ASSESSMENT OF NATURAL RADIOACTIVITY LEVELS OF SOME NIGERIAN MARBLE DEPOSITS

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Abstract: The natural radioactivity levels of some marble deposits in parts of Nigeria were carried out to evaluate possible radiological hazard associated with them. This will help to assess the possible radiological risks to human health. The collected samples were pulverised, dried at 110^{0}C in order to remove moisture, and sealed in plastic beakers and kept for about four weeks for equilibrium to be reached between ^{226}Ra and its progeny ^{214}Pb. The natural radioactivities of the collected marble samples were measured using the gamma spectrometer which contains a NaI (Tl) detector connected to Multichannel Analyser (MCA). Results of measured γ-ray spectra and activity concentrations of the marble samples are; ^{232}Th (9.72$\pm$ 4.02 – 25.83$\pm$9.74 Bq/Kg), ^{238}U (14.17$\pm$6.05 – 27.19$\pm$6.14 Bq/Kg) and ^{40}K (104.07$\pm$29.78 – 302.74$\pm$60.11 Bq/Kg). The mean radium equivalent Ra_{eq} value obtained was 60.27 BqKg^{-1} which is lower than the limit of 370 Bq/Kg set by the Organisation for Economic Cooperation and Development. The absorbed gamma dose rate in air was estimated to be in the range of 20.12 – 39.44 nGyh^{-1} which is lower than the world average value of 55nGyh$^{-1.}$ The annual effective dose equivalent ranged from 24.68 – 48.37 µSv with an arithmetic mean of 34.65 µSv; it was also found to be lower the average value (70 µSv) recommended by the United Nations Committee on the Effect of Atomic Radiation (UNSCEAR). The results indicate that, at present, the radiation hazard from radionuclides in all the marble samples analyzed is within permissible limits. Therefore, it poses no radiation threat to the human population as well as other environmental elements living around these areas.

Keywords: Marble, radionuclides, radiation, effective dose, hazards

Introduction

Marbles are metamorphic equivalence of granular limestone or dolomite (i.e., rock composed of calcium-magnesium carbonate) that has been recrystallized under the influence of heat, pressure, and aqueous solutions. Commercially, it includes all decorative calcium-rich rocks that can be polished, as well as certain serpentines (verd antiques). They are generally massive and occur interbedded with such metamorphic rocks like mica. Marbles are used principally for constructions and monuments, interior decoration, statuary, table tops, and novelties.

Radionuclide components of building materials may lead to exposure to radioactive elements (^{238}U, ^{235}U and ^{232}Th) that may be injurious to the environment and inhabitants. The longer an individual stays indoor, the higher the risk of indoor and outdoor exposures to radiation from the building materials.

Marble deposits in Nigeria are known to be Precambrian and they occur in most cases within the migmatite-gneiss-schist-quartzite complex as relicts of sedimentary carbonate rocks. These are upper Proterozoic schist belt Meta sediments which are normally marked by a general absence of carbonates. Such marble appear to be limited to the western portions of the south and central parts of the country. Several of these marble deposits are currently being exploited for cement e.g. Okpella and Obajana and decorative stones e.g. Jakura, Kwakuti and Igbetti (Bamidele & Yomi, 2013).

Research has shown that building materials (such as granite, marble, sand, etc.) may cause significant gamma dose indoors due to their natural radionuclide components (Ravisankar *et al*., 2012). Bearing in mind the global interest in using marbles for construction/ornamental purposes, there is need to assess its radiological risk associated with these deposits (Aslam *et al*., 2012).

Knowledge of the level of these deposits' natural radioactivity will help in developing standards and guideline for its uses and management.

Materials and Methods

Field work/sampling

Nine (9) samples were gotten randomly from 3 different quarry sites, the Bua cement Plant in Okpella Edo state , Dangote cement plant in Obajana Kogi State and a local mine in Igarra Edo state, Nigeria. The study area lies within latitudes 7° 11' N and 7° 55' N and longitudes 6° 3' E and 6° 25' E (Fig. 1). Each sample was collected in a polythene bag, labelled carefully at each location and sent to the laboratory for analysis.

