

RESEARCH ARTICLE

HEAVY METAL CONCENTRATION AND RADIOLOGICAL HAZARD ASSESSMENT OF SELECTED BASEMENT ROCKS OF IGARRA, SOUTHWESTERN NIGERIA

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ABSTRACT

The study assessed heavy metal concentration and radiological hazards in selected basement rocks from Igarra, used in construction. Twenty rock samples were collected from two quarry sites (Calc-silicate-gneiss and Lamprophyre), Ten (five from each) were then carefully picked and analyzed for natural radioactivity and heavy metal concentrations using X-ray Fluorescence spectrometry (XRF). Standard conversion factors were applied to convert radioactive metals into activity concentrations of radionuclides, and radiological hazard indices were calculated. The mean heavy metal concentrations followed the order: Fe > Cr > Zn > Ni > Pb > Cu > Co > Th > Sn > Ra > As > Cd and Fe>Cr>Zn>Pb>Ni>Cu>Th>Co>Sn>Ra>As>Cd for calc-silicate-gneiss and lamprophyre respectively. The average activity concentrations of ²²⁶Ra, ²³²Th, and ⁴⁰K varied between 19.34-74.65 Bq/kg, 28.18-195.29 Bq/kg, and 970.3-2115.88 Bq/kg respectively. Lamprophyre had higher activity concentrations and radiological indices, including radium equivalent activity, external and internal hazard indices, gamma representative index, absorbed dose rates, annual effective dose equivalents and excess lifetime cancer risk, compared to Calc-silicate-gneiss. Although both rock types exhibited activity concentrations, gamma indices, and absorbed dose rates and excess lifetime cancer risk (outdoor) above the world average, radium equivalent activity, external and internal hazard indices, annual effective doses and excess lifetime cancer risks (indoor) were within safe levels. The study concludes that while the radiological impact is tolerable, quarry workers might face higher exposure due to elevated outdoor radiation levels. Additionally, some trace metals exceeded Earth's crust averages, presenting potential toxicity risks if inhaled or ingested. While the rocks are deemed safe for construction, their use in interior decoration is not recommended to avoid potential long-term radiation exposure indoors.

KEYWORDS

Activity Concentration, radiation exposure, basement rock, X-ray fluorescence spectrometer, quarry workers

1. INTRODUCTION

Rock is basically an aggregate of mineral/s, rock materials are materials derived from sedimentary, metamorphic and Igneous rocks. In southwestern and other parts of Nigeria, rocks outcrop well and has being widely used for various construction purposes mainly because of their strength (Ademeso and Oji, 2020). Naturally occurring radioactive materials (NORMs), which involves the natural radionuclides ⁴⁰K, ²³⁸Th, and ²³⁵U as well as their many offspring, are largely constituted in rocks. NORMs are highly enriched in earthy materials including minerals, rocks, soil and water; nevertheless, because of the native geology of a region, the NORMs' concentrations and impacts differ from one location to another (UNSCEAR, 2000). It becomes necessary for earthy material such as soil, rocks and minerals to be monitored within the environment to be sure of their radiation impact because harmful elements and radioactive materials that make them up can be re-distributed as a result of dust from quarrying and mining processes to mine and nearest environment. This processes can of waters, soil and foods be contaminated, leading to major radiation risk (Osimobi et al., 2018; Nabayaogo et al., 2021). Modern day uses have increased the importance of rocks as they are now used for road, building and dam construction, shafts and tunnels, caverns, radioactive waste disposal etc (Oji and Ademeso, 2020). Numerous local mining and rock quarrying companies have established themselves in Nigeria due to the vast amount of mineral ore resources and rocks that are evenly

distributed in different parts of the country. Rock mining, which involves the excavation of outcrop and unexposed rocks in the subsurface and their subsequent crushing into different sizes, has the potential to increase the risk levels and radiation dose rates of nearby residents and workers by redistributing radionuclides in form of dust from the quarry site to soil and air of nearby environment (Ofomola et al., 2023). Products from rock quarries, which are widely used as building and road construction materials, might also expose people indoors to more radiation from buildings (Gbenu et al., 2016; Alausa et al., 2019). Natural radionuclides and likely harmful substances found in rocks during quarrying can find their way into human system via the ingestion of contaminated water and food crops grown in nearby soil, as well as through the inhalation of dust particles in the air (Ofomola et al., 2023). The abundance of these materials, which could constitute radiation sources and at the same time are required for use as construction materials, needed to be checked whether it meets safety requirements in line with safe indoor and outdoor standards for human (UNSCEAR, 2000; IAER, 2003). In Igarra and other parts of Nigeria, rocks outcrop well and has being commonly used for various construction purposes without evaluating the level of natural radionuclides in them to ascertain their suitability and safety of the dweller and end user of radiation risk (Oji and Ademeso, 2020; Ofomola et al., 2023). The incessant and excessive radiation exposure which has resulted into loss of life and properties in Southwestern and other parts of Nigeria has become worrisome. Most of these radiation exposures which

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arises from negligence of not using the appropriate rock materials that will not pose radiological risk during and after construction. Several researches has also been carried out on petrographic attributes, geochemistry, and physico-mechanical characteristics of rocks (Olade and Elueze, 1979; Rahaman, 1976; Elueze, 2000; Oji and Ademeso, 2020; Ademeso and Oji, 2020), but little or no study has been conducted on evaluating the natural radionuclides of this easily assessed rocks from the study area in order to know if the rocks are safe for use without posing any health risk. This research therefore seek to evaluate heavy metal concentration and radiological hazard indices of this easily assessed rocks in Igarra that are being quarried and use for different construction purposes.

2. STUDY AREA

Igarra is a town in the northern part of Edo state, Nigeria, situated along

Auchi-Ibillo route. It is situated between latitudes $7^{\circ}05'N$ and $7^{\circ}20'N$ and longitude $6^{\circ}00'E$ and $6^{\circ}10'E$ (Figure 1).

