Volume 16, No 3 | International Journal of Radiation Research, July 2018

Evaluation of radiological hazards due to natural radioactivity in bituminous soils from tar-sand belt of southwest Nigeria using HpGe-Detector

M.O. Isinkaye[1*], N.N. Jibiri[2], S.I. Bamidele[2], L.A. Najam[3]

[1]*Department of Physics, Radiation, Health and Environmental Physics Group, Ekiti State University, Ado Ekiti, Nigeria*
[2]*Department of Physics, Radiation and Health Research Laboratory, University of Ibadan, Ibadan, Nigeria.*
[3]*Department of Physics, College of Science, Mosul University, Mosul, Iraq*

► ***Original article***

Corresponding authors:
Dr. M.O. Isinkaye,
Fax: *+234 803 0516026*
E-mail:
matthewisinkaye@eksu.edu.ng

Revised: June 2017
Accepted: August 2017

Int. J. Radiat. Res., July 2018; 16(3): 351-362

DOI: 10.18869/acadpub.ijrr.16.3.351

ABSTRACT

Background: Oil exploration is known to have great impact on the environment due the presence of natural radionuclides in crude oil and bitumen. ***Materials and Methods***: In this study, high purity germanium (HpGe) detector was used to determine the activity concentrations of 40K, 226Ra and 232Th in bituminous soil and viscous bitumen samples collected from 5 different locations within the tar-sand belt of southwest Nigeria. Soil samples were collected also from a non tar-sand area to serve as control. ***Results:*** The average concentrations of ^{40}K, ^{226}Ra and ^{232}Th in the bituminous-soil samples were 139.32, 28.21 and 27.13 Bq kg^{-1}, respectively for Agbabu, 16.09, 18.71 and 17.99 Bq kg^{-1}, respectively for Ilubirin, 33.98, 38.90 and 29.82 Bq kg^{-1}, respectively for Iju Oke, 35.01, 30.06 and 21.52 Bq kg^{-1}, respectively for Ode Aye, 7.99, 4.77 and 4.08 Bq kg^{-1}, respectively for Ode Irele. Their respective values were 306.82, 23.52 and 23.14 Bq kg^{-1} for the non bituminous-soil. The natural radioactivity levels of ^{40}K, ^{226}Ra and ^{232}Th in the viscous bitumen samples ranged from below detection level (BDL)-30.74, 2.02-36.33 and 3.38-33.71 Bq kg^{-1}, respectively. The estimated gamma dose rate was higher in the non-bituminous soil than that of bituminous soil. ***Conclusion:*** All the radiation hazard indices estimated in this study are lower than the acceptable limits. It can therefore be concluded that the soil and bitumen samples are safe for use as materials for building and road constructions.

Keywords: *Natural radioactivity; radiation hazards; bitumen; tar-sand; HpGe detector.*

INTRODUCTION

Exposure to ionizing radiation comes from radionuclides of natural and artificial origin [1]. Naturally occurring radionuclides are present in different ecosystems in the earth environment. The concentrations of these radionuclides in different environmental matrices depend on the geological formations in the local environments. Radionuclides of natural origin come from two main sources: cosmogenic and primordial sources. Cosmogenic radionuclides are products of cosmic radiations interactions with atmospheric molecules, while primordial radionuclides are created with the earth. Cosmogenic radionuclides include ^{3}H, ^{7}Be, ^{14}C and ^{22}Na, while primordial radionuclides are the long-lived radionuclides such as ^{40}K, ^{238}U, ^{235}U, and ^{232}Th and their daughters. Constant amount of cosmogenic radionuclides are usually observed in the earth's environment due to the balance between the rate at which they are produced and the rate at which they decay [2]. The main contributors to the environmental

background radiation are the terrestrial radionuclides, ^{40}K, ^{226}Ra and ^{232}Th, which are not uniformly spread in soils, as such they vary according to geology and geography of different environment [3-5]. Their concentrations in soil and rocks depend on the mineral make up of the under-laying bedrock [6]. A good knowledge of natural radioactivity content of soil and rocks plays a major role in radiation protection practices and geo-scientific research [7].

Tar sand generally consists of sand, heavy oil, mineral-rich clay and water [8]. The heavy oil in tar sand is called bitumen. Bitumen consists essentially of hydrocarbons and typically comprises at least 80% carbon and 15% hydrogen. The remainders are oxygen, sulphur, nitrogen and traces of various metals [9]. The Nigerian tar-sand belt lies on the onshore areas of the Eastern Dahomey-Benin basin with an estimated reserve of bitumen and heavy oil around 120 x 4300 m^3 [10, 11]. Estimated probable reserve of untapped bitumen deposit within Ondo State in a 4.5 km × 55 km area is about 16 billion barrels [12]. In Nigeria, bitumen typically occurs both on the sub-surface and surface as seepages and outcrops. Road construction accounts for about 70 % uses of bitumen. It is used mainly as glue or binder when mixed with aggregate particles to create asphalt concrete. Its other main uses are for bituminous waterproofing products [13]. In the quest for diversification of economy and reduction of over dependence on oil and gas, Nigeria as a nation is opting for ways of exploiting her naturally abundant mineral resources. In this instance, more emphasis is on solid minerals. It is on this premise that interest is geared towards the exploitation of its vast bitumen deposits. Taking the past environmental impacts of oil and gas exploitation in the country into account, it is of concern that there might be a high level of radionuclides presence in the tar-sand deposit and it is feared that the future exploitation might have some negative impact on the environment and the population. Renewed interest in the exploration and exploitation of the vast bituminous sand deposit of Nigeria and recent reported cases of possible high levels of radioactive materials in some bituminous nodules in Czech Republic [14] and in northern Saskatchewan, Canada [15] account for the need to study the presence and level of radionuclides within the bituminous soil of the tar-sand belt of Nigeria. The aim of the research work therefore, is to evaluate the natural radioactivity contents of bituminous soil in order to assess the radiological hazards associated with the tar-sand belt of southwest Nigeria.