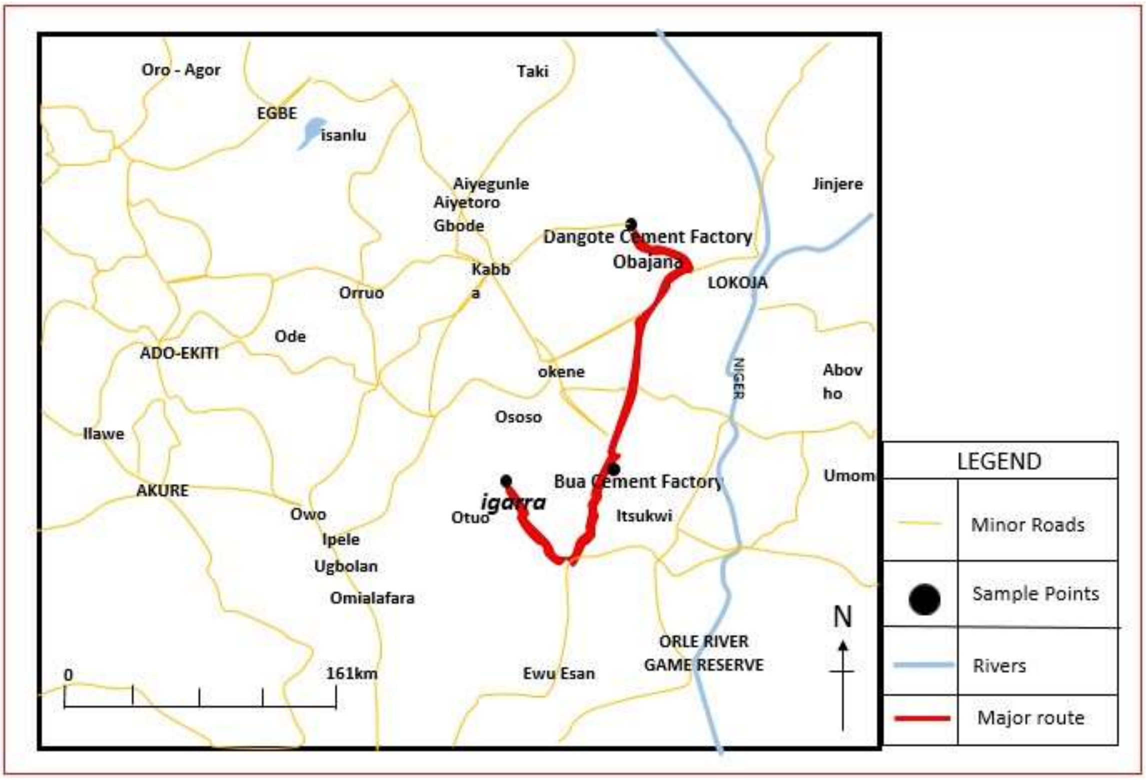

Fig. 1: Location map of the study areas (Google Earth)

Laboratory analysis

The laboratory studies were carried out at the Energy research centre at the Obafemi Awolowo University (OAU), Nigeria. The marble samples were pulverised to powdered form in the laboratory; this was done to have the same matrix and sieved through fine mesh (2 mm). The sieved pieces were then dried at 110^{0}C in order to remove the moisture. The samples were then sealed in plastic beakers and kept for about four weeks for equilibrium to be reached between ^{226}Ra and its progeny (Mustapha *et al.*, 1997). The natural radioactivities of the collected marbles were measured using the gamma spectrometer which contains a NaI (Tl) detector connected to MCA. The counting system consists of a 7.6x7.6 cm NaI (Tl) Detector Model Bircom Preamplifier Model 2001, Amplifier Model 2020 ADC model 8075 HVPS Model 3105. The detector was quoted at 25% efficiency and calibration was achieved using IAEA-375 Reference soil supply by the international Atomic Energy Agency. A mass of 200g of each sample sealed and put in the container were kept for twenty eight (28) days for attainment of secular equilibrium after which each of the container was placed directly on top of the detector for counting. The same container geometry was used for each sample background and with a counting time of 36,000 sec. For quality assurance, the gamma ray spectroscopy analysis adopted in this work was used by several. The radionuclides identified with reliable regularity belong to the series one headed by ^{238}U and ^{232}Th, as well as the non-series ^{40}K.

The photopeak used to identify ^{40}K was at 1,461KeV, while those for ^{238}U were ^{214}Bi at 1,764 and 609.3KeV and for 232Th, ^{228}Ac and ^{201}TI at 911.0 and 583.5 KeV, respectively.

Results and Discussion

Natural radionuclide concentrations measured in the samples collected at all locations are as presented in Table 1.

