



Determination of concentrations and Annual Effective Dose of Pb, Cr, Rn in Groundwater Sources in Shika and Zaria City, Kaduna State, Nigeria

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ABSTRACT: The levels of some physicochemical parameters, heavy metals and ^{222}Rn in some underground water of Shika and Zaria, Nigeria are reported. The Cr in the hand-dug wells and borehole water was in the range of 0.008 ± 0.006 mg/L to 0.338 ± 0.39 mg/L for the rainy, and 0.09 ± 0.13 mg/L to 0.66 ± 0.06 mg/L for the dry season; while Pb ranged from 0.001 ± 0.00 mg/L to 0.862 ± 0.569 mg/L for rainy season in Shika and Zaria. The ^{222}Rn concentration ranged from 0.1 ± 0.0141 Bq/L to 66.56 Bq/L for rainy and 1.5 ± 0.0141 Bq/L to 71.53 ± 0.007 Bq/L for dry season. The borehole samples have higher ^{222}Rn than the permissible limit and most physicochemical parameters of Shika water were within the safe limit. The highest annual effective dose was $14.30 \mu\text{Sv/year}$ and $12.0 \mu\text{Sv/year}$ in the rainy and dry seasons respectively. There was significant difference between the parameters across the season. Therefore, caution should be taken to avoid the elevation of these elements in water bodies as a result of anthropogenic activities.

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African countries have a long history of using surface and groundwater sources. Deterioration in the quality and quantity of surface water and public water supply system, in many developing countries have led to dependence on groundwater sources (Okonko *et al.*, 2008; Adelana *et al.*, 2008). Water shortage or its pollution can cause severe decrease in productivity and deaths of living species (Galadima and Garba, 2012).

Heavy metals exist in water in colloidal particulate and dissolved phases (Adepoju-Bello *et al.*, 2009). They also exist in water bodies from natural origin such as eroded minerals, leaching of ore deposits and volcanic extruded products (Igwilon *et al.*, 2006).

Rock, soil and water contain ^{238}U , ^{232}Th and their decay products. Since the late 1980s, radon has been identified to be of health concern, causing lung cancer among others. Radon is a radioactive gas, formed when uranium or radium decays. It escapes from the earth's crust through cracks and crevices in the bedrock and either dissolves in ground water or seeps through foundation cracks into the environment/human habitations (Shakir *et al.*, 2011). So, the quality of groundwater is affected by the characteristics of the media through which the water passes on its way to the ground water zone of saturation (Adeyemi *et al.*, 2007). Radiation from

natural sources account for the majority of human exposure to radiation, with radon decay product being the largest contributor (Tso and Li, 1987; UNSCEAR, 2000). Adelekan and Abegunde (2011) reported Cr in hand-dug wells near automobile mechanic villages in Ibadan, Nigeria to be lower than the limits set by WHO for drinking water. Also, the levels of Pb in selected underground water have been assessed by various studies (Ekwumemgbo *et al.*, 2011). The work of Emad, (2014) showed that groundwater samples in Jordan Valley contained radon-222 in the range of 0.28 ± 1.5 to 44.31 ± 3.2 Bq L⁻¹ by using RAD7 instrument. In addition, well water was reported to have the highest radon content compared to reverse osmosis (drinking water), mineral water and tap water by Abdul Malik (2015). The well water recorded Ra above the maximum contamination limit of 300 pCi/L recommended by United State Environmental Protection Agency. The aim of this work is to determine the radon concentration in groundwater (hand dug well and borehole) in Shika and Zaria city, as well as the lead and chromium concentration in the water samples.

MATERIALS AND METHODS

Site Description: The areas of study are Shika and Zaria city metropolis, in Kaduna State, Nigeria, having scarcity of public water supply; so leading to dependence on groundwater sources for domestic

usage. These areas are bound by Longitude $7^{\circ} 42^1$ and latitude $11^{\circ} 3^1$ (Zaria city); and Longitude $7^{\circ} 33^1$ and Latitude $11^{\circ} 11^1$ (Shika). The sampling points where the water samples were collected randomly during the rainy and dry season of 2016 are showed in the map below ($n = 20$).

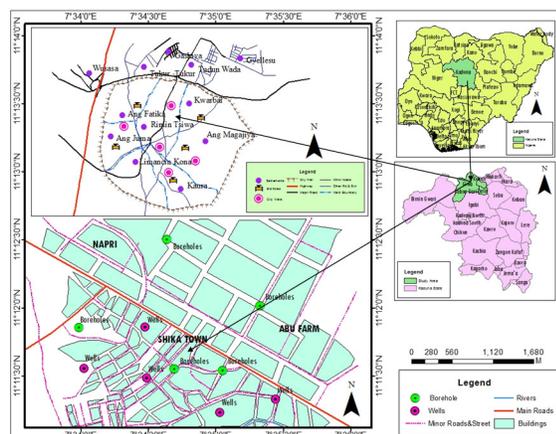


Fig 1: Map of Shika and Zaria City Showing Location of Wells and Boreholes. Source: Zaria Quirk Bird Satellite Image 2015.

