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Seasonal Dynamics of Heavy Metal Contamination and Associated Health Risk Assessment in the Water Resources of Riruwai Mining Area, North-Western Nigeria

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Seasonal Dynamics of Heavy Metal Contamination and Associated Health Risk Assessment in the Water Resources of Riruwai Mining Area, North-Western Nigeria

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Abstract

Heavy metal pollution from metal mining constitutes a major environmental concern worldwide due to its severe adverse effects on public health. In this study, the cancer and non-cancer risks of heavy metals in water resources of the Riruwai mining area were investigated. A total of 31 water samples were collected from five different locations, which include underground mining ponds (RGWI), tap water (RGW2), mining ponds (RGW3), boreholes (RGW4) and well water (RGW5) during both dry and rainy seasons. The concentrations of arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), manganese (Mn), lead (Pb), and zinc (Zn) were determined using Microwave Plasma Atomic Emission Spectrometry (MP-EAS), and cancer and non-cancer risks were evaluated using the U.S. EPA human health risk assessment model. The results of the analysis indicated that the heavy metal concentrations varied significantly across sampling locations ($p \leq 0.05$), with higher levels observed during the rainy season and exceeding the regulatory limits in RW1 and RW2 samples. The hazard quotient (HQ) values for all heavy metals were less than unity ($HQ < 1$) for both adults and children across all seasons, indicating no significant non-cancer health risks. Total cancer risk (TCR) values for As, Cd, Cr, and Pb were below the acceptable limit of 1×10^{-4}, which suggests no probable carcinogenic risk. Children exhibited higher HQ and TCR values than adults, which demonstrate greater vulnerability to heavy metal toxicity. It recommends continuous monitoring and remediation efforts to prevent future health consequences, particularly for the vulnerable children's populations.

Keywords: Heavy metals, health risk assessment, mining area, surface water, non-cancer risk, cancer risk, Riruwai

1. Introduction

Pollution from metal mining constitutes a major environmental concern worldwide due to its severe adverse effects on public health and ecological systems [1, 2]. Mining activities are intrinsically linked to elevated concentrations of heavy metals that would otherwise remain at natural background levels in the absence of anthropogenic disturbance [3, 4]. Heavy metals are particularly problematic environmental contaminants because they do not undergo chemical degradation in the environment. Instead, they persist and accumulate in sediments, soils, and water bodies for extended periods, creating long-term sources of contamination that pose sustained risks to surrounding ecosystems and human populations [5, 6].

Water is indispensable for maintaining human health and welfare, with access to clean drinking water now universally recognized as a fundamental human right [7-9]. However, mining operations have been documented to cause deleterious effects on water resources through the release of toxic metals from various environmental matrices, including soils, sediments, surface water, and groundwater [4, 10, 11]. Substantial quantities of hazardous heavy metals are discharged into the environment during mining operations, potentially triggering significant environmental degradation and public health challenges [12, 13]. Consequently, the assessment of human health risks associated with water consumption in mining areas is absolutely essential to safeguard both human well-being and environmental integrity.

In recent years, risk assessment has emerged as a valuable and promising tool for analysing environmental and occupational hazards [14, 15]. This discipline has gained increasing prominence in modern toxicological and epidemiological practice, serving both hazard evaluation and disease control and prevention at the population level [16]. Human risk assessment is defined as the process of estimating the probability of occurrence of an event and the probable magnitude of adverse health effects on human exposures to environmental hazards over a specified time period [17]. It serves as an efficient methodology for evaluating the relationship between environmental quality and public health outcomes, providing quantitative measures expressed in terms of hazard degree [18].

According to the United States Environmental Protection Agency [19], risk assessment comprises four fundamental steps: (i) hazard identification, (ii) hazard characterization, (iii) exposure assessment, and (iv) risk characterization. Hazard identification aims to determine the presence, concentrations, and spatial distribution of contaminants at any given location. Exposure assessment quantifies the intensity, frequency, and duration of human exposure to

environmental contaminants, typically by measuring the average daily intake (ADI) of identified heavy metals through ingestion, inhalation, and dermal contact pathways for both adults and children in the study area [20]. Risk characterization represents a critical step in the human risk assessment decision-making process [16]. During this phase, both non-carcinogenic and carcinogenic risks are evaluated [19]. Non-carcinogenic risk is calculated by comparing exposure levels over a defined period with a reference dose derived from the same exposure duration. The ratio of exposure to toxicity is termed the hazard quotient (HQ). The HQ approach assumes the existence of an exposure threshold below which even sensitive populations are unlikely to experience adverse health effects; exceeding this threshold raises concerns about potential non-carcinogenic effects, with higher HQ values indicating greater health risks. Carcinogenic risk, in contrast, is determined from the slope factor (SF) of the dose-response curve in the low-dose region, where the relationship between exposure dose (mg/kg/day) and response is expressed as the probability of developing cancer [21, 22]. Based on this assumption, SF is a constant, and cancer risk is directly proportional to intake. The lifetime exposure (ADDlife) is derived from exposure assessment by distributing cumulative exposure over the expected lifespan (e.g., 70 years) [19, 23].

Although no official outbreak of heavy metal poisoning has been reported in the Riruwai mining area, residents, particularly those directly engaged in mining activities, frequently report various illnesses consistent with symptoms of heavy metal toxicity. These include gastrointestinal disturbances, neurological symptoms, dermatological conditions, and other non-specific health complaints that mirror the clinical manifestations of chronic heavy metal exposure [24]. This observation underscores the urgent need for systematic investigation of heavy metal levels in the study area to prevent potential negative health consequences for local communities.

Despite the recognized importance of environmental health assessments, comprehensive human health risk evaluations in the Riruwai mining area remain insufficient. The present study addresses this critical research gap by conducting a thorough investigation of heavy metal contamination in water samples and its associated health risks. This research is essential for protecting public health and the environment by providing scientific evidence to inform policy decisions, guide remediation efforts, and promote sustainable mining practices in the region.

Furthermore, the findings will contribute to the broader understanding of mining-related environmental contamination in Nigeria and similar settings across sub-Saharan Africa.

2. MATERIALS AND METHODS

2.1 Description of the study area

Riruwai, the headquarters of Doguwa Local Government Area, is situated in the extreme southern part of Kano State. It lies between latitude 10°43'97"N and 10°45'01"N and longitude 8°43’03"E and 8°47'39”E, covering an area of 129 km² [25]. Riruwai is bordered in the north and east by Zainabi, Ragada in the west, and Dariye Shere in the south [26]. The map of Riruwai is shown in Figure 1. Riruwai has the highest elevation in the whole of Kano; it has an average height of 1100 m above sea level. It was reported to have a contour value greater than 580 m and a slope that is greater than 18° above sea level [27]. It is also called the foot slope of the Jos Plateau. Riruwai is endowed with spectacular landscapes, well-rounded hills, rolling topography with intermountain plateaus, dissected hills, and ridges [28, 29]. Köppen's climate classification categorized the climate as tropical savanna. The area has two distinct seasons: rainy (April-October) and dry (October-April) seasons. The mean annual rainfall is between 400 and 1,200 mm/annum [28]. Riruwai has an estimated population of 150,645 people based on the 2006 census report. The projected population is 257,479 people as of 2015 at a 3.2% growth rate [30].

