

Evaluation of Heavy Metals Pollution Status of the Groundwater around Riruwai Mining Area, Kano State, Nigeria

H. Badamasi, U.F. Hassan, H. M. Adamu, and N. M. Baba

ABSTRACT

The aim of this study was to investigate the heavy metals pollution status of the groundwater of Riruwai mining area, Kano State, Nigeria. A total of 31 groundwater samples were collected from five sampling locations which include: underground mining site (RGW1), tap water, (RGW2), surface mining ponds (RGW3), borehole (RGW4) and the well water samples (RGW5) during the dry and rainy seasons. The concentrations of seven heavy metals (As, Cd, Cr, Hg, Mn, Pb and Zn) and some physical parameters (pH, EC, and TDS) were determined using Atomic Absorption Spectrometer and Deluxe Water and Soil Analysis Kit respectively. The results of the analysis revealed that pH, EC and TDS were within the desirable limits recommended by WHO and NSDWQ in all sampling locations except in RGW1 and RGW3 for both seasons. The concentrations of heavy metals (mg/dm³) ranged as follow: As (ND to 0.15), Cd (ND to 0.1), Cr (ND to 0.25), Hg (ND to 0.09), Mn (0.12 to 0.66), Pb (0.003 to 0.06) and Zn (2.29 to 11.75), and As (0.005 to 0.20), Cd (0.001 to 0.15), Cr (0.001 to 0.17), Hg (ND to 0.14), Mn (0.16 to 0.92), Pb (0.007 to 0.09) and Zn (2.85 to 14.05) during the dry and rainy seasons respectively. The heavy metals concentrations changed along with the sampling sites in decreasing order of RGW1 > RGW2 > RGW3 > RGW4 > RGW5 in both seasons. The concentrations of all heavy metals were above the desirable limits recommended by WHO and NSDWQ during both seasons except well water samples (RGW5) and some few locations where the heavy metals were not detected. Therefore, it is recommended that water resources of the Riruwai mining area should be monitored closely, and more efforts should be made to reduce heavy metals concentrations level, particularly As, Cd, Cr and Zn.

Keywords: Atomic Absorption Spectrometer, Concentrations, Heavy metals, Riruwai

Published Online: May 28, 2021

ISSN: 2684-446X

DOI : 10.24018/ejgeo.2021.2.3.140

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I. INTRODUCTION

Groundwater is among the most significant and essential resources that occurs in a permeable geologic formations known as aquifers [1]. Approximately 2 billion people across the globe depend on groundwater as the main source of water for human consumption and agricultural practices [2]. Rapid population growth, industrial development, agricultural practices, and mining activities has contributed to the groundwater overutilization for many years, placing unprecedented pressure on global groundwater supplies [3]. Mining activities are major anthropogenic activities causing water pollution and they are well known for their deleterious effects on the groundwater [4]. Mine tailings and other mining-related operations are the major source of contaminants, mainly of heavy metals in water. 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 [5]. Heavy metals are of serious importance to human health and ecosystem owing to their toxic effects and

persistence in the environment [6]. During mining and smelting processes, heavy metals are usually discharged from mining areas by erosion, weathering, and leaching into nearby soil, surface, and groundwater [7]. A study conducted by Giri and Singh [8] affirmed that 50% of the groundwater samples were highly polluted with respect to heavy metals like Cu, Ni, Co, Cr, Mn and Pb in the proximity of copper mining region. A groundwater of Udege Mbeki Mining District, North-Central, Nigeria was reported by Okegye and Gajere [9] to be contaminated with heavy metals. The present study sought to investigate the groundwater quality status related to heavy metals pollution in the mining area of Riruwai, Kano State, Nigeria. The research would provide baseline data for policy makers and the general public on the heavy metals metal pollution status of the study area for future environmental monitoring.

II. MATERIALS AND METHODS

A. Materials

In preparing 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 [10]. Angstrom Atomic Absorption Spectrometer with the model AAS320 was used for the determination of heavy metals in the groundwater samples.

B. Methods

1. Description of the study area

Riruwai, the headquarters of Doguwa Local Government Area is located in the 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 km² (Fig. 1). 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 [11]. Riruwai is among the younger granite complexes in Nigeria. It is situated amidst the assemblage of metamorphic and calc-alkaline meta-igneous rocks that subsequently changed from Precambrian to Cambrian ages [12].