Physicochemical Parameters of the Water Sample: The methods used to determine the physicochemical parameters of water samples collected in the rainy and dry season of 2016 were those described by APHA (1995). The pH, temperature, total dissolve solids (TDS), colour and conductivity of the water were measured *in-situ*. In order to maintain quality assurance, triplicate determination of the samples were made and the data presented as means.

Metal Determination: To 10.0 cm^3 of each water sample collected wet digestion was carried out with 10.0 cm^3 concentrated HCl and concentrated HNO_3 acid mixture (3:1) on a hot plate at 90°C (Mendham *et al.*, 2008).

After digestion, each of the digest was filtered using a Whatman number 42 filter paper. The filtrate was analysed for heavy metals using a Plasma Atomic Absorption Spectrophotometer (Varian AA240FS) at the Multi-user Laboratory, Ahmadu Bello University, Zaria – Nigeria. The total Pb was determined at 405.781 nm and Cr at 425.433 nm .

Quality assurance to validate the atomic absorption spectrometry equipment was carried out by spiking experiment. To 50 cm^3 of the Multi-element standard solution (MESS) prepared, was drawn with a graduated pipette and used to spike 50 cm^3 of pre-digested groundwater sample from Shika, Nigeria in a 100 cm^3 beaker. The spiked water sample and 10 cm^3 of unspiked water sample was then digested. Then the

concentrations of Cr and Pb in the spiked and unspiked samples were used to calculate the percentage recovery (Omoniyi *et al.*, 2016a).

Analysis of Ground Water for ^{222}Rn Determination: The water samples were analyzed as soon as possible (maximum of three days) after collection to achieve maximum accuracy, because the composition of the sample may change if samples are left for long before performing the analysis.

Sample Preparation and Analysis: About 10 mL each of the samples was added into a scintillation vial containing 10 mL of the insta-gel scintillation cocktail. The vials were sealed tightly and shaken for more than two minutes to extract ^{222}Rn in water phase into the organic scintillator.

Sample Analysis: The prepared samples were analyzed using a liquid scintillation counter (Tri-Carb-LSA1000) located at the Center for Energy Research and Training (CERT), Ahmadu Bello University, Zaria–Nigeria. The samples were analyzed after they were allowed to stand for three hours after preparation in order to establish radioactive equilibrium between ^{222}Rn and its daughter progeny. The liquid scintillation counter was calibrated prior to the analysis using IAEA ^{226}Ra standard solution. For the calibration, the ^{222}Rn standard samples were counted for 60 minutes. Background count measurements were also made for the same time period (60 min). The ^{222}Rn activity concentration was calculated using the following equation (Galan Lopez *et al.*, 2004).

$$\text{Rn} \left(\frac{\text{Bq}}{\text{L}} \right) = \frac{100 \times (\text{SC} - \text{BC}) \exp(\lambda t)}{60(\text{CF}) \times (\text{D})} \quad 1$$

Where, Rn = radon level in Bq/L; SC = sample count rate (count min^{-1}); BC = background count rate (Count min^{-1}); K = calibration value; T = elapsed time from sampling to testing given in minutes.

Also, the annual effective doses due to the intake of radon were calculated from the mean activity concentration using the following equation:

$$\text{ERn} = \text{DFRn} \cdot \text{Iw} \cdot \text{A}^{222}\text{Rn} \quad 2$$

where DFRn is the effective dose per unit intake of radon in water for adults, taken as 10^{-8} Sv/Bq from UNSCEAR 1993 report; and Iw is the water consumption rate (l/a) taken to be 2 L per day .

RESULTS AND DISCUSSION

Physicochemical Parameters of the Water Sample: The temperature for the water samples as presented in

Table 1 were within the WHO (1993) acceptable limit of 25°C for drinking water, except for sample 6 and 9 from Zaria boreholes that were 27.00 ± 0.00°C and 26.00 ± 0.00°C) respectively during the rainy and dry season and sample 11 and 13 from Samaru boreholes, being 24.00 ± 0.00 and 23.00 ± 0.00°C respectively during dry season. The deviation of these temperature might be as a result of absorbed heat from the sun or from bedrock beneath, because temperature is due to flux of heat coming beneath the ground or chemical reaction due to the decomposition of organic matter (Chapman, 1997). The pH of the water samples are in the range of 6.5-9.5 for the wells and boreholes water during the rainy and dry season, except for sample 5 from Zaria well, 8 from Zaria borehole and 10 Zaria borehole with pH of 6.10 ± 0.14, 6.40±0.00 and 6.45± 0.00 respectively; and these were below the recommended range of 6.5 to 9.5 set by WHO (1997), which could be attributed to sewage or waste dumping, so through leaching of these contaminants into the soil which ultimately increase the soil acidity and consequently the pH is lowered as observed (WHO, 1997). The electrical conductivity was highest in ZWS3 with value 970.50±0.71 µs/cm and lowest in