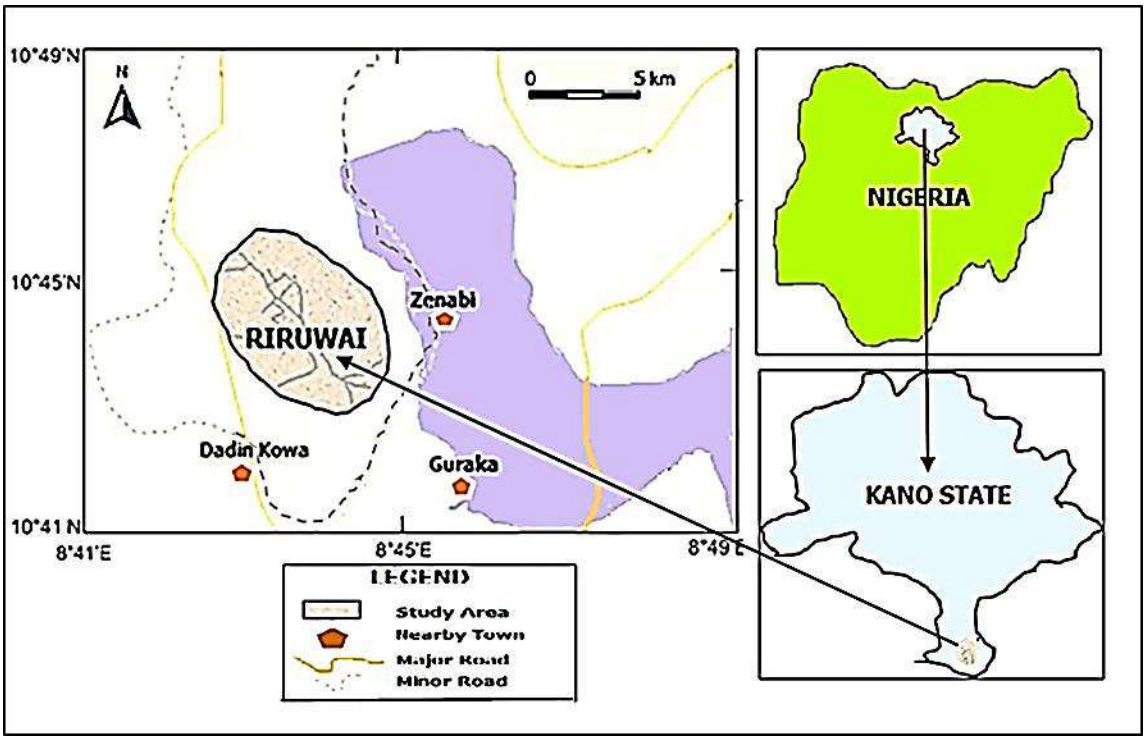


Figure 1. Geographical Map of the Study Area

2.2 Sampling of water

A total of 31 water samples were collected from five sampling sites, which include underground mining ponds (RGWI), tap water (RGW2), mining ponds (RGW3), boreholes (RGW4), and well water (RGW5). All the samples were separately collected in polyethylene bottles that were pre-washed with 20.00% HNO_3 and distilled water, except for the determination of mercury, where borosilicate glass bottles were used to minimize Hg^{2+} loss and contamination, as reported by Bravo et al. [31]. During sampling, two separate sets of bottles in each sampling location (1000 cm^3 each) were filled with water. A few drops of 65.00% HNO_3 were added to the first set of bottles of water sample (bringing the pH of the sample to below 2.00) to minimize precipitation and adsorption onto container walls [32] and were used to determine heavy metal concentrations. The second set of bottles was not acidified and was used to measure pH, electrical conductivity (EC), and total dissolved solids (TDS) in the field. To obtain a constant pH and EC, the samples were collected after 15 minutes of pumping [32]. The acidified samples in the first set of bottles were transported to the laboratory for heavy metal and radionuclide analyses.

2.3 Determination of Heavy Metals in Water Samples

A filtered water sample (500.00 cm^3) was placed in a 1000 cm^3 beaker, evaporated to 50.00 cm^3 on a hot plate at a temperature of 80°C, allowed to cool, and quantitatively transferred into a 250 cm^3 beaker. 10.00 cm^3 of concentrated trioxonitrate(V) acid was added, and the resulting solution was heated slowly at 80°C until a clear solution was obtained [32]. The digest was allowed to cool, filtered using Whatman filter paper number 42 into a 100 cm^3 volumetric flask, and made up to the mark with deionized water. The levels of arsenic, cadmium, chromium, mercury, manganese, lead, and zinc were determined using a Microwave Plasma Atomic Emission Spectrometer (Model Number 4200; Agilent, USA).

2.4 Human Health Risk Assessment

2.4.1 Average daily intake (ADI) of heavy metals

The average daily intakes (*ADIs*) of the investigated heavy metals in water, soil, and food crop samples were computed using the following equations [33].

$$ADI_{oral} = \frac{C_{water} \times IR_{water} \times EF \times ED}{BW \times AT} \quad (1)$$

$$ADI_{dermal} = \frac{C_{water} \times SA \times K_p \times ABS \times EF \times ED \times CF}{BW \times AT} \quad (2)$$

Where:

ADI = Average daily intake of heavy metals due to ingestion, inhalation, dermal contact and oral of water (mg/dm^3)

C = Heavy metal concentration in water (mg/dm^3)

IR = Ingestion rate of water (mg/dm^3)

CF = Conversion factor (kg/mg)

ED = Exposure duration (years)

BW = Body weight of the exposed individual (kg)

AT = Time period over which the dose is averaged (days)

EF = Exposure frequency (days/year)

SA = Exposed skin surface area (m^2)

ABS = Dermal absorption factor (no unit)

2.4.2 Non-cancer risks assessment of heavy metals

Non-cancer risks are evaluated in terms of hazard quotient (HQ). It was estimated by dividing ADI by the toxicity threshold value, which was referred to as the chronic reference dose (RfD) in mg/kg/day of a specific heavy metal as shown in equation 3 [34, 35]. HQ ≤ 1.00 indicates no adverse health effects, while HQ > 1.00 signifies likely adverse health effects [19].

