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Assessment of the Contamination of Some Food Crops Due to Mineral Deposits in Ondo State, Nigeria.

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ABSTRACT

The most valuable minerals are found in large quantities in southwest Nigeria, particularly in Ondo State. As a result of the mineral presence, several areas of Ondo State are currently connected to significant levels of naturally occurring radioactivity. If properly managed and controlled, the mineral reserves are a boon to the Nigerian government, but the risks involved in their exploration and utilization also pose a serious threat to the state. It has an impact on the resources of land, air, and water used for agriculture and human habitation. As a result, the government wants to guarantee that food security is negatively impacted. That is, the Federal government of Nigeria works to ensure that everyone has access to enough safe, nutrient-dense food. This work allowed for the prediction of likely radiological health implications by analyzing baseline radiation levels in some of the most significant food crops in Ondo State. Because they meet the majority of food's nutritional needs, maize (Zea mays), yam (Dioscorea alata), and cassava (Manihot esculenta) tubers were gathered from the State's farmlands. The main crops grown and consumed in the communities are maize, yam, and cassava, thus these were the ones picked. Above all, there would have been additional food products including meat, vegetables, fish, and water if there hadn't been budgetary limitations. To ensure thorough coverage of the study area, Ondo State was split up into zones. The samples of maize (Zea mays), yam (Dioscorea alata), and cassava (Manihot esculenta) were dried at room temperature until they achieved a constant weight. For 28 days, they were maintained in a 1-liter Marinelli beaker after being ground, blended, and packaged in 250 g. This allowed them to reach secular equilibrium. Gamma-ray spectroscopy was utilized to ascertain the activity concentrations of Thorium-232, Potassium-40, and Radium-226 in the food samples. When measuring radioactivity concentration, the Hyper Pure Germanium (HPGe) detector is superior to other detectors in several ways, including high energy resolution, sensitivity, peak shape, stability, minimal background noise, and high accuracy. Nevertheless, HPGe detectors are more costly, necessitate liquid nitrogen, and are more vulnerable to radiation harm. To calibrate the Hyper Pure Germanium detector, standard radioactive sources were first used. Every sample was subjected to a 10-hour gamma counting process at Obafemi Awolowo University in Ile-Ife. In yam, the mean activity concentrations of Ra-226, Th-232, and K-40 were 1.91 ± 0.10 Bq/kg, 2.34 ± 0.21 Bq/kg, and 48.84 ± 3.14 Bq/kg, in that order. For Th-232, 2.19 ± 0.07 Bq/kg, Ra-226, and K-40, the mean value of the radionuclide content in maize was 2.83 ± 0.21 Bq/kg, 2.19 ± 2.16 Bq/kg, and 2.19 respectively. In cassava, the mean activity concentrations for Ra-226, Th-232, and K-40 were 2.52 ± 0.31 Bq/kg, 1.94 ± 0.21 Bq/kg, and 45.12 ± 3.31 Bq/kg each. In zones six through eight, the average committed effective doses for yam eating were 0.55 μSv/y, for maize it was 0.39 μSv/y, and for cassava, it was 0.49 μSv/y. The yearly dosage recommendation for the general public, which is 0.35 μSv/y, is exceeded by these figures. Therefore, the results of this work's values indicate that some foods consumed in particular areas of Ondo State are contaminated radioactively. However, as gamma-emitting radionuclides are significant contributors to human internal exposure by ingestion, inhalation, or bodily wounds, we advise that systematic and suitable procedures also need to be devised for the monitoring of these radionuclides by NESREA. To keep an eye on and evaluate the environmental state of Nigeria's mining sites and industrial operations, the National Environmental Standards and Regulations Enforcement Agency (NESREA) was founded by the Federal government. The federal agency is keeping an eye on the mining exploration and exploitation activities in the states of Kogi, Zamfara, Osun and same could also be applied to Ondo State

