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Activity and Mass Concentration of ^{226}Ra, ^{228}Ra and ^{232}Th in Groundwater around the Zona Uranium Occurrence, Peta Gulf Syncline, Northeast Nigeria

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Abstract In this study, eighteen groundwater samples were collected from wells in villages around Zona, an area reported to host uranium mineralization and these were analyzed for mass/activity concentration of ^{226}Ra, ^{228}Ra and ^{232}Th. Consumption of groundwater with elevated levels of ^{226}Ra, ^{228}Ra and ^{232}Th may result to cancer, kidney and/or developmental defects in humans and other animals. The results obtained were compared for compliance with international guidelines for radionuclides in drinking water. Results of the study showed that activity concentration of ^{226}Ra, ^{228}Ra and mass concentration of ^{232}Th ranged from 0.05 to 6.7pCi/L, 0.2 to 4.8pCi/L and 0.02 to 1.10µg/L, respectively. The higher levels of ^{226}Ra in the studied samples compared with ^{228}Ra in same sample might be as a result of ^{226}Ra being part of ^{238}U decay series as a results of which ^{226}Ra is found over wide range of aquifer, it might also be an indication of secondary mineralization of uranium. Based on international guidelines regulating these radionuclides in groundwater, levels recorded at the time of the study fall within permissible limits of 20pCi/L for ^{226}Ra and ^{228}Ra while ^{232}Th which is insoluble in water, therefore, has no regulated limit. All radionuclides analyzed fall within international guideline despite occurrence of uranium mineralization in the study area.
Keywords *Activity Mass Concentration, Radionuclides, Ionizing Radiation*

1. Introduction

Regulating radionuclide levels in drinking water is gradually receiving global attention because of its health implications. In developing countries, the major health threat from water contamination has been bacterial and viral infection. However, for several decades now chemicals and radiological aspect of drinking water quality are receiving attention. Water can be radioactive due to the presence of naturally occurring radionuclides (NORs), which originates from the earth's crust, and are widely

distributed in the environment; in water, soils, rocks and air. Exposure to radioactivity increases the risk of various cancer cases to humans. Radon gas, Polonium, Lead and Bismuth increase the risk of lungs and stomach cancer, uranium and thorium increase toxicity risks to the kidneys and bones while radium increases the risk of bone cancer (bone sarcomas) and head carcinomas.

It is imperative to investigate the mass/activity concentration levels of these radionuclides in groundwater supply of the area because of the reported uranium occurrence. Because, once exposure is insured, it is not reversible; therefore, prevention is the best approach.

In this study, eighteen water samples were collected from wells in villages around Peta Gulf Syncline in the Upper Benue trough, northeastern Nigeria (Figure 1) and analyzed for mass/activity concentration of ^{226}Ra, ^{228}Ra and ^{232}Th. The results were compared for compliance with international guidelines for radionuclides in drinking water.

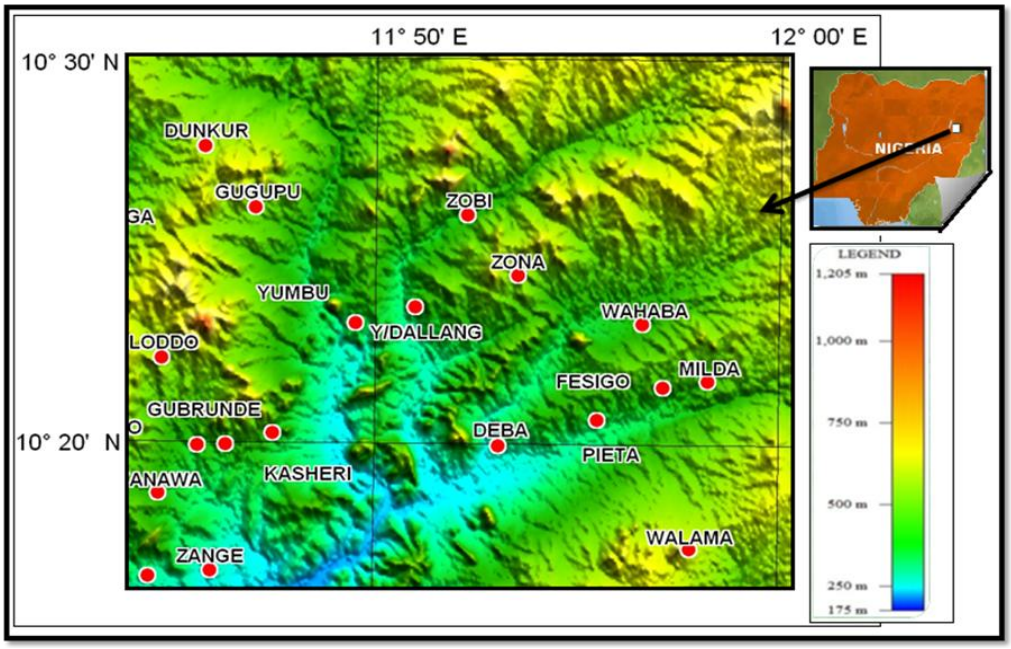

Figure 1: *Digital Elevation Model of the Study Area Showing Sampled Points [Inset is a Map of Nigeria Showing Location of the Study Area (Globalmapper 13)]*