Table 1: Assessment of radioactivity levels of Obajana, Okpella and Igarra marble deposits

S/N as Sample Code	Radioactive content (Bq Kg $^{-1}$)			Dose rate((μSv/hr.) for γ	
	K-40	U-238 (Ra-226)	Th-232 (Ra-228)	Before Lab analysis	After Lab analysis
		Obajana			
Marb-1	247.42+ 40.07	17.83 + 8.14	19.92 + 8.46	0.18	0.17
Marb-2	133.29 + 29.11	27.19 + 6.14	25.83 + 9.74	0.19	0.20
Marb-3	302.74 + 60.11	26.23 + 5.71	24.18 + 7.63	0.19	0.19
		Igarra			
Marb-1	129.94 + 34.45	14.17 + 6.05	13.43 + 5.42	0.13	0.14
Marb-2	104.07 + 29.78	27.11 + 10.02	19.84 + 7.15	0.19	0.21
Marb-3	214.39 + 40.17	18.25. + 7.09	17.47 + 6.49	0.16	0.17
		Okpella			
Marb-1	210.89 + 38.14	20.91 + 6.30	15.81 + 4.25	0.16	0.15
Marb-2	124.08 + 28.97	19.10 + 5.36	13.67 + 5.31	0.14	0.13
Marb-3	198.53 + 40.02	14.82 + 4.66	9.72 + 4.02	0.12	0.10

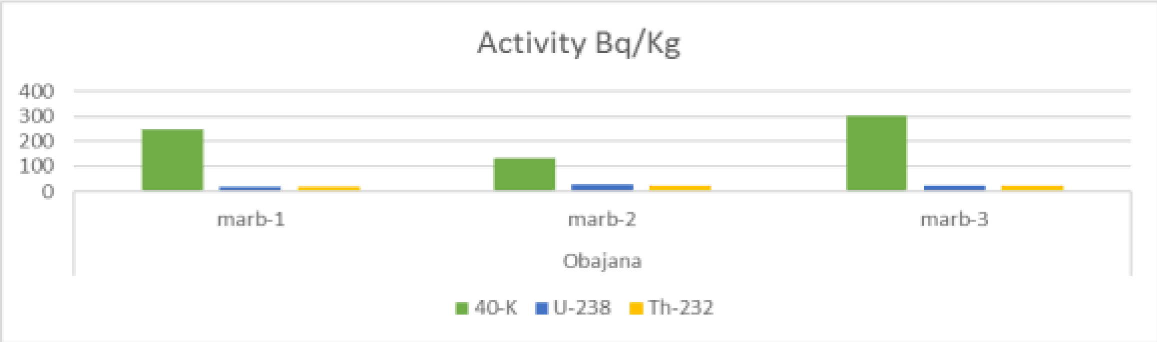

Fig. 2: Pictorial representation of 40K, 238U, and 232Th in the Obajana marble samples

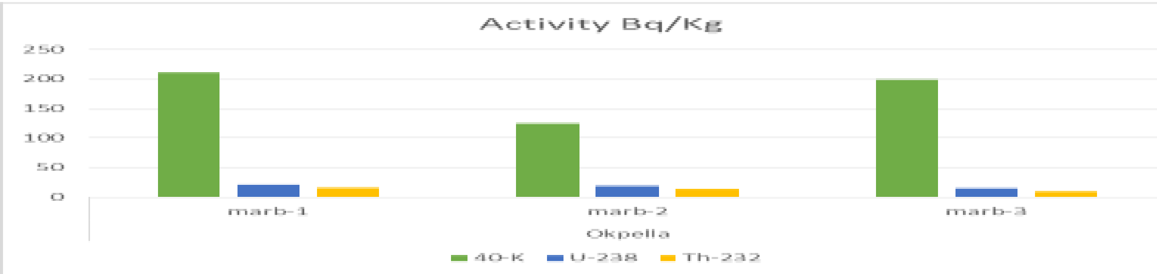

Fig. 3: Histogram representation of 40K, 238U, and 232Th in the Okpella marble samples

Obajana: Three (3) marble samples were collected at the Dangote cement factory in Obajana Kogi state. The average specific activity concentrations for the various radionuclides were 227.82 ± 43.10 Bq/Kg, 23.75 ± 6.66 Bq/Kg, and 23.31 ± 8.61 Bq/Kg for ^{40}K, ^{238}U and ^{232}Th respectively. The result indicates that ^{40}K has the highest activity in all samples from Obajana with the highest value of ^{238}U being 27.19 ± 6.14 Bq/Kg. The Obajana marble (marb-3) has the highest value of ^{40}K (302.74 ± 60.11 Bq/Kg). ^{232}Th recorded the lowest average radionuclide value of 23.31 ± 8.61 Bq/Kg (Fig. 2).

