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Assessment of Radiological Hazards Associated with ^{40}K, ^{232}Th and ^{232}U in Water Samples from New Calabar River, Rivers State, Nigeria

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Abstract
An assessment of radiological hazards associated with intake of ^{40}K, ^{232}Th and ^{232}U in river water samples from New Calabar River, Rivers State, Nigeria, was carried out in this study with the aid of Sodium Iodide (NaI) gamma-ray detector. The water samples were collected into sterile plastic containers and treated by adding 16 ml, 1 M HNO_3 solution. This helped to reduce pH of water sample to less than 2, and also allowed for secular equilibrium to be established prior to analysis. Results revealed that mean activity concentration of ^{40}K, ^{232}Th and ^{232}U are 62.43±3.26, 4.18±0.24, and 9.37±1.19 Bql^{-1} respectively while mean total annual effective dose ($mSvy^{-1}$) in infants (0-1and 1-2)y, children (2-7 and 7-12)y, and adults (12-17 and >17)y are (8.45 and 4.448), (2.999 and 2.666), and (5.347 and 3.207) respectively. Mean absorbed dose and annual effective dose equivalent are 9.461±0.802 $nGyh^{-1}$ and 11.285±0.962 mSv yr^{-1}respectively. Mean annual gonad dose equivalent, radium equivalent and excess lifetime cancer risk are 65.304±5.716 Bql^{-1}; 19.506±1.806 Bql^{-1} and 39.550±3.343 E-3, respectively. Mean activity concentration of ^{40}K and ^{232}Th are above recommended safe limits of 10.0 and 0.1 Bql^{-1} respectively, while that of ^{232}U was slightly below 10 Bql^{-1} recommended safe limit. All radiological hazard indices considered in this study are above the recommended safe limits hence the river water source is radiologically polluted and unsafe for human consumption. Provision of alternative and safe water supplies, as well as further research studies on areas not captured in this study are recommended.

Keywords: Sediments, Radioelements, Equilibrium, Concentration, Radiological Hazards

Introduction

Natural radioactivity refers to the presence of radioactive elements in the environment, primarily from naturally occurring radioactive materials in the earth's crust (Jegede et al., 2017; Orosun et al., 2022). These radioactive elements are always present in river water but at different levels or concentrations (Tzortzis et al., 2004; Al-Hamali, 2020). Natural radioactivity in river water primarily comes from the dissolution of radionuclides, such as Uranium which is present in trace amounts in rocks and soils, and is often mobilized into water bodies (Rathore, 2018). Oni and Adagunodo (2019) highlighted that thorium which is found in rocks, soil, and water; and Radon is a radioactive gas released from soil and groundwater, is dissolved into water sources and is also a decay product of uranium. The natural radioactivity in river water can affect both water quality and public health. The exposure to radionuclides in drinking water can lead to internal contamination and subsequent health risks (Davou & Mangset, 2015). Exposure to high levels of uranium and thorium has been linked to renal toxicity, bone and kidney cancer (UNSCEAR, 2000) while Radium, a decay product of uranium and thorium, has been linked to an increased risk of bone cancer and leukemia (Ononugbo and Anyalebechi, 2017), and exposure to radon causes lung cancer (Jegede et al., 2017). The intake of K-40, which is generally considered a low-level radiation exposure, can still contribute to the total body radiation dose. This is particularly significant in areas where the background radiation from natural sources is already high, such as the Niger Delta region (Akinmoladun et al., 2020). The Niger Delta region of Nigeria, including Rivers State, is one of the most ecologically sensitive areas in the country. It is characterized by an intricate network of rivers, wetlands, and creeks, which serve as vital sources of water for domestic, agricultural, and industrial uses (Ojobo & Adowei, 2021). However, the region faces significant environmental challenges, including the contamination of water bodies by natural and anthropogenic pollutants (Nwochigoziri et al., 2023). Among the most concerning contaminants are naturally occurring radioactive materials (NORMs), such as ^{40}**K**, ^{232}**Th**, and ^{232}**U.** These radioactive elements can enter river water through leaching from surrounding soils and rocks (Tchokossa et al., 2011), potentially posing radiological hazards to the

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local populations. The aim of this study is to assess radiological hazards associated with intake of radionuclides in water samples from New Calabar river, Rivers State, Nigeria.

There are several studies carried out on natural radioactivity in surface water (river, lakes and reservoirs), in various parts of Nigeria, especially the Niger Delta region. Some of the studies include the assessment of: natural radioactivity in Imo river, Southern Nigeria (Akpofure et al., 2020); natural radioactivity in some rivers in the Niger Delta (Nwachukwu et al., 2023); annual effective dose of radionuclides in infants due to intake of river water from New Calabar river, Rivers State, Nigeria (Igbudu & Briggs-Kamara, 2023), and annual effective dose of radionuclides in children due to intake of water samples from New Calabar river, Rivers State, Nigeria (Igbudu et al., 2023). Others are assessment: of radiological properties of river water in Southern Niger Delta, Nigeria (Eze et al., 2021); radiological health risk associated with surface water from Delta and Bayelsa States, Niger Delta region, Nigeria (Olaiya et al., 2022); radiological hazards and health risks associated with intake of ^{40}K, ^{232}Th and ^{232}U in river water samples from various locations within Rivers State (Akinmoladun et al., 2020), and radiological risk associated with intake of ^{232}Th and ^{232}U through drinking water in Rivers State (Eze et al., 2022). Findings indicated that certain surface water (rivers), especially those close to oil and gas production, extraction, mining or exploration, and gas flaring activities showed high level of natural radionuclides while those without such activities exhibited level of radionuclides within the acceptable range (Nwachukwu et al., 2023; Igbudu et al., 2023). According to Olaiya et al. (2022), oil production activities, particularly the gas flaring processes, contributed to elevated levels of radon in river water, thereby further complicating the health risks of inhabitants within the study area. Furthermore, factors such as effluent discharge and release of industrial wastes into the river water (Ononugbo & Anyalebechi, 2017), water's pH, temperature, and ionic composition caused by the solubility and mobility of radionuclides in river water (Ikhuoria et al., 2006), contributed to the increased level of certain radionuclides, particularly radon and radium in river water samples (Tchokossa et al., 2011). The concentration of uranium and radium in surface and underground water are usually above recommended safe limits in certain locations, particularly around oil exploration sites (Akpofure et al., 2020). According to Igbudu and Brigg-Kamara (2023) and Igbudu et al. (2023) surface and ground water supplies within the Niger Delta region have been found to show high level of radionuclides above the recommended safe limits, thereby posing radiological health risks on the inhabitants of such area that rely on the water supplies for domestic and agricultural purposes. This is due to several anthropogenic activities such as domestic, medical, electronic and industrial wastes discharge into the river, sand mining, and bunkering (Ononugbo & Anyalebechi, 2017). These activities increase the level of radionuclides in the water resources in Niger Delta, especially the New Calabar river. Generally, the activity concentration or level of radionuclides in both surface and underground water resources within Niger Delta region vary from location to location, and are influenced by the presence of radionuclides (thorium and uranium) bearing rocks beneath the earth, and other anthropogenic activities taking place within such study area (Agbalagba et al., 2013; Igbudu & Briggs-Kamara, 2023).

