DETERMINATION OF RADON-222 CONCENTRATION FROM THE MINING SITES OF MARU, ANKA AND BUKKUYUM AREAS IN ZAMFARA STATE, NIGERIA.

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ABSTRACT.
Natural radionuclides such as Uranium-238 (^{238}U), Thorium-232 (^{232}Th), Radium-226 (^{226}Ra) and Potassium-40 (^{40}K) and heavy metals are normally exposed to the surface during mining activities. When inhaled (as dust) or ingested (by drinking contaminated water) in significant concentrations, they can lead to health challenges. In this research work, wastewater was collected from gold-mining sites of Anka, Maru, and Bukkuyun Local Government Areas of Zamfara State, Nigeria. Radon concentration was measured using Liquid Scintillation Counter. Results from the analysis show that, the average mean Radon concentration was 174.9Bq/L, 115.3Bq/L and 137.4Bq/L for Anka, Bukkuyum and Maru respectively. These revealed that, Anka has the highest ^{222}Rn concentration while Bukkuyum has the lowest concentration. Results also show that about 90% of samples exceed the permissible limit of 100 Bq/L by the World Health Organization (WHO) and European Union (EU). This implies that, most public premises and workplaces in Zamfara State have high Radon concentrations in the air.

Keywords: Mining sites, Radiological hazard, Activity concentration, Wastewater.

INTRODUCTION.

Naturally occurring radionuclide materials such as ^{40}K, ^{238}U, ^{232}Th, ^{222}Ra are prevalent in the environment, resulting in human exposure throughout human history. Anthropogenic activities such as mining, has led in high environmental concentrations of these contaminants (Kamunda *et al.,* 2017). Naturally, the Earth's environment varies according to the geological formation. This is largely responsible for the uneven distribution of radionuclides and natural resources in the earth environment. The soil serves as a means of migration for transportation of radionuclides to the environment. Occurring radionuclides within certain environment are hazardous owing to the fact that the activity concentrations of radioactive materials are considered the principal indicator to the radiological contamination in the environment (Amos *et al.,* 2019). These activities are liable for a series of environmental and human health problems and by producing huge quantities of waste into the environment. Even with comparatively effective mining activities, high levels of natural radionuclides and heavy metals are released into the atmosphere and water leaving a repercussion of environmental contamination in neighboring communities. These levels of natural radionuclides, enters the human body. If large concentrations of these radionuclides build up in the human body, this can lead to health effects such as development of cancers, cardiovascular and respiratory diseases (Kamunda *et al.,* 2016). The risk of cardiovascular and respiratory mobility, asthma, lung cancer, inflammation and mortality may increase when these radioactive particles are ingested or inhaled. However, when considering internal exposure, larger particles are less of a concern because they are unable to penetrate deep into the lungs and can be easily expelled by coughing (Madzunya *et al.,* 2020). Therefore, it is important to monitor radionuclides in areas around mines. Natural radionuclides such as Uranium-238 (^{238}U), Thorium-232 (^{232}Th), Radium-226 (^{226}Ra) and Potassium-40 (^{40}K), and heavy metals are normally exposed to the surface during mining activities. They enter the human body

when inhaled (as dust) or ingested (by drinking contaminated water). An intake of large concentrations of these radionuclides and heavy metals can lead to health effects such as development of cancers.

Assessment of radiological risk from the soils of artisanal mining areas of Anka, North Western Nigeria was carried out by Amos *et al* (2019).