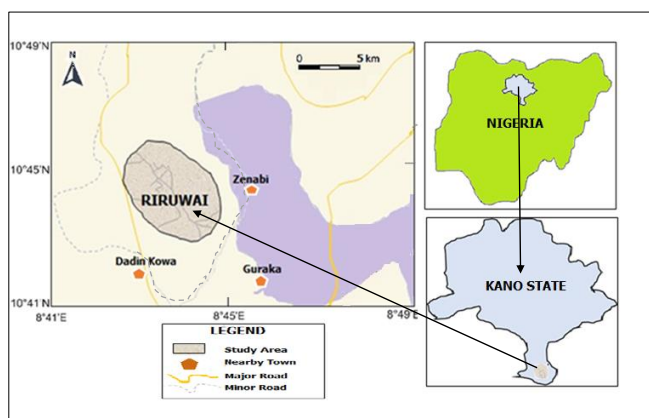


Fig. 1. Map showing the study Area.

2. Sampling of the groundwater samples

Sampling was performed in February (dry season) and August (rainy season) of 2020 to get an idea of the seasonal variations of the heavy metal concentrations. A total of 31 groundwater samples were collected from five sampling sites which include underground mining pond (RGW1), tap water (RGW2), mining ponds (RGW3), borehole (RGW4) and the well water (RGW5). All the samples were collected in polyethylene bottles which were pre-washed with 20.00 % of HNO₃ and deionized water, except for the determination of Hg where borosilicate glass bottles were used to minimize Hg²⁺ loss and contamination as reported by Bravo et al. [13]. During sampling, two bottles were filled with water from each sampling site and then filtered. A few drops of 65.00 % of HNO₃ were added to one bottle of water samples (bringing the pH of the samples below 2.00) to minimize precipitation and adsorption onto container walls [14] and was used to determine heavy metals concentrations. The second bottle was not acidified and was used to measure pH, electrical conductivity (EC) and total dissolved solids (TDS). To get

constant pH and EC, the samples were collected after 15 min of pumping of the samples. The pH, EC and TDS were measured on the spot using Deluxe Portable Water and Soil Analysis Kit (Model 1024 G). The samples were placed in an ice-box and transported to the laboratory for further analysis.

3. Concentration and digestion of the groundwater samples

A 500.00 cm³ of the filtered water sample (in a 1000 cm³ beaker) was placed on a hot plate and evaporated to 50.00 cm³. The sample was allowed to cool and transferred into a 250 cm³ beaker. 10.00 cm³ of concentrated HNO₃ was added and the resulting solution was heated slowly at 80 °C until a clear solution was obtained [14]. 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 then transferred into a 100 cm³ volumetric flask. More deionized water was added to the solution to make it up to the mark.

4. Determination of heavy metals in the groundwater samples

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

5. Quality control and statistical analysis

All samples were analyzed in triplicate. The standard solutions of all heavy metals were prepared by successive dilution of certified standards (1000 mg/dm³) procured from Sigma Aldrich and the calibration curve of each metal was constructed. Blank determinations were carried out to correct any background contamination from reagents, filter papers or other systemic sources of error. All statistical analyses were carried out using SPSS 23.0 (SPSS Inc., Chicago, USA). All graphs were plotted using OriginPro 2016 (Originlab Corporation, USA) software.

III. RESULTS AND DISCUSSION

A. Results

1. Heavy metals concentrations and some physical parameters of the groundwater samples

The mean concentrations of arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), manganese (Mn), lead (Pb) and zinc (Zn) and some selected physical parameters (pH, electrical conductivity, and total dissolved solid) were determined respectively in water samples from five different sampling sites (underground mining site, tap water, mining pond, borehole and well water) during the dry and rainy seasons are presented in Tables I and II.

