Determination of Elemental Concentration of Natural Radionuclide in Soils of Industrial Communities, South-South Nigeria

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***Abstract*—** The elemental concentration of natural radionuclides in soil of some communities in South-South Nigeria with history of oil spillage, gas flaring, oil bunkering and operation of illegal artisanal oil refining activities was determined and measured with gamma ray spectroscopy. The activity concentration values of radionuclides in soil were converted to elemental concentration values. The result showed that the mean value of elemental concentrations in the soil samples ranged from 1.44±0.34 to 2.58±0.26ppm for uranium, 5.60±0.81 to 8.33±1.16ppm for thorium and 0.35±0.03 to 1.54±0.06% for potassium. These mean elemental concentration values are respectively lower than the worldwide standard of 2.7ppm, 11ppm and 1.3ppm in the soil of the five sampled communities except for the potassium value in the soil at Bunu-Tai that was higher than the permissible standard by 0.24%. The Th/U elemental ratio in the soil samples at Eleme and Bunu-Tai communities are respectively 4.68 and 4.84 and are over 1.6 times higher than the theoretical standard value of 3.0 for normal continental crust indicating an enrichment of thorium and depletion of uranium radionuclides in these communities. The Th/U elemental ratio in the soil samples at Ban-Ogoi, Bodo and Giokoo communities are respectively over 1.4 times lower than the 3.0 standard for normal continental crust showing a depletion of thorium and enrichment of uranium in those communities. Relative depletion/enrichment of natural radionuclides occurred in soils of the sampled communities arising from alteration of natural processes by anthropogenic/metamorphic activities.

***Keywords*—** Artisanal oil Refining, Elemental Concentration, Enrichment/Depletion, Oil Bunkering, Soil.

I. INTRODUCTION

The earth crust contains naturally occurring radioisotopes such as the radionuclides from the ^{238}U and ^{232}Th series/products, and ^{40}K at trace levels in all ground formations. The concentrations of all these elements depend on the geology of a local environment as well as other natural and anthropogenic processes like oil and gas exploration and production industries, operation of illegal artisanal oil refining/oil bunkering activities, uncontrolled discharge of industrial waste into the environment and deposition of particulate matter from gaseous emission from gas flare stacks. Aside from elevation of the radionuclide levels and the terrestrial radiation dose in the soil and rocks, these activities from various sources have inevitably led to alterations in the quality of the soil since it is considered contaminated when chemicals are present or other alterations have been made to its natural environment (Gowd et. al., 2010). The specific levels of terrestrial environmental radiation are related to the geological composition of each lithologically separated area, and the content of the rock from which the soils originate in each area in the radioactive elements of thorium (Th), uranium (U) and potassium (K) (Tzortzis and Tsertos, 2004). The International Atomic Energy Agency (2003), Eisenbud (1987), and Eisenbud and Gesell (1997) reported that the average concentration of uranium, thorium and potassium in the earth crust respectively is in the range of 2-3ppm, 8-12ppm, and from about 0.1% for limestone through 1% for sandstones to as much as 3.5% for some granite.

The elemental abundance of the original Th, U, and K concentrations in rocks and soils may vary because of alteration of metamorphic processes (Verodoya et. al., 2001) and the elemental abundance of Th/U, K/U and K/Th ratios may allow us to study the enrichment/depletion processes as a result of the complex metamorphic history, environmental degradation/pollution history, alteration and/or weathering that affected the investigating rocks/soil (Chiozzi et. al., 2002). Thus, the Th/U, K/U and K/Th ratios provides an indication whether relative depletion or enrichment of radioisotopes had occurred in an environment. Findings by Tzortzis and Tsertos (2004) and Al-Hamarneh and Awadaliah (2009) revealed that the theoretical value of elemental ratios of Th/U for normal continental crust is about 3.0. This study aimed to determine the elemental concentration of natural radionuclides in the soil of an industrial area in the south-south Nigeria with history of illegal activities of oil bunkering, artisanal oil refining of crude oil and gas as well as gaseous emission of particulate matter from

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such operations. Knowledge of the elemental concentration of naturally occurring radionuclides in the soil of the study area would provide a better understanding on the spatial distribution of radionuclides in order to ascertain whether there has been relative enrichment or depletion of radionuclides in the soils.

