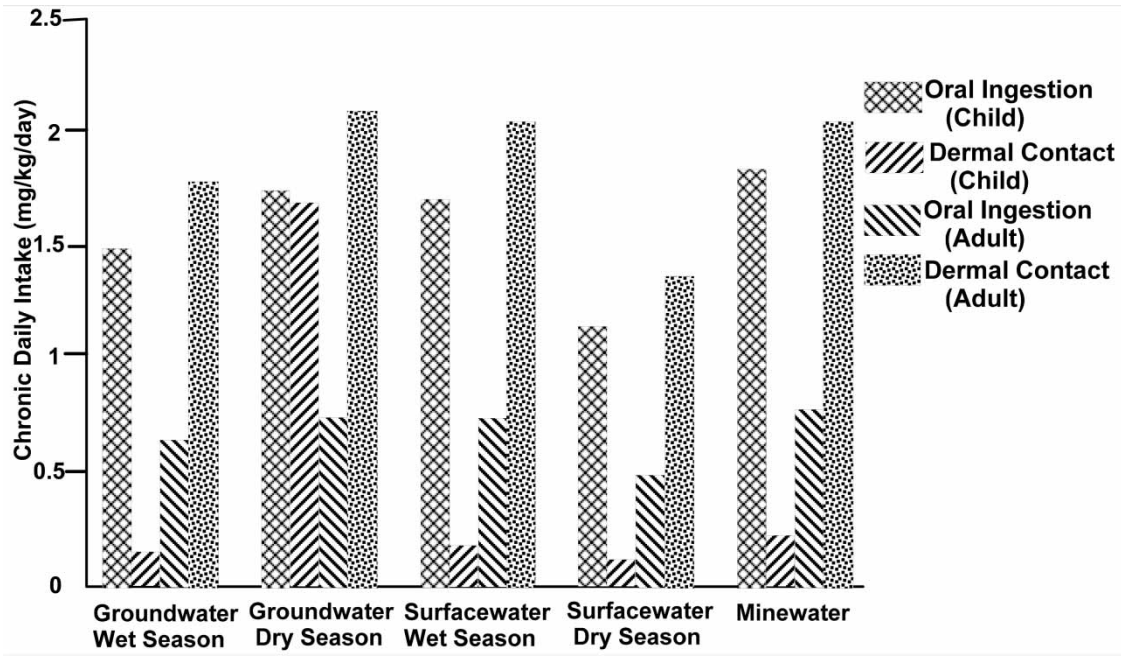


Figure 3 | Chronic daily intake of heavy metals in water by kids and adults.

Table 6 | Hazard quotients of metals for non-carcinogenic health risks

	HQ oral ingestion												HQ dermal contact					
	F	Mn	Cr	Co	Ni	Cu	Zn	As	Cd	Pb	Fe	Total HQ	Mn	Cr	Cu	Zn	Cd	Total HQ
Child																		
GWS	0.37	2.21	13.09	0.13	0.13	0.29	0.12	10.18	0.86	0.94	0.62	28.89	321.48	52.34	13.41	5.83	171.03	564.08
GDS	0.47	0.85	18.49	0.06	0.06	0.90	0.15	7.64	0.79	0.90	2.33	32.59	123.20	73.96	41.52	7.15	158.00	403.82
SWS	0.32	3.89	9.14	0.04	0.04	0.55	0.06	4.23	0.14	0.61	3.00	21.98	567.21	36.55	25.00	2.90	27.90	659.55
SDS	0.40	1.93	18.20	0.03	0.03	0.75	0.03	0.73	0.06	0.14	1.05	23.28	46.20	5.67	3.79	0.30	2.35	58.29
MW	0.33	2.17	8.78	0.02	0.02	0.94	0.07	14.07	0.42	3.76	1.58	32.13	315.46	35.11	43.44	3.41	83.00	480.40
Adults																		
GWS	0.04	0.23	2.64	0.02	0.02	0.03	0.01	1.03	0.09	0.38	0.07	4.51	32.41	10.56	1.36	0.36	17.24	61.90
GDS	0.05	0.09	3.73	0.01	0.01	0.10	0.01	0.77	0.08	0.04	0.02	4.87	12.42	14.92	4.19	0.44	15.93	47.88
SWS	0.04	0.40	1.85	0.01	0.01	0.06	0.01	0.43	0.02	0.25	0.31	3.32	57.18	7.37	2.52	0.18	2.82	70.05
SDS	0.04	0.20	3.67	0.01	0.01	0.08	0.01	0.08	0.01	0.06	0.11	4.23	28.30	14.68	3.46	0.07	1.11	47.60
MW	0.04	0.22	1.77	0.01	0.01	0.10	0.01	1.42	0.05	1.52	0.16	5.26	31.80	7.08	4.38	0.21	8.37	51.83