SBW4 with value 55.00±0.00 µs/cm. All the water samples had conductivity level below the WHO maximum contaminant level of 1200 µs/cm. The physicochemical parameter of some water samples assessed by Ishaku and Ezeigbo (2010) showed that the conductivity of about 33.3 % of the sampling sites were above the WHO maximum contaminant level, further the high conductivity level at the sites mentioned could be linked to sewage materials and leaching of inorganic contaminants (Harison, 1992).

The colour intensity of the water samples across the sampling points ranged from 5.00 to 10.00 Hazen; with all being below the standard limit of 15 Hazen unit for drinking water (WHO, 1997). This indicates that the selected water samples have good aesthetic property. As presented in Table 1, the total dissolved solid contents of the water from all the sampling points were below WHO maximum contaminant levels of 1000 mg/L. Higher total dissolved solid reduce water clarity, which could contribute to decrease in photosynthetic activities and might lead to an increase in water temperature (NRCC, 2011). This might also explain the good water colour reported in this study.

Table 1: Physicochemical parameters of Shika and Zaria wells and Boreholes during Rainy and Dry season

SAMPLE ID	Temp (°C) Rainy	Temp (°C) Dry	pH Rainy	pH Dry	EC (µs/cm) Rainy	EC (µs/cm) Dry	Colour (Unit) Rainy	Colour (Unit) Dry	TDS(Mg/L) Rainy	TDS (Mg/L) dry
1	25.00±1.41	25.00±0.00	7.35±0.07	9.00±0.00	960.50±0.71	74.00±0.00	5.00±0.00	10.00±0.00	480.50±0.71	431.00±1.41
2	25.50±0.71	25.00±0.00	7.25±0.07	8.50±0.71	428.50±0.71	785.00±18.38	5.00±0.00	5.00±0.00	741.00±1.41	885.00±1.41
3	25.50±0.71	25.00±0.00	7.20±0.00	9.00±0.00	970.50±0.71	899.50±0.71	5.00±0.00	5.00±0.00	452.50±0.71	601.00±
4	25.00±0.00	25.00±0.00	7.30±0.00	8.00±1.41	462.00±0.00	398.00±0.00	5.00±0.00	5.00±0.00	753.00±0.00	132.00±0.00
5	26.00±0.00	25.00±0.00	6.10±0.14	8.50±0.71	603.50±0.71	685.50±0.71	5.00±0.00	5.00±0.00	290.50±0.71	293.00±
6	27.00±0.00	25.00±0.00	6.70±0.00	8.00±0.00	406.00±0.00	582.00±0.00	5.00±0.00	5.00±0.00	922.50±0.71	312.00±0.00
7	26.00±0.00	25.00±0.00	6.70±0.00	8.50±0.71	804.50±0.71	900.00±0.00	5.00±0.00	5.00±0.00	560.00±0.00	593.00±
8	25.50±0.71	25.00±0.00	6.40±0.00	8.50±0.71	584.00±0.00	894.00±0.00	5.00±0.00	5.00±0.00	271.50±0.71	740.00±0.00
9	26.00±0.00	25.00±0.00	6.65±0.07	9.00±0.00	706.50±0.71	801.00±0.00	5.00±0.00	5.00±0.00	490.50±0.71	610.00±2.83
10	25.50±0.71	25.00±0.00	6.45±0.07	9.00±0.00	625.50±0.71	865.00±0.00	5.00±0.00	5.00±0.00	322.00±0.00	432.00±
11	25.00±0.00	24.05±0.07	8.00±0.00	8.50±0.00	122.00±1.41	147.00±	5.00±0.00	5.00±0.00	60.50±0.71	73.00±
12	26.00±0.00	25.00±0.00	7.25±0.35	7.65±0.07	271.50±0.71	507.00±0.00	5.00±0.00	5.00±0.00	209.50±0.71	255.00±
13	25.05±0.07	23.00±0.00	7.55±0.07	7.50±0.00	187.00±0.00	195.00±0.00	5.00±0.00	5.00±0.00	90.50±0.71	101.00±1.41
14	25.75±0.35	25.00±0.00	7.85±0.07	7.49±0.02	57.00±0.00	55.00±0.00	5.00±0.00	5.00±0.00	28.00±0.00	41.00±1.41
15	25.50±0.71	25.00±0.00	7.65±0.07	7.38±0.03	98.00±0.00	81.00±0.00	5.00±0.00	5.00±0.00	46.00±0.00	41.00±1.41
16	26.00±0.00	25.00±0.00	7.60±0.00	7.20±0.02	120.50±0.71	277.00±0.00	5.00±0.00	10.00±0.00	58.00±0.00	139.00±0.00
17	25.75±0.35	25.00±0.00	7.50±0.00	6.95±0.07	351.50±0.71	325.00±0.00	5.00±0.00	5.00±0.00	176.00±0.00	171.00±
18	26.50±0.71	25.00±0.00	7.20±0.00	7.19±0.02	254.50±0.71	277.00±0.00	5.00±0.00	10.00±0.00	132.00±0.00	139.00±0.00
19	25.00±0.00	26.00±0.00	7.55±0.07	6.95±0.07	62.00±0.00	57.00±0.00	5.00±0.00	5.00±0.00	30.00±0.00	29.00±0.00
20	25.00±0.00	25.00±0.00	8.28±0.04	6.95±0.07	96.50±0.71	948.00±0.00	5.00±0.00	5.00±0.00	468.00±0.00	470.00±0.00
WH std		25		6.5-9.5		1200		15		1000

