Evaluation of Radionuclides Concentration in Soil and Sediment Samples from Warri Refinery and Petrochemical Company (WRPC) and Environs In Delta State Nigeria.

[1]Edomi .O. and [1]Esi, O. E.

[1]Dept of Laboratory Science .Tech. (Physic Unit), Delta State School, Burutu, Delta State, Nigeria

E-Mail: ovieedomi2@gmail.com 07034645296

ABSTRACT

Evaluation of radionuclides concentration in soil and sediment samples from Warri refinery and petrochemical company (WRPC) and environs in Delta State, Nigeria have been conducted using NaI (TL) spectrometer with the purpose of proving a baseline data on the radiation level and the distribution of activity concentration in this region were a lot of oil and gas activities are taking place. The activity concentration of ^{40}K in soil and sediment varies from 155.22±32.27 to 420.47±1.37 and 425.48±8.43 to 762.09±12.27 (Bq/kg), with an average values of 273.83±11.98 and 573.86±9.14 (Bq/kg), that of ^{238}U ranges 13.19±5.12 to 37.77±2.37 and 36.84±2.26 to 71.42±3.20 (Bq/kg) with a mean values of 26.24±3.21 and 46.92±2.28 (Bq/kg), while that of ^{232}Th varies 16.98±2.57 to 36.13±2.53 and 28.42±2.09 to 40.34±1.17 (Bq/kg) with a mean values of 27.79±3.53 and 36.64±2.21 (Bq/kg) respectively. The mean value results obtained for radionuclides were compared with previous literature values obtained in other environments and also with the world wide average, the results shows conformity except the average value results for sediment samples which revealed a high level deviation of activity concentration in the study areas compared with worldwide recommended average values. And this is attributed to oil and gas activities, and also Uranium is moderately been soluble in water. The calculate mean values for radiological hazard parameters in soil and sediment samples are lower than their respective allowable international average values except excess lifetime cancer risk which is higher than international stipulations for both soil and sediment samples. The implication is that the study environment is been threatened radiologically and over exposure of individuals may have significant effect. However, gas flaring and other oil and gas activities in the region should be reduce to permissible allowable level.

Keywords: Soil, sediment, radionuclides, exposure, environment.

1.0 INTRODUCTION

There are several radionuclides substance found in our environment due to their spontaneous disintegration which result in emission of toxic gases that are and harmful to man and the entire ecosystem. Despite the dangerous effects of radiation to man, when properly harnessed are beneficial. Presently, the application of man-made radiation source in medicine and other disciplines can no longer be over emphasized.

Radionuclides are naturally present in air, water, soil, sediment, and even in human body due to food, injection, inhalation via the air, food, water, soil and sediment, (Innocent, (2011)). There is nowhere on planet earth that naturally occurring radioactive materials (NORMs) are not found (Avwiri, 2011). The geologic formation that contained crude oil deposit also constitutes NORMs. Large quantity of the crude oil (Petroleum) present in the earth's crust was formed at the site of Ancients Sea by the decay of Sea-Life. As a result of this, petroleum deposit often occurs in aquifers containing brine (salt-water). Radionuclides along with other dissolved in the brine precipitate (separate and settle) forming various waste such as mineral sealed inside pipes, sludge, contaminate equipments and produce water. Due to the extraction processes, the radionuclides are concentrated and are exposed to the surface environment which are contacted by man due to pollution of the areas as typified as TENORM (EPA, 2012).

The W.R.P.C sited in Uvwie L.G.A in Delta State, Nigeria was built and commissioned in 1978 with a planned to process 100,000 barrels of crude oil per day but was later de-bottlenecked to process 125, 000 barrels per day in 1987.The marketable products of the (WRPC) are premium motor spirit (PMS) (Petrol), Kerosene. Liquefied petroleum gas (LPG) and carbon black e.t.c. Over the years, Nigeria economy solely depends on the sales of these produce to her counterpart. This now served as a means of livelihood and income generation.

Due to the activities of the oil and gas, vis-à-vis the production processes has culminated in the release of harmful effluents and radioactive substances which defiles and pollute the aquatic life and the environment at large. Several researchers has discussed impact of

oil and gas activities on the physical environment owing to their area of interest, (Ikoku, 2000).

Previously existing literatures revealed that several studies has been carried out on activity concentration in soil, water and sediment in different locations, Avwiri *et al.* (2007), Edomi *et al.* (2019), Gyuk *et al.* (2017), Kolo, (2014), Esi *et al.* (2017), and Mokobia *et al.* (2017). However, studies have not been advanced to W.R.P.C and its environs, hence investigating the activity concentration in the study sites and its radiological health status is now necessary.

2.1 STUDY AREA

The study areas are Ekpan, Ubeji and Jeddo in Uvwie Local Government Area of Delta State, Nigeria. Delta State is Located in the Niger Delta region of Nigeria. The State shares borders with Edo State, Anambra, Bayelsa and Atlantic Ocean (Map of Study Area).