TABLE I: LEVELS OF HEAVY METALS AND SOME SELECTED PHYSICAL PARAMETER IN THE WATER SAMPLES OF RIRUWAI, KANO STATE DURING THE DRY SEASON

Parameters	Sampling Locations					WHO	NSDWQ
	RGW1	RGW2	RGW3	RGW4	RGW5		
pH	5.61 ± 0.14	6.82 ± 0.06	5.31 ± 0.02	6.79 ± 0.03	6.88 ± 0.05	6.5-9.5	6.5-8.5
EC (µS/cm)	1500 ± 9.50	469.00 ± 5.23	1722.00 ± 3.00	523.00 ± 2.08	423.00 ± 2.52	1400	1000
TDS (mg/dm ³)	960.00 ± 3.61	300.16 ± 2.11	1102.08 ± 1.53	314.72 ± 2.00	270.72 ± 2.08	—	500
As (mg/dm ³)	0.15 ± 0.02	0.02 ± 0.00	0.21 ± 0.02	0.02 ± 0.01	ND	0.01	0.01
Cd (mg/dm ³)	0.11 ± 0.00	ND	0.08 ± 0.01	0.01 ± 0.007	ND	0.003	0.003
Cr (mg/dm ³)	0.13 ± 0.01	0.04 ± 0.01	0.25 ± 0.03	ND	ND	0.05	0.05
Hg (mg/dm ³)	0.09 ± 0.03	ND	0.07 ± 0.01	ND	ND	0.006	0.001
Mn (mg/dm ³)	0.66 ± 0.02	0.14 ± 0.03	0.50 ± 0.01	0.30 ± 0.01	0.12 ± 0.01	—	0.2
Pb (mg/dm ³)	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 (mg/dm ³)	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 (2011), NSDWQ = Nigerian Standards for Drinking Water Quality (2007)

TABLE II: LEVELS OF HEAVY METALS AND SOME SELECTED PHYSICAL PARAMETER IN THE WATER SAMPLES OF RIRUWAI, KANO STATE DURING THE RAINY SEASON

Parameters	Sampling Locations					WHO	NSDWQ
	RGW1	RGW2	RGW3	RGW4	RGW5		
pH	5.87 ± 0.10	7.63 ± 0.05	5.98 ± 0.02	7.53 ± 0.02	7.64 ± 0.07	6.5-9.5	6.5-8.5
EC (µS/cm)	1700 ± 11.50	501.00 ± 1.53	1951.00 ± 2.51	589.00 ± 1.88	498.00 ± 2.56	1400	1000
TDS (mg/dm ³)	1088.00 ± 2.00	320.64 ± 2.51	1248.64 ± 2.08	376.96 ± 2.00	318.72 ± 2.00	—	500
As (mg/dm ³)	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 (mg/dm ³)	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 (mg/dm ³)	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 (mg/dm ³)	0.14 ± 0.03	ND	0.09 ± 0.00	0.003 ± 0.00	ND	0.006	0.001
Mn (mg/dm ³)	0.92 ± 0.05	0.17 ± 0.01	0.73 ± 0.03	0.49 ± 0.05	0.16 ± 0.03	—	0.2
Pb (mg/dm ³)	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 (mg/dm ³)	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 (2011), NSDWQ = Nigerian Standards for Drinking Water Quality (2007)

B. Discussion

1. Physical parameters of the groundwater samples

The pH of the water is a very important water quality parameter, and its measurement is crucial in evaluating water quality. This is due to the fact that pH regulates the solubility of hazardous metals in the aquatic ecosystem, which can have a severe impact on aquatic organisms and human health [15]. The pH of the groundwater as depicted in Tables I to II ranged from 5.31 (mining pond) to 6.88 (well water), with 5.61 (underground mining site), 6.79 (borehole) and 6.82 (tape water) falling in between the lowest and highest pH values during the dry season. During the rainy season, the pH values varied from 5.87 (underground mining site) to 7.64 (well water). The pH of 5.98 (mining ponds), 7.53 (boreholes) and 7.63 (tape water) fell in between the lowest and highest values. Generally, the pH values of all sampling locations were higher during the rainy season and decreased in the order of well water > tap water > borehole > underground mining site > mining pond. Mining pond location was having lowest pH (more acidic) value while the highest pH (slightly alkaline) value was recorded in the well water samples for both seasons. The decreased pH values observed at all sampling sites during the dry season is most likely due to dissolved mineral ions generated by evapotranspiration. Likewise, the increase in pH during the rainy season might be attributed to the diluting action of dissolved ions [16]. The pH values in all the samples were within the permissible limits for drinking water recommended by the WHO and the NSDWQ for both seasons except for underground mining site and mining pond. These results were in good agreement with

those reported by Singh and Kamal [1] and Rahman et al. [17]. The low pH values in underground mining sites and mining ponds may be due to the formation of sulfuric acid from the oxidation of pyrite in the ore [18].