Key: 1- ZWS1, 2- ZWS2, 3- ZWS3, 4- ZWS4, 5- ZWS5, 6- ZBS1, 7- ZBS2, 8- ZBS3, 9- ZBS4, 10- ZBS5, 11- SBW1, 12- SBW2, 13- SBW3, 14- SBW4, 15- SBW5, 16- SWW1, 17- SWW2, 18- SWW3, 19- SWW4, 20- SWW5, ZWS- Zaria well, ZBS- Zaria borehole, SBW- Shika borehole, SBW- Shika well

Heavy Metal Content of the Water Samples: From the spiking experiment, the mean % recovery in ascertaining the quality assurance ranged from 78.6 ± 0.21 to 89.11 ± 0.32. This signals accuracy of the atomic absorption spectrophotometer. The result of the levels of Pb and Cr in the selected groundwater as presented in Table 2 shows that during the rainy season of 2016, all the water samples contain Cr below the detection limit of the AAS machine, except for samples 6 (ZBS1) having 0.008±0.006 mg/L and 10 (ZBS5) having 0.009±0.006 mg/L; though found to be below the standard permissible limit of Cr in water

(0.050 mg/L); the study indicated that sample 7 (ZBS2) and 8 (ZBS3) have mean Cr concentration of 0.338 ± 0.39 mg/L and 0.236 ± 0.169 mg/L which are above the permissible limit of Cr in water (WHO, 1993). This might be as a result of increase in industrial process such as tanning, paint production, and pigment production, as these involve the use of Cr compound and are therefore the most frequent source of hexavalent Cr (Marques, 2000).

The report of this study is similar to that by Saba and Ebrahim (2016) for 100 well water in the plain of

Ardabil, having Cr content lower than the allowed amount stated by the national standard. Also, Adefemi and Awokunmi (2010) reported that water samples from selected hand-dug wells in Itaogbolu area of Akure, Ondo State, Nigeria contained Cr (0.0 - 0.4 mg/L) that was within the maximum allowable limit set by World Health Organization for drinking water.

Further, the result for Pb concentration in the water samples collected in the rainy season indicated that it was in the range of 0.001 ± 0.001 to 0.862 ± 0.0569 mg/L. The borehole water samples generally recorded lower Pb than the hand-dug well water, especially for the samples collected from Zaria city, Nigeria. This trend is similar to the study by Ehi-Eromosele and Okiei (2012) in which Pb concentrations in surface, ground and tap waters collected in some part of Lagos metropolis, Nigeria were determined using Differential Pulse Anodic Stripping Voltammetry (DPASV), the ranking of Pb content was: Tin-can Lagoon (0.215 mg/L) > Lagos Lagoon (0.110 mg/L) > well water, Lawanson, Surulere (0.080 mg/L) > Borehole near Odo Iyaaloro stream, Mende (0.070 mg/L) > Borehole, Olusosun, Ojota (0.033 mg/L) (Ehi-Eromosele and Okiei; 2012). Therefore, the higher levels of Pb in some well water than borehole in Shika and Zaria, Nigeria can be explained by the depth difference, while other variables like closeness to dumpsites, streams, local craft and industrial activities could also be significantly relevant. During the rainy season, all the water samples had Pb concentrations above the tolerable limit of 0.01 mg/L set by WHO 1993, except for sample 1 and 2, which