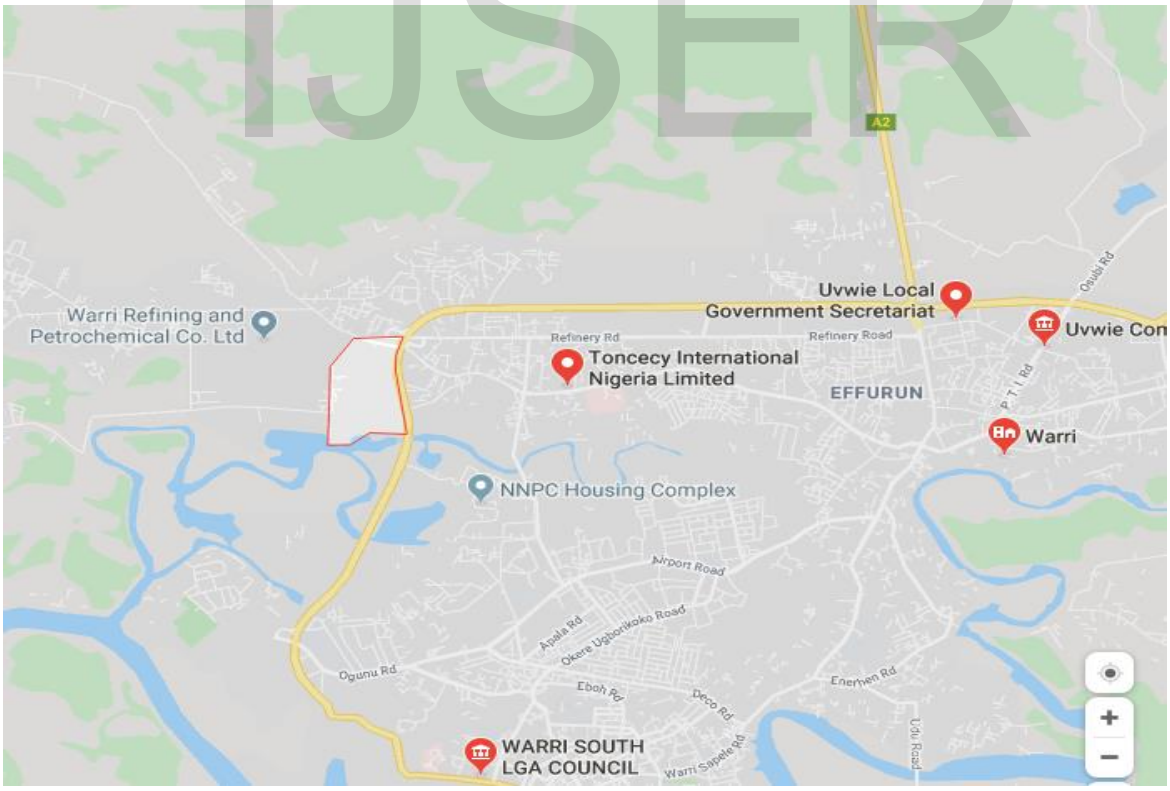

Figure 1: Map of Study Area

2.2 MATERIALS AND METHODS

2.3 SAMPLE COLLECTION AND PREPARATION

Nine soil and sediment samples were collected from three oil producing communities (Ekpan, Ubeji and Jeddo) within W.R.P.C in Uvwie Local Government of Delta State. Three each for soil and sediment samples were collected from each community. Samples were collected at the depth of 0.2m (20cm). At the point of sampling, the sampled soil and sediment were sealed in a black polythene bag and were properly labeled to avoid cross contamination before taking to laboratory for gamma counting. Samples were collected using standard methods, following the procedures of Murty and Karunakara (2008) and Baykara and Dogru (2009). The samples were oven dried at about 100^0c for about ten hours after removing stones, pebbles and plant debris, the soil and sediment were sequently crushed and passed through a fine mesh sieve of 100cm to homogenize them. Sealed soil and sediment samples were then sealed in 300ml plastic containers and stored for four weeks to allow Uranium to reach equilibrium with its progeny before subsequently determination of the specific activity concentration using, a thallium activated sodium iodide [(NaI(TI)] detector at the Centre for Energy Research and Development (CERD) of Obafemi Awolowo University Ife, Ile-Ife. They were further subjected to gamma spectroscopy to determine radionuclide concentration in the samples for the purpose of identifying radionuclides present in them.

2.4 NATURAL RADIOACTIVITY MEASUREMENT AND GAMMA COUNTING

Prior to gamma counting, the energy calibration was made by measuring standard sources of known radionuclides with defined energy within the range of 88.03 to 1274.51 KeV. The energy calibration above obtained was used to identify each radionuclide in the unknown source by matching their photo peak energy channel number with corresponding energies in nuclear data. Each sealed samples was then placed on the sodium iodide detector and counted for 3600 seconds. The gamma ray counting of sample was performed on a lower gamma spectrometer consisting of a detector (NaI)

connected to ORTEC456 amplifier. This was enclosed in a 100mm thick lead shield to screen off the environmental radiation. A sample-90 computer program used to match gamma energies to a library of possible isotopes was used to analyses the spectra. The background spectra obtained were used to correct the calculated sample activities. The radionuclides detected were calculated using the expression (IAEA; 1989) as:

$$(A)_S = \frac{(R_n)_S\, M_S}{\frac{(R_n)_{sd}\, M_{sd}}{(A)_{sd}}} = \frac{(R_n)_S\, M_S\, (A)_{sd}}{(R_n)_{sd}\, M_{sd}} \quad (1)$$

Where

$(A)_S$ is the activity concentration of radionuclide (Bq/kg)

$(R_n)_s$ is Net Peak Area of the radionuclide

M_s is the Mass of the sample (kg)

$(A)_{sd}$ is the activity concentration of the standard source (Bq/kg)

$(R_n)_{sd}$ is the net peak area of the radionuclide in the standard source sample.