$$HQ = \frac{ADI}{RfD} \quad (3)$$

Table I: Exposure Parameters Used for Human Health Risk Assessment (USEPA , 2004)

			Human Exposure	
Parameter	**Unit**	**Symbol**	**Child**	**Adult**
Body weight	kg	*BW*	14	55
Exposure frequency	days/years	*EF*	350	350
Exposure duration	years	*ED*	6	30
Ingestion rate	kg/day	*IR*	200	100
Inhalation rate	cm^3/day	IR_{air}	10	20
Exposed skin surface area	cm^2	*SA*	0.21	0.58
Soil to skin adherence factor	mg/cm^2	*AF*	2×10^{-3}	7×10^{-4}
Dermal absorption factor	—	*ABS*	0.1	0.1
Dermal exposure ratio	—	*FE*	0.61	0.61
Particulate emission factor	cm^3/kg	*PEF*	1.3×10^{9}	1.3×10^{9}
Conversion factor	g/cm^3	*CF*	1×10^{-6}	1×10^{-6}
Average time (carcinogens)	days	*AT*	25550	25550
Average time (non-carcinogens)	days	*AT*	2190	10950

Table 2. Reference Doses and Gradient Factors of Heavy Metals of Different Exposure Pathways

Heavy Metals	As	Cd	Cr	Hg	Mn	Pb	Zn
RfD_I	0.0003	0.003	0.003	0.0003	0.033	0.0035	0.3
RfD_D	0.00009	0.0005	0.00005	0.0003	0.00184	0.000525	0.06
RfD_{Inh}	0.000015	0.000015	0.0000286	0.000086	0.0000143	0.00352	0.3
SF	1.5	6.3	42	----	----	0.0085	----

2.4.3 Cancer risk assessments of heavy metals

Cancer risks were estimated by calculating the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogens as presented in equation 4. The slope factor (*SF*) converts the estimated daily intake of a toxin averaged over a lifetime of exposure directly to the incremental risk of an individual developing cancer [33].

$$Cancer\ Risk = ADI \times SF \quad (4)$$

Where, $Cancer\ Risk$ = cumulative probability of an individual developing cancer over a lifetime, *SF* = slope factor (mg/kg/day) and *ADI* = Cumulative chronic daily intake averaged over expected life span (mg/kg/day). The total cancer risk (*TCR*) of an individual was finally calculated from the average contribution of the individual heavy metals for all the pathways using equation 5 [33].

$$TCR = RISK_{Ing} + RISK_{Inh} + RISK_{Derm} \quad (5)$$

A *TCR* of less than 1 x 10^{-4} is generally considered an acceptable range, when *TCR* exceeds 1 x10^{-4}; there is likelihood of cancer risk [36].

3. RESULTS AND DISCUSSION

3.1 Concentrations of heavy metals in water samples

The results of some heavy metal levels in water samples around Riruwai mining area are presented in Tables 3 and 4.

Table 3. Concentrations of Some Heavy Metals (mg/dm^3) in the Water Samples Analysed during Dry Season

Parameters	Sampling Locations					WHO	NSDWQ
	RGW1	RGW2	RGW3	RGW4	RGW5	[40]	[41]
As	$0.21^{a} \pm 0.02$	$0.15^{a} \pm 0.02$	$0.02^{b} \pm 0.00$	$0.02^{b} \pm 0.01$	$0.0006^{b} \pm 0.00$	0.01	0.01
Cd	$0.08^{a} \pm 0.01$	$0.11^{b} \pm 0.00$	$0.0009^{c} \pm 0.00$	$0.01^{c} \pm 0.007$	$0.0009^{c} \pm 0.00$	0.003	0.003
Cr	$0.25^{a} \pm 0.03$	$0.13^{b} \pm 0.01$	$0.04^{c} \pm 0.01$	$0.0007^{c} \pm 0.00$	$0.0008^{c} \pm 0.00$	0.05	0.05
Hg	$0.07^{a} \pm 0.01$	$0.09^{a} \pm 0.03$	$0.0005^{b} \pm 0.00$	$0.0008^{b} \pm 0.00$	$0.0005^{b} \pm 0.00$	0.006	0.001
Mn	$0.50^{a} \pm 0.01$	$0.66^{a} \pm 0.02$	$0.14^{b} \pm 0.03$	$0.30^{b} \pm 0.01$	$0.12^{b} \pm 0.01$	—	0.20
Pb	$0.08^{a} \pm 0.02$	$0.06^{a} \pm 0.01$	$0.007^{b} \pm 0.00$	$0.04^{a} \pm 0.02$	$0.003^{b} \pm 0.00$	0.01	0.01
Zn	$17.43^{a} \pm 0.07$	$11.73^{b} \pm 0.03$	$5.26^{c} \pm 0.03$	$4.88^{d} \pm 0.01$	$2.29^{e} \pm 0.03$	—	3.00

Values were mean ± standard deviation (n = 3). **RGW1** = mining pond, **RGW2** = underground mining sites, **RGW3** = tap water, **RGW4** = borehole, **RGW5** = well water. Values on the same row with the same superscript letters were statistically the same ($p > 0.05$), while those with different superscript letters on the same row were significant as revealed by one-way ANOVA and the Tukey HSD post-hoc test ($p \leq 0.05$).

Table 4. Concentrations of Some Heavy Metals (mg/dm^3) in the Water Samples Analysed during the Rainy Season

Parameters	Sampling Locations					WHO	NSDWQ
	RGW1	RGW2	RGW3	RGW4	RGW5	[40]	[41]
As	$0.35^{a} \pm 0.04$	$0.20^{b} \pm 0.03$	$0.03^{c} \pm 0.01$	$0.04^{c} \pm 0.01$	$0.005^{c} \pm 0.001$	0.01	0.01
Cd	$0.11^{a} \pm 0.01$	$0.15^{b} \pm 0.01$	$0.009^{c} \pm 0.00$	$0.02^{c} \pm 0.01$	$0.001^{c} \pm 0.00$	0.003	0.003
Cr	$0.32^{a} \pm 0.05$	$0.17^{b} \pm 0.03$	$0.06^{c} \pm 0.01$	$0.008^{c} \pm 0.00$	$0.001^{c} \pm 0.00$	0.05	0.05
Hg	$0.09^{a} \pm 0.00$	$0.14^{b} \pm 0.03$	$0.0009^{c} \pm 0.00$	$0.003^{c} \pm 0.00$	$0.0008^{c} \pm 0.00$	0.006	0.001
Mn	$0.73^{a} \pm 0.03$	$0.92^{b} \pm 0.05$	$0.17^{c} \pm 0.01$	$0.49^{a} \pm 0.05$	$0.16^{c} \pm 0.03$	—	0.20
Pb	$0.10^{a} \pm 0.04$	$0.09^{a} \pm 0.03$	$0.03^{a} \pm 0.02$	$0.06^{a} \pm 0.01$	$0.007^{b} \pm 0.001$	0.01	0.01
Zn	$20.03^{a} \pm 0.06$	$14.05^{b} \pm 0.08$	$7.01^{c} \pm 0.03$	$5.90^{c} \pm 0.03$	$2.85^{d} \pm 0.02$	—	3.00

Values were mean ± standard deviation (n = 3). **RGW1** = mining pond, **RGW2** = underground mining sites, **RGW3** = tap water, **RGW4** = borehole, **RGW5** = well water. Values on the same row with the same superscript letters were statistically the same (p >

0.05), while those with different superscript letters on the same row were significant as revealed by one-way ANOVA and the Tukey HSD post-hoc test ($p \leq 0.05$).