Sowole and Egunjobi (2019) assessed the activity concentrations of ^{40}K, ^{238}U and ^{232}Th in surface soil samples from different locations at Igbokoda, Ondo State in Nigeria where crude oil exploration was taking place. The mean excess lifetime cancer risk for outdoor exposure was 0.2132×10^{-3}. The values of mean external and internal hazard indices, mean radium equivalent activity, mean absorbed dose rate, mean annual effective dose equivalent and mean excess lifetime cancer risk were within the recommended limits of 1.0 Bq kg^{-1}, 370 Bq kg^{-1}, 55.00 nGy hr^{-1}, 1.0 mSv yr^{-1} and 1.45×10^{-3} respectively. The determination of radiological hazard indices from surface soil to individuals in Angwan Kawo gold mining sites, Niger State, Nigeria was carried out by Esiole *et al* (2019). The radionuclide concentrations were determined using the sodium iodide (NaI (TI)) detector with a low background configuration. The results obtained show that the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K for all the soil and mill tailing samples analyzed were within the acceptable limits set by regulatory agencies and as such, the radiological health risks to the people living in the studied areas is insignificant. Innocent *et al* (2014) conducted research on radiological safety assessment of some mine sites at Gusau and environs, Nigeria. The radiation hazard indices were estimated for soil samples collected from abandoned mine sites. The γ-ray spectrometry was used to determine the quantity and quality of radioactivity in the soil samples randomly collected from 10 abandoned mine sites in the area of study. The mean values of gamma index level, external and internal hazard indices were 0.48, 0.35 and 0.39 respectively. The mean absorbed dose rate of the samples was found to be 59.7 $nGy.h^{-1}$, while the mean annual effective dose was estimated to be 0.073 $mSv.y^{-1}$. From the hazard indices information, it was concluded that the radiation level in the study areas was within the safety limit.

The aim of this study is to evaluate the human risk associated with the exposure to Radon-222 and heavy metals in soil, water, and sediments in the samples collected from Anka, Maru, and Bukunyum Local Government Areas of Zamfara State. Twenty soil samples were collected from agricultural, mining and mine processing areas in Anka, Zamfara State. The measurement of activity concentration of ^{226}Ra, ^{232}Th and ^{40}K was performed using the gamma-ray spectrometer equipped with a high purity germanium detector.

STUDY AREA.

The study sites are located in three (3) local government areas of Zamfara State, Northwest Nigeria between 6° 00′ – 7° 00′ E of the longitude and 12° 00′ – 13° 00′ N of the latitude.

Bukkuyum is a local government area in Zamfara State, Nigeria. Located on latitude 12º 07′ 60.00″ N and longitude 5º 27′ 59.99″ E, it has an area of 3214 km^2 and a population of 211,633 according to the 2006 census. Anka falls between latitude 11º 51′ N and 12º 08′ N, and longitude 5° 51' E and 6° 08′ E with a population of 263,400 (Buba, 2016). The Anka River is the main water body in the study area. The geology of Anka is characterized by the Anka schist belt that hosts the lead mineralization, and the lead-

copper-silver-gold polymetallic association. Anka is well known for artisanal gold exploitation for several decades and the mineral is hosted by schists, phyllites and quartzites associated with sub-regional structural elements subsidiary to the Anka fault (Waziri *et al.*, 2013). Maru is situated at latitude 12. 33° N and longitude 6.41° E, and 339 meters elevation above the sea level. Maru is characterized by old igneous rocks, formed during the Precambrian Paleozoic era (Innocent *et al.*, 2014). Mineral deposits such as, smectite, kaolinite, feldspars, granite, pegmatite, quartz, migmatites, amphibolites, monazite, zircon, thorianite, ferruginous quartz, meta-sandstone, porphyritic biotite and many others abound in the study area.

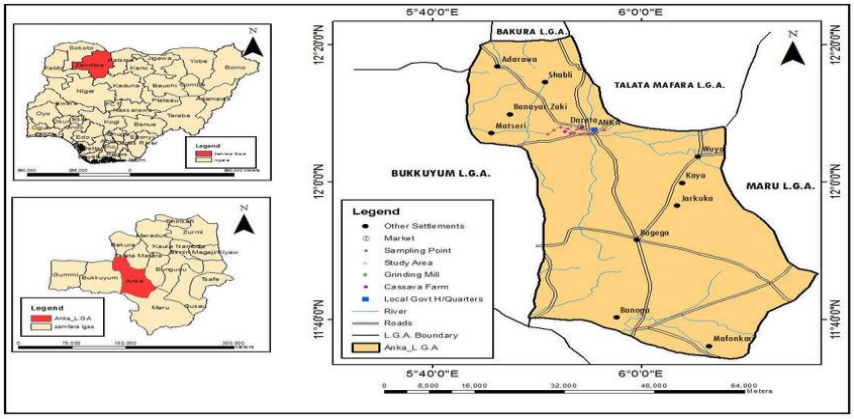

Figure 1: Geological map of the study area.