Materials and Methods

Study Area

This study area is new Calabar river in Rivers State, located in the Niger Delta region of Nigeria. It is a stretch of river that flows from its source at Elele-Alimini across several communities' river banks, including the popular Choba bridge, through a distance of about 150 Km, and discharges into the Atlantic Ocean (Igbudu & Briggs-Kamara, 2023). The study area is characterized by a complex system of rivers and creeks that may be impacted by both natural and anthropogenic sources of radioactivity. The water quality in Rivers State is influenced by oil spills and the use of chemical fertilizers (Ononugbo & Anyalebechi, 2017) which can further exacerbate the risks associated with exposure to elevated radiation levels in drinking water. Some rivers in Rivers State maintain relatively low levels of natural radioactivity while some, especially those near industrial zones may pose serious health risks due to the presence of high level of natural radioactivity (Otu, 2012). This is because the region has been subjected to environmental stressors from both natural and anthropogenic sources, including oil exploration, industrial activities, and mining. The new Calabar river is a major source of water supplies for domestic (cooking and drinking), recreational (swimming), and agricultural purposes (Igbudu & Briggs-Kamara, 2023). The river is also a point of discharge of domestic, industrial, electronic, hospital and radioactive wastes (Ononugbo & Anyalebechi, 2017), thereby increasing the concentrations of radionuclides in the river.

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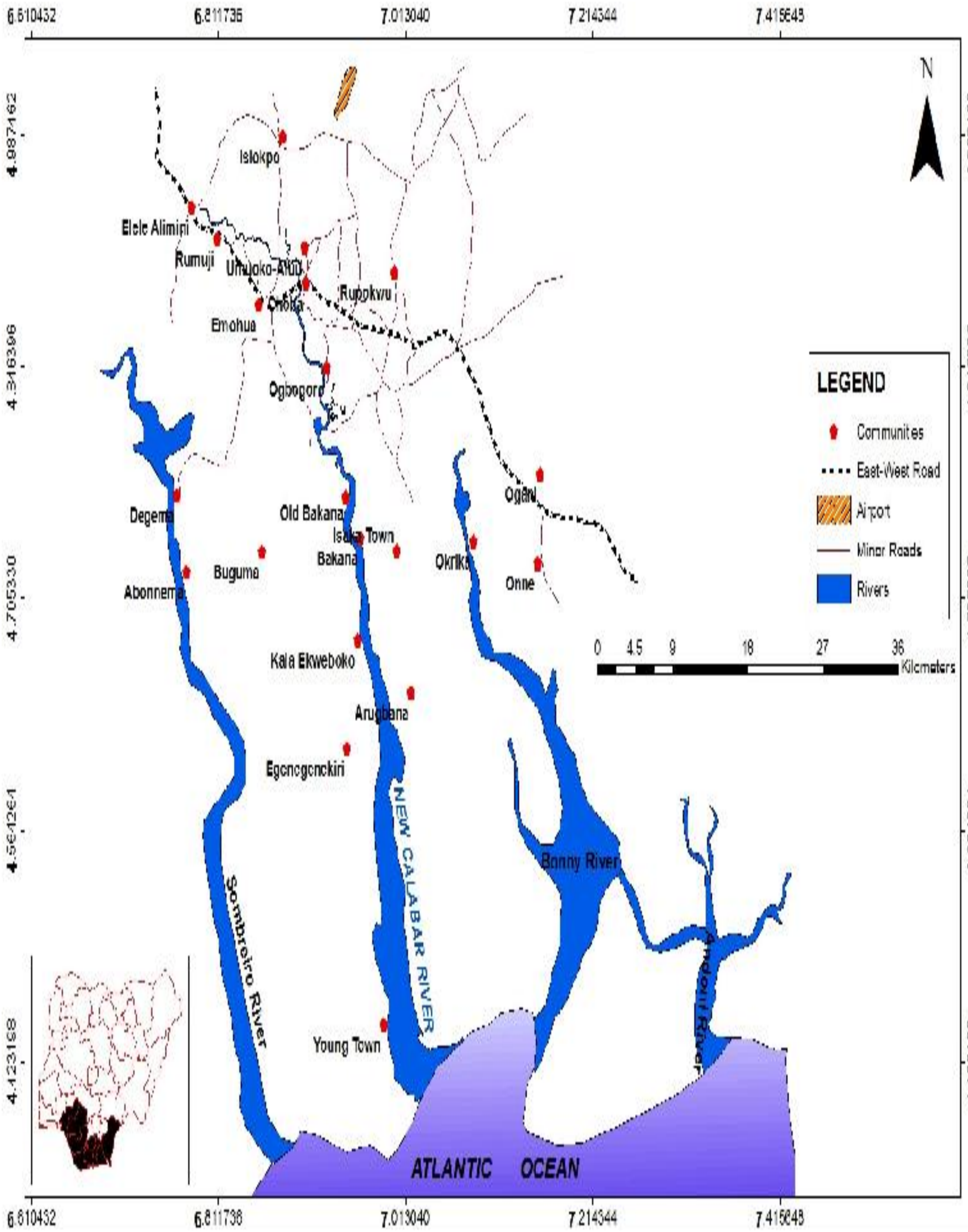

Fig. 1: Map of Lower Niger Delta showing the New Calabar River drainage system and the communities through which it traverses (Source: Francis and Elewuo, 2012).