The Peta Gulf Syncline is a fault bounded pull-apart sub-basin filled with the Bima Formation (Lower Cretaceous) which has three siliclastic members: (i) B_1: medial fan coarse-grained to micro-conglomeritic sandstones; (ii) B_2: full fluvial median-grained sandstones with minimal fines, and (iii) B_3: lacustrine and flood basin deposits comprising alternating fine-grained sand stone and siltstone/claystone (Suh *et al.,* 2000). According to Suh *et al*. (2000), the only significant uranium occurrence in the Peta Gulf Syncline is found around Zona (Zona uranium anomaly). Other localized mineralization around has been reported by Arabi *et al.* (2012), Elegba *et al*. (1993), Funtua *et al*. (1985; 1988; 1992; 1997) and Okujeni *et al*. (1987; 1990; 1994) around Gubrunde, Kanawa and Dali (all around the study area).

2. Materials and Methods

Groundwater samples were collected from eighteen hand dug wells, the dominant source of water for domestic activities in the area using standard procedure described in EPA water sampling protocol (EPA, 2004). The sites sampled were selected in a manner that covers all localities surrounding the entire areas reported to host uranium mineralization. In order to have a fresh sample from each well,

the well was purged for about fifteen minutes before sampling. The low density plastic bottles in which samples were collected were washed with distilled water followed by second washing with the sample before it was filled at a minimum flow. A sampling reproducibility test was performed *in-situ* by measuring five successive samples from same site and the results showed no deviation. Procedures adopted for analysis of Radium and Thorium is detailed in Eichrom procedures (Eichrom, 2006; Moon et al., 2003).

The test method is based on the utilization of solid phase extraction of radium from water samples. The detection of the ^{226}Ra is by alpha spectrometry and ^{228}Ra via ^{228}Ac by gas flow proportional beta counter.

An aliquot of the sample is measured into a beaker; barium carrier and ^{133}Ba were added. Radium and Barium were sorbed on an ion exchange column, eluted, evaporated to dryness, and dissolved in 0.095M HNO_3. The dissolved solution was loaded on solid phase extraction column. ^{228}Ac was selectively sorbed on a solid phase extraction column, while ^{226}Ra and ^{133}Ba passed through the column. ^{228}Ac was eluted with 0.35M HNO_3, and is precipitated with cerium fluoride. The precipitate was collected on a filter paper and counted for beta radiation. ^{226}Ra and ^{133}Ba were collected and precipitated with barium sulfate. The precipitate was collected on a filter. ^{133}Ba was counted using a gamma counter while Ra-226 is counted via alpha spectrometry.

The relation given below was used to calculate ^{228}Ra activity:

$$^{228}\text{Ra (pCi/L)} = \frac{A}{2.22 \times E \times V \times Y \times e^{-\lambda t2}} X \frac{\lambda t_2}{1-e^{-\lambda t_2}}$$

Where:

A = Net count rate, cpm
E = Counting efficiency expressed as fraction
Y = ^{133}Ba (Ra) yield expressed as fraction
V = Sample volume (liters)
t_1 = Decay time of ^{228}Ac, from start of rinse until start of counting (minutes)
t_2 = Counting time (minutes)
λ = Decay constant of ^{228}Ac ($1.88*10^{-3}$ min^{-1})

While for ^{226}Ra activity, the relation given below was used

$$^{226}\text{Ra (pCi/L)} = \frac{S - B}{2.22 \times E \times V \times Y}$$

Where:

S = Sample counts per minute
B = Background counts per minute
E = Efficiency of counter
V = Volume of samples in liters
Y= ^{133}Barium yield.

Thorium was separated from uranium by Eichrom resins (Horwitz, E.P., 1993; Horwitz, E.P., 1992; Kressin, I.K., 1977; Maxwell, S.L., 1993; Nelson, D., 1992) prior to measurement by alpha Spectrometry as described in Eichrom, 2001. A calcium phosphate precipitation technique was used to concentrate and remove actinides from water samples. Tracer was used to monitor chemical

recoveries and correct results to improve precision and accuracy. In this work, 97% chemical recovery achieved.

3. Results and Discussion

The result for samples analyzed is shown in Table 1 and Figure 2. Results for Radium are presented in pCi/L and Bq/L. The highest ^{226}Ra activity concentration (6.7pCil/L) was recorded at Yimirdallang (Figure 2, Table 1 (Y/DALLANG)), some few kilometers southwest of the Zona uranium mineralized area.