Electrical conductivity (EC) is a measure of an ability of substances to conduct electricity. Higher EC values indicates the enrichment of dissolve ions and pollution load in the groundwater [19]. The EC values ranged from 423.00 µS/cm (well water) to 1722.00 µS/cm (mining pond), with 469.00 µS/cm (tape water), 523.00 µS/cm (borehole) and 1500.00 µS/cm (underground mining site) fell in between the lowest and highest EC values during dry season. During the rainy season, the EC values ranged from 498.00 µS/cm (well water) to 1951.00 µS/cm (mining pond). The EC of 501.00 µS/cm (tape water), 589.00 µS/cm (borehole) and 1700.00 µS/cm (underground mining site) fell in between the extreme values. The findings of this research revealed that EC values decreased during the dry season and increased during the rainy season. This was consistent with the findings of Silas et al. [15]. All EC values were within the threshold values recommended by WHO and NSDWQ except in underground mining water and mining pond water samples. The highest EC value of 1953.51 µS/cm was found at the mining pond in the rainy season, while the lowest EC value of 420.48 µS/cm was recorded in the well water. The higher EC values in underground mining site and mining pond might be due the presence of excess ions in the water [20]. According to Abida and Harikrishna [21] the conductivity values below 50.00 µS/cm are regarded as low, while those between 50.00 – 600.00 µS/cm are said to be medium and values above 600.00 µS/cm are considered to be high. In this

study, all the water samples were below 600.00 $\mu\text{S}/\text{cm}$ except for underground mining site and mining pond which were above 600.00 $\mu\text{S}/\text{cm}$, indicating high conductivity high conductivity.

Total dissolved solids (TDS) are the inorganic ions and smaller quantities of organic matter that exists as solution in water. TDS values varied from 270.72 mg/dm^3 (well water) to 1102.08 mg/dm^3 (mining pond), with 300.16 mg/dm^3 (tap water), 314.72 mg/dm^3 (borehole) and 960.00 (underground mining site) falling in between the lowest and highest values of TDS determined during the dry season. During the rainy season, the TDS values spread from 318.72 mg/dm^3 (well water) to 1951.00 mg/dm^3 (mining pond), with 320.64 mg/dm^3 (tap water), 376.96 mg/dm^3 (borehole) and 1088.00 mg/dm^3 (underground mining site) fell in between the lowest and highest TDS values. The highest value of TDS was found in the rainy season at mining pond while the lowest was recorded at the well water. All values of TDS were within the permissible limit suggested by NSDWQ with the exception of water samples from underground mining site and mining pond in both dry and rainy seasons. Zhu et al. [22] reported similar results when they studied the effects of mining activities on groundwater hydrochemistry and heavy metals migration in the Yangtze Metallogenic Region, Eastern China.

2. Levels of heavy metals in the groundwater samples

The concentrations of arsenic (As) ranged from ND (well water) to 0.21 mg/dm^3 (mining pond) with 0.02 mg/dm^3 (tap water and borehole) and 0.15 mg/dm^3 (underground mining site) falling in between extreme concentrations during the dry season. During rainy season, the concentration of As varied between 0.35 mg/dm^3 in the mining pond location and 0.005 mg/dm^3 in the well water. The As concentration of 0.003 mg/dm^3 (tap water), 0.004 mg/dm^3 (borehole) and 0.20 mg/dm^3 (underground mining site) were in the middle of the range. The higher concentrations levels of As were found during the rainy season with mining pond site having the highest As concentration while the lowest concentration was detected at well water samples. Similar results were reported by Obasi and Akudinobi [23] when they studied the levels of heavy metals in water resources of lead–zinc mining communities of Abakaliki, Southeast Nigeria. The concentrations of As were above allowable limits recommended by WHO and NSDWQ in all sampling locations and for all seasons except in the well water. This indicated that the ground water has been polluted by As. Lower levels of As exposure have been linked to nausea, vomiting, decreased erythrocyte, leukocyte production and irregular heartbeats, whilst long-term exposure has been connected to the development of skin lesions, internal malignancies, lung illness, peripheral vascular disease, hypertension and cardiovascular disease [24].