The levels of arsenic during the dry season as presented in Table 3 ranged from 0.0006 mg/dm³ (well water) to 0.21 mg/dm³ (mining pond), such that 0.02 mg/dm³ and 0.15 mg/dm³ were, respectively, found in tap water/borehole water and underground mining sites. Table 4 shows that the level of arsenic during the rainy season spread from 0.005 mg/dm³ (well water) to 0.35 mg/dm³ found in the mining pond. Concentrations of 0.03, 0.04, and 0.20 mg/dm³ found in tap water, borehole, and underground mining sites, respectively, were found between the extreme concentrations of arsenic in the study area. The higher concentrations of arsenic were found during the rainy season, with the mining pond site having the highest arsenic concentration, while the lowest concentration was detected in the well water sample. The observed values of arsenic were in good agreement with literature values of 0.0041 mg/dm³ and 0.005 mg/dm³ found in well water during both seasons, as respectively reported by [37] and [38]. Obasi and Akudinobi [39] reported a higher arsenic level of 4.13 mg/dm³ in water resources of lead-zinc mining communities of Abakaliki, Southeast Nigeria.

All the observed values of arsenic in both seasons were higher than the 0.01 mg/dm³ permissible limit set by [40] and [41], with the exception of 0.0006 mg/dm³ and 0.005 mg/dm³, respectively, found in well water samples during dry and rainy seasons. It is therefore evident that water samples from the mining pond, underground mining site, tap water, and borehole were not safe for human consumption. Arsenic is a toxic element that can cause a range of health problems, including skin lesions, cancer, cardiovascular disease, and diabetes [42]. Mining activities may release arsenic into the environment through various processes, such as weathering of rocks and minerals, leaching from mine waste, and runoff from mine sites. Once released, arsenic can enter the water supply and contaminate local water sources, including rivers, lakes, and groundwater [43, 44].

As shown in Tables 3 and 4, the concentrations of cadmium ranged from 0.0009 (well and tap water) to 0.11 mg/dm³ (underground mining site). The values of 0.01 mg/dm³ (borehole) and 0.08 mg/dm³ (mining pond) lay between the lowest and highest concentrations of cadmium during the period of the dry season. During the rainy season, the concentration of cadmium was found to spread from 0.001 mg/dm³ (well water) to 0.15 mg/dm³ (underground mining site), such

that 0.009 mg/dm³ (tap water), 0.02 mg/dm³ (borehole), and 0.11 mg/dm³ (mining pond) were, respectively, found between the lowest and highest observed concentrations. The experimental values of cadmium in the present study were comparable to a reported literature value of 0.17 mg/dm³ determined in water samples from the Gold Mining Area of the Prestea Huni Valley District, Ghana [45].

The concentrations of cadmium in all sampling sites and seasons were above [40] and [41] acceptable limits of 0.003 mg/dm³ except in tap and well water. This demonstrated that water from mining ponds, underground mining sites, and boreholes should not be used for human consumption due to the high levels of cadmium beyond the limits of national and international regulatory bodies. Exposure to high concentrations of cadmium in water may have harmful effects on human health and the environment. Cadmium is a toxic metal, and exposure to high levels can lead to acute and chronic health problems, including kidney damage, respiratory problems, cancer, and developmental effects in children [46, 47].

The concentrations of chromium ranged from 0.0007 (borehole) to 0.25 mg/dm³ (mining pond). The levels of 0.0008, 0.04, and 0.13 mg/dm³ found in well water, tap water, and underground mining sites lay between the lowest and highest concentrations in the dry season. During the rainy season, the concentrations of chromium ranged from 0.001 (well water) to 0.32 mg/dm³ (mining pond). Chromium concentrations of 0.008 mg/dm³ (borehole), 0.06 mg/dm³ (tap water), and 0.17 mg/dm³ (underground mining water) fell between the extreme concentrations of observed chromium. The observed concentration of chromium in this study was lower than a literature value of 0.74 mg/dm³ determined in water samples from the chromite mine environment of Sukinda, India [48]. The concentrations of chromium in borehole and well water were within WHO [40] and NSDWQ [41] permissible limits in all the seasons, whereas the concentrations of chromium in mining ponds and underground mining sites were above the allowable limit. In the tap water sample, the concentration of chromium is above the WHO [40] and NSDWQ [41] recommended limit during the rainy season and below the limit during the dry season. Considering the high levels of chromium in mining ponds and underground mining sites as well as the high levels of chromium in tap water that exceed the legally allowable limit, water from these sample locations should not be used for drinking or other domestic purposes. Chromium is a naturally occurring metal found in rocks, soil, plants, and animals. It can exist in

various forms, including trivalent chromium (Cr^{3+}) and hexavalent chromium (Cr^{6+}). While Cr^{3+} is an essential nutrient required in small amounts for glucose metabolism in the body, Cr^{6+} is a potent carcinogen and toxic to humans. Epidemiological studies have linked long-term exposure to Cr^{6+} in water to an increased risk of lung, kidney, and gastrointestinal cancers. Other negative effects of Cr^{6+} include skin irritation, respiratory and reproduction problems, and liver and kidney damage [49, 50].

The concentrations of mercury ranged from 0.0005 (tap water and well water) to 0.09 mg/dm³ (underground mining site), such that 0.0008 mg/dm³ (borehole) and 0.07 mg/dm³ (mining pond) were found between the lowest and highest concentrations during the dry season, respectively. In the rainy season, the observed levels of mercury spread from 0.0008 (well water) to 0.14 mg/dm³ (underground mining site). The levels of 0.0009 mg/dm³ (tap water), 0.003 mg/dm³ (borehole), and 0.09 mg/dm³ (mining pond water) fell between the observed extreme concentrations. The measured levels of mercury in boreholes, tap water, and well water were in accordance with published literature values of 0.0008 mg/dm³ in both seasons that were reported by [37] when they studied heavy metal contamination of soil and water in a former mining area of Rudňany, Slovakia. In both seasons, the concentrations of mercury at the mining pond and underground mining site were above the recommended limits of 0.006 and 0.001 mg/dm³ set by [40] and [41], respectively. The levels of mercury in tap water and well water were, however, lower than the [40] and [41] threshold limits. This indicates that the water from the mining pond and underground mining site should not be used for consumption. Exposure to mercury through contaminated water can cause a range of health issues, including nervous system and kidney damage, developmental disorders in children and in severe cases, even death [51].