Materials

The materials used in this study are: Sodium Iodide NaI (Tl) gamma-ray detector. It is a crystal doped with thallium, and was used to analyze the water samples as well as to determine the activity concentration of the radionuclides present in the water samples. The global positioning system (GPS), was used to measure the coordinates of sample locations and sampling points, sterilized 50 cl plastic containers were used for collection of water samples. Others are **w**ater samples from the New Calabar river, digital pH meter for measuring the pH of water samples, and HNO_3 solution for dilution and reduction of samples' pH to less than 2.

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Methods

Preparation of Water Samples

Sterilized 50 cl plastic sample containers were thoroughly washed three times with detergents and hard brush, and rinsed with distilled water. The water samples were collected into the plastic bottles and treated with nitric acid solution in order to reduce the pH of the water samples (Igbudu et al., 2023), and to e**nsure** that water samples in the container do not interfere with the gamma rays (Ononugbo & Anyalebechi, 2017). The water samples in the containers were labelled and well packed in a refrigerator for about 24 hours. They were transported to laboratory for analysis.

Gamma Ray Detector

The gamma ray detector was calibrated using a standard radioactive source of known energy (Cs-137 or Co-60). Two types of calibration were carried out on the gamma ray detector. They are **e**nergy calibration which uses the gamma-ray peaks from the calibration source to calibrate the energy scale of the spectrometer, and the **e**fficiency calibration which involves determination of the detector's efficiency for different energy levels, using standard sources and comparing the counts with the expected values. The background radiation in the setup was measured without any water sample so as to account for any ambient radiation and ensure that measurements of the sample are not influenced by environmental radiation. The background spectrum was recorded and later subtracted.

Analysis of Water Samples

During analysis, the water samples were placed inside the well of the NaI detector, and an appropriate counting time was set. The counting time depends on activity level of the sample, and ranges from a few minutes to several hours. The sensitivity of NaI detector depends on the specific isotope being measured, volume of water sample, and detector's calibration. In order to obtain accurate measurements, volume of water was made sufficient to produce a measurable signal, but not too large such that it overwhelms the detector's efficiency. Background radiation spectrum was subtracted from the sample spectrum in order to eliminate interference from environmental radiation. The concentration of the radioactive isotope in the water samples were calculated, using known calibration factor. The results were finally reported in terms of activity concentration for each detected isotope.

Estimation of Radiological Hazard Indices

Several studies have utilized radiological hazard indices to assess the potential risks associated with drinking water contaminated with ^{40}**K**, ^{232}**Th**, and ^{232}**U**. The common indices include:

Activity Concentration

The activity concentration of radionuclides in water samples was estimated after subtracting decay corrections, using Eq. (1): (Avwiri et al., 2014; Igbudu et al., 2023)**:**

$$A_c(Bql^{-1}) = \frac{C_a}{P_\gamma(M_s/V_s)\varepsilon_\gamma\, t_c} \qquad (1)$$

where**:** A_c is activity Concentration (Bql^{-1}), C_a is the net peak area of a peak at energy, ε_γ is efficiency of the detector for a γ-energy of interest; V_s is sample volume; t_c is total counting time; and P_γ is abundance of the γ-line in a radionuclide'

Total Annual Effective Dose (TAED)

The is a measure of total radiation exposure an individual receives from radionuclides (^{40}K, ^{232}Th and ^{232}U) in water samples over the course of a year. It is obtained by adding up individual doses from each of the radionuclides in water samples for each category of age of population that consumes the water, using Eq. (2): (Ajayi & Adesida, 2009; Ononugbo & Anyalebechi, 2017):

$$\text{TAED (mSvy}^{-1}) = \sum A_c I_A C_F \qquad (2)$$

where: A_c is activity concentration (Bql^{-1}) of the radionuclide in the water sample; I_A is daily water consumption (Ld^{-1}); and C_F is dose conversion factor (mSvBq^{-1}).

Absorbed Dose (AD)

This is the rate at which radiation energy is absorbed by tissues, and is a measure of the potential for biological damage to organs. The WHO has set safe limit of 1.0 nGyh^{-1} for the absorbed dose in drinking water (Ononugbo and Anyalebechi, 2017; WHO, 2017), with values above this threshold indicating potential health risks. The absorbed dose was estimated using Eq. (3): (Avwiri et al., 2014; Eke & Emelue, 2019; Mbonu & Ben, 2021; Samaila & Tampul, 2021):

$$\text{AD (nGyh}^{-1}) = 0.462\, C_U + 0.604\, C_{Th} + 0.0417\, C_K \qquad (3)$$

where: C_K, C_{Th} and C_U are activity concentrations of ^{40}K, ^{232}Th and ^{232}U respectively while 0.0417, 0.604, 0.462 are conversion factor for ^{40}K, ^{232}Th and ^{232}U respectively.

Annual Effective Dose Equivalent (AEDE)
This is the measure of total radiation risk to an individual organism, and is used to determine the quantity of radiation the human body absorbed per year. It also determines degree of long-term effect that might occur in the future due to exposure to radiation (Ugbede & Benson, 2018). It was estimated using Eq. (4): (Avwiri et al., 2014; Ereh & Zhang, 2018; Sowole & Egunjobi, 2019):
AEDE ($mSvy^{-1}$) = D ($nGyh^{-1}$) × 8760 hr × 0.2 × 0.7 (Sv/Gy) × 10^{-6} (4)
where**:** D is absorbed dose ($nGyh^{-1}$); 8760 is the total hour in a year; 0.7 is dose conversion factor (Sv/Gy) and 0.2 is the occupancy factor for outdoor measurement.

