CONTRIBUTIONS OF NATURAL RADIONUCLIDES IN CHEMICAL FERTILIZERS TO FARM SOIL RADIOACTIVITY AND COMMITTED EFFECTIVE DOSES TO HUMAN

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CERTIFICATION

I certify that the work described in this thesis was carried out under my supervision by **Fasae Kolawole Peter (35885)** in the Department of Physics, University of Ibadan.

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DEDICATION

This research work is dedicated

To

The almighty God

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My special gratitude goes to the almighty God, the Lord Jesus Christ and the Holy Spirit; the maker of Heaven and earth, the father of all and the creator of all things. He is worthy of all my praises.

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TABLE OF CONTENTS

CONTENTS **PAGE**

LIST OF TABLES

LIST OF FIGURES

Figures **Page**

ABSTRACT

The use of chemical fertilizers to replenish depleted soil nutrients due to over cultivation and erosion is a common practice. Natural radionuclides in these fertilizers can cause some radiological adverse health effects to animal, through indirect ingestion of fertilizer, including consumption of plants grown with fertilizers. Information on the level of contribution of chemical fertilizers to farm soil radioactivity and radiological health effects in Nigeria are scanty. This study was designed to assess the contributions of chemical fertilizers to farm soil radioactivity and Committed Effective Doses (CEDs) to human.

Samples of commonly used Nitrogen-Phosphorus-Potassium (NPK:15-15-15) and Single Superphosphate (SSP) fertilizers were collected from retail markets in southern and northern Nigeria, respectively. Three partitions (0.55m^2 each) of rain-fed experimental farm was filled with Virgin Soil (VS), which was collected from government reserved forest in Ekiti State. The fertilizers (NPK and SSP) were applied separately to VS with NPK (VS_{NPK}) and VS with SSP (VS_{SSP}) using broadcasting method at 1.0 kg/m^2. The third partition served as the control (VS_C). Seeds of Tomato (*Solanum esculentum* K. Karsten) and vegetable (*Amaranthus hybridus* Linnaeus) were sown on the partitions after one week of fertilizers application. The contributions of chemical fertilizers to farm soil radioactivity and their transfer factors to plants were investigated using standard method. The activity concentrations of natural radionuclides (^{40}K, ^{226}Ra and ^{232}Th) in the fertilizers, soil and plant samples were measured using Sodium Iodide doped with Thallium (NaI(Tl)) detector. The CEDs were determined using standard equation as contained in Radioactivity in Food and the Environment (RIFE) documents. Data were analysed using descriptive statistics and one way ANOVA at $\alpha_{0.05}$.

The Mean Activity Concentrations (MACs) of ^{40}K, ^{226}Ra and ^{232}Th in NPK and SSP were 4754.0±192.0, 156.0±99.0 and 9.4±4.0 Bq/kg; 301.0±36.0, 696.0±113.0 and 14.7±2.7 Bq/kg, respectively. The MACs of ^{40}K, ^{226}Ra and ^{232}Th in soil samples of the VS_C, VS_{NPK} and VS_{SSP} were 204.0±2.4, 43.0±2.3 and 7.0±1.7 Bq/kg; 352.0±1.9, 62.0±1.7 and 8.0±1.9 Bq/kg; 285.0±3.3, 66.0±2.0 and 10.0±1.4 Bq/kg, respectively. The MACs of the three radionuclides in tomato samples of the VS_C, VS_{NPK} and VS_{SSP} were 64.0±1.4, 18.0±1.7 and 7.0±1.7 Bq/kg; 125.0±2.1, 33.0±2.0 and 8.0±1.9 Bq/kg; 122.0±1.7, 51.0±1.4 and 10.0±1.4 Bq/kg, respectively

The MACsin the vegetable samples of the VS_C, VS_{NPK}, and VS_{SSP} were 72.0±1.4, 22.0±1.7 and 8.0±2.6 Bq/kg; 133.0±1.7, 45.0±1.9 and 10.0±1.9 Bq/kg; 142.0±2.3, 57.0±1.7 and 13.0±2.1 Bq/kg for ^{40}K, ^{226}Ra and ^{232}Th, respectively. Differences in MACs were significant in samples considered. Use of NPK and SSP contributed 72.0, 44.0, 14.0% and 40.0, 53.0, 43.0%, respectively to the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in the VS_{NPK} and VS_{SSP} compared to the VS_C farm soil. Radionuclide transfer factors in the VS_C, VS_{NPK} and VS_{SSP} ranged from 0.36-0.66, 0.35-0.56 and 0.43-0.78, respectively. The CEDs due to consumption of tomatoes and vegetable of VS_{NPK} and VS_{SSP} were 0.22 and $0.33 \mu Sv/y$; 0.11 and $0.14 \mu Sv/y$, respectively, which are lower than the recommended CED of $0.1 mSv/y$ by International Commission on Radiological Protection (ICRP). The NPK and SSP fertilizers in the VS_{NPK} and VS_{SSP} contributed 54.0 and 130.0 %, respectively to the CED (tomatoes), 37.0 and 73.0 %, respectively to CED (vegetables) when compared to plants in the VS_C.

Chemical fertilizers contribute to farm soil radioactivity and the committed effective doses to human is elevated more by Single Superphosphate fertilizer.

Keywords: Radiological effect, Farm soil radioactivity, Radionuclide transfer factors, Chemical fertilizer

Word count: 498

CHAPTER ONE

1.0 INTRODUCTION

1.1 The Concept of Radioactivity

The nucleus of an atom consists of neutrons and protons collectively called nucleons. The electrons in the electron cloud counteract the positive charges of the protons in the atomic nucleus with their negative electrical charges, hence, making the atom to be electrically neutral. It has been found that the stability of nucleus depends upon its neutron to proton ratio (N/Z) . Light nuclei (A < 20) have N/Z ratio close to unity. For heavy nuclei (A > 20 the N/Z ratio increases progressively due to dominance of number of neutrons. Radioactive decay is the process in which an unstable atomic nucleus spontaneously loses energy by emitting ionizing particles and radiation to form a more stable nucleus. This decay, or loss of energy, results in an atom of one type, called the parent nuclide transforming to an atom of a different type, named the daughter nuclide (Vasilyeva and Starkov, 1996).

A heavy charged alpha particles which are basically helium atom (He^{++}) and the light beta particles (e^+, e^-) with the accompanying neutral and much lighter particles called neutrinos are emitted in natural radioactivity. Where the N/Z ratio is lower than the requirement for stability, a radioactive nuclide can decay by β emission or k-electron capture. These transformations are expressed in the equation below (Vasilyeva and Starkov, 1996).

Positron emission:

$$^{11}X_6 \rightarrow {}^{11}_{5}Y + {}_{+}e^0 \qquad (p^+ \text{ emisions}) \qquad 1.1$$

A k electron capture (this is not very common and occurs in case of nuclei with low N/Z ratio and having insufficient energy for positron emission transformation is given by:

$${}^{7}_{4}X + {}_{-1}e^0 \rightarrow {}^{7}_{3}Y + \upsilon \qquad (\text{k-capture}) \qquad 1.2$$

The daughter nucleus produced by β - emission or k - electron capture, has a ratio $^{N+1}/_{Z-1}$ A radioactive nuclide would be neutron rich and would decay by β -

emission to produce a daughter nucleus with a lower N/Z ratio of $(N-1)(Z+1)$ (Vasilyeva and Starkov, 1996):

$$^{14}X_6 \quad \rightarrow \quad ^{14}_{7}Y \quad + \quad _{-1}e^0 \qquad 1.3$$

$$^{29}_{13}X \quad \rightarrow \quad ^{29}_{14}Y \quad + \quad _{-1}e^0 \qquad 1.4$$

When the value of Z becomes greater than 82, Some nuclides attain greater stability by α-emission which reduces the initial N/Z value to $N-2 \big/ Z-2$

$$^{238}_{92}X \quad \rightarrow \quad ^{234}_{90}Y \quad + \quad ^{4}_{2}He \qquad 1.5$$

Radioactivity is a random process, meaning that it is physically impossible to predict whether or not a given atomic nucleus will decay and emit radiation at any given moment, it follows a well defined probability distribution whose characteristic rate can be predicted. If a sample contains N radioactive nuclei, then the rate $-dN/dt$ at which nuclei will decay is proportional to N:

$$\frac{dN}{dt} = -\lambda N \qquad 1.6$$

in which λ the disintegration constant (or decay constant) has a characteristic value for every radionuclide.

$$dN/N = -\lambda dt \qquad 1.7$$

$$N = N_o e^{-\lambda t} \qquad 1.8$$

where N_0 is the number of unstable nuclei at time $t=0$ and N is the number of nuclei remaining at any subsequent time. Equation (1.8) shows that the amount of the initial radionuclide decays exponentially with time.

The rate of decay of a radioactive sample is described as the activity of the sample. The activity A of a radioactive sample is the number of disintegration per unit time. This is measured in the unit called Becquerel (Bq). The activity of a sample varies directly with the number of radioactive atoms in the sample. This relationship is described by the expression (SCC., 2016):

$$A = \lambda N = \frac{dN}{dt} \qquad 1.9$$

Where A is the activity of the sample, N is the number of radioactive atoms present, and λ is a decay constant representing the fractional rate of decay of the sample in units of time. If the activity A_0 of a radioactive sample is known at some time $t = 0$, then the activity A at a later time t can also be computed with the expression:

$$A = A_0 e^{-\lambda t} \qquad 1.10$$

The characteristic decay rate of a nuclear species is usually quoted as the half life, which is the time required for one half of the initial number of nuclei to decay. If $t_{1/2}$ is the half life then

$$t_{1/2} = 0.693/\lambda \qquad 1.11$$

For natural unstable radionuclides, the half-life, $T_{1/2}$ ranges from fractions of seconds (e.g. 164 µs for ^{214}Po) to billions of years (e. g. 4.5×10^9 years for ^{238}U). Many of the natural radionuclides still remain in the earth crust, despite series of disintegration that had occurred over time and that accounts for their radioactivity in natural matrices.

1.2 Radioactive Decay Series

All natural elements with atomic numbers Z > 83 are radioactive. These elements decay either by emission of α-particles (energetic helium nuclei), or by emission of negative β-particles (energetic electrons). The four distinct natural decay series: uranium, actinium, thorium, and neptunium are shown in Table 1.1 shows They are often designated as the 4n, 4n+1, 4n+2, 4n+3 decay series according to the divisibility of their mass number by 4, where n is an integer. Only three of these decay series' are found in nature: uranium, actinium, and thorium. The longest lived member of all these series are sufficiently long- lived to survive till the present time and are found in varying amount in the earth depending on the local geology. The isotope ^{237}Np has a half-life much shorter

Table 1.1: The natural decay series

Series/Mass changing	**First isotope**	**Half-life** (years)	**Last isotope**
Uranium (4n+2)	^{238}U	4.49×10^{9}	^{206}Pb
Actinium (4n+3)	^{235}U	7.10×10^{8}	^{207}Pb
Thorium (4n)	^{232}Th	1.39×10^{10}	^{208}Pb
Neptunium (4n+1)	^{237}Np	2.14×10^{6}	^{209}Bi

Source: Vasilyeva and Starkov (1996)

than the geological age of the Earth (5 billions years). Virtually all Neptunium had decayed within the first 50 millions years after the Earth was formed. Among the four series only thorium and uranium series contribute appreciably to population exposure (Vasilyeva and Starkov, 1996). The naturally radioactive series of Uranium and Thorium are shown in Figures 1.1 and 1.2 respectively.

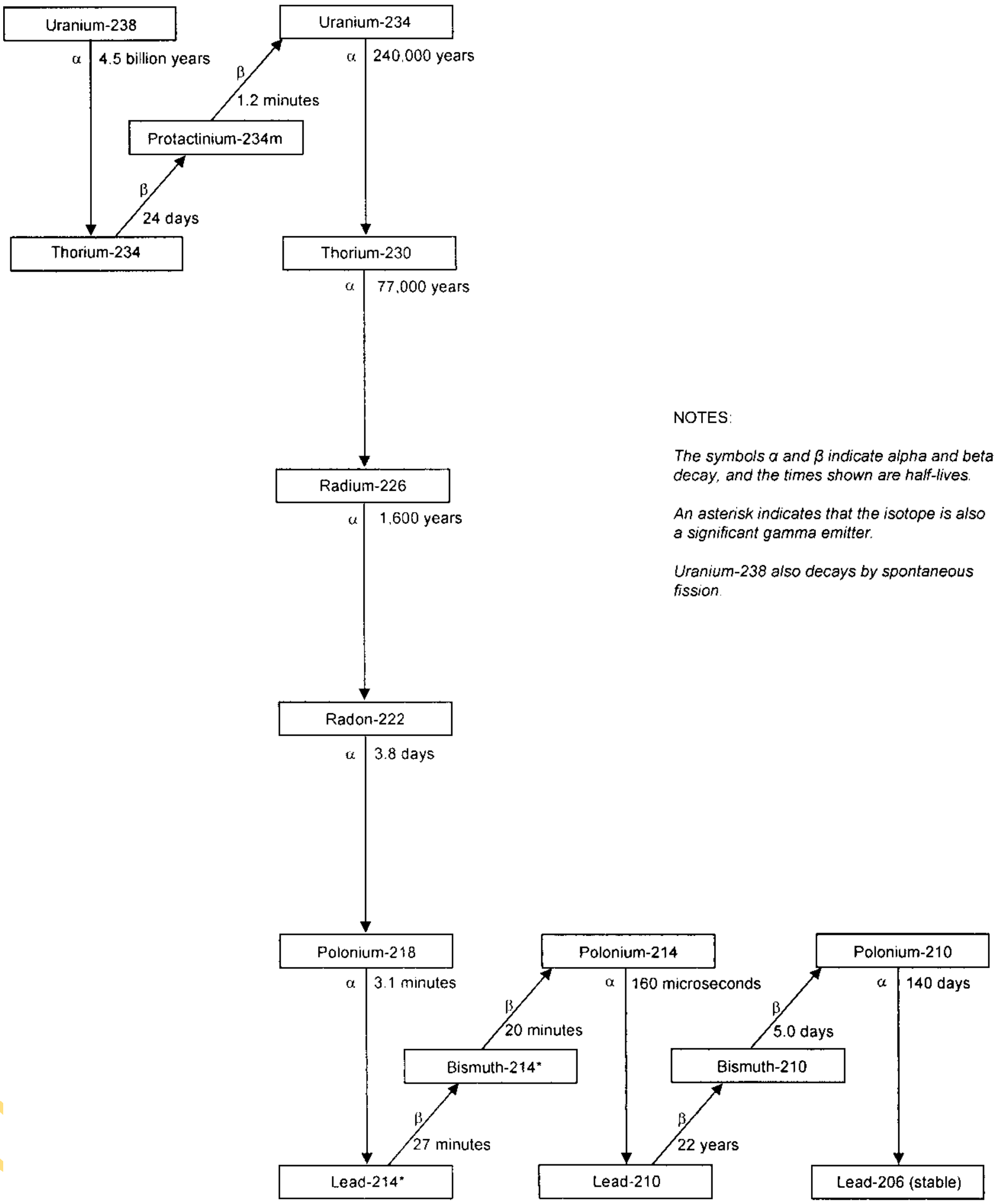
Radioactive decay continues to produce new radioactive daughters until lead-208 is reached, which is a stable daughter. Natural uranium consists of two series: the uranium series, headed by ^{238}U and the actinium series, headed by the uranium isotope ^{235}U. The latter accounts for only 0.72% of the atoms in natural uranium. The various members of the thorium and uranium series emit a mixture of α-, β-, and γ-radiation. In addition, the primordial radionuclide ^{40}K also contributes to the dose rate, because of its presence in minerals like feldspar. The radioactivity of potassium is due to its isotope potassium-40. This nucleus has a complicated decay involving electron capture, β- and β + decay and γ -radiation. The radioisotope ^{40}K is present in natural potassium with an abundance of 0.018% and has a half life of 1.28×10^{9}y. Potassium is widely distributed in nature, with concentration varying from about 0.1% for limestone, 1% for sandstones and 3.5% for some granite (Sabol and Weng, 1995).

1.3 Biological Effect of Radiation

The mechanism of the biological effect of radiation is through ionization and excitation of atoms and molecules in the tissue. All biological damage effects begin with the consequence of radiation interactions with the atoms forming the cells.

1.4 Interaction of Radiation with Cells

If radiation interacts with the atoms of the DNA molecule, or some other cellular component critical to the survival of the cell, it is referred to as a direct effect. Such an interaction may affect the ability of the cell to reproduce and, thus, survive. If enough atoms are affected such that the chromosomes do not replicate properly, or if there is significant alteration in the information carried by the DNA molecule, then the cell may be destroyed by "direct" interference with its life-sustaining system.