II. THE STUDY AREA

The study areas are five communities comprising Eleme, Bunu-Tai, Ban-Ogoi, Bodo and Giokoo. Eleme lies within Latitude 04º46'37.6"N and Longitude 007º07'51.0"E, Bunu-Tai lies within Latitude 04º45'41.0"N and Longitude 007º14'29.4"E, Ban-Ogoi lies within Latitude 04º36'43.4''N and Longitude 007º06'41.0''E, Bodo lies within Latitude 04º44'46.2''N and Longitude 007º06'32.1''E while Giokoo lies within Latitude 04º37'41.0"N and Longitude 007º16'21.1"E. The five communities respectively belong to Eleme Local Government Area (LGA), Tai LGA and Gokana LGA of Rivers State, Nigeria (Figure 1). The general topography is relatively flat lying and consists of terrestrial and marine environment. Due to the crude oil spills that polluted the land, the terrestrial environment has patchy regenerating vegetation which consisted mostly of scanty and secondary type residual grasses. Each of the five communities is within 1,000m radius of the spilled sites, gas flaring at flow stations, oil bunkering and illegal artisanal oil refining activities. The soils are dark brown loamy soil to clay loam soil (Avwiri and Agbalagba, 2014.

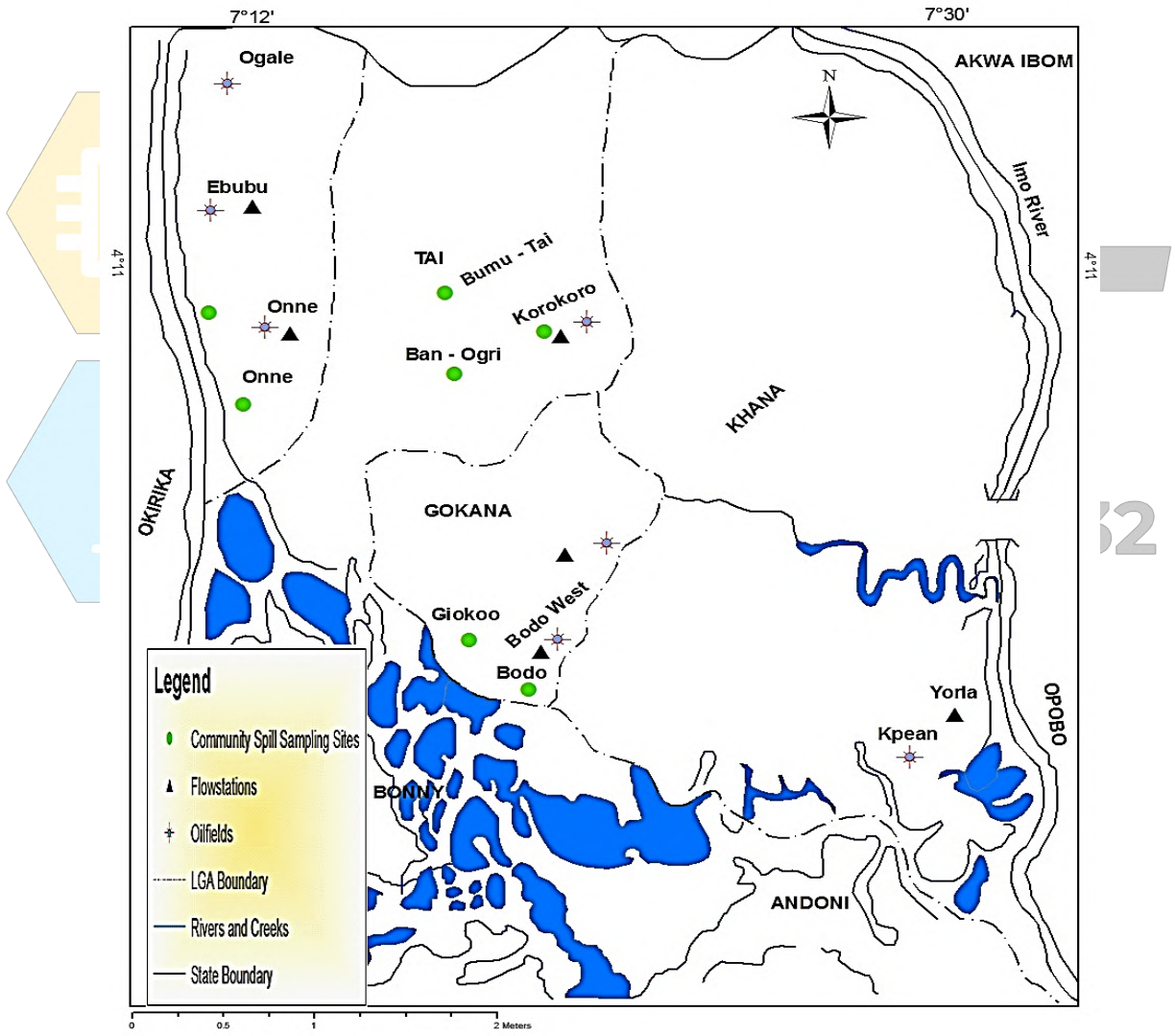

Figure 1: *Map of the Study Area*

Regional Geology

The study area falls within the Niger Delta region which is made up of thick clastic sedimentary sequence with age ranging from Eocene to Recent and it sits astride the Niger flood plains, which overlies the Benin formation that is often called the coastal plain sand (Tattam, 1943). This formation consists predominantly of coarse grained sandy soils with few shale intercalations. The

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unconsolidated, highly porous sands of the Benin formation is a fresh water bearing sands zone (Amajor, 1991), and all aquifers in this region are located within this lithio-stratigraphic unit. The Benin formation comprises multiple layers of clay, clay conglomerates, peat and/or lignite all of variable thickness and texture and covered by overburden soil (Short and Stauble, 1967).

III. MATERIALS AND METHOD

Sample Collection and Preparation

The sampling strategy adopted was the purposive and stratified sampling methods, and samples were collected according to internationally established experience (ASTM, 1983, 1986; IAEA, 2004). The sites were split into sampling areas and were divided into cells of 50m by 50m grids. The grid blocks were assigned numbers, where a number generator such as N identical cards was used to select the grid points at which samples were collected within defined boundaries of the area concerned. Five cores were drilled in a zigzag pattern (randomly) within each cell and samples were collected from the cores within a 10-foot radius of the centre point for the sample. The samples so collected at different points randomly were mixed together thoroughly to give a composite sample. Each sampling point was selected independent of the location of all other sampling points such that all locations within the area of study had equal chance of being selected.