Annual Gonad Dose Equivalent (AGDE)
This is a measure of potential threat to sensitive cells such as the gonad cells (UNSCEAR, 2000) due to radiation exposure to a certain level. It was estimated using Eq. (5): (Eke & Emelue, 2019):
$AGDE = 3.09C_U + 4.18C_{Th} + 0.314C_K$ (5)
where: C_U, C_{Th} *and* C_K *are* Activity concentrations of ^{232}U, ^{232}Th and ^{40}K respectively while 3.09; 4.18 and 0.314 are conversion factor for C_U, C_{Th} *and* C_K respectively.

Radium Equivalent (Raeq)
This is one of the most widely used radiation hazard indices. It is a summative measure of the radioactivity of uranium, thorium, and radium, providing a single value for the overall radiological risk in a water body. It was estimated using Eqs. (6) and (7): (Avwiri et al., 2014; Eke & Emelue, 2019):
$Raeq = \left[\frac{C_U}{370} + \frac{C_{Th}}{259} + \frac{C_K}{4810}\right] \times 370$ (6)
$Raeq = C_U + 1.43C_{Th} + 0.077C_K$ (7)
where: C_U, C_{Th} *and* C_K *are* activity concentrations of ^{232}U, ^{232}Th and ^{40}K respectively while 1, 1.43 and 0.077 are the respective conversion factors.

Excess Lifetime Cancer Risk (ELCR)
This is a radiological hazard index used to predict the probability of an individual developing cancer over a human lifetime due to continued exposure to radiation. It was estimated using Eq. (8): (Avwiri et al., 2014; Samaila & Tampul, 2021):
ELCR = AEDE × DL × RF (8)
where: $AEDE$ is annual effective dose equivalent; DL is duration of life time (approximately 70 years); and RF *is* fatal risk factor per Sievert (Sv^{-1}), approximately 0.05 for stochastic effect for general public.

Results
Table 1 represents the activity concentration of radionuclides of (^{40}K, ^{232}Th and ^{232}U) in river water samples from new Calabar River while Table 2 represents the estimated radiological hazard indices due to intake of radionuclides in river water samples. Fig. 1 represents mean total annual effective dose for six different age groups (infants, children and adults) while Fig. 2 represents the mean radiological hazard indices and the world average value.

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Table 1: Activity Concentrations (Bql^{-1}) of radionuclides ^{40}K, ^{232}Th and ^{232}U in the Water from New Calabar River (Igbudu & Briggs-Kamara, 2023).

Sample Location	Sample Code	Location Latitude N	Location Longitude E	Activity Concentration *(Bq L^{-1})* ^{40}K	^{232}Th	^{232}U
Iwofe Jetty Water Front	P1	4º 48’36.86’’	6º 55’44.94’’	40.05±2.12	4.54±0.27	5.70±0.84
(L1)	P2	4º 48’33.06’’	6º 55’42.01’’	36.07±1.91	3.90±0.23	11.04±1.56
Ogbogoro Water Front	P1	4º 50’55.09’’	6º 55’24.42’’	14.89±0.78	2.07±0.12	4.52±0.60
(L2)	P2	4º 48’52.07’’	6º 55’50.71’’	28.31±1.49	2.81±0.17	12.05±1.62
Rumuokparali Water	P1	4º 52’16.76’’	6º 54’15.47	99.40±5.23	5.39±0.32	6.79±0.97
Front (L3)	P2	4º 52’30.92’’	6º 54’13.33’’	66.52±3.37	1.74±0.10	6.53±0.64
Choba Market Water	P1	4º 53’48.24’’	6º 55’13.17’’	31.69±1.60	4.21±0.24	6.34±0.64
Front (L4)	P2	4º 53’50.88’’	6º 53’54.26’’	55.99±2.96	2.76±0.17	10.15±1.39
Omuihuechi Aluu	P1	4º 53’50.88’’	6º 54’97.69’’	40.37±2.13	3.17±0.19	10.76±1.50
Water Front 1 (L5)	P2	4º 53’28.63’’	6º 54’08.24’’	137.04±7.20	3.55±0.21	9.54±1.37
Omuihuechi Aluu	P1	4º 54’46.18’’	6º 53’52.96’’	63.43±3.35	6.43±0.38	6.31±0.88
Water Front 2 (L6)	P2	4º 54’40.19’’	6º 53’51.45’’	95.31±5.00	1.03±0.06	25.29±3.03
Choba Bridge Water	P1	4º 53’48.24’’	6º 55’13.17’’	24.62±1.25	4.74±0.27	8.20±0.82
Front (L7)	P2	4º 53’50.88’’	6º 53’54.26’’	93.00±4.89	4.99±0.30	15.09±2.04
Mini Onuah Stream,	P1	5º 04’31.36’’	6º 41’53.26’’	13.38±0.68	5.85±0.34	12.53±1.25
Elele Alimini (L8)	P2	5º 04’24.30’’	6º 44’10.33’’	70.77±3.73	6.01±0.36	5.50±0.77
Mini Ezi Stream, Elele	P1	5º 03’29.30’’	6º44’23.25’’	266.11±13.99	4.87±0.29	13.71±2.04
Alimini (L9)	P2	5º 02’29.20’’	6º 44’07.86’’	76.65±4.06	4.95±0.29	0.48±0.07
Rumuji/Ibaa Bridge	P1	4º 56’44.87’’	6º 47’42.40’’	72.64±3.68	3.83±0.22	14.07±1.38
Water Front (L10)	P2	4º 56’40.33’’	6º 47’41.05’’	10.38±0.54	5.89±0.35	4.61±0.63
Alimini Water Front,	P1	4º 55’29.27’’	6º50’02.94’’	40.37±2.13	4.55±0.27	9.22±1.20
Oduoha Emohua (L11)	P2	4º55’45.99’’	6º49’58.90’’	94.99±4.99	3.98±0.24	23.67±3.11
Ogbodo Water Front	P1	4º55’25.36’’	6º 50’24.69	19.92±1.05	7.04±0.42	0.72±0.11
Oduoha Emohua (L12)	P2	4º 55’25.75’’	6º 50’23.66’’	59.95±3.04	4.95±0.28	1.20±0.12
Ogbodo,Water Front 2	P1	4º 55’19.59’’	6º 50’21.70’’	22.12±1.12	2.51±0.15	1.82±0.18
Oduoha Emohua (L13)	P2	4º 55’08.25’’	6º 50’13.62’’	79.83±4.04	1.53±0.09	9.87±0.97
Mgbuitanwo Emohua	P1	4º 52’55.02’’	6º 53’35.78’’	11.01±0.58	4.36±0.09	12.54±1.74
Water Front (L14)	P2	4º 52’56.37’’	6º 53’34.90’’	83.36±4.39	5.47±0.33	14.24±1.93
Min.				**10.38±0.54**	**1.03±0.06**	**0.48±0.07**
Max				**266.11±13.99**	**7.04±0.42**	**25.29±3.03**
Mean				**62.43±3.26**	**4.18±0.24**	**9.37±1.19**
SD				**51.580**	**1.540**	**6.008**
WAV				**10.0**	**0.10**	**10.0**