had mean Pb concentration of 0.0075 ± 0.005 and 0.001 ± 0.001 mg/L respectively. This is similar to the report of Ehi-Eromosele and Okiei (2012) for the Pb contents in selected groundwater in Lagos, Nigeria. Though contradicts the report of Adelekan and Abegunde (2011) on the Pb levels in groundwater near automobile mechanic villages in Ibadan, Nigeria, the study indicated that Pb content was lower than the threshold amount stated by WHO (1997). Also, the study of the chemical quality of groundwater in Sajjad, Zarrin hahr, showed that the mean concentration of lead was lower than the drinking water standards. The level of Pb in the groundwater of Shika and Zaria are not statistically different ($P < 0.05$). The high lead level raises health concern, in children this can cause consequences which may be irreversible including learning disabilities, behavioural problems, and mental retardation on a long term basis (WHO, 2012). Table 2 also shows the level of Pb and Cr in the water samples during the dry season of 2016, it shows that most of the samples contained Pb and Cr below detection limit (BDL), except Shika borehole water and some wells, that have mean Cr concentration above the permissible limit of 0.05 mg/L Cr. High concentration of Cr can destroy biological membrane and are carcinogenic (Metze *et al.*, 2005). Also, the mean Pb concentration in the water samples collected during the dry season of 2016 for all the sampling point were found to be below detection limit. This might be as result of no runoff from washing of pesticides, fertilizers, herbicides and animal waste from agricultural sources in the dry season.

Table 2: Concentration (mg/L) of Cr and Pb in Water Samples from Shika and Zaria City during the rainy season

Site	Samples	Rainy season		Dry Season	
		Cr(mg/L)	Pb(mg/L)	Cr(mg/L)	Pb(mg/L)
Zaria Well Water	ZWS1	BDL	0.0075 ± 0.005	BDL	BDL
	ZWS2	BDL	0.001 ± 0.001	BDL	BDL
	ZWS3	BDL	0.862 ± 0.569	BDL	BDL
	ZWS4	BDL	0.039 ± 0.028	BDL	BDL
	ZWS5	BDL	0.0557 ± 0.040	BDL	BDL
Zaria Borehole Water	ZBS1	0.008 ± 0.006	0.063 ± 0.044	BDL	BDL
	ZBS2	0.338 ± 0.39	0.0475 ± 0.034	BDL	BDL
	ZBS3	0.236 ± 0.167	0.301 ± 0.203	BDL	BDL
	ZBS4	BDL	0.046 ± 0.032	BDL	BDL
	ZBS5	0.009 ± 0.006	0.031 ± 0.021	BDL	BDL
Shika Borehole Water	SBW1	BDL	0.023 ± 0.016	0.12 ± 0.00	BDL
	SBW2	BDL	0.070 ± 0.049	0.11 ± 0.01	BDL
	SBW3	BDL	0.046 ± 0.033	0.12 ± 0.02	BDL
	SBW4	BDL	0.073 ± 0.052	0.11 ± 0.02	BDL
	SBW5	BDL	0.093 ± 0.066	0.11 ± 0.08	BDL
Shika Well Water	SWW1	BDL	0.069 ± 0.049	0.10 ± 0.02	BDL
	SWW2	BDL	0.051 ± 0.036	0.66 ± 0.06	BDL
	SWW3	BDL	0.048 ± 0.034	0.09 ± 0.13	BDL
	SWW4	BDL	0.031 ± 0.022	BDL	BDL
	SWW5	BDL	0.044 ± 0.030	BDL	BDL
WHO		0.05	0.01	0.05	0.01

BDL- below detection limit

Radon Concentration in Water: Table 3 shows the ^{222}Rn content in the water samples during rainy and dry season of Shika community and Zaria metropolis, Nigeria. The lowest ^{222}Rn was 0.10 ± 0.014 Bq/L (SWW4) and the highest was 66.56 ± 0.03 Bq/L (SBS1) in the rainy season. The highest concentration of ^{222}Rn was found during the dry season in ZBS1 (71.53 ± 0.01 Bq/L). The ^{222}Rn concentration obtained in both the rainy and dry seasons were found to be generally lower than the standard permissible limit for ^{222}Rn intake set by world Health Organization and United State Environmental Protection Agency (11.04 Bq/L). This shows that most groundwater in Shika and Zaria community can be said to be safe for drinking during both season. However, some has higher than the recommended level in water. Also, the borehole water sample from Shika metropolis have ^{222}Rn concentration ranging from 0.80 Bq/L to 11.05Bq/L during the rainy season, and ^{222}Rn concentration between 5.63 Bq/L to 44.08 Bq/L during the dry season of 2016. During the rainy season ^{222}Rn concentration were found to be lower than the World Health Organization (WHO, 1993; UNSCEAR, 1993 maximum permissible value of 10Bq/L and 11.1Bq/L. Therefore, most of the water samples contained tolerable level of ^{222}Rn during the rainy season. Whereas BWS5 have ^{222}Rn concentration of 44.08 Bq/L which is almost four times the permissible limit during dry season, SBW5 has the highest concentration of ^{222}Rn (44.08 Bq/L), this might be as a result of less volume of water in the boreholes compare to the rainy season volume of water. The relatively high ^{222}Rn in the dry season than the rainy season, may be related to the radon source (^{238}U and

^{226}Ra) in the water-rock system present in the areas especially Zaria. This could pose greater health risk when consumed for a long period of time (Lawal, 2008), because wells sunk in areas that are rocky tend to show high content of granites to which radon is associated (Berazina *et al.*, 2005).

