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Health Risk Assessment of Heavy Metals through the Consumption of Drinking Water from Riruwai Mining Area Kano State, Northern Nigeria

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ABSTRACT

The objective of this research is to study the health risk of heavy metals associated with the consumption of drinking water from the Riruwai mining area Kano State, Northern Nigeria. Water samples were collected from a variety of sources, including underground mining areas (RGW1), tap water samples (RGW2), mining pond water samples (RGW3), borehole water samples (RGW4), and well water samples (RGW5). The concentrations of Arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), and Zinc (Zn) were determined using atomic absorption spectrophotometer, and the measured concentrations of these metals were used to compute human health risk using the United State Environmental Protection Agency's (USEPA) model. The results of the study indicated that the concentrations of As, Cd, Cr, Hg, Mn, Pb, and Zn were ranged from 0.005-0.35, 0.001-0.15, 0.01-0.32, ND-0.14, 0.16-0.92, 0.007-0.10, and 2.85-20.03 mg/dm3 respectively. The mean concentrations of all the heavy metals were above the desirable limits recommended by WHO and NSDWQ during both seasons except in RGW5 and few locations where the heavy metals were not detected. For non-carcinogenic risk assessment, the HQ values of children were considerably higher than that of the adults in all sampling stations. The HQ values were less than one (HQ > 1) in both adults and children. For carcinogenic risk assessment, the total cancer risk (TCR) of Cr, Hg, Pb, and Zn were within the tolerable limit of less than $1x10^{-6}$ in all sampling sites, whereas As and Cd exceeded the tolerable limit in the underground mining site, mining pond and borehole water samples. Children were more vulnerable to cancer and non-cancer risks from heavy metals than adults. High values of cancer and non-cancer risks in children call for more attention to this group of people. The researchers recommended that the water resources of the Riruwai mining area should be continuously monitored for heavy metals especially As, Cd, Cr, and Zn, and preventative measures should be put in place to protect the health of the inhabitants of the study area.

Keywords: *Adults, Carcinogenic risk, Children, Heavy metals, Drinking water, Non-carcinogenic risk, Riruwai,*

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1. INTRODUCTION

Water is essential for human health and well-being and is recognized as a fundamental human right [1]. Water resource contamination remains a major concern in several regions of developing countries, particularly in sub-Saharan regions where contaminated water poses significant risks to human health and the environment [2]. Water pollution is one of the most significant environmental problems in the world in recent years since many human population around the world uses groundwater as a source of drinking water [3]. In Nigeria, poorly regulated population growth, urbanization and inappropriate management of water resources have adversely impacted both the quality and quantity of water [4].

Mining has made a major contribution to Nigeria's socio-economic growth. However, the accompanying environmental degradation through ore transportation, extraction, smelting and disposal of tailings and wastewater is a serious concern to the state [5]. Previous studies have shown that the extensive mining activities have deleterious effects on the groundwater resources due to the release of toxic metals from various environmental components such as soils, sediments, surface water and groundwater [6]. Substantial quantities of hazardous heavy metals are discharged into the environment during mining operations, which may cause significant environmental and health challenges [7]. Heavy metals are important to human health and ecosystem due to their toxic effects and persistence in the environment [8]. Human exposure to heavy metal is a major cause of concern due its non-biodegradability and persistence in the environment [9].

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The exposure of heavy metals by human body can take place through various pathways, which include direct ingestion, inhalation, and dermal contact [10]. Acute or chronic exposure to heavy metals may lead to variety of human health challenges, including dermal, pulmonary, cardiac, haematological, hepatic, renal, fertility, immunological and carcinogenic problems [11, 12]. The problem of heavy metals pollution in water resources is much more severe in developing nations like Nigeria due to laxity in environmental laws and improper monitoring of water resources as well as the presence of discriminate illegal mining activities [13].

Human risk assessment is described as the method of assessing the likelihood of event occurrence and the intensity of potential harmful effects on human exposure to environmental hazards across a specific period of time [14]. It is an effective way to assess the relationship between the environment and human health, that could be quantitatively evaluated in based on the degree of hazard [15]. According to USEPA (2004) risk assessment comprises of four fundamental steps, viz. (1) hazard identification, (2) hazard characterization, (3) exposure assessment and (4) risk characterization. Hazard Identification is essentially intended to measure metals that are present at any particular location, their concentrations and spatial distribution. The objective of the exposure assessment is to measure the magnitude, frequency and duration of human exposure to an environmental pollutant. Exposure assessment is generally performed by measuring the average daily intake (*ADI*) of heavy metals previously identified through ingestion, inhalation and dermal contact by adults and children from the study location [16]. Non-carcinogenic and carcinogenic risks are usually estimated during Risk characterization stage [17]. Carcinogenic risk is an incremental probability of any individual to develop cancer during his/her lifetime due to chemical exposure under contaminated environment [18]. Non-carcinogenic risk signified the effect of heavy metals within shortest period of exposure that may be exposed of a few hours to 1 year [19]. The ratio of exposure to toxicity is called hazard quotient (*HQ*). The larger the value of *HQ* above one (unity), the greater the level of concern [20]. The life time exposure (ADD_{life}) can be obtained from the earlier exposure assessment by distributing the exposure incurred over the exposure duration over expected life span [17].

Riruwai community, located in the extreme southern part of Kano State, Northern Nigeria is predominantly a mining community. Large scale mining commenced in 1979 with nearly 900 tons of Zn-Sn ore production per day. The mining activities was closed after five years of continued operation. Artisanal and small mining activities are still taking place in the area. A research conducted by Nigerian Mining Cooperation reported that close to five million tons of mineral Ore containing tin and Zinc were found in the area. Riruwai has an estimated population of 150,645 people based on the 2006 census report [21]. To the best of our knowledge, no any scientific research was carried out to study the health risk of heavy metals through the consumption of drinking water in the study area. Therefore, this prompted us to carry out research.

2. MATERIALS AND METHODS

2.1 Materials

In preparing of the solutions, analytical grade reagents were used throughout the study without further purification. All glass and plastic wares were soaked overnight in 10.00 % (v/v) nitric acid, washed three times with distilled water and finally three times with deionized water. The wares were oven dried at 50.00-60.00 °C [22]. Angstrom Atomic Absorption Spectrophotometer with the model AAS320 was used for the determination of heavy metals in water samples.

2.2 Methods

2.2.1 *Description of the Study Area*

Riruwai, the headquarters of Doguwa Local Government Area is situated in the extreme southern part of Kano State, Northern Nigeria. It lies between latitude 10°43''97''N - 10°45'01"N and longitude 8°43''3"E - 8°47'39" E covering an area of 129 km^2. Riruwai has the highest elevation in the whole of Kano having an average height of 1100 m above the sea level. It was reported to have a contour value greater than 580 m and slope of greater than 18 ° above sea level. The Köppen's climate classification categorized the climate as tropical savanna. The area is characterized by two distinct seasons: rainy (April – October) and dry (October-April) seasons [23]. A topographical map of Riruwai is shown in Figure 1.