According to the study, Semi-pelitic phyllites, quartzbiotite schist, mica schist, calc-silicate gneiss and marble, and meta-conglomerate are the main rock types that have been revealed in the area (Odeyemi, 1988). All of these rock types have undergone at least two episodes of deformation. Pan African granites like the Igarra batholiths and other minor intrusives including pegmatite, aplite, dolerite, lamprophyre, and syenite later intruded these supracrustal rocks and the underlying basement. More so, , categorized the main rock in the area as (a) The gneiss-migmatite-quartzite complex; (b) The schist belts which are low to medium grade supracrustal and meta-igneous rocks; (c) The Pan African granitoids (older granites) and other related rocks such as charnockitic rocks and syenites; and (d) Minor felsic and mafic intrusives (Figure 2) (Adekoya et al., 2003).

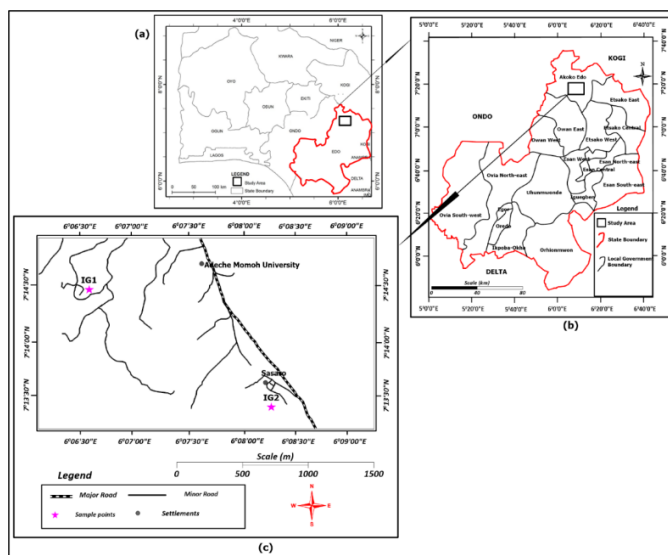


Figure 1: Map of southwestern Nigeria showing the study area (a), insert is the map of Edo state showing the study area (b) and the location map of the study area (Modified after federal ministry of land and housing, 2010)

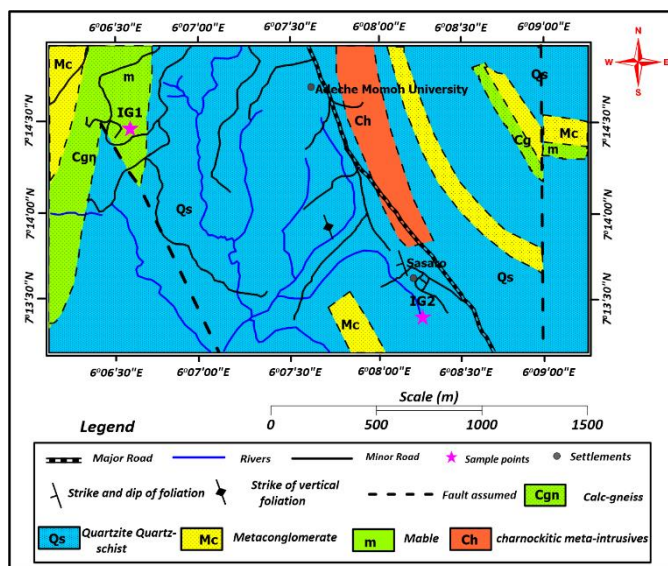


Figure 2: Geological map of the study area showing the sample location (Modified from geological map of Lokoja sheet 62, Geological survey agency of (Nigeria, 1966))

3. METHODOLOGY

3.1 Sampling and preparation

Twenty (20) fresh rock samples were randomly collected from Cal-silicate-gneiss and Lamprophyre quarry site, the samples were carefully placed in labeled bags for easy identification and transported to the engineering geology laboratory, Federal University of Technology Akure for processing. Ten (10) samples (five from each types) were then carefully selected from the rock samples and were fully pulverized spontaneously. The samples were oven dried at temperature of $110^{\circ}C$ until steady mass was attained. Weighing was done again at one-hour intervals until there was no noticeable change in weight. To create

homogeneous fine-grained samples, the dry samples were ground into a fine powder and subsequently sieved through a 2 mm mesh sieve. 200g of the dried samples were weighed and put into radon-impermeable, cylindrical plastic containers that were the same size as the detector (70 mm in height by 60 mm in diameter). In order to prevent radon-222 from escaping, the containers were triple sealed. To do this, Vaseline jelly was first applied to the container cap's inner rim. In addition, after capping, the space between the container and cap assembly were filled with candle wax, and then masking tape is used to tighten the seal. In accordance, the secured container containing the samples were left for four weeks to allow for parent and daughter radionuclides to get temporal equilibrium before starting fluorescence spectroscopy analysis (Ajayi et al., 2018).

3.2 Radionuclides activity measurement in rock

The samples were analyzed for natural radioactive elements (Radium, Thorium and Potassium) in the rock samples using X-ray Fluorescence spectrometer (XRF) Pananalytical Axiosm AX model at Temsol Consults Limited laboratory Ibadan. Standard conversion factors (Table 1) and equations were then used to calculate the activity concentration of radionuclides in accordant and evaluate the radiological hazard indices associated with the rock samples respectively (Hanfi et al., 2021; Beretka and Mathew, 1985; UNSCEAR, 2000).