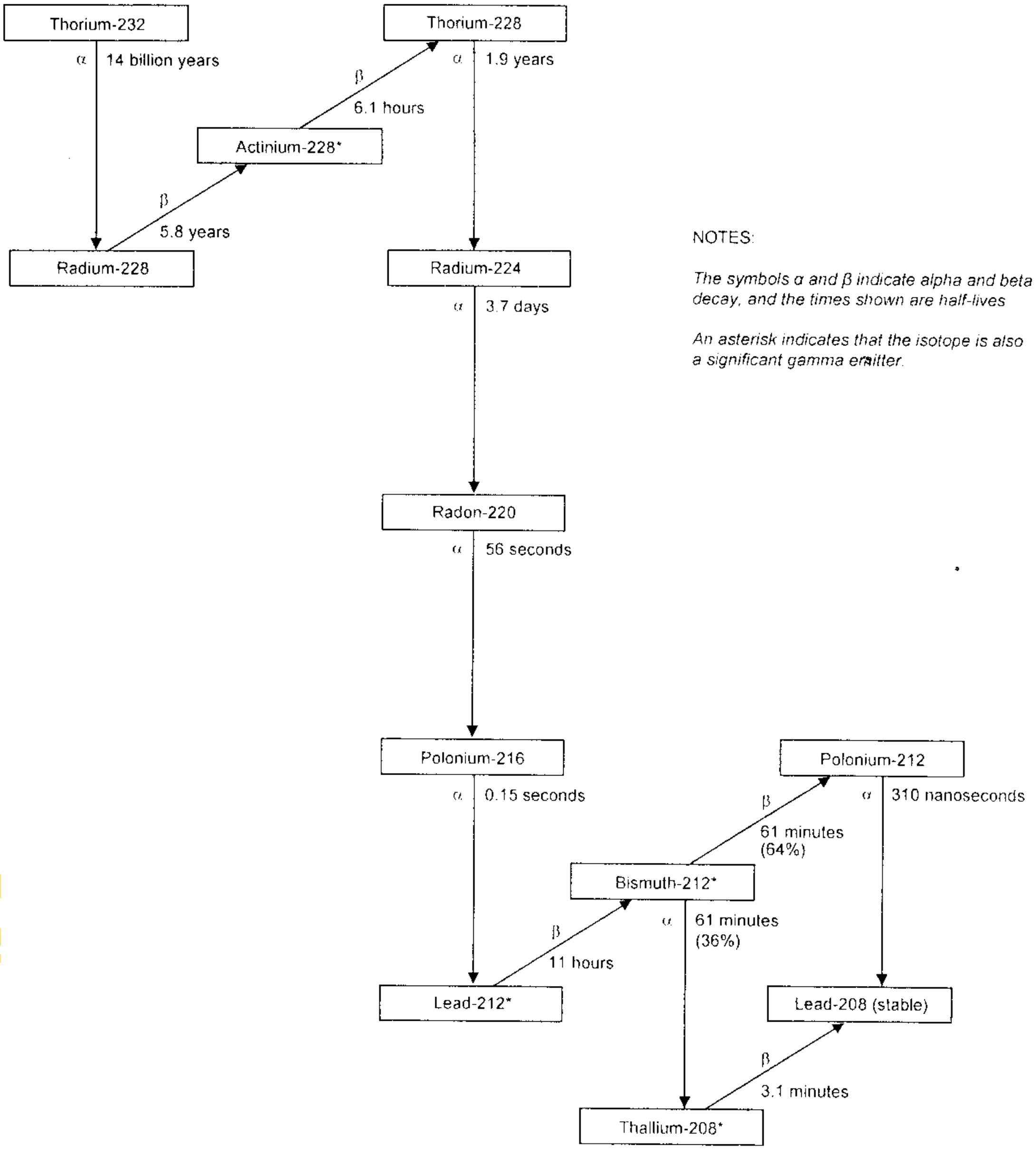
NOTES:

The symbols α and β indicate alpha and beta decay, and the times shown are half-lives.

An asterisk indicates that the isotope is also a significant gamma emitter.

Uranium-238 also decays by spontaneous fission.

Figure 1.1: Natural Decay Series: Uranium-238 (Argonne National Laboratory, EVS, 2005)



NOTES:

The symbols α and β indicate alpha and beta decay, and the times shown are half-lives

An asterisk indicates that the isotope is also a significant gamma emitter.

Figure 1.2: Natural Decay Series: Thorium -232 (Aronne National Laboratory, EVS, 2005)

In the indirect effect, when radiation interacts with water, it may break the bonds that hold the water molecule together, producing fragments such as hydrogen (H) and hydroxyls (OH). These fragments may recombine or may interact with other fragments or ions to form compounds, such as water, which would not harm the cell. However, they could combine to form toxic substances, such as hydrogen peroxide (H_2O_2), which can contribute to the destruction of the cell. The (OH) radical which is known to be the most effective in causing damage, can attract a hydrogen atom from the deoxyribose moiety of the DNA molecule yielding a highly reactive site on DNA in the form of a DNA radical. Thus this process arises from the irradiation of an adjacent water molecule rather than the DNA molecule itself (BEIR, 1990).

Not all living cells are equally sensitive to radiation. Those cells which are actively reproducing are more sensitive than those which are not. This is because dividing cells require correct DNA information in order for the cell's offspring to survive. A direct interaction of radiation with an active cell could result in the death or mutation of the cell, whereas a direct interaction with the DNA of a dormant cell would have less of an effect. As a result, living cells can be classified according to their rate of reproduction, which also indicates their relative sensitivity to radiation. This means that different cell systems have different sensitivities. Lymphocytes (white blood cells) and cells which produce blood, gonad and epithelia are constantly regenerating, and are, therefore, the most sensitive. Reproductive and gastrointestinal cells are not regenerating as quickly and are less sensitive. The nerve and muscle cells are the slowest to regenerate and are the least sensitive cells (USNRC Technical Training Center, 2009). Cells in human body, have a tremendous ability to repair damage. As a result, not all radiation effects are irreversible. In many instances, the cells are able to completely repair any damage and function normally.

If the damage is severe enough, the affected cell dies. In some instances, the cell is damaged but is still able to reproduce. The daughter cells, however, may be lacking in some critical life-sustaining component, and they die. The other possible result of radiation exposure is that the cell is affected in such a way that it does not die but is simply mutated. The mutated cell reproduces and thus perpetuates the mutation. This could be the beginning of a malignant tumor.

At low doses such as that received everyday from background radiation, cellular damage is rapidly repaired. Muscle and nerve cells are relatively insensitive to radiation, and therefore, so are the muscles and the brain. In general radiation sensitivity of a tissue is proportional to the rate of proliferation of its cells and inversely proportional to the degree of cell differentiation (Princeton, 2007; USNRC Technical Training Center, 2009). The schematic diagram of cell damaging effect of radiation is shown in Fig.1.3.

Biological effects of radiation are typically divided into two categories:

The first category consists of exposure to high doses of radiation over short periods of time producing acute or short term effects. The second category represents exposure to low doses of radiation over an extended period of time producing chronic or long term effects.

1.5 Justification for this Study

Fertilizers are chemical compounds that provide necessary chemical elements and nutrients to plants, as such have become essential to the agricultural field all over the world. Different types of fertilizers, such as phosphate, NPK etc. used for agricultural purposes are essential components of agricultural activities that help to increase the crop production and to improve the nutrient-deficient properties of lands. Fertilizers usually employed in agriculture contain traces of heavy metals and relatively high concentrations of naturally occurring radionuclides. Phosphate containing fertilizers have been used worldwide to increase the quantities of micronutrients, which are continuously taken off from the soil due to farming activities. Also, the concentration of ^{238}U and its decay products tends to be elevated in phosphate deposits of sedimentary origin, therefore when this rock is processed into phosphate fertilizers, most radionuclides come into fertilizers. Thus, fertilizers redistribute naturally occurring

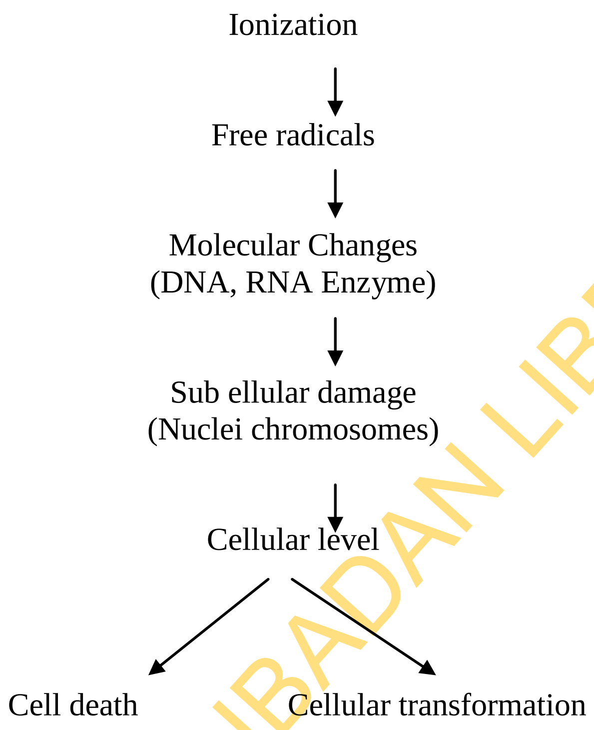


Figure 1.3: Schematic Diagram of Cell Damaging Effect of Radiation

radionuclides at trace levels throughout the environment and become a source of radioactivity. Hence, the use of such fertilizers is the main anthropogenic source of the uranium input to the farm soil in the environment (about 73 % of the total input of uranium) (Stojanovic et al., 2012).

However, a possible negative effect of fertilizers is the contamination of cultivated lands by some naturally occurring radionuclide materials (NORM)

Plants take some fraction of the radioactivity present in the fertilizers applied to soil. The soil to plant transfer factor is broadly used as one of the parameters to estimate the intake of radionuclides through food ingestion. Human beings are internally and externally exposed to radioactivity due to ingestion of plants raised on fertilized soil and inhalation of rock and fertilizer dust (Todorovic et al., 2016).

Some of the main components in fertilizers are nitrogen, phosphorus and potassium. These added components, as well as other added heavy metals and chemicals in fertilizers, are responsible for many adverse health effects (Aktar et al., 2009). The heavy metals may accumulate in the soil with repeated applications of chemical fertilizers for crop nutrients and thus increase the levels of toxic heavy metals in thesoils. This has generated an environmental concern over the years. Also due to handling and use of chemical fertilizer, some fertilizers particles may be ingested, which could contribute to the committed effective dose to humans. When radioactive elements are inhaled, ingested (swallowed) or absorbed into the blood stream, sensitive living tissue can be exposed to radiation. Radionuclides may reach the gastrointestinal tract directly by ingestion or indirectly by transfer from the respiratory tract. The exposure routes to human are shown in Figure 1.4.

Although radionuclide concentrations in the environment have been extensively studied in Nigeria and some countries (UNSCEAR, 2000; Amrani and Tahtat, 2001; Baba *et al*., 2004; El Afifi *et al*., 2006; Monika *et al*., 2010; Ademola and Ademonehin, 2010; Jibiri and Biere, 2011; Faanu *et al*., 2011; Ademola and Obed, 2012; Kaleel and Mohanad, 2012; Innocent et al., 2013; Augustine *et al*., 2014; Augustine *et al*., 2014; Rajeshwari *et al*., 2014; and Jassim *et al*., 2016) information on the level of contribution of chemical

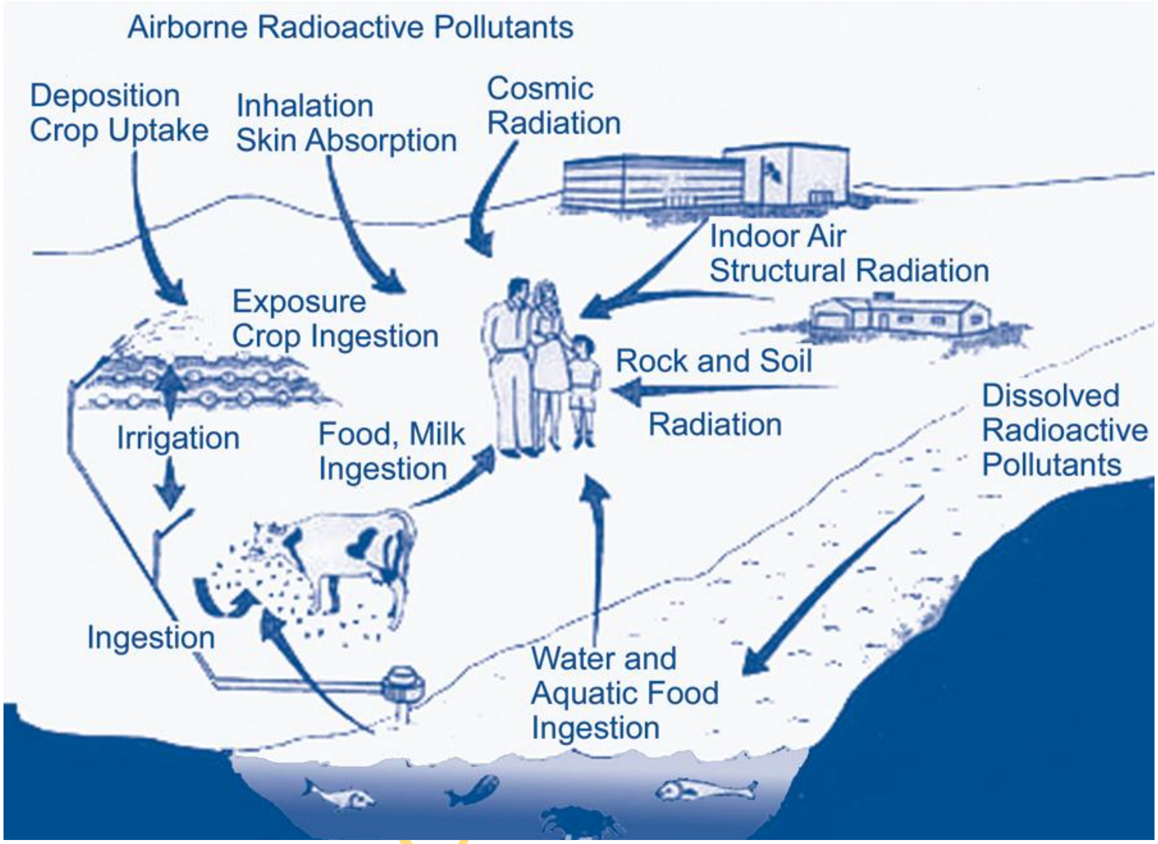


Fig. 1.4: **Radionuclides Exposure Route to Human (U.S. D O E)**

fertilizers to farm soil radioactivity and radiological health effects in Nigeria have not been adequately addressed. Despite the good number of brands of chemical fertilizers by different manufacturing companies sold in retail market outlets in the country, information on the level of contribution of the chemical fertilizers to farm soil radioactivity and radiological health effects are scanty. This study was designed to assess the contributions of chemical fertilizers to farm soil radioactivity and committed effective doses to human.

1.6 Aim and Objectives of the Study

In view of the large amount of chemical fertilizer distributed and used by the farmers in parts of Nigeria, it is imperative to assess the contribution of chemical fertilizers to farm soil radioactivity and the committed effective doses to man. The aim of the present study is to determine the contribution of chemincal fertilizers to farm soil radioactivity and radiological effect on human. The objectives of the study are as follows:

i. to determine the activity concentrations of gamma emitting radionuclides ^{40}K, ^{226}Ra and ^{232}Th in the different brands of NPK (15-15-15) fertilizer from the different fertilizer companies, sold in retail markets across the major commercial cities of southwestern, Nigeria.

ii. to determine the gross alpha and gross beta activities of the NPK (15-15-15) fertilizer and Single Superphosphate fertilizer in order to estimate the commited effective doses due to ingestion and handling of fertilizer samples during application.

iii to determine the activity concentration of ^{40}K, ^{226}Ra and ^{232}Th in the cultivated fertilized farm soil and virgin soil in order to determine the contribution of chemical fertilizer to farm soil radioactivity.

iv investigate the transfer ratio of radionuclides from soil to some vegetables

v to determine the activity concentration of ^{40}K, ^{226}Ra and ^{232}Th in the soil and plant samples of the experimental farms in order to evaluate the committed effective doses to man.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Radioactivity in the Environment

Natural environmental radioactivity and the associated external exposure due to gamma radiation depend mainly on the geological and geographical conditions, and appear at different levels in the soils of each region in the world (UNSCEAR, 2000). The specific levels of terrestrial environmental radiation are related to the composition of each lithologically separated area, and to the content of the rock from which the soils originate (Habshi, 1980). Terrestrial radionuclides, also known as primordial radionuclides, are present everywhere in the environment including the human body. The prominent Primordial radionuclides (and their decay products) with half-lives which are comparable to the age of the earth exist in measurable quantity in the earth's environment are ^{232}Th , ^{238}U and ^{40}K their respective contributions to natural radiation exposure dose is about 55.8% for ^{238}U, 14% for ^{232}Th,and 13.8% for ^{40}K (UNSCEAR, 1993, Ngachin, 2008).

Studies in science has contributed immensely to environmental radioactivity due to the proliferation of nuclear applications such as nuclear weapons, nuclear tests, radioactive effluent discharges, release of radioactive wastes to the environment, nuclear power reactors' accidents such as the Chernobyl nuclear power plant in 1986. The United Nation Scientific Committee on Effects of Atomic Radiation (UNSCEAR) had evaluated the average annual dose from combined effects of both natural and Artificial radioactivity as 82% from natural sources, 17% from medical applications, 0,9% from radioactive elements and 0.04% from production of nuclear energy, while others such as industrial use of radionuclides account for the remaining 0.06%.

Naturally occurring radiation and environmental radioactivity has led to the performance of extensive surveys in many countries of the world (UNSCEAR, 2000). Such investigations can be useful for both the assessment of public dose rates and the performance of epidemiological studies, as well as to keep reference–data records, in order to ascertain possible changes in the environment radioactivity due to nuclear, industrial, and other human activities. Natural environmental radioactivity arises mainly from primordial radionuclides, such as ^{40}K and the nuclides from the ^{232}Th and ^{238}U series and their decay products, which occur at trace levels in all ground formations (Akhtar *et al*., 2005; Yousef *et al*. 2007). The natural radioactive chains from ^{238}U, ^{235}U and ^{232}Th produce a group of radionuclides with a wide range of half-lives. Most of the radioisotopes are alpha emitters, so when they are ingested or inhaled, they significantly contribute to the radiation dose that people receive (Scholten and Timmernans,2005; Abel-Ghany, 2009). On the other hand, both uranium and thorium are always present in soil, their gamma radiation causes external exposures with the consequent absorbed doses.

Building and industrial materials, also contribute to environmental radioactivity in two ways. by gamma radiation mainly ^{226}Ra, ^{232}Th, ^{40}K and their progenies to a whole body dose and in some cases by beta radiation to a skin dose, also by releasing the noble gas radon, its radioactive daughters, which are deposited in the human respiratory tract (Quindos,1987). Enhanced or elevated levels of natural radionuclides in such materials may cause doses in the order of several mSv y^{-1} (Ngachin *et al*. 2007).

2.2 Chemical Fertilizers

Chemical fertilizers are referred to as inorganic fertilizer, they are made up with different formulations to suit a variety of specified uses. The principal reasons for applying fertilizers are:

(i) Balancing the soil: to bring the composition of nutrients in a soil up to the mix required by crops, or add nutrients that are in short supply.

(ii) Replacing: to replace the nutrients, that has been harvested.

(ii) Feeding soil organisms: the use of fertiliser to feed organisms from the woody substances in it.

Direct fertilization may include one or several nutrients; there are single or simple fertilizers such as $NaNO_3$, $MgNO_3$ and SSP fertilizers.