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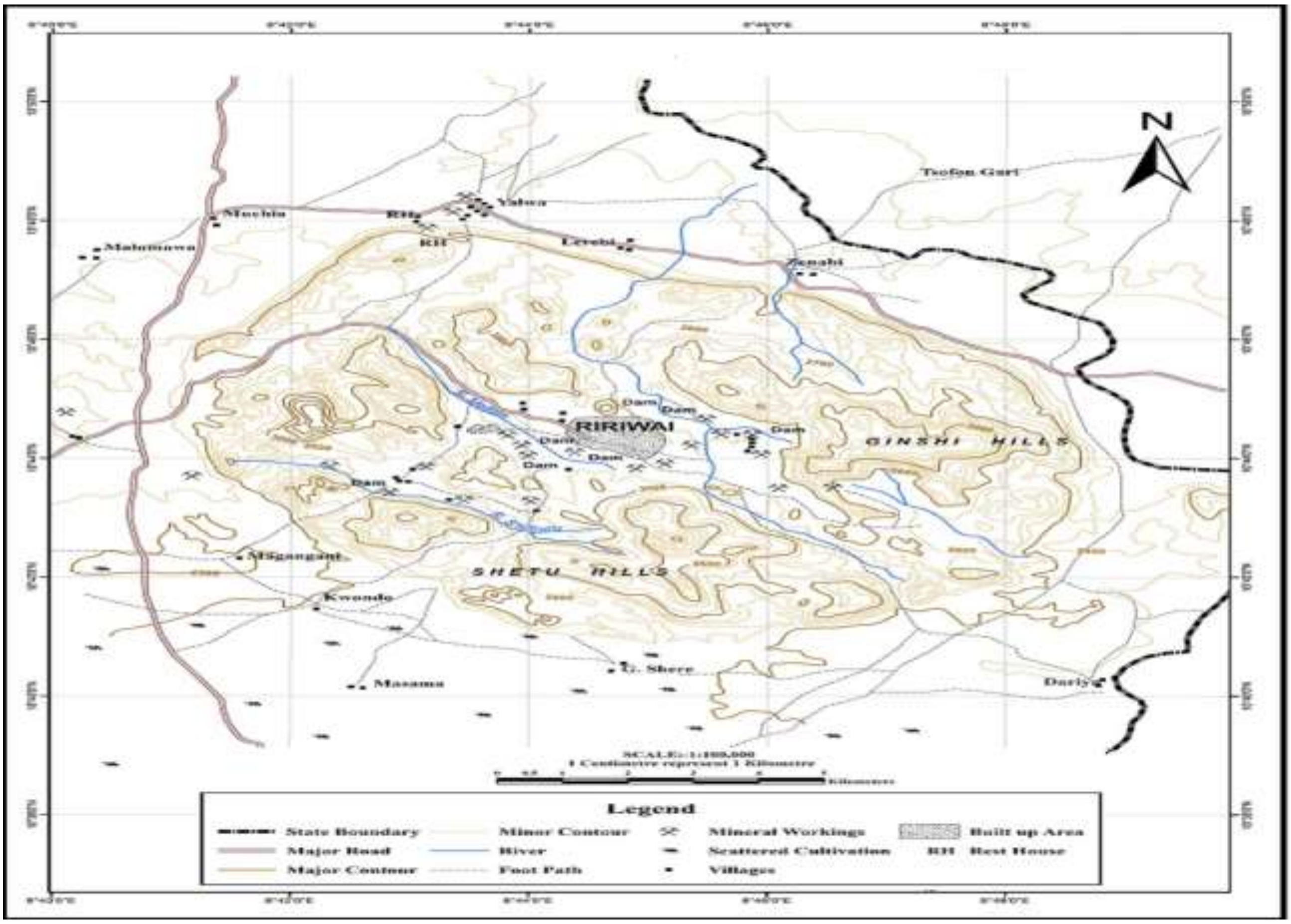

Figure 1. A topographical map showing the study Area

2.2.2 Sampling of Water Samples

A total of 31 water samples were collected from five sampling locations, including the underground mining Area (RGWI), tap water (RGW2), mining ponds (RGW3), borehole (RGW4) and the well water (RGW5) during the dry season (February, 2020) and rainy season (August, 2020). All the samples were collected in a polyethylene bottles which were pre-washed with 20.00 % of HNO_3 followed distilled water except for the determination of Hg where, borosilicate glass bottles were used to minimize Hg^{2+} lost and contamination as reported by Bravo *et al*. (2018). During sampling, the bottles were filled with water from each sampling site and then filtered. A few drops of 65.00 % of HNO_3 were added (bringing the pH of the samples below 2.00) to minimize precipitation and adsorption onto container walls [24]. The samples were placed in an ice-box and transported to the laboratory for further analysis.

2.2.3 Concentration and Digestion of Water Samples

A 500.00 cm^3 of the filtered water sample in a 1000 cm^3 beaker was placed on a hot plate and evaporated to 50.00 cm^3. It was allowed to cool and transferred into a 250 cm^3 beaker. A 10.00 cm^3 of concentrated nitric acid (HNO_3) was added, and the resulting solution was heated slowly at 80 °C until a clear solution was obtained (APHA, 2005). Slow heating was done to avoid metal loss due to evaporation. The digested sample was allowed to cool, filtered through Whatman filter paper No. 42 and transferred into a 100 cm^3 volumetric flask. The final solution was made up to the mark with more deionized water.

2.2.4 Determination of Heavy Metals in the Water Samples

The levels of seven heavy metals namely: As, Cd, Cr, Hg, Mn, Pb and Zn were analyzed using Angstrom Atomic Absorption Spectrophotometer (Angstrom AAS-320, Boston, USA) by selecting suitable wavelength for each elements. Three replicate determinations were run for each sample and the instrument was re-calibrated after analysis of ten samples.

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2.2.5 Health Risk Assessment

The health risk assessment was carried out using USEPA recommended health risk assessment model. In this study, seven heavy metals (As, Cd, Cr, Hg, Mn, Pb and Zn) were considered for human health risk assessment.