Keywords: Exploration, Radiation, Health, Mineral, Spectroscopy. Gamma-Rays

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1. Introduction

Due to its onshore and offshore crude oil production, which accounts for up to 10% of Nigeria's total output and reserves, Ondo State is one of the oil-producing states in the nation. Additionally, Ondo State contains commercially significant amounts of liquefied natural gas, which has prompted the state to build a natural gas facility (KPMC 2008). Ondo State contains enormous quantities of several solid minerals, including bitumen, kaolin clay, coal, tin, limestone, iron ore, and marble (MSMD 1990). Fig.1 represents the map of Ondo State showing the various positions where various solid minerals are deposited. There are known to be significant negative environmental effects from the exploration and utilization of certain minerals. Malignant disease development and most likely other health problems in humans have been linked to radiation. All living creatures, including humans, have been exposed to radiation since the beginning of time since it is a ubiquitous part of the environment (Kendall et al., 2006). One of the radiation sources found in the environment, in water, in food that humans eat, and in the soil that is used to build human settlements is radionuclides.

Therefore, to determine whether the environment in which these food crops are grown is polluted, it is required to evaluate the quantities of Ra-226, Th-232, and K-40 in the food crops in Ondo State (Nwankpa, 2017). To estimate the uptake and retention of these radionuclides in the human body, it is also required to determine how much Th-232 and Ra-226 are consumed through the food chain. Ra-226 and Th-232 daily intakes were found to be influenced by food crops and vegetables in research conducted by Shiraishi et al. (2000) and Okeji et al. (2012). Coal and oil exploration are two more sources of radionuclides in the environment. These sources contain remnants of primordial radionuclides. Natural radioactive materials (NORM) are emitted during the extraction and burning of crude oil, specifically in the form of light fly ash from coal that escapes through the plant's exhaust and from oil during the burning of brine. In addition to being radioactive, phosphate rocks that are mined for fertilizers include large quantities of uranium and radon, which are released into the environment during the ores' extraction and processing (Ahmed and Arabi, 2005). Natural occurring radioactive materials (NORM) are used in conventional industries such clothes, construction, luminous paint, colouring, and burning lime. These materials can get enriched and released into the environment during industrial processes. When consumed or inhaled, radionuclides are dispersed throughout the body in accordance with the element's metabolism, and the radiation's sensitivity varies between the organs. (Kendall and others, 2009). Some of the system's atoms become ionized as a result of energy being deposited or absorbed in the biological system via interactions between the ionizing radiation and the organs. The dose, physical characteristics, intensity, and energy distribution inside the organism all affect how the ionizing radiation affects man.

2. Materials and Method

With a predicted population of 4.75 million, the study region (Ondo State) has a total land mass of approximately 14789 km². Latitudes 5°45' N and 8°15' N and longitudes 4°30' E and 6° E are where Ondo State is located (NPC 2016). This work allowed for the prediction of likely radiological health implications by analyzing baseline radiation levels in some of the most significant food crops in Ondo State. Because they meet the majority of food's nutritional needs, maize (Zea mays), yam (Dioscorea alata), and cassava (Manihot esculenta) tubers were gathered from the State's farmlands. The main crops that are grown and consumed in the communities are maize, yam, and cassava. More significantly, other dietary items including meat, vegetables, fish, and water would have been included in this effort except for financial limits.

Sites for industry, farmlands, water resources, and mineral resources were carefully considered when selecting locations for the sampling. The research region was thoroughly covered by dividing Ondo State into eight zones (refer to fig. 3 and table 2). Every food crop was gathered in three samples per zone. The gathered food crops, samples of manihot esculenta (cassava), yam (Dioscorea alata), and maize (Zea mays), were dried at room temperature until they attained a constant weight. To attain secular equilibrium, they were ground, blended, and packaged in 250 g in a 1-liter Marinelli beaker. They were then stored for a complete month.