(a) Nitrogenous fertilizers (vigorous growth of plant parts)

(b) Phosphatic fertilizers (promotes vigorous growth and sturdy roots of plants)

(c) Potassium fertilizers (cell wall and membrane development)

Different types of chemical fertilizers are classified according to the three principal elements, namely Nitrogen (N), Phosphorous (P) and Potassium (K), and may, therefore, be included in more than one group. There are multi-nutrient fertilizers which contain two or more macronutrients, such as NP, PK, NK and NPK. The product name "NPK" is normally followed by three numbers to indicate the percent of N, P_2O_5 and K_2O which the product contains, e.g. 15-15-15 indicates that this particular grade contains 15% N (nitrogen compounds), 15% P_2O_5 (phosphorus compounds) and 15% K_2O (potassium compounds). The reason why there are so many different types of chemical fertilizers in different formulations is because different plants require different nutrients.

Phosphate rocks together with potassium ores and nitrogenous compounds are the main raw materials used for fertilizers' industrial production. As a matter of fact phosphorus, potassium and nitrogen are essential elements for plants growth. Phosphorus can be found in nature in a combined state in fluorapatite Ca5(PO4)3F, hydroxylapatite Ca5(PO4)3(OH) and chlorapatite Ca5(PO4)3Cl ores, the main constituents of phosphate rocks (Adel G. E. Abbady, 2005). The Nitrogen is processed and produced from Ammonia; Phosphate rock digestion enables a considerable part of the phosphorus to be supplied, while potassium is produced from potassium salts (potash).

2.3 Radioactivity in Chemical Fertilizer

Phosphate materials used for production of phosphate fertilizers contain a minor quantity of radioactive material, which are mainly various members of the uranium and thorium series, and radioactive potassium. Fertilizer plants cause environmental harm through emissions of radioactive gases into the air, discharges into water, and storage and solid waste problems into the environment. Actions should be undertaken to minimize the emissions and to clean up spills and solid wastes (UNSCEAR, 1988; Diab *et al.*, 2008). Through the various stages of production, Uranium and Thorium with their decay products may reach the commercial fertilizers used in agriculture. The introduction of natural radionuclides also occurs in areas far from the production zone through the utilisation of fertilizers for soil enrichment and the conveyance of solid wastes to landfills (Pfister *et al*., 1976).

Phosphate rocks contain relatively high concentrations of naturally occurring radioactive materials from the uranium and thorium decay series (^{238}U and ^{232}Th). Such rocks like granites, sandstone and mineral rocks (granite, canotite and pitchblend) are known to be rich in uranium. Phosphate rock is the starting raw material for all phosphate products. It can be of sedimentary, volcanic or biological origin. Concentrations of ^{232}Th series and ^{40}K in phosphate rocks of all types are similar to those observed normally in soil, whereas the concentration of ^{238}U and its decay products tend to be elevated in phosphate deposits of sedimentary origin. A typical concentration of ^{238}U in sedimentary phosphate deposits is 1500 Bq/kg (UNSCEAR, 1993; Ashraf *et al*. 2001). Mining, milling, transporting of phosphate ores, manufacturing of phosphate fertilizers and using phosphate fertilizers containing uranium are ways in which the workers, public and the environment are exposed to enhanced doses of radiations (IAEA, 2004; Othman and Al-Masri, 2007).

The primary potential environmental radiation problem associated with phosphate rock mining and processing is related to mining debris and processing waste products. While these materials do not present a direct radiation hazard, problems may be created by their use. Occupational exposures mainly occur during mining, processing and transportation of phosphate rock, as well as during transportation and utilization of phosphate fertilizers (UNSCEAR, 1988). Nitrogen-Phosphrus-Potassium (NPK) fertilizers can contain elevated levels of the uranium series and potassium-40. One factor that impacts the amount of radioactivity in the chemical fertilizer is its nitrogen, phosphorous and potassium content

Natural radionuclides are present in air breathed by humans, in food, drinking water as well as the ground from which human settlements are built. When ingested or inhaled, naturally occurring radionuclides are distributed among body organs according to the metabolism of the element involved, which normally exhibits varying sensitivities to radiation (Thomas, *et al*., 2011). The release of radionuclides into environment contaminates food according to the type of soil, its chemical characteristics, the physical and chemical forms of the radionuclides in the soil, radionuclide uptake by particular plant and finally the level of accumulation by particular foodstuffs (Shanthia, et al., 2009). Studies from other countries (Tahir *et al*., 2009; Ashraf and Al-Sewaidan, 2008; Becegato et al., 2008; Wassila and Ahmed, 2011; El-Bahi *et al*., 2004; Ahmed and El-Arabi, 2005; Oni *et al*., 2014) have shown that chemical fertilizers contain some concentrations of radioactive elements, hence they can contribute to radioactivity in soil, plant and environment.

2.4 Radioactivity in Soil

The amount of radioactivity in the soil varies widely; hence it is important to monitor the terrestrial background radiation mainly due to natural radionuclides in soil. Soil from waste dump sites may contain naturally occurring radionuclides in significant amounts and the resulting external radiation exposure pathway to the population has been subjects for study (Oni *et al*., 2011; Kaleel and Mohanad, 2012). Many have measured the activity concentration of natural radionuclides in soil to ascertain the levels of contamination, these are presented in Table 2.1

2.5 Radioactivity in Farm Soil

The use of different types of fertilizers in the agricultural sector for the purpose of enhancing crop yield has become very common nowadays, fertilizers are usually used in reclaiming the land and improving the properties of crops. Despite their positive values in enhancing crop productivity, (Meserecordias et al., 2014) research has shown that phosphate rocks contain a substantial concentration of uranium, thorium, radium and their decay products, these radionuclides are redistributed throughout the agricultural soils of the world (Mlwilo *et al*., 2007). Hence, the use of chemical fertilizer may enhance natural radionuclide contents in the farm soils and through root uptake be accumulated in the leaves. It is important to note that using phosphate fertilizers over a period of many years could increase the radium and uranium content of the soil. This consequently, increases the radiation dose which would cause diseases for human body.

Table 2 .1: Activity concentrations (Bq/kg) of soil samples reported in literatures

Country	**Activity Concentrations (Bq/ kg)**			**References**
	^{40}K	**^{238}U**	**^{232}Th**	
Nigeria	505.1	55.3	26.4	Augustine, *et al*., 2014
Nigeria	384.2	39.8	17.7	Ademola and Obed, 2012
Nigeria	240.2	13.3	40.0	Ademola and Ademonehin, 2010
Nigeria	426.5	12.1	60.1	Innocent *et al*., 2013
Egypt	337	78	33	El Afifi *et al*., 2006
Algeria	422	41	27	Amrani and Tahtat, 2001
Ghana	162.1	13.6	24.2	Faanu *et al*., 2011
Palestine	120	34.5	23.8	Kaleel and Mohanad, 2012
India	260.6	68	59	Rajeshwari *et al*., 2014
Turkey	488	47.3	36.3	Baba *et al*., 2004
Poland	529	40	58	Monika,*et al*., 2010
Iraq	453.9	21.2	9.7	Jassim *et al*., 2016
Nigeria	505.1	55.3	26.4	Augustine, *et al*., 2014
Egypt	264.1	31.12	10.96	Diab *et al*.**,** **2008**
Nigeria	2550.4 - 3208	33.1 - 39.9	51.98 - 56.08	Jibiri and Biere, 2011
Nigeria	1062	129	147	Jibiri et al, 2011
World average	420	35	30	UNSCEAR, 2000

The research reports on the activity concentrations of the radionuclides in cultivated farm soils in Nigeria and other countries are presented later in Table: 4.24.

2.6 Radioactivity in Vegetables

Plants are the primary recipients of the radionuclides from soil. These radionuclides can get transferred into plants along with the nutrients during mineral uptake and accumulate in various parts and even reach edible portions. Studies on the radioactivity of the consumable parts of a vegetable assume importance as it is necessary to estimate the ingestion dose to the public (Jibiri *et al*., 2007; Islaml, *et al*., 2014). It is noted that one of the major direct contaminations of man by ionizing radiations is done through the food chain. Therefore, accurate estimation of the occurrence of natural radionuclides in foods will provide information from which the estimation of the average radiation exposure of the public in some localities can be made. Also, the knowledge of intakes of some radionuclides (such as ^{238}U and ^{232}Th) is important for estimating the metabolic parameters of up-take and retentions of those radioelements in human body (Thomas, *et al*., 2011). The leaves which constitute the eatable part of the plant, are commonly consumed in the country, hence, it is important to understand the behavior of natural radionuclides in the environment because such information can be used as the associated parameter values for radiological assessment.

The low mobility of radioactive elements in soil holds them in the root zone. Plants assimilate the radioactive substances with others necessary for their growth, then dangerous isotopes may get into animal tissues and finally as food into organisms of human beings (Chibowski, 2000). Radioelements contents have been measured in various food and drinking water samples by several methods, but their concentrations differ from place to place. Previous studies have shown that there are three food categories, namely: fish and shellfish, cereals (excluding rice) and vegetables, found to be the main contributors to the daily intakes (Thomas *et al*., 2011). The activity concentration of the naturally occurring radionuclides in food and vegetables have been studied in Nigeria and other countries to determine the level of contamination, this is presented in Table 2.2.

Table 2.2: The Activity concentrations of Vegetables reported in literatures

Country	**Vegetable**	**Activity Concentration (Bq/kg)**			**References**
		^{40}K	**^{238}U**	**^{232}Th**	
Cameroon	Vernonia	302 ± 36 (115 - 460)	42 ± 15 (20 – 50)	17 ± 7 (9 – 22)	Thomas, *et al.*, 2011
Nigeria (Delta State	water leaf (Talinum triangulare)	36.48 –68.02	2.33 – 5.18	1.26 – 2.98	Tchokossa, *et al.*, 2013
Bangladesh (Jamalpur)	Ladies finger	1274-4860	5.5-7.4	8-2.4	Selina and Aleya, 2012
Bangladesh (Kustia)	Red amaranth	870-2531	4.22-20	5.5-23	Selina and Aleya, 2012
Nigeria (Jos)	Tomatoes *(Lycopersicum* spp*)*	32.37±14.44	3.84 ± 0.06	3.96 ± 0.17	Jwanbot, *et al.*, 2012
Egypt	Tomatoes *(Lycopersicum* spp*)*	49.48 ±3.45	0.96 ±0.30		Saleh, *et al.*, 2007
World average Value	Root vegetables/ fruits		0.003	0.0005	UNSCEAR, 2000

2.7 Radiation Detection and Principles of Scintillation Spectrometry

Instruments used for detecting and measuring nuclear radiations are based on the ionization and excitation radiations produced in the atom and molecules of the medium through which they pass. Whatever the type of radiation, the general principle is that the radiation gives up some or all of its energy to the medium of the detector, either by ionizing it directly or by causing the emission of the charged particles which in turn produce ionization in the medium. The response of the specific type of detector is based on the fundamental mechanism by which radiation interact and lose their energy in the detector.

2.8 Interaction of Gamma-radiation with Matter

There are three major processes by which gamma rays can interact with atoms of matter when absorbed or scattered. These processes however lead to partial or complete transfer of gamma-ray photon energy to an electron. These interactions are Photoelectric effect.

2.8.1 Compton scattering

In this process interaction takes place between the incident gamma ray photon and an electron that is loosely bond to an atom of the absorbing material, the electron is considered free because its binding energy is much smaller than the energy of the incident photon, hence it is regarded as an elastic scattering. The photon collides with the electron and transfers a fraction of its energy to the electron; the electron is ejected from the atom along with the scattered photon. The photon is scattered at an angle θ with respect to its original direction and its energy is reduced from hv to hv^1. Thus its frequency is changed and its wavelength increases from λ to λ^1 . The electron is scattered at an angle ϕ and its energy is almost equal to $hv - hv^1$. The change in wavelength, $\Delta\lambda$ is given by

$$\Delta\lambda = \lambda - \lambda^1 = \frac{h}{m_0 c}(1 - \cos\theta) \qquad (2.1)$$

m_0 is the rest mass of an electron $\Delta\lambda$ is referred to as Compton shift and h is the planck's constant.

Because all angles of scattering are possible, the energy transferred to the electron can vary from zero to a large fraction of the gamma ray energy. The energy of the scattered photon E^1_γ is given in terms of the scattering angle θ and the initial photon energy E_γ as:

$$E_\gamma = \frac{E_\gamma}{1+(\frac{E_\gamma}{m_0c^2})\{1-\cos\theta\}} \qquad (2.2)$$

Where m_0c^2 is the rest mass energy of the electron, which is 0.511MeV.

The kinetic energy of the scattered electron is given by

$$E_e = E_\gamma - E^1_\gamma \qquad (2.3)$$

2.8.2 Photoelectric Effect

Photoelectric effect process involves interaction of and incoming gamma ray photon with the atom of the absorbing medium in which the photon is completely absorbed resulting in the ejection of an energetic electron in its place from one of the bound states, usually K-shell. This ejected electron is known as a photoelectron and its energy is:

$$E_e = hv - E_b \qquad (2.4)$$

where E_b is the binding energy of the photoelectron in its original shell and *hv* is the energy of the incident photon. For gamma ray energies of more than a few hundred KeV, the photoelectron carries off the majority of the original photon energy, which it loses in ionization and excitation of the absorber atom. The peak resulting from photoelectric interaction is termed photopeak and the number of counts under a photopeak per unit time is proportional to the activity of the source. Besides the ejection of photoelectron, the interaction also creates an ionized atom with a vacancy in one of its bond shells. This vacancy is promptly filled by electrons from the higher shells resulting in the production of characteristic x-rays. The photoelectric effect is the predominant absorption process at low gamma energies. The probability that a photon will interact with matter, expressed by the cross-section σ (m^2), depends on the photon energy E_γ and the composition of the matter. For photoelectric effect, the cross-section is approximately given by IAEA (2003b):

$$\sigma = \text{constant } (\frac{Z^n}{E_\gamma^3}) \quad (2.5)$$

where n varies between 4 and 5 over the gamma energy region of interest and Z is the atomic number of the absorber. Equation 2.11 Indicates that the probability of photoelectric absorption depends strongly upon the atomic number of the absorbing material. This is the primary reason why high Z materials such as lead are used to shield radiation detectors from nuclear radiation sources.

2.8.3 Pair production

Pair production takes place when the photon energy is above 1.02 MeV or $2m_oc^2$, under the influence of the electromagnetic field of a nucleus, the photon is absorbed completely and replaced by a positron and an electron pair. The total energy of the Compton scattering and pair production is equal to the energy of the initial photon as given in the energy equation below:

$$hv = (E_e + m_0 c^2) + (E_p + m_0 c^2) \quad (2.6)$$

where E_e , E_p and m_0 are the kinetic energies of the electron, positron and mass of electron, respectively. The particles lose their kinetic energies E_e and E_p, by excitation of the absorption crystal. The positron then annihilates with an electron to produce two photons, each with 0.511 MeV energy in approximately 180^0 (oppositely directed) to conserve momentum.

The final light output is therefore usually due to one of three possible coincident sequences following the initial pair production.

(a) Both gammas resulting from the annihilation interaction may lose their kinetic energies to the crystal. Since the time interval between pair production and annihilation is as short as 10^{-6}s, a light pulse size given by the total energy hv of the incident photon, that is a photopeak, will result. This is added to the photopeak due to photoelectric absorption.

(b) One of the annihilation photon may escape. A “single-escape peak” then occurs at a pulse height given by $hv - 0.511MeV$.

(c) Escape of both annihilation photons giving rise to a “double-escape peak” corresponding to $hv - 1.02MeV$

2.9 Principle of Scintillation Spectroscopy

The scintillation process is one of the oldest and most useful methods available for detecting ionizing radiations and spectroscopy of a wide range of radiations. Scintillation detectors operate on the principle that ionization and excitation of certain organic and inorganic materials when they absorb radiation energy lead to excited electronic state and the subsequent return of the excited electrons to ground state is accompanied by the emission of light. Therefore, a scintillation detector is a transducer that changes the kinetic energy of an ionizing radiation into a flash of visible light.

Sodium iodide thallium activated NaI(Tl) detector, which is optically coupled to a photomultiplier tube is most frequently used for gamma-ray measurement. The thallium activator, which is present as an impurity in the crystal structure to the extent of about 0.2% converts the energy absorbed in the crystal into light. The high density of the crystal, together with its high effective atomic number, result in a high detection efficiency which makes it ideal for low-level gamma spectrometry. The crystal, NaI (Tl) is highly hygroscopic and so, it is usually enclosed in a light metal like aluminum with optical window through which it is coupled to a photomultiplier.

NaI (Tl) crystal has an excellent light yield to primary or secondary electrons, which is the highest of any known scintillation material (Canberra, 1983). Its response to gamma-rays is close to linear over most of the significant energy range. The light released with each interaction in the crystal is weak relative to normal room light intensity, a photomultiplier tube (PMT) is therefore used to detect and record this light. The PMT converts the visible light photons to electrical pulses which are sorted by height, counted and stored in a multichannel analyzer (MCA) which displays the resulting spectrum. A Canberra 7.6 mm × 7.6 mm NaI (Tl) crystal was used in this study.

A schematic diagram of sequence of events in a scintillation detector crystal, which is coupled to a photomultiplier tube, is shown in Figure 2.1.

2.9.1 Principle of radiation detection by a NaI(Tl) crystal

When an incoming gamma radiation with energy $E = hv$ is incident on the NaI(Tl) crystal, there is photoelectric absorption, the energy of the photon is completely dissipated in the crystal producing N number of secondary photons in the visible range. The number of the secondary photons is given by:

$$N = \frac{Eq}{W_0} \tag{2.7}$$

where q is the luminescence quantum efficiency, which is the probability of a photoelectric interaction of the incident photon, W_0 is the average energy to produce a single photon which about 3eV for NaI(Tl) crystal. When these photons strike the photo sensitive cathode of the photomultiplier tube, they cause photoelectrons to be ejected from the cathode. The electrons are then accelerated to a second electrode, called dynode, whose potential is about 100V positive with respect to the photocathode. Each of the electrons that impinge the dynode causes several other electrons to be ejected from the dynode, thereby multiplying the original photocurrent. At the first dynode the number of photoelectrons is given by:

$$N_d = \frac{Eq}{W_0} m C_{pe} g_c G \tag{2.8}$$

where m is a factor between 0 and 1 depending on the degree of spectral matching between the scintillation spectrum and the spectral responses of the photocathode, C_{pe} is the photo-quantum efficiency of the window-cathode system, g_c is the efficiency with which the first dynode collects the number of electrons arriving it and G is the light collection efficiency of the photocathode which gives the ratio of the number of photoelectrons emitted at the photocathode to the number of photons incident on it.

G is determined by the self-absorption, reflection loses, light trapping, optical flaws and the optical geometry of the photocathode.