SD = Standard Deviation, WAV = World Average Value, (±) = Associated Uncertainty Error

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Table 2: Estimated Radiological Hazard Indices due to intake of radionuclides (^{40}K, ^{232}Th and ^{232}U) in river water samples

Sample Code	Radiological Hazard Indices AD ($nGyh^{-1}$)	AEDE ($mSvy^{-1}$)	AGDE (Bql^{-1})	Ra_{eq}(Bql^{-1})	ELCR ($\times 10^{-3}$)
L1P1	7.046±0.640	8.641±0.785	49.166±4.390	15.275±1.389	30.243±2.747
L1P2	8.960±0.939	10.989±1.152	61.742±6.381	19.394±2.036	38.461±4.032
L2P1	3.959±0.359	4.855±0.440	27.295±2.600	8.626±0.832	16.992±1.540
L2P2	8.445±0.913	10.357±1.120	57.870±6.184	18.248±1.978	36.249±3.920
L3P1	10.537±0.859	12.923±1.053	74.723±5.977	22.152±1.831	45.230±3.685
L3P2	6.842±0.497	8.391±0.609	48.338±3.454	14.140±1.042	29.368±2.131
L4P1	6.793±0.507	8.331±0.622	47.139±3.483	14.793±1.106	29.158±2.177
L4P2	8.691±0.868	10.659±1.064	60.481±5.935	18.408±1.861	37.306±3.724
L5P1	8.569±0.897	10.509±1.100	59.175±6.098	18.401±1.936	36.781±3.850
L5P2	12.266±1.060	15.043±1.300	87.348±7.372	25.168±2.224	52.650±4.550
L6P1	9.444±0.776	11.582±0.952	66.292±5.359	20.389±1.681	40.537±3.332
L6P2	16.280±1.645	19.892±2.017	112.379±11.183	34.102±3.501	69.622±7.059
L7P1	7.678±0.594	9.416±0.728	52.882±4.055	16.874±1.302	32.956±2.548
L7P2	13.864±1.328	17.003±1.629	96.688±9.093	29.387±2.845	59.510±5.701
L8P1	9.880±0.811	12.117±0.995	67.372±5.497	21.925±2.260	34.580±2.838
L8P2	9.122±0.729	11.187±0.894	43.288±5.055	19.543±1.572	39.154±3.129
L9P1	20.372±0.869	24.984±1.066	146.279±11.909	41.164±3.532	87.444±3.731
L9P2	6.408±0.377	7.859±0.462	46.242±2.703	13.460±0.798	27.506±1.617
L10P1	11.843±0.924	14.524±1.133	82.295±6.339	25.140±1.978	50.834±3.965
L10P2	6.120±0.525	7.506±0.644	42.124±3.579	13.832±1.172	26.271±2.254
L11P1	8.691±0.806	10.659±0.988	60.185±5.505	18.834±1.760	37.306±3.458
L11P2	17.300±1.790	21.217±2.195	119.604±12.180	36.675±3.847	74.259±7.682
L12P1	5.415±0.348	6.641±0.427	37.907±2.425	12.321±0.792	23.243±1.494
L12P2	6.044±0.351	7.412±0.430	43.214±2.496	12.894±0.754	25.942±1.505
L13P1	3.279±0.220	4.021±0.270	23.061±1.535	7.103±0.480	14.073±0.945
L13P2	8.813±0.671	1.995±0.823	61.960±4.642	18.205±1.410	6.982±2.880
L14P1	8.886±0.882	10.898±0.468	60.430±5.934	19.623±1.914	38.143±1.638
L14P2	13.359±1.274	16.383±1.562	93.041±8.691	28.481±2.740	57.340±5.467
Min.	**3.279±0.220**	**4.021±0.270**	**23.061±1.535**	**7.103±0.480**	**14.673±0.945**
Max.	**20.372±0.869**	**24.984±1.066**	**146.279±11.909**	**41.164±3.532**	**87.444±3.731**
Mean	**9.461±0.802**	**11.285±0.962**	**65.304±5.716**	**19.506±1.806**	**39.550±3.343**
SD	**3.947**	**5.165**	**28.166**	**8.025**	**18.091**
WAV	**1.0**	**0.1**	**1.0**	**370.0**	**0.29E-3**