2.2.5.1 *Exposure assessment*

For health risk assessment of heavy metals in the water samples, two pathways connected to human exposure routes which include oral and dermal contacts are usually considered. Average daily intakes from water ingestion (ADI_{oral}) and from dermal contact (ADI_{derm}) were computed using the following relation [25]:

$$ADI_{oral} = \frac{C_{gw} \times IR_{gw} \times EF \times ED}{BW \times AT} \quad (2)$$

$$ADI_{derm.} = \frac{C_{gw} \times SA \times CF \times AF \times ABS \times EF \times ED}{BW \times AT} \quad (3)$$

Where:

ADI = Average daily intake of Heavy metals from ingestion and dermal contact for groundwater (mg/kg/day)

C_{gw} = Heavy metals concentration in the groundwater (mg/dm^3)
IR_{gw} = Ingestion rate for groundwater (dm^3/day)
CF = Conversion factor (dm^3/cm^3)
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 (cm^2)
AF = Soil to skin adherence factor (mg/cm^2)
ABS = Dermal absorption factor (no unit)

The various parameter values used for $ADI_{oral.}$ and ADI_{derm} computations are presented in Table 1. In order to reduce uncertainty of USEPA model due to the human and geographical differences, average *BW* for children and adults in the study area were generated using site-specific questionnaire.

Table 1: Exposure Parameters used for Health Risk Assessment (USEPA, 2011)

			Human Exposure	
Parameter	**Unit**	**Symbol**	**Child**	**Adult**
Body weight	kg	BW	14[a]	55[a]
Exposure frequency	days/years	EF	365	365
Exposure duration	years	ED	6	30
Ingestion rate	kg/day	IR	0.0001	0.0001
Exposed skin surface area	cm^2	SA	7422	18182
Soil to skin adherence factor	mg/cm^2	AF	0.07	0.2
Dermal absorption factor	—	ABS	0.001	0.001
Conversion factor	L/cm^3	CF	0.001	0.001
Average time (carcinogens)	days	AT	65 × 70	365 × 70
Average time (non-carcinogens)	days	AT	365 × ED	365 × ED

[a]Average body weights generated from the study area using questionnaire

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2.2.5.2 *Non-carcinogenic risk assessment*

In order to evaluate the non-cancer health risk for exposure to heavy metals, hazard quotient (*HQ*) were also calculated for both oral and dermal pathway. If the value of *HQ* exceeds 1, there is an unacceptable risk of adverse non-carcinogenic effects on health, while if the *HQ* is less than 1, it was considered an acceptable level [26]. *HQ* was calculated using the formula:

$$HQ = \frac{ADI}{RfD} \tag{4}$$

Where: *ADI* and *RfD* (mg/kg/day) are average daily intake and reference dose for heavy metals respectively. The values of *RfD* for As, Cd, Cr, Hg, Mn, Pb and Zn were 0.0003, 0.003, 0.003, 0.0003, 0.033, 0.0035 and 0.3 mg/kg-day respectively.

2.2.5.3 Carcinogenic risk assessment

The total carcinogenic risks (*TCR*) due to the exposure with heavy metals were computed using the following relation:

$$TCR = ADI \times SF \tag{5}$$

Where: *SF* is the carcinogenic slope factor and *ADI* is the average daily intake. The value of *SF* for As, Cd, Cr and Pb were 1.5, 6.3, 0.19, and 0.0085 mg/kg/day respectively. Hg, Mn and Zn have no available *SF* hence, they were not included in the computation of carcinogenic risks. The acceptable or tolerable risk levels for carcinogens suggested by the USEPA range from 10^{-4} (1 in 10,000) to 10^{-6} (1 in 1,000,000) [25].

2.2.6 *Quality Control and Statistical Analysis*

All analyses were performed in triplicate. Blank determinations were carried out to correct any background contamination from reagents, filter papers or other systemic sources of error. Statistical analyses were conducted using SPSS 23.0 (SPSS Inc., Chicago, USA). Graphs were plotted using Origin Pro 2016 (Origin lab Corporation, USA) software.

3. RESULTS AND DISCUSSION

3.1 Results

3.1.1 *Heavy Metals Concentration in the Water Samples*

The mean concentrations of As, Cd, Cr, Hg, Mn, Pb and Zn determined in water samples from five different sampling locations (RGW1, RGW2, RGW3, RGW4 and RGW5) during the dry and rainy seasons are presented in Tables 2 and 3.

Table 2: Levels of Heavy Metals in the Water Samples of Riruwai Mining Area during the Dry Season

Heavy Metals (mg/dcm^3)	Sampling Locations					WHO (mg/dcm^3)	NSDWQ (mg/dcm^3)
	RGWI	RGW2	RGW3	RGW4	RGW5		
As	0.15 ± 0.02	0.02 ± 0.00	0.21 ± 0.02	0.02 ± 0.01	ND	0.01	0.01
Cd	0.11 + 0.00	ND	0.08 ± 0.01	0.01 ± 0.007	ND	0.003	0.003
Cr	0.13 ± 0.01	0.04 ± 0.01	0.25 ± 0.03	ND	ND	0.05	0.05
Hg	0.09 ± 0.03	ND	0.07 ± 0.01	ND	ND	0.006	0.001
Mn	0.66 ± 0.02	0.14 ± 0.03	0.50 ± 0.01	0.30 ± 0.01	0.12 ± 0.01	—	0.2
Pb	0.06 ± 0.01	0.007 ± 0.00	0.08 ± 0.02	0.04 ± 0.02	0.003 ± 0.00	0.01	0.01
Zn	11.73 ± 2.61	5.26 ± 0.03	17.43 ± 0.07	4.88 ± 0.01	2.29 ± 0.03	—	3

Values are mean ± standard deviation (n = 3), ND = Not detected, RGW1 = Underground mining area water samples, RGW2 = Tap water samples, RGW3 = Mining pond water samples, RGW4 = Borehole water samples, RGW5 = Well water samples, WHO = World Health Organization, NSDWQ = Nigerian Standard for Drinking Water Quality

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Table 3: Levels of Heavy Metals in the Water Samples of Riruwai Mining Area during the Rainy Season

Heavy Metals (mg/dcm^3)	Sampling Sites					WHO (mg/dcm^3)	NSDWQ (mg/dcm^3)
	RGWI	RGW2	RGW3	RGW4	RGW5		
As	0.20 ± 0.03	0.03 ± 0.01	0.35 ± 0.04	0.04 ± 0.01	0.005 ± 0.001	0.01	0.01
Cd	0.15 + 0.01	0.009 ± 0.00	0.11 ± 0.01	0.02 ± 0.04	0.001 ± 0.00	0.003	0.003
Cr	0.17 ± 0.03	0.06 ± 0.01	0.32 ± 0.05	0.008 ± 0.00	0.001 ± 0.00	0.05	0.05
Hg	0.14 ± 0.03	ND	0.09 ± 0.00	0.003 ± 0.00	ND	0.006	0.001
Mn	0.92 ± 0.05	0.17 ± 0.01	0.73 ± 0.03	0.49 ± 0.05	0.16 ± 0.03	—	0.2
Pb	0.09 ± 0.03	0.03 ± 0.02	0.10 ± 0.04	0.06 ± 0.01	0.007 ± 0.001	0.01	0.01
Zn	14.05 ± 0.08	7.01 ± 0.03	20.03 ± 0.06	5.90 ± 0.03	2.85 ± 0.02	—	3