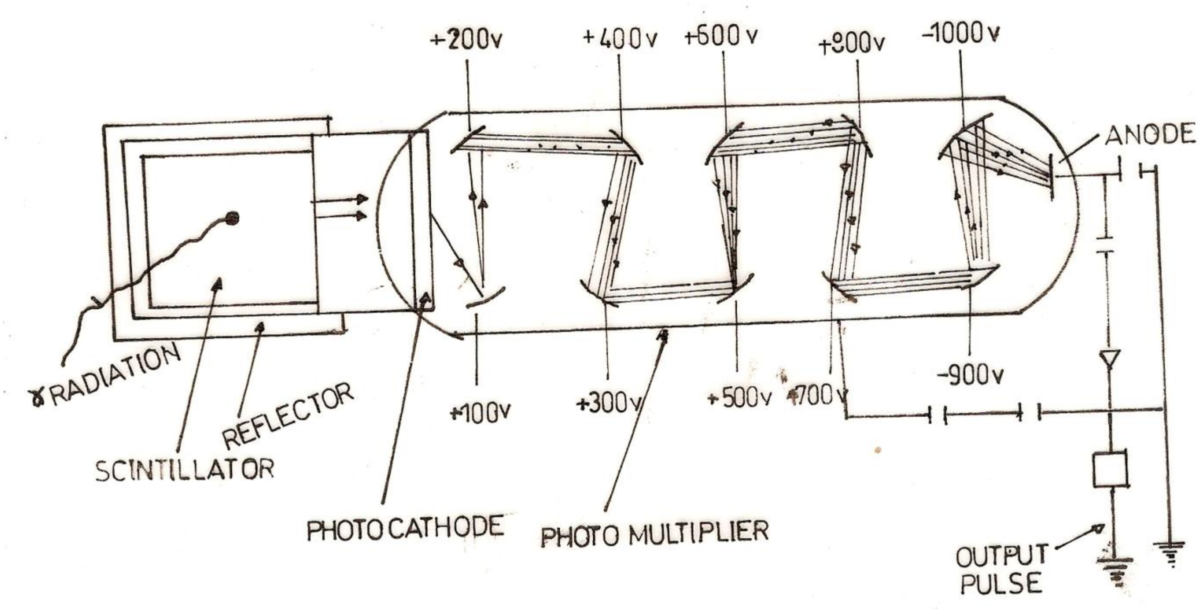


Figure 2.1: A schematic representation of the sequence of events in the detection of gamma ray photon by a scintillation detector.

The NaI(Tl) unit may be coated with reflectors like MgO or Al_2O_3 thereby making self-absorption small, in order to make G approximately equal to unity. The term $mC_{pe}g_c$ depends in a complex manner on the wavelength of the emitted. The factor C_{pe} depends on the cathode material and its thickness while g_c depends on the structure of the dynode. The N_d electrons given by the above equation are multiplied by k successive dynodes to give an overall gain M

$$M \quad = \quad \prod_{i}^{k} m_i \qquad\qquad (2.9)$$

where m_i is the multiplication at the *ith* dynode and is roughly proportional to the voltage between the dynodes. The total number of electrons Q, at the last dynode collected at the anode is given by

$$Q \;=\; N_d\, M \qquad\qquad (2.10)$$

The multiplication is roughly proportional to the voltage between the dynodes. Therefore, the overall gain of a photomultiplier tube is a sensitive function of the applied voltage (Knoll, 1989). The total number of electrons collected at the anode has a linear proportionality in magnitude to the energy of the initial incident photon.

Apart from the number of electrons given by equation 2.12, there are a number of electrons produced due to thermionic emission in the photomultiplier tube. The number of electrons with thermal energy greater than the work function of the photo cathode which are emitted as thermionic electrons is a function of temperature as given in the equation (Birks,1964).

$$n_T \quad = \quad AT e^{-\left\{\frac{Qe}{kT}\right\}} \qquad\qquad (2.11)$$

where T is the absolute temperature, e is the electronic charge, k is the Boltzman constant, A and Q are characteristics of the cathode material.

These thermionic electrons are multiplied in the PM tube and constitute the dark current, in other words they produce in the PM tube in the absence of incident radiation. The pulses form part of the background of the energy spectrum, this may constitute a problem when weak sources or low energy radiation are being measured.

2.9.2 Gamma-ray spectrometry

Gamma-rays of various energies and intensities are emitted by most radioactive sources, energy spectrum is produced when these emissions are collected and analysed with a gamma spectrometer. The fast electrons, which result from the three most common processes of energy transfer by gamma-rays, earlier discussed, provide very useful information on energy and intensity of the incident gamma-rays. A detailed analysis of this spectrum is typically used to determine the identity and the quantity of gamma-ray emitters present in the source. This is possible, because the system has the ability to differentiate between radiation energies and radiation sources in the samples. A gamma-ray spectrometer normally consists of an energy sensitive radiation detector, a pulse sorter called multichannel analyzer (MCA), and associated amplifiers and data readout devices Gamma spectroscopy systems are selected to take advantage of several performance characteristics. These characteristics determine the response of the detector to gamma radiation and also give a measure of how good the detector can modify the gamma-rays. Two of the most important include detector resolution and detector efficiency, other factors that affect the shape of the pulse amplitude include, escape event, dead time, accidental summing and the characteristics compton edge (Heath, 1964).

2.9.3 Detector resolution

Two pulses produced by gamma-rays of the same energy may be of slightly different heights, called photopeaks and sorted into two close channels, that is gamma rays detected in a spectroscopic system produce peaks in the spectrum. The photopeaks due to monoenergetic gamma rays is therefore not a single line but a distribution spread over a number of close channels due to statistical fluctuations involved in the processes.

The width of the peaks is determined by the resolution of the detector, a very important characteristic of gamma spectroscopic detectors. In most spectra the horizontal position of the peak is determined by the gamma ray's energy, and the area of the peak is determined by the intensity of the gamma ray and the efficiency of the detector.

The energy resolution of a detector is defined as the ratio of the full width of a photopeak at half-maximum amplitude (FWHM) to the energy E corresponding to the highest point in the photopeak expressed as a percentage. In scintillation spectrometry, resolution R can also be defined quantitatively as the number of channels between the half maximum point in the photopeak divided by the channel number E_p of the photopeak and multiplied by 100%:

$$R = \frac{\Delta E}{E_p} \times 100\% \qquad (2.13)$$

R^2 is inversely proportional to the gamma energy E, and that a system must conform to this rule for its performance to be reliable (Farai, 1989). The smaller the energy spread ΔE, the better the ability of a detector to separate full energy peaks that are close together.

The Gaussian shape of the spectrum photopeaks in NaI(TI) detector is due to mainly its poor energy resolution. The detector system used in this work has a resolution of about 8% at 662 KeV of ^{137}Cs. The resolution is low when compared to the resolution of other gamma spectrometers like litium drifted germanium (Ge(Li)) and the hyper pure germanium (HPGe) detectors, it is suitable for distinguishing the photopeaks due to the three primodial radionuclides measured in this study. Three spectra of interest were obtained separately in turn using IAEA standard calibration sources RGK-1 (K_2SO_4), RGU-1(U-Ore) and RTh-1 (Th-Ore). K-40 can be identified from the 1.460MeV peak, while ^{238}U and ^{232}Th can also be identified from 1.760 MeV peak and 2.614 MeV peak respectively. The other photopeaks of the ^{238}U and ^{232}Th, especially at the lower energy regions overlap and cannot be distinguished by the detector crystal as shown in Figure 2.2. The evaluation of radioactivity concentrations of the radionuclides carried out in this work was done using these photopeaks.

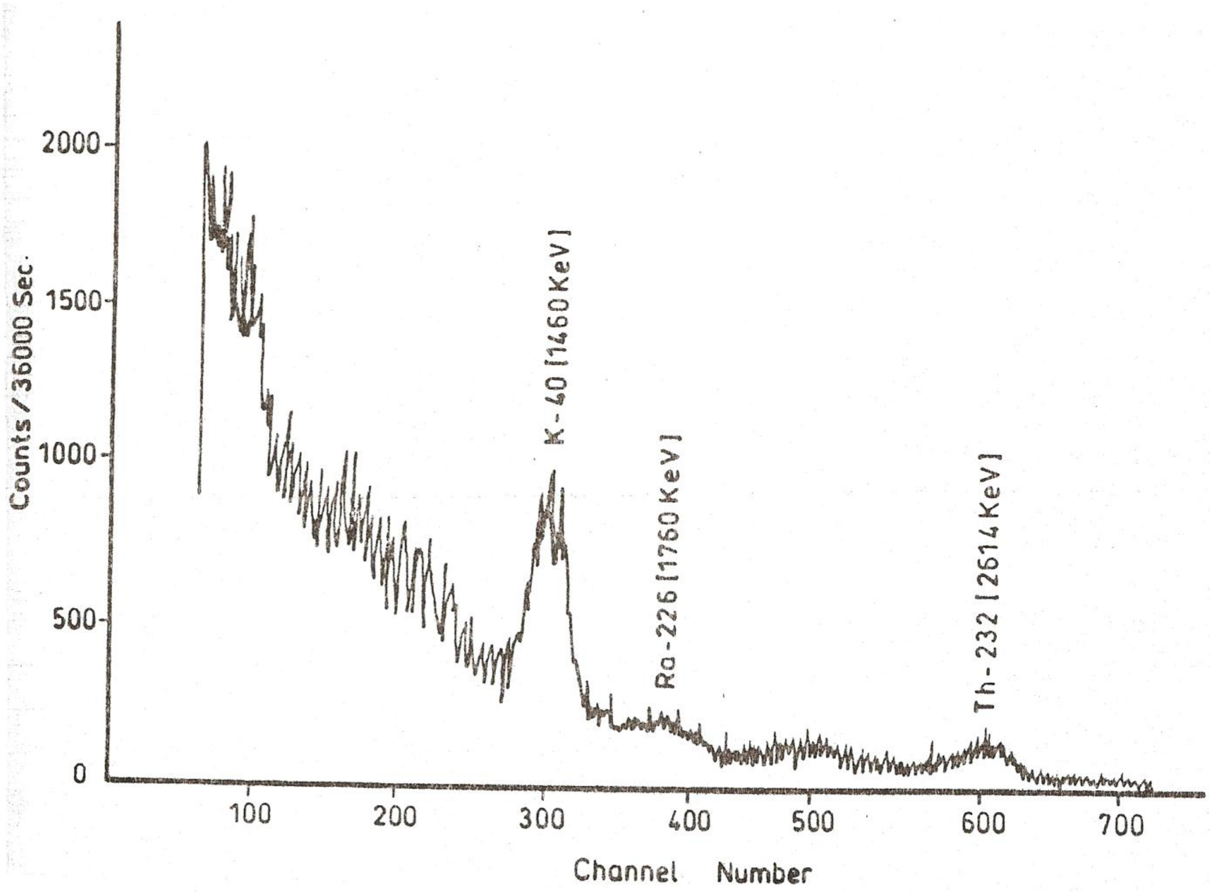


Figure .2.2: A typical spectrum of the radionuclides in a sample taken with NaI (TI) Crystal detector.

2.9.4 The Efficiency of the detector

The intrinsic detection efficiency of any device operated in pulse mode is defined as the probability that a quantum of radiation incident on the detector will produce a recorded pulse. In other words, the efficiency of the detector is the probability that an emitted gamma ray will interact with the detector and produce a count, since not all gamma rays emitted by the source and pass through the detector will produce a count in the system. In case of radiations of low intensity, a high detection efficiency is important to minimize the total time needed to record enough pulses for good statistical accuracy in the measurement. Detection efficiency is further subdivided into two types: total efficiency and peak efficiency. The total efficiency gives the probability that an incident quantum of radiation produces a pulse, regardless of size, from the detector. The peak efficiency is defined as the probability that the quantum will deposit all its initial energy in the detector. Since there are almost always ways in which the quantum may deposit only part of its energy and then escape from the detector, the total efficiency is generally larger than the peak efficiency.

Several factors such as volume and shape of the detector crystal, the absorption cross section in the crystal, the dimensions of the source and the distance and position from the source to the detector (source-detector geometry) determine the efficiency of the detector (Perez-Andujar and Pibisa, 2004). The dimension of the source and source-detector geometry factors can be optimized so as to achieve maximum efficiency for a detector due to multiple interactions enhanced in detectors of large volume, the peak efficiency for gamma-ray detectors improves significantly with increasing size.

Detector efficiency is usually measured by taking a gamma spectrum of a source of known activity, and comparing the rates in each peak to the count rates expected from the known intensities of each gamma ray. The energy of the gamma rays being detected is an important factor in the efficiency of the detector. The detail efficiency calibration process in this work is discussed in the next chapter.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Measuring System

The measuring system used for radioactivity measurement in this study is a 7.6 cm × 7.6 cm Na (Tl) by Bicron (Model No: 802) scintillation detector coupled to a photomultiplier tube through a preamplifier/amplifier base to a canberra series 10 plus (Model: 1104) multichannel analyzer (MCA). The MCA is a complete system having all functions needed for spectroscopic analysis. The set up of the measuring system is shown in Figure 3.1. The detector is a 7.6cm × 7.6cm Na(Tl) crystal located inside a lead castle C it is interfaced with the MCA through a 50 Ω coaxial cable. The MCA electronic system consists of an internal spectroscopic amplifier (AMP), a 100 MHZ Wilkinson type analog to digital converter (ADC), control logic (CL) with input and output devices and multichannel scaling input, 4 k memory (M), display and analysis (DAL) and screen display (SD). The measuring system has a unique advantage of operating on batteries, which can be trickle-charged. The batteries can run continuously for eight (8) hours, this will prevent interruption in counting in case of power failure. The MCA has facilities to supply a stabilized extra high voltage (EHT) bias to the detector.

Preliminary investigations of some spectral characteristics were performed before the counting of the samples. These preliminary measurements include; (i) channel – energy dependence, (ii) Detector efficiencies and of the system at various gamma energies (iii) Detection Limit. All these were determined in order to evaluate the performance and reliability of the detector system for the measurement.

3.1.1 Energy Calibration

The energy calibration was carried out to relate channel numbers to gamma-rays energy in MeV. After a preset counting time of 7200 s., the channels of the various photopeaks corresponding to known gamma energies were identified.

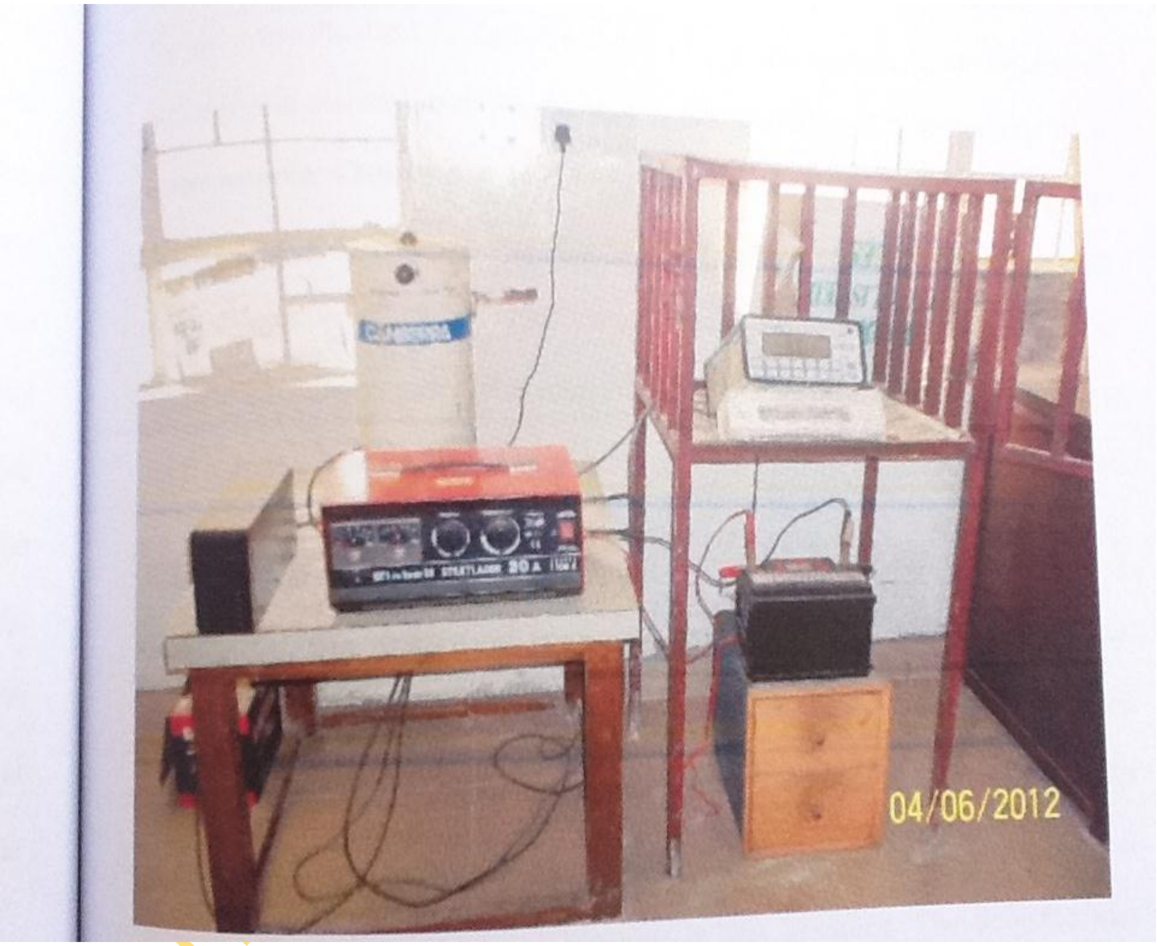


Fig. 3.1 Measuring Assembly.

The channel numbers were obtained from gamma energies of some known radionuclides from standard reference sample from Nucleus Inc. Oak Ridge, TN USA and geological certified reference material for radiometric measurement from International Atomic Energy Agency (IAEA) Vienna. A linear equation was obtained with which the gamma energy (E) in MeV corresponding to a channel number (N) can be obtained for a fixed setting including geometry of the spectrometric system. The energy calibration equation obtained is given by equation 3.1. Table 3.1 presents the channel numbers corresponding to the gamma energies while the calibration curve is shown in Figure 3.2.

$$E\ (\text{MeV}) = 3.857 \times 10^{-2} * \text{CH No} + 4.15 \times 10^{-2} \qquad 3.1$$

This equation was stored in the memory of the MCA so that the channel numbers are read in units of gamma-ray energy (MeV), in order that the various radionuclides that may be present in the fertilizer and soil samples could be identified through the gamma energies they emit.