MATERIALS AND METHODS

Study location

The study area falls entirely within Ondo State in southwest Nigeria. The State lies between latitude 5^0 45′ and 7^0 52′ N and longitudes 4^0 20′ and 6^0 03′ E. The state has a population of over 3 million people according to the Nigeria National Population Commission report of 2006. The elevation ranges from 50 to 250 m above the sea level. The area falls within the tropical rainforest region with two distinct climatic seasons, which are; dry (harmattan) season from November to April and wet (rainy) season from May to October. The geology of the state includes the region of sedimentary rocks in the south, and the region of PreCambrian Basement Complex rocks in the north. The sedimentary rocks are mainly of the postCretaceous sediments and the Cretaceous Abeokuta Formation. The tar-sand belt lies within the sedimentary rocks region (figure 1).

Collection of samples

A total of 35 samples were collected for analysis. Five bitumen impregnated soil, otherwise known as bituminous sand and one viscous bitumen samples were collected each from Agbabu, Ilubinrin, Ode Irele, Ode Aye and Iju Oke. Five soil samples were also collected from Ajue, which has no history of bitumen occurrence to serve as control. The geographical coordinates of the sampling locations are imposed on the map of Ondo State as shown in figure 1. The soil samples were collected to the depth of 0 – 15 cm from the surface at each location using a hand trowel. After collection, the

soil samples were placed in polythene bags and carefully labeled to prevent samples mix up. The samples were properly marked and taken to Radiation and Health Physics Laboratory, Department of Physics, University of Ibadan, Nigeria, for processing before gamma spectrometry.

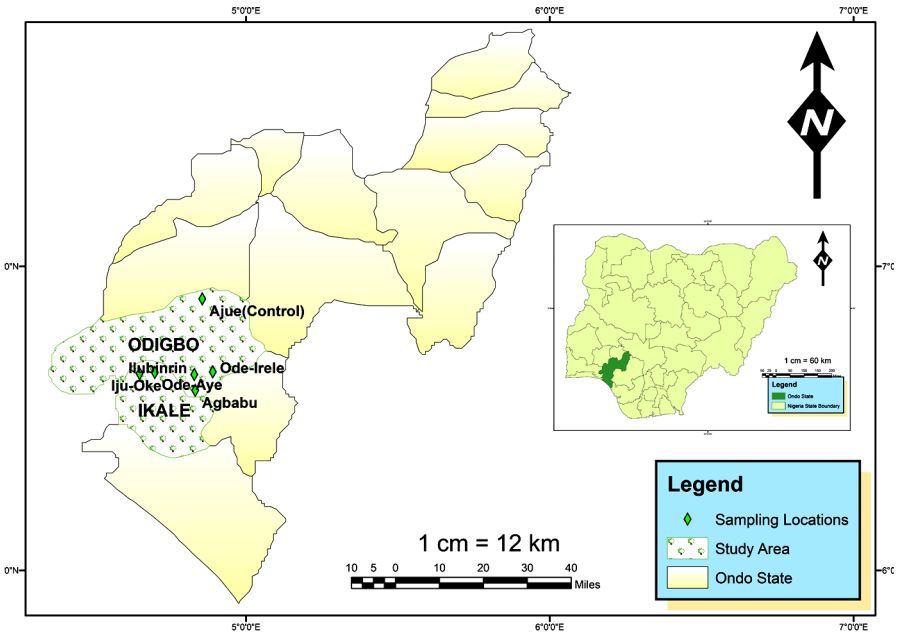

Figure 1. Map of Ondo State showing the study locations.

Sample Preparation

Each soil sample was dried under the laboratory condition until constant weight was achieved. The dried samples were pulverized and homogenized using a motorized grinder and allowed to pass through a sieve of 200 µm mesh size. The homogenized soil samples were then dried in a temperature controlled oven at 105^{0}C for about 24 h in order to eliminate organic matter content of the soil samples. The samples were then packed and sealed in cylindrical plastic containers of 9 cm × 7 cm dimension to prevent the escape of radiogenic gases such as radon. The weights of the sealed samples were recorded using an electronics weighing balance. In order to achieve radioactive secular equilibrium between parent radionuclides and their respective daughters, the sealed containers were stored for a period of 4 weeks [17].

Experimental setup

The radioactivity measurement was done using high purity germanium (HpGe) detector crystal coupled to ORTEC Multi-Channel Analyzer (MCA). The detector is an ORTEC coaxial N-type HpGe detector from Oak Ridge, TN, USA. The detector crystal is placed inside a cylindrical lead shield of 5 cm thickness with internal diameter of 24 cm and height of 60 cm. MAESTRO-32 evaluation software was used for spectrum acquisition and processing. The MCA consists of an analogue to digital converter (ADC), Control Logic (CL) with input and output devices, High Voltage Power Supply (HVPS), Electronic cooling system which cools the detector to a liquid Nitrogen temperature. Also present are automobile rechargeable batteries of four Nexus ultra-power NUP- SMF 200 which serve as a back up to the system, Central Processing Unit (CPU) and Digital display monitor are employed to display the spectrum.

The energy calibration was done by obtaining the relationship between peak position in the spectrum and the corresponding gamma-ray

energy. The height of each pulse output from a photomultiplier tube which was viewed on the display output and the channel corresponding to it is directly proportional to the initial gamma energy producing the pulse. The calibration was done using gamma emitter sources of known energies. These are americium-241 (59.45 keV), cesium-137 (661.66 keV), cobalt-60 (1173.23 keV), cobalt-60 (1332.5 keV), cobalt-60 (2505.72 keV) obtained from International Atomic Energy Agency (IAEA) in Austria. The gamma emitter sources were exposed to the HpGe detector and gamma spectrum was acquired. The counting time was 36000 s. The calibration sources were counted long enough in order to obtain a well-defined photo-peak while the gain of the system was adjusted so that the photo-peak of ^{137}Cs was about one-third the full scale. This ensured that the range of all radionuclides of interest was covered. The channel number that corresponds to the centroid of each full energy peak (FEP) on the MCA was recorded and the slope and intercept calculations were automatically done by the system.