Table 1: *Radionuclides Levels in Groundwater of the Study Area*

S/N	Latitude	Longitude	^{226}Ra (pCi/L)	^{226}Ra (Bq/L)	^{228}Ra (pCi//L)	^{228}Ra (Bq//L)	^{232}Th (µg/L)
1	$10^0$16'.4	$11^0$45'.6	1.8±0.0486	0.0666	1±0.025	0.037	0.11±0.013
2	$10^0$23'.3	$11^0$50'.6	4.3±0.116	0.1591	2.9±0.073	0.1073	0.08±0.002
3	10021.4	$11^0$58'.2	0.9±0.0243	0.0333	0.3±0.008	0.0111	0.07±0.001
4	10020.4	$11^0$55'.3	0.7±0.0189	0.0259	0.3±0.008	0.0111	0.63±0.012
5	10019.6	$11^0$53'.0	6.7±0.1809	0.2479	4.2±0.105	0.1554	0.04±0.001
6	$10^0$24'.2	$11^0$53'.3	1.5±0.0405	0.0555	1.2±0.03	0.0444	0.05±0.001
7	$10^0$23'.3	$11^0$50'.6	0.6±0.0162	0.0222	0.1±0.003	0.0037	0.02±0.001
8	$10^0$23'.1	$11^0$49'.3	0.3±0.0081	0.0111	<dl		0.03±0.001
9	$10^0$23'.1	$11^0$41'.5	1±0.027	0.037	0.2±0.005	0.0074	0.3±0.006
10	$10^0$26'.4	$11^0$41'.3	1.5±0.0405	0.0555	0.7±0.018	0.0259	0.15±0.003
11	$10^0$22'.1	$11^0$44'.4	2±0.054	0.074	1±0.025	0.037	0.11±0.002
12	$10^0$19'.6	$11^0$46'.2	2.1±0.0567	0.0777	1.6±0.04	0.0592	1.1±0.021
13	$10^0$20'.1	$11^0$47'.3	0.9±0.0243	0.0333	1±0.025	0.037	0.05±0.001
14	$10^0$19'.5	$11^0$45'.4	0.2±0.0054	0.0074	<dl		0.02±0.001
15	$10^0$16'.0	$11^0$40'.5	1±0.027	0.037	0.5±0.013	0.0185	0.22±0.004
16	$10^0$21'.3	$11^0$57'.1	0.9±0.0243	0.0333	0.2±0.005	0.0074	0.31±0.006
17	$10^0$23'.1	$11^0$56'.4	0.7±0.0189	0.0259	<dl		0.07±0.001
18	$10^0$17'.2	$11^0$57'.5	4.2±0.1134	0.1554	3.3±0.083	0.1221	0.04±0.001

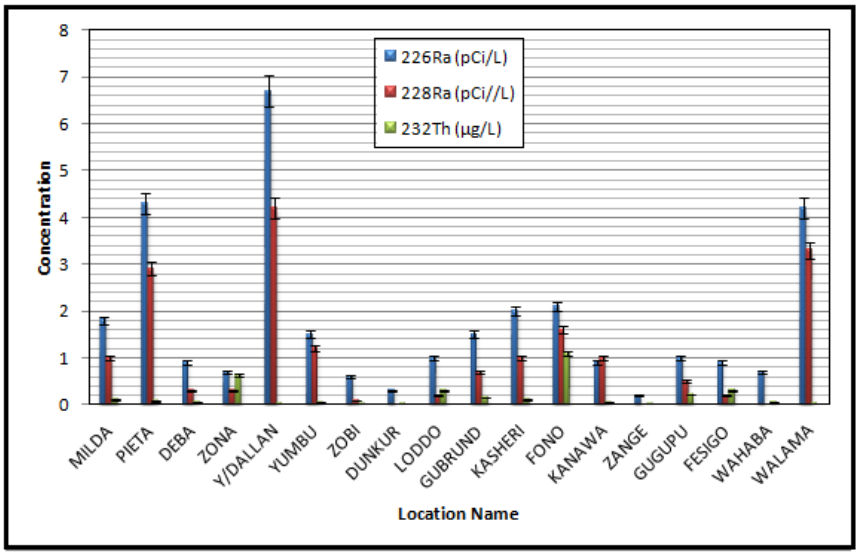

Figure 2: *A Graph of Levels of Studied Radionuclide in Groundwater of the Study Area*

As can be seen on the map of configuration of water table and groundwater flow direction (Figure 6), the high ^{226}Ra activity concentration (Figure 3) might have originated from the Zona uranium mineralized area and transported to this area by groundwater as indicated by the flow direction (Figure 6). Analytical protocol specified by the U.S. Environmental Protection Agency (USEPA) in the interim regulations of 1996 recommends that if ^{226}Ra in drinking water exceed 3pCi/L, then the sample is tested for ^{228}Ra. Current WHO guidelines have set ^{226}Ra and ^{228}Ra maximum contaminant limits at 20pCi/L.