Table 7 | Hazard quotients of metals for carcinogenic health risks

	Child					Adults				
	HQ Cr	HQ As	HQ Cd	HQ Pb	Total HQ	HQ Cr	HQ As	HQ Cd	HQ Pb	Total HQ
GWS	1.96×10^{-2}	4.58×10^{-1}	2.61×10^{-7}	2.86×10^{-3}	4.80×10^{-1}	8.41×10^{-3}	1.96×10^{-1}	1.12×10^{-7}	1.22×10^{-3}	2.06×10^{-1}
GDS	2.42×10^{-2}	2.86×10^{-1}	2.61×10^{-7}	2.02×10^{-3}	3.12×10^{-1}	1.19×10^{-2}	1.47×10^{-1}	1.03×10^{-7}	1.17×10^{-3}	1.60×10^{-1}
SWS	1.37×10^{-2}	1.89×10^{-1}	4.25×10^{-8}	1.85×10^{-3}	2.05×10^{-1}	5.87×10^{-3}	8.14×10^{-2}	1.82×10^{-8}	7.93×10^{-4}	8.81×10^{-2}
SDS	2.73×10^{-2}	3.24×10^{-2}	1.67×10^{-8}	4.24×10^{-4}	6.01×10^{-2}	1.17×10^{-2}	1.39×10^{-2}	7.16×10^{-9}	1.82×10^{-4}	2.58×10^{-2}
MW	1.96×10^{-2}	6.33×10^{-1}	1.27×10^{-7}	1.15×10^{-2}	6.58×10^{-1}	5.64×10^{-3}	2.71×10^{-1}	5.42×10^{-8}	4.92×10^{-3}	2.81×10^{-1}

3.1 liters of water per day for healthy living. Findings revealed that inhabitants of the area drink water provided by shallow wells situated close to active mining pits which might infiltrate the aquifer and pollute it.

Oral intake of metals

The HQs for non-carcinogenic and carcinogenic health risks are presented in Tables 6 and 7, respectively. For children, the total HQ for metals in groundwater for non-carcinogenic health risks during the wet and dry seasons through ingestion is 28.89 and 32.59, respectively. For surface water during the wet and dry seasons, the total HQ is 21.98, while during the dry season, it is 23.28. For mine water, the HQ is 32.13. For adults, the total HQ for non-carcinogenic health risks for metals during the wet season is 4.51, while during the dry season, it is 4.87. For surface water, the total HQ during the wet season is 3.32, while during the dry season, it is a total of 4.23. For mine water, the total HQ is 5.26.

Dermal contact

For children, the total HQ of metals through dermal contact in groundwater during the wet and dry seasons is 564.08 and 403.82 (Table 6). For surface water, HQ through dermal contact during the wet and dry seasons are 659.55 and 58.29. For mine water, HQ, it is 480.40. For grown-ups, total HQ through dermal contact for wet and dry seasons is 61.90 and 47.88, respectively, while for surface water during the wet season, it is 70.05 and 47.60 for dry and wet seasons. For mine water, it is 51.83. For kids, the total HQ for carcinogenic health risks of metals in groundwater during the wet and dry seasons is 2.05×10^{-1} and 1.06×10^{-1} (Table 7). For surface water during the wet and dry seasons, it is 8.80×10^{-2} and 2.57×10^{-2} respectively. For mine water, it has a total of 2.81×10^{-1}. For adults, the total HQ for carcinogenic health risks of metals in groundwater during wet and dry seasons are 2.05×10^{-1} and 1.06×10^{-1} (Table 7). For surface water during the wet and dry seasons, it is 8.80×10^{-2} and 2.57×10^{-2} each. For mine water, it has a total of 2.81×10^{-1}. For children, the hazard index (HI) for metals in groundwater during the wet and dry seasons is 0.48 and 0.31, respectively. The HI for surface water during the wet and dry seasons is 0.21 and 0.06, respectively. The carcinogenic HI for mine water for children is 0.66. For adults, the HI for metals in groundwater for both wet and dry seasons is 0.21 and 0.16, while for surface water during the wet and dry seasons, the HI is 0.08 and 0.02 each. For mine water, the HI is 0.28.