Radioactivity measurement

Each sample was placed directly on the HpGe detector and counted for 10 h. The counting system exhibited high detection efficiency since the number of pulse under a photo peak is proportional to the intensity of the radiation reaching the detector volume. The net area or count under the corresponding peaks in the energy spectrum was computed by subtracting counts due to Compton scattering of higher peaks and other background sources from the peaks from the net area, the activity concentration was obtained using equation 1 [18]:

$$C_S = \frac{M_{st}A_s}{M_s A_{st}} C_{st} \quad (1)$$

Where; C_S is the concentration of radionuclide in the sample (Bqkg^{-1}), C_{st} is the concentration of radionuclide in the standard (Bqkg^{-1}), M_{st} is the mass of the standard sample (kg), M_S is the mass of the sample (kg), A_{st} the net area of the standard and A_s is the net area of sample. The energy peaks used for determination of activity of ^{226}Ra in the samples were 295 keV and 352 keV of ^{214}Pb and 609 keV, 1120 keV and 1764 keV of ^{214}Bi , for 232Th, 583 keV and 2614 keV of ^{208}Tl, 911 keV and 969 keV of ^{228}Ac were used, while 40K was determined from 1460 keV gamma line [19]. The background counts in the detector assembly were determined using an empty container sealed under identical measurement conditions and having the same geometry as the container used for the sample measurement. It was determined prior to the measurement of the samples. This procedure is important because of the existence of natural radionuclides in building materials, cosmic rays entering the atmosphere and contribution from other radioactive sources which might be present in the laboratory.

EVALUATION OF RADIOLOGICAL PARAMETERS

The gamma absorbed dose rate

The absorbed dose rate in air at 1m above the ground surface can be calculated based on the recommendation given by United Nations Scientific Committee on the Effects of Atomic Radiation [1]. This quantity is used to measure the radiation exposure to human body in order to evaluate the amount of radiological hazards to humans due to the concentrations of ^{226}Ra, ^{232}Th and ^{40}K in soil. The absorbed dose rate (DR) at 1m above the ground (in nGyh^{-1}) was calculated using equation 2 [6]:

$$DR(nGy\ h^{-1}) = 0.462A_{Ra} + 0.604A_{Th} + 0.0417A_K \quad (2)$$

Where; A_{Ra}, A_{Th} and A_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K, respectively.

The annual effective dose

In order to determine the radiological impact of the results obtained, the annual effective dose needs to be determined for an individual exposed at the calculated dose rate. The annual effective dose in unit of mSv y^{-1} was obtained by converting the total absorbed dose in nGy h^{-1} and multiplies by occupancy factor OF, of one year expressed in seconds, using equation 3 [6]:

$$E = DR \times OF \times CF \quad (3)$$

Where; E is the annual effective dose, CF is

the conversion factor for absorbed dose in air to external effective dose in adults and is given as 0.7 Sv/Gy [2], DR is the calculated absorbed dose rate at 1m above the ground and OF is the occupancy factor, which is given as 0.2 (assuming that individuals spend 20% of their time outdoors) × number of hours per annum. Thus, OF becomes:

$$OF = 0.2 \times 24 \times 365\ d \cong 1750\ h\,y^{-1} \quad (4)$$

The value obtained will be compared with the ICRP recommendation for effective protection of both radiation workers and the member of the public from ionizing radiation.

Radium equivalent activity

The radium equivalent activity is a single quantity that is used to account for the radiation doses accruing from ^{226}Ra, ^{232}Th and ^{40}K. It is one of the mostly used hazard indices in radiation protection assessment [20]. The radium equivalent activity is estimated based on the assumption that 370 Bq kg^{-1} of ^{226}Ra, 259 Bq kg^{-1} of ^{232}Th and 4810 Bq kg^{-1} of ^{40}K produce the same gamma dose rate [21]. Radium equivalent activity can be calculated from the following relation (equation. 5) suggested by Beretka and Mathew [22]:

$$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_K \quad (5)$$

Where, A_{Ra} is the activity concentration of ^{226}Ra in Bq kg^{-1}, A_{Th} is the activity concentration of ^{232}Th in Bq kg^{-1} and A_K is the activity concentration of ^{40}K in Bq kg^{-1}.

Internal radiation hazard index (H_{in})

The internal radiation hazard index (H_{in}) is used to reduce the maximum permissible concentration of ^{226}Ra to half the values appropriate for the external exposure alone. The radionuclide radon-222 which is a progeny of ^{226}Ra poses threats to the respiratory organs, when accumulated in large quantity in the indoor air. For the safe use of a material in the construction of dwellings, the maximum value of the internal hazard index should be less or equal to unity [23]. The internal exposure to ^{222}Rn and its radioactive daughters can be controlled by the internal hazard index [22, 23]. The internal hazard index is calculated as:

$$H_{in} = \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \leq 1 \quad (6)$$

Where; A_{Ra}, A_{Th} and A_K are the specific activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in Bq kg^{-1}, respectively.

External radiation hazard index (H_{ex})

The estimation of external hazard index (H_{ex}) is an important tool in the assessment of the suitability of any material used in the construction of dwellings from the radiological point of view. The external hazard index due to gamma radiation is calculated using equation 7 [22]:

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \leq 1 \quad (7)$$

Where; A_{Ra}, A_{Th} and A_K are the specific activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in Bq/kg, respectively. The external hazard index is gotten from the expression of the radium equivalent through the supposition that its m aximum permissible value corresponds to the upper limit of Ra_{eq} (370Bq/kg) ($H_{ex} = \frac{Ra_{eq}}{370}$), therefore the external dose rate does not exceed 1.5 mGy. In order to limit the external gamma dose of materials to 1.5 mGy/y for the radiation hazard to be negligible or insignificant, the external hazard index must be in conformity with the criterion of $H_{ex} \leq 1$ [24].