Table 1: Conversion of radioactive element concentration to activity concentration (BqKg⁻¹) (IAEA, 2003; Hanfi et al., 2021)

Radioactive element	Concentration	Activity concentration (BqKg ⁻¹)
⁴⁰ K	1% K in rock	313
²³⁸ U	1 ppm U in rock	12.35
²³² Th	1 ppm Th in rock	4.06
²²⁶ Ra	1ppm Ra in rock	12.35

3.3 Heavy metal concentration analysis in rock

Two grams of each sample were considered and oven dry at a temperature of 110°C for a minimum of 4 hours. After cooling, overnight, the samples were roasted at 850°C in a furnace to eliminate extra air and moisture content, and they were then weighed once more. Six grams of X-ray flux were added to 0.7 grams of the dried samples, which had been measured into glass discs, in order to lower the melting point of the samples and enable full homogenization. 35.3% lithium tetraborate (Li₂B₄O₇) and 64.7% lithium metaborate (LiBO₂) make up the X-ray flux. Care was taken when adding X-ray flux as observed by Willis and Duncan (2013) that flux should be dry and free of CO₂, because many fluxes are hygroscopic hence they can also adsorb CO₂ from air. Thus, Platinum crucibles were employed in a gas fusion chamber to fuse the samples (CLAISSE-M4 GAS FUSION Model). By adding lithium bromide (LiBr), a releasing agent, the fused discs were also released from the platinum crucible in the gas fusion chamber. About 2.5g of LiBr was weighed and dissolved in 100 ml of water to help the samples come out of the crucible. Six drops of the dissolved releasing agent were then mixed with the samples. During fusion (melting) the samples were subjected to a temperature of about 1100°C in the chamber after which the samples were completely fused into a glass disc. After cooling, the discs were labeled and transferred into a desiccator. The fused discs were thereafter loaded into the XRF Spectrometer chamber which is made of reinforced plastic and stainless steel. The model of the wavelength dispersive XRF machine through which analysis was conducted is Pananalytical AxiosmAX. The automated lever system is connected to a clamp and rubber plate which picked the disc by suction, lower it into the stainless steel loader while the clamp will grip the loader, lift it up and drop it into a hollow portion within the chamber that is in direct contact with the X-ray beam. It takes about 12 minutes for each sample to be analyzed. The lever system completes a cycle of operation by returning the sample disc to its original place. The XRF spectrometry operational settings was set at 4 kW, 60 kV (160 mA).

3.4 Assessment of radiological hazard parameters in the rocks

3.4.1 Radium equivalent activity (Ra_{eq})

Radium equivalent activity (Ra_{eq}) is a quantity that estimates the hazards of the materials containing the radionuclides ²³²Th, ²²⁶Ra, and ⁴⁰K, it is expressed in becquerels per kilogram (Bqkg⁻¹). According to the equation, the same amount of gamma radiation is produced by 370Bqkg⁻¹ of ²²⁶Ra, 259Bqkg⁻¹ of ²³²Th, and 4810Bqkg⁻¹ of ⁴⁰K (Beretka and Mathew, 1985; Shuaibu, 2017). The following relation, as specified, was used to evaluate the Ra_{eq} (UNSCEAR, 2000).

$$Ra_{eq} (BqKg^{-1}) = A_{Ra} + 1.43A_{Th} + 0.077A_K \quad (1)$$

Where A_{Ra}, A_{Th}, and A_K are the activity concentrations of ²²⁶Ra, ²³²Th, and ⁴⁰K in the samples

3.4.2 External hazard index (H_{ex}) and internal hazard index (H_{in})

The H_{ex} and H_{in} were computed using Eqs. (2) and (3), respectively, to record the external and internal exposure of the radiation originating from ²²⁶Ra, ²³²Th, and ⁴⁰K in the materials under examination (Krishnamoorthy et al., 2018; Ademola et al., 2014; Gbenu et al., 2016).

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \quad (2)$$

$$H_{in} = \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \quad (3)$$

Where A_{Ra}, A_{Th} and A_K are the activity concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K in materials respectively. H_{ex} and H_{in} values must be ≤ 1, which falls under the dose equivalent limit of 1mSv⁻¹, as proposed by the International Commission on Radiological Protection (ICRP, 1996), for the radiation threat to be considered minimal.

3.4.3 Gamma representative index (I_γ)

When materials with a potential radiological concern are to be used for construction, the gamma representative index (I_γ), is a useful parameter for screening them (Jibiri and Okeyode, 2012; Gbenu et al., 2016). It is described as stated in eq. (4).

$$I_{\gamma} = \frac{A_{Ra}}{150} + \frac{A_{Th}}{100} + \frac{A_K}{1500} \quad (4)$$

According to Jibiri and Okeyode (2012), values of I_γ ≤ 1 indicate a radiologically safe rock that is consistent with the annual effective dose limit of ≤ 1mSv.

3.4.4 Absorbed dose rate (DR)

During quarrying activity, the presence of ²²⁶Ra, ²³²Th, and ⁴⁰K in rocks may result in radiation risk. The outdoor radiation absorbed dose rate (DR_{outdoor}), in air at a height of one meter above the ground was thus computed using conversion factors of 0.462, 0.604, and 0.0417 for ²³⁸U, ²³²Th, and ⁴⁰K, respectively, in order to evaluate the dosage levels (Beretka and Mathew, 1985; UNSCEAR, 2000). It is expressed as follows;

$$DR_{outdoor} = 0.462A_{Ra} + 0.604A_{Th} + 0.0417A_K \quad (5)$$

$$DR_{indoor} = 0.92A_{Ra} + 1.1A_{Th} + 0.08A_K \quad (6)$$

Additionally, as indicated by Eq. (6), the indoor absorbed dose rate (DR_{indoor}) due to gamma ray emission from naturally occurring radioactive materials in construction materials (such rock blocks) is calculated using the data from Qureshi et al. (2014) and Beretka and Mathew (1985).

Note A_{Ra}, A_{Th} and A_K are the activity concentration of ²²⁶Ra, ²³²Th and ⁴⁰K respectively.

3.4.5 Annual effective dose (AED)

The annual effective dose is the annual dose received by people, which is estimated from the absorbed dose rate by applying a dose conversion and time occupancy factors (UNSCEAR, 2000). UNSCEAR (2000) stated adult outdoor time occupancy factor to be 0.2 (20%), while that of indoor to be 0.8 (80%). Both the outdoor and indoor AED in units of mSv⁻¹ was calculated using the following equations (UNSCEAR, 2000)

$$AED_{outdoor} = DR_{outdoor} \times 8760h \times 0.2 \times 0.7SvGy^{-1} \times 10^{-1} \quad (7)$$

$$AED_{indoor} = DR_{indoor} \times 8760h \times 0.8 \times 0.7SvGy^{-1} \times 10^{-6} \quad (8)$$

Where DR is the absorbed dose rate in air in nGy⁻¹, 8760 is the total hours in a year; 0.7 SvGy⁻¹ is the dose conversion factor and the factor 10⁻⁶ converts the nano scale to milli.