3.1.2 Detector Efficiency

The detection efficiency of a gamma spectrometer is the ratio of the net count under a photopeak after a preset counting time to the number of gamma photon incident on the detector crystal at a fixed geometry. The effieciency calibration was to convert the area under photopeak to concentration of the radionuclides in units of Bq kg^{-1}.

For the purpose of finding the detection efficiency, and hence, the activity of the source, a reference standard gamma source prepared from Rocketdyne Laboratories, Canoga Park, California, USA, which is traceable to a mixed standard gamma source (No 48722 – 356) by Analytics Inc. Atlanta, Georgia (USA) was used. The standard gamma source has certified activity concentrations of 7.24, 578.40, 20.90 and 10.47 Bq kg^{-1} for ^{137}Cs, ^{40}K, ^{226}Ra and ^{232}Th respectively. The source was counted for 10 h. The detection efficiency ε_p for each of the four gamma energies was determined using equation 3.2:

Table 3.1: The channel numbers corresponding to the gamma energies

Nuclide	Energy (MeV)	Channel number
Cs – 137	0.662	54
Co – 60	1.173	100
Co – 60	1.333	114
K – 40	1.460	124
Bi – 214	1.760	148
Tl – 208	2.614	222

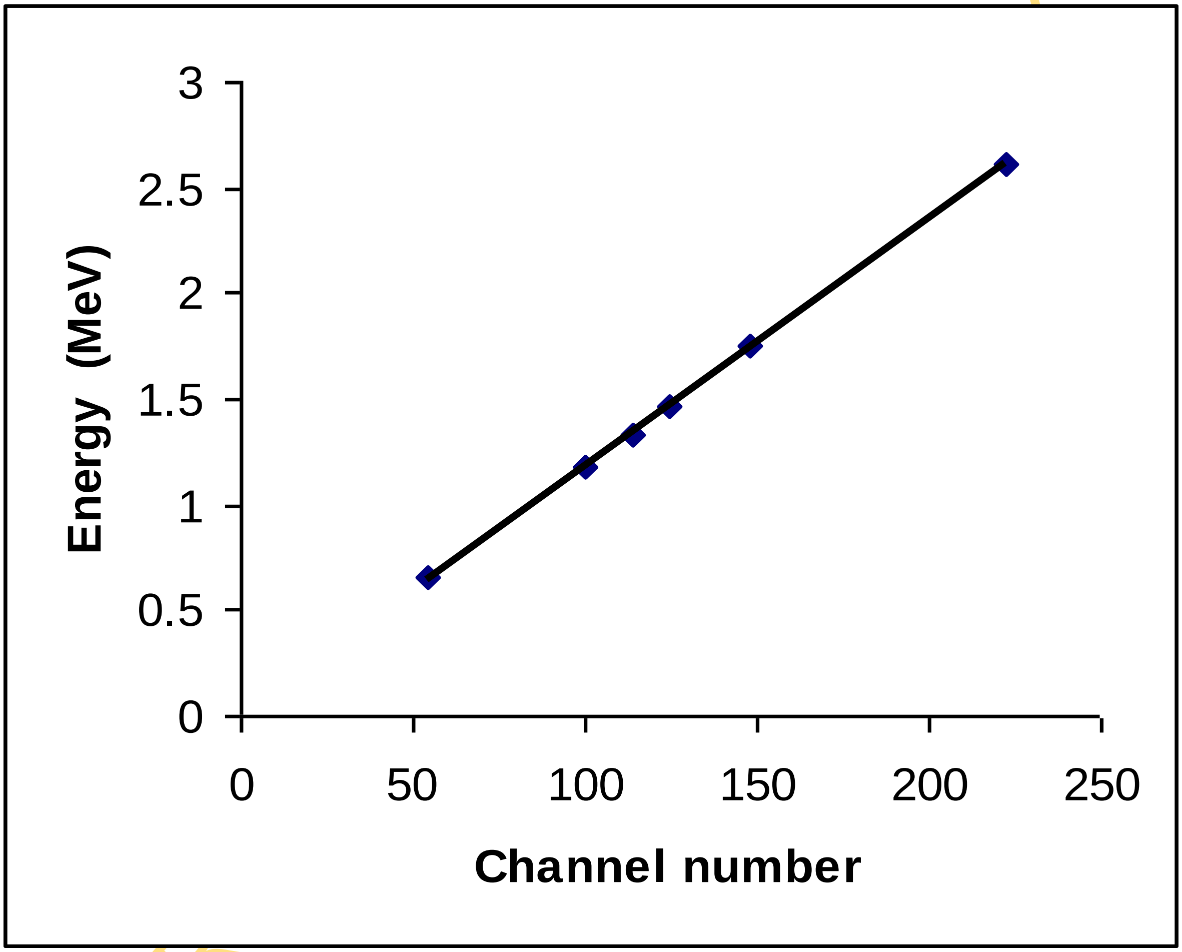


Figure 3. 2: Energy calibration curve.

$$\varepsilon_p = \frac{A}{tYmA_{ref}} \qquad 3.2$$

where A is the net area under each photopeak above background, A_{ref} is the activity concentration of the reference source, m is the mass in kg, t is the counting time and Y is the gamma yield.

The detection efficiency ε_p for each of the four gamma energies are given in Table 3.2, while the detection efficiency as a function of the γ – ray energy is shown in Figure 3.3.

3.1.3 Detection Limit

The lower limit of detection (LLD) is the ability of a detector system to quantify radiation levels slightly above any unavoidable background radiation. It can also be defined as the smallest amount of sample activity that will yield a net-count sufficiently large so as to imply its presence. The size of the quantity is governed by a preselected statistical risk, the probability of concluding falsely that sample activity is present (Pasternack and Harley, 1971). The detection limit of each radionuclide in a sample depends on the background count, the acquisition time and the detection efficiency of the measuring system (Rybach, 1988; Chiozzi *et al*., 2000). The detection limit (DL) of a measuring system describes its operating capability without the influence of the sample. The LLD given in Bq kg^{-1} which is required to estimate the minimum detectable activity in a sample, was obtained using the equation (Jibiri, and Emelue,2009)

$$DL(Bq\ kg^{-1}) \quad = \quad 4.65\frac{\sqrt{C_b}}{t_b}k \qquad 3.3$$

Where C_b is the net background count in the corresponding peak, t_b is the background counting time (s) and k is the factor that converts counts per second (cps) to activity concentration (Bq kg^{-1}) as given in equation (1). With the measurement system used in this work, detection limits obtained were 17.3 Bq kg^{-1}, 4.2 Bq kg^{-1}, and 5.1 Bq kg^{-1} for ^{40}K, ^{226}Ra and ^{232}Th, respectively as shown in Table 3.3. Values below these numbers were taken in this work as being below the lower limit of detection (<LLD) of the detector.

Table 3.2: Efficiencies at different gamma energies

Radionuclide	Activity A,(Bq kg^{-1})	Energy (MeV)	Yield Y	Area (counts)	Efficiency (× 10^{-2}) cps/Bq
^{137}Cs	7.24	0.662	0.852	2476	5.57
^{40}K	578.40	1.460	0.107	8342	1.87
^{226}Ra	20.90	1.760	0.159	400	1.67
^{232}Th	10.47	2.614	0.358	364	1.35

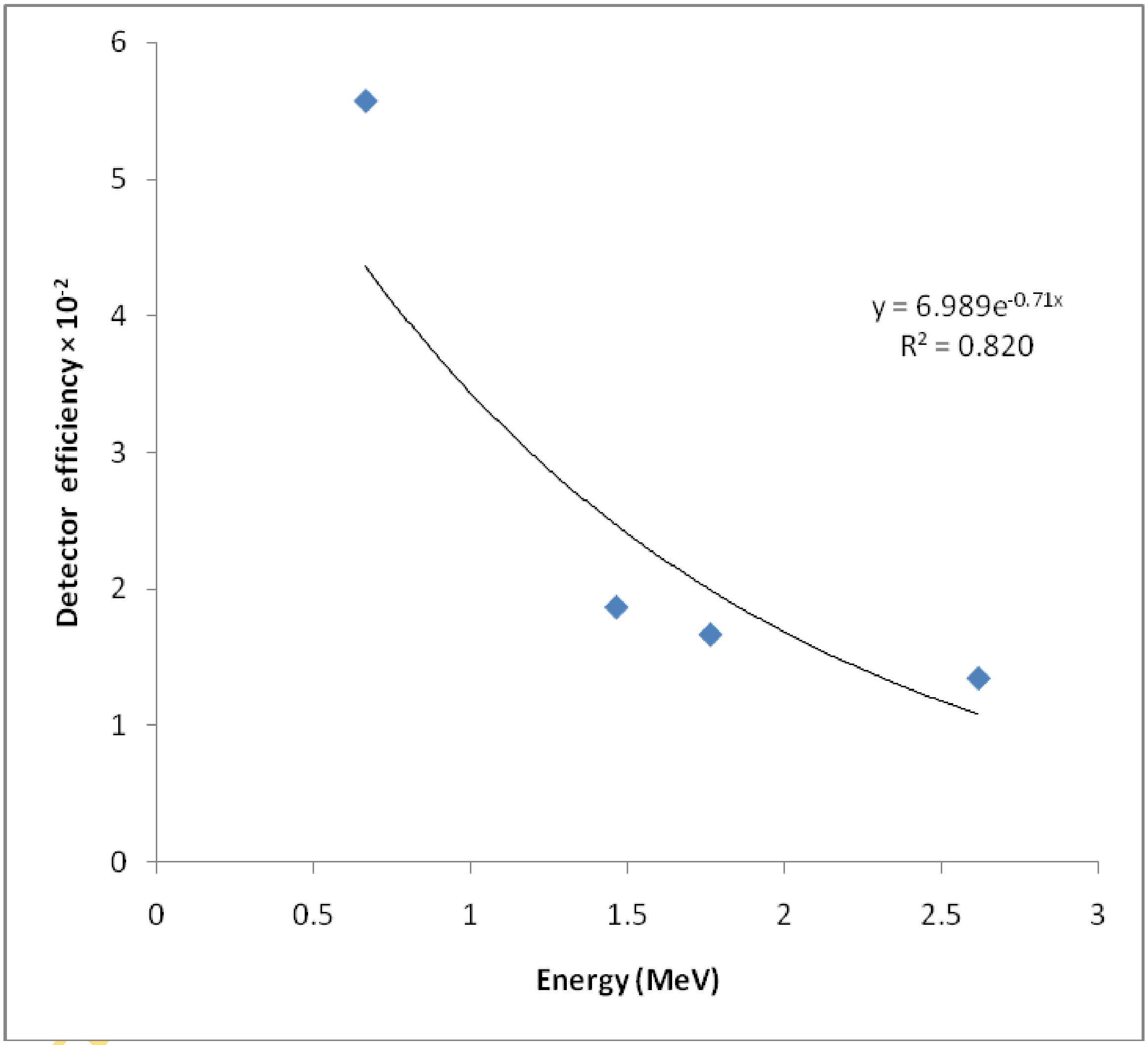


Figure 3.3: Detection efficiency curve of the detector.

Table 3.3: Lower limit of detection (LLD) for full energy peaks of the radionuclides

Radionuclides	Radionuclides Corresponding to full-energy peak	Energy (MeV)	LLD	
			Cps	Bq kg^{-1}
^{137}Cs	^{137}Cs	0.662	*	*
^{40}K	^{40}K	1.460	0.0068	17.3
^{226}Ra	^{214}Bi	1.765	0.0021	4.2
^{232}Th	^{208}Tl	2.615	0046	5.1

- **No ^{137}Cs peak was observed in the background spectrum.**

3.5 Collection of Samples

3.5.1 Collection of fertilizer samples

Eighty samples of different brands of NPK (15-15-15) fertilizers were collected from the local retail outlets in the commercial city centers in six states of the southern part of Nigeria, located between latitude 5° 28′ N and 8° 30′ N and between longitude 3° 22′ E and 5° 46′ E. The samples were collected in the main markets of the cities of Abeokuta, Akure, Ado – Ekiti, Ibadan, Lagos and Osogbo where agricultural inputs are sold on retail. This made the agricultural inputs available for local farmers.

Samples of the chemical fertilizers were also collected directly from the abandoned stock piles of the two old and famous fertilizer producing companies in Nigeria; the National Fertilizer Company (NAFCON), Onne, Port- Harcourt, Rivers State, Nigeria and the Federal Super-phosphate fertilizer Company, Kaduna, Kaduna State, Nigeria (NSPFC). Though, these two companies are no longer producing fertilizers in the country, their products were once dominant in the Nigerian markets and were widely sold across all the regions of the country for more than two decades. The samples from these companies were collected in order to determine the concentration levels of natural radionuclides in their products and compare with the present common products in the Nigerian markets available to the farmers. Samples of Single Super Phosphate fertilizer (SSP) and phosphate rocks samples were also collected from the National Super Phosphate fertilizer Company located in Kaduna, Northern region of Nigeria while NPK fertilizer samples were collected from Onne, southern region of Nigeria.

In Nigeria, the SSP type of fertilizers are only used in the northern region of Nigeria because of the low fertility of farmland in the region (FSFC, 1999) while NPK is widely used in the southern region where the soil fertility is relatively good for agricultural purposes. The map of Nigeria indicating the states from where chemical fertilizer samples were collected is shown in Figure 3.4. The four fertilizer companies whose products are common in southwestern Nigeria, and whose products were collected from retail outlets for this study are presented in Table 3.4.

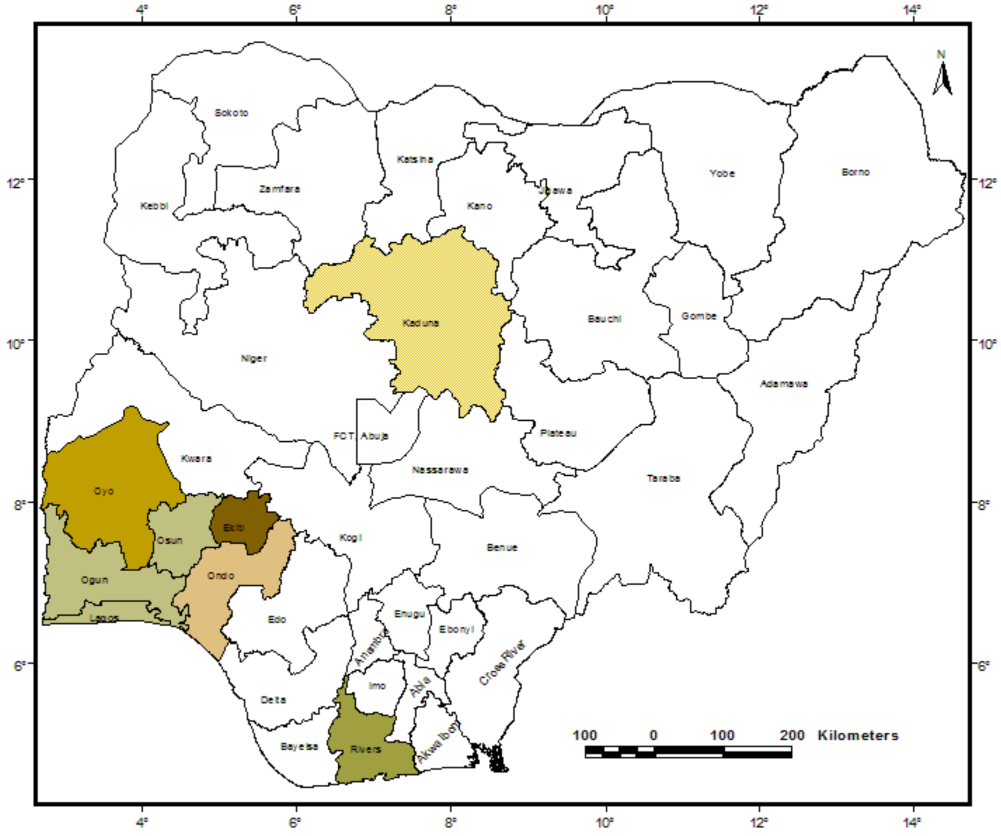


Fig. 3.4: Map of Nigeria showing States where samples were collected

Also presented in Table 3.4 are samples of Single Superphosphate (SSP), Phosphate Rock from Kaduna, in northern Nigeria. The raw materials for production of NPK fertilizer; urea ($NH_2 . CO . NH_2$) and Potash (Aluminium Potassium Sulphate: $AlK(SO_4)_2 12H_2O$) were also collected in order to investigate whether they contribute to radioactivity in NPK fertilizer.

3.5.2 Collection of farm soil samples

3.5.2.1 Farm soils from Northern Nigeria

The knowledge of the dynamics of the radionuclides, ^{40}K, ^{226}Ra and ^{232}Th deposition and downward distribution through the soil in the rooting zone is important for predicting the radionuclides transfer to man. The effective root zone depth is the depth of soil used by the main body of the plant roots to obtain most of the stored moisture and plant food. The root zone of vegetable has been estimated to be 12.0 – 15.0 cm contains a large portion of the nutrient-absorbing roots (FSE, 2005). It is also important to know the activity concentrations of the radionuclides within the upper soil horizons (root zone) where it is readily available for root uptake and transfer to plants. In light of this, vertical profile was considered in the sample collection, ranging between 0 – 5 cm depth, 5 – 10 cm depth and 10 – 15 cm depth from each of the farm locations. The farm soil samples were collected using a soil auger to a depth of 15.0 cm and placed into polythene bags.

Farm soil samples were collected in two cultivated farms in the Northern part of Nigeria: Prison farm of the Nigerian Prison Services Kaduna, and the School of Agriculture Kaduna. The farms were visited during the planting season in the month of June to ensure the application of fertilizer in the cultivated farms. Single Superphosphate (SSP) fertilizer is readily available in the city and the credibility of the farms is not in question hence, the farms were chosen for this study. The samples were collected in the month of November after harvesting season. Three farm soil samples were collected at each point (with respect to vertical profile as earlier stated) of the seventeen locations within the Nigerian Prison Services Kaduna farm and three farm soil samples at each point of the seventeen locations in the School of Agriculture Kaduna.