Representative gamma index

Another veritable tool that can be used to examine whether the sample meet these limits of dose criteria is the representative gamma index ($I\gamma r$). This index is used to estimate the level of ϒ- radiation hazard associated with the natural radionuclides in specific investigated samples. The expression is proposed by OECD [25] and is given as:

$$I_{\gamma r} = \frac{A_{Ra}}{150} + \frac{A_{Th}}{100} + \frac{A_K}{1500} \quad (8)$$

Where; A_{Ra}, A_{Th} and A_K are as defined above. The representative gamma index helps us to correlate the annual dose rate due to the excess external gamma radiation caused by superficial material. It is used as screening tool to identify

materials that may become health concerns when used as building materials.

RESULTS

The activity concentrations of three naturally occurring radionuclides (^{40}K, ^{226}Ra and ^{232}Th) were determined in bituminous soil and viscous bitumen samples collected from five different populated settlements within the tar sand belt area of southwest Nigeria. Samples were also collected from a location outside the tar sand belt but within the same geological region to serve as control (figure 1). The statistics of the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th expressed in Bq kg^{-1} is presented in table 1. From the table, the highest mean concentration of ^{40}K (139.32 ± 97.88 Bq kg^{-1}) for the tar-sand belt was obtained in Agbabu, while the lowest mean concentration (7.99 ± 4.47 Bq kg^{-1}) of the same radionuclide was obtained in Ode-Irele. For ^{226}Ra, the highest mean concentration of 38.90 ± 2.07 Bq kg^{-1} was observed at Iju-Oke, while the lowest mean concentration of 4.77 ± 1.30 Bq kg^{-1} was observed at Ode-Irele. Also for ^{232}Th, the highest mean concentration of 29.83 ± 1.40 Bq kg^{-1} was observed at Iju-Oke, while the lowest mean concentration of 4.08 ± 1.28 Bq kg^{-1} was obtained at Ode-Irele. Ode-Irele presented the lowest concentrations of the three radionuclides considered in the study. The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in viscous bitumen samples collected from the five locations in the study area are shown in table 2. From the table, the activity concentrations for ^{40}K, ^{226}Ra and ^{232}Th ranged from BDL-30.74, 3.38 -33.71 and 2.02-36.33 Bq kg^{-1}, respectively. In the entire tar-sand belt, the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in the collected bituminous soil samples were found to be in the range of 1.79-240.82, 3.52-41.37 and 2.36-30.69 Bq kg^{-1} with average values of 46.48 ± 41.08, 24.13 ± 1.81 and 20.11 ± 2.62 Bq kg^{-1}, respectively. For the control site (Ajue), the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th ranged from 181.61-343.15, 19.57-27.86 and 19.36-28.41 Bq kg^{-1}, with average values of 306.82 ± 78.70, 23.52 ± 3.27 and 23.13 ± 3.70 Bq kg^{-1}, respectively. The activity concentration of ^{40}K in bitumen samples is generally below the detection limit of the HpGe detector employed in this study except at two locations (Ilubinrin and Iju-Oke). Ilubinrin, Iju-Oke and Ode-Irele presented ^{226}Ra and ^{232}Th concentrations in bitumen samples that are comparable to their corresponding values in soil samples. Agbabu and Ode-Aye values are much lower in bitumen samples in comparison to soil samples. The average concentrations of ^{40}K, ^{226}Ra and ^{232}Th measured in both the bitumen and bituminous-soil samples were lower than the world wide average value of 420, 32, and 45 Bq kg^{-1}, respectively [1]. The only exceptions are the soil and bitumen samples from Iju Oke whose average values of 38.90 Bq kg^{-1} and 33.71 Bq kg^{-1}, respectively, for ^{226}Ra are higher than the world average crustal value.

Table 1. The activity concentrations of 40K, 238U and 232Th in bituminous soils from tar-sand belt of Ondo State.

Location	Size	^{40}K (Bqkg^{-1})		^{226}Ra (Bqkg^{-1})		^{232}Th (Bqkg^{-1})	
		Mean	Range	Mean	Range	Mean	Range
Agbabu	5	139.32±97.88	36.56-240.82	28.21±4.62	22.07-34.65	27.13±7.30	15.95-33.67
Ilubirin	5	16.01±6.76	9.74-24.44	18.71±2.26	17.45-22.74	17.99±1.74	16.15-20.36
Iju-Oke	5	33.98±12.43	16.49-50.07	38.90±2.07	35.71-41.37	29.79±1.37	27.38-30.69
Ode-Aye	5	35.01±2.12	32.98-38.15	30.06±5.50	26.77-39.59	21.52±1.40	19.91-23.69
Ode-Irele	5	7.99±4.47	1.79-14.31	4.77±1.30	3.52-6.96	4.08±1.28	2.36-5.77
Ajue (Control)	5	306.82±78.70	181.61-395.00	23.52±3.27	19.36-28.41	23.14±3.70	19.36-28.41