Water samples from Zaria metropolis have the concentration of ^{222}Rn in the range of 23.41 to 66.56 Bq/L during rainy season and 17.81 Bq/L to 71.53 Bq/L during dry season. All the water samples have ^{222}Rn concentration higher than the permissible limit stated by WHO (1993) and USEPA (1991). Also having radon concentration above the standard limit during rainy season. This may be as a result of the natural processes, industrial or agricultural activities and increase human activities in the area where the borehole are located (Garba *et al.*, 2008). High concentration of ^{222}Rn was recorded in boreholes in Zaria because most of them are deeper and are therefore closer to the surface sub-soil which are underlined by older granite, also Zaria has high human, agricultural activities, and natural process than Shika (Garba *et al.*, 2008). As presented in Table 4, during the rainy season of 2016, the selected groundwater in Shika and Zaria metropolis, Nigeria has the lowest annual effective dose being $0.90 \mu\text{Sv/year}$ (SWW4) and the highest was $14.30 \mu\text{Sv/year}$ (SBS1). On the other hand, the lowest annual effective dose during the dry season was $1.0 \mu\text{Sv/year}$ in several sites (SWW4) and the highest was $12.0 \mu\text{Sv/year}$ in ZWS1. The borehole samples recorded higher ^{222}Rn concentrations and higher annual effective doses compared to the well water samples.

Table 3: ^{222}Rn Concentration in Water Sample from Shika and Zaria

S/No.	Sample ID	Rn(Bq/L) Rainy season	Rn (Bq/L) Dry season	Annual effective dose ($\mu\text{Sv/year}$) -R ($\mu\text{Sv/L}$) -D
1	ZWS1	4.02±0.03	60.07±0.01	12.81- 12.0
2	ZWS2	0.16±0.00	53.02±0.01	10.63- 11.0
3	ZWS3	2.50±0.14	28.55±0.00	6.21- 6.0
4	ZWS4	2.23±0.03	2.26± 0.03	0.90-1.0
5	ZWS5	25.75±0.01	1.53±0.01	5.31 -5.0
6	ZBS1	66.56±0.03	71.53±0.01	14.30 - 14.0
7	ZBS2	24.04± 0.03	26.49±0.01	5.30 - 5.0
8	ZBS3	54.41±0.01	17.81±0.01	3.60 -3.0
9	ZBS4	23.41±0.00	30.70±0.00	6.20 - 6.0
10	ZBS5	59.60±0.00	31.41±0.01	6.20 -6.0
11	SBW1	2.90±0.00	5.85±0.07	1.17 - 1.0
12	SBW2	11.05±0.07	6.63±0.01	1.32 - 1.0
13	SBW3	8.18± 0.03	5.71±0.01	1.14 - 1.0
14	SBW4	0.80±0.00	11.04±0.01	2.20 -2.0
15	SBW5	8.50±0.14	44.08±0.01	1.80- 2.0
16	SWW1	5.38±0.00	11.04±0.00	2.20 - 2.0
17	SWW2	1.79±0.014	9.34± 0.03	1.87 - 2.0
18	SWW3	3.33±0.014	5.29±0.01	1.06 - 1.0
19	SWW4	0.10±0.014	6.68±0.03	1.34 - 1.0
20	SWW5	0.81±0.00	6.68±0.00	1.34 -1.0
Standard		11.10		/

Scientists believe that exposure to ^{222}Rn is the second leading cause of cancer. When it decays, it shoots off alpha particles which are a heavy, electrically charged, sub-atomic particles consisting of two protons and two neutrons. If an alpha particle strikes chromosomes in a lung cell, it can alter the way the cell reproduces. And the calculated annual effective dose due to the intake of ^{222}Rn in drinking water (hand-dug well and borehole) at Shika and Zaria was within the permissible limit. The variation in the radon concentration could be a function of the geological structure of the area, depth of the water source and geo-hydrological processes that occur in the area as well as the anthropogenic activities. From the study, there was negative and positive correlation between the amount of ^{222}Rn , Cr, Pb and physicochemical parameter of the water sample, also there was significant difference between the parameters across the season.