$(M)_{sd}$ is the mass of standard (kg)

Calculation of Radiological Hazard Parameter

i. Radium Equivalent Activity Index

The radium equivalent index permit a single index or number to explain the gamma output from different constituents of Uranium, Thorium and Potassium in soil and sediment samples in the communities under study. Accordingly it is expressed (Esi et, al 2017) as:

$$Ra(eq) = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad (2)$$

Where C_{Ra}, C_{Th} and C_K are concentration of Uranium, Thorium and Potassium respectively.

ii. Absorbed Dose Rate (D)

The gamma radiation population doses of those living in the area is given as (Esi et, al 2018)

$$D = 0.462A_u + 0.621A_{Th} + 0.0417A_k \quad (3)$$

Where "D" is the absorb dose rate in $nGyh^{-1}$ and A_u, A_{Th} and A_k are concentration of Uranium, Thorium and Potassium respectively.

iii. Internal Hazard Indice (H_{in})

This describes the hazardous nature of radon and its progeny in our body respiratory organs, due to consumption of water and food particles into our body. The H_{in} is expressed (Edomi *et al*., 2019) as:

$$H_{in} = \frac{C_{Ra}}{185} + C_{Th}/259 + C_K/48104 \quad (3)$$

For the internal hazard to be less effective its should be less than unity.

iv. External Hazard Indice

The internal hazard indice measures the internal effect of radiation while this measures the external effect of radiation arising from radiation hazard in the environment. This effect is as a result of long lived radionuclides which have significant effects on human exposure. It is expressed as:

$$H_{ex} = C_{Ra}/370 + C_{Th}/259 + C_K/48103 \quad (4)$$

Where C_{Ra}, C_{Th}, and $C_{K,}$ are activity concentration of Uranium, Thorium and Potassium respectively. For the effect to be insignificant it must be less than one.

V. Annual Effective Dose Equivalent AEDE (Outdoor and Indoor)

The expression for the annual effective dose rate was given (Esi *et al.*, 2017) as:

AEDR = D ($Gyrh^{-1}$) x 8760 ($nGyrh^{-1}$) x 0.7 x $103/109$ x 0.2 x 10^{-3} (5)

EFFECTIVE DOSE = D x 1.2264 x 10^{-3}

EFFECTIVE DOSE ($m\int vyr^{-1}$) = D(mGyr/h) x 8760 nGyr/hr x 0.7 x $(103/109)$nGyr x 0.8 x 10^{-6} (6)

Where D is the dose rate (UNSCEAR, 2000) has recommended 0.7 Sv/Gy as the conservation coefficient from the absorbed dose in the air to effective dose are 0.2 $(5/24)$ and 0.8 $(19/24)$ respectively as the volumes for the indoor and outdoor occupancy factors.

VI. Excess Lifetime Cancer Risk (ELCR)

The equation for the Excess Lifetime Cancer Risk (ELCR) was expressed by (Taskin, 2009) as:

ELCR = AEDE x RF x DL (7)

Where AEDE is the annual effective dose rate, "DL" is the duration of Life estimated to be 54.5 years for Nigerian life time expectancy (W.H.O, 2015) and RF is the risk factor i.e Fatal cancer risk per sievert, for stochastic effects, KRP uses RF as 0.05 for the public.

Table 1: Specific Activities in Soil and Sediment Samples

S/N	Sample Code	Soil Sample Activity Concentration (Bq/kg)			Sediment Sample Activity Concentration (Bq/kg)		
		K-40	U-238	Th-232	K-40	U-238	Th-232
1	EKPSS A	372.04±9.23	24.77±2.10	22.74±8.20	591.48±1.40	37.13±3.18	28.42±2.09
2	EKPSS B	323.60±5.28	34.20±1.60	19.30±4.87	521.32±2.38	42.18±1.22	34.61±3.14
3	EKPSS C	420.47±1.37	37.77±2.37	36.13±2.53	680.43±22.58	53.45±1.09	43.39±1.31
4	UBESS A	163.85±6.31	20.32±4.08	32.17±1.38	425.48±8.43	71.42±3.20	38.75±0.34
5	UBESS B	227.21±7.46	32.11±2.24	16.98±2.57	681.42±1.25	45.66±2.14	35.62±3.30
6	UBESS C	306.69±13.14	27.17±4.71	27.52±2.37	762.09±12.27	44.83±3.12	34.92±4.20
7	JEDSS A	155.22±32.27	13.19±5.12	19.56±1.77	529.05±7.74	36.84±2.26	40.34±1.17
8	JEDSS B	253.01±19.51	28.43±3.36	26.12±2.09	487.06±8.12	48.45±1.21	39.27±2.18
9	JEDSS C	228.39±12.39	32.12±6.20	35.42±3.14	486.44±10.61	42.36±1.21	34.45±2.19

Table 2: Mean Specific activity Concentration of K-40, U-238 and Th-232 (Bq/Kg) of Soil and Sediment samples

S/N	CODE	Soil samples			Sediment samples		
		^{40}K	^{238}U	^{232}Th	^{40}K	^{238}U	^{232}Th
1	EKPSS	373.70±5.29	26.12±5.20	32.25±2.02	597.74±11.30	44.25±1.83	35.47±2.18
2	UBESS	232.58±9.30	25.56±2.11	26.53±3.68	622.99±7.31	53.97±2.82	36.43±2.61
3	JEDSS	212.21±21.35	27.03±2.33	24.58±4.89	500.85±8.82	42.55±2.19	38.02±1.84
	Average	272.83±11.98	26.24±3.21	27.79±3.35	573.86±9.14	46.92±2.28	36.64±2.21
	UNSCEAR; 2000	400	35	30	400	35	30