The concentrations of manganese ranged from 0.12 (well water) to 0.66 mg/dm³ (underground mining site) such that 0.14 mg/dm³ (tap water), 0.30 mg/dm³ (borehole), and 0.50 mg/dm³ (mining pond) fell between the lowest and highest observed values during the dry season. During the rainy season, the concentrations of manganese varied from 0.16 (well water) to 0.92 mg/dm³ (underground mining site). Manganese concentrations of 0.17 mg/dm³ (tap water), 0.49 mg/dm³ (borehole), and 0.73 mg/dm³ (mining pond) fell between the lowest and highest observed concentrations. The observed concentrations of manganese in this study were lower than a literature value of 1.74 mg/dm³ determined in the mine pit water, surface water, and

groundwater systems of the largest manganese mining areas in Ghana [52]. The concentrations of manganese in all the sampling locations with the exception of well water (RGW5) and tap water (RGW3) were higher than the [41] recommended limit of 0.20 mg/dm³ in both seasons. Based on these findings, it is evident that the water from the mining pond, underground mining site and borehole is polluted with manganese and should not be used for drinking or other household uses. Exposure to high levels of manganese in water can affect the nervous system, causing symptoms such as tremors, muscle weakness and loss of coordination. High levels of manganese exposure can also cause stomach pain, nausea and diarrhoea [53].

The concentrations of lead ranged from 0.003 (well water) to 0.08 mg/dm³ (mining pond). The levels of 0.007 mg/dm³ (tap water), 0.04 mg/dm³ (borehole), and 0.06 mg/dm³ (underground mining site) fell between the lowest and highest observed concentrations of lead during the dry season. During the rainy season, the concentrations of lead ranged from 0.007 mg/dm³ (well water) to 0.10 mg/dm³ (mining pond). The lead concentrations of 0.03 mg/dm³ (tap water), 0.06 mg/dm³ (borehole), and 0.09 mg/dm³ (underground mining site) lay between the lowest and highest observed concentrations. The concentrations of lead in all sampling sites were above the [40] and [41] desirable limits of 0.01 mg/dm³ except for well water, where lead concentrations were below the desirable limit in all the seasons. The concentration of lead in tap water during the dry season is, however, lower than the [40] and [41] allowable limits. This indicates that only water from well water samples may be safe for human consumption. The experimental values of lead in the present study were comparable to a reported literature value of 0.17 mg/dm³ determined in water samples from the Gold Mining Area of the Prestea Huni Valley District, Ghana [45]. Lead contamination in drinking water can have several harmful effects on human health. Lead exposure can cause acute and chronic kidney damage, which can lead to kidney failure over time [54]. It can also interfere with the production of red blood cells, leading to anemia. Lead exposure can affect both male and female reproductive systems, leading to fertility issues and complications during pregnancy, and damage to the nervous system, leading to symptoms such as headaches, memory loss, and seizures [55].

The concentrations of zinc ranged from 2.29 (well water) to 17.43 mg/dm³ (mining pond). The experimental values of 4.88 mg/dm³ (borehole), 5.26 mg/dm³ (tap water), and 11.73 mg/dm³ (underground mining site) were found, respectively, between the observed extreme

concentrations during the dry season. During the rainy season, the concentrations of zinc ranged from 2.85 mg/dm³ (well water) to 20.03 mg/dm³ (mining pond), such that 5.90 mg/dm³ (borehole), 7.01 mg/dm³ (tap water), and 14.05 mg/dm³ (underground mining site) were found between the lowest and highest observed concentrations of zinc. The highest zinc concentration of 20.03 mg/dm³ was found in the mining pond samples (RGW3) during the rainy season, while the lowest (2.29 mg/dm³) was observed in well water samples during the dry season. The concentration of zinc in all sampling locations exceeded the desirable limit of 3.00 mg/dm³ recommended by [41] during both seasons. This shows that water from all the sampling locations might be contaminated by zinc, and consumption of such water may be detrimental to the health of the residents and should therefore be avoided. Zinc is an important dietary element that plays a vital role in various bodily functions such as immune system functioning, wound healing, and cell growth and division when it is at an optimal level. However, consumption of high levels of zinc can cause nausea, vomiting, diarrhea, anaemia, a weakened immune system, and nervous system problems [56, 57].

Generally, the observed concentrations of the studied heavy metals varied significantly ($p \leq 0.05$) along the sampling locations as obtained from one-way ANOVA results. The levels of heavy metals in mining ponds and underground sites as well as arsenic and zinc in tap water and boreholes were found to be greater than the threshold limits. This, therefore, indicates that water in the afore-mentioned locations was polluted with heavy metals. Previous studies established that mining areas were characterized by high concentrations of heavy metals resulting from mine tailings and mine waste [58]. Muhire et al. [59] reported that concentrations of heavy metals in water were generally higher on mining sites than in non-mining areas and even higher than international standards when they evaluated the environmental impacts of mining on Gishwati Protected Reserve in Rwanda. High levels of heavy metals in these locations might be linked to the weathering and dissolution of bedrocks and ore minerals in the area, and it could be due to the phenomenon of leaching and heavy metal precipitation from the overburden dumps and tailing ponds [60, 39, 61]. It might also be due to the acidity of sampling locations, particularly mining ponds and underground mining sites, since heavy metals' mobility and availability in water increase as a result of a decrease in pH [62, 63]. The heavy metals varied seasonally with higher concentrations during the rainy season, but the independent t-test result revealed no

statistically significant difference between the seasons ($P \leq 0.05$). High levels of heavy metals during the rainy season might be attributed to the dissolution of heavy metals from their ores [39]. Jiang et al. [64] discovered that predominant wind direction, erosion of mine tailings, and rainwater runoff were playing significant roles in the widespread dispersal and transfer of heavy metals from soil to water.

3.2 Risks Assessment of Heavy Metals in Water Samples

3.2.1 Non-cancer risk assessment

The results of the non-cancer health risks of heavy metals from five different sampling sites, which include mining pond (RGW1), underground mining site (RGW2), tap water (RGW3), borehole (RGW4), and well water (RGW5) during both the dry and rainy seasons, were depicted in Figures 2 and 3.