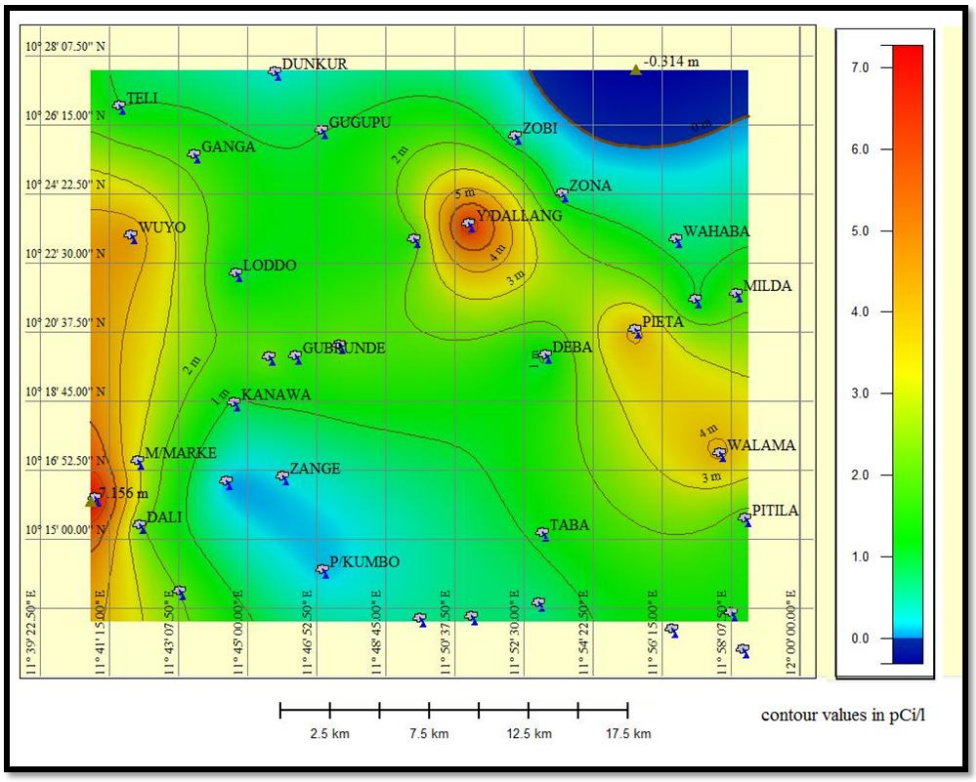

Figure 3: *Map of ^{226}Ra Activity Concentration in Groundwater of the Study Area (Contour Values are in pCi/L)*

The setting of separate guideline value for Radium by USEPA was because Radium is believed to be the most radiotoxic of the radionuclides in drinking water (Cothern, 1987). Of all the samples studied, only two (Pieta and Yimirdallang) had ^{226}Ra >3pCi/L (Figure 3) which requires test for ^{228}Ra according to the EPA regulation of 1996.

The activity concentrations of Radium (Figures 3 and 4) in all the studied water samples fall below the EPA's MCL of 20pCi/L for both ^{226}Ra and ^{228}Ra. This means that based on Radium concentration in the studied samples, all the studied water sample are Radium compliant. Thorium levels recorded in the studied groundwater samples ranged from below the detection limit to 1.1µg/L (Table 1, Figure 5). Thorium is not a regulated contaminant in the WHO, EPA and NIS guidelines and therefore, no health guidelines were proposed for it by these bodies.