Okpella: Three (3) samples were collected from this mining site. The radionuclides identified at Bua Cement Factory in Okpella have an average specific activity concentration of 177.83 ± 35.71 Bq/Kg, 18.28 ± 5.44 Bq/Kg, and 13.07 ± 4.53 Bq/Kg for ^{40}K, ^{238}U and ^{232}Th respectively. The result indicates that ^{40}K has the highest activity in all samples from this site with a value of 210.89 ± 38.14 Bq/Kg. The highest value of ^{238}U was 20.91 ± 6.30 Bq/Kg. ^{232}Th had the lowest activity in all samples 9.72 ± 4.02 Bq/Kg (Fig. 3).

Igarra: The radionuclides identified at the local quarry in Igarra Edo State have an average specific activity concentration of 149.47 ± 34.8 Bq/Kg, 19.84 ± 7.72 Bq/Kg, and 16.91 ± 6.35 Bq/Kg. The result indicates that ^{40}K has the highest activity in all samples with a value of 214.39 ± 40.17 Bq/Kg. The highest value of ^{238}U was 27.11 ± 10.02. ^{232}Th had the lowest activity in all samples 13.43 ± 5.42 Bq/Kg (Fig. 4).

A combined activity concentrations graph for the various radionuclides in the studied marble samples is presented in Fig. 5.

Table 2 shows the average radionuclide concentrations of ^{40}K, ^{238}U & ^{232}Th in the mining areas. ^{40}K had the highest average radionuclide value of 185.04+37.87 Bq/Kg, ^{232}Th had the lowest average radionuclide value in the areas with a value of 17.76+6.50 Bq/Kg.

Table 2: Average Radionuclide Concentration of ^{40}K, ^{238}U & ^{232}Th

Prim Radi	Obajana			Igarra			Okpella			Av Radi Value $BqKg^{-1}$
	Marb-1	Marb-2	Marb-3	Marb-1	Marb-2	Marb-3	Marb-1	Marb-2	Marb-3	
^{40}K	247.42±40.07	133.29±29.11	302.74±60.11	129.94±34.45	104.07±29.78	214.39±40.17	210.89±38.14	124.08±28.97	198.53±40.02.	185.04±37.87
^{238}U	17.83±8.14	27.19±6.14	26,24±5.71	14.17±6.05	27.11±10.02	18.25±7.09	20.91±6.30	19.10±5.36	14.82±4.66	20.62±6.61
^{232}U	19.92±8.46	25.83±9.74	24.18±7.63	13.43±5.42	19.84±7.15	17.47±6.49	15.81±4.25	13.67±5.31	9.72±4.02	17.76±6.50

Prim Radi = Primordial Radionuclide; **Av Radi =** Average Radionuclide

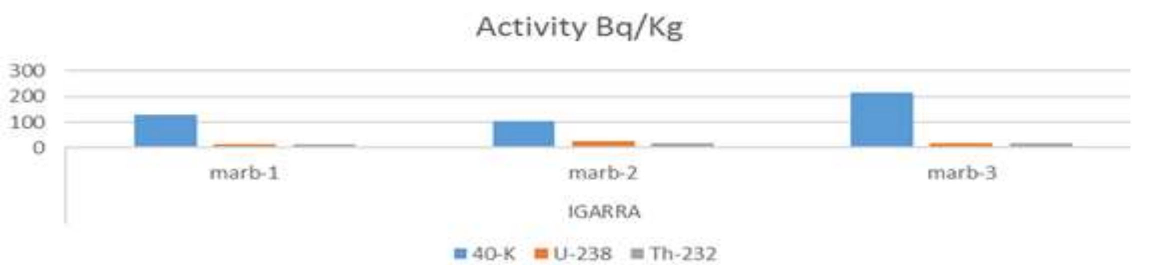

Fig. 4: Histogram representation of ^{40}K, ^{238}U, and ^{232}Th in the Igarra marble samples