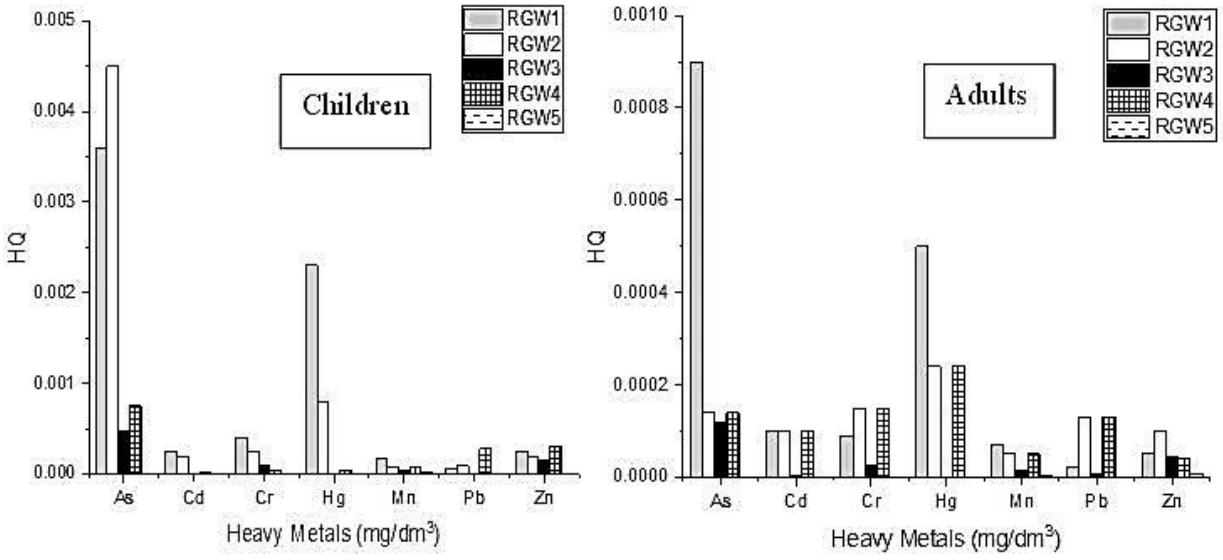


Figure 2: Non-carcinogenic Risks (HQ) of Heavy Metals in Water Samples during the Dry Season

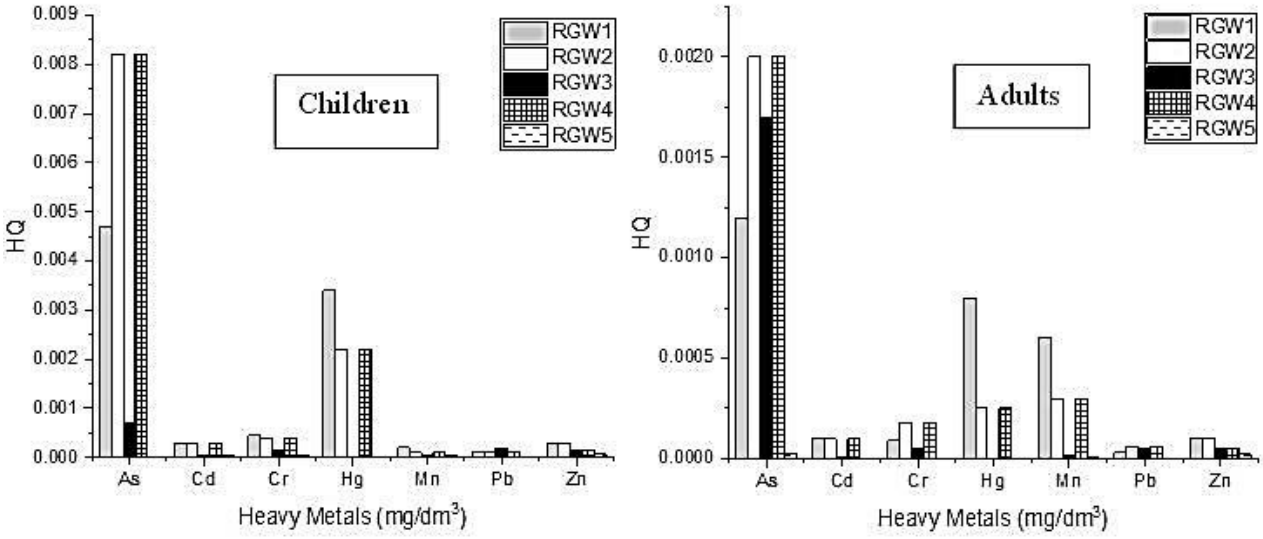


Figure 3: Non-carcinogenic Risks (HQ) of Heavy Metals in Water Samples during the Rainy Season

3.2.2 Cancer risk assessment

The results of total cancer risk (TCR) of heavy metals from five different sampling locations, which include mining pond (RGW1), underground mining site (RGW2), tap water (RGW3), borehole (RGW4), and well water (RGW5) around Riruwai Mining Area during both the dry and rainy seasons, were shown in Figures 4 and 5.

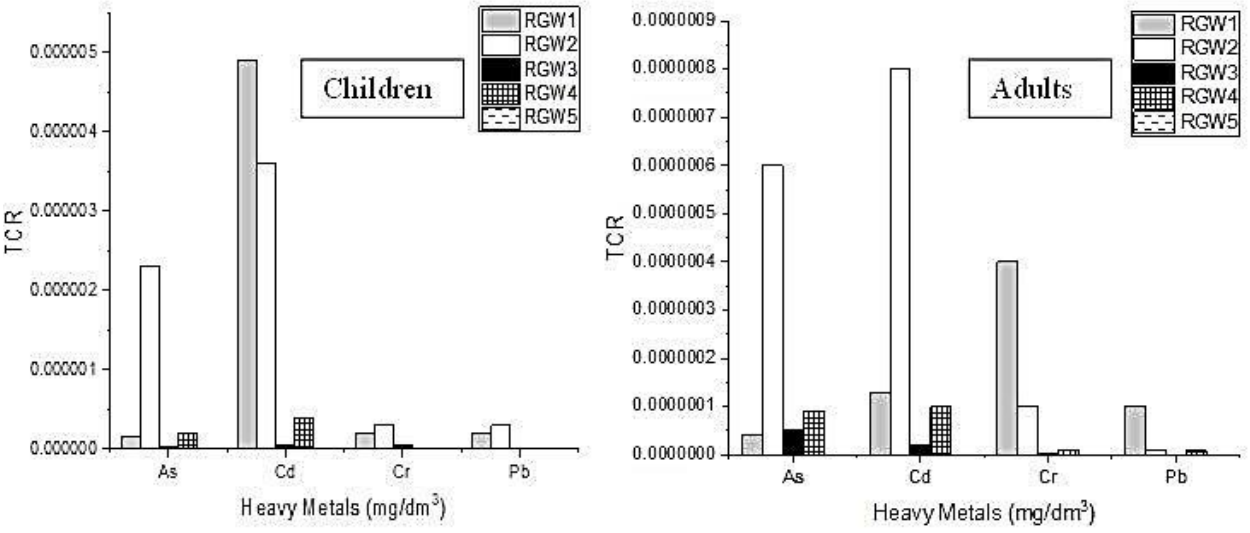


Figure 4. Total Cancer Risks (HQ) of Heavy Metals in Water Samples during the Dry Season