Five samples of soil were collected from the five communities. Two samples each of soil were randomly collected from Eleme, Bunu-Tai, Ban-Ogoi, Bodo and Giokoo communities across the grids and were thoroughly mixed together to get a composite sample. The site of soil collection have close proximity with the oil spilled sites, flow stations flaring gases, and areas of oil bunkering and illegal artisanal refining activities. Three samples of soil were also collected from areas without history of oil spillage, gas flaring; oil bunkering and artisanal oil refining activities located about 57km away from the sampling communities which serves as control samples. The soil samples were collected with soil auger. The soil auger was cleaned with acid, detergent and rinsed with tap water before it was used to drill to a depth of 20cm. Avwiri and Agbalagba (2014) recommended that sampling for the average activity concentration in soil be taken in the top 20cm as this is the acceptable international compromise arising from alternate measures that are often based on deposition per unit area assuming atmospheric fallout. For each site, soil samples of about 2kg (wet weight) were collected and put in labeled vacuum black plastic bag directly after collection to prevent them from atmospheric humidity. The samples were transported to the laboratory where stones and organic materials were removed then air dried for room temperature to constant weight and sun-dry at 25±2^{o}C to remove the moisture content. The samples were further oven dried at a temperature of 105^{o}C for 1-2 hours to remove any remaining moisture content. The removal of the moisture took care of self absorption in each of the sample. The dried samples were pulverized into fine grains so as to increase the total emission area and then were passed through a sieve mesh of 150µm so that clay and mineral particle may homogenize. Thereafter, a sample of 250±0.05% was weighed and sealed with adhesive tape in air tight plastic containers of diameter 6.5cm that could seat in the detector head. The sealing with adhesive tape was to prevent the escape of the gaseous radionuclides in the samples. The samples were left for 4 weeks in order to allow for secular equilibrium between the long-lived parent radionuclide and their short-lived daughter radionuclides (^{226}Ra up to ^{210}Pb and ^{228}Th up to ^{208}Pb) in the ^{238}U and ^{232}Th decay series before counting.

Sample Analysis

The activity of the natural radiouclide of the prepared soil samples were counted at the Centre for Energy Research and Training, Zaria with gamma ray spectrometer detector for 36,000 seconds to produce strong peaks at gamma emmiting energies at 1,460Kev. The detector is a Thallium activated Canberra 7.6cm x 7.6cm sodium iodide [NaI(TI)] detector (model 803 series) coupled to a Canberra series 10 plus Multichannel-Analyzer through an ORTEC 456 amplifier base. The detector, enclosed in a 10 cm thick lead shielding lined with 1.5mm thick cadmium and 0.8mm thick copper, was connected to a computer program Maestro window that matched gamma energies to a library of possible isotopes. The lead shield was to reduce environmental background radiation. The ^{238}U and ^{232}Th activities were determined indirectly through the activities of their daughter products. The activities of ^{238}U was determined from the average activities of ^{214}Pb at 352kev and ^{214}Bi at 609Kev while that of ^{232}Th was determined from average activities of the decay products of ^{208}Ti at 583kev and ^{228}Ac at 911Kev. The activity of ^{238}U in the samples was calculated after subtracting decay correction. The background spectra measured under the same conditions for both the standard and sample measurements were used to correct the calculated sample activity concentrations. The net area under each photopeak, after background corrections, was used to calculate the activity concentration (Cs) of

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each radionuclide in the soil in accordance with Arogunjo *et. al*. (2005):

$$Cs\ (Bq/kg) = \frac{C_n}{\varepsilon P_\gamma M_s} \quad \ldots\ldots\ldots\ldots (1)$$

Where: Cs is the activity concentration of radionuclide in the sample, C_n is the count rate under each photo peak due to each radionuclide, ε is the detector efficiency for the specific γ-ray, P_γ is the absolute transition probability of the specific γ-ray, M_s is the mass of the sample (kg).

Correlation between ^{238}U and ^{232}Th, ^{238}U and ^{40}K, and ^{232}Th and ^{40}K

The elemental concentrations of natural radionuclides in soil was determined by converting the activity concentrations of ^{238}U (Bq/kg), ^{232}Th (Bq/kg) and ^{40}K (Bq/kg) (Table 1) to the elemental concentrations of Uranium (eU) in ppm and Thorium (eTh) in ppm and the percent of Potassium-40 (%K) using the conversion factors recommended by the IAEA Technical Report No. 1363 as follows:

1ppm eU = 12.35Bq/Kg of ^{238}U …… (2)
1ppm eTh = 4.06Bq/kg of ^{232}Th …… (3)
1%K = 313Bq/kg of ^{40}K …… (4)