THEORETICAL BACKGROUND.

Radioactive Decay Law and Activity

Radioactive decay law states that a radioactive substance decays exponentially with time. Mathematically it is expressed as (Ghoshal, 2012):

$$N_t = N_o e^{-\lambda t} \quad (1)$$

where N_o is the initial number of nuclei present at time $t = 0$, N_t is the number of nuclei present after time t and λ is the radioactive decay constant.

The activity of a radioactive source (A) is the number of disintegration per second which is measure in Becquerel and expressed by calculus notation as (Ghoshal, 2012):

$$At = \frac{d_{Nt}}{d_t} = -\lambda N_t \quad (2)$$

Substituting for N_t from equation 1 into equation 2 gives (Ghoshal, 2012):

$$A_t = A_o e^{-\lambda t} \quad (3)$$

where A_t is the activity of radioactive substance at time t and A_o is the activity of radioactive substance at time $t = 0$

Specific Activity

Specific activity is the activity per unit mass or volume of a radioactive sample. It is measured in Becquerel per Kilogram $^{Bq}/_{Kg}$, $^{Bq}/_{L}$ and also in $^{Bq}/_{m^3}$ (Ghoshal, 2012):

$$\text{Specific activity} = {}^{\lambda N}/_{M} \quad (4)$$

where M is the mass of the radioactive substance and N is the number of nuclei present.

Activity concentration.

Calculations of number of counts per second for the photo peak and activity concentrations of each detected radionuclides was based on the concept of secular equilibrium being. The activity concentration in BqL^{-1} (A) in the samples was obtained as follows (Uosif *et al.*, 2015):

$$AA(BqL^{-1}) = \frac{100 \times (SC-BC) \times \exp\lambda t}{60 \times CF \times D} \quad (5)$$

where $C_{Rnw}(BqL^{-1})$ is the concentration of Radon – 222 in Becquerel per liter, SC the sample count, BC the background count ($countmin^{-1}$), T the time elapsed between sampling to count and λ the decay constant (1.2 X 10^{-4} min^{-1}). CF is the calibration factor, D the fraction of ^{222}Rn in the cocktail in 22 ml total capacity vial for 10 ml of sample, 10 ml of cocktail and 2 ml of air.

Annual effective dose rate (AEDR).

The annual effective dose of ^{222}Rn in drinking water is given by (UNSCEAR, 2000):

$$E = K \times G \times C \times T \times 1000 \quad (6)$$

where E is the annual effective dose (mSv/y), K the conversion coefficient of ^{222}Rn (Sv/Bq) which is equal to 1.8 X 10^{-9} Sv/Bq and G the daily consumed water (L/d), which is equal to 2.723 L/d. C is the concentration of ^{222}Rn (Bq/L), T the time span of water consumption (365 days) and 1000 the conversion coefficient of Sv to mSv.

MATERIALS AND METHOD.

The materials used for this research include, disposable hypodermic syringe (20 ml, 10 ml capacities), Liquid Scintillation Counter (Packard Tri-Card LSA 1000TR), digital weighing balance and X-ray fluorescent (XRF).

Sample collection and preparation.

