Determination of Radionuclide Concentrations, Hazard Indices and Physiochemical Parameters of Water, Fishes and Sediments in River Kaduna, Nigeria

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Abstract: The radionuclide concentrations in fishes, water and sediments were analyzed using the (NaI) gamma-ray spectrophotometer and from the activity concentrations their radiological health indices were mathematical computed and the physiochemical parameters of River Kaduna, Nigeria were also carried out. The result of the physiochemical parameters analysed in the river showed that BOD had mean value of 0.070mg/L ± 0.003, COD mean value was 3.84 ± 0.07mg/L, TSS obtained was 0.018 mg/L ± 0.023, Conductivity and TDS mean results were 0.38 ± 0.001 mScm and 0.18 ± 0.026 mg/l respectively while the pH and temperature were 6.70 ± 0.01 and 24.00 ± 0.04°C respectively. The results of the samples analysed showed that the activity concentrations of $^{226}$Ra in fishes was 3.83±0.44 Bq/Kg, in water was 29.85±0.32 Bq/L and in sediments was 23.97±1.60Bq/Kg, $^{40}$K was 149.78±5.041 Bq/Kg, 32.18±0.322 Bq/L, 52.61±0.965 Bq/Kg for fish, water, sediment respectively. $^{232}$Th was 11.4025±0.9437 Bq/Kg, 68.53±0.0786 Bq/Kg, 15.57±0.4325 Bq/L for fishes, sediment and water respectively. Radium equivalent dose, absorbed dose rate and annual gonad equivalent dose mean results were 70.76Bq/Kg, 31.62Gy/h¹ and 217.01mSvyr⁻¹ respectively. Internal and external hazard mean indices were 0.24 and 0.19 respectively. However, the results are below the control samples obtained. This showed that the water, fishes and sediments are within the ICRP/UNSCEAR standards and minimal or no anthropological radiological degradation.

Keywords: Radionuclide, Hazard Indices, River Kaduna, Sediments, Gamma ray spectroscopy.

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I. Introduction

In many developing countries like Nigeria, soils and aquatic environments are affected by mine waste disposal, acid deposition, sewage, sludge and other anthropogenic activities. Radioactive materials can enter water in several ways by being deposited in surface water from the air, by entering ground water or surface water from the ground through erosion, seepage or human activities such as mining, farming, industrial activities and by dissolving from underground mineral deposits as water flows through them. Natural radiations are the major contributor of ionizing radiation in the environment [1]. Natural occurring radioactive materials (NORM) such as $^{226}$Ra, $^{232}$Th and $^{40}$K in the environment are due to bedrock formations which are weathered resulting in mineral leaching that leads to contamination. Others includes, releases from fertilizers, agrochemicals, research and medical facilities and mines, these form the bulk of radionuclides in ground and surface water [1].

The radiological implication of these radionuclides is due to gamma exposure of the body and irradiation of the human populace, as well as the environment. Therefore, the assessment of radionuclides from natural sources is of particular importance as natural radionuclides are the largest contributor to the external dose of world population.

Furthermore, since naturally occurring radioactive materials can contaminate the environment and pose a risk to human health. The estimation of the radiation dose distribution is vital in assessing the health risks and serve as a reference for documenting changes in environmental radioactivity due to anthropogenic activities [2].

Hence, the inquisitions for knowledge of radiological health hazard indices in the environment is basically to enable one arrive at a scientific acceptable inference and conclusion regarding health status and risks associated with impacted environment. An increment in the radiological burden leads to health issues associated with ionizing radiation [3].
II. Map Of River Kaduna

III. Materials and method

3.1 Description of the study area

3.1.1 River: The Kaduna River

Kaduna River is located at (Lat.10.52° N, Long 7.44° E) and it occupies the central position of the northern Nigeria. Kaduna River originates from the Kujuma hills in Plateau Nigeria and flows for 210km before reaching Kaduna town and stretches down 100km into the shiroro dam project areas where it finally empties into River Niger [4]. A storage reservoir is built at the Kagimi dam in the northern part of the city off the Kaduna – Jos highway. It is the main water supply source for Kaduna town and industries and serves various purposes; domestic, fishing and industrial uses, also peasant farmers along the coast of the river use water from the river to irrigate their food crops especially vegetables during the dry season. There are six major drains that discharge effluents into Kaduna River, these are:

1. Romi drain: This drain contains effluents from a refinery, paper factory, automobile industry, bottling and brewing operations.
2. Makera drain: This drain contains effluents from textile and bottling operation.
3. Kakuri drain: This drain contains effluents from textiles and fertilizer industries.
4. Rafin dai drain: This drain contains effluents from brewing and flour milling activities.
5. Rigasa drain: This drain contains effluent from glass and chemical plants.
6. Nasarawa drain: This drain consists for domestic effluents [5]

3.2 Materials

3.2.1 Lists of materials

Mortar and pestle, Aluminum foil, Sieving mesh (2mm), Masking tape, Plastic containers, Conical flask (250 mL), Beakers (250 mL), Crucibles, Candle, wax/ Vaseline.

3.2.2 List of equipments

pH meter (Hanna instrument), Conductivity meter (model DDS 307), Analytical weighing balance (Mettler AE 166), Oven (Cole Medical England Vol AC 220v/50Hz 0607034), Gamma ray spectrophotometer (NaI) TI

3.2.3 List of Chemicals and their assay

The chemical and reagents were manufactured by British drug house limited.
Sulphuric acid ------------ purity 98%, specific gravity 1.84 g/cm³
Phosphoric acid ------- purity 80%, specific gravity 1.63 g/cm³
Phenanthroline Ferroin indicator
Ferrous ammonium sulphate solution
Potassium dichromate solution

IV. Sampling

The water and sediments sampling were done at various point source along the Kaduna river. Two species of fish (Cat fish and Tilapia fish) were collected from the river. The fishes were of same approximate size and length of about 30 cm long and 5 - 7 cm wide to establish the age limit.

4.1 Fish sample preparation

The fresh fish samples collected were carefully kept in plastic containers with ice to keep the temperature at less than 5 °C and labeled before being transported to the laboratory for identification. The fishes were oven dried at 80 °C ± 5 °C. The dried fish samples was then pulverized to fine texture using mortar and pestle, then 200g was weighed and packed in plastic containers and carefully sealed with vaseline and candle wax for 4 weeks in order to establish secular radioactive equilibrium between the natural radionuclides and their respective progenies before it was analysed using the gamma-ray spectrophotometer.

4.2 Sediment sample preparation

Sediment samples were obtained from point sources along the rivers. At each point sediment samples were taken superficially by using pre-cleaned disposable plastic containers and packed separately in polythene bags. The samples were transported to the laboratory and air-dried in the laboratory at room temperature to reduce the moisture and then oven dried at 105 °C to constant weight and then grounded using mortar and pestle and sieved to fine texture of ≤ 2mm diameter. About 200g of the sediment was then measured and stored in plastic containers, sealed with Vaseline, candle wax and masking tape for about twenty eight (28) days in order to allow for Ra and its short lived progeny to attain secular equilibrium before analyses using the gamma-ray spectrophotometer.

4.3 Water sample preparation

About 100 mL of water sample were collected from different point source along the Kaduna river using clean prewashed container with screw caps and homogenously mixed before 200 mL was measured and stored for 28 days in order to establish secular radioactive equilibrium between the 226Ra and its respective progenies before analysed using the gamma-ray spectrophotometer. The physiochemical parameters of the water sample collected were carried out at the Nigeria Defence Academy chemistry laboratory except for the pH and temperature which were done in-situ.

V. Principles of gamma ray spectrometer (NaI) TI

The radiological analysis was carried out using a 76 x 76mm NaI (Tl) detector crystal optically coupled to a photomultiplier tube (PMT). The assembly has a preamplifier incorporated into it and a 1kilovolt external source. The detector is enclosed in a 6cm lead shield with cadmium and copper sheets. This arrangement is aimed at minimizing the effects of background and scattered radiation.