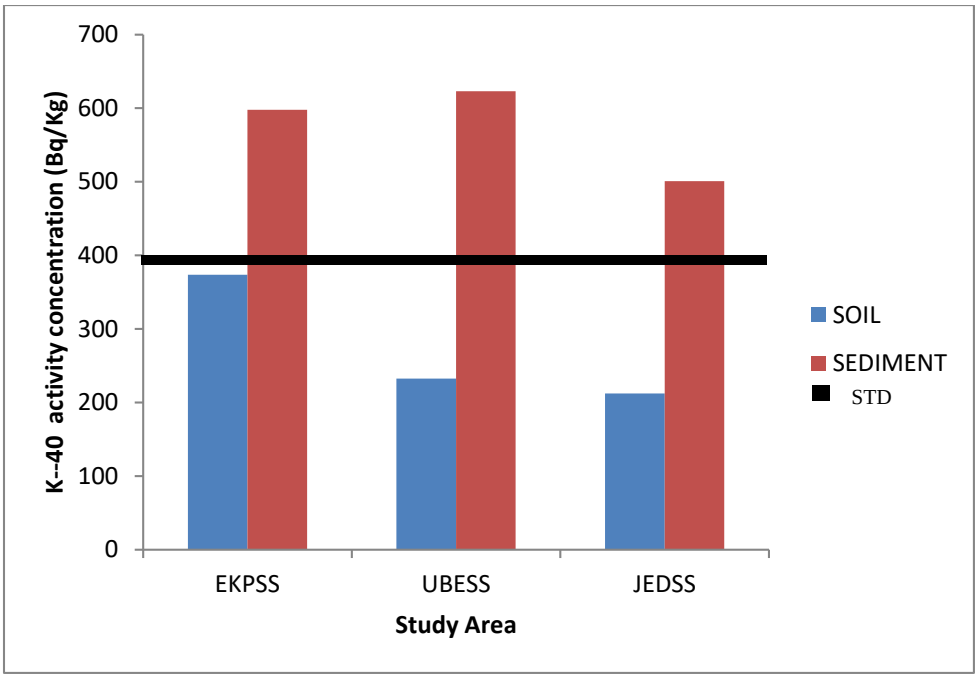

Figure 2: Inter comparison of K-40 activity conc. in the soil and sediment samples from the study area

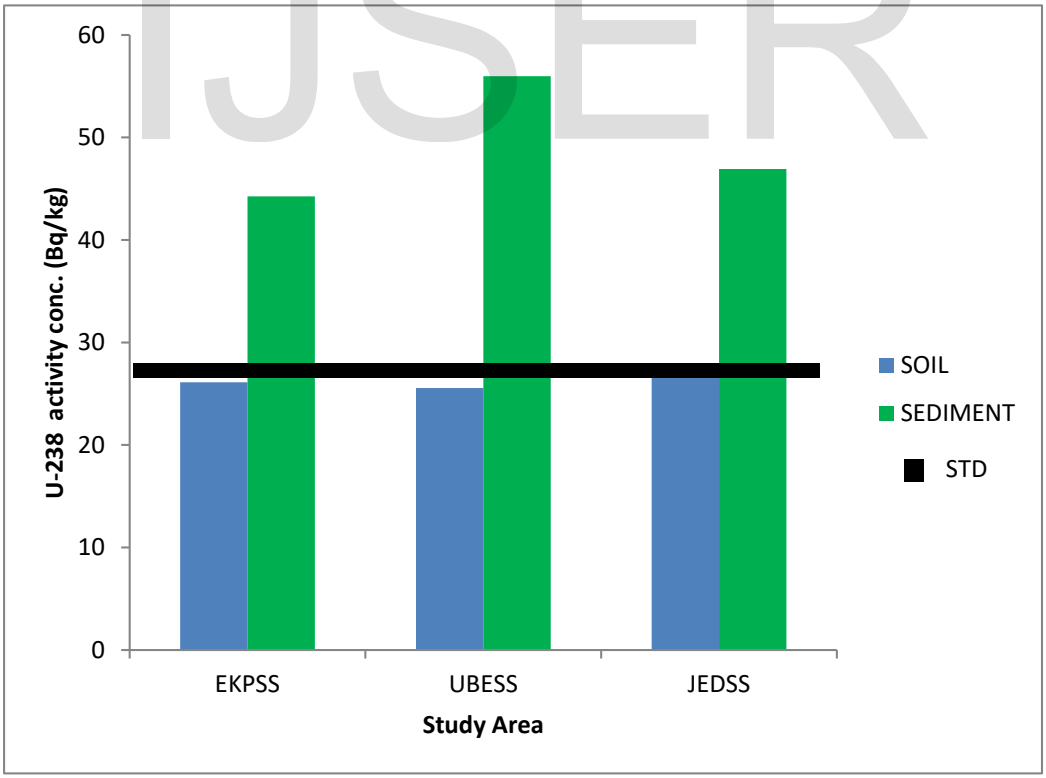

Figure 3: Inter comparison of U-238 activity in the soil and sediment samples from the study area