3.4.6 Excess lifetime cancer risk (ELCR)

According to Ugbede, (2020), Eq. (9) was used to compute the ELCR, which predicts the chance of cancer formation by individual over a lifetime owing to exposure to low-level radiation, in order to assess the danger of cancer among workers and residents. Also, the assessment among indoor occupants due to gamma ray emission from naturally occurring radioactive components in building materials (such rock blocks), ELCR was calculated using the report from Qureshi et al. (2014) and ICRP (1991), as indicated in Eq. (10).

$$ELCR_{outdoor} = AED_{outdoor} \times DL \times RF \quad (9)$$

$$ELCR_{indoor} = AED_{indoor} \times DL \times RF \quad (10)$$

Where AED is the annual effective dose, DL is average duration of life taken to be 70 years (Ugbede, 2020) and RF stands for risk factor having value of 0.05 Sv⁻¹ (ICRP, 2007).

3.5 Statistical analysis

The acquired data's were subjected to multivariate analysis of Pearson correlation in order to measure linear relationship between them. The analysis was carried out using the Statistical Microsoft Excel 2020. The correlation coefficient values ≥ 0.5 were considered as strong.

4. RESULTS AND DISCUSSION

4.1 Activity concentrations of radionuclides in the rocks

The results of activity concentrations of ^{40}K , ^{226}Ra and ^{232}Th of the rocks samples are provided in Table 2 and Figure 3. The activity concentrations in the cal-silicate-gneiss samples for ^{40}K , ^{226}Ra and ^{232}Th ranged from 970.3 to 1899.91 Bqkg $^{-1}$ with an average of 1695.21 Bqkg $^{-1}$, 19.34 to 62.74 Bqkg $^{-1}$ with an average of 47.71 Bqkg $^{-1}$ and 28.18 to 64.15 Bqkg $^{-1}$ with an average of 51.43 Bqkg $^{-1}$ separately. While in the lamprophyre samples, the values extended from 1064.2 to 2115.88 Bqkg $^{-1}$, 38.07 to 74.65 Bqkg $^{-1}$ and 35 to 195.3 Bqkg $^{-1}$ for ^{40}K , ^{226}Ra and ^{232}Th respectively. The average concentrations were valued as 1377.2 Bqkg $^{-1}$, 52.5 Bqkg $^{-1}$ and 80.92 Bqkg $^{-1}$ respectively. As can be seen, all of the samples under investigation show the presence of radionuclides in them, but in varying concentrations. Also, the concentrations of ^{40}K in both samples surpass those of ^{226}Ra and ^{232}Th (Figure 3). As a result, ^{40}K made up a greater portion of the samples' overall radioactivity concentration. The activity concentrations of ^{232}Th in all the samples were higher than those of ^{226}Ra , this is consistent with the results of Gbenu *et al.*, (2016) and Okeyode *et al.*, (2018) on quarry rocks in other parts of southwestern Nigeria and Obiora *et al.*, (2020) on

cretaceous rock deposits in the Abakaliki-Ishiagu environs, where uranium and radium levels were lower than those of thorium nuclides. ^{40}K show higher concentration in cal-silicate-gneiss than those of lamprophyre while ^{226}Ra and ^{232}Th were higher in lamprophyre than those of cal-silicate-gneiss (Figure 3). The study's activity concentration values for the radionuclides (^{226}Ra , ^{232}Th , and ^{40}K) were contrasted with those of comparable investigations conducted in other nations and with the global average (Table 3). The observed variations in the activity concentrations of radionuclides in rock samples across nations may be caused by variations in the chemical and mineralogical compositions of the rocks in those nations (Ofomola *et al.*, 2023; Endjambi *et al.*, 2024). Additionally, the observed variation in NORMs may be caused by variations in the magmatic origin from which the rocks are formed (Moura *et al.*, 2011). The mean activity concentrations of the analyzed rocks were higher than that of the worldwide average of 33 Bqkg $^{-1}$ for ^{226}Ra , 45 Bqkg $^{-1}$ for ^{232}Th and 420 Bqkg $^{-1}$ for ^{40}K (UNSCEAR, 2000).

Table 2: Activity concentration of radionuclides in the rocks

Sample ID	Rock Names	Activity Concentration of Radionuclides (Bqkg $^{-1}$)		
		^{40}K	^{238}Ra	^{232}Th
IG1a	Calc-Silicate-Gneiss	1881.13	38.07	54
IG1b	Calc-Silicate-Gneiss	970.3	62.25	64.15
IG1c	Calc-Silicate-Gneiss	1868.61	19.34	28.18
IG1d	Calc-Silicate-Gneiss	1899.91	62.74	56.03
IG1e	Calc-Silicate-Gneiss	1856.09	56.17	54.81
Mean		1695.21	47.71	51.43
IG2a	Lamprophyre	1064.2	38.07	35.08
IG2b	Lamprophyre	2115.88	74.65	195.29
IG2c	Lamprophyre	1298.95	51.71	47.3
IG2d	Lamprophyre	1154.97	48.24	42.87
IG2e	Lamprophyre	1252	49.85	84.08
Mean		1377.2	52.50	80.92

Table 3: Activity concentration values of ^{40}K , ^{232}Th , and ^{226}Ra are compared to those of other countries

Countries	Activity Concentrations Ranges (Bq/kg)			References
	^{226}Ra	^{232}Th	^{40}K	
Nigeria (Igarra)	47.71 – 52.50	51.43 – 80.92	1377.2-1695.21	Present Study
Nigeria (Igbeti)	14 - 487	209 - 3680	429 - 5953	Ajetunmobi <i>et al.</i> , 2022
Coorg	BDL-34.11	16.46-160.84	96.72 - 933.68	Prakash, <i>et al.</i> , 2017
Chika Manguluru	143.9 - 760.9	45.9 - 450.7	316.8- 985	Manjunatha <i>et al.</i> , 1998
Kali river, India	41.0 - 322.6	BDL - 26.1	147.2- 2739	Narayana <i>et al.</i> , 2007
Cyprus	1- 588	1- 906	50 - 160.6	Michalis <i>et al.</i> , 2003
Pakistan	33	32	57	Iqbal <i>et al.</i> , 2000
Sudetes Mountain, Poland	31—122	25 - 62	320 - 1200	Malczewski <i>et al.</i> , 2004
Wadi Karim area, Egypt	14.0 - 227	10.5- 183.0	2299 - 7356	El-Arabi, 2007
Piedmont, Italy	397	211	1265	Lucia <i>et al.</i> , 2006
Turkey	15.85	33.8	359	Osmanlioglu, 2006
World Average	35	45	420	UNSCEAR, 2000