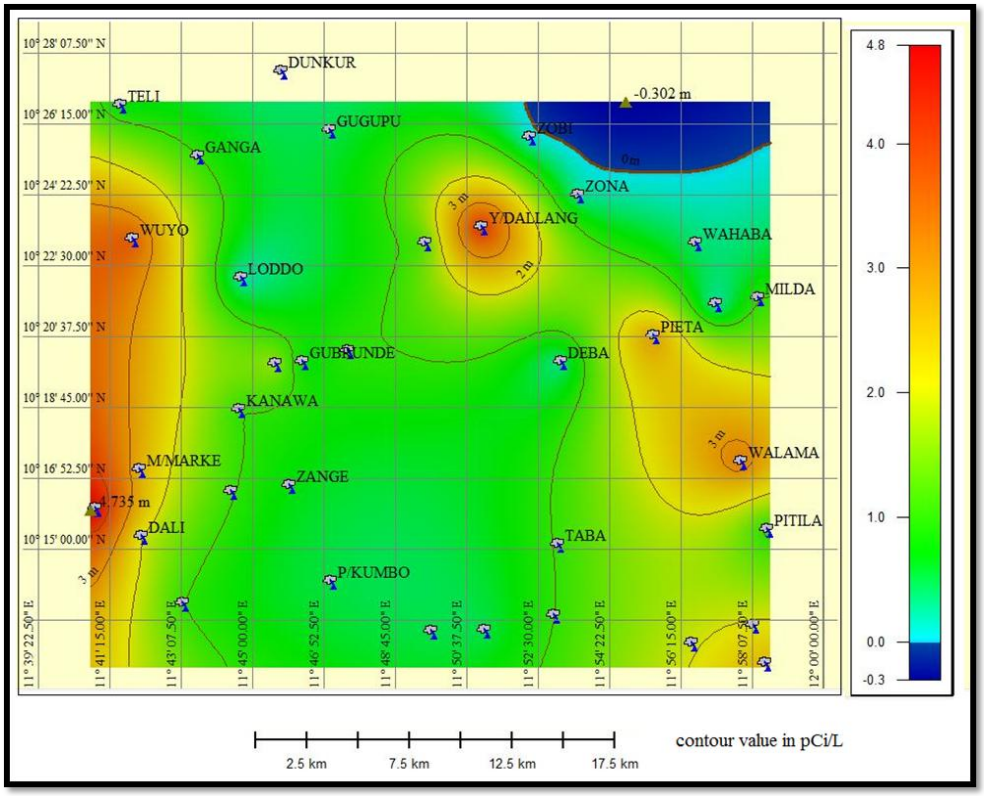

Figure 4: *Map of ^{228}Ra Activity Concentration in Groundwater of the Study Area (Contour Values are in pCi/L)*

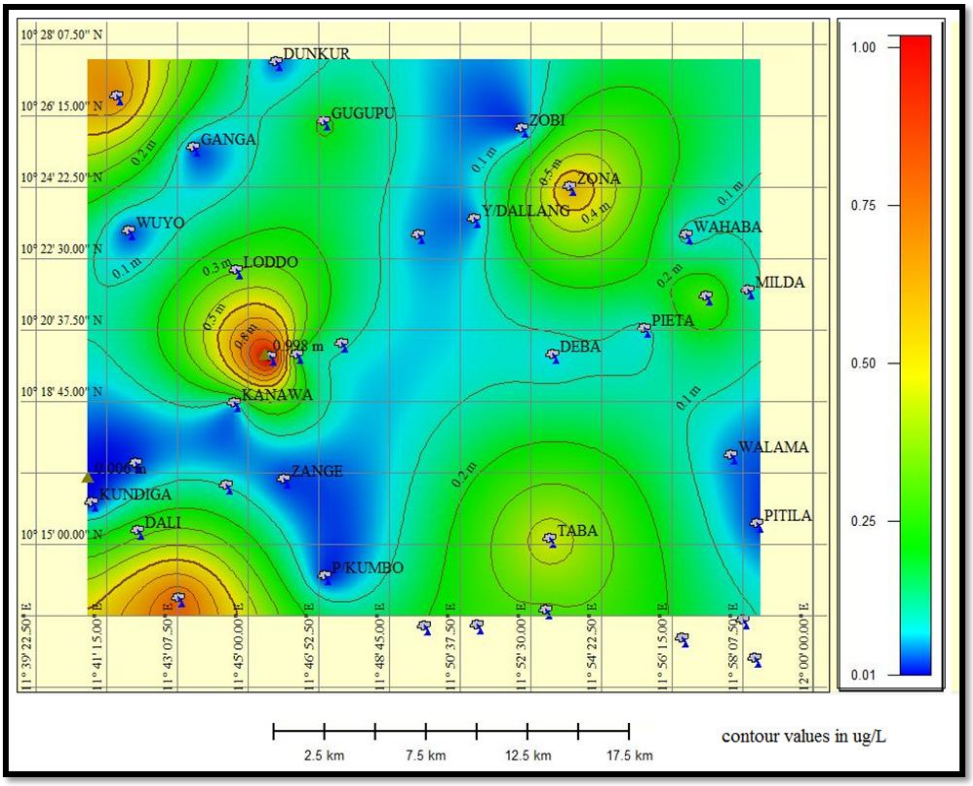

Figure 5: *Map of ^{232}Th Concentration in Groundwater of the Study Area (Contour Values are in µg/L)*

A comparison of Uranium levels in groundwater in the study area (Table 2) and that elsewhere within and outside Nigeria showed that Uranium levels in groundwater from the study area are higher than those from the basement area around Zaria as reported by Onoja (2011).

For Radium, the values from the study area are lower than those reported from other areas in Nigeria by Garba (2010) (Table 2). Awodugba (2008) and Amakum and Jibiri (2010) reported Uranium and Thorium levels in boreholes and wells from southwestern Nigeria to be much higher than those obtained both in this study and from Zaria (Table 2) implying greater effects from ionizing radiation and chemical toxicity after long term consumption of water from those parts of Nigeria.