The results of the various radiological parameters used to evaluate the exposure of the populace to the gamma radiation from the naturally occurring radionuclides considered in this study are presented in table 3. The external exposure to gamma dose was evaluated through the calculation of outdoor air-absorbed dose rates due to terrestrial gamma rays at 1 m above the ground from ^{40}K, ^{226}Ra and ^{232}Th using the formula provided in equation 2. The results show that the air-absorbed dose rates ranged from 3.70-44.00 nGy h^{-1}. Iju-Oke has the highest mean outdoor air-absorbed gamma dose rates of 37.40 ± 1.87 nGy h^{-1}, while Ode-Irele has the lowest mean value of 5.00 ± 1.43 nGy h^{-1}. The annual outdoor effective dose was calculated and the mean value for the various locations presented in table 3. It could be seen from the table that the annual outdoor effective dose to which humans are exposed in the study area ranged from 30.57-53.89 μSv y^{-1} with a mean of 43.16 ± 8.36 μSv y^{-1} for Agbabu, 22.61-29.02 μSv y^{-1} with a mean of 24.72 ± 2.67 μSv y^{-1} for Ilubinrin, 42.08-48.18 μSv y^{-1} with a mean of 45.82 ± 2.29 μSv y^{-1} for Iju-Oke, 32.32-41.62 μSv y^{-1} with a mean of 34.72 ± 3.88 μSv y^{-1} for Ode-Aye and 4.54-8.94 μSv y^{-1} with a mean of 6.12 ± 1.76 μSv y^{-1} for Ode-Irele. The results of the radiological hazard assessment show that the overall tar-sand belt average air-absorbed dose rate is 25.23 ± 2.18 nGy h^{-1}. This value is about 1.5 order of magnitude lower than the mean air-absorbed dose rate of 37.63 ± 3.97 nGy h^{-1} obtained outside the tar-sand belt. The overall mean value of outdoor effective dose within the tar-sand belt is 30.91 ± 2.67 μSv y^{-1}. This value is lower than the 46.10 ± 4.86 μSv y^{-1} obtained for the control sites.

Table 2. The activity concentrations of ^{40}K, ^{238}U and ^{232}Th, radium equivalent activity (Raeq) and representative gamma index (Iγr) in viscous bitumen from tar-sand belt.

Location	Activity concentration (Bq kg^{-1})			Radiological indices	
	^{40}K	^{226}Ra	^{232}Th	Ra_{eq}	$I_{\gamma r}$
Agbabu	BDL	3.38	2.02	6.85	0.04
Ilubirin	30.74	28.41	28.08	71.07	0.49
Iju-Oke	7.37	33.71	36.33	85.10	0.59
Ode-Aye	BDL	4.06	4.47	10.28	0.07
Ode-Irele	BDL	6.98	12.26	22.24	0.17
Tar-sand mean	19.06	16.63	15.31	39.11	0.27

Table 3. The mean radiological parameters obtained in bituminous and non-bituminous soils from tar-sand belt.

Location	Radiological parameters					
	D_R (nGy/h)	EDR (μSv/y)	Ra_{eq}	H_{in}	H_{ex}	I_γ
Agbabu	35.23	43.16	77.74	0.29	0.21	0.55
Ilubirin	20.18	24.72	45.67	0.17	0.12	0.32
Iju-Oke	37.40	45.82	84.17	0.33	0.23	0.58
Ode-Aye	28.35	34.72	63.53	0.25	0.17	0.44
Ode-Irele	5.00	6.12	11.22	0.04	0.03	0.08
Tar-sand belt	25.23	30.91	56.46	0.22	0.15	0.39
Ajue (Control)	37.63	46.10	80.22	0.28	0.22	0.59

DR=dose rates, EDR=effective dose rates, Raeq=radium equivalent activity, Hin=internal hazard index, Hex=external hazard index and Iγ=representative level index

The radium equivalent activities due to the presence of naturally occurring radionuclides (^{40}K, ^{226}Ra and ^{232}Th) were calculated based on their activities in the bituminous soil samples using equation 5. The highest value of radium equivalent activity obtained in bituminous soil samples is found to be 96.17 Bq kg^{-1}, while the lowest value is 8.21 Bq kg^{-1}. The overall mean value for the study area is 56.46 ± 4.21 Bq kg^{-1}. The location-based mean values ranged from 11.22 ± 3.20 Bq kg^{-1} in Ode-Irele to 84.17 ± 4.15 Bq kg^{-1} in Iju-Oke. In the control locations, the radium equivalent activity varies from 74.08 to 94.35 Bq kg^{-1} with a mean of 80.22 ± 8.29 Bq kg^{-1}. The overall mean radium equivalent activity is lower at the bituminous soil locations than the control sites. For the bitumen samples, the radium equivalent activity varies from 6.35 Bq kg^{-1} at Agbabu to 85.10 Bq kg^{-1} at Iju-Oke with an average value of 39.11 ± 36.38 Bq kg^{-1}. The calculated values of external and internal hazard indices vary from 0.02-0.26 and 0.03-0.35 with mean values of 0.15 ± 0.01 and 0.22 ± 0.02, respectively for the bituminous soil samples. For the control sites (Ajue), the values range from 0.20-0.25 and 0.26-0.33 with mean values of 0.22 ± 0.02 and 0.28 ± 0.03, respectively for external and internal hazard indices. Lastly on the radiological hazards assessment, the representative level index was calculated for the bituminous soil and the viscous bitumen samples. The results indicate that the highest mean value of 0.58 ± 0.03 was obtained in Iju-Oke, while the lowest mean value of 0.08 ± 0.02 was obtained in Ode-Irele for the bituminous soil samples with a total mean value of 0.39 ± 0.04 and overall range of 0.06 to 0.69. For the non-bituminous soil, the gamma representative index ranges from 0.58 to 0.70 with a mean of 0.59 ± 0.06, while for viscous bitumen samples, the value ranges from 0.04 to 0.59 with a mean of 0.27 ± 0.25.

DISCUSSION

From the results of the activity concentrations of the natural radionuclides obtained for the bituminous soil samples, low values of standard deviations were noticed indicating that the three radionuclides were uniformly distributed within the study area. The distribution also reflects the uniformity in the geology of the study environment. A comparison between the mean activity concentrations of the three radionuclides observed for the tar-sand belt and the control site shows that ^{40}K is about five order of magnitude higher at the control site to the tar-sand belt (table 4). ^{226}Ra and ^{232}Th fall within the same range for the tar-sand belt and the control site. From the results, it is observed that the occurrence of bitumen caused depletion in the ^{40}K content of the soil samples. The results of this study show that ^{40}K, ^{226}Ra and ^{232}Th account for 51%, 27% and 22%, respectively, of the total radioactivity levels in the tar-sand belt of southwest Nigeria.