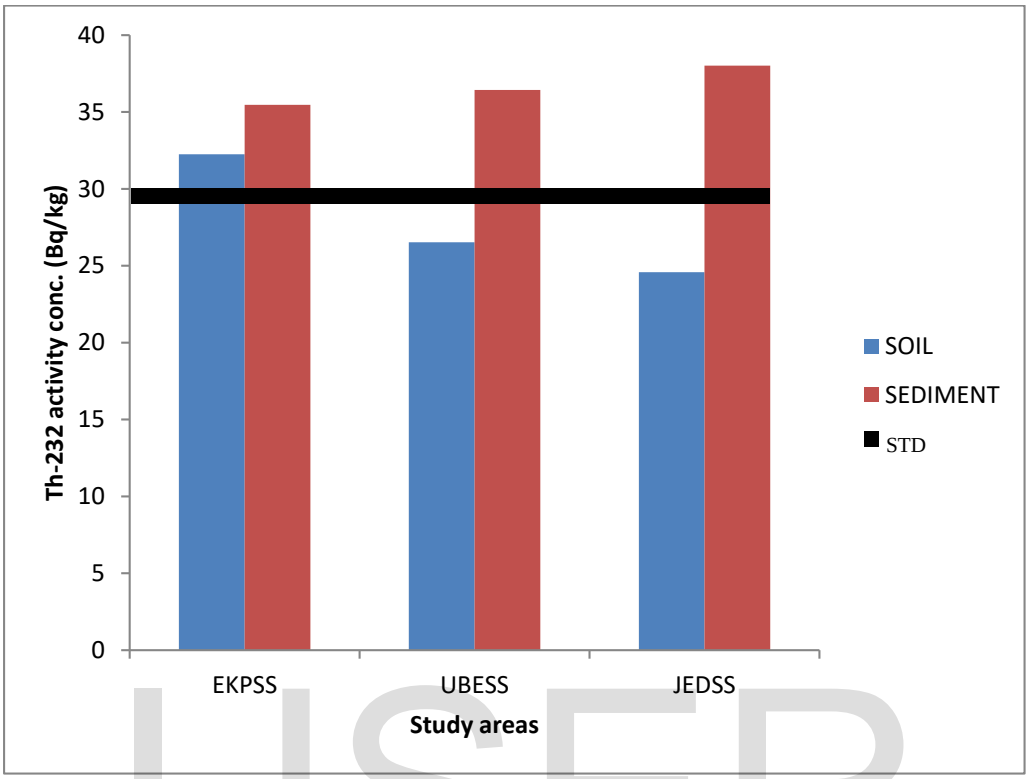

Figure 4: Inter comparison of Th-232 activity in the soil and sediment samples from the study area

Table 3: Calculated Mean Values for Hazard Indices in Soil and Sediment Samples

S/N	CODE	Soil Samples							Sediment Samples						
		Raeq	D	H_{in}	H_{ex}	AEDR (Outdoor)	AEDR (Indoor)	ELCR ($X10^3$)	Raeq	D	H_{in}	H_{ex}	AEDR (Outdoor)	AEDR (Indoor)	ELCR ($X10^3$)
1	**EKPSS**	101.02	47.67	0.343	0.273	58.46	233.8	6.371	140.99	67.39	0.580	0.388	82.64	330.5	9.006
2	**UBESS**	81.48	37.98	0.288	0.219	46.57	186.3	5.076	154.03	73.53	0.562	0.416	90.17	360.7	9.829
3	JEDSS	78.51	36.60	0.285	0.212	44.88	179.5	4.891	141.10	64.15	0.480	0.366	78.67	314.6	8.572
	Average	87.00	40.75	0.305	0.234	49.97	199.8	5.446	145.4	68.35	0.540	0.390	83.82	355.1	9.135