The concentration of cadmium (Cd) ranged from ND (well water and tap water) to 0.11 mg/dm^3 (underground mining site) with 0.01 mg/dm^3 (borehole) and 0.08 mg/dm^3 (mining pond) falling in between the lowest and highest concentrations of Cd for the period of dry season. During the rainy season, the concentration of Cd spread from 0.001 mg/dm^3 (well water) to 0.15 mg/dm^3 (underground mining site) with 0.009 mg/dm^3 , 0.02 mg/dm^3 and 0.11 mg/dm^3

falling in between the lowest and highest concentrations. The concentrations of Cd in all sampling sites were above WHO and NSDWQ acceptable range except in tap water and well water samples. High levels of Cd in mining pond, underground mining site and borehole could be linked to the weathering and subsequent dissolution of the chalcopyrite and pyrite ores in the area [23]. The concentrations of chromium (Cr) ranged from ND (well water and borehole) to 0.25 mg/dm^3 (mining pond) with 0.04 mg/dm^3 and 0.13 mg/dm^3 falling between the lowest and highest concentrations in the dry season. During the rainy season, the concentration of Cr ranged from 0.001 mg/dm^3 (well water) to 0.32 mg/dm^3 (mining pond). The Cr concentrations of 0.008 mg/dm^3 , 0.06 mg/dm^3 and 0.17 mg/dm^3 lied in between the extreme concentrations level of Cr. The concentration of Cr in borehole and well water was within the WHO and NSDWQ permissible limits for all seasons whereas the concentration of Cr in mining pond and underground mining site were above allowable limit. In tap water sample, the concentration of Cr was above the WHO and NSDWQ recommended limit during the rainy season and below the limit during the dry season. This was in good agreement with results reported by Prasad et al. [25]. Cr has reported to cause anemia, irritations and ulcers in the small intestine and stomach, damage sperm and neurological effects [26].

The concentration of mercury (Hg) ranged from ND (tap water, borehole and well water) to 0.09 mg/dm^3 with 0.07 mg/dm^3 falling between the lowest and highest concentration during the dry season. During the rainy season, the concentration of Hg spread from not detected (well water and tap water) to 0.14 mg/dm^3 with 0.003 mg/dm^3 (borehole) and 0.09 mg/dm^3 fell in between the observed extreme concentration levels. The concentrations of Hg were not detected in the water samples from tap water and well water in all the seasons. The concentration of Hg was detected only during the rainy season in borehole water sample which was below WHO and NSDWQ limits. However, the concentrations of Hg in the underground mining site and mining pond were above WHO limit of 0.006 mg/dm^3 and NSDWQ limits of 0.001 mg/dm^3 in both the seasons, which indicates contamination of water from underground mining site and mining pond water samples. Hg and its compounds affect the neurological system, causing irritation, memory issues, and loss of hearing or vision [23].

The concentration of manganese (Mn) ranged from 0.12 mg/dm^3 (well water) to 0.66 mg/dm^3 (underground mining site), with 0.14 mg/dm^3 (tap water), 0.30 mg/dm^3 (borehole) and 0.50 mg/dm^3 (mining pond) falling between the lowest and highest observed values during the dry season. During the rainy season, the concentration of Mn spread from 0.16 mg/dm^3 (well water) to 0.92 mg/dm^3 (underground mining site). The Mn concentrations of 0.17 mg/dm^3 (tap water), 0.49 mg/dm^3 (borehole) and 0.73 mg/dm^3 (mining pond) lied in between the lowest and highest observed concentration levels. The highest concentrations of Mn (0.92 mg/dm^3) were obtained in underground mining site during the rainy season while the lowest value of 0.12 mg/dm^3 was found in well water sample. High concentration of Mn especially in the rainy season might be attributed to the dissolution of manganese from the chalcopyrite and siderite ores which underlie the area. It has

been established that Mn^{2+} predominates in most groundwater at pH of 4.00–7.00 but may become oxidized under alkaline conditions at $pH > 8.00$ [23]. The concentrations of Mn were above WHO and NSDWQ in all sampling stations with the exception of well water and tap water samples. This demonstrated that 60% of water samples analyzed were contamination by Mn.