IV. RESULTS AND DISCUSSION

The mean value of elemental concentrations in the soil samples are found to range from 1.44±0.34 to 2.58±0.26ppm for uranium, 5.60±0.81 to 8.33±1.16ppm for thorium and 0.35±0.03 to 1.54±0.06% for potassium. While the revised values of the UNSCEAR (2008) permissible limits are 2.7ppm for uranium, 11ppm for thorium and 1.3% for potassium. These mean values are derived by transforming the corresponding worldwide average activity concentrations of 33Bq/kg, 45Bq/kg and 420Bq/kg (UNSCEAR, 2008) for ^{238}U, ^{232}Th and ^{40}K radionuclides into uranium, thorium and potassium elemental concentrations respectively, using equations 2, 3 and 4.The result (Table 2) showed that the mean values of the elemental concentration of uranium, thorium and potassium in the soil of the five sampled communities are respectively lower than the revised (UNSCEAR, 2008) standard of 2.7ppm, 11ppm and 1.3ppm except for the potassium value at Bunu-Tai soil which is higher than the permissible standard by 0.24%.

The relationship between uranium and thorium can be considered in terms of the Th/U ratio (Table 2 and Figure 1). The obtained result of the average elemental ratio for Th/U for the soil samples in the study area are respectively 4.68 and 4.84 at Eleme and Bunu-Tai communities. These values are over 1.6 times higher than the theoretical value of 3.0 for normal continental crust. Therefore, there is an enrichment of thorium and depletion of uranium radionuclides in these communities (Figure 1). Again, the Th/U elemental ratio for the soil samples at Ban-Ogoi, Bodo and Giokoo communities are respectively 2.17, 2.44 and 2.82. These values are over 1.4 times lower than the 3.0 standard for normal continental crust; hence there is depletion of thorium and enrichment of uranium in those communities. Tzortzis and Tsertos (2004) and Al-Hamarneh and Awadaliah (2009) asserts that a high or low value of the Th/U ratio is an indication of a depletion of uranium or an enrichment of thorium due to alteration of natural processes in the area. The Th/U elemental ratio of the three community soil samples are over 1.6 times higher than the theoretical value for normal continental crust of 3.0 (Tzortzis and Tsertos, 2004; Al-Hamarneh and Awadaliah, 2009). It is also over 1.4 times lower than the theoretical value of 3.0 in the other 3 community soils at Ban-Ogoi, Bodo and Giokoo. However, the Th/U ratio in this study is found to be higher than the 2.33±0.02 and 1.85±0.001 for soil and sediment of Mini-Okoro/Oginigba creek at PortHarcourt obtained by Avwiri et. al. (2014) and the 2.04±0.35 obtained by Tzortzis and Tsertos (2004) for elemental concentration of surface soil in Cyprus. The Th/U elemental ratio of this study is also higher than the 2.93±1.46 and 2.88±1.34 values for soils stemming from the limestone and basalt plateaus respectively that were obtained by Al-Hamarneh and Awadallah (2009) in their work on soil radioactivity levels and radiation hazard assessment in the highlands of northern Jordan.

Table 1: *Mean Activity of Radionuclides in the community's Soil Samples*

S/No	Sample Name	Specific Activity (Bqkg^{-1})		
		^{238}U	^{232}Th	^{40}K
1	SS_{Eleme}	17.77±4.2	27.37±5.4	208.20±10.6
2	$SS_{Bunu\text{-}Tai}$	21.24±2.2	33.82±4.7	483.15±18.2
3	$SS_{Ban\text{-}Ogoi}$	31.84±3.2	22.75±3.3	110.44±9.6
4	SS_{Bodo}	30.29±3.7	24.25±2.4	248.90±15.4
5	SS_{Giokoo}	29.51±3.3	27.42±2.1	210.20±10.5
UNSCEAR (2008) Standard		**33**	**45**	**420**