The activity concentrations of Radium-226, Thorium-232, and Potassium-40 were determined in the food samples using Gamma-ray spectrometry. The Hyper Pure Germanium (HPGe) detector used has several advantages over other detectors in the measurement of radioactivity concentration such as, (i) High energy resolution: it offers a superior energy resolution, typically 0.1-2 keV, (ii) sensitivity: it is more sensitive especially for low-energy gamma rays, (iii) peak shape and stability: HPGe detectors provide better peak shapes and stability, making them ideal for precise spectroscopy, (iv) low background noise reducing interference and improving detection limits and high accuracy. However, HPGe detectors are more expensive, require Liquid nitrogen and more sensitive to radiation damage. The detector has a resolution of about 8% at 0.662 MeV of Cs-137. The detection Energy calibration of the system was carried out using a standard reference source (IAEA- 444) prepared by the Radiochemical Centre, Amersham, England. To get the best resolution possible, the spectrometer system was calibrated to obtain the 0.5 KeV per channel and to locate the 662-KeV photopeak of the 137Cs gamma line at about one-third of full scale. This was accomplished by setting the amplifier's coarse gain, fine gain, and shaping time at 20, 0.5, and 4.0 μs, respectively, and its gain range and LLD at 4K, 8K, and 0.3V. This configuration remained the same for the duration of the measurements. Until a well-defined picture peak was obtained, the sources were tallied.

A statistical error level of less than one percent serves as the foundation for a well-defined photopeak in this work. Every identified photopeak was examined by gathering pertinent data about it from the S100 program. The centroid is one piece of such information. Plotting the channel numbers against the gamma ray energies revealed the centroid of each of the different full energy peaks on the MCA (Figure 1). The gamma counting, which lasted for 10 hours for each sample, was carried out in the Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria. The MAESTRO software program installed in the detector system automatically searches for the peak, evaluates the peak position in energy, and identifies the radionuclides by use of the nuclide library. It calculates the net peak areas, subtracts the background count, and then displays the activity concentration in selected units [Galmore 2002]. Also, an empty Marinelli beaker was counted under identical geometry as the samples in other to determine the background spectrum distribution which was subtracted from the values [Nwankpa 2004].

K-40 was measured at the photopeak of gamma transmission at 1460 KeV, while Ra-226 and Th-232 were measured at the photopeaks of Bi-214 and Tl-208, respectively, at 1760 KeV and 2614 KeV.

Table 1: Channels for Various Energies of the Energy Calibration Sources

Standard Source	Energy(KeV)	Channel
^{152}Eu	344.27	284.28
^{137}Cs	661.70	610.04
^{152}Eu	778.89	734.89
	1112.02	1076.31
^{60}Co	1173.24	1140.25
	1332.50	1305.56
^{152}Eu	1407.95	1387.83