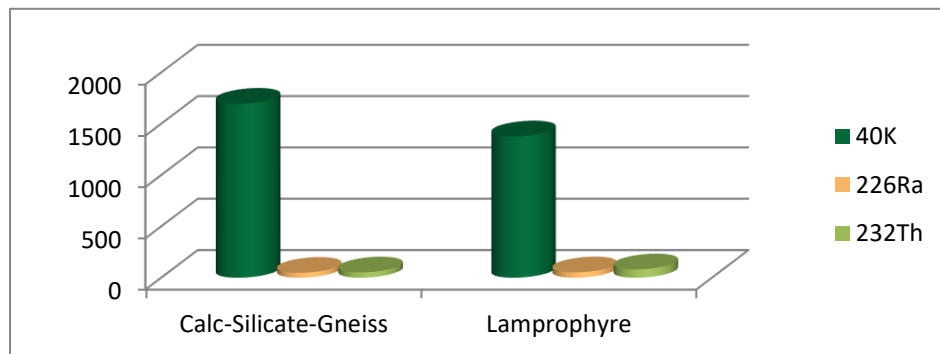


Figure 3: Average activity concentrations in (Bq/kg) of ^{226}Ra , ^{232}Th and ^{40}K .

4.2 Radiological hazard assessment in the rocks

Table 4 shows the evaluated radiological hazard indices for both rock samples. Compared to calc-silicate-gneiss, lamprophyre had higher average values of the various hazard indices assessed (Figure 4a and 4b). This may be due to the variation in the chemical and mineralogical components as well as differences in geological formation of the rocks. The values of radium equivalent activity in the samples were less than 370 Bqkg⁻¹ acceptable global level (UNSCEAR, 2000). In the calc-gneissic samples, the values extended from 203.52 to 289.16 Bqkg⁻¹ with an average of 251.80 Bqkg⁻¹, while in the lamprophytic samples, the range was 170.17 to 516.84 Bqkg⁻¹ with an average of 274.27 Bqkg⁻¹. The comparatively low values of R_{eq} in calc-gneissic and lamprophytic samples indicate that the rocks do not pose a serious concern to public health because of their radium equivalent rate. Also, the values of H_{ex} and H_{in} were < 1 with averages of 0.680 and 0.809 respectively in the calc-silicate-gneiss and 0.741 and 0.882 respectively in the lamprophyre. Since none of the samples showed readings higher than the allowable limit of 1 (UNSCEAR, 2000), it may be concluded that they provide no radiation concern and are acceptable for use as building materials. The gamma representative index (I_γ), a criterion for identifying construction materials with potential radiological health implications, is another index that was assessed. The calc-gneissic samples had an average gamma representative index (I_γ) of 1.962, while the lamprophyre samples had an average of 2.07. A material with negligible radiological risk needs to have I_γ value of less than 1 (Ofomola et al., 2023). As noticed, the rock samples' I_γ value is

greater than 1, buttressing the fact that the rocks exhibit high gamma radiation level. As a result, these rocks shouldn't be used in interior design for buildings because they could cause hazards. To investigate the radiation exposure from the quarry rocks, the absorbed dose rates (DR) in air were computed. The values of the DR (outdoor and indoor) extended from 103.88 to 142.05 nGy⁻¹ and 103.72 to 140.14 nGy⁻¹ with a mean of 123.8 and 122.3 nGy⁻¹ respectively in calc-silicate-gneiss whereas in lamprophyre it ranges from 83.15 to 240.68 nGy⁻¹ and 81.99 to 237 nGy⁻¹ with a mean of 130.56 and 128.80 nGy⁻¹ respectively (Table 4). The average value of DR due to outdoor and indoor in the studied rock samples exceed the global average value (Figure 4a) of 59 nGy⁻¹ and 84 nGy⁻¹ (UNSCEAR, 2000), while the average values of the annual effective dose (outdoor and indoor) rates are below the global average value (Table 4) of 1.0 mSv/y (ICRP, 2007) showing insignificant radiological impact to people outdoor (both to the quarry work and dweller within the environment) and indoor occupancy. Both samples' radiation doses remain below the thresholds that can cause acute effects and within the worldwide range (UNSCEAR, 2000). More so, the mean value of the excess lifetime cancer risk outdoor for the study is above the acceptable limit of 0.29×10^{-3} , (UNSCEAR, 2000) while the indoor is below the limit of 2.84×10^{-3} (Qureshi et al., 2014). The value of $ELCR_{indoor}$ shows that though the rocks emit gamma radiation but at negligible level that may not impact on the indoor occupancy (people living within the confinement of the building) when used for building purpose, on the other hand, lifelong or extended exposure to the environment might lead to dose buildup, which raises the likelihood of any health risks.