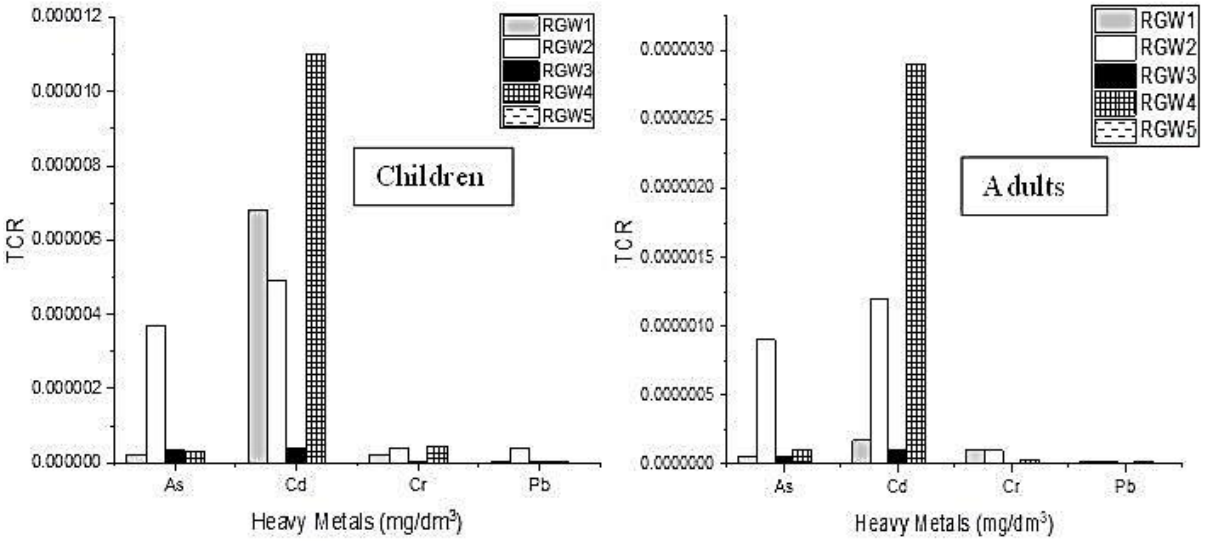


Figure 5. Total Cancer Risks (HQ) of Heavy Metals in Water Samples during the Rainy season

In water samples as shown in Figures 2 and 3, *HQ* values of arsenic ranged from 1.00 x 10^{-8} to 5.00 x 10^{-3} in children during the dry season. The highest value was recorded in mining pond water samples, while the lowest value was obtained in the well water. During the rainy season, *HQ* values of arsenic were spread from 1.00 x 10^{-6} (well water samples) to 8.33 x 10^{-3} (mining pond water samples).

In the adult population, *HQ* values of arsenic ranged from 1.00 x 10^{-9} (well water samples) to 1.27 x 10^{-3} (mining pond) and 1.19 x 10^{-4} (well water samples) to 2.12 x 10^{-3} (mining pond water samples) during the dry and rainy seasons, respectively. *HQ* values of arsenic in all sampling sites, populations, and seasons were less than the threshold limit of one. This implies that arsenic might unlikely pose non-cancer risks to the inhabitants of the study area.

The *HQ* values of cadmium ranged from 1.00 x 10^{-11} to 1.90 x 10^{-4} in children during the dry season. The highest value was detected at the mining pond, and the lowest value was found in the well water samples. During the rainy season, *HQ* values of cadmium ranged from 2.38 x

10^{-5} (well water samples) to 2.62 x 10^{-4} (mining pond water samples). In the adult population, *HQ* values of cadmium ranged from 2.00 x 10^{-7} (well water samples) to 4.84 x 10^{-5} (mining pond) and 6.06 x 10^{-7} (well water samples) to 6.67 x 10^{-5} (mining pond water samples) during the dry and rainy seasons, respectively. *HQ* values of cadmium in all sampling sites, populations, and seasons were less than the threshold limit of one. This shows that cadmium is unlikely to pose non-cancer risks to the residents of the study area.

The *HQ* values of chromium ranged from 1.00 x 10^{-7} to 5.95 x 10^{-4} in children, with the highest value detected at the mining pond and the lowest value found in well water samples during the dry season. During the rainy season, *HQ* values of chromium ranged from 2.38 x 10^{-5} (well water samples) to 7.62 x 10^{-4} (mining pond water samples). In the adult population, *HQ* values of chromium ranged from 51.00 x 10^{-8} (well water samples) to 1.51 x 10^{-4} (mining pond water samples) and 6.06 x 10^{-7} (well water samples) to 1.94 x 10^{-4} (mining pond water samples) during both the dry and rainy seasons, respectively. All sample sites, populations, and seasons had *HQ* values that were lower than one. This shows that residents of the study area were unlikely to be at risk from non-cancer effects of chromium.

The *HQ* values of mercury ranged from 1.00 x 10^{-10} to 1.67 x 10^{-3} in children during the dry season. The highest value was observed at the mining pond, while the lowest value was found in well water. During the rainy season, the *HQ* values of mercury ranged from 1.00 x 10^{-7} (well water samples) to 2.14 x 10^{-3} (mining pond). In the adult population, the *HQ* values of mercury ranged from 1.00 x 10^{-9} (well water samples) to 4.24 x 10^{-4} (mining pond) and 1.00 x 10^{-5} (well water samples) to 5.45 x 10^{-4} (mining pond water samples) during the dry and rainy seasons, respectively. *HQ* values of mercury in all sampling sites, populations, and seasons were less than the threshold limit of one. This shows that mercury might not pose non-cancer risks to the residents of the study area.

The *HQ* values of manganese spread from 2.59 x 10^{-5} (well water samples) to 1.40 x 10^{-4} (underground mining pond water samples) in children during the dry season. During the rainy season, *HQ* values of manganese ranged from 3.46 x 10^{-5} (well water samples) to 2.00 x 10^{-4} (mining pond water samples). In the adult population, *HQ* values of manganese ranged from 6.61 x 10^{-6} (well water samples) to 5.10 x 10^{-5} (mining pond) and 8.81 x 10^{-6} (well water samples) to

3.60 x 10^{-5} (mining pond water samples) during the dry and rainy seasons, respectively. *HQ* values of manganese in all sampling sites, populations, and seasons were less than the threshold limit of one. This indicates that manganese might not pose non-cancer risks to the residents of the study area.