Table 3.4: Fertilizer Companies, Cities and Number of Samples Collected

Fertilizer Companies	Cities	No of Samples
(GFCN)	Ibadan	6
(ITL/TAK)	Ibadan	4
(GFCN)	Ado-Ekiti	4
(ITL/TAK)	Ado-Ekiti	6
(MAGIC)	Abeokuta	5
(F & C)	Abeokuta	5
(GFCN)	Akure	10
(F & C)	Lagos	9
(MAGIC)	Osogbo	10
NAFCON	Onne	9
Single Superphosphate Fertilizer(SSP)	Kaduna	12
Phosphate Rock	Kaduna	13
Urea ($NH_2 . CO . NH_2$)		5
Potash (Aluminium Potassium Sulphate: $AlK(SO_4)_2 12H_2O$)		5

The samples were randomly collected in order to have a good representative sampling of the entire cultivated farms.

3.5.2.2 Farm soil from southern Nigeria

At the NPK fertilized farm located around the National Fertilizer Company, Onne, Port- Harcourt, in southern Nigeria, three farm soil samples were collected at each point (with respect to vertical profile as earlier stated) of the eighteen locations within the farm.

3.5.2.3 Virgin soil samples

The Virgin soil (VS) are soil from a land that has not been cultivated in the last ten years. They are known to contain more humus, nitrogen and rich in other plant nutrients in the root zone. There are different views on the duration to which soil could be regarded as virgin, Akhtar and Tufail (2009) regarded virgin soil as cultivated soil for one year without fertilizer. In this study, the prefered soil has not been cultivated in the last 50 years to ensure no contamination due to fertilizer application. Sixty virgin soil samples in this study were collected from government reserved forests in Ado – Ekiti, Ikere – Ekiti and Egbe – Ekiti all in Ekiti State, Nigeria. These are forests where Teak and Melina trees were planted without application of chemical fertilizer for over 50 years (EKSG, 2012). The virgin soil used is loamy in nature; it shares the property of sandy soil and clay soil.

3.5.2.4 Experimental farm soil

In order to compare, validate measurements and to investigate the contribution of fertilizer to farm soil radioactivity, an experimental agricultural farm bed was established. The bed was made of wooden planks with dimensions of 21.0 cm by 55.0 cm by 3.0 m, it was partitioned into three equal portions of area 0.55 m^2 each, and filled with the same virgin soil collected from the government reserved forest in Ado Ekiti as stated in session 3.5.2.3. The depth of the agricultural bed was within the rooting zone of vegetable.

3.5.2.5 Application of chemical fertilizers

Single superphosphate (SSP) fertilizer was applied to the soil of the first partition at the rate of 1.0 kg/ 0.55 m^2 (VS_{SSP}), no fertilizer was applied to the second partition, this served as the control farm (VS_C). NPK (15-15-15) from Fertilizer and Chemical Company (F &C) brand was applied to the soil of the third partition (VS_{NPK}). The NPK (15-15-15) from Fertilizer and Chemical Company (F &C) was the available brand as the time the experimental farm was established. The experimental agricultural bed is shown in Fig.3.5.

3.5.2.6 Sowing vegetables Seeds

Vegetables supply most of the nutrients that are deficient in other food materials. This includes supply of minerals, especially calcium and iron. Vegetables are acid neutralizers, prevent constipation and promote digestion. Amaranthus and other vegetables are rich sources of vitamins A, B, and C. some vegetables are also rich sources of carbohydrate and cheap sources of protein. Vegetables are generally needed to have balanced diets and overcome nutritional deficiencies, and make our staple food more palatable and enhance their intake. They have short growing period, may be harvested two or three times by topping or young leaf removal.

Tomatoes (*Lycopersicum esculentum* K. Karsten) plant and Vegetable (*Amaranthus hybridus* Linnaeus) are largely eaten daily by people of all strata and animals in Nigeria, their rooting zone is between 0 – 20cm (FSE, 2005), hence they were used as experimental plants in this study. The seeds of Tomatoes (*Lycopersicum esculentum* K. Karsten) and Vegetable (*Amaranthus hybridus* Linnaeus) were sown using broadcasting method in the three partitions one week after the application of fertilizer**.** In broadcasting, seeds are spread over the prepared land by throwing small quantities of the seeds into the air close to the surface of the prepared land (Rebecca, 2012). Broadcasting is the normal practice in sowing seeds of most leafy vegetables such as *Celosia*, *Amaranthus hybridus*. Six weeks after sowing, the vegetable plants were matured and havested. The Tomatoes (*Lycopersicum esculentum* K. Karsten) were matured and harvested at fifty days (50days) after planting since the havesting period of tomato is from 35 days to 60 days (Jones, 2015).

Fig. 3.5: Cultivated Experimental Farm

3.5.3 Sample Preparation

The fertilizer and the cultivated farm soil samples were dried at 80 °C in a temperature controlled oven until there was no detectable change in the mass of the samples. The dried samples were thoroughly crushed, ground and pulverized to fine powder.

The uprooted matured plants were thoroughly washed under running water, dried at a low temperature of 40 °C to avoid being denatured or burnt. Both the dried tomatoes and vegetable samples were pulverised into powder. The powder was passed through a 2 mm sieve. Due to the limited space of the detector shield, only 200 g of the fertilizer samples and soil samples (dry weight) were used for analysis. The samples after weighing were transferred to radon-impermeable cylindrical plastic containers of uniform size (60 mm height by 65 mm diameter) and were sealed for a period of about 30 days. This was done in order to allow for radon and its short-lived progenies to reach secular radioactive equilibrium prior to gamma spectroscopy. The reference soil was also transferred to a container of the same material and dimensions as were used for the fertilizer samples. This was to ensure that the geometry configuration remained the same. To avoid distribution of the gamma radiation emitting decay products in the gas room on top of the sample masses, the containers were filled up almost totally (filling height 60 cm). With this filling height the sample masses were approximately 200 g corresponding to the sample size limit capacity of the detector. The variations of the effective sample density caused by this are seen not to affect the activity results within the experimental error of the measurement technique employed in this work.

Differences between the effective atomic numbers in the chemical composition of the fertilizers and the standard samples would not affect the results since the mass attenuation co-efficient does not depend on the atomic number in the energy range under consideration to a very good approximation up to an atomic number of 40 (Zr) (Pfister *et al.*,1976). Thus self absorption correction could be neglected. From the relative photon emission intensities and from the energy peak efficiencies the activities of the gamma emitting decay products could be calculated which equal the activities of the parent nuclides under the conditions of radioactive equilibrium. The standard reference sample used is a soil sample prepared from Rocketdyne Laboratories California; USA which is traceable to a mixed standard gamma source (Ref. No. 48722-356) by Analytic Inc. Atlanta, Georgia.

3.5.4 Radioactivity measurement

A low-level gamma spectrometry system consisting of a 76 mm by 76 mm NaI(Tl) detector (Model No 802-series, Canberra Inc.) couple to a canberra series 10 plus multi channel analyzer (MCA) (Model No 1104) through a preamplifier base was used in the present study.

The detector has a resolution of about 8% at energy of 0.662 MeV. This was enough to distinguish the gamma energies of interest in the study. The choice of radionuclide to be detected as a reference was made based on the fact that the NaI (Tl) detector used in the present study has a poor energy resolution. Hence the photons emitted by them would be sufficiently discriminated if their emission probability and their energy were high enough and the surrounding background continuum was low enough. Therefore, the activity concentration of ^{214}Bi (determined from its 1.760 Mev gamma ray peak) was chosen to provide an estimate of ^{226}Ra in the food samples, while that of the daughter radionuclide ^{208}Tl (determined from its 2.615 Mev gamma ray peak) was chosen as an indicator of ^{232}Th.

^{40}K was determined by measuring the 1.460 Mev gamma rays emitted during the decay of ^{40}K. ^{137}Cs was also considered and quantified by looking for 0.662 Mev gamma rays peak. The presence of ^{137}Cs isotope in a sample is an indicator for any potential environmental contamination due to nuclear accidents and weapon tests (Sutherland et. al, 1990). The standard reference food sample used for the efficiency calibration was obtained from the IAEA traceable to source Ref No IAEA-152. While the standard reference soil sample used for efficiency calibration was from Rocketdyne Laboratories California, USA, which is traceable to a mixed standard gamma source (Ref No 48722-356) by Analytic Inc., Atlanta, GA, USA.

Both the fertilizer and soil samples were placed symmetrically on top of the detector and measured for a period of 36000 seconds (10 h). The net area under the corresponding peaks in the energy spectrum was determined by subtracting counts due to Compton scattering of higher peaks and other background sources from the total area of the peaks. From the net area of a certain peak, the activity concentrations in the samples were obtained using Equation (3.1) (Olomo, 1990; Akinloye and Olomo, 2000; Farai and Ademola, 2001).

$$C(Bq/kg) = \frac{C_n}{\varepsilon I_\gamma m_s} \tag{3.1}$$

Where C is the activity concentration of the radionuclide in the food or soil sample expressed in Bq/kg, C_n is the count rate under the corresponding peak, ε is the detector efficiency at the specific gamma-ray energy, I_γ is the gamma yield or absolute transition probability of the specific gamma and m_s is the mass of the sample measured in kg. Equation 3.1 can be expressed as (Jibiri and Ajao, 2005, Jibiri and Bankole, 2006, Jibiri et al 2007)

$$C(Bq/kg) = \frac{C_k}{A_k} A \tag{3.2}$$

where C_k is the activity concentration of the radionuclide in a standard reference sample having the same geometry or matrix as the investigated sample expressed in (Bq/kg), A_k is the net area of the peak in the reference sample spectrum and A is the net area of the corresponding peak in the sample spectrum.

3.5.5 Sample counting for gross alpha and gross beta.

In order to give an approximate idea of the amount of radionuclides in fertilizer and soil, the gross alpha and gross beta activities were measured, this gives the degree of contamination and consequent committed effective doses due to inadvatent ingestion of the chemical fertilizers and the fertilized soil.

The gross alpha and beta equipment used is AN EURISYS MEASURE- IN- 20. Low background multiple (eight) channel alpha and beta counter. It is a gas flow proportional counter with 450 μg/cm^3 thick window of diameter 60 mm. The radiation level within the measuring system is less than 1.0 msv/hr. The counting system incorporates an anti-coincident guard counters used to eliminate the influence of high energy cosmic radiation that would enter the measuring environment. The counting gas is an argon-methane mixture at the ratio of 90% and 10% respectively. The chambers are covered with 10 cm thick lead and the inside dimensions are 480 x 280 x 105 mm^3. The system is connected to a micro-processor IN-SYST, a spreadsheet programmed QUARTTRO-PRO and a graphic programm. For the alpha activity, the standards were Pu – 239 sources of activity measurements for the eight sources varying from 133.3 Bq to 185.8 Bq at 2π-stearadians. The radionuclide impurity in each of them varied from 0.74 – 0.82% (Akpa et al 2004). The Beta standards are strontium-90 beta sources of diameter 38mm and an active film of 12 mg/cm^3 thick. For eight channels, there are eight sources of activities varying from 105.1 Bq to 117.7 Bq at 4π-stearadians. Cerca and LEA Laboratories in France certified all measurements with certificate No. CT001271/00/1778 – 1783 (Akpa *et al*, 2004). The radionuclide impurity in each of them is less than 0.1%. The beta and alpha specific activities were calculated using the following equation 3.3 (Akpa *et al*, 2004):

$$Specific\ \ Activity(\alpha,\beta)(Bq/kg)=\frac{Counting\ \ Rate(\alpha,\beta)-Background\ counting\ rate(\alpha,\beta)}{Sample\ Eff\ \times Channel\ Eff\ \times Weight\ of\ \ sample} \quad (3.3)$$

3.5.6 Committed Effective Dose Due to Inadvertent Ingestion of Chemical Fertilizers During Handling by Farmers in the Farm

The ingestion of soil and dust is a potential route of exposure for both adults and children to environmental chemicals. Children, in particular, may ingest significant quantities of soil due to their tendency to play on the floor indoors and on the ground outdoors. Children may ingest soil and dust through deliberate hand-to-mouth movements, or unintentionally by eating food that has dropped on the floor. Adults may also ingest soil or dust particles that adhere to food, cigarettes and hands (EPA, 2011). Therefore farmers may ingest particles of chemical fertilizer particles that adhere to their hands during application to agricultural farm soil.

The resulting biological damage from this pathway may substantially increase the risk of cancer in addition to external natural sources of radiation exposure in farm. The annual committed dose due to gross alpha and gross beta activity following inadvertent ingestion of particles of chemical fertilizer can be estimated using the equation 3.4 (Ismail *et al*, 2009)

$$E = I\,AC \times 365 \qquad 3.4$$

where E (mSv/y) is the annual committed dose, I (kg) is the daily ingested particles of fertilizer, A (Bq/ kg) is the activity; C (Sv/Bq) is a dose conversion factor in.

3.5.7 The Radiation Hazard Parameters in Samples

The results of the activity concentrations of the samples were used to assess the potential radiological hazards associated with the samples by estimating the radiological indices compare with values obtained from other studies .

3.5.7.1 Radium equivalent activity

The radium equivalent activity is defined as weighted sum of the activity concentrations of the radionuclides given by the equation 3.5 (Beretka and Mathew, 1985):

$$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_K \qquad (3.5)$$

3.5.7.2 Gamma representative index

Gamma representative index ($I_{\gamma r}$) can be used to estimate the level of gamma radiation hazard associated with the natural radionuclides. This index is defined by the equation 3.6 (El-Zakla, 2007):

$$I_{\gamma r} = 0.0067A_{Ra} + 0.01A_{Th} + 0.00067A_K \qquad (3.6)$$

where A_{Ra}, A_{Th} and A_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K respectively in Bq kg^{-1}.

3.5.7.3 **Absorbed dose rate**

The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th measured in each of the samples indicate the quantity of radioactivity present but do not provide a measure of radiation risk in the form of an absorbed dose rate. Natural radionuclides contribute to the absorbed dose, and this depend on the natural specific activity concentration of ^{226}Ra, ^{232}Th and ^{40}K (Kurnaz *et al*., 2007), the radiation energy and the dose absorbed by the individuals (Jibiri, 2000).

The total absorbed dose rate (nGy/h) in air at 1m above the ground surface due to gamma radiations in the ^{40}K, ^{226}Ra and ^{232}Th can be calculated using the equation 3.7 (Beck *et al*, (1972) , UNSCEAR (1988) and UNSCEAR (2000)):

$$D = 0.042A_K + 0.429A_{Ra} + 0.667A_{Th} \tag{3.7}$$

where $A_{k,}$ A_{Ra} and A_{Th} are the activity concentration of the radionuclides.

3.5.7.4 Annual effective dose rates due to the fertilized farm soils

The annual effective dose rate gives the radiological hazard to which an individual is exposed. In order to estimate the annual effective doses, the conversion coefficient (0.7 Sv.Gy^{-1}) and outdoor occupancy factor (0.2) implying that 20% of time is spent outdoors, on the average were used (UNSCEAR, 2000). There are two additional factors that must be considered. The first is a factor (F) which converts Gy to Sv that accounts for the biological effectiveness of the dose in causing damage in human tissue. The second is the occupancy factor (T) that specifies the proportion of the total time spent outdoors. The effective dose rate outdoors, in units of mSv h^{-1} or µSv per year, is calculated by using the following equation 3.8 (Abbady et al., 2006):

$$H_E = DTF \tag{3.8}$$

where D is the calculated absorbed dose rate (nGy h^{-1}), T is the outdoor occupancy time (0.2 × 24 h × 365.25) = 1753 hy^{-1}, and F is the conversion factor (0.7 × 10^{-6} Sv Gy^{-1}).

3.5.8 Radionuclide transfer factor

The accumulation of radionuclides in farm soil is a complicated process dependent on many factors. Soil properties are a factor influencing radionuclide accumulation. One of the integral indicators of radionuclide behaviour in soils of different types is the transfer factor (TF) (Alexakhin and Korneyev, 1992). This is defined as "concentration of radionuclide per unit weight of plant" divided by "concentration of radionuclide per unit weight of dry soil" The transfer factor is given by equation 3.9:

$$Transfer\ Factor = \frac{Radioactivity\ concentration\ in\ Plant\,(Bq\,kg^{-1})}{Radioactivity\ concentration\ in\ soil\,(Bq\,kg^{-1})} \qquad 3.9$$

3.5.9 Committed effective doses

The effective committed dose due to dietary intake is provided by the following equation 3.10 adapted from an ICRP publication (ICRP, 2000):

$$D = \sum\sum C_{f\,j} M_f h_j \qquad 3.10$$

where D (mSv) is committed effective dose, C_{fj} (Bq kg^{-1}) is radioactivity of radionuclide *j* in food *f*, M_f (kg) is the average daily intake of food *f*, and h_j is the committed effective dose coefficient. The dose coefficient for adult (mSv Bq^{-1}) used are 2.8×10^{-4} µSv Bq^{-1} for ^{226}Ra and 2.3×10^{-4} µSv Bq^{-1} for ^{232}Th. ^{40}K is of limited interest because, as an isotope of an essential element, it is homoestatically controlled in the human cells. In this work the committed effective dose due to the radionuclides ^{226}Ra and ^{232}Th intake were calculated using the consumption rate of 15.0 kg y^{-1} for green vegetable (RIFE, 2005) and 7.19 kg y^{-1} for tomatoes (Jibiri *et al*. 2007) in the study area.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Activity Concentrations of Radionuclides in Chemical Fertilizers

The activity concentrations of radionuclides measured in NPK (15-15-15) fertilizer samples commonly used in Nigeria were determined using equation 3.2. The activity concentration values obtained for the samples from the south western region of Nigeria, with respect to the fertilizer manufacturing companies and their respective fertilizer products are presented in Table 4.1. The average activity concentrations of the radionucldes in different brands of NPK fertilizer in the region under consideration are presented in Table 4.2. The activity concentrations determined in single superphosphate fertilizers and Phosphate rock are also presented in Table 4.2

The quoted errors in the mean values in the tables are the arithmetic standard deviations at 95% confidence interval and hence they represent the spread in the values in each city, except in cases where only one sample was analyzed. For these cases, the reported error terms represent measurement uncertainty. It is observed that the activity concentration of the radionuclides in the fertilizer samples in the region is homogeneously distributed in contents with over 80% of the values in all the cities per brand type lying within ±1σ. As could be observed from Table 4.1, ^{40}K exhibits the highest radionuclide concentrations in all the NPK (15-15-15) fertilizer samples considered in this study. Specifically, the NPK fertilizer produced by Golden Fertilizer Company Nigeria has the highest mean activity concentration of 5089 ± 111 Bq kg^{-1} for ^{40}K in the city of Akure while the least mean value of 3972 ± 417 Bq kg^{-1} was obtained in Abeokuta from the NPK produced by Magic Premium Fertilizer Company. Also the while the least mean value of 9.9 ± 7.3 Bq kg^{-1} was obtained in Osogbo from the NPK produced by Magic Premium Fertilizer Company.