Values are mean ± standard deviation (n = 3), ND = Not detected, RGW1 = Underground mining area water samples, RGW2 = Tap water samples, RGW3 = Mining pond water samples, RGW4 = Borehole water samples, RGW5 = Well water samples, WHO = World Health Organization, NSDWQ = Nigerian Standard for Drinking Water Quality

3.1.2 *Health Risks Assessment*

3.1.2.1 *Non-carcinogenic risk assessment*

The results of non-carcinogenic health risk (in terms of hazard quotient, *HQ*) of heavy metals from five different sampling sites (underground mining area, tap water, mining pond, borehole and well water) are depicted in Figures 2 to 6.

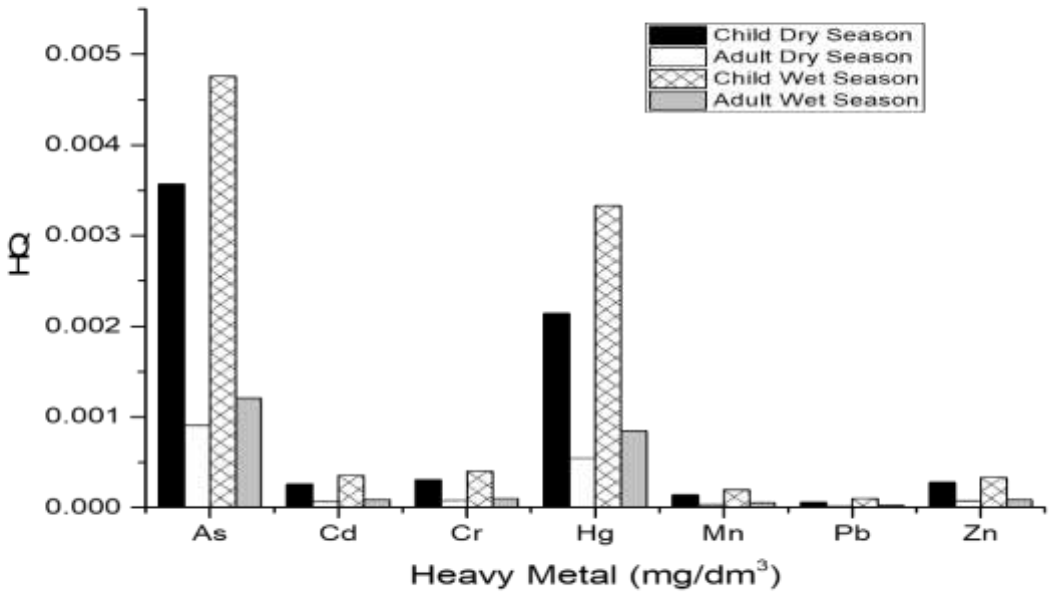

Figure 2*: *Total Health Quotient (HQ) of Heavy Metals from Riruwai Underground Mining Area Water Samples

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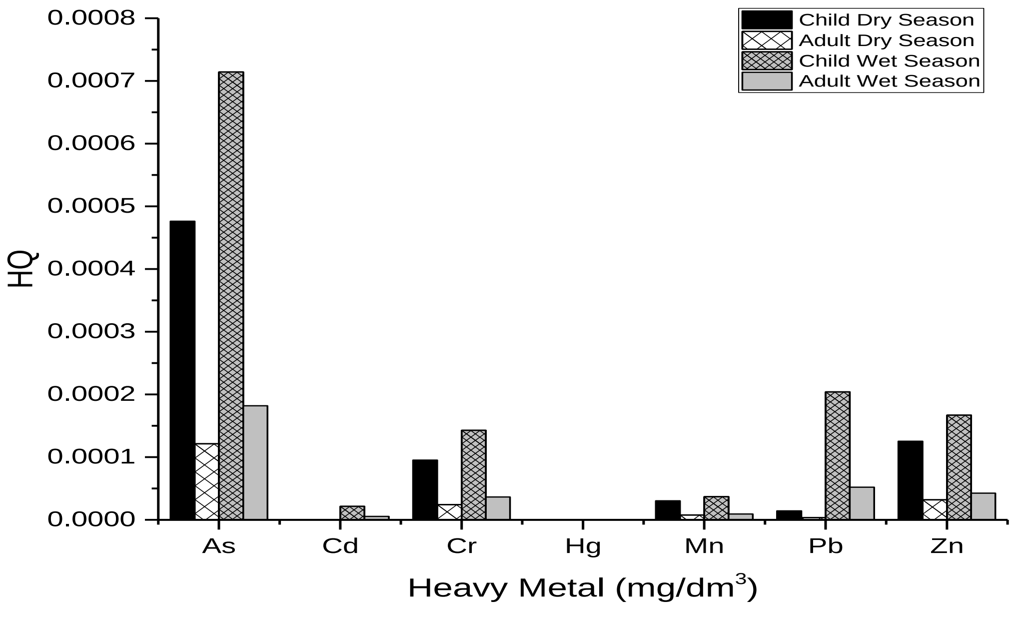