D = Absorbed Dose, AEDE = Annual Effective Dose Equivalent,

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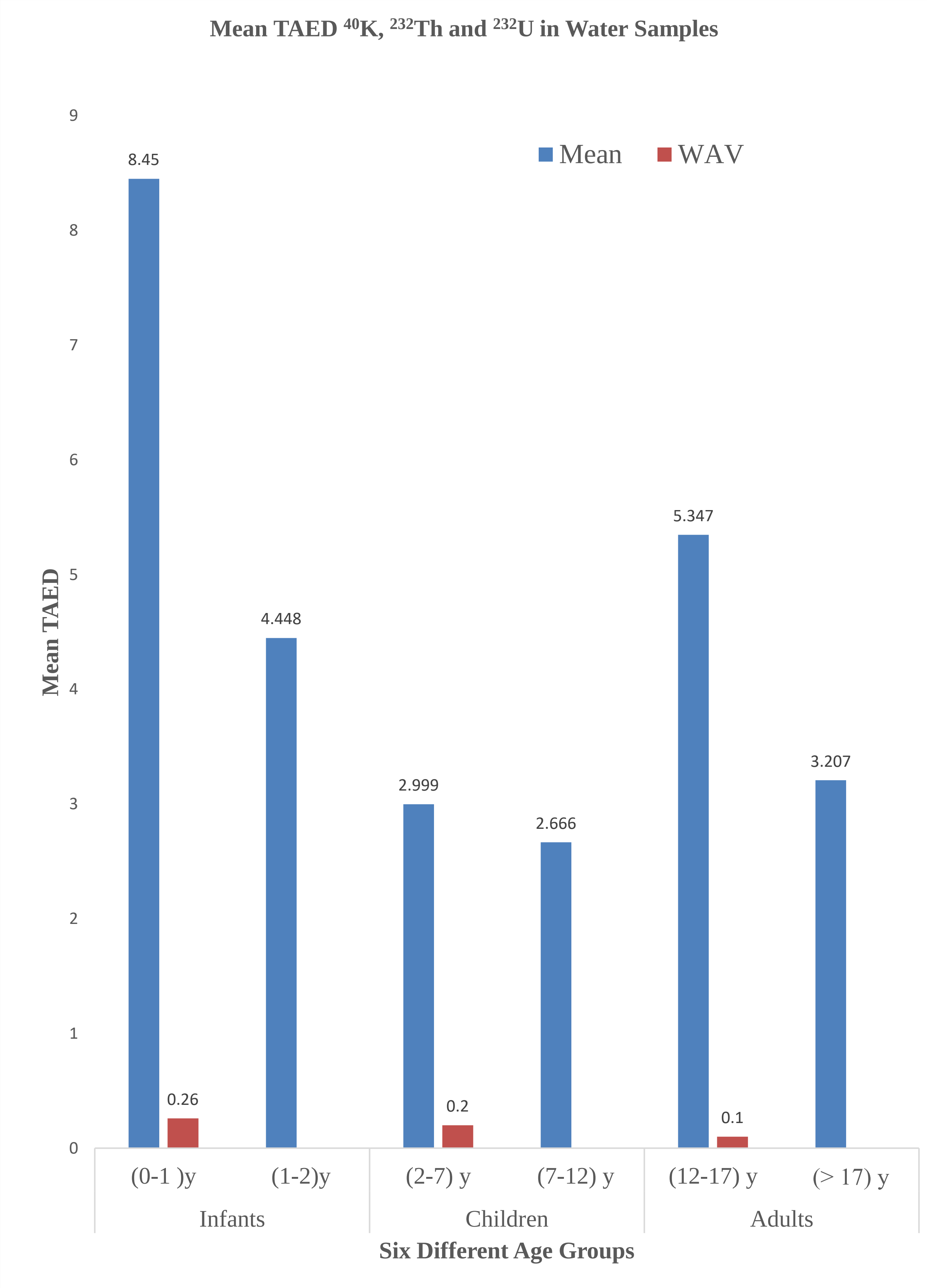