Table 4: Estimated radiological hazard indices of the rocks

Sample ID	Rock Names	Radiological Hazard Indices									
		R_{eq} (Bqkg ⁻¹)	H_{ex}	H_{in}	I_γ	DR (nGy ⁻¹) Outdoor	DR (nGy ⁻¹) Indoor	AED (mSvyr ⁻¹) Outdoor	AED (mSvyr ⁻¹) Indoor	ELCR (x10 ⁻³) Outdoor	ELCR (x10 ⁻³) Indoor
IG1a	Calc-Silicate-Gneiss	260.13	0.702	0.805	2.048	128.65	127.38	0.158	0.625	0.553	2.188
IG1b	Calc-Silicate-Gneiss	228.7	0.618	0.786	1.703	107.97	106.03	0.132	0.52	0.462	1.82
IG1c	Calc-Silicate-Gneiss	203.52	0.55	0.602	1.656	103.88	103.23	0.127	0.506	0.445	1.771
IG1d	Calc-Silicate-Gneiss	289.16	0.781	0.95	2.245	142.05	140.14	0.174	0.687	0.609	2.405
IG1e	Calc-Silicate-Gneiss	277.47	0.749	0.901	2.16	136.45	134.72	0.167	0.661	0.585	2.314
Mean		251.796	0.680	0.809	1.962	123.8	122.3	0.152	0.600	0.531	2.100
IG2a	Lamprophyre	170.17	0.46	0.562	1.314	83.15	81.99	0.102	0.402	0.357	1.407
IG2b	Lamprophyre	516.84	1.396	1.597	3.861	240.68	237.76	0.295	1.166	1.033	4.081
IG2c	Lamprophyre	219.37	0.592	0.732	1.683	106.62	105.04	0.131	0.515	0.459	1.803
IG2d	Lamprophyre	198.47	0.536	0.666	1.52	96.34	94.87	0.118	0.465	0.413	1.628
IG2e	Lamprophyre	266.49	0.72	0.854	2.008	126.02	124.31	0.155	0.61	0.543	2.135
Mean		274.268	0.741	0.882	2.077	130.562	128.794	0.160	0.632	0.561	2.211
Permissible World limit/Average		370^a	≤1^a	≤1^a	≤1^a	59^d	84^a	1.0^c	1.0^c	0.29^a 0.37^b	2.84^b
Recommendation as used in these references ^a UNSCEAR (2000), ^b Qureshi (2014), ^c ICRP (2007), ^d UNSCEAR (2000)											