NPK fertilizer produced by ITL/TAK and F & C fertilizer companies has the highest mean activity concentration of 451 ± 14 Bq kg^{-1} and 337 ± 91 Bq kg^{-1} for ^{226}Ra in Ibadan and Lagos respectively

Table 4.1: The range and mean concentrations of the radionuclides in the samples of fertilizer produced by different companies and sold on retail markets in southwestern Nigeria

STATE (Company)		^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{232}Th (Bq kg^{-1})
Oyo	Mean	4687 ± 400	13.6 ± 9.3	9.4 ± 2.3
(GFCN)	Range	(3991 - 5184)	(2.7 - 26.3)	(6.1 - 12.2)
Oyo	Mean	4470 ± 331	450.6 ± 14.3	
(ITL/TAK)	Range	(4039 – 4845)	(435.3 – 467.5)	BDL
Ekiti	Mean	5083 ± 133.6	18.8 ± 4.9	7.0 ± 5.4
(GFCN)	Range	(4987 - 5279.9)	(14.6 – 24.8)	(1.9 – 12.6)
Ekiti	Mean	4941 ± 219	386± 94.6	3.4 ± 2.6
(ITL/TAK)	Range	(4625-5169)	(289 – 532)	(BDL – 3.5)
Ogun	Mean	3972 ± 417	13.0 ± 9.3	
(MAGIC)	Range	(3284 – 4392)	(2.4 – 27.6)	BDL
Ogun	Mean	4608 ± 274	316 ± 75.4	
(F & C)	Range	(4244 – 4975)	(203 – 388)	BDL
Ondo	Mean	5089 ± 111	12.0 ± 5.9	15.1 ± 2.8
(GFCN)	Range	(4853 – 5196)	(6.0 – 20.7)	(11.2 – 19.7)
Lagos	Mean	4506 ± 393	336.8 ± 91.1	
(F & C)	Range	(3867 – 4951)	(209 – 472)	BDL
Osun	Mean	4678 ± 438	9.9 ± 7.3	8.3 ± 2.6
(MAGIC)	Range	(3569 – 5132)	(2.0 – 26.3)	(4.2 – 11.1)
Rivers	Mean	4935 ± 223	11.3 ± 4.4	15.0 ± 3.0
(NAFCON)	Range	(4649 – 5249)	(7.0 – 18.2)	(11.2 – 19.0)

Table 4.2: Range and Mean activity concentrations (Bq kg^{-1}) of ^{40}K, ^{226}Ra and ^{232}Th in different brands of NPK fertilizers for the region under study

Brand of Fertilizer	No of samples	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{232}Th (Bq kg^{-1})
GFCN	20	3992-5280 (4953 ± 50)	BDL-26.3 (14.8 ± 10.0)	BDL -19.7 (10.5 ± 3.3)
ITL/TAK	10	4039-5169 (4706 ± 60)	289-532 (418 ± 20)	BDL -7.0 (5.3 ± 3.7)
MAGIC	16	3284-5132 (4567 ± 50)	BDL - 27.6 (10.0 ± 8.3)	<**BDL** – 11.1 (6.7 ± 3.5)
F & C	14	3867 – 4951 (4557 ± 55)	203 – 472 (326.6 ± 18.5)	BDL
NAFCON	6	4649.1 – 5249.1 (4935 ± 49)	7.0 – 18.2 (11.3 ± 4.4)	11.2 – 19.0 (15.0 ± 3.6)

The NPK fertilizer produced by GFCN Fertilizer Company has the highest mean activity concentration of 15.1 ± 2.8 Bq kg^{-1} for ^{232} Th in the city of Akure while the least mean value of 3.4 ± 2.6 Bq kg^{-1} was obtained in Ado-Ekiti from the NPK produced by ITL/TAK fertilizer company. The mean activity concentrations 4935±49, 11.3±4.4 and 15.0±3.6 Bq kg^{-1} of radionuclides in the NPK fertilizer samples collected from NAFCON compare well with the values obtained in other NPK samples from other companies. This indicates that possibility of mixture of fertilizer brands may not alter the activity concentrations of the radionuclides in the NPK fertilizer. Potassium activity concentration was found to be exceptionally high in all the fertilizer samples and may be because of its importance in crop production for the farmlands in the region. Potassium (K) an essential nutrient for plant growth is classified as a macronutrient. Soils can supply some K for crop production, but when the supply from the soil is not adequate, K must be supplied in a fertilizer. Potassium is associated with movement of water, nutrients, and carbohydrates in plant tissue. If potassium is deficient or not supplied in adequate amounts, growth is stunted and yields are reduced. Various research efforts have shown that potassium stimulates early growth, increases protein production, improves the efficiency of water use among other effects. Potassium is vital for stand persistence, longevity, and improves resistance to diseases and insects. Its high content in these brands of fertilizer will increase its content in soil for plant uptakes and good produce yields. The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th obtained for phosphate rock from Sokoto are 536.2±45.3 Bq kg^{-1}, 1038±28.4 Bq kg^{-1}and 257.9±35.6 Bq kg^{-1}, respectively as presented in Table 4.3.

Naturally occurring radionuclides may be trapped in the earth's crust during the formation of the parent rocks (Gbadebo, 2011) and end up in soils as part of rock cycle through weathering (USEPA, 2007). This may account for the higher activity concentration values of the radionuclides in the phosphate rock in Nigeria, it may also be based on the differences in the geology across the countries. Also, the variation in the levels of the radionuclides may be due to the alteration caused by metamorphic process. The variation in the activity concentrations of the radionclides in the soils and rocks across the world may be related to the composition of the bedrocks and the distribution

Table 4.3: The mean and range of activity concentrations of the radionuclides in single superphosphate fertilizer and the phosphate rocks

Sample	No of Samples	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{232}Th (Bq kg^{-1})
SSP Range	12	301 ± 36 (221 – 353)	696 ± 113 (437 – 814)	14.7 ± 2 (BDL – 18)
Phosphate Rock	13	536 ±45	1038 ± 28	258 ± 36
Urea (NH_2 . CO . NH_2)	5	882.1 ± 6 (880 – 884)	10.0 ± 1.6 (9 – 11)	68.3 ± 8.0 (67.6 – 68 7)
Potash (Aluminium Potassium Sulphate: $AlK(SO_4)_2 12H_2O$)	5	629.8 ± 5.2 (628 – 635)	11 ± 2 (10 – 12)	190 ± 40 (189 – 192)

of the isotopes in the rocks and the processes in which they are released (weathering, erosion and deposition), (Verdoya *et al*, 2001).

The results of the activity concentrations of the radionuclides in the raw material used in the production of NPK fertilizer, mainly phosphate rock (a source of phosphorus), urea and potash are presented in Table 4.3. Phosphate rock has a mean activity concentration value of 1038±28 Bq/kg which indicates that the major contributor to radioactivity in fertilizer is phosphate rock, it may be responsible for the elevated activity concentration of 696 ± 113Bq kg^{-1} for ^{226}Ra. The comparison of the ranges and the mean activity concentrations of the radionuclides determined in this study with ranges and mean of the measured values in some other countries in the world is presented in Table 4.4.

The activity concentrations of ^{226}Ra and ^{232}Th in NPK fertilizer samples from the fertilizer samples in the states and fertilizer manufacturing companies were analysed using Analysis of Variance (ANOVA) at 0.05 confidence level. It shows the existence or absence of significant difference between two or more groups of experimental results. The obtained p = 0.000119, There were significant differences ($p < 0.05$) in the activity concentrations of ^{226}Ra in the NPK fertilizer samples across six states in the southern region of Nigeria.

The p = 0.41 was obtained for ^{40}K in the NPK fertilizer samples, there were no significant differences ($P > 0.05$) in the activity concentrations of ^{40}K in the NPK fertilizer samples across the states considered. The $p = 1.08\times10^{-13}$ was obtained for ^{232}Th, there were significant differences ($P < 0.05$) in the activity concentrations of ^{232}Th across the states in this study. The average activity concentration of Thorium in the fertilizer samples from Ondo State has the highest value. This is significantly different from the mean values obtained from samples in other states.

The distribution pattern were investigated using box plots, this provide a useful way to visualise the range and other characteristics of responses for a large group. The boxplot for the activity concentrations of the naturally occuring radionuclides ^{226}Ra, in NPK fertilizer samples is shown in Figure 4.1.

Table 4.4: The Comparison of mean and range activity concentrations of the radionuclides in NPK and SSP in the present work and other studies in the world

Country	Sample	Activity Concentration (Bq kg^{-1})			References
		^{40}K	^{226}Ra	^{232}Th	
Pakistan	NPK	885	386	38	Tahir et al (2009)
USA	NPK	200	780	49	Guimond and Windham (1975)
Germany	NPK	720	520	15	Khan et al(1996)
Saudi Arabia	NPK	2818	75	23	Ashraf and Al-Sewaidan (2008)
Finland	NPK	3200	54	11	Mustonen (1985)
Brazil	NPK	603	647.6	753.9	Becegato et al (2008)
Algeria	NPK	11644	134.7	131.8	Wassila and Ahmed (2011)
Nigeria	NPK	4729	143	9	Present work
Egypt	SSP	446 – 882	301	125 – 239	El-Bahi et al.(2004)
Egypt	SSP	4	66	366	Ahmed and El-Arabi (2005)
Nigeria	SSP	301	696	14.7	Present work

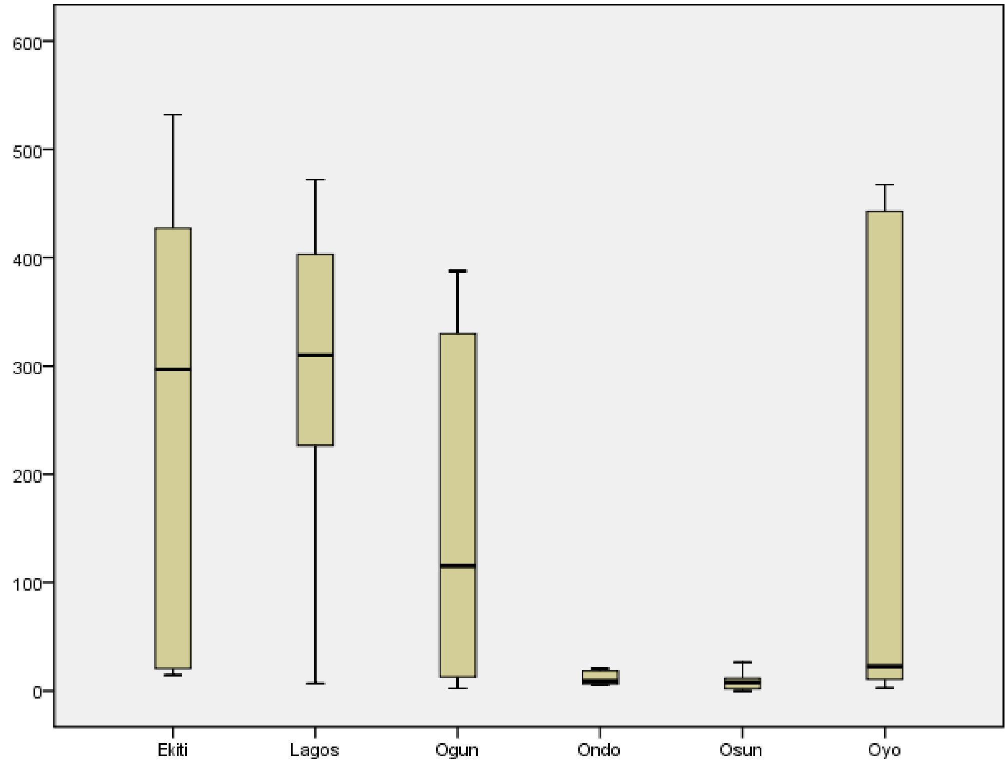


Figure 4.1: Activity concentrations of ^{226}Ra in NPK fertilizer samples from the southwestern States

The figure shows that the median in the group of activity concentration values of the fertilizer samples from Lagos State exhibit the highest value. The plot shows a normal distribution compared to values obtained for samples from Ekiti state which is negatively skewed and Oyo and Ogun States that are positively skewed. The values for Ondo and Osun States show little or no dispersion (spread) in the activity concentration values, while all other group of values show a higher degree of dispersion.

The boxplot for the activity concentrations of ^{232}Th in NPK fertilizer samples is presented in Figure 4.2. The figure presents the fertilizer samples from Ondo State with the highest median value having a normal distribution while values from Osun and Oyo States are negatively skewed, but the values in Lagos and Ogun States are below the detection limit.

The boxplot for the activity concentrations of ^{40}K in NPK fertilizer samples is presented in Figure 4.3. Samples of NPK fertilizer in Ekiti State exhibit the highest median as shown by the band inside the boxplot, though it showed little dispersion, while all other samples showed a higher degree of dispersion.

The activity concentrations of ^{226}Ra and ^{232}Th in NPK fertilizer samples from the fertilizer manufacturing companies were analysed using Analysis of Variance (ANOVA). The p-values are 2×10^{-16} and 1.96×10^{-13} respectively. There were significant differences ($P < 0.05$) in the activity concentrations of ^{226}Ra and ^{232}Th in brands of NPK fertilizers sold on retail in southern Nigeria. ANOVA test on activity concentrations of ^{40}K gives $p = 0.60$, There were no significant differences ($P > 0.05$) in the activity concentrations of ^{40}K in the NPK fetilizer samples in all the fertilizer samples from the fertilizer companies in the study area.

The Boxplot distribution for the activity concentrations of the naturally occuring radionuclides ^{226}Ra in brands of NPK fertilizer samples are shown in Figure 4.4. The ITL/TAK brand of fertilizer samples show a higher degree of dispersion and exhibit the highest median, it is also negatively skewed while the samples from Fertilizer and Chemical Company is positively skewed. Other samples from Magic Fertilizer, Golden Fertilizer and NAFCON companies show a very low degree of dispersion.

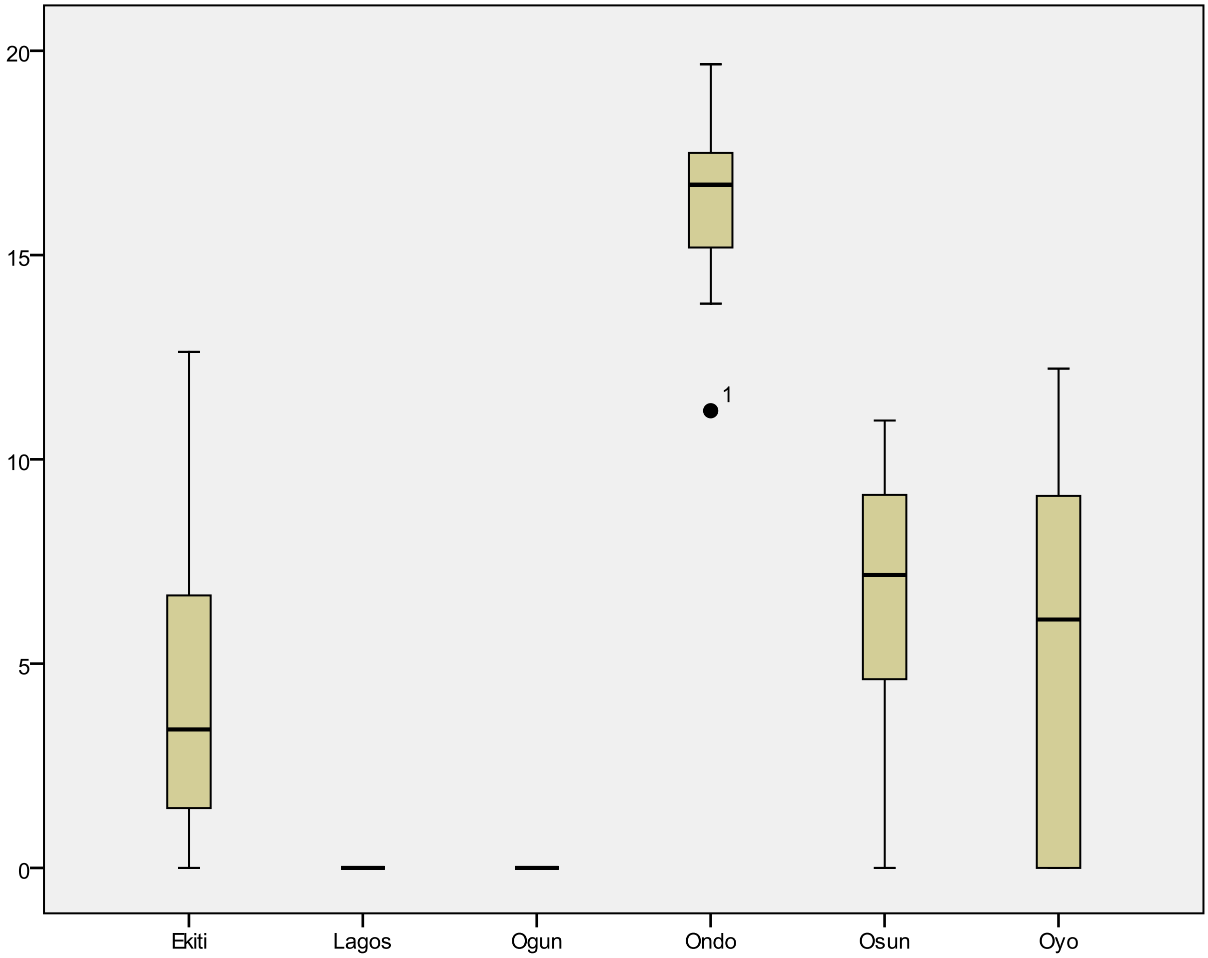


Figure 4.2: Activity concentrations of ^{232}Th in NPK fertilizer samples from the southwestern States