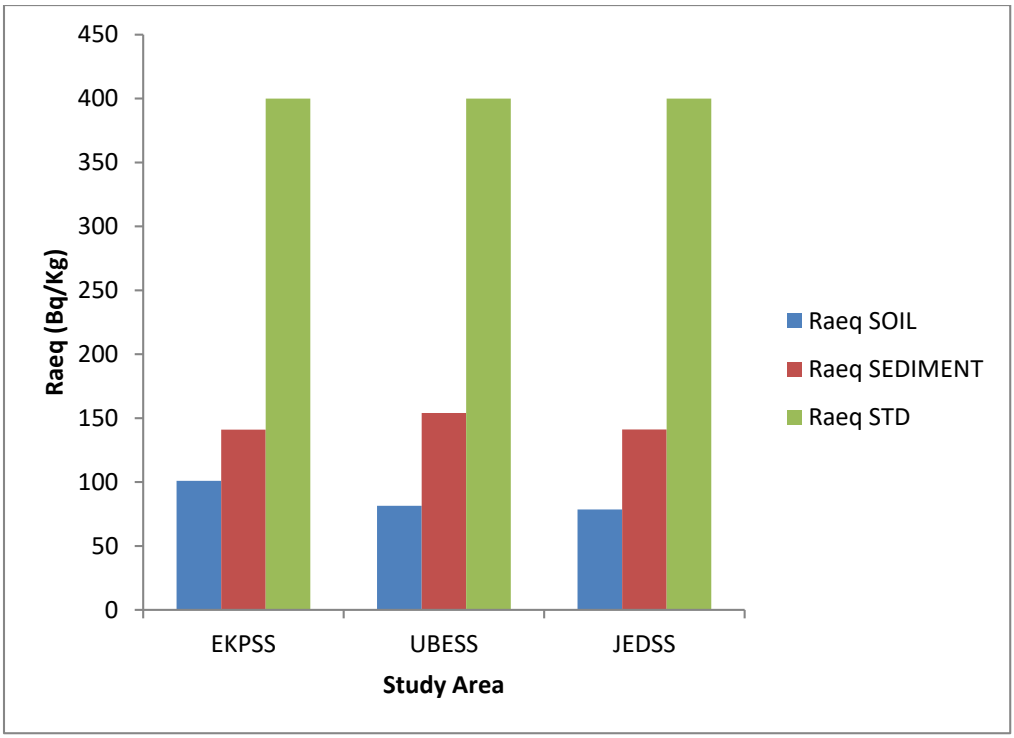

Figure 5: Radium equivalent in soil and sediment samples against UNSCEAR average

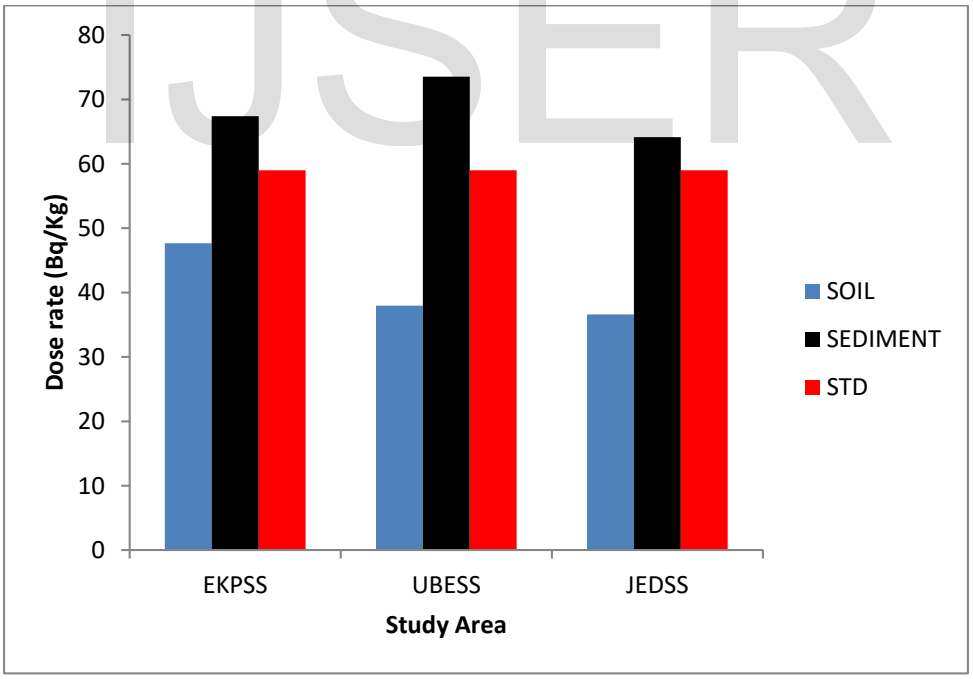

Figure 6: Dose rate in soil and sediment samples against UNSCEAR average

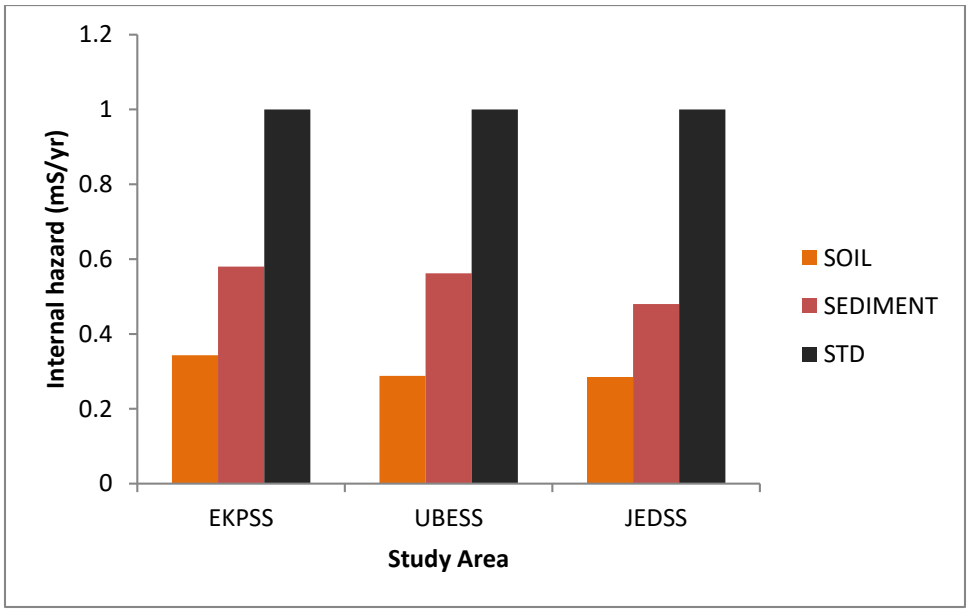

Figure 7: Internal hazard in soil and sediment samples against UNSCEAR average