A total of ninety (90) soil samples were collected by random sampling method from the mine sites at selected locations in three (3) local government areas of the state (Maru, Anka and Bukkuyum). The soil samples were packed in air tight polyvinyl chloride (PVC) containers from the areas of surveillance, properly sealed and labeled for easy identification and then transported to the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Nigeria. Stream sediment samples were also collected randomly around the mining sites with stainless steel trowel to the depth of 0 to 15 cm stream water and sediment covering both dry and wet seasons. Sediment samples were air dried for four days and kept in labeled polythene bags. Sample preparations were carried out in the Materials Science and Development Section (MSDS) Laboratory of the Center for Energy Research and Training (CERT), Zaria. The preparation for water samples for radioactivity analysis was rather straightforward; HNO_3 was introduced to the water sample at the collection point and sealed in their containers to reduce the absorption of radioactivity by the surrounding walls of the containers. 10 ml of each sample was added into a vial containing 10 ml of toluene based cocktail (scintillator) using a hypodermic syringe. The vials were tightly capped and shaken vigorously for three (3) minutes to extract Radon-222 in water phase into the organic scintillator. In a similar manner a blank sample for the background was prepared using distilled water that has been kept in a glass bottle for at least 21 days. The prepared samples were allowed to stand undisturbed for at least three (3) hours each in order for ^{222}Rn and its alpha decay products to attain equilibrium before counting the sample for sixty (60) minutes in a liquid scintillation counter.

Sample analysis.

The prepared samples were analyzed using Liquid Scintillation Counter (Tri-Carb

LSA 1000TR) model located at the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Nigeria, after they were allowed to stay for three hours for equilibrium to be attained between ^{222}Ra and its daughter progeny. Measurements were carried out within 24 hours after preparation in order to avoid leakage of ^{222}Rn gas. Radiation emitted from the samples transferred energy to the organic scintillator which in turn emits light photons. This way each emission result is a pulse of light in form of digit. The activity concentration of ^{222}Ra was calculated from the samples and background results obtained using equation (5). The annual effective dose of ^{222}Rn through drinking water was calculated using equation (6) as proposed by the United Nation Committee on the Effects of Atomic Radiation. The samples investigated in this experiment were sampled from the vicinity of the contaminated area from the mining sites of Anka, Maru and Bukkuyum. The soil samples were dried, homogenized and sieved at 250 µm particle sizes. XRF analyzes were carried out at the Center for Energy Research and Training, Ahmadu Bello University, Zaria using energy-dispersive XRF analyzer having an excitation source a miniaturized 30 kV X-ray tube.

RESULTS AND DISCUSSION.

The activity concentrations of Radon-222 of the forty (40) samples collected at different locations of the selected areas under study is presented in the table 1.

Table 1: Results of Radon concentration and their corresponding annual effective dose.

S/N	Sample ID	Sample Coordinate	pH	Rn(Bq /L)	AED (mSv/y)
1	A 4	N 11º 59.867 E 005º 48.391	8.05	233.8	0.418
2	A 5	N 11º 59.486 E 005º 45.458	9.37	198.8	0.356
3	A 6	N 11º 59.827 E 005º 45.463	8.36	141.8	0.255
4	A 7	N 11º 59.821 E 005º 45.442	8.48	137.5	0.247
5	A 8	N 11º 59.833 E 005º 45.462	8.58	99.10	0.178
6	B 10	N 12º 05.516 E 005º 57.489	8.29	71.04	0.128
7	B 11	N 12º 05.531 E 005º 57.513	8.31	117.8	0.212
8	B 12	N 12º 05.848 E 005º 57.508	8.12	116.8	0.210
9	D 10	N 12º 03.315 E 005º 52.400	8.20	176.9	0.318
10	H 10	N 12º 16.853 E 006º 26.603	8.18	104.1	0.187
11	C 13	N 12º 16.093 E 006º 26.506	8.07	131.8	0.237
12	D 11	N 12º 16.093 E 006º 26.506	8.59	97.80	0.176
13	D 12	N 12º 01.807 E 005º 57.305	8.48	152.7	0.275
14	E 8	N 12^0 19.38 E005º 198330	9.38	104.4	0.188
15	F 10	N 12º 15.716 E 006º 21.207	8.66	118.0	0.212
16	F 11	N 12º 15.755 E 006º 21.195	8.42	116.9	0.210
17	F 12	N 12º 15.742 E 006º 21.205	8.25	118.6	0.213
18	G 4	N 11º 59.877 E 005º 48.405	8.43	120.5	0.217
19	G 5	N 11º 59.875 E 005º 48.411	8.52	145.3	0.262
20	G 6	N 11º 59.859 E 005º 48.412	8.02	140.5	0.253
21	H 1	N 12º 21.126 E 006º 16.079	8.27	124.3	0.224
22	H 2	N 12º 17.1481E 006º 78.698	8.44	102.5	0.185
23	I 13	N 12º 20.958 E 006º 16.300	8.34	85.20	0.153
24	I 14	N 12º 03.320 E 005º 52.382	9.50	100.8	0.181
25	I 15	N 12º 01.797 E 0055º 7.29	8.27	271.4	0.489
26	I 16	N 12º 01.115 E 005º 57.382	8.19	130.2	0.234