***Figure 3*: Total Health Quotient (HQ) of Heavy Metals from Riruwai Tap Water Samples**

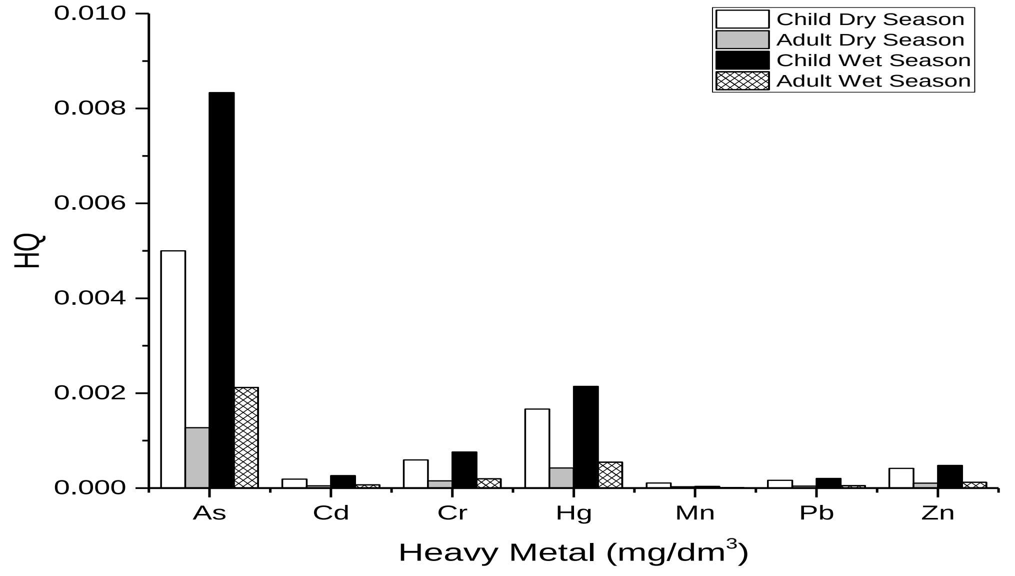

***Figure 4*: Total Health Quotient (HQ) of Heavy Metals from Riruwai Mining Pond Water Samples**

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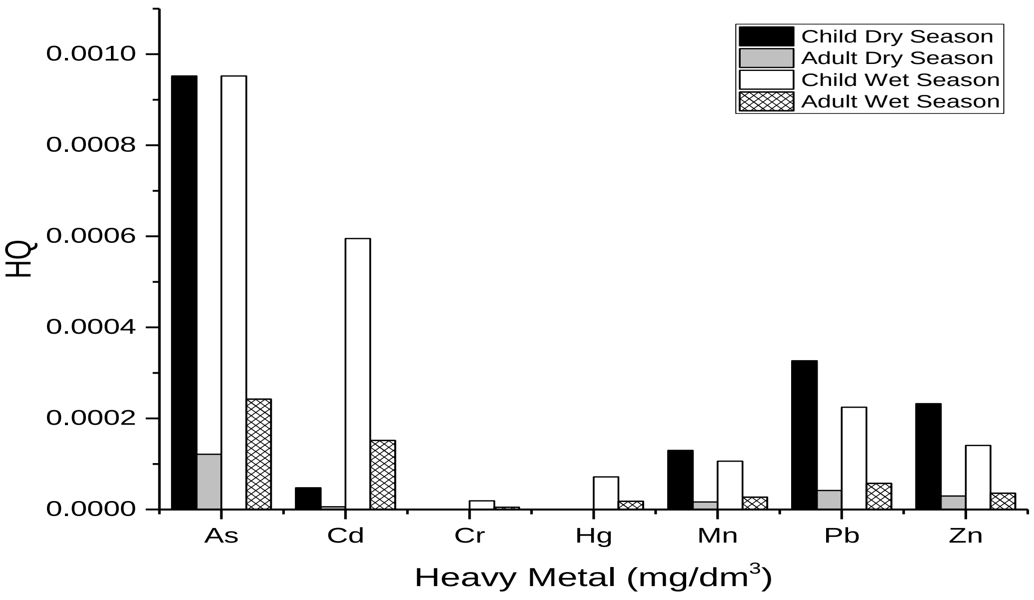

Figure 5: Total Health Quotient (Quotient) of Heavy Metals from Riruwai Borehole Water Samples

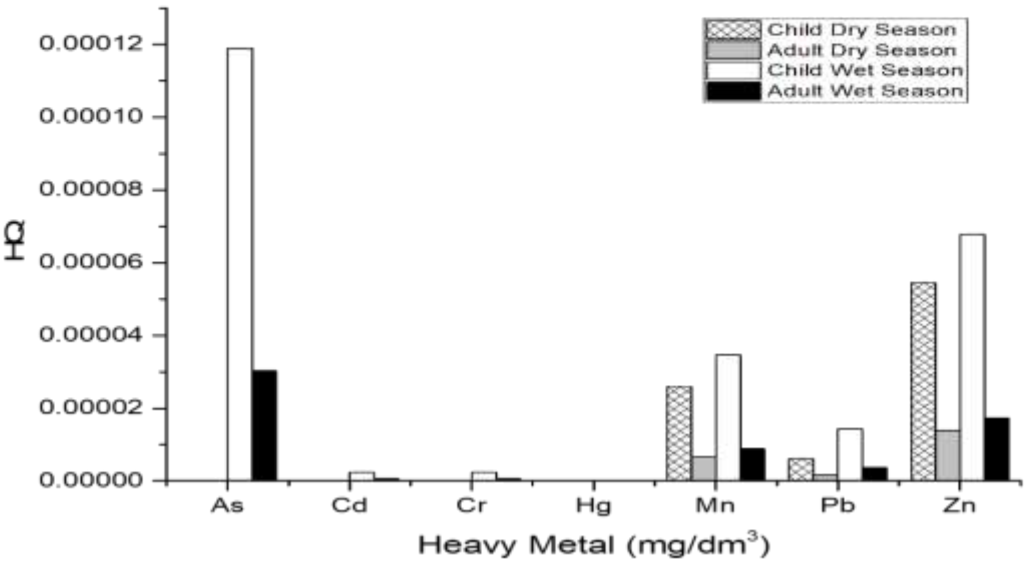

Figure 6: Total Health Quotient (HQ) of Heavy Metals from Riruwai Well Water Samples

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3.1.2.2 *Carcinogenic risk assessment*

Figures 7, 8, 9, 10 and 11 showed the results of total cancer risk (*TCR*) for underground mining area, tap water, mining pond, borehole and well water samples.

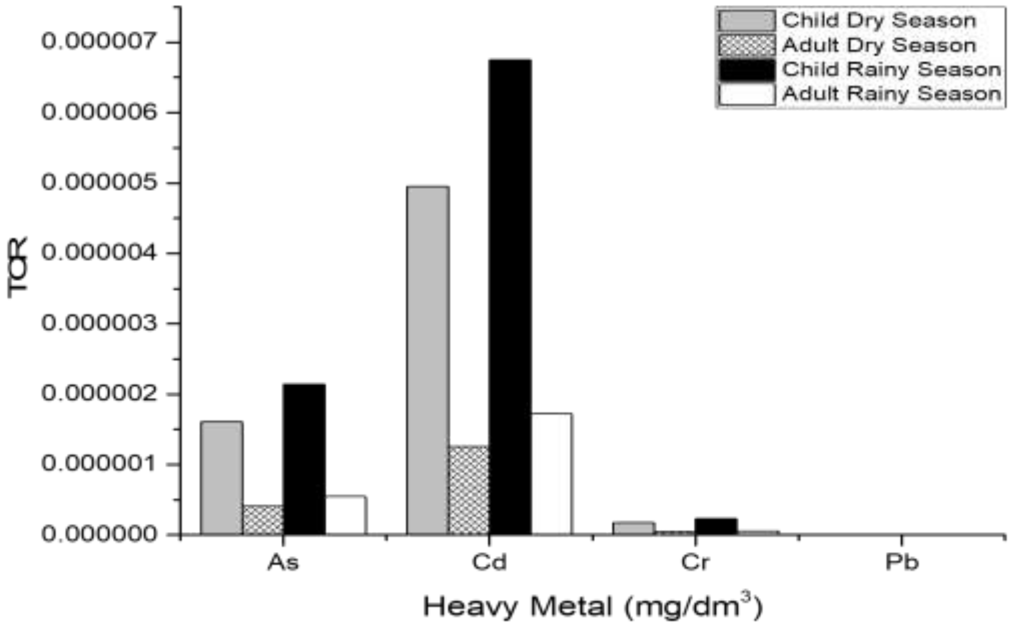

Figure 7: Total Cancer Risk (TCR) of Heavy Metals from Riruwai Underground Mining Area Water Samples