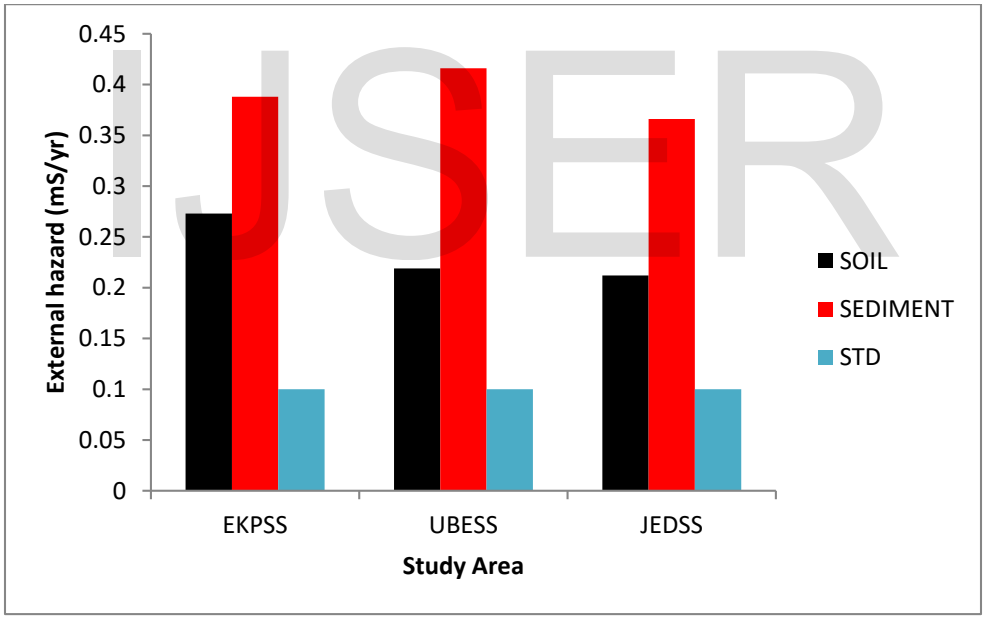

Figure 8: External hazard in soil and sediment samples against UNSCEAR average

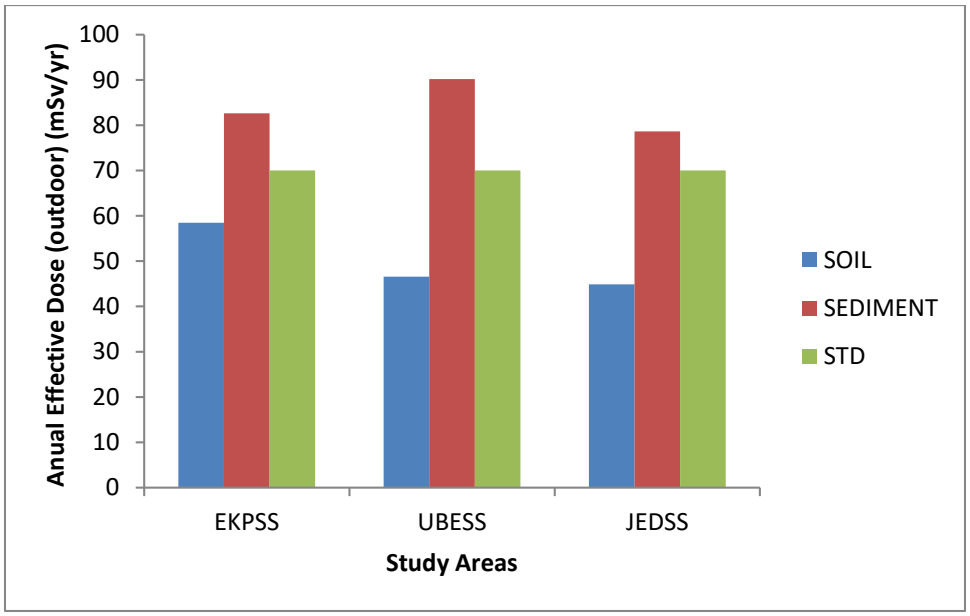

Figure 9: Annual Effective Dose (outdoor) in soil and sediment samples against UNSCEAR average

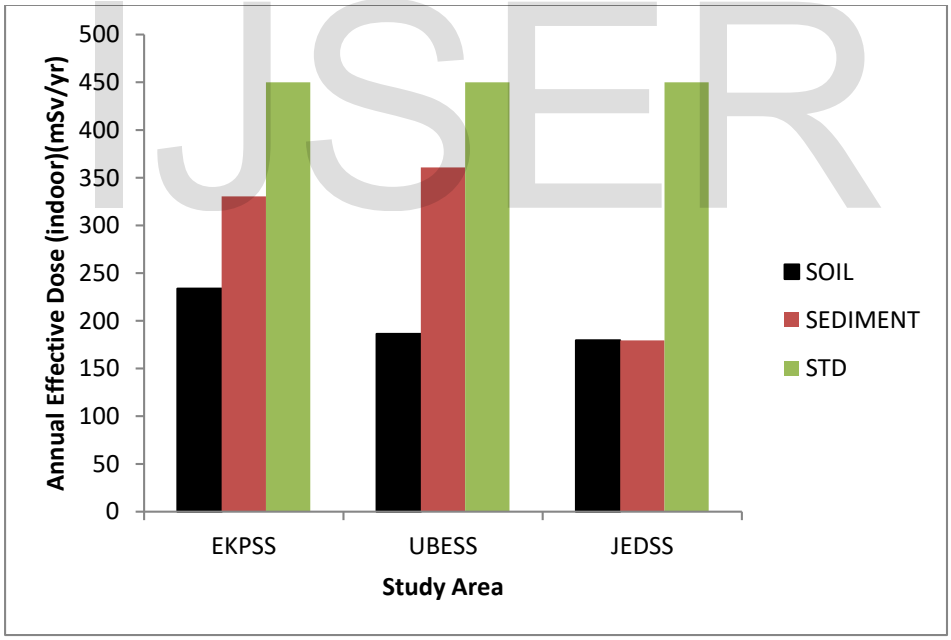

Figure 10: Annual Effective Dose (indoor) in soil and sediment samples against UNSCEAR average