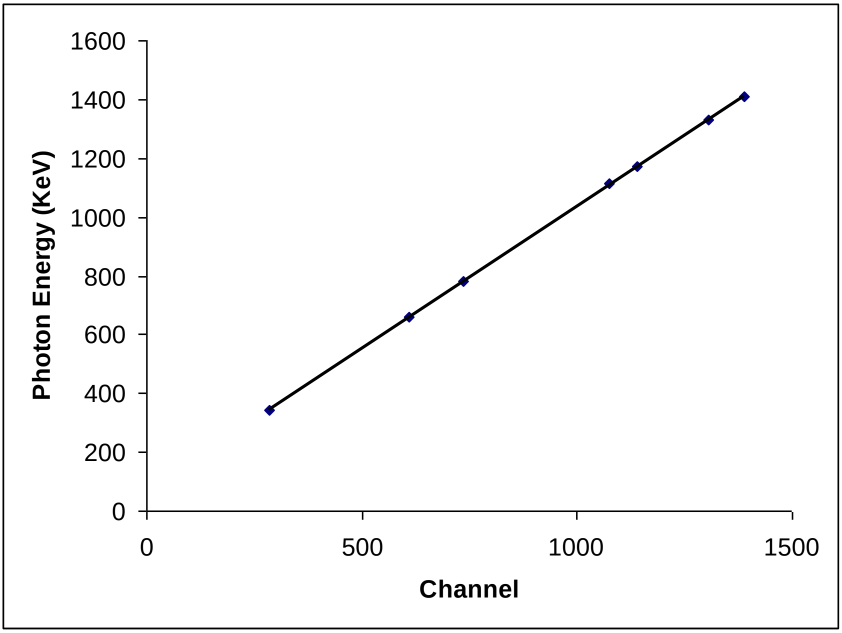

Fig. 1: Energy Calibration Curve

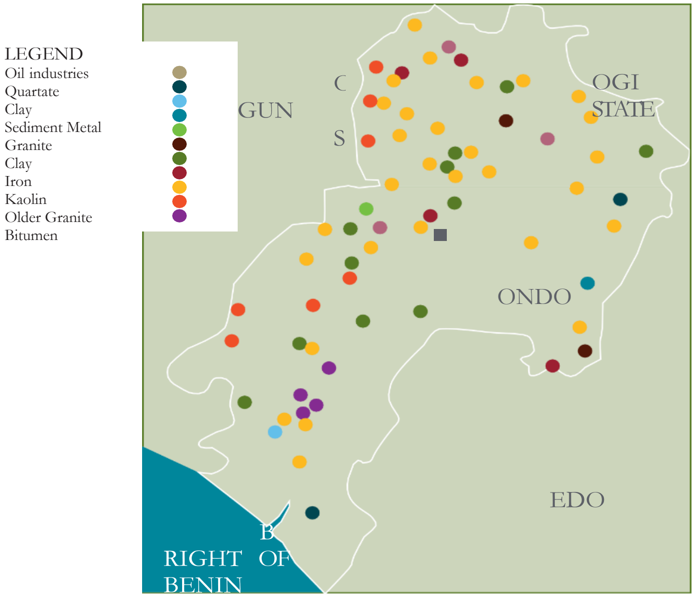

Fig. 2: Ondo State map showing the location of key mineral resources (adapted from KPMG international)

.Fig. 3: Ondo State map showing the local government areas (adapted from Research Gate images)

Table 2: Zonal Demarcation on Local Government Basis

Zone	Local government areas
1	Akoko North West, Akoko North East, Akoko South East, and Akoko South West
2	Owo, and Ose
3	Ifedore, Akure North and Akure South
4	Ile-Oluji/Okeigbo and Ondo East
5	Ondo West and Idanre
6	Odigbo
7	Okitipupa and Irele
8	Ilaje and Ese Odo

To understand how Ondo State was divided into 8 zones, compare fig. 2 and fig. 3. Table 2 shows how the 8 zones are allotted to the 18 local government areas in the State and signifies the solid mineral deposited in each zone.

3. Radiation Hazard Indices

The committed effective dose (E) to the public from radionuclides Th-232 and U-238(Ra-226) that are consumed by food crop consumers is calculated using (1) and (2), as per Mizdaq (2000) and Rzama (1994).

$$E_u = I_u \, x \, e_{gu} \quad (1)$$

$$E_{Th} = I_{Th} \, x \, e_{Th} \quad (2)$$

The ICRP ingestion dose coefficients for Th-232 and U-238 (Ra-226) radionuclides are denoted by eg_{Th} and eg_u, respectively, and the annual intake of these radionuclides is expressed as $E = E_u + E_{Th}$, Iu (Bq) and I_{Th} (Bq) [ICRP 1996]. For age groups over 17, the ICRP values of the ingestion coefficient for Th-232 (eg_{Th}) and U-238 (eg_u) radionuclides are 2.3×10^{-7} Sv/Bq and 4.5×10^{-8} Sv/Bq, respectively. Akinloye et al. (1999) defined radionuclide intake as the activity concentration of radionuclides multiplied by usage or food intake. Food crops are used in Nigeria at a rate of 0.55×10^{-3} kg/day (0.2 kg/yr) [FAO 1992]. Because there are insufficient site-specific data, this number is chosen. NCRP (1984) states that the general consumption pattern is used when a population's pattern of food consumption is normal.