The concentration of lead (Pb) ranged from 0.003 mg/dm^3 (well water) to 0.08 mg/dm^3 (mining pond), with 0.007 mg/dm^3 (tap water), 0.04 mg/dm^3 (borehole) and 0.06 mg/dm^3 (underground mining site) falling between the lowest and highest observed concentrations of Pb during the dry season. During the rainy season, the concentration of Pb ranged from 0.007 mg/dm^3 (well water) to 0.10 mg/dm^3 (mining pond). The Pb concentrations of 0.03 mg/dm^3 (tap water), 0.06 mg/dm^3 (borehole) and 0.09 mg/dm^3 (underground mining site) fell in between the lowest and highest observed concentrations. The highest concentration of Pb was detected in the mining pond water samples during the rainy season while the lowest was recorded in well water samples during the dry season. The concentrations of Pb in all sampling sites were above the desirable limit except for well water, where the Pb concentrations were below the desirable limit in all the seasons and tap water during the dry season. Higher concentration of Pb in almost all samples analyzed is indicating that the groundwater in the study area was contamination by Pb. Davies et al. [27] established that the high concentration of Pb in groundwater of mining sites can be linked to the high immobility of Pb especially, at a low pH. Pb is a highly toxic metal whose widespread uses has caused extensive environmental degradation and health problems in many parts of the world.

The concentrations of zinc (Zn) ranged from 2.29 mg/dm^3 (well water) to 17.43 mg/dm^3 (mining pond) with 4.88 mg/dm^3 (borehole), 5.26 mg/dm^3 (tap water) and 11.73 mg/dm^3 (underground mining site) falling between the observed extreme concentrations during the dry season. During the rainy season, the concentrations of Zn ranged from 2.85 mg/dm^3 (well water) to 20.00 mg/dm^3 (mining pond), with 5.90 mg/dm^3 (borehole), 7.01 mg/dm^3 (tap water) and 14.05 mg/dm^3 (underground mining site) falling in between the lowest and highest observed concentrations of Zn. The concentration of Zn in all sampling locations exceeded the desirable limit of 3.00 mg/dm^3 recommended by NSDWQ in both seasons. The highest Zn concentrations of 20.00 mg/dm^3 was found in the mining pond water (RGW3) during rainy seasons, while the lowest (2.29 mg/dm^3) was observed in well water samples during the dry season. This indicated that 100 % of groundwater samples analyzed were contaminated by Zn. Previous studies had established that mining areas are well characterized by high concentration of heavy metals resulted from mine tailings and mine waste [5]. The observed high values of Zn might be associated with the phenomenon of leaching due to heavy metals precipitation from the overburden dumps and tailing ponds [1]. Zn is an important metal required for optimal growth and development; but, in higher concentrations, it is poisonous [28]. The toxicity of Zn in human may occur if zinc concentration reaches 3 mg/dm^3 in water. The toxicity is characterized by symptoms of irritability, muscular stiffness and pain, loss of appetite and nausea [29].

3. Seasonal variations of heavy metals and some physical parameters of the groundwater samples

Heavy metals and physical characteristics of water samples showed marked seasonal variations as shown in Tables I and II, with the highest concentrations recorded during the rainy season and lower concentrations reported during the dry season. High concentrations of heavy metals and some physical parameters in the rainy season might be due to the rainfall during the rainy season which not only dilutes the heavy metals but also helps in their leaching [30]. However, independent statistical t-test revealed no statistically significant difference between the means of two seasons in all the groundwater samples analyzed.

IV. CONCLUSION

The findings of this study revealed that the mean concentrations of As, Cd, Cr, Hg, Mn, Pb, Zn and some physical parameters (pH, EC and TDS) varied with the sampling sites, with higher values reported during the rainy season. The pH, EC and TDS were within the desirable limits recommended by WHO (2011) and NSDWQ (2007) in all sampling locations except for underground mining sites (RGW1) and mining pond (RGW3) samples during dry and rainy seasons. While 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. The study demonstrates heavy metal contamination of the groundwater of Riruwai mining area, and it is suggested that water resources in the area should be carefully monitored, and more efforts should be made to reduce heavy metal concentrations, particularly As, Cd, Cr, and Zn, in the area.

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