Table 2: *Mean Elemental Concentration of ^{238}U, ^{232}Th (ppm) and ^{40}K (%) in Soil Samples with their Ratios*

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S/No	Community/Sample Name	Elemental concentration			Elemental concentration Ratios		
		^{238}U (ppm)	^{232}Th(ppm)	^{40}K (%)	Th/U	K/U	K/Th
1	Eleme (SS_{Eleme})	1.44±0.34	6.74±1.33	0.67±0.03	**4.68**	0.47	0.09
2	Bunu-Tai ($SS_{Bunu-Tai}$)	1.72±0.18	8.33±1.16	1.54±0.06	**4.84**	0.89	0.18
3	Ban-Ogoi ($SS_{Ban-Ogoi}$)	2.58±0.26	5.60±0.81	0.35±0.03	2.17	0.14	0.06
4	Bodo (SS_{Bodo})	2.45±0.29	5.97±0.59	0.79±0.05	2.44	0.33	0.13
5	Giokoo (SS_{Giokoo})	2.39±0.27	6.75±0.52	0.67±0.03	2.82	0.28	0.09
UNSCEAR (2008), Tzortzis and Tsertos (2004), Al-Hamarneh and Awadallah (2009), Avwiri et. al, (2014) Standard		**2.7**	**11**	**1.3**	**3.0**		

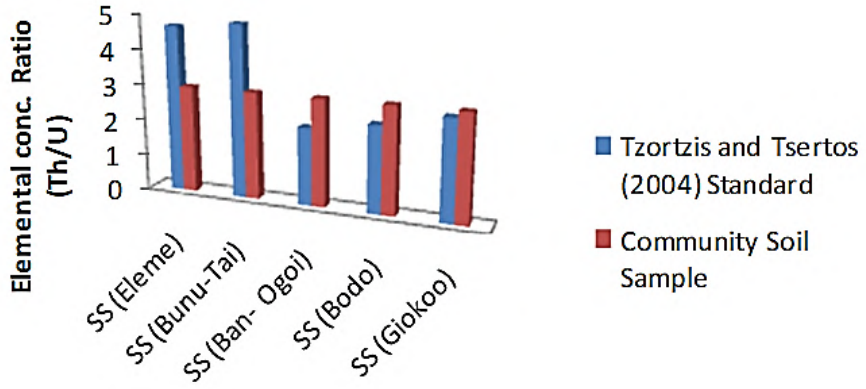

Figure 1: *Th/U Elemental ratio of the community soils compared to the standard*

V. CONCLUSION

The activity concentration of natural radionuclides (^{238}U, ^{232}Th and ^{40}K) in the soil samples in an environment with history of oil spillage, illegal artisanal oil refining, oil bunkering activities and gas flaring have been measured by gamma ray spectroscopy. The result showed that the activity concentrations of the three radionuclides in soil of the five sampled communities are within the permissible limits. The study finds that there was enrichment of thorium radionuclides in the soils at Eleme and Bunu-Tai, but a depletion of thorium in the soils of Ban-Ogoi, Bodo and Giokoo communities. The elemental concentration of thorium radionuclide is enriched by a factor of 1.68 and 1.84 respectively at Eleme and Bunu-Tai communities above the permissible theoretical value of 3.0 for normal continental crust. This implies that the topsoil of the continental crust in these communities have been enriched with thorium by 56% and 61% respectively. There is also a depletion of thorium or enrichment of uranium in the soils at Ban-Ogoi, Bodo and Giokoo communities by a factor of 0.83, 0.56 and 0.18 respectively below the permissible standard of 3.0. This means that concentration of thorium radionuclides in the soil of these 3 communities have been depleted by 28%, 17% and 6% respectively. Thus the elemental concentration of uranium is higher in the soil of those three communities. There was therefore relative depletion/enrichment of natural radionuclides in soils of the five sampled communities arising from alteration of natural processes in the environment by anthropogenic/metamorphic activities.

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ISSN: 2582-6832

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