Generally, the annual effective dose obtained in this study was less than half the total natural radiation exposure of $2400 \mu\text{Sv}/\text{year}$. Also, the effective doses are also within the World Health Organisation (WHO) recommended reference level of $100 \mu\text{Sv}$ per year for intake of radionuclides in water (IAEA, 2001). So the water samples studied are safe for drinking. Notwithstanding, periodical assessment of the levels of heavy metals and radionuclides in the water sources and the environment at large is imperative. In comparison to the work of Nada (2013), this study had higher mean radon concentration. Nada (2013) reported that the radon concentrations in groundwater of Aucashat city (Iraq) was in the range of 8.02 ± 0.14 to $11.7 \pm 0.16 \text{ Bq}/\text{L}$, with an average of $9.35 \pm 1.24 \text{ Bq}/\text{L}$, and the annual effective dose from ingestion (stomach) was 840 to $1230 \mu\text{Sv}/\text{y}$; from inhalation (lung) it was 2250 to $3280 \mu\text{Sv}/\text{y}$ and for whole body was from 3090 to $4510 \mu\text{Sv}/\text{y}$. Though, the annual effective dose from ingestion of water was higher than reported for the groundwater of Shika and Zaria, Nigeria. Also the result from this study is lower than the measured radon concentration range of 374.89 ± 37 to $6409.03 \pm 130 \text{ pCi}/\text{L}$ reported by Abdul Malik *et al.* (2015) for well water of selected areas in Pulau Pinang and Kedah using RAD7 and Rad H_2O accessories ($1 \text{ pci} = 0.037 \text{ bq}$). In addition, the well water has radon above the maximum contamination limit (MCL) of $300 \text{ pCi}/\text{L}$ recommended by United State Environmental Protection Agency (USEPA). In an era of acute water shortage from public water supply system, digging of well and drilling of boreholes is the order of the day, so consideration should be given to installation of water treatment system to remove radon.

Conclusion: From the study most of the physicochemical parameters in the groundwater studied are within the WHO safe limit. Also the levels of Cr and Pb, except Pb in the water collected in the rainy season was below the limit. The ^{222}Rn concentration in the ground water sources were found to be within the maximum permissible limit, except for the samples collected from Zaria metropolis. So, periodic assessment of radon in water and the environment at large is recommended.

REFERENCES

- Abdul Malik, MFI; Rabaiee, NA; Jaafar, MS (2015). Determination of radon concentration in water using Rad7 and Rad H_2O accessories. AIP Conference Proceedings, 1657: 1.
- Adefemi, SO; Awokunmi, EE (2010). Determination of physico-chemical parameters and heavy metals in water samples from Itaogbolu area of Ondo-State, Nigeria. *Afr. J. Environ. Sc. Tech.* 4(3): 145-148.
- Adelana, SMA; Abiye, TA; Nkhuwa, DCW; Tindinugaya, C; Oga, MS (2008). Urban groundwater management and protection in Sub-Saharan Africa. In: Adelana, SMA; MacDonald, AM *Applied groundwater studies in Africa, International Association of Hydrogeologists, selected papers*, p. 222-259.
- Adelekan, BA; Abegunde, KD (2011). Heavy metals contamination of soil and groundwater at automobile mechanic villages in Ibadan, Nigeria. *Int. J. Phys. Sc.* 6(5): 1045-1058.
- Adepoju-Bello, AA; Ojomide, OO; Ayoola, GA; Coker, HAB (2009). Quantitative analysis of some toxic metals in domestic water obtained from Lagos metropolis. *The Nig. J. Pharm.* 42(1): 57-60.
- Adeyemi, O; Oloyede, OB; Oladiji, AT (2007). Physiochemical and microbial characteristics of leachate contaminated group water. *Asian J. Biochem.* 2 (5): 343-348.
- APHA (1995). Standard methods for examination of waters and wastewaters, 15th ed. American Public Health Authority. Washington D.C 1193.
- Berazina, EV; Elansky, NF (2005). Spatial distribution of ^{222}Rn concentrations and its fluxes in the lower atmosphere over continental Russia. *Radiophys.* 23(2): 67-69.