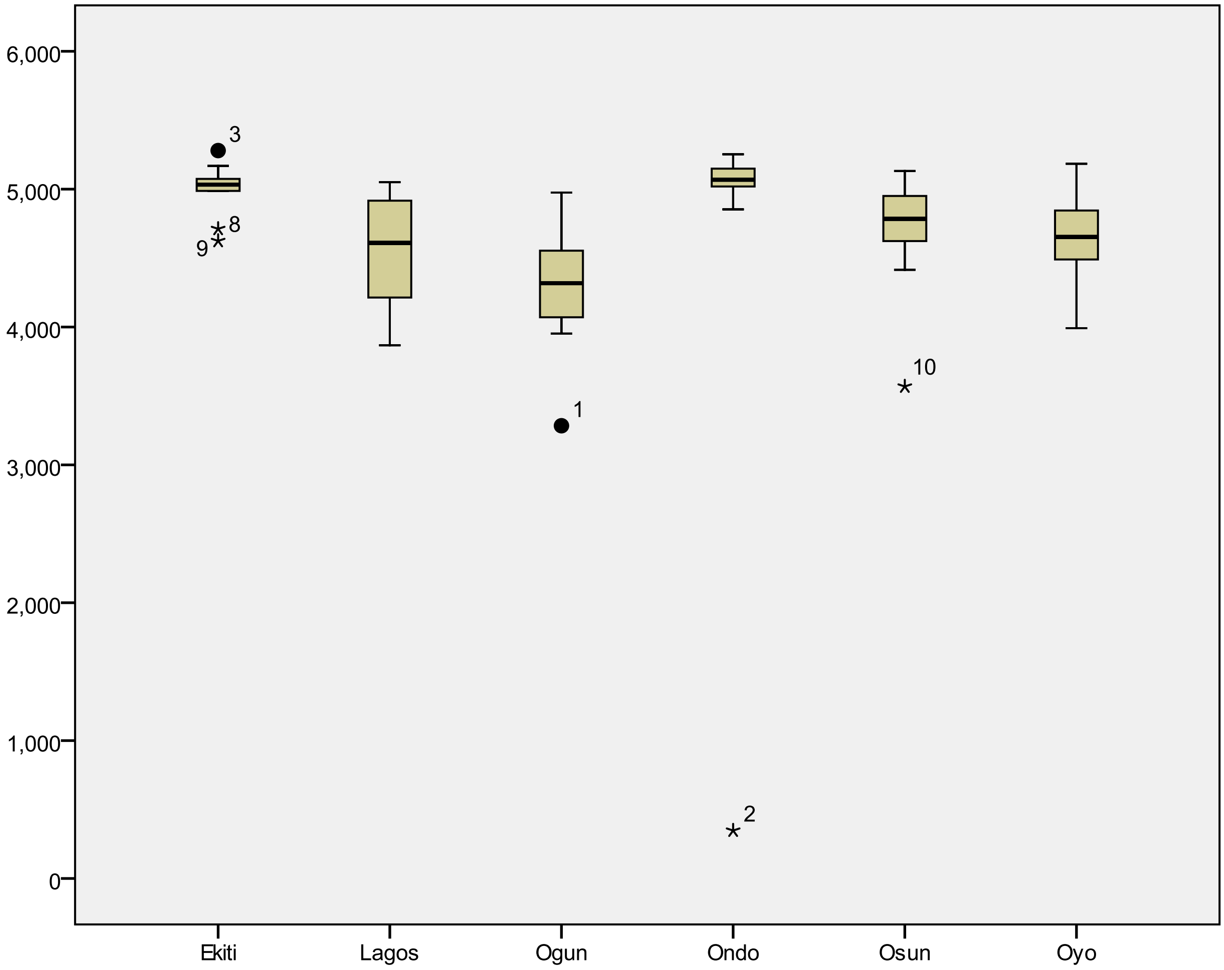


Figure 4.3: Activity concentrations of ^{40}K in NPK fertilizer samples from the southwestern States

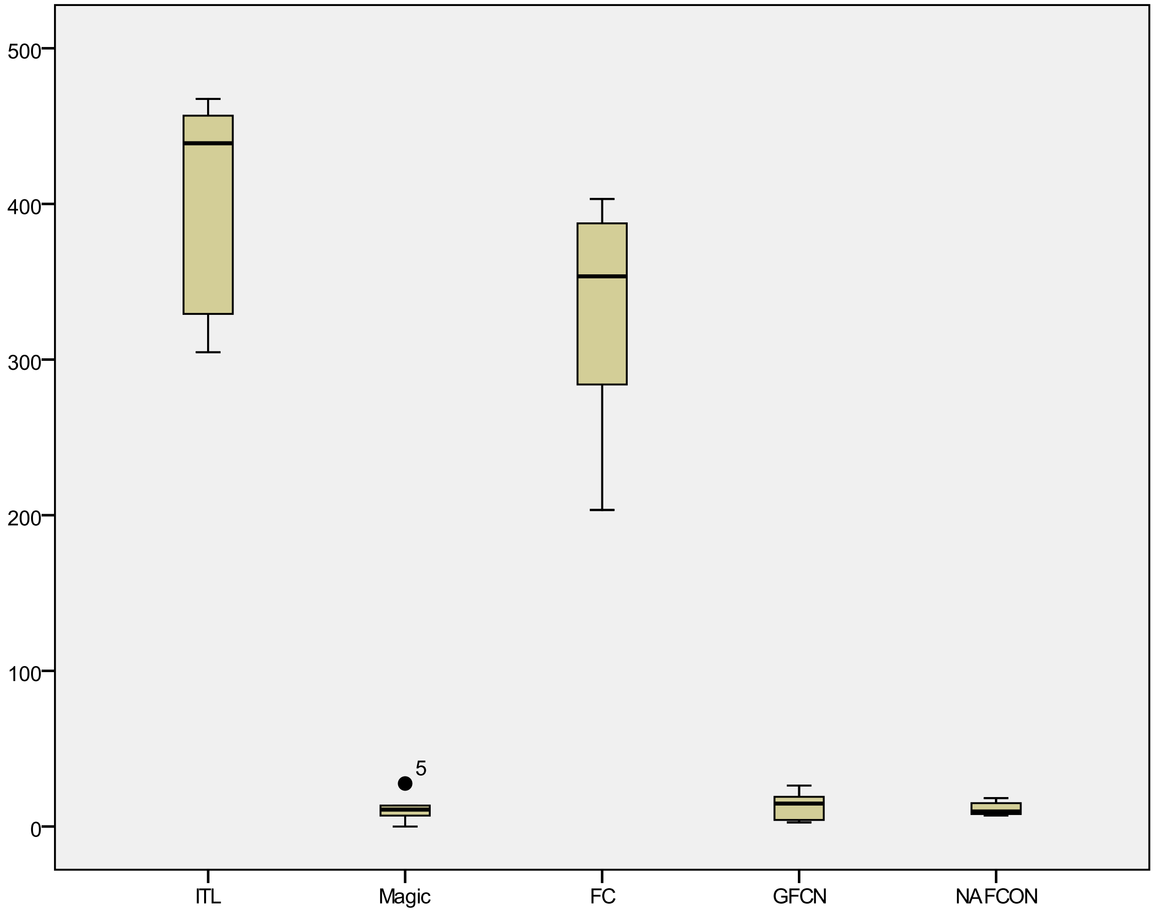


Figure 4.4: The activity concentrations of ^{226}Ra in NPK fertilizer of the fertilizer producing companies in Nigeria

The Boxplot distribution for the activity concentrations of the naturally occuring radionuclides ^{232}Th in brands of NPK fertilizer samples are shown in Figs. 4.5. The NAFCON brand of fertilizer samples show a high degree of dispersion and exhibit the highest median, it is also positively skewed while the samples from ITL/TAK Company is positively skewed with a low median. The samples from Magic fertilizer company show the highest degree of dispersion and a normal distribution while samples from Golden fertilizer company are negatively skewed and samples from Fertilizer and Chemical company samples are below the detection limit.

The Boxplot for the activity concentrations of the naturally occuring radionuclides ^{40}K in brands of NPK fertilizer samples are shown in Figs. 4.6.

4.3 Gross Beta and Gross alpha activity concentrations in Fertilizer

The gross alpha and beta activity concentration of single superphosphate, NPK fertilizers are presented in Table 4.5. The errors in Tables 4.5 are combined uncertainties in the counting measurements. The gross beta activity concentration varied from 2410 Bq/kg to 4560 Bq/kg in the NPK (15-15-15) fertilizers with the highest value obtained in the samples from Ondo State followed by the value obtained from samples from Lagos State. The gross beta activity concentration value of 1340 Bq/kg was obtained in the Single Superphosphate fertilizers. This gross beta activity concentration value is lower than the least activity concentration values obtained in NPK fertilizer as presented in Table 4.5. This indicates that there are more beta emitters in the NPK fertilizers than in the SSP fertilizers; this may be attributed to the high concentration of ^{40}K in the fertilizers.

The gross alpha activity concentrations varied from 10.0 Bq kg^{-1}-100 Bq kg^{-1}across the samples. The Superphosphate fertilizer exhibits the highest gross alpha activity concentration of 100 Bq kg^{-1}, which correlates with an activity concentration value of 696± 113 Bq kg^{-1} for ^{226}Ra in Table 4.3. NPK fertilizer has the least value of 10.0 Bq kg^{-1}, this also correlates with activity concentrations obtained in Table 4.1.

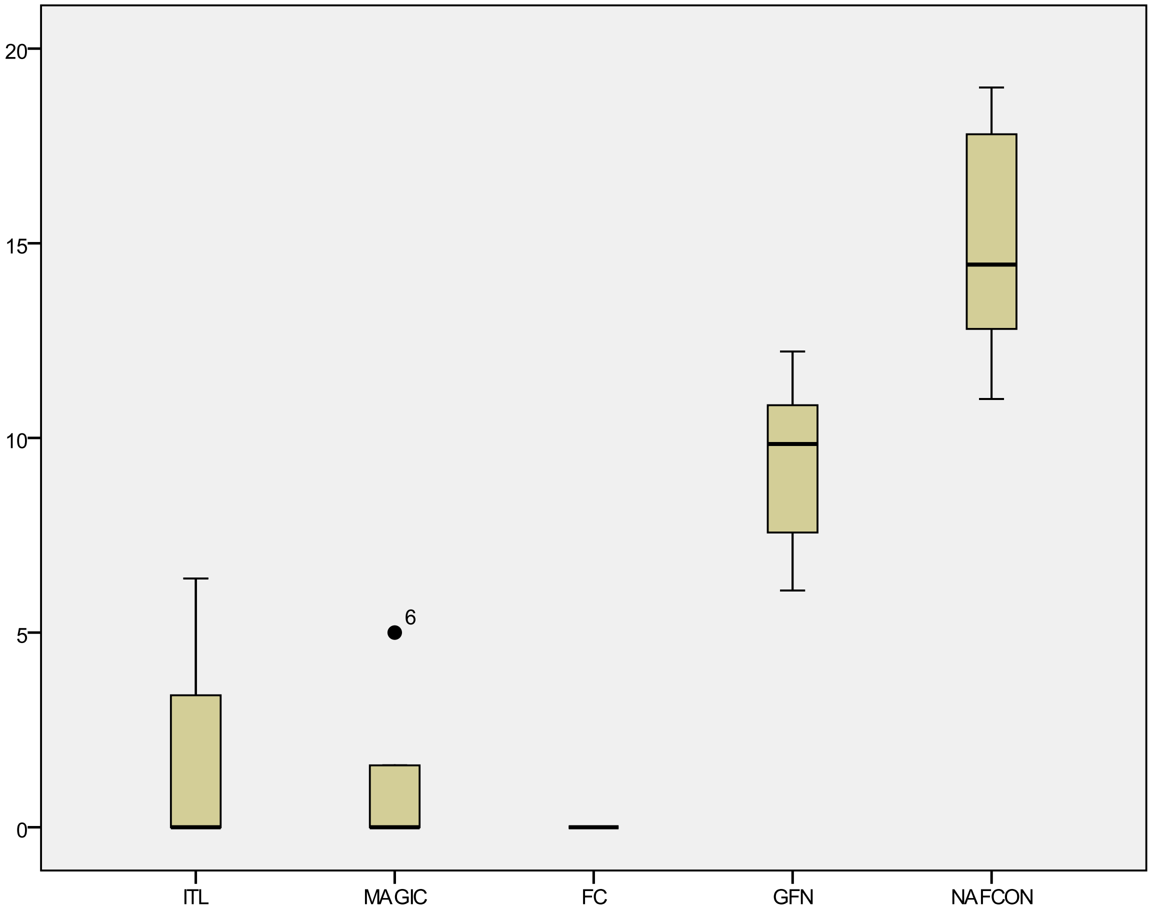


Figure 4.5: The activity concentrations of ^{232}Th in NPK fertilizer of the fertilizer producing companies in Nigeria

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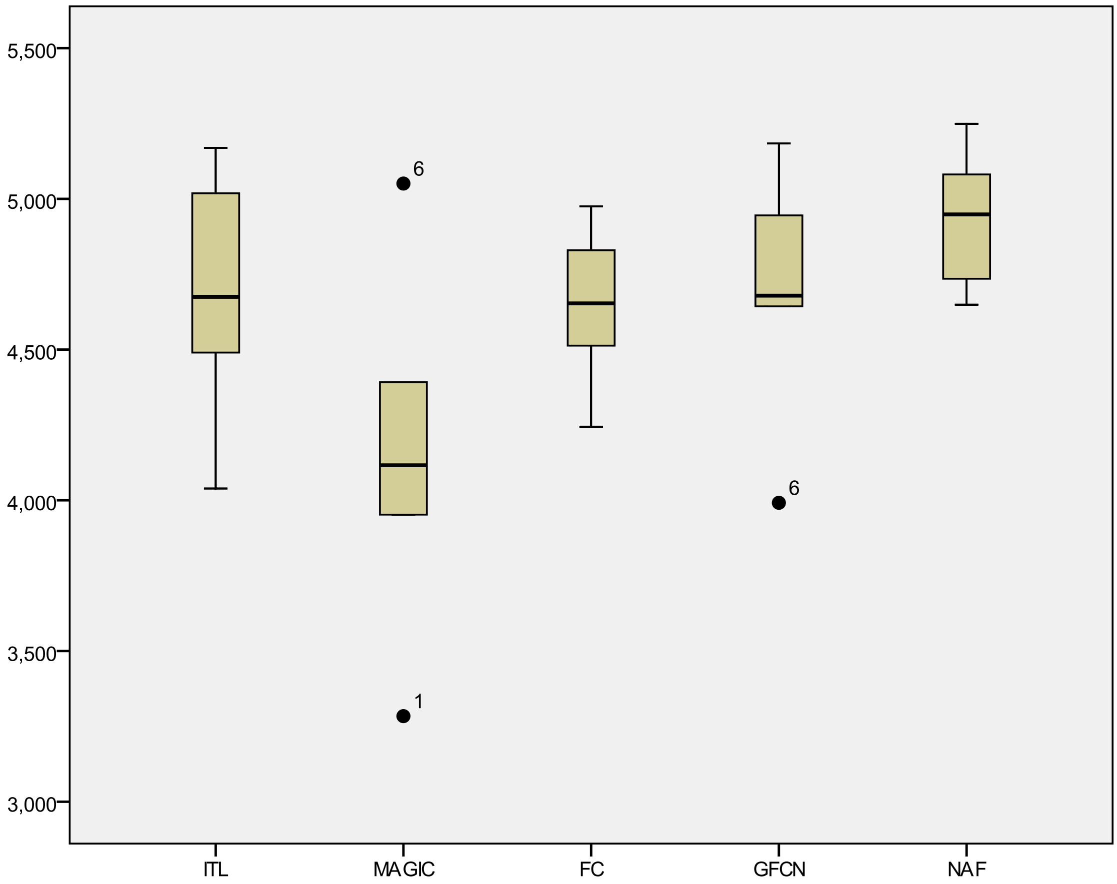

Figure 4.6: The activity concentrations of ^{40}K in NPK fertilizer of the fertilizer producing companies in Nigeria

Table 4.5: The gross alpha and beta activity concentrations (Bq kg^{-1})in super phosphate and NPK fertilizer samples

Samples	No of Samples	State (capital city)	Alpha Activity (Bq kg^{-1})	Beta Activity (Bq kg^{-1})
Superphosphate	12	Kaduna	100 ± 20	1340 ± 70
SSP 1		(Kaduna)	(90 – 105)	(1320 – 1350)
NPK	6	Oyo	30 ± 20	2410 ± 80
		(Ibadan)	(25 – 34)	(2400 – 2440)
NPK	6	Ogun	10 ± 10	2470 ± 80
		(Abeokuta)	(8 – 12)	(2460 – 2480)
NPK	6	Osun	10 ± 10	2420 ± 80
		(Osogbo)	(7 – 11)	(2410 -2430)
NPK	6	Ondo	90 ± 20	4560 ± 140
		(Akure)	(80 – 100)	(4540 – 4560)
NPK	6	Lagos	60 ± 20	3510 ± 100
		(Lagos)	(55 – 70)	(3560 – 3600)
NPK	6	Ekiti	20 ± 10	2640 ± 80
		(Ado-Ekiti)	(14 – 26)	(2630 – 2660)

However, this result showed that SSP is enriched in alpha emitters compared to NPK fertilizers. It was also observed that low activity concentration of ^{40}K may be associated with SSP and high values with NPK fertilizers. It was also observed that NPK fertilizers exhibited a high activity concentration values of 451±14 Bq kg^{-1} and BDL for ^{226}Ra and ^{232}Th respectively as presented in Table 4.1 earlier. This is an indication that Ra-226 may contribute more of the alpha emitters than Th-232 since the activity concentration of ^{232}Th was below the detection limit. This study showed that there is a positive correlation ($R^2 = 0.85$ and $R^2 = 0.76$) between the gross beta and alpha activities with the gamma activity concentration values in the fertilizer samples. High ^{226}Ra and ^{40}K concentrations will indicate high gross alpha and beta activities in the samples as shown in Figures 4.7 and 4.8. This is in agreement with the study by Aytas (2012).

4.3 Committed Effective Dose (CED) Due To Inadvertent Ingestion of Chemical Fertilizers During Handling by Farmers in the Farm

Inadvertent ingestion of fertilizer is assumed to occur through hand to mouth transfer of fertilizer during handling and fertilizer dust present on the skin and clothing. In this work the adopted quantity of fertilizer inadvertently ingested daily is 5.0×10^{-5} kg which corresponds to 0.02kg/y (EPA, 2011). The committed dose was estimated by using the values of the gross alpha, beta activities in Table 4.5 and the dose conversion factor 2.8×10^{-7} Sv/Bq (ICRP, 2000). The total committed effective dose due to the gross alpha, beta and gamma activity concentrations via the ingestion of chemical fertilizers were calculated using the equation 3.4. The CED ranged from 0.295 μSv/y to 1.190 μSv/y. The estimated total committed effective dose values for NPK fertilizers are lower than the recommended committed dose of 0.1 mSv/y (ICRP, 2000), as presented in Table 4.6. The high activity concentration values of ^{226}Ra in SSP may account for this elevated value.