The data acquisition software is Maestro by Canberra Nuclear Products. The samples were measured for a period of 29000 seconds, for each sample. The spectrometer was calibrated against reference material with known activity concentration of 40K, 226Ra, 232Th. 40K was measured directly using its 1460 keV gamma ray line whereas 226Ra and 232Th were measured using the photo peaks of their respective progenies: 214Bi (1760 keV) and 208Ti (2615 keV). The peak area of each energy in the spectrum was used to compute the activity concentrations in each sample by the use of the following equation:

\[
C \left( \text{Bq.kg}^{-1} \right) = \frac{C_n}{C_{nk}} \tag{7}
\]

Where,

\[
C = \text{activity concentration of the radionuclides in the sample given in Bq/Kg}
\]

\[
C_n = \text{count rate (counts per second)} \quad \text{Net Count}\quad \text{Count per second (cps)} = \frac{\text{Net Count}}{\text{Live Time}}
\]

\[
C_{nk} = \text{Calibration factor of the detecting system.}
\]
VI. Radiological Parameters

6.1 Radium equivalent index (Raeq)
This is a radiological index which represents the activity levels of $^{226}$Ra, $^{232}$Th and $^{40}$K by a single quantity and also takes into account the radiation hazards associated with them. It is mathematically defined by [8] as:

$$Ra_{eq} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_{K}}{4810}$$

Where: $C_{Ra}$, $C_{Th}$, and $C_{K}$ are the activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K respectively. In the above relation, it has been assumed that 10 Bqkg$^{-1}$ of $^{226}$Ra, 7 Bqkg$^{-1}$ of $^{232}$Th and 130 Bqkg$^{-1}$ of $^{40}$K produce equal gamma dose. The maximum value of Ra$_{eq}$ in soil must be less than 370 Bqkg$^{-1}$ [8] otherwise it is regarded as being above standard.

6.2 External hazard index (H$_{ex}$)
External hazard index is a widely used hazard Index which represents the external exposure and it is defined by [8] as:

$$H_{ex} = \frac{C_{Ra}}{370} + C_{Th}/259 + C_{K}/4810$$

6.3 Internal hazard index (H$_{in}$)
In addition to external hazard index, radon and its short-lived products are also hazardous to the respiratory organs. The internal exposure to radon and its daughter progenies is quantified by the internal hazard index H$_{in}$, which is given by the equation:

$$H_{in} = \frac{C_{Ra}}{185} + \frac{C_{Th}}{259} + \frac{C_{K}}{4810}$$

The values of the indices (H$_{ex}$, H$_{in}$) must be less than unity for the radiation hazard to be negligible [9].

6.4 Absorbed dose rate (D)
Absorbed dose rate is a measure of energy deposited in a medium by ionizing radiation. It is equal to the energy deposited per unit mass of the medium, and so has the unit J/kg. Absorbed dose rate therefore is absorbed dose divided by the time it takes to deliver that dose unit Gy/s. The absorbed dose rates in outdoor (D) due to gamma radiations in air at 1m above the ground surface for the uniform distribution of the naturally occurring radionuclides ($^{226}$Ra, $^{232}$Th and $^{40}$K) were calculated based on guidelines provided by [8]. The conversion factors used to compute absorbed - dose rate (D) in air per unit activity concentration in Bq/kg (dry weight) corresponds to 0.462 nGy/h for $^{226}$Ra (of U – series), 0.621 nGy/h for $^{232}$Th and 0.0417 nGy/h for $^{40}$K [8] [10].

$$D (nGy/h) = 0.462 C_{Ra} + 0.621 C_{Th} + 0.0417 C_{K}$$

6.5 Annual gonad equivalent dose (AGED)
This is a measure of threat to sensitive cells from exposure to a particular level of radiation. These sensitive cells include the gonads, surface cells and the bone marrow. Annual gonad equivalent dose is calculated using the equation [3].

$$AGED (mSvyr^{-1}) = 3.09 C_{Ra} + 4.18 C_{Th} + 0.314 C_{K}$$

Where: $C_{Ra}$, $C_{Th}$, and $C_{K}$ are activity concentrations of $^{226}$Ra, $^{232}$Th, and $^{40}$K respectively.