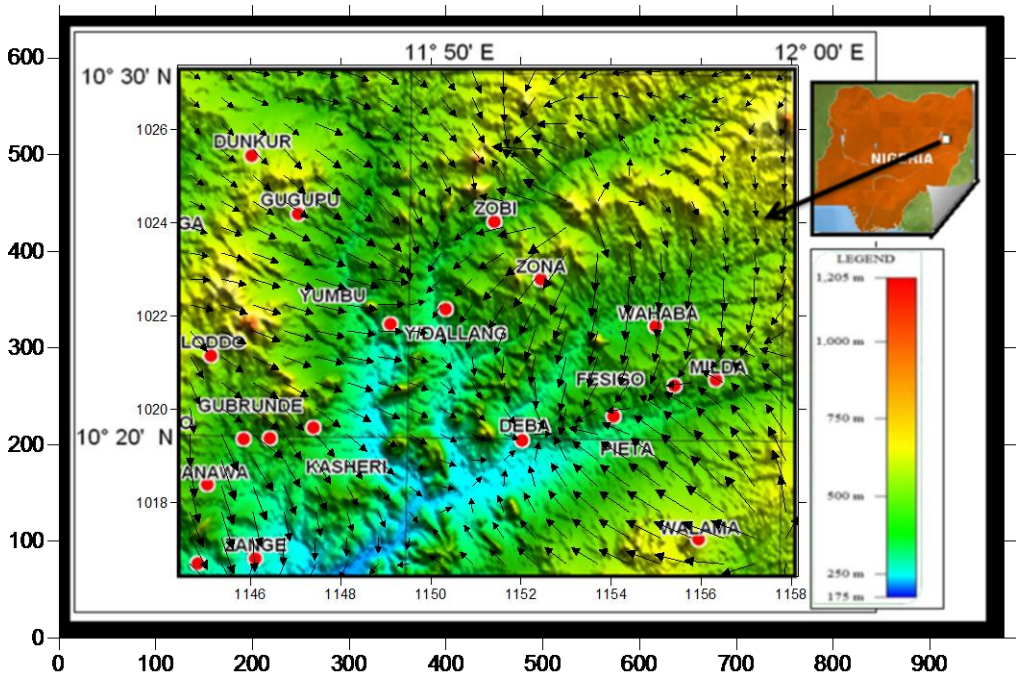

Figure 6: *Superimposed Configuration of Water Table with Groundwater Flow Direction on Digital Elevation Model of the Study Area*

According to Akerblom and Lindgren (1997), as a result of hydrogeochemical processes occurring in the subsurface, Uranium and its decay products such as Radium may be enriched on the surface of fractures (Figure 7) and based on other previous studies by Gascogne (1997), Langmuir and Riese (1985) and Lingmuir and Melchor (1985), radium appears to be stabilized in solution where high concentration of Ca^{2+}, Mg^{2+} and Cl^{-} prevails, because these ions compete for adsorption sites.

Table 2: *Comparison of U, ^{226}Ra, ^{228}Ra and ^{232}Th Values in Groundwater from the Study Area with Other Reported Value within and outside Nigeria (* are Average Values)*

Worker	Radionuclide		
	^{226}Ra (pCi/L)	^{228}Ra (pCi/L)	^{232}Th (µg/L)
This work (NE, Nigeria)	0.05±0.002 - 7.3±0.19 (*1.87)	0.1±0.003 - 4.8±0.12 (*1.53)	0.01±0.001 - 1.1±0.021 (*0.206)
Garba (2010) (NW, Nigeria)	0.81 - 5.4 (*2.7)	13.5 - 5.14 (*2.43)	
Onoja (2011) (NW, Nigeria)			2.7E5 - 0.00973 (*0.0016)
Amakum and Jibiri(2010) (SW, Nigeria)			
Awodugba (2008) (SW, Nigeria)			297.00±2.58 (*117)

Also, according to Arabi et al. (2012), groundwater from the study area had high Calcium and Magnesium which makes the water very hard; therefore, these might be the reason for Radium stability in groundwater of the area.

Radium itself is not soluble and does not form any soluble complexes that enhance its dissolution into groundwater, but because it is a bone seeker, it is the radionuclides of greatest human-health concern. According to Cothern (1987), the estimated risk of developing cancer from exposure to total Radium of 5pCi/L is about 10^{-5}.

The most important factor affecting Radium levels in groundwater is the distribution of the parent isotope, and because each Radium isotope comes from separate decay series headed by very different elements, there are very important differences.

The higher levels of ^{226}Ra in the studied samples compared to ^{228}Ra in same sample is as a result of ^{226}Ra being part of ^{238}U decay series. Uranium can be transported in groundwater over long distance and its occurrence can be influenced significantly by secondary process, as a result, ^{226}Ra can be found over a wide range of aquifer types.