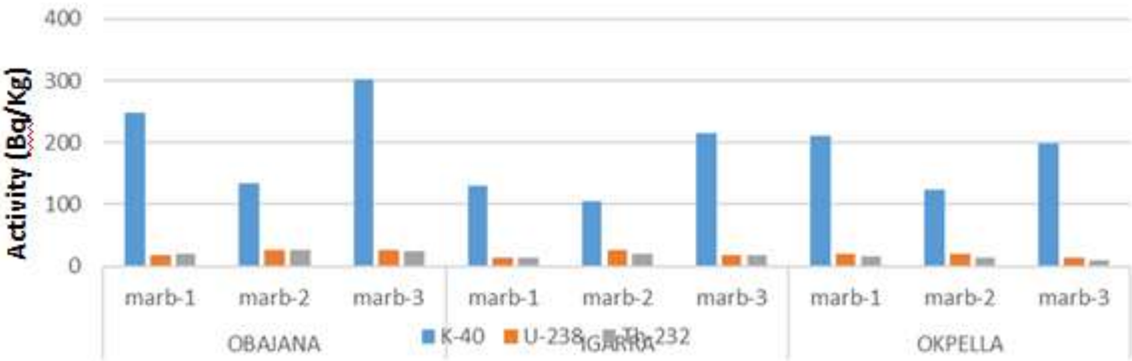

Fig. 5: A combined histogram view of ^{40}K, ^{238}U, and ^{232}Th in the Igarra, Okpella and Obajana marble samples

Radiological effects, indices and hazard assessment

One of the main objectives of radioactivity measurement in environmental studies is not to simply determine the activity concentrations of ^{238}U, ^{232}Th, and ^{40}K, but also to estimate the radiation exposure dose and assess the biological effects on humans (Akinmosin *et al*, 2016).

In this study, five (5) related quantities were deduced, these includes;

i. Absorbed dose rate (D)
ii. Radium equivalent activity (Raeq)
iii. Annual effective dose equivalent
iv. External hazard index (H_{ex})
v. Internal hazard index (H_{in})

These radiological parameters can be calculated from the measured activity concentrations of the three main primordial radionuclides in the samples.

i. **Absorbed dose rate:** The absorbed dose at 1m above the soil or rock containing the naturally occurring radionuclide is calculated from (UNSCEAR, 2000):

$$D\ (nGy\ h\text{-}1) = 0.604C_{Th} + 0.462C_u + 0.042C_k$$

Where: C_{Th}, C_u, C_k are the activity concentration (Bq Kg-1) of ^{232}Th, ^{238}U, and ^{40}K, respectively.

The total absorbed dose rates calculated for all analysed samples are shown in Table 3. The value of the total mean absorbed dose rate 1.0 m above the ground level ranges from 20.12 – 39.44 $nGyh^{-1}$, with an average of 28.25 $nGyh^{-1}$. Figs. 6 and 7 show the graphical representation of the absorbed and total absorbed dose rates of the marble samples. The average absorbed dose rates for all the samples are lower than the world average value of 55 $nGyh^{-1}$ (Fares *et al.*, 2011).

ii. Radium equivalent activity (Raeq): This was carried out to determine the gamma radiation hazards associated with the marble rocks collected from the various sites. The radium equivalent activity was determined using the following formula:

Raeq = Au + 1.43ATh + 0.077Ak (Beretka and Mathew, 1985)

Where: Au, ATh, and AK are the activity concentrations of U, Th and K in BqKg-1 respectively.

Table 3 shows the calculated Radium activity of the marble samples collected from the 3 mining sites. The calculated Raeq values range from 43.38 BqKg-1 in Igarra (Marb-1) to 84.12 BqKg-1 in Obajana (Marb-3) with an average Raeq value of 60.27 BqKg-1. The graphs of the radium equivalent in the various areas are shown in Figure 8. All the values of Raeq in the studied samples are found to be lower than the criterion limit of 370 Bqkg-1 (NEA-OECD, 1979). The results of this study show that the average value of Ra eq obtained for the marble is 60.27 Bq kg-1 which is less than the recommended value of 370 Bq kg-1. As such, this does not pose any radiological hazard when used for construction purposes.

iii. External hazard index: This was carried out to determine the gamma radiation hazards associated with the marble rocks collected from the various sites. The external hazard index was determined using the following formula:

$$H_{ex} = \frac{A_u}{370} + \frac{A_{th}}{259} + \frac{A_k}{4810} \leq 1 \quad \text{(Krieger, 1981)}$$

Table 3: Radium equivalent activity, Dose rate, external hazard index, internal hazard index and annual effective dose

Location	Sample No	Radium equivalent activity $BqKg^{-1}$	Dose Rate (nGyh-1)	External Hazard Index	Internal Hazard Index	Annual Effective Dose(μSv)
Obajana	Marb-1	65.37	30.66	0.18	0.22	37.60
	Marb-2	74.39	33.76	0.20	0.27	41.40
	Marb-3	84.12	39.44	0.23	0.30	48.37
Igarra	Marb-1	43.38	20.12	0.12	0.16	24.68
	Marb-2	63.49	28.88	0.17	0.25	35.42
	Marb-3	59.74	27.99	0.16	0.21	34.33
Okpella	Marb-1	59.76	28.07	0.16	0.22	34.43
	Marb-2	48.20	22.29	0.13	0.18	27.34
	Marb-3	44.01	23.03	0.12	0.16	28.24

The result presented in Table 3 shows that the value of the External hazard index ranges from 0.12 – 0.23. The marble in Obajana (Marb-3) possesses the highest external index level of 63.10 while the Igarra marble (Marb-1) and Okpella (Marb-3) possesses the least external hazard index. The average H_{ex} value for the samples was 0.16. These values being less than 1 as recommended by the International Committee on Radiological Protection (ICRP) show that the samples are safe for exposure to human activities. Fig. 9 is a graphical representation of the H_{ex}.