VII. Physico-Chemical Parameters

7.1 Chemical Oxygen Demand (COD)
A portion of sample (10 mL) was measured using measuring cylinder into refluxing flask. 5 mL of 0.42M potassium dichromate solution was then measured and added into the flask followed by 10-15 mL concentrated sulphuric acid and 0.5 mL of silver sulphate and then swirled to mix. The bottom of the flask was immersed in a water bath to allow it cool, since it is an endothermic reaction.

Sample was then refluxed on the hot plate for 2 hours and allowed to cool at room temperature, 50 mL of distilled water was added followed by addition of 2-5 drops of phenanthroline ferroin indicator and swirled. It was then titrated against 0.25 mol.dm$^{-3}$ ammonium sulphate solution from blue green to reddish brown [11]. From the result COD was calculated using the formula.

$$COD \text{ mg/l} = (A – B) \times M \times 8000$$

Volume of Sample taken

Where A= volume of blank, B= volume of sample, M= molarity of ferrous ammonium sulphate.

7.2 Biochemical Oxygen Demand (Winkler methods)
200 mL of the sample was measured using the measuring cylinder into a 250 mL BOD bottle and then wrapped in a black polythene bag and then kept in a cupboard for 5 days without light interferances.
After incubating for 5 days, on the 5th day 2 mL of manganese chloride was added and 2 mL of alkaline iodide (a mixture of potassium iodide KI and sodium hydroxide NaOH) and then swirled to mix. 2 mL of concentrated sulphuric acid was then added followed by 2 – 3 drops of starch indicator. The solution was then titrated against sodium thiosulphate solution (0.25mol.dm⁻³) till the solution became colorless indicating the end point. From the results obtained, BOD was then calculated using the formula;

\[ \text{BOD mg/L} = \frac{D_1 - D_0}{\text{Vol sample}} \]

Where, \( D_1 \) = Dissolved oxygen after 5 days; \( D_0 \) = Dissolved oxygen on first day at lab; Vol. sample = Volume of sample used.

### 7.3 Measuring pH of a liquid using a pH meter

The pH of the sample was measured using pHep pocket size pH meter in-situ. Prior to use, it was rinsed with deionized water and immersed into the sample already taken in a container. Reading was taken when the reading on the meter stabilizes [12]

### 7.4 Measurement of Electrical Conductivity and Total Dissolved Solid (EC and TDS)

The electrical conductivity and total dissolved solids was measured using conductivity meter of model DDS 307. Prior to use, the electrical conductivity meter was calibrated by measuring the conductivity of a standard solution of known conductivity (distilled water). The probe was rinsed thoroughly before and after calibration using deionized water and carefully blotted. Enough sample of the water was collected in a beaker so that the probe tip can be submerged in the sample; Readings on the meter was taken while the meter stabilized [13].

### 7.5 Measurement of Total Suspended Solids

The TSS was determined by recording the increase in weight of the dried filter paper with pore size of 5 μm after 100 mL of the sample was measured and filtered through it after which the filter paper was oven dried at 110 °C and weighed until a constant weight is obtained [13]. The TSS was calculated using the formula;

\[ \text{TSS} = \left[ \frac{(A - B)}{C} \right] \times 1000 \text{ mg/L} \]

Where \( A \) = weight of filter + solids (g); \( B \) = weight of filter (g); \( C \) = volume of sample filtered (mL).

### VIII. Results

Results are shown in table 1 – 3 below. Table 1 shows the activity concentration of radionuclides while table 2 shows the calculated radiological hazard indices at River Kaduna. Table 3, shows the results of the physiochemical parameters.