The *HQ* values of lead spread from 6.12 x 10^{-6} (well water samples) to 1.63 x 10^{-4} (underground mining pond water samples) in children during the dry season. During the rainy season, *HQ* values of lead ranged from 1.43 x 10^{-5} (well water samples) to 2.04 x 10^{-4} (mining pond water samples). In the adult population, *HQ* values of lead spread from 1.56 x 10^{-6} (well water samples) to 4.16 x 10^{-5} (mining pond) as well as 3.63 x 10^{-6} (well water samples) to 5.19 x 10^{-5} (mining pond water samples) during the dry and rainy seasons, respectively. *HQ* values of lead in all sampling sites, populations, and seasons were less than the threshold limit of one, indicating that lead might not pose non-cancer risks to the residents of the study area.

The *HQ* values of zinc ranged from 5.45 x 10^{-5} to 4.15 x 10^{-4} in children, with the highest value detected in the mining pond water samples and the lowest value found in well water samples during the dry season. During the rainy season, *HQ* values of zinc ranged from 6.79 x 10^{-5} (well water samples) to 4.77 x 10^{-4} (mining pond water samples). In the adult population, *HQ* values of zinc ranged from 1.39 x 10^{-5} (well water samples) to 1.06 x 10^{-4} (mining pond) and 1.72 x 10^{-5} (well water samples) to 1.21 x 10^{-4} (mining pond water samples) during the dry and rainy seasons, respectively. All sample sites, populations, and seasons had *HQ* values that were lower than one. This shows that residents of the study area were unlikely to be at risk from non-cancer effects of zinc.

As shown in Figures 4 and 5, the *TCR* of arsenic in children ranged from 1.00 x 10^{-8} to 2.25 x 10^{-6}, with the highest value found in the mining pond water and the lowest value found in well water samples during the dry season. During the rainy season, *TCR* values of arsenic ranged from 1.00 x 10^{-6} (well water samples) to 3.75 x 10^{-6} (mining pond water samples). In the adult population, *TCR* values of arsenic ranged from 1.00 x 10^{-11} (well water samples) to 5.72 x 10^{-7} (mining pond) as well as 1.00 x 10^{-9} (well water samples) to 9.55 x 10^{-7} (mining pond water samples) during both dry and rainy seasons, respectively. *TCR* values of arsenic in all the

sampling locations, population, and seasons were less than the tolerable limit of 1.00×10^{-4}. This indicates that there is no probable cancer risk to the residents of the study area.

The *TCR* of cadmium ranged from 1.00×10^{-9} (well water samples) to 3.60×10^{-6} (mining pond water samples) during the dry season in the children's population. During the rainy season, *TCR* values of cadmium ranged from 1.00×10^{-7} (well water samples) to 3.75 x 10-6 (mining pond water samples). In the adult population, *TCR* values of cadmium ranged from 1.00×10^{-11} (well water samples) to 9.16×10^{-7} (mining pond) and 1.00×10^{-9} (well water samples) to 1.26×10^{-6} (mining pond water samples) during the dry and rainy seasons, respectively. *TCR* values of cadmium in all the sampling locations, population, and seasons were less than the tolerable limit of 1.00×10^{-4}. This implies cadmium might not pose cancer risk to the residents of the study area.

The *TCR* of chromium spread from 1.00×10^{-8} (well water samples) to 3.39×10^{-7} (mining pond water samples) during the dry season in the children's population. During the rainy season, *TCR* values of chromium ranged from 1.00×10^{-7} (well water samples) to 4.34×10^{-7} (mining pond water samples). In the adult population, *TCR* values of chromium ranged from 0.00 (well water samples) to 8.63×10^{-8} (mining pond) and 1.00×10^{-9} (well water samples) to 1.11×10^{-7} (mining pond water samples) during the dry and rainy seasons, respectively. *TCR* values of chromium in all the sampling locations, population, and seasons were less than the tolerable limit of 1.00×10^{-4}. This shows that there is no probable cancer risk to the residents of the study area.

The *TCR* of lead ranged from 1.82×10^{-10} (well water samples) to 4.85×10^{-9} (mining pond water samples) during the dry season in the children's population. During the rainy season, *TCR* values of lead ranged from 4.25×10^{-10} (well water samples) to 6.07×10^{-9} (mining pond water samples). In the adult population, *TCR* values of lead ranged from 4.64×10^{-11} (well water samples) to 1.23×10^{-9} (mining pond) and 1.08 x 10-10 (well water samples) to 1.54×10^{-9} (mining pond water samples) during the dry and rainy seasons, respectively. *TCR* values for arsenic were less than 1.00×10^{-4} in all sample sites, populations, and seasons. This implies that people of the study area were unlikely to develop arsenic-induced cancer.

Generally, arsenic had the highest *HQ* value in both children and adults in all sampling locations and seasons. *HQ* values of other heavy metals varied along the sampling locations. *The HQ* values of children were considerably higher than those of the adults in all the sampling locations. *HQ* values were less than one ($HQ < 1$) in both populations and seasons. This indicated that the heavy metals might not pose adverse health effects. However, high *HQ* values in children compared to the adults implied that children were more susceptible to heavy metal pollution than adults. This might be due to behavioral and physiological characteristics of children [65], as children were more vulnerable to toxic contaminants than adults [66, 21]. Similar results were reported by Zhang et al. [67] and Hussain et al. [68].

TCR values of all the heavy metals were within the safe limit in all the sampling locations, populations, and seasons. This indicates that consumption of the examined water samples investigated may not cause cancer risk. TCR values in all the studied heavy metals were higher in children than in adults. This indicates that children were more vulnerable to cancer risk from heavy metals than the adults were. This also corroborates with the findings of Vesković and Onjia [69], who investigated the risks of exposure to heavy metals in the water from Mashhad, Iran. Children were more susceptible to cancer risks because of their high water and calorific intakes as well as their high breathing rates [70, 71].

Conclusion

This study investigated the cancer and non-cancer risks associated with heavy metals specifically arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), manganese (Mn), lead (Pb), and zinc (Zn) in water samples from the Riruwai mining area in Kano State, Nigeria. The results indicated significant contamination of water resources, with heavy metal concentrations exceeding regulatory limits, particularly in samples RGW1 and RGW2. Although the risk assessments showed no immediate adverse effects from heavy metal exposure for the general population, children were identified as being more vulnerable to such contamination. This highlights the urgent need for protective measures aimed at this sensitive group. Consequently, the study advocates for ongoing monitoring and robust risk management strategies to protect public health and avert potential health crises in this mining community.

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