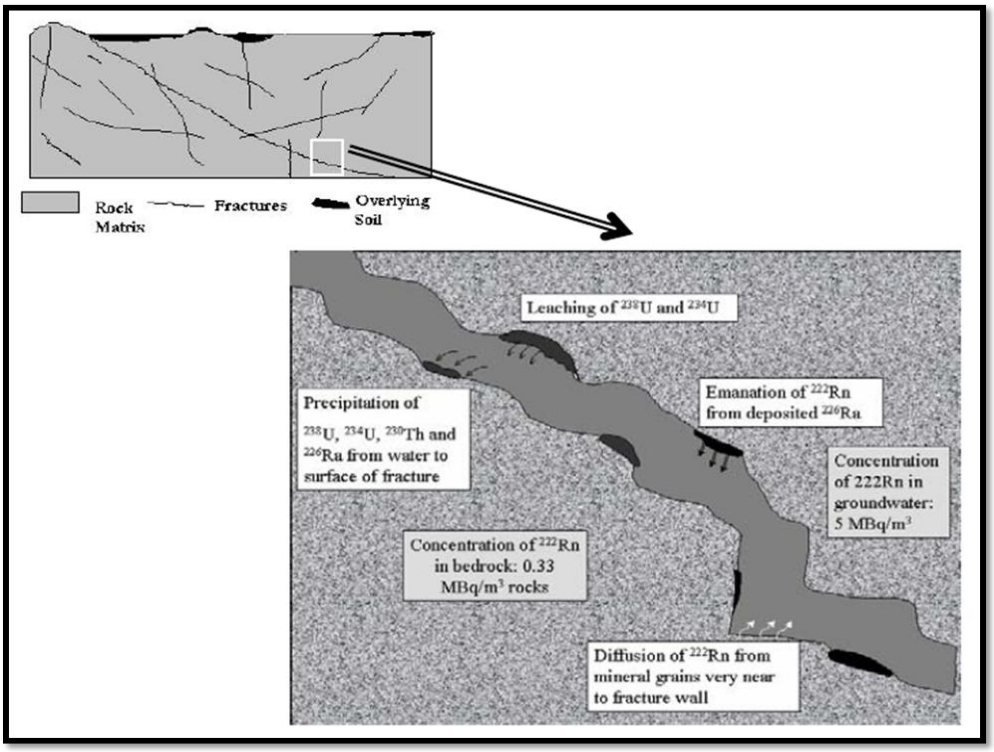

Figure 7: *Radionuclides Migration in Crystalline Rocks (Akerblom and Lindgren, 1997)*

^{226}Ra is more likely to occur at elevated levels because its parent Uranium can be concentrated into secondary deposits by groundwater. ^{226}Ra is also the third alpha-recoiled progeny in the decay series, making it more susceptible to dissolution. Uranium concentrations above 30µg/L has been reported around Yimirdallang and Kundiga (further southwest of the study area) by Arabi et al. 2012, these might have been responsible for substantive ^{226}Ra levels in groundwater of the area while in contrast, ^{228}Ra which is part of the ^{232}Th decay series is lower in sample groundwater samples because Thorium is extremely insoluble and is not subject to mobilization by groundwater. As a result, ^{228}Ra is directly controlled by the distribution of Thorium in the aquifer solids. Where there has been no secondary enrichment of Uranium, ^{228}Ra is generally the dominant Radium isotope in solution, primarily due to the higher natural abundance of Thorium over Uranium.

4. Conclusion

The levels of ^{226}Ra, ^{228}Ra and ^{232}Th in groundwater of the study area indicate the likelihood that Radium distribution in groundwater of the study area might have been controlled by groundwater movement and the distribution of their parent isotopes. Higher ^{226}Ra when compared with ^{228}Ra might be an indication of secondary mineralization of Uranium while low ^{228}Ra levels might indicate the non-solubility of Thorium because an important consequence of the significance in difference in the solubility of the parent isotopes of ^{226}Ra versus ^{228}Ra is that Uranium could be preferentially leached

out of an aquifer, leaving Thorium behind. Consequently the gross alpha and ^{226}Ra would be low. When ^{226}Ra is low it means that ^{228}Ra is even lower and the analysis for ^{228}Ra would not be triggered as recommended by EPA.

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References

Akerblom G., et al. *Mapping of Groundwater Radon Potential*. European Geologist. 1997. 5; 13-22.

Amakum C.M., et al. *Chemical and Radiological Risk Assessment of Uranium in Borehole and Well Water in the Odeda Area, Ogun State, Nigeri*a. International Journal of the Physical Sciences. 2010. 5 (7) 1009-1014.

Arabi A.S., et al. *Activity Concentration of Uranium in Groundwater from Uranium Mineralized Areas And it's Neighborhood*. Journal of Radioanalytical and Nuclear Chemistry. 2012. 293 (1) 135-142.

Awodugba A.O., et al. *Assessment of Radiological Concentration in Water Supply from Boreholes in Ogbomosho Land, Western Nigeria*. Indoor and Built Environment. 2008. 17 (2) 183-186.

Cothern C.R., 1987a: *Development of Regulations for Radionuclides in Drinking Water.* Radon, Radium and Other Radioactivity in Groundwater, Lewis Publishers, Chelsea MI, USA, 1-11.

Elegba S.B., et al. *Distribution Pattern of REE and Other Elements in the Host Rocks of the Gubrunde Uranium Occurrence, NE Ni*geria. Journal of Radioanalytical and Nuclear Chemistry. 1993. 7; 365-373.