#### TABLE 1: Activity concentration of radionuclide’s of $^{226}$Ra, $^{40}$K, $^{232}$Th at River Kaduna

<table>
<thead>
<tr>
<th>S/N</th>
<th>Sample ID</th>
<th>K-40 (Bq/Kg)</th>
<th>Error± (Bq/Kg)</th>
<th>Ra-226 (Bq/Kg)</th>
<th>Error± (Bq/Kg)</th>
<th>Th-232 (Bq/Kg)</th>
<th>Error± (Bq/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fish</td>
<td>149.78</td>
<td>5.04</td>
<td>3.84</td>
<td>3.44</td>
<td>11.40</td>
<td>0.94</td>
</tr>
<tr>
<td>2</td>
<td>Water</td>
<td>32.18</td>
<td>0.32</td>
<td>29.85</td>
<td>0.32</td>
<td>15.57</td>
<td>0.43</td>
</tr>
<tr>
<td>3</td>
<td>Sediment</td>
<td>52.61</td>
<td>0.97</td>
<td>23.97</td>
<td>1.59</td>
<td>68.53</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>Control</td>
<td>926.96</td>
<td>10.14</td>
<td>34.56</td>
<td>6.87</td>
<td>16.87</td>
<td>11.25</td>
</tr>
<tr>
<td>5</td>
<td>World standard</td>
<td>≤ 400</td>
<td>≤35</td>
<td>≤30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### TABLE 2: Calculated hazard indices at River Kaduna

<table>
<thead>
<tr>
<th>S/N</th>
<th>Kaduna fish</th>
<th>Ra eq (Bq/Kg)</th>
<th>External hazard index (Hex)</th>
<th>Internal hazard index (Hin)</th>
<th>Absorbed Dose rate (D) nGy⁻¹</th>
<th>AGED mSvyr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Kaduna fish</td>
<td>31.68</td>
<td>0.09</td>
<td>0.09</td>
<td>14.99</td>
<td>106.55</td>
</tr>
<tr>
<td>2</td>
<td>Kaduna sediment</td>
<td>126.03</td>
<td>0.34</td>
<td>0.41</td>
<td>55.21</td>
<td>377.07</td>
</tr>
<tr>
<td>3</td>
<td>Kaduna water</td>
<td>54.59</td>
<td>0.15</td>
<td>0.23</td>
<td>24.66</td>
<td>167.42</td>
</tr>
<tr>
<td>4</td>
<td>Average value</td>
<td>70.76</td>
<td>0.19</td>
<td>0.24</td>
<td>31.62</td>
<td>217.01</td>
</tr>
<tr>
<td>5</td>
<td>Control</td>
<td>130.06</td>
<td>0.35</td>
<td>0.45</td>
<td>64.95</td>
<td>468.37</td>
</tr>
<tr>
<td>6</td>
<td>World standard</td>
<td>≤370</td>
<td>1.00</td>
<td>1.00</td>
<td>60.00</td>
<td>300.00</td>
</tr>
</tbody>
</table>