4. Results and Discussion.

Table 3: The Mean Specific Activities for Maize, Yam and Cassava (Bq/Kg)

Zone	Food crop	Ra-226	Th-232	K-40
	maize	2.60 ± 0.49	2.63 ± 0.51	31.41 ± 2.14
1	yam	1.48 ± 0.08	1.82 ± 0.12	38.81 ± 2.80
	cassava	2.02 ± 0.91	1.90 ± 0.60	43.04 ± 3.43
	maize	2.50 ±0.59	1.79 ± 0.27	29.98 ± 2.34
2	yam	3.02 ± 0.72	1.29 ± 0.32	34.76 ± 3.11
	cassava	2.20 ± 0.32	1.54 ± 0.16	34.14 ± 2.34
	maize	2.64 ± 0.59	2.17 ± 0.46	29.69 ± 2.32
3	yam	1.09 ± 0.08	1.90 ± 0.13	35.21 ± 1.36
	cassava	2.48 ± 0.52	2.05 ± 0.49	44.61 ± 3.56
4	maize	2.41 ± 0.73	1.89 ± 0.38	29.74 ± 1.23
	yam	1.71 ± 0.13	1.43 ± 0.16	35.87 ± 4.24

	cassava	1.88 ± 0.63	1.70 ± 0.57	42.86 ± 2.44
	maize	2.42 ± 0.44	1.94 ± 0.27	31.52 ± 1.38
5	yam	1.79 ± 0.21	1.98 ± 0.17	38.27 ± 1.13
	cassava	1.75 ± 0.24	1.79 ± 0.26	39.14 ± 1.36
	maize	5.61 ± 0.42	4.07 ± 0.59	50.07 ± 2.13
6	yam	9.82 ± 0.08	7.94 ± 0.12	49.98 ± 2.11
	cassava	8.06 ± 0.14	6.81 ± 0.27	43.77 ± 3.46
	maize	11.97 ± 2.13	7.75 ± 0.18	47.99 ± 3.14
7	yam	10.19 ± 0.13	12.03 ± 0.42	57.89 ± 4.38
	cassava	12.05 ± 0.55	10.25 ± 0.46	40.31 ± 4.79
	maize	13.77 ± 0.13	9.79 ± 0.22	46.12 ± 2.45
8	yam	12.20 ± 0.23	11.93 ± 0.07	59.50 ± 3.68
	cassava	11.91 ± 0.57	13.30 ± 0.39	53.38 ± 2.23

Table 4: Annual Intake of Ra-226 & Th-232 and Committed Effective Doses for Maize, Yam and Cassava

Zone	Food crop	Annual intake Ra-226, Th-232 (Bq/kg)		Committed effective doses (μSv/y		
		Ra-226	Th-232	E_U	E_{Th}	E
1	Maize	0.52	0.53	0.02	0.12	0.14
	Yam	0.30	0.37	0.01	0.08	0.09
	Cassava	0.44	0.38	0.02	0.09	0.11
2	Maize	0.50	0.36	0.02	0.08	0.10
	Yam	0.60	0.26	0.03	0.06	0.09
	Cassava	0.44	0.31	0.02	0.07	0.09
3	Maize	0.54	0.43	0.02	0.10	0.12
	Yam	0.22	0.38	0.01	0.09	0.10
	Cassava	0.50	0.41	0.02	0.09	0.11
4	Maize	0.48	0.38	0.02	0.08	0.10
	Yam	0.34	0.29	0.01	0.07	0.08
	Cassava	0.38	0.34	0.02	0.08	0.10
5	Maize	0.48	0.39	0.02	0.09	0.11
	Yam	0.36	0.40	0.01	0.09	0.10
	Cassava	0.35	0.36	0.01	0.08	0.09
6	Maize	1.12	0.81	0.05	0.19	0.24
	Yam	1.96	1.59	0.09	0.37	0.46
	Cassava	1.61	1.36	0.07	0.31	0.38
7	Maize	2.39	1.55	0.11	0.36	0.47
	Yam	2.04	2.41	0.09	0.45	0.54
	Cassava	2.41	2.05	0.11	0.37	0.48
8	Maize	2.75	1.96	0.12	0.35	0.47
	Yam	2.44	2.39	0.11	0.55	0.66
	Cassava	2.38	2.66	0.11	0.51	0.62

The radioactive mean activity concentrations of Th-232, K-40, and Ra-226, respectively, range from 1.09 ± 0.08 to 12.20 ± 0.23 Bq/kg, 1.29 ± 0.32 to 12.03 ± 0.42 Bq/kg, and 34.76 ± 3.11 to 59.50 ± 3.68 Bq/kg in the yam samples. Within the maize samples, the mean activity concentration of radionuclides varies: 1.79 ± 0.27 to 9.79 ± 0.22 Bq/kg for Th-232, 2.41 ± 0.73 to 13.77 ± 0.13 Bq/kg for Ra-226, and 29.69 ± 2.32 to 50.07 ± 2.13 Bq/kg for K-40. The mean activity concentrations for cassava vary from

1.75 ± 0.24 to 12.05 ± 0.55 Bq/kg for Ra-226, 1.54 ± 0.16 to 13.30 ± 0.39 Bq/kg for Th-232, and 34.14 ± 2.34 to 53.38 ± 2.23 Bq/kg for K-40.