EPA, 2000: *National Primary Drinking Water Regulations; Radionuclides*. United State Environmental Protection Agency (EPA). Final Rule, 231.

EPA, 2005: *Human Health Fact Sheet*. Argonne National Laboratory, US, 17.

EPA, 2010: *The Analysis of Regulated Contaminant Occurrence Data from Public Water Systems in Support of the Second Six-Year Review of National Primary Drinking Water Regulations*. Office of Ground Water and Drinking Water, Washington, DC.

Funtua, 1985: *An Orientation Biogeochemical Survey on Some Mineral Occurrences in the Peta Syncline, Sheet 153(Wuyo*). Unpublished B.Sc. Thesis, Ahmadu Bello University, Zaria, Nigeria, 42.

Funtua, 1988: *Geology and Genesis of Uranium Mineralization at Kanawa, Gubrunde Horst Northeastern Nigeria*. Unpublished M.Sc. Thesis, Ahmadu Bello University, Zaria, Nigeria., 88.

Funtua, 1992*: Geolgy and Geochemistry of Uranium Mineralization in Mika Northeastern Nigeria*. Unpublished Ph.D. Thesis, Ahamdu Bello University, Zraia, Nigeria, 181.

Funtua, I.I., et al. *Radon Emanation Study of Uranium Ore Samples from N.E. Nigeria*. Applied Radiation and Isotopes. 1997. 46 (6) 867-869.

Garba, 2008: *Narural Radioactivity of Groundwater in the Precambrian Rocks Around Zaria, North-Central Nigeria*. Unpublished Ph.D. Thesis, Department of Geology, Ahmadu Bello University, Nigeria, 218.

Gascogne. High Levels of Uranium and Radium in Groundwater at Canada's underground Research Lab, Lac du Bonnet, Manitoba, Canada, Applied Geochemistry. 1987. 4; 577-591.

Horwitz. *Separation and Preconcentration of Uranium from Acidic Media by Extraction Chromatography*. Analytica Chimica Acta. 1992. 266; 25-37.

Horwitz. *Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatograph*y. Analytica Chimica Acta. 1993. 281; 361-372.

Kressin. *Electrodeposition of Plutonium and Americium for High Resolution Alpha Spectrometry*, Analytical Chemistry. 1977. 49; 842-846.

Langmuir D. *The Thermodynamic Properties of Radium*. Geochimica et Cosmochimica Acta. 1985. 49; 1593-1601.

Langmuir D., et al. The Geochemistry of the Ca, Sr, Ba and Ra Sulfates in Some Deep Brines from Palo Duro Basin Texas, Geochimica et Cosmochimica Acta. 1985. 49; 2523-2432.

Maxwell, 1993: High Speed Separations to Measure Impurities in Plutonium-238 Oxide and Trace Radionuclides in Waste, 34th ORNL-DOE *Conference on Analytical Chemistry in Energy Technology*. Gatlinburg, TN.

Moon D.S., et al. Pre-concentration of Radium Isotopes from Natural Waters using MnO_2 Resin. Applied Radiation and Isotopes. 2003. 59; 225-262.

Nelson, 1992: *Improved Methods for the Analysis of Radioactive Elements in Bioassay and Environmental Samples.* 38th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry. Santa Fe, NM, US.

Okujeni. *Biogeochemical Investigation into Possible Use of Leaf and Bark Samples of Some Savanah Trees in Prospecting Uranium in Upper Benue Trough.* Nig. Jour. Sci Res., 1987. 1; 57-64.

Okujeni C.D. *A Geochemical Orientation Survey for Uranium in the Peta Syncline and Gubrunde Horst, Upper Benue Trough, Nig*eria. Nieria Journal of Scientific Research. 1990. 3; 27-38.

Okujeni C.D. Geochemical and Gamma Spectrometric Analysis of Ores and Host Rocks of the Kanawa Uranium Occurrence in NE, Nigeria. Journal of Radioanalytical and Nuclear Chemistry. 1994. 178 (2) 375-385.

Onoja, 2011: Determination of Natural Radioactivity and Committed Effective Dose Calculation in Borehole Water Supply in Zaria, Nigeria. Unpublished PhD Thesis, Department of Physics, Ahmadu Bello University, Zaria, Nigeria, 190.

Suh C.E. Host Rock Geology and Geochemistry of the Zona Uranium Occurrence, Peta Gulf Syncline (Upper Benue Trough), Northeast Nigeria. Journal of African Earth Sciences. 2000. 31; 619-632.

WHO, 2004: *Guidelines for Drinking Water Quality*, Vol. 1. World Health Organization, Geneva, 1-494.

WHO, 2008: *World Health Organization Guidelines for Drinking Water Quality*. (Third Edition Incorporating the First and Second Addenda) Vol.1. Recommendation, NCW Classifications Washington, 473.

WHO, 2011: *Guidelines for Drinking Water Quality*, (Fourth Edition) WHO Library Cataloguing-in-Publication Data, NLM Classification. Washington, 541.