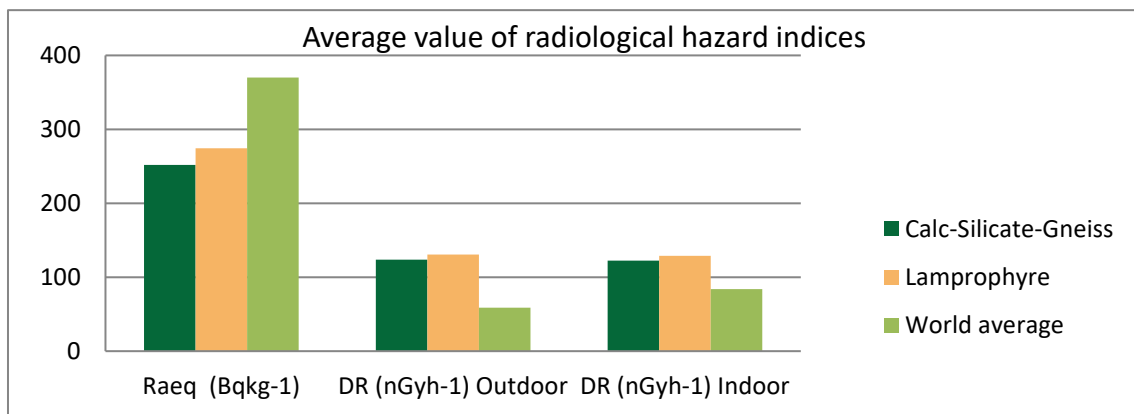


Figure 4a: Average radiological hazard indices

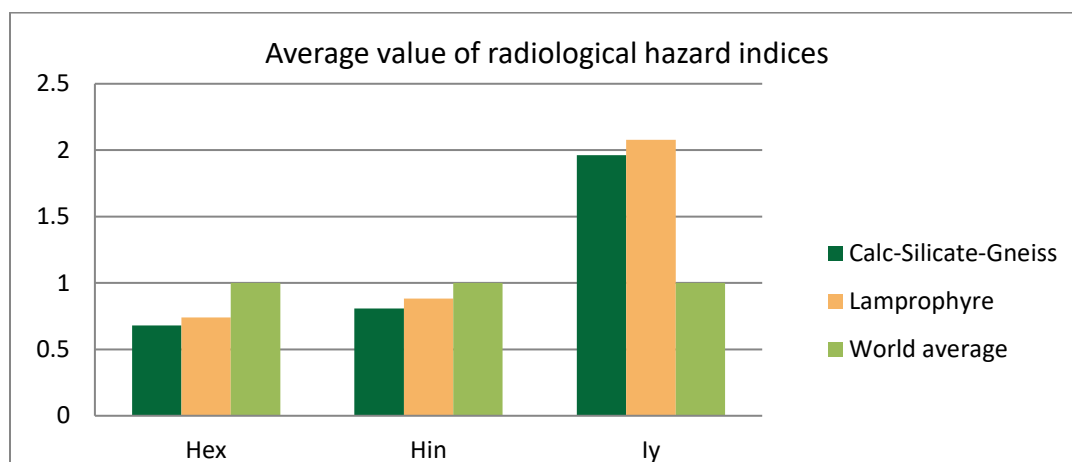


Figure 4b: Average radiological hazard indices

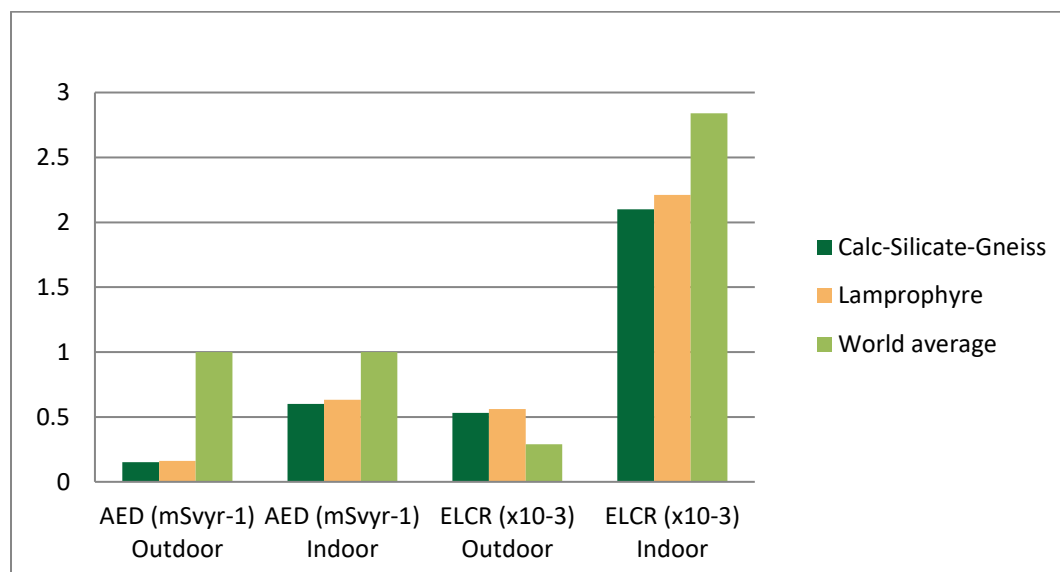


Figure 4c: Average radiological hazard indices

4.3 Concentrations of heavy elements in rocks

Table 7 displays the heavy element concentrations in the samples of Igarrá rocks that were analyzed. For the calc-silicate-gneiss, the concentration of elemental composition are in the range of 19- 45 ppm, 10- 83 ppm, 0.1-0.5 ppm, 2600-36100 ppm, 5-260 ppm, 1-5 ppm, 6.94-15.8 ppm, 1.56-6.06 ppm, 5-67 ppm, 2-93 ppm, 1-23 ppm and 4-7 ppm for Pb, Zn, Cd, Fe, Cr, As, Th, Ra, Cu, Ni, Co, and Sn respectively, with mean value of 37.3, 59.9, 0.5, 14200, 118.6, 5.0, 12.7, 3.9, 23.8, 45.8, 15.6 and 5.72 respectively. The average elemental concentration in the calc-silicate-gneiss sample were described in this manner Fe>Cr>Zn>Ni>Pb>Cu>Co>Th>Sn>Ra>As>Cd. Also the mean value of the elemental concentration in lamprophyre are 51.4 ppm, 59.6 ppm, 0.5 ppm, 25620 ppm, 125.2 ppm, 5 ppm, 19.9 ppm, 4.3 ppm, 35.2 ppm, 44.6 ppm, 15.4 ppm and 6.6 ppm for Pb, Zn, Cd, Fe, Cr, As, Th, Ra, Cu, Ni, Co, and Sn respectively. The average elemental concentration in this rock sample were described in this manner Fe>Cr>Zn>Pb>Ni>Cu>Th>Co>Sn>Ra>As>Cd independently. As regards their average concentrations, the value of Cobalt, copper, nickel, zinc and iron are below the earth's crust averagewhile other element such as chromium, lead, thorium, tin, radium, arsenic and cadmium were higher for both rock studied, suggesting them to be toxic when the dust is been inhaled or ingested (Turekian and Wedepohl, 1961). Fe has the highest concentration among other elemental compositions under study, which is consistent with reports that natural soil and rock formations contain a sizable amount of Fe, as shown by certain research. (Faridullah et al., 2017; Hançerlioğulları and Eyüboğlu, 2020; Yahaya et al., 2021). Pb-Zn deposits with modest variability may be the source of the Pb and Zn contents in the rocks (Ofomola et al., 2023). In rocks, the presence of these metals may lead to serious health issues for workers in quarry locations, including pulmonary and respiratory disorders. Residents of the host environment may inhale polluted dust during quarrying, which might result in a significant accumulation of harmful elements along the nasal cavity. These elements could then be carried to blood vessels via the thin lining of the air sac. Accordingly, blood tests from residents of quarry host communities in Ago Iwoye, Ogun state, Nigeria, clearly show considerable

exposure to Zn, Cu, and Mn (Odeyemi et al., 2021).

4.4 Analyzing natural radionuclides and radiological danger indices in rocks by statistical means

The Pearson correlation coefficient was used to determine the degree of relationship between the radionuclides and radiological parameters in the study. The results are shown in Table 6, with values between -0.5 and 0.5 being regarded as not correlated. The result demonstrates that there are distinct relationships between radionuclides and radiological hazard indices. Strong positive correlations between the pairs $^{226}\text{Ra}/^{232}\text{Th}$, $^{226}\text{Ra}/\text{H}_{\text{in}}$, $^{232}\text{Th}/\text{H}_{\text{in}}$, and $^{40}\text{K}/\text{H}_{\text{in}}$ were observed in the calc-silicate-gneiss (Table 6). This suggests that the exposure levels of the quarry workers and residents surrounding the rock to these naturally occurring radionuclides, ^{40}K , ^{232}Th , and ^{226}Ra , are in close proximity to (H_{in}). The only radiological hazard index that has a strong positive correlation with radionuclides is the internal hazard index (H_{in}) while others are weak. This indicates that an increase in the level of exposure to the radionuclides will result to increase in the internal radiological hazard index (H_{in}). Also there are strong correlations that exists between the radiological hazard indices with the highest having 1.00 except between DR and ELCR that are weak. Fusun et al., 2020, Ajetunmobi, 2018, and Ghada and Arafat, 2018 reported the trend of positive correlation between estimated radiological parameters in their study. The very low correlation that exist between the gamma representative index and the radionuclides in the calc-silicate-gneiss indicated that the gamma representative index values (though greater than the world threshold limit) do not hinder the rocks from being used as building materials (Ajetunmobi et al., 2022). In contrast with Lasun et al., 2019, which reported positive correlations between the gamma representative index and ^{226}Ra (0.99), ^{232}Th (0.57), external and internal indices (0.98, 0.99), and radium equivalent (0.99). In the lamprophytic rock, there are strong correlations between the radionuclides with the highest being 0.99 (Table 6). This suggests that exposure levels to these naturally occurring radionuclides fall within a close range. This trend was also observed in the positive correlation that exists between the estimated radiological parameters. It was also noted

that there is a high correlation between the radionuclides and radiological parameters. This high correlation that exist may hinder the use of the

lamprophyre as interior decoration in building.