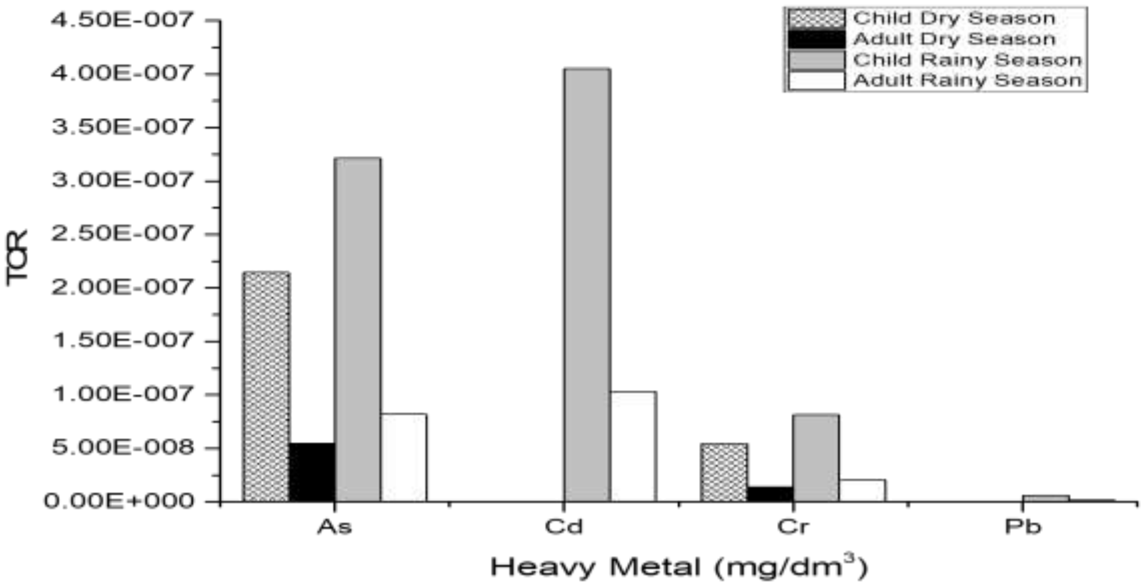

Figure 8: *Total Cancer Risk (TCR) of Heavy Metals from Riruwai Tape Water Samples*

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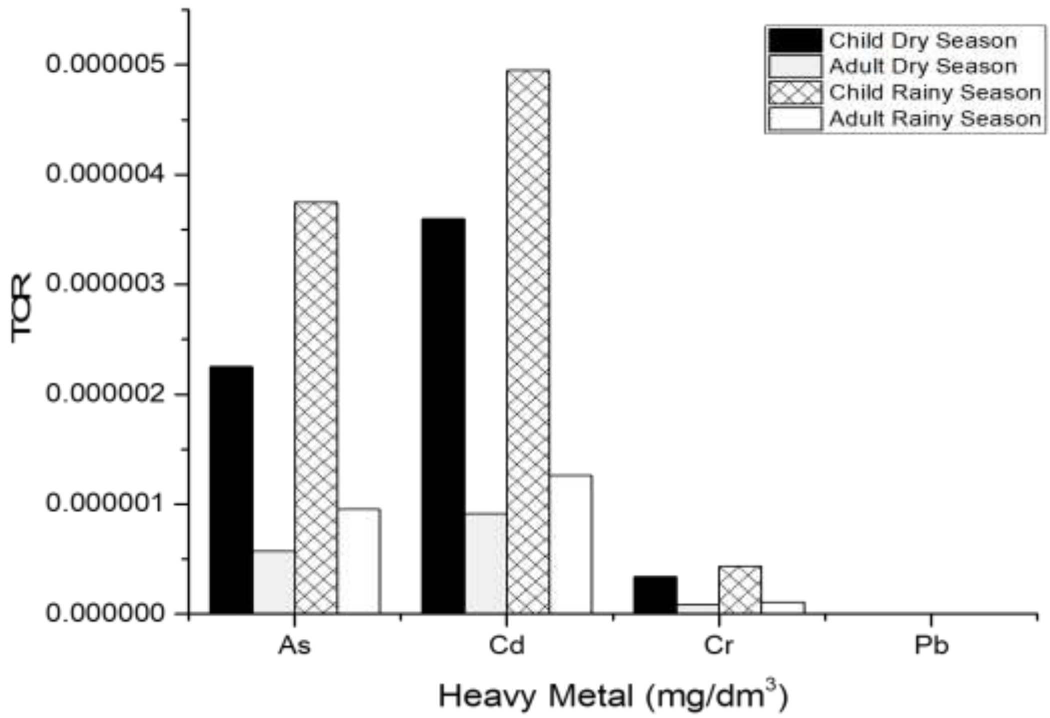

Figure 9: *Total Cancer Risk (TCR) of Heavy Metals from Riruwai Mining Pond Water Samples*