Table 4. Comparison of mean activity concentrations of 40K, 226Ra and 232Th in viscous bitumen, bituminous-sand and non-bituminous soil samples.

Sample type	^{40}K (Bqkg^{-1})	^{226}Ra (Bqkg^{-1})	^{232}Th (Bqkg^{-1})
Bitumen	19.06	16.63	15.31
Bituminous sand	46.48	24.13	20.11
Non-bituminous sand	306.82	23.52	23.13

When compared with values obtained for other environmental matrices around the world (table 5), the activity concentrations of ^{226}Ra and ^{232}Th in bituminous soil and bitumen samples compare very well with values obtained for sediment and soil samples from other locations around the world but much lower than values obtained in rock samples. The activity concentrations of ^{40}K in bituminous soil and bitumen show significant deviation from values obtained for other environmental samples. As shown in table 5, the activity concentrations of ^{226}Ra is higher than values obtained in sediment samples from Coruh River (Turkey) [26], Hunza

River (Pakistan)[27] and Kutubdia Island (Bangladesh) [28] but lower than those obtained in Wei River (China)[29] and Oguta Lake (Nigeria) [30]. Rock samples from Eastern desert (Egypt) [31] show lower concentrations of ^{226}Ra and ^{232}Th than bituminous soil from the study area while rocks from India [32], Brazil [33] and Nigeria [34] possess higher concentrations of the ^{226}Ra and ^{232}Th than bituminous soil except phosphate rock from Nigeria with lower values of ^{226}Ra. When compared with soil samples from other locations, the value of ^{226}Ra in bituminous soil is lower than activity concentrations obtained in Kucuk Menderes, Dikili, Rize (Turkey) [35-37] and Jordan[38] but higher than those from Tripoli (Libya) [39] and Niger Delta (Nigeria) [40]. For ^{232}Th, the activity concentrations obtained in bituminous soil is lower than values obtained in sediments of Hunza [27] and Wei Rivers [29], Kutubdia Island [28] and Oguta Lake [30] but higher than mean value from Coruh River [26]. In comparison with values obtained for soil samples from other locations, bituminous soil in this study presents lower concentration of ^{232}Th than soil of Kucuk Menderes [35], Rize [37], Jordan [38] and Niger Delta [40] but higher than those from Dikili (Turkey) [36] and Tripoli (Libya) [39]. ^{40}K in bituminous soil from tar-sand belt is lower than values obtained for sediment, rock and soil samples from other locations considered in this study.

Table 5. Comparison of the activity concentration of 226Ra, 232Th and 40K bituminous soil and viscous bitumen with values for other matrices from different countries.

Location	Sample type	Activity concentration (Bq kg^{-1})		
		^{40}K	^{226}Ra (^{238}U)	^{232}Th
Turkey (Coruh River)[26]	Sediment	510.2 ± 157.6	11.4 ± 3,4	18.3 ± 5.5
Pakistan (Hunza River)[27]	Sediment	173.96	11.65	21.37
Bangladesh (Kutubdia Island)[28]	Sediment	475.51	15.39	38.35
China (Wei River)[29]	Sediment	833.3	33.1	21.8
Nigeria (Oguta Lake)[30]	Sediment	1023 ± 474	47.89 ± 18.67	55.37 ± 32.74
Egypt (Eastern desert)[31]	Rock	405.7 ± 29.5	15.64 ± 1.14	14.46 ± 1.08
India (Ramanagara and Tumkur)[32]	Rock	869.29 ± 3.78	41.08 ± 2.12	86.26 ± 2.94
Brazil[33]	Rock	1648	31	73
Nigeria[34]	Phosphate rock	323.7	BDL	616.5
Turkey (Kucuk Menderes)[35]	Soil	744.8	48.4	20.5
Turkey (Dikili)[36]	Soil	579.2	28.7	17.6
Turkey (Rize)[37]	Soil	771.57	85.75	51.08
Jordan[38]	Soil	442.6	52.9	24.0
Libya (Tripoli)[39]	Soil	270	10.5	9.5
Nigeria (Niger Delta)[40]	Soil	210 ± 49	18 ± 3.4	22 ± 4.4
Nigeria (Tar-sand belt)[This study]	Soil	46.48	24.13	20.11
Nigeria (Tar-sand belt)[This study]	Bitumen	19.06	16.63	15.31

BDL=below detection limit

All the values of absorbed dose rates obtained are far lower than the world average value of 60 nGy h^{-1} reported in UNSCEAR [1] for areas with normal background radiation level. The study area could therefore be identified as one of the few locations in the world with very low background radiation levels. In normal background areas, the average worldwide outdoor effective dose from terrestrial radionuclides is 70 μSvy^{-1} [19]. All the annual outdoor effective doses (mean, minimum and maximum) obtained in this study are much lower than the worldwide average value for normal background dose received from radionuclides of terrestrial origin. Figure 2 shows the graphical distribution of the annual effective doses in the study area.