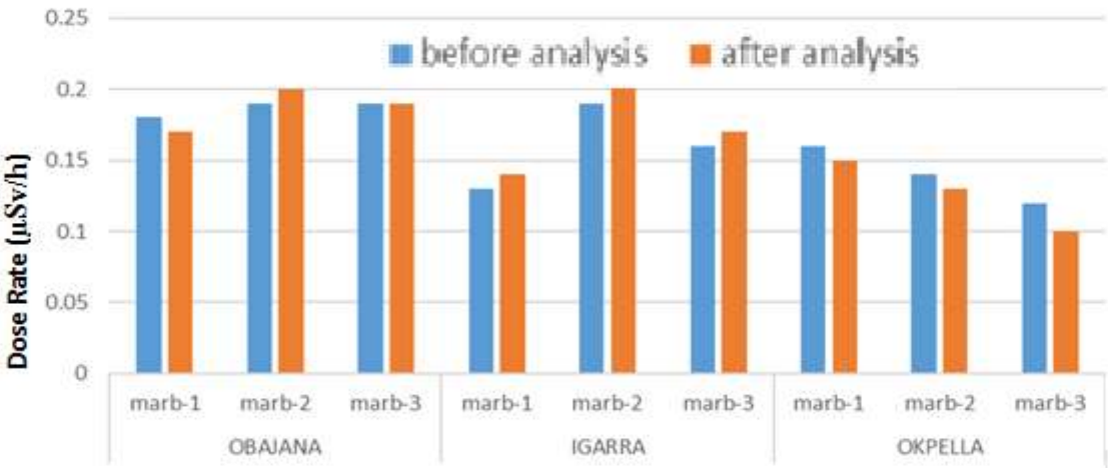

Fig. 6: **Graphical representation of the absorbed dose rates from gamma radiation**