These values fall within the average ranges of 8(1-9) Bq/kg, 3(2-10) Bq/kg and 50(25-75) Bq/kg for Ra-226, Th-232 and K-40 respectively (UNSCEAR 2000). Table 2 data clearly show that K-40 is the main source of radionuclide content in all food crops, with the greatest amounts seen in yam and maize (Nwankpa and Essiett, 2010). The findings indicate that the radionuclide contents of food crops from zones 1 through 5 do not significantly differ from one another. Additionally, this study has demonstrated that the number of naturally occurring radionuclides varies throughout Ondo State. Since it might be significantly impacted by the kind of plant, water transportation (Tchokossa, 1998), organic metabolism, groundwater, and other various factors, this is explained by the heterogeneity of minerals deposited (Shiraishi 2000). Nonetheless, the three food crops' activity concentrations of Ra-226, Th-232, and K-40 in zones 6–8 exceed the permissible safe level. This may be related to the production of crude oil in the zones and the illicit mining of certain minerals. According to Table 4, the average yearly intake of Th-232 and Ra-226 from yam diet was 1.01 and 1.03 Bq/kg, respectively. The mean yearly intake of Th-232 and Ra-226 for maize was 0.80 Bq/kg and 1.10 Bq/kg, respectively, whereas for cassava it was 1.07 Bq/kg and 0.98 Bq/kg. It was found that the three food crops' yearly consumption values of Ra-226 were less than the recommended threshold of 5.7 Bq/kg.

Furthermore, the three food crops' yearly Th-232 intake values were less than the diet's 1.5 Bq/kg reference (UNSCEAR, 2000). These food crops would not increase dietary intakes of radionuclides from the thorium series (Amaral, 2005).

In certain parts of Ondo State, the committed effective doses from yam, maize, and cassava consumption exceed the reference value of 0.35 μSv/y specified in (UNSCEAR, 2000). Comparing zones 6–8 to other zones, it can be shown that the committed effective doses in certain zones are higher than the reference value. Certain research locations are radiological unsafe for residential and agricultural use, according to the values of hazard indices [Ahmed, 2014]. The food crops that are grown and eaten in those areas are almost always tainted. You may remember that zones 6–8 are rich in minerals like granite, bitumen, and crude oil. These zones are home to several illicit mining operations, particularly zone 8, where unmanaged mineral resource exploitation and unlawful crude oil mining have deteriorated the ecosystem. The local populations in these areas are unaware of the hazardous state of the environment and the radioactive influence on their health. The majority are farmers, and agricultural goods are their source of income. People struggle to survive and ignore government agencies that are trying to reposition them because of political bias and the government's callous disregard for their well-being.

Additional natural resources that have already been utilized in zones 7 and 8 are ball clay, which is used to make ceramics, and silica sand, which is used to make glass (Agwu, et al 2016). Therefore, the people of Ondo State are seriously at risk due to the unlawful mining of certain minerals. Nonetheless, we advise that systematic and suitable procedures be developed for the assessment of gamma-emitting radionuclides as well, as they are significant sources of internal exposure for humans through ingestion, inhalation, or bodily wounds.

It is thought that to put an end to illicit mining, the federal and state governments must play a significant role. When communities have access to social amenities like power, water, and education, this might be feasible. A portion of the issue stems from foreign partners who support illicit mining to maximize earnings. Nigeria has the personnel, expertise, and tactics to stop illicit mining and keep an eye on mineral exploration; but, the corruption of public servants, local authorities, and other players has complicated the implementation of all mining legislation.

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