Health risks posed by HMs

In this study, it was also found that HI values of metals in all water samples for non-carcinogenic health risks were higher for both children and adults (Figure 4). This implied that inhabitants of this area are exposed to non-carcinogenic health risks, which are facilitated by mining activities. For children, Mn, Cr, As, Cu, Zn, and Cd contributed more to the higher HI values, while for adults, Cr, As, Mn, Cr, Cu, and Cd played major roles in the increased HI values for non-carcinogenic health risks. All the water in this area has an HI > 1, which implies that oral ingestion and contact with the contaminated water may cause non-carcinogenic health risks. For carcinogenic health risks, HQ for all the metals was above the recommended 1×10^{-5} except for Cd, which has lower values. All the water has HI values higher than 1×10^{-5}, which shows that residents of this area are exposed to carcinogenic health issues. This study showed that children are more susceptible to these health risks than adults. Exposure to lead can cause damage to the brain and nervous system of children. It can also lead to slowed growth and development and may cause learning and behavioral problems. A high amount of Pb in children may also contribute to an increase in hearing and speech problems (CDC 2022). The presence of Cd in the human body may lead to renal and hepatic dysfunction, pulmonary edema, testicular damage, osteomalacia, and damage to the adrenals

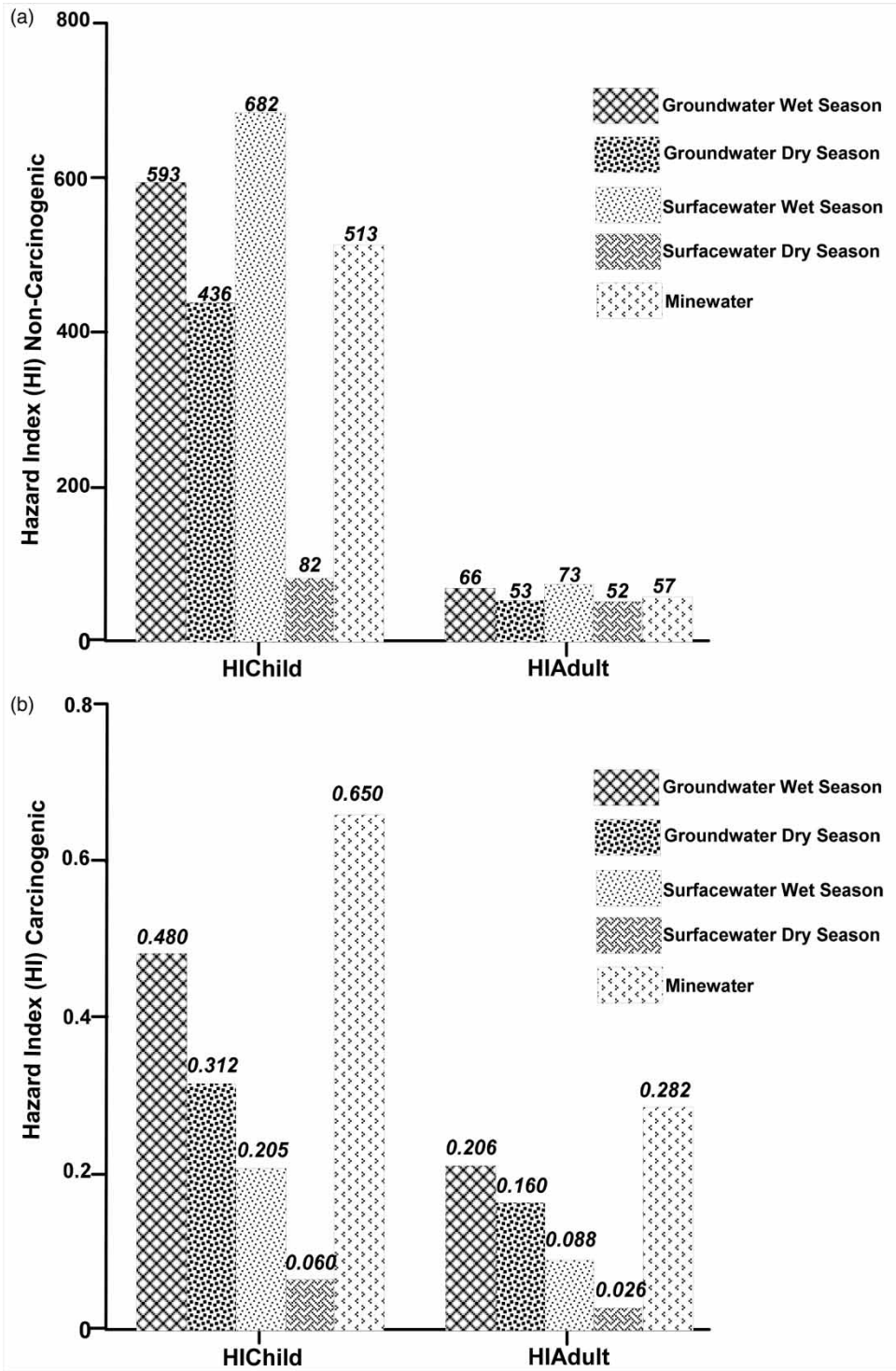


Figure 4 | Hazard index (HI) for non-carcinogenic and carcinogenic health risk.

and hemopoietic system (Tinkov *et al.* 2018). It can also lead to coronary heart disease, stroke, and peripheral artery disease (IARC 1993). Arsenic water can be harmful to the eyes, skin, liver, kidneys, lungs, and lymphatic system. Exposure to arsenic can also cause cancer (CDC 2019). High zinc intakes can cause nausea, dizziness, headaches, gastric distress, vomiting, and loss of appetite (Ryu & Aydemir 2020). Exposure to high doses of copper can cause health problems. Short-term exposure to

high levels of copper can cause gastrointestinal distress. Long-term exposure and severe cases of copper poisoning can cause anemia and disrupt liver and kidney functions (Abedi & Aghasi 2019). Nickel contact can cause a variety of side effects on human health, such as allergies, cardiovascular and kidney diseases, lung fibrosis, and lung and nasal cancer (Genchi *et al.