Fig. 1: Mean TAED of ^{40}K, ^{232}Th and ^{232}U in Water Samples and WAV

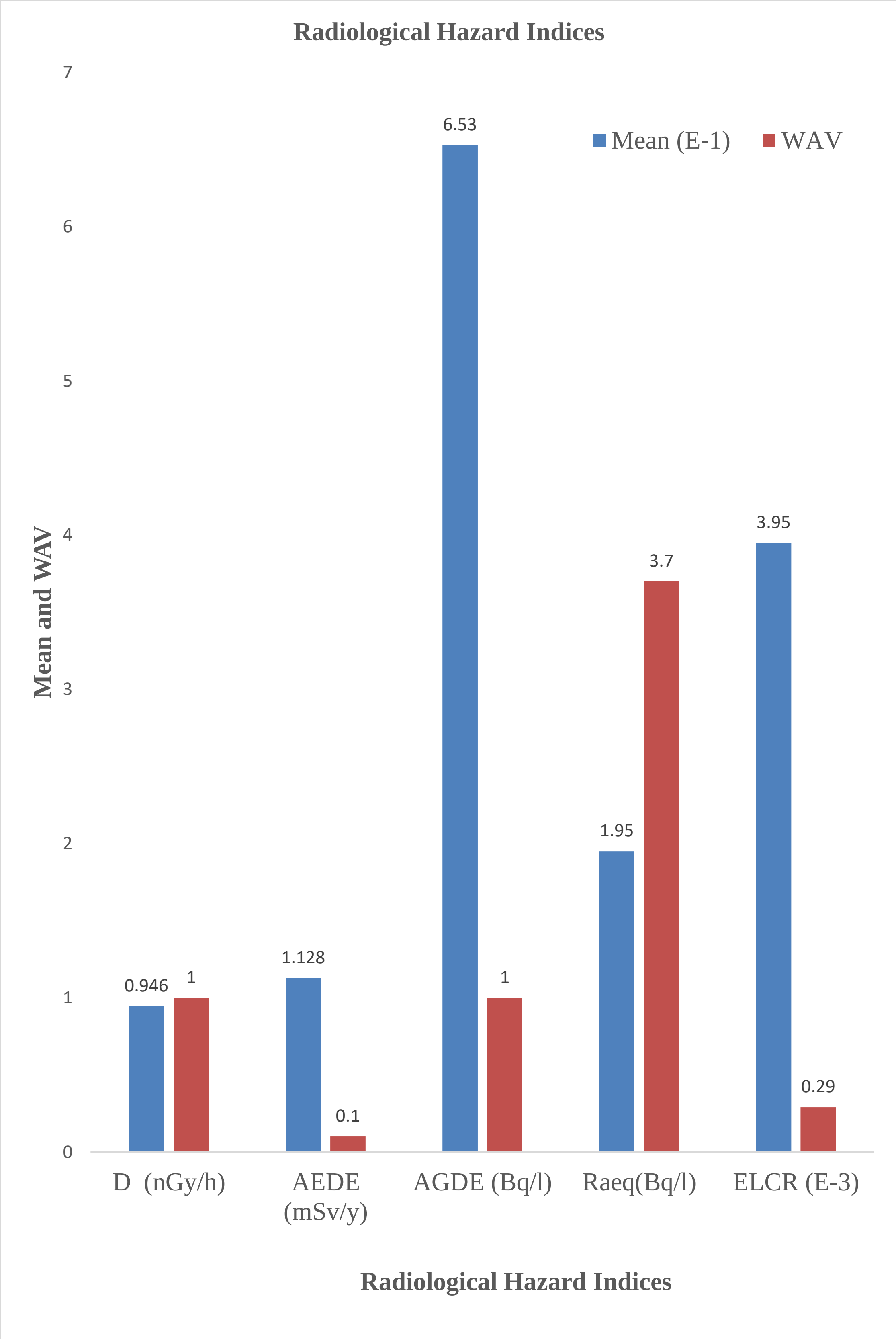

Fig 2: Mean radiological hazard indices in water samples and world average values.

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Discussion

The study on the assessment of radiological hazards associated with intake of ^{40}K, ^{232}Th and ^{232}U in water samples from the New Calabar River, Rivers State, Nigeria was conducted. The radioelements in the water samples as well as their activity concentration were determined using NaI gamma-ray detector.

Activity Concentration

The activity concentration of the radionuclides in water samples was estimated using Eq. (1): (Avwiri et al., 2014; Igbudu et al., 2023). The minimum and maximum values of ^{40}K, ^{232}Th and ^{232}U are (10.38±0.54 and 266.11±13.99) Bql^{-1}, (1.03±0.06 and 7.04±0.42) Bql^{-1}, and (0.48±0.07 and 25.29±3.03) Bql^{-1} respectively while their mean activity concentrations are 62.43±3.26, 4.18±0.24, and 9.37±1.19 Bql^{-1} respectively. The ^{40}K is most dominant radionuclide in the water samples, followed with ^{232}U while ^{232}Th is the least. The mean value of ^{40}K in this study is higher than the mean values of: 15.82±2.03 Bql^{-1} obtained in surface water in coastal communities in Ndokwa East, Delta State (Ononugbo & Anyalebechi (2017); 32.1±3.5 Bql^{-1} obtained in river water around three Oil Mining Lease (OML) fields in some communities in Niger Delta, Nigeria (Agbalagba et al., 2013); 48.78±13.67 Bql^{-1} obtained in produced water samples from flow station waste pit within oil and gas fields onshore of Delta State (Avwiri et al., 2013); 7.51±0.56 Bql^{-1} obtained from borehole water supply in some communities in Ogbia Local Government Area, Bayelsa State (Anekwe et al., 2023); 49±15 Bql^{-1} obtained from community water supplies in oil and gas producing area in Delta State, Nigeria (Tchokossa et al., 2011); 4.94±0.06 Bql^{-1} mean value obtained from Mini Okoro/Oginigba creek in Port Harcourt (Avwiri et al., 2014); 19.09±10.05 Bql^{-1} obtained from sachet drinking water produced in Nigeria (Ajayi and Adesida, 2009); and 129.67±8.27 Bql^{-1} obtained from drilled well water supplies across some cities in Ondo and Ekiti States (Ayodele et al., 2020). The abundance of ^{40}K in the river water samples might be due to some anthropogenic activities such as application of N-P-K fertilizer during agricultural practices, effluent discharge of organic components rich in potassium into the water body (Agbalagba et al., 2013), oil and gas exploration, exploitation and flaring activities by multinational and international oil companies located within study area (Igbudu et al., 2023), as well as pipeline vandalization (Tchokossa et al., 2011) that give rise to oil spillage into the water body. Potassium are also largely present naturally in the soil, minerals and rocks beneath the earth, and are released in liquid phase into the river through weathering process and surface water run-off into the river (Ononugbo & Anyalebechi, 2017).

The mean activity concentration of ^{40}K and ^{232}Th (62.43±3.26 Bql^{-1} and 4.18±0.24) are higher than internationally recommended safe limits of 10.0 Bql^{-1} and 0.1 Bql^{-1} respectively (WHO, 2017; UNSCEAR, 2000) while that of ^{232}U (9.37±1.19 Bql^{-1}) was slightly below the recommended safe limit of 10.0 Bql^{-1}. Findings in this study indicated that the water supplies in the study area are radiologically polluted and unfit for human consumption since they possess serious health risks to the public that make use of it.

Total Annual Effective Dose

The TAED for six different age groups due to intake of radionuclides in water samples was estimated using Eq. (2): (Ajayi & Adesida, 2009; Ononugbo & Anyalebechi, 2017). Results in Fig. 1 showed that total annual effective dose in ($mSvy^{-1}$) ranged from (3.187±1.676 to 15.215±1.676) and (1.296±0.096 to 9.199±0.994) in infants (0-1 and 1-2)y respectively, with mean values of 8.450±0.784 and 4.448±0.426 respectively. The TAED in children (2-7 and 7-12)y ranged from (0.875±0.066 to 6.251±0.607) and (0.750±0.058 to 5.822±0.660) respectively with mean values of 2.99±0.299 and 2.660±0.291 respectively. The TAED in adults (12-17 and >17)y ranged from (1.431±0.117 to 12.532±1.455) and (0.959±0.073 to 6.800±0.821) respectively, with mean values of 5.347±0.619 and 3.207±0.334 respectively. Mean TAED ($mSvy^{-1}$) in infants, children and adults exceeded recommended safe limits of 0.26, 0.20 and 0.10 respectively. This implies that the river water samples are radiologically polluted and unfit for human consumption.