#### TABLE 3: Physiochemical parameters

<table>
<thead>
<tr>
<th>PARAMETERS</th>
<th>River Kaduna</th>
<th>WHO</th>
<th>FEPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD (mg/L⁻¹)</td>
<td>0.070 ± 0.003</td>
<td>10.000</td>
<td>10.000</td>
</tr>
<tr>
<td>Conductivity mS.Cm⁻¹</td>
<td>0.380 ± 0.001</td>
<td>3000</td>
<td>4000</td>
</tr>
<tr>
<td>TSS (mg/L⁻¹)</td>
<td>0.018 ± 0.023</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>24.00 ± 0.04</td>
<td>25-30</td>
<td>&lt;40</td>
</tr>
</tbody>
</table>
The gamma-ray spectrometric analysis for all the samples showed that the activity concentration for $^{40}$K in fish, water and sediment sampled were 149.78 Bq/Kg, 32.18 Bq/Kg and 52.61 Bq/Kg respectively with an average mean value of 78.19 Bq/Kg. That of $^{226}$Ra was 3.84 Bq/Kg, 29.85 Bq/Kg and 23.97 Bq/Kg for the fish, water and sediment samples respectively with an average mean value of 19.22 Bq/Kg. The activity concentration of $^{232}$Th was 11.40 Bq/Kg, for the fish, 15.57 Bq/Kg for water and 68.53 Bq/Kg for the sediments with an average mean value of 31.84 Bq/Kg. From all the samples results assayed, $^{232}$Th is observed to be higher than the world set standard 30 Bq/Kg [8] and this could be attributed to the high use of fertilizers in the surrounding farms, variation in geological structure and abundance of radioactive thorium minerals such as monozite, zircon and thorianites [14]

In the environment $^{232}$Th are very radiotoxic and carcinogenic, they substitute for Ca in the bones and teeth. Long term exposure increases the chances of developing lung diseases and lung, pancreas and bone cancer.

From table 2, the values of the radiological hazard indices show that the radium equivalent activity for the fish, water and sediment samples were 31.68 Bq/Kg, 54.59 Bq/Kg and 126.03 Bq/Kg respectively with an average mean value of 70.76 Bq/Kg. The mean values of the external and internal hazard index and the absorbed dose rates are 0.19, 0.24 and 31.62 nGyh$^{-1}$ respectively. Furthermore, the annual gonad equivalent dose has a mean average of 217.01 mSvyr$^{-1}$. This is in agreement with the results reported by [15] where 187.2 Bq/Kg, 0.51, 85.3 nGyh$^{-1}$ were obtained for the radium equivalent dose, external hazard index and absorbed dose rate respectively. This indicates that the results obtained are within the permissible limits recommended by the ICRP/UNSCEAR; hence, Fishes, water and soils from this river is safe for use and consumption.

The values of the physiochemical water quality parameters of river Kaduna area presented as shown in table 3 above. Also presented in the table are the standard safe limits of the determined physiochemical parameter as recommended by to the international body, the World Health Organization and Federal Environmental Protection Agency. As can be observed from table 3, the pH obtained was 6.7 ± 0.01, which falls within the internationally accepted standard of 6.5 - 8.5 for water. The concentration of the total suspended solids (TSS) was 0.018 ± 0.023 mgL$^{-1}$, this is much lesser than the specified safe limit of 10 mgL$^{-1}$ by WHO and FEPA and this low level is an indication that there is no significant influence on turbidity. The total dissolved solid concentration is related to the conductivity. The low TDS concentration of 0.18 observed indicated low conductivity levels were 0.38 ± 0.001 mS.cm$^{-1}$ was obtained. The Bio-chemical Oxygen Demand and Chemical Oxygen Demand were 0.070 ± 0.03mgL$^{-1}$ and 3.84 ± 0.07 mgL$^{-1}$ respectively. These low values obtained suggest that the River contains low organic load which support aquatic life. The temperature obtained was 24.0 ± 0.02°C, which puts it well within the range set accepted internationally.

### IX. Discussions

The radionuclide’s concentrations, radiological hazard indices and physiochemical properties were estimated in water, fish and sediment samples from river Kaduna. The results showed that the activity concentrations were within the permissible limits except for $^{232}$Th concentration in the sediment samples. The hazard indices results obtained are within the international set standards of ICRP and UNSCEAR except for the sediment where 377.07 mSvyr$^{-1}$ was obtained.

The physiochemical water quality parameter for the water sample, BOD, COD, TDS, TSS, pH, conductivity and temperature were within the acceptable limits indicating that the radionuclide concentrations have no significant effect on the water quality.

### X. Conclusion

The authors are grateful for the support and technical co-operation provided by the Center for Energy Research and Training (CERT), Zaria and Nigeria Defence Academy, Kaduna for giving us access to their facilities to use during this research.
References