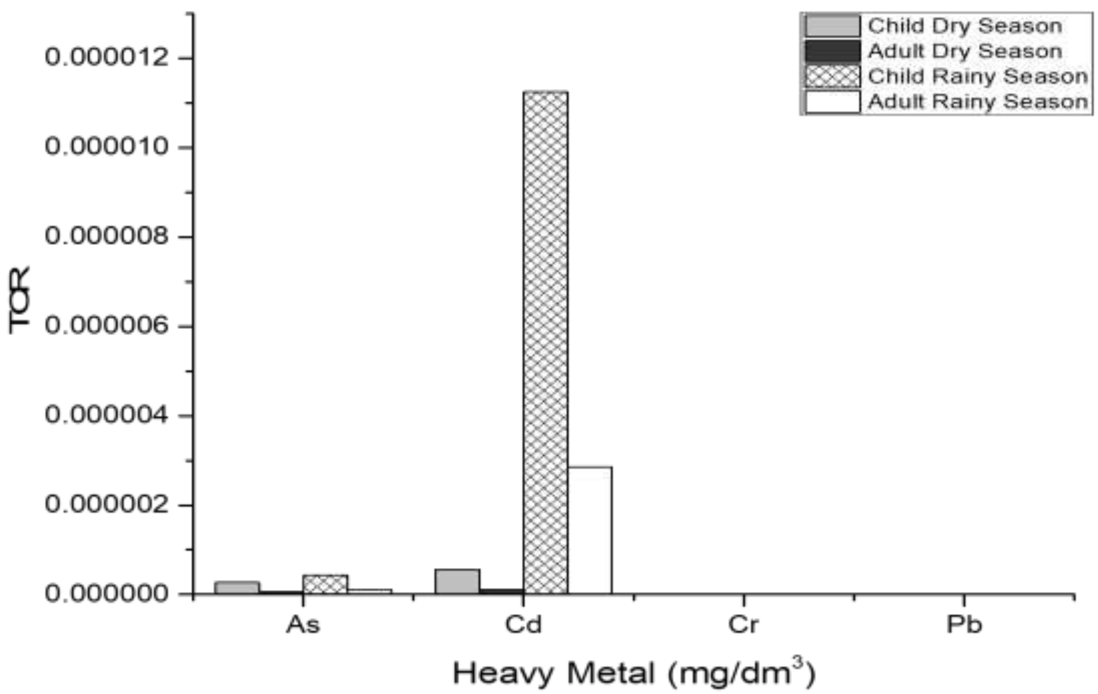

Figure 10: *Total Cancer Risk (TCR) of Heavy Metals from Riruwai Borehole Water Samples*

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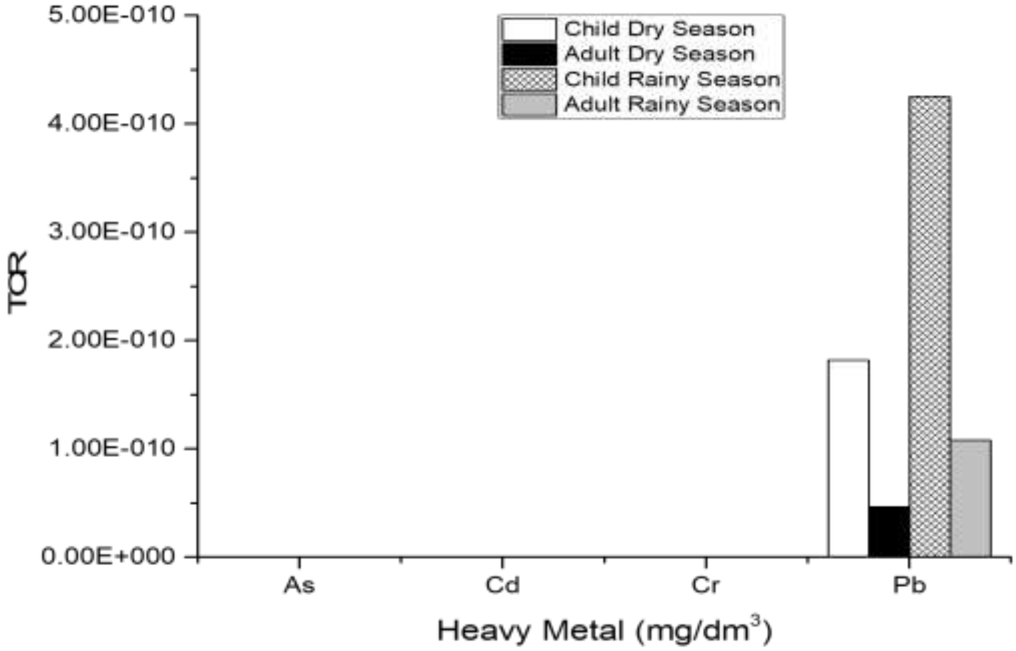

Figure 11*: *Total Cancer Risk (TCR) of Heavy Metals from Riruwai Well Water Samples

3.2 Discussion

3.2.1 *Levels of Heavy Metals in the Water Samples*

The concentrations of As, Cd, Cr, Hg, Mn, Pb and Zn were ranged from 0.005-0.35, 0.001-0.15, 0.01-0.32, ND-0.14, 0.16-0.92, 0.007-0.10, 2.85-20.03 mg/dm^3 during the dry season and 0.005-020, 0.001-0.15, 0.001-0.17, ND-0.14, 0.16-0.92, 0.007-0.09, 2.85-14.05 mg/dm^3 during rainy season. In RGW1 and RGW3, the mean concentrations of all heavy metals surpassed the desirable limits recommended by WHO and NSDWQ during all seasons. This indicates the contamination of RGW1 and RGW3 sampling locations by heavy metals. During the dry season, the concentrations of heavy metals were detected in the following locations: Cd (RGW2 and RGW5), Cr (RGW4 and RGW5), Hg (RGW2, RGW4 and RGW5). During the rainy season, only Hg were beyond the instrument detection limit in RGW2 and RGW5. This suggests that RGW2, RGW4 and RGW5 samples were not polluted by Cd, Cr and Hg. Nienie et al. [2] reported similar results when the studied the seasonal variability of water quality by traceable metals in Sub-urban Area in Kikwit, Democratic Republic of the Congo. The findings were also consistent with those reported by He et al. [10]. It has been reported by several authors that the water resources of the mining areas are well characterized by high levels of heavy metals [7, 9, 10].

3.2.2 *Health Risk Assessment*

3.2.2.1 *Non-carcinogenic risk assessment*

The non-carcinogenic risk is usually expressed in terms of hazard quotient (*HQ*). The results of non-carcinogenic health risk of heavy metals as depicted in Figure 2 to 6 revealed that the *HQ* values of arsenic (As) ranged from 0.00 to 5.00 x 10^{-3} for children, with highest value recorded in mining pond water samples and the lowest value obtained in the well water samples during the dry season. During the rainy season, the *HQ* values of As were spread from 0.00 (well water samples) to 8.33 x 10^{-3} (mining pond water samples). For the adults population, the *HQ* values of As ranged from 0.00 (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. The *HQ* values of cadmium (Cd) ranged from 0.00 to 1.90 x 10^{-4} for children, with highest value detected at the mining pond and lowest value found in the well water samples during the dry season, During the rainy season, the *HQ* values of Cd ranged from 2.38 x 10^{-5} (well water samples) to 2.62 x 10^{-4} (mining pond water samples). For the adults population, the *HQ* values of Cd ranged from 0.00 (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. The *HQ* values of chromium (Cr) ranged from 0.00