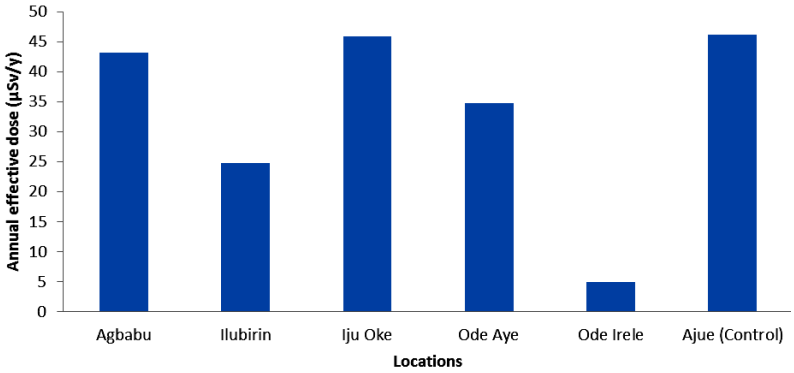

Figure 2. Distribution of annual effective dose (μSv y^{-1}) in the study area.

The average values of the radium equivalent activities vary as bitumen < bituminous soil < normal soil. The radium equivalent values obtained in this study are much lower than the recommended limit of 370 Bq kg^{-1} for building materials and far lower than 740Bq/kg recommended for materials used for road construction [6,19,25,41]. This implies that the bituminous soil and the bitumen samples could used for building and road constructions without fear of excessive exposure to gamma radiation. The results also show values of external and internal hazard indices lower than unity, which is the upper limit for both external and internal hazard indices recommended by European Commission [42] as the maximum limit for material to be used for construction purposes. The gamma representative indices obtained in all the locations are lower than unity indicating that there are little or no radiological concerns as far as utilizing the materials for road construction and as components of building materials. These results are consistent with the results of an earlier research carried out by Isinkaye [8] in one of the locations considered in this study.

CONCLUSION

The natural radioactivity levels of bitumen-impregnated soil and viscous bitumen samples collected from the tar-sand belt of southwest Nigeria have been determined in this study. The results show that the activity content of soil and viscous bitumen from tar-sand belt are lower than those in soils of non-bituminous area. The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th for the study area are much more lower than their average crustal values obtained for areas with normal background radiations around the world. The results of this study show that the tar-sand belt of southwest Nigeria can be categorized as area with low level of natural background radiation.

***Conflicts of interest*:** *Declared none.*

REFERENCES

1. UNSCEAR (2008) Sources and Effects of Ionization Radiation. United Nations Scientific Committee on the Effects of Atomic Radiation. Report to the General Assembly with Scientific Annexes. Volume II. Scientific Annexes C, D and E. New York
2. Mikhail B (2008) Exposure from environmental radioactivity: International Safety Standards. *Applied Radiation and Isotopes,* ***66****: 1546-1549*.
3. Miah FK, Roy S Touhiduzzaman M, Alam B (1998) Distribution of radionuclides in soil samples in and around Dhaka City. *Applied Radiation and Isotopes,* ***49****: 133-137*.
4. UNSCEAR (2000) Sources, Effects and Risks of Ionizing Radiation, Ney York: United Nations. Annex A and B
5. Arogunjo MA, Farai IP, Fuwape IA (2004) Impact of oil and gas industry to the natural radioactivity distribution in the Delta region of Nigeria. *Nigeria Journal of Physics,* ***16****: 131-136*.
6. Maphoto KP (2004) Determination of natural radioactivity concentrations in soil: a comparative study of windows and full spectrum analysis. Unpublished PhD Thesis: The University of the Western Cape
7. Einsenbud M (1963) Environmental Radioactivity: McGraw -Hill Book Company, New York, *pp 135-163*.
8. Isinkaye MO (2007) Radiometric assessment of natural radioactivity levels of bituminous soil in Agbabu, south-west Nigeria. *Radiation Measurements,* ***43****: 125-128*.