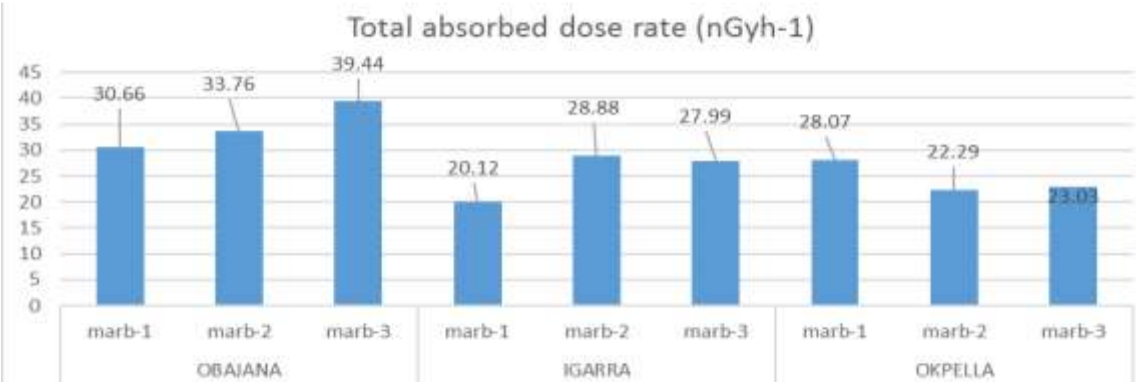

Fig. 7: Graphical representation of the total absorbed dose rate

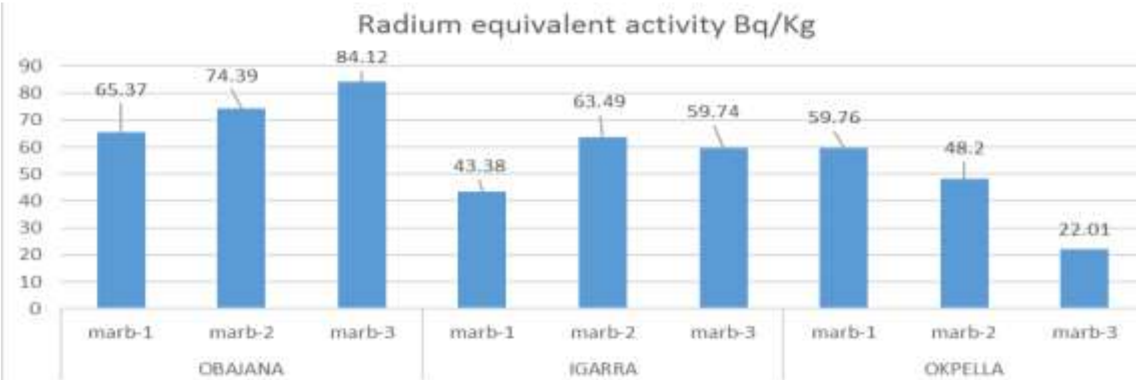

Fig. 8: Graphical representation of the Radium equivalent activity

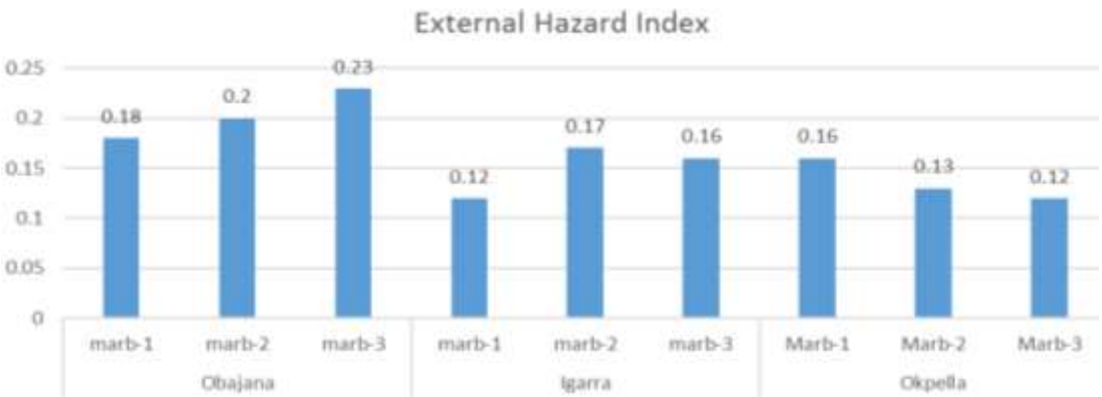

Fig. 9: Graphical representation of the external hazard index

iv. Internal hazard index (H_{in}): The internal exposure to 222Rn and its progenies is controlled by the internal hazard index (H_{in}). The internal hazard index was calculated using the formula:

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The values obtained for the internal hazard index are shown above in Table 3. The values ranged from 0.16 – 0.30 with an average value of 0.22. The highest value of H_{in} was found in Obajana (Marb-3) with a value of 0.30 while the lowest was found in Okpella (Marb-3) with a value of 0.16. The Hin of the study areas is <1 (Maximum value recommended by UNSCEAR. This implies that the radiation in these areas is below the recommended H_{in}, as shown in Fig. 10; and as such poses no threat to the human population.

v. Annual effective dose equivalent: the annual effective dose resulting from the absorbed dose is also obtained from:

E= D (nGy h-1) x (8760 h y-1) x 0.2 x 0.7 (Sv/G y-1)

Where: D (nGy h-1) is the dose rate in air from outdoor terrestrial gamma radiation and 0.7 (Sv Gy h-1) is the dose conversion factor and 0.2 is the outdoor occupancy factor as shown in Table 3. The annual effective dose was found to vary between 24.68 – 48.37 µSv with a mean of 34.65 µSv.