* 2020). Ingestion of too much copper from water may lead to headaches, vomiting, diarrhea, stomach cramps, nausea, liver damage, and kidney disease. High levels of copper may damage red blood cells and reduce their ability to carry oxygen. Male fertility may be affected by high levels of copper (MDH 2023). A high intake of Cr in water may cause allergic dermatitis (skin rash or inflammation), liver damage, kidney problems, and nerve tissue damage. It can also affect sperm count in men and may lead to stunted growth in infants (Edwards 2019). Accumulated Cr in the human body can also lead to asthma, nasal ulcers, convulsions, and acute gastroenteritis (Edwards 2019). Elevated intakes of manganese may have adverse effects on the nervous system. These health effects include behavioral changes and other nervous system effects, which include movements that may become slow and clumsy (ATSDR 2014). It can also cause sperm damage and adverse changes in sexual performance in males (ATSDR 2014). It may also lead to inflammation of the kidneys and kidney stone formation (ATSDR 2014). In children, it may affect the brain, which can lead to a decrease in the ability to learn and can also lead to difficulty in speech and walking (ATSDR 2014). Fluorine water may cause dental fluorosis, skeletal fluorosis, arthritis, bone damage, osteoporosis, muscular damage, fatigue, joint-related problems, and chronic issues. In extreme conditions, it could adversely damage the heart, arteries, kidney, liver, endocrine glands, neuron system, and several other delicate parts of a living organism (Solanki *et al.* 2022).

CONCLUSIONS

This study revealed that the water around the Arufu Pb–Zn–F area is contaminated by HMs (Cr, Co, Ni, Cu, Zn, As, Cd, Sb, Ba, Pb, and Fe). The major sources of water pollution in the area are artisanal mining and mineral dressing. The concentrations of studied metals were above the WHO and Nigerian standards for drinking water quality for all climatic seasons except for Cu, Zn, As, Cd, and Sb, which are lower than the standard limit in surface water obtained during the dry season. Contamination assessment showed that the water is highly polluted by HMs and that they pose high ecological risks in the area. Health risk assessment uncovered that HMs in water pose both carcinogenic and non-carcinogenic health risks to kids and adults in the area.

This study has some limitations. Some variables used in this for evaluating ecological and human health risks were mainly derived from the USEPA guidelines. The values of these variables may not be appropriate for people living in Nigeria. Furthermore, only a limited number of toxic substances were considered in this study and used for health risk evaluations. Mining activities in the area might have released other toxic substances, which might be higher than those reported in this study. Affirmation of the impact of these HMs using clinical methods should be considered. Strict measures on mining activities should be introduced in the country to safeguard public and environmental health.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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