27	I 17	N 12º 01.799	E 005º 57.291	7.77	125.6	0.226
28	I 18	N 12º 01.807	E 005º 57.3051	8.27	106.5	0.192
29	I 19	N 12º 06.693	E 005º 55.403	8.01	120.5	0.217
30	M 10	N 12º 03.345	E 005º 54.354	7.39	169.6	0.305
31	M 11	N 12º 03.334	E 005º 52.412	7.94	111.8	0.201
32	L 10	N 12º 02.330	E 005^0 52.346	7.73	139.6	0.251
33	X 1	N 12º 17.122	E 006º 78.2991	9.82	116.2	0.209
29	X2	N 12º 60.707	E 005º57.554	9.09	138.0	0.248
35	X 3	N 12º 02.728	E 005º 44.511	7.99	127.7	0.229
36	K 10	N 11º 59.825	E 005º 45.460	8.42	120.5	0.217
37	K 11	N 11º 59.486	E 005º 45.486	8.48	139.1	0.250
38	J 8	N 12º 17.148	E 006º 08.698	9.82	171.1	0.308
39	J 9	N 12º 20.760	E 006º 16.614	9.09	143.7	0.259
40	J 10	N 12º 06.739	E 005º 16.382	7.99	247.9	0.446

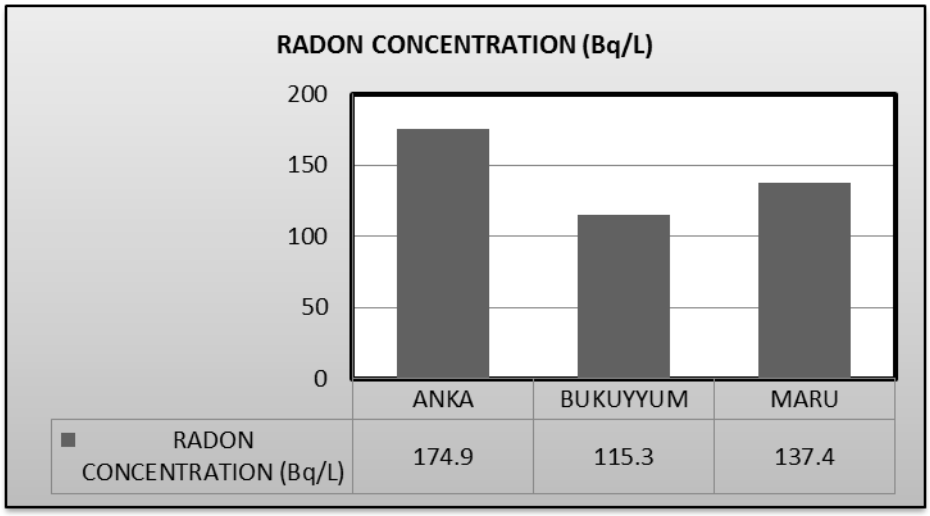

Figure 2: A plot of Mean ^{222}Rn concentration for the three selected Local Government Areas.