Absorbed Dose

The absorbed dose ($nGyh^{-1}$) due to ingestion of the radionuclide in the water sample was estimated using Eq. (3): (Avwiri et al., 2014; Eke & Emelue, 2019; Mbonu & Ben, 2021; Samaila & Tampul, 2021), with the aid of activity concentration of ^{40}K, ^{232}Th and ^{232}U (Table 1). Results in Table 2 indicated that the absorbed dose ($nGyh^{-1}$) due to ingestion of radionuclides in the water samples ranged from 3.279±0.220 to 20.372±0.869, with the mean value of 9.461±0.802 $nGyh^{-1}$. The maximum value occurred in sample collected from Mini Ezi stream while the minimum value occurred in sample collected from Ogbodo Water front 2. The mean absorbed dose exceeded the internationally recommended safe limit of 1.0 $nGyh^{-1}$ (UNSCEAR, 2010; WHO, 2017). This also implies that the river water supplies are radiologically polluted and unfit for human consumption since they contain some radiological hazards capable of causing human health risks. The findings in this study are synonymous to the mean value of: 22.16 $nGyh^{-1}$ recorded from surface water in Eagle, Atlas and Rock cement companies in Port Harcourt (Avwiri, 2005); 1.64 $nGyh^{-1}$ recorded from Mini-Okoro/Oginigba creek (Avwiri et al., 2014); 1.521

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$nGyh^{-1}$ recorded from packaged drinking water in Ilorin and Ogbomoso (Orosun et al., 2022) and 6.68 $nGyh^{-1}$ recorded from produced water from selected flow stations in Delta State (Avwiri et al., 2013).

Annual Effective Dose Equivalent (AEDE)

The AEDE was estimated using Eq. (4): (Avwiri et al., 2014; Ereh and Zhang, 2018; Sowole and Egunjobi, 2019), with the aid of the values of the absorbed dose (Table 2). Results in Table 2 further revealed that annual effective dose equivalent in this study ($mSvy^{-1}$) ranged from 4.021±0.270 to 24.984±1.066 with mean value of 11.2851±0.962 $mSvy^{-1}$. The maximum value was recorded in sample collected from Mini-Ezi stream while the minimum value was recorded in sample from Ogbodo water front 2. The mean annual effective dose equivalent (Fig. 2) is higher than the internationally recommended safe limit of 0.1 $mSvy^{-1}$ (UNSCEAR, 2010; WHO, 2017). The water samples in this study contain some radiological hazards, and are unsafe for human consumption.

Annual Gonad Dose Equivalent (AGDE)

The AGDE (Bql^{-1}) was estimated using Eq. (5): (Eke & Emelue, 2019), with the aid of results in Table 1. Results (Table 2) showed that annual gonad dose equivalent (Bql^{-1}) due to ingestion of radionuclides in water samples ranged from 23.061±1.535 to 146.279±11.909, with mean value of 65.304±5.716 Bql^{-1}. The minimum value was recorded in samples collected from Ogbodo water front 2 while the maximum value was recorded in Mini-Ezi stream. The mean annual gonad dose equivalent exceeded the internationally recommended safe limit of 1.0 Bql^{-1}, indicating that the water samples are unsafe for consumption since they contain radiological hazards that risk human health.

Radium Equivalent (Raeq)

The Raeq (Bql^{-1}) in the water samples was estimated using Eqs. (6) and (7) (Samaila & Tampul, 2021), with the aid of results in Table 1. Results in Table 2 showed that the radium equivalent (Bql^{-1}) due to ingestion of river water samples ranged from 7.103±0.480 to 41.164±3.532, with mean value of 19.506±1.806 Bql^{-1}. The minimum value was recorded in sample collected from Ogbodo water front 2 while the maximum value was recorded in Mini-Ezi stream. The mean radium equivalent is below the internationally recommended limit of 370 Bql^{-1} (UNSCEAR, 2010). Though this value does not pose immediate health risk to humans, but might occur later as a result of continuous exposure to radiation.

Excess Lifetime Cancer Risk

The excess lifetime cancer risk due to intake of water samples from New Calabar River was estimated using Eq. (8): (Avwiri et al., 2014; Samaila & Tampul, 2021), with the aid of results in Table 1. Results (Tab. 2) showed that the excess lifetime cancer risk ranged from 14.673±0.945 to 87.444±3.731E-3, with mean value of 39.550±3.343 E-3. The maximum value was obtained in sample collected from Mini-Ezi stream and minimum in sample collected from Ogbodo water front 2. The mean excess lifetime cancer risk is above the internationally recommended safe limit of 0.29 E-3. This implies that the water sample under study are radiologically polluted and unsafe for human consumption. This finding is similar to 38.552 E-3, 52.072 E-3 and 30.189 E-3 mean values obtained from surface water samples in Ogba/Egbema/Ndoni Local Government Area (Ononugbo et al., 2013) for infants, children and adults respectively.

Conclusion

This study assesses the radiological hazards associated intake of radioelement: ^{40}K, ^{232}Th and ^{232}U in water samples from the new Calabar river, Rivers State, Nigeria. The water samples were analyzed in the laboratory with the aid of sodium Iodide (NaI) gamma ray detector, and the activity concentration of the radioelements were obtained. The study revealed that the mean activity concentration of the radionuclides is above the internationally recommended safe limits of 10.0, 0.10 and 10.0 Bql^{-1} for **K-40**, **232-Th** and **232-U** respectively. The mean TAED in infants, children and adults due to ingestion of radionuclides in water samples exceeded the internationally recommended safe limits of 0.26, 0.20 and 0.10 $mSvy^{-1}$ respectively. The mean: absorbed dose, annual effective dose equivalent, annual gonad dose equivalent and excess lifetime cancer risk exceeded their respective internationally recommended safe limits of 1.0 $nGyh^{-1}$, 0.1 $mSvy^{-1}$, 1.0 Bql^{-1} and 0.29 E-3 respectively. These imply that the water supplies are radiological contaminated, polluted and harmful since they contain radiological hazards capable of causing health risks on consumers. The mean radium equivalent is below the internationally recommended limit of 370 Bql^{-1} (UNSCEAR, 2010). Though, this value doesn't pose immediate health risk to humans, but it's most likely to occur as a result of continuous exposure to radiation. Generally, the water samples under study are considered unsafe for human consumption since the mean values of all radiological parameters considered are above internationally recommended safe limits, except that of radium equivalent.

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Recommendations

Provision of alternative, clean, and good drinking by government, especially at the local level, Non-Government Organizations (NGO), and philanthropists are recommended for the inhabitants of the study area.

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