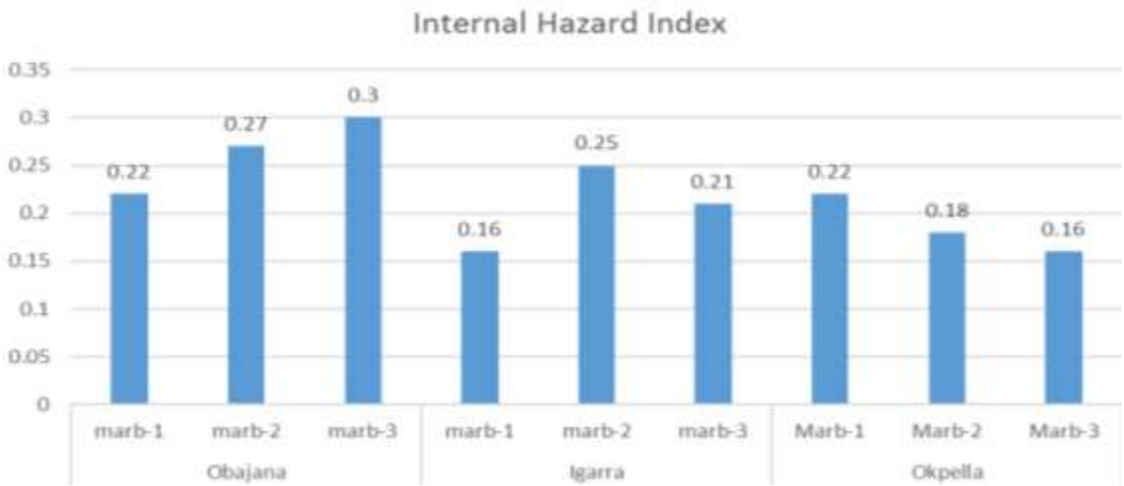

Fig. 10: Graphical representation of the internal hazard index

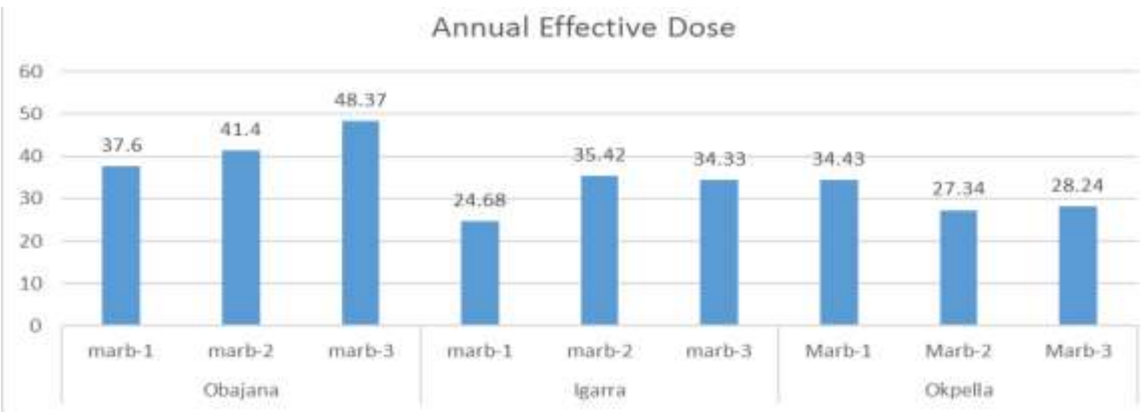

Fig. 11: Graphical representation of the annual effective dose of the marble samples

Figure 11 shows the graphical representation of the annual effective dose equivalent. The annual effective doses recorded at the study areas were lower than the worldwide average value (70 µSv y-1) recommended by the UNSCEAR (2000). This implies that the marble samples in these quarry sites and the people around the areas are not prone to excess radiation, hence the marble deposits in these areas are safe to be used for engineering and other commercial purposes.

Conclusion

The activity concentrations in the nine (9) marble samples from Obajana, Okpella and Igarra areas were determined employing high-resolution gamma ray spectroscopy. The results of the investigation showed that primordial radionuclides, namely ^{238}U, ^{232}Th and ^{40}K, were present in all samples. The activity concentrations of ^{238}U, ^{232}Th and ^{40}K were found to range from (17.83$\pm$ 8.14) to (27.19$\pm$ 6.14) $BqKg^{-1}$ for ^{238}U, (9.72$\pm$ 4.02) to (25.83$\pm$ 9.74) $BqKg^{-1}$ for ^{232}Th, and (104.07$\pm$ 29.78) to (302.74$\pm$ 60.11) $BqKg^{-1}$ for ^{40}K. The activity concentrations of the analyzed marble rocks in the study areas are generally low when compared with the worldwide average concentrations of ^{40}K (500 Bq/kg), ^{226}Ra (50 Bq/kg), and ^{232}Th (50 Bq/kg) for normal background radiation environment. ^{40}K had the highest mean activity concentration followed by ^{232}Th and ^{238}U. This can be due to the natural abundance of 40K, ^{232}Th and ^{238}U. ^{40}K is found in most terrestrial materials with an abundance of 0.012% while ^{232}Th is about 4 times more abounding than ^{238}U. Therefore, the activity level of ^{232}Th is expected to be higher than that of ^{238}U. The marble deposits in this study are generally safe, and do not pose any immediate environmental threat to its inhabitants.

Conflict of Interest

Authors have declared that there is no conflict of interest reported in this work.

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