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to 5.95 x 10^{-4} for children, with highest value detected at the mining pond and lowest value found in the well water samples during the dry season, During the rainy season, the *HQ* values of Cr ranged from 2.38 x 10^{-5} (well water samples) to 7.62 x 10^{-4} (mining pond water samples). For the adults population, the *HQ* values of Cd ranged from 0.00 (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 the dry and rainy seasons respectively. The *HQ* values of mercury (Hg) ranged from 0.00 to 1.67 x 10^{-3} for children, with highest value detected at the mining pond and lowest value found in the well water samples during the dry season, During the rainy season, the *HQ* values of Hg ranged from 0.00 (well water samples) to 2.14 x 10^{-3} (mining pond water samples). For the adults population, the *HQ* values of Hg ranged from 0.00 (well water samples) to 4.24 x 10^{-4} (mining pond) and 0.00 (well water samples) to 5.45 x 10^{-4} (mining pond water samples), during the dry and rainy seasons respectively. The *HQ* values of manganese (Mn) spread from 2.59 x 10^{-5} (well water samples) to 1.40 x 10^{-4} (underground mining pond water samples) for children during the dry season, During the rainy season, the *HQ* values of Mn ranged from 3.46 x 10^{-5} (well water samples) to 2.00 x 10^{-4} (mining pond water samples). For the adults population, the *HQ* values of Mn stretched 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. The *HQ* values of lead (Pb) ranged from 6.12 x 10^{-6} (well water samples) to 1.63 x 10^{-4} (underground mining pond water samples) for children during the dry season. During the rainy season, the *HQ* values of Pb ranged from 1.43 x 10^{-5} (well water samples) to 2.04 x 10^{-4} (mining pond water samples). For the adults population, the *HQ* values of Pb spread from 1.56 x 10^{-6} (well water samples) to 4.16 x 10^{-5} (mining pond) and 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. The *HQ* values of zinc (Zn) ranged from 5.45 x 10^{-5} to 4.15 x 10^{-4} for children, with highest value detected at the mining pond water samples and lowest value found in the well water samples during the dry season, During the rainy season, the *HQ* values of Hg ranged from 6.79 x 10^{-5} (well water samples) to 4.77 x 10^{-4} (mining pond water samples). For the adults population, the *HQ* values of Zn 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. Among the heavy metals, Arsenic was said to have the highest *HQ* value in both children and adults in all sampling locations and the highest *HQ* value was detected in mining pond water while the lowest was found in well water samples. The *HQ* values of other heavy metals (Cd, Cr, Hg, Mn, Pb and Zn) changed along the sampling stations. Generally, the *HQ* values of children were considerably higher than that of the adults in all sampling locations. Similar results were reported by Zhang *et al*. [27] and Ghahramani *et al*. [28]. The *HQ* values were less than one ($HQ > 1$) in both adults and children during all the seasons. This was indicating that the heavy metals did not pose adverse health effects. However, higher *HQ* values in children than the adults imply that children are more susceptible to heavy metals pollution than the adults. This might be due to the behavioral and physiological characteristics of children as children are more vulnerable to toxic contaminants [29].

3.2.3.2 *Carcinogenic risk assessment*

The results of total cancer risk (*TCR*) which were shown in Figures 7 to 11 indicated that for children, the *TCR* of arsenic (As) ranged from 0.00 to 2.25 x 10^{-6}, with highest value detected at the mining pond and lowest value found in the well water samples during the dry season. During the rainy season, the *TCR* values for As ranged from 0.00 (well water samples) to 3.75 x 10^{-6} (mining pond water samples). For the adults population, the *TCR* values of As ranged from 0.00 (well water samples) to 5.72 x 10^{-7} (mining pond) and 0.00 (well water samples) to 9.55 x 10^{-7} (mining pond water samples), during the dry and rainy seasons respectively. The *TCR* of cadmium (Cd) ranged from 0.00 (well water samples) to 3.60 x 10^{-6} (mining pond water samples) during the dry season for children population. During the rainy season, the *TCR* values of Cd ranged from 0.00 (well water samples) to 3.75 x 10^{-6} (mining pond water samples). For the adults population, the *TCR* values of Cd ranged from 0.00 (well water samples) to 9.16 x 10^{-7} (mining pond) and 0.00 (well water samples) to 1.26 x 10^{-6} (mining pond water samples), during the dry and rainy seasons respectively. The *TCR* of chromium (Cr) spread from 0.00 (well water samples) to 3.39 x 10^{-7} (mining pond water samples) during the dry season for children population. During the rainy season, the *TCR* values of Cr ranged from 0.00 (well water samples) to 4.34 x 10^{-7} (mining pond water samples). For the adults population, the *TCR* values of Cr ranged from 0.00 (well water samples) to 8.63 x 10^{-8} (mining pond) and 0.00 (well water samples) to 1.11 x 10^{-7} (mining pond water samples), during the dry and rainy seasons respectively. The *TCR* of lead (Pb) ranged from 1.82 x 10^{-10} (well water samples) to 4.85 x 10^{-9} (mining pond water samples) during the dry season for children population. During the rainy season, the *TCR* values of Pb ranged from 4.25 x 10^{-10} (well water samples) to 6.07 x 10^{-9} (mining pond water samples). For the adults population, the *TCR* values of Pb ranged from 4.64 x 10^{-11} (well water samples) to 1.23 x 10^{-9} (mining pond) and 1.08 x 10^{-10} (well water samples) to 1.54 x 10^{-9} (mining pond water samples), during the dry and rainy seasons respectively. The *TCR* for all heavy metals were higher in children than the adults. This indicates that children were more vulnerable to cancer risk from heavy metals than the adults. Similar trends were reported by Alidadi *et al*. [30]. The *TCR* for As and Cd were greater than the safe limit of 1 x 10^{-6} in the underground mining area, mining pond water and borehole water samples both children and adults and during dry and rainy seasons.

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4. CONCLUSION

The present study reveals that the mean concentrations of all the heavy metals were above the desirable limits recommended by WHO and NSDWQ during both seasons except in well water (RGW5) samples and few locations where the heavy metals were not detected. For non-carcinogenic risk, the *HQ* values of children were considerably higher than that of the adults in all sampling locations and all seasons. The *HQ* values were less than one ($HQ > 1$) in both adults and children during all the seasons. This was indicating that the heavy metals did not pose adverse health effects. However, higher *HQ* values in children than the adults implied that children are more susceptible to heavy metals pollution than the adults. For carcinogenic risk assessment, the *TCR* for As and Cd were greater than the safe limit of 1×10^{-6} in the underground mining area, mining pond water and borehole water samples both children and adults and during dry and rainy seasons. This suggests a carcinogenic risk for children and adults exposed to heavy metals through ingestion and dermal routes. Therefore, water resources of Riruwai mining area should be properly monitored for heavy metals especially As, Cd, Cr and Zn and preventative measures should be put in place to protect the health of the inhabitants of study area.

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