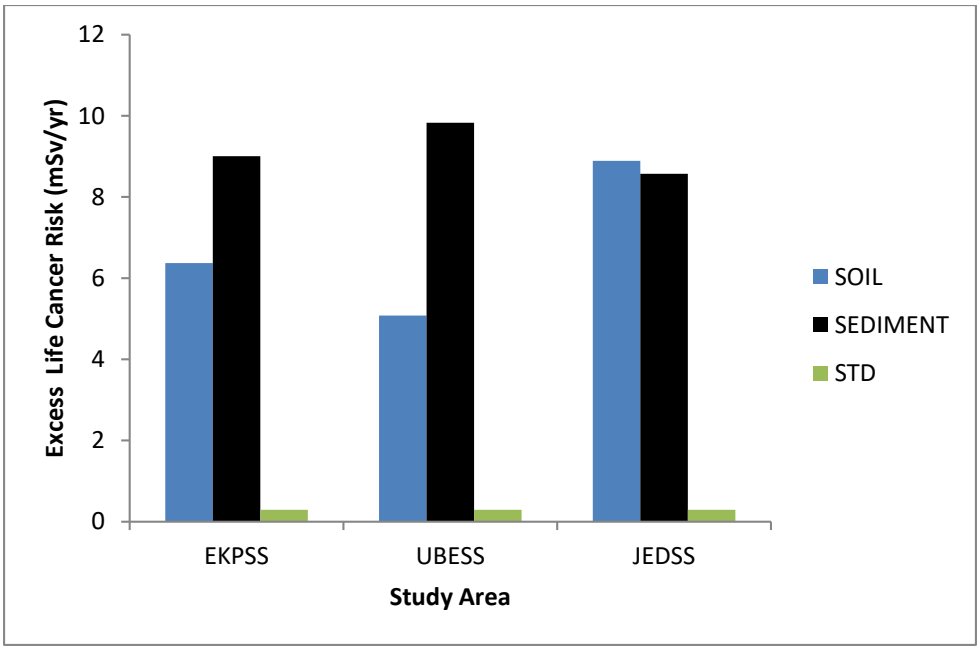

Figure 11: Excess life cancer risk in soil and sediment samples against UNSCEAR average

2.5 DISCUSSION OF RESULTS

Three naturally occurring radionuclides (^{40}K, ^{238}U and ^{232}Th) were determined in soil and sediment samples measured around Warri refinery and environs, and the results for the specific activities concentration in soil and sediment samples are presented in Table 1 and 2. For the specific activity concentration of ^{40}K in soil and sediment samples in the studied areas ranges from 155.22±32.27 to 420.47±1.37 and 425.48±8.43 to 762.09±12.27 (Bq/kg) with an average values of 272.83±11.98 and 573.86±9.14 (Bq/kg). The minimum and maximum values of activity concentration in soil been observed at JEDSSA and EKPSSC and for sediments UBESSA and UBESSC. While for ^{238}U, the activity concentration ranges 13.19±5.12 to 37.77±2.37 and 36.84±2.26 to 71.42±3.20 (Bq/kg) with an average values of 26.24±3.21 and 46.92±2.28 (Bq/kg). The lowest and highest values been recorded at JEDSSA and EKPSSC and for sediment samples is at JEDSSA and UBESSA respectively. On the other hand, the activity concentration of ^{232}Th in soil and sediment ranges from 16.98±2.57 to 36.13±2.53 and 28.42± 2.09 to 40.34±1.17 (Bq/kg) respectively with an average values of 27.79±3.53

and 36.64±2.2 (Bq/Kg). The minimum and maximum values for soil and sediment are observed at UBESSB and EKPSSC, and EKPSSA and EKPSSC for sediment.

The activity concentration averages value results obtained in the study areas in soil samples are far less than the obtained average value results for sediment samples. However this values are comparable with other studies carried out in different location in Nigeria, Esi et,al (2017), Gyuk et al (2017), Mokobia et, al (2003) and Ibrahim et, al (2013).

The average value results for sediment samples is higher than the world wide recommended values (UNSCEAR, 2008) of 400, 35 and 30 (Bq/kg) for Potassium, Uranium and Thorium respectively. The high concentration in sediment samples can be attributed to oil and gas activities which includes gas flaring in the study environments. This is shown in figure 2 to 4 graphically. Also Uranium is moderately soluble in water.

The mean values calculated for radiation hazard parameter in soil and sediment samples in the study sites are Raeq (87.00 and 145.4 Bq/kg), D (40.75 mʃvy^{-1} and 68.35nGyh^{-1}), H_{in} (0.305 and 0.540), H_{ex} (0.234 and 0.390) AEDR (Outdoor) (49.97 and 83.82mʃvy^{-1}), AEDR (Indoor) (199.8 and 335.1mʃvy^{-1}) and ELCR (5.44x10^{-3} and 0.135x10^{-3}) respectively. Comparing these averages, results only excess lifetime cancer risk exceeds its limit for both soil and sediment samples as shown in figure 5 to 12. The implication is that the chances of having cancer by the populace are significant. Therefore, oil and gas activities and the use of sand/sediment as building materials in these region may poses health challenges on the member of the public and those residing in these eminent.

2.2 CONCLUSION

Evaluation of radionuclide concentration in soil and sediment samples from Warri refinery and petrochemical company and environs in Delta State, Nigeria has been conducted. The average values obtained for radionuclides in soil samples in the study areas are below the world permissible values. Nevertheless, the obtained average results for ^{238}U, ^{40}K and ^{232}Th in sediment samples are highly above the (UNSCEAR, 2000) worldwide limit of 400Bq/kg, 35Bq/kg and 30Bq/kg for potassium, Uranium and

Thorium respectively. Comparably, the obtained results are in tandem with existing literatures. Edomi et al (2019), Esi et, al (2017), Kolo (2014). More so, the mean values calculated for radiation hazard, parameter in soil and sediment samples revealed that excess lifetime cancer risk is higher than its limit for both soil and sediment samples while every other health parameters are below their respective average values. The implication is that the chances of having cancer by the populace are significant. Therefore, oil and gas activities and the use of soil and sediment as building materials in the region poses serious threat and health challenges on the populace and public in general.

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