The ^{222}Rn activity concentration due to contribution from the three selected areas for this study ranged from 71.04 (Bq/L) to 247.9 (Bq/L) with sample J10 leading the activity concentration and sample B10 having the lowest activity concentration as shown in the table 1. Figure 2 shows the frequency distribution pattern for all the three (3) local Government Areas. These results show that the average mean Radon concentration is 174.9Bq/L, 115.3Bq/L and 137.4Bq/L for Anka, Bukkuyum and Maru respectively. Anka has the highest ^{222}Rn concentration followed by Maru and then Bukkuyum which has the lowest concentration as shown in the figure 2. The results show that the mean ^{222}Rn concentration is higher than the recommended limit of 100 Bq/L by the World Health Organization and European Union. This high ^{222}Rn concentration may be attributed to the fact that radon is very high around the mining sites where mining activities are taking place. The concentration may also be as a result of ^{222}Rn release from the surrounding geological formation. High concentration of ^{222}Rn has been of great concern about its health effects. Therefore, drinking or bathing with the groundwater can give rise to exposure of humans to its radiation and may result in cancer and even death in extreme situation (USEPA, 1999). The annual effective dose due to ingestion of ^{222}Rn in the collected samples varied from 0.128 to 0.446 mSv/y, with an average of

0.2444 mSv/y for all the selected areas under study.

Figure 3 shows the average AED of ^{222}Rn due to ingestion representing the three Local Government Areas of Zamfara State where mining activities are taking place.

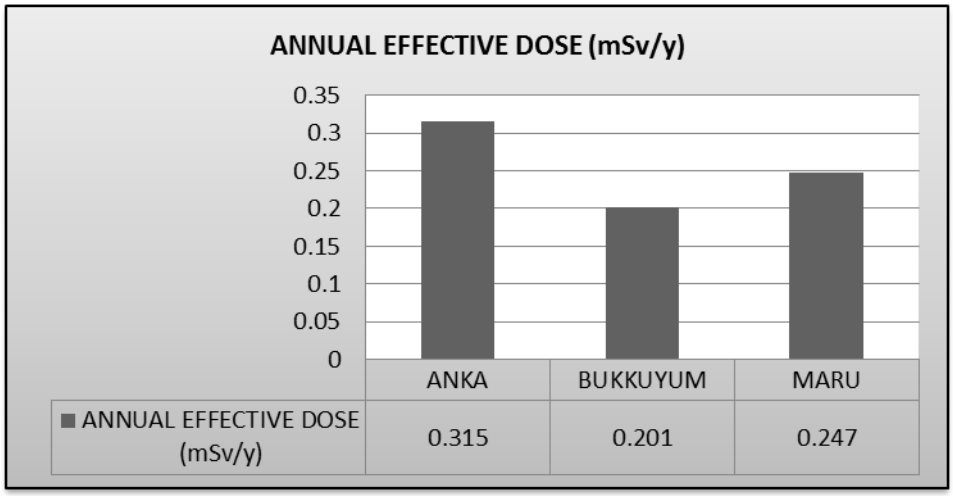

Figure 3: Annual Effective Dose (AED) for the three selected Local Government Areas.

The mean values for the annual effective dose due to ingestion of ^{222}Rn in the water sample collected from the mining sites are 0.315mSv/y, 0.201mSv/y and 0.247 mSv/y for Anka, Bukkuyum and Maru respectively with Anka having the highest annual effective dose due to ingestion of ^{222}Rn followed by Maru and then Bukkuyum with the lowest value as show in the table above. International organizations have established recommended limits for ^{222}Rn concentration in water but Nigeria has not introduced any legal regulation concerning permissible radon concentration in water yet, therefore, there is need for radon concentration in water to be investigated thoroughly so that guidelines for regulations on the radon concentrations in Nigeria would be established.

CONCLUSION.

Radon-222 assessment was conducted on wastewater sources of artisanal and local mining areas of Anka, Bukkuyum and Maru local Government Areas of Zamfara State, Northwest Nigeria and the result presented. The radon concentrations and the computed mean annual effective dose were found to be above WHO and EU recommended limits. Lifetime cancer risks from water sources in the study area were also considered to be high for adults and children.

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