9. BP (2007) Bitumen: Bringing Technology to the Surface. BP Australia Pty Ltd
10. Arotupin DJ, Olalemi AS, Ijabamido DM (2013) Evaluation of bacteria and physicochemical qualities of tar sand soil from Gbelejuloda, Ondo State, Nigeria. *FUTA Journal of Research in Sciences,* ***1****: 118-122*.
11. Adegoke OS, Ibe EC. (1982) The tar sand and heavy crude resources of Nigeria. Proc. 2nd International Conference on Heavy crude and tar sands. Caracas, Venezuela, 7-17 February, pp. 280-285
12. MMSD (2010) Tarsands and Bitumen Exploration Opportunities in Nigeria. E Report of Ministry of Mines and Steel Development. Available at: www.mmsd.gov.ng/ Downloads/Tarsand%20&%20Bitumen.pdf
13. Abraham H. (1938) Asphalts and Allied Substances: Their Occurrence, Modes of Production, Uses in the Arts, and Methods of Testing (4th ed). New York: D. Van Nostrand Co. Inc.
14. Bohdan K, Karel Z, Jorges S, Jan J *et al.* (1999). Bitumen in the late variscan hydrothermal vein-type uranium deposit in Czech Republic: Sources, radiation-induced alteration, and relation to mineralization. *Economic Geology*, ***94****: 1093-1114*.
15. Alexandre P and Kyser TK (2006) Geochemistry of Uraniferous Bitumen in the Southwest Athabasca Basin, Saskatchewan, Canada. *Economic Geology*, ***101****: 1605 – 1612*.
16. Hasan MM, Ali, MI, Paul IO, Haydar MA, Islam, SMA (2013) Measurement of Natural Radioactivity in Coal, Soil and Water Samples Collected from Barapukura Coal Mine in Dinajpur District of Bangladesh. *Journal Nuclear and Particle Physics*, ***3 (4)****: 63-71*.
17. Roessler, CE, Smith ZA, Bolch WE, Prince RJ (1979) Uranium and radium-226 in Florida phosphate materials. *Health Physics,* ***37 (3)****: 269-277*.
18. Isinkaye, MO (2013) Natural radioactivity levels and the radiological health implications of tailing enriched soil and sediment samples around two mining sites in Southwest Nigeria. *Radiation Protection and Environment*, ***36(3)****: 122-127*.
19. Faisal BMR, Haydar MA, Ali MI, Paul D, Majumder RK, Uddin MJ (2014) Assessment of Natural Radioactivity and Associated Radiation Hazards in Topsoil of Savar Industrial Area, Dhaka, Bangladesh. *Journal Nuclear and Particle Physics,* ***4****: 129-136*.
20. Abd El-Hadi, E, Abdullah IAE, Abd El-Bast A, Shaban H, Imran IS (2012) Natural radioactivity of environmental samples and their impact on the population at Assalamia Alhomira Area in Yemen. *Geosciences* ***2(3)****: 125-132*.
21. Kohshi C, Takao I, Hideo V (2001) Terrestrial gamma radiation in Koshi Protectorate, Japan. *Journal of Health Science*, ***47 (4)****: 362-372*.
22. Beretka J and Matthew PJ (1985) Natural radioactivity of Australian building materials, industrial wastes and by-products. *Health Physics,* ***48****: 89-95*.
23. Iqbal M, Tufail M, Mirza SM (2000) Measurement of natural radioactivity in marbles found in Pakistan using NaI(Tl) gamma ray spectrometer. *Journal of Environmental Radioactivity,* ***51 (2)****: 255-265*.
24. Jibiri NN, Alausa SK, Farai IP (2009) Radiological hazard indices due to activity concentration of natural radionuclides in farm soils from two high background radiation areas in Nigeria. *Int J Low Radiation,* ***6 (2)****: 79-95*.
25. OECD (1979) Exposure to radiation from the natural radioactivity in building materials. Report by a Group of Experts of the OECD. Nuclear Energy Agency, Paris, France.
26. Kobya Y, Taşkın H, Yeşilkanat CM, Varinlioğlu A, Korcak S (2015) Natural and artificial radioactivity assessment of dam lakes sediments in Çoruh River, Turkey. *Journal of Radioanalytical and Nuclear Chemistry,* ***303 (1)****: 287-295*.
27. Qureshi AA, Tariq S, Din KU, Manzoor S, Calligaris C, Waheed A (2014) Evaluation of excessive lifetime cancer risk due to natural radioactivity in the rivers sediments of Northern Pakistan. *Journal of Radiation Research and Applied Sciences,* ***7 (4)****: 438-447*.
28. Rashed-Nizam QM, Tafader MK, Zafar M, Rahman MM, Bhuian AKMSI, Khan RA, Kamal M, Chowdhury MI, Alam MN (2016) Radiological risk analysis of sediment from Kutubdia Island, Bangladesh due to natural and anthropogenic radionuclides. *Int J Radiat Res,* ***14(4)****: 373-377*.
29. Lu X., Zhang X, Wang F (2008) Natural radioactivity in sediment of Wei River, China. *Environmental Geology,* ***53 (7)****: 1475-1481*.
30. Isinkaye MO and Emelue HU (2015) Natural radioactivity measurements and evaluation of radiological hazards in sediment of Oguta Lake, South East Nigeria. *Journal of Radiation Research and Applied Sciences,* ***8 (3)****: 459-469*.
31. Harb S, El-Kamel AH, El-Mageed AA, Abbady A, Wafaa R (2008) Concentration of U-238, U-235, Ra-226, Th-232 and K-40 for some granite samples in eastern desert of Egypt. In Proceedings of the 3rd Environmental Physics Conference*, pp. 19-23*.
32. Rangaswamy DR, Srilatha MC, Ningappa C, Srinivasa E, Sannappa J (2016) Measurement of natural radioactivity and radiation hazards assessment in rock samples of Ramanagara and Tumkur districts, Karnataka, India. *Environmental Earth Sciences,* ***75 (5)****: 1-11*.
33. Anjos RM, Veiga R, Soares T, Santos AMA, Aguiar JG, Frascá MHBO, Brage JAP, Uzêda, D, Mangia L, Facure A, Mosquera B (2005) Natural radionuclide distribution in Brazilian commercial granites. *Radiation Measurements,* ***39 (3)****: 245-253*.
34. Okeji MC, Agwu KK, Idigo FU (2012) Natural radioactivity in cultivated land in the vicinity of a phosphate fertilizer plant in Nigeria. *Radiation Physics and Chemistry,* 81 (12): 823-1826.
35. Aközcan S (2014) Natural and artificial radioactivity levels and hazards of soils in the Kücük Menderes Basin, Turkey. *Environmental Earth Sciences,* ***71 (10)****: 4611-4614*.
36. Tabar E, Kumru MN, Ichedef M, Saç MM (2013) Radioactivity level and the measurement of soil gas radon concentration in Dikili geothermal area, Turkey. *Int J Radiat Res,* ***11 (4)****: 253-261*.
37. Dizman S, Görür FK, Keser R (2016) Determination of radioactivity levels of soil samples and the excess of lifetime cancer risk in Rize province, Turkey. *Int J Radiat Res,* ***14(3)****: 237-244*.

38. Ahmad N, Hussein AJA (1998) Radiation doses in Jordanian dwellings due to natural radioactivity in construction materials and soil. *Journal of Environmental Radioactivity*, ***41 (2)****: 127-136*.
39. Shenber MA (1997) Measurement of natural radioactivity levels in soil in Tripoli. *Applied Radiation and Isotopes*, ***48 (1)****: 147-148*.
40. Agbalagba EO and Onoja RA (2011) Evaluation of natural radioactivity in soil, sediment and water samples of Niger Delta (Biseni) flood plain lakes, Nigeria. *Journal of Environmental Radioactivity*, ***102 (7)****: 667-671*.
41. UNSCEAR (1993) United Nations Scientific Committee on the Effects and Risk of Ionizing Radiation, Report to the General Assembly, with Scientific Annexes, United Nations, New York.
42. EC (1999) Radiological protection principles concerning the natural radioactivity of building materials. Radiation Protection 112, Directorate-General, Environment, Nuclear Safety and Civil Protection, European Commission, Luxembourg.