- Chapman, D (1997). Water Quality Assessment: A guide to the use of biota, sediment and water in environmental analysis, Second edition. London: E and SPON. p. 1-21, 58-124, 413-613.
- Ebrahimi, A (2010). Chemical quality of groundwater in the area Sajjad golden city. *Health Systems Res. J.* 6 (4): 34 - 39.
- Ehi-Eromosele, CO; Okiei, WO (2012). Heavy metal assessment of ground, surface and tap water samples in Lagos metropolis using anodic stripping voltammetry. *Resources and Environ.* 2(3): 82-86
- Ekwumemgbo, AP; Eddy, NO; Omoniyi, KI (2011). Heavy metals concentrations of water and sediments in oil exploration zone of Nigeria. Heavy Metals in the Marine Environment, 15TH ICHMET: 579-582.
- Emad, A (2014). Radon-222 concentrations in the groundwater along Eastern Jordan Rift. *J. Appl. Sc.* 14: 309-316.
- Galan, LM; Martin, SA; Gomez, EV (2004). Application of ultra-low level liquid scintillation to the determination of ²²²Rn in groundwater. *J. Rad. Anal. Nucl. Chem.*, 261(3), 631-636.
- Garba, NN; Rabi'u, N; Yusuf, AM; Isma'ila, A (2008). Radon: its consequences and measurement in our living environs. *J. Res. in Phys. Sc.* 4(4): 23-25.
- Galadima, A; Garba, ZN (2012). Heavy metals pollution in Nigeria: Causes and consequences. *Elixir Pollut.* 45: 7917-7922.
- Harrison, RM (1992). Understanding our Environmental Chemistry and Pollution. Cambridge University Press, 2nd edition, p. 46-49.
- IAEA (2001). Water for people, water for life. The United Nation World Water Development Report. <http://www.unesdoc.unesco.org/images/0012/001295/129556e.pdf>.
- Igwilo, IO; Afonne, OJ; Maduabuchi, UT; Osisakwe, OE (2006). Toxicological study of the Anam River in Otuocha, Anambra State, Nigeria, *Arch. Environ. Occupation Health.* 61(5): 205-208.
- Ishaku, JM; Ezeigbo, HI (2010). Groundwater quality monitoring in Jemeta-Yola Area of North-eastern Nigeria. *J. Water Resources.* 20(2): 1-14.
- Karahan, G (1997). Determination of environmental natural radioactivity of Istanbul and annual effective dose equivalent of natural radiation, PhD Thesis, Istanbul Technical University, Istanbul.
- Lawal, MG (2008). Natural radioactivity of groundwater in N.W. Precambian Rocks of sheet 102, Zaria. Unpublished Ph.D Thesis, Department of Physics, Ahmadu Bello University, Zaria-Nigeria.
- Mendham, J; Denney, RC; Barnes, JD; Thomas, MJK (2008). Quantitative Chemical Analysis 6th edition. Vogel text book, Pearson education, p. 642.
- Marqués, MJ; Salvador, AA; Morales-Rubio, A; de la Guardia, M (2000). Chromium speciation in liquid matrices: a survey of the literature. *Fresen J. Analyt. Chem.* 367: 601.613.
- Metze, D; Jakubowski, N; Klockow, D. (2005). In: Cornelis, R; Crews, H; Caruso, J; Heumann, KG. Handbook of elemental speciation II: species in the environment, food, medicine and occupational health. Wiley, New York
- Nada, FT (2013). Uranium and radon concentration in ground water in Aucashat city (Iraq) and the associated health effects. *Adv. Applied Sc. Res.* 4(3): 167-171.
- Natural Research Council of Canada, NRCC (2011). Effect of sodium and potassium in the Canadian Environment. No 150154 Associate committee on Scientific Criteria for Environmental Quality Ottawa.
- Okonko, IO; Adejoye, OD; Ogunnusi, TA; Fajobi, EA; Shittu, OB (2008). Microbiological and physicochemical analysis of different water samples used for domestic purposes in Abeokuta and Ojota, Lagos Nigeria. *Afr. J. Biotech.* 7(5): 617-621.
- Omoniyi, KI; Ekwumemgbo, PA; Isuwa, B (2016a). Post flooding assessment of the heavy metal pollution of water and fish of rivers Niger and Benue in Lokoja, Nigeria. A paper presented at the 5th International Conference on Chemical, Ecology and Environmental Sciences (ICEES-2016), 5th - 6th May, 2016, Dubai (UAE).
- Omoniyi, K; Abechi, SE; Akpa, RU (2016b). Determination of the physicochemical properties and radiation health hazard indices of 'Nzu clay' obtained from Azonogogo, Delta State and Uzella

- River in Edo State, Nigeria. *Nig. J. Mat. Sc. Eng.* 7 (1): 87-94.
- Saba, H; Ebrahim, F (2016). Determination cadmium and lead pollution resources of Ardabil Plain underground waters. *Open J. Ecol.* 06(09): 554-561
- Shakir, KM; Naqvi, AH; Azam, A; Srivastava, DS (2011). Radium and radon exhalation studies of soil. *Iran. J. Radiation Res.* 8(4): 207 - 210.
- Tso, MW; Li, C (1987). Indoor and Outdoor ^{222}Rn daughters in Hong Kong, *Health Phys.* 53(2):175-180.
- United States Environmental Protection Agency (USEPA) (2002). Drinking Water from Household Wells.
<http://www.epa.gov/safewater/drinklink.html>
- UNSCEAR (2000) United Nations Scientific Committee on the Effect of Atomic Radiation, Sources and Effects of Ionizing Radiation, United Nations, New York. p. 56-64.
- WHO (1997). World Health Organization guidelines for drinking water quality 2nd edition vol. 2. *In Health Criteria and other supporting information, WHO, Geneva.*
- WHO (1993). World Health Organization guidelines for drinking water quality 2nd edition vol. 2. *In Health Criteria and other supporting information, WHO, Geneva.*
- WHO (2012). Water, Sanitation and Health. World Health Organization, Geneva