Table 5: Comparison of the study's estimated radiological parameters with those of other nations

Countries	R _{eq} (Bqkg ⁻¹)	H _{ex}	H _{in}	DR (nGyh ⁻¹) Outdoor	AED (mSvyr ⁻¹) Outdoor	ELCR (x10 ⁻³) Outdoor	References
Present Study (IG1)	251.796	0.680	0.809	123.8	0.152	0.531	Present Study
Present Study (IG2)	274.268	0.741	0.882	130.562	0.160	0.561	Present Study
Egypt	56.00	0.15	0.18	28.60	40	-	El-Arabi, 2006
China	190.0	0.51	0.59	-	0.65	-	Xinwei <i>et al.</i> , 2006
Turkey	-	-	-	44	0.30	-	Wafaa, 2004
Turkey				43.2			Ahmet, 2006
Cyprs	-	-		1209	2970	-	Michalis <i>et al.</i> , 2003

Table 6: Radiological hazard indices and radionuclides' Pearson correlation coefficients in the rocks

	²²⁶ Ra	²³² Th	⁴⁰ K	R _{eq}	H _{ex}	H _{in}	I _y	DR _{outdoor}	DR _{indoor}	AED _{outdoor}	AED _{indoor}	ELCR _{outdoor}	ELCR _{indoor}
Calc-silicate-gneiss													
²²⁶ Ra	1												
²³² Th	0.807	1											
⁴⁰ K	-0.177	-0.261	1										
R _{eq}	0.428	0.332	0.144	1									
H _{ex}	0.430	0.332	0.143	1	1								
H _{in}	0.712	0.562	0.562	0.918	0.919	1							
I _y	0.248	0.170	0.306	0.962	0.961	0.783	1						
DR _{outdoor}	0.274	0.186	0.282	0.971	0.971	0.806	0.999	1					
DR _{indoor}	0.250	0.167	0.307	0.961	0.961	0.784	0.999	0.999	1				
AED _{outdoor}	0.269	0.186	0.284	0.97	0.970	0.803	0.999	0.999	0.999	1			
AED _{indoor}	0.250	0.168	0.306	0.961	0.961	0.784	0.999	0.999	1	0.999	1		
ELCR _{outdoor}	0.268	0.184	0.286	0.969	0.968	0.801	0.999	0.206	0.206	1	0.999	1	
ELCR _{indoor}	0.250	0.168	0.305	0.961	0.961	0.784	0.999	0.212	1	0.999	1	0.999	1
Lamprophyre													
²²⁶ Ra	1												
²³² Th	0.881	1											
⁴⁰ K	0.953	0.944	1										
R _{eq}	0.927	0.993	0.975	1									
H _{ex}	0.927	0.993	0.975	1	1								
H _{in}	0.939	0.989	0.979	0.999	0.999	1							
I _y	0.929	0.992	0.977	0.999	0.999	0.999	1						
DR _{outdoor}	0.931	0.991	0.978	0.999	0.999	0.999	1	1					
DR _{indoor}	0.931	0.991	0.978	0.999	0.999	0.999	1	1	1				
AED _{outdoor}	0.931	0.991	0.978	0.999	0.999	0.999	1	1	1	1			
AED _{indoor}	0.931	0.992	0.978	0.999	0.999	0.999	1	1	1	1	1		
ELCR _{outdoor}	0.931	0.991	0.978	0.999	0.999	0.999	1	1	1	1	1	1	
ELCR _{indoor}	0.931	0.991	0.978	0.999	0.999	0.999	1	1	1	1	1	1	1

Table 7: Concentrations of heavy metals in igarra rocks.

Sample ID	Concentration of Heavy Metal in PPM											
	Pb	Zn	Cd	Fe	Cr	As	Th	U	Cu	Ni	Co	Sn
Calc-silicate-gneiss												
IG1a	45	83	<0.5	38100	260	<5	13.3	3.07	29	93	23	5
IG1b	41	10	<0.5	2600	5	<5	15.8	5.02	5	2	1	7
IG1c	19	58.3	<0.5	7900	95	<5	6.94	1.56	67	45	15	4
IG1d	43	72	<0.5	8300	110	<5	13.8	5.06	8	48	18	4.6
IG1e	41	76	<0.5	14100	123	<5	13.5	4.53	10	41	21	8

Table 7(cont): Concentrations of heavy metals in igarra rocks.

Mean	37.28	59.85	<0.5	14200	118.6	<5	12.67	3.85	23.8	45.8	15.6	5.72
Lamprophyre												
IG2a	45	35	<0.5	4800	10	<5	8.64	3.07	3	4	1	3
IG2b	73	66	<0.5	31000	150	<5	48.1	6.02	31	50	16	16
IG2c	45	69.1	<0.5	30200	148	<5	11.65	4.17	101	71	21	5.01
IG2d	46	65.3	<0.5	31200	156	<5	10.56	3.89	21.4	45	18	4.87
IG2e	48	62.4	<0.5	30900	162	<5	20.71	4.02	19.5	53	21	4.20
Mean	51.4	59.55	<0.5	25620	125.2	<5	19.93	4.23	35.18	44.6	15.4	6.62
Earth crust Average	14	70	0.15	46700	102	1.8	9.6	2.7	60	84	25	2.3

Earth Crust Average ([Turekian and Wedepohl, 1961])

5. CONCLUSION

Heavy metal concentration and radiological hazard assessment of selected basement rocks of Igarra that are used for construction materials have been investigated. The results indicate that all of the estimated radiological indices, including the mean activity concentration of ^{40}K and ^{232}Th , were higher in lamprophyre than in calc-silicate-gneiss. Also, it was determined that while the radium equivalent, external and internal indices, annual effective doses, and excess lifetime cancer risks (indoor) were within the average, the mean activity (^{226}Ra , ^{232}Th , and ^{40}K) concentration, the gamma representative indices, absorption dose rates, and excess lifetime cancer risk (outdoor) in both rocks were higher than the world average. The study concludes that while the radiological impact is tolerable as presented by most indices, quarry workers might face higher exposure due to elevated outdoor radiation levels. Additionally, some trace metals exceeded Earth's crust averages, presenting potential toxicity risks if inhaled or ingested. While the rocks are deemed safe for construction, their use in interior decoration is not advised to avoid potential long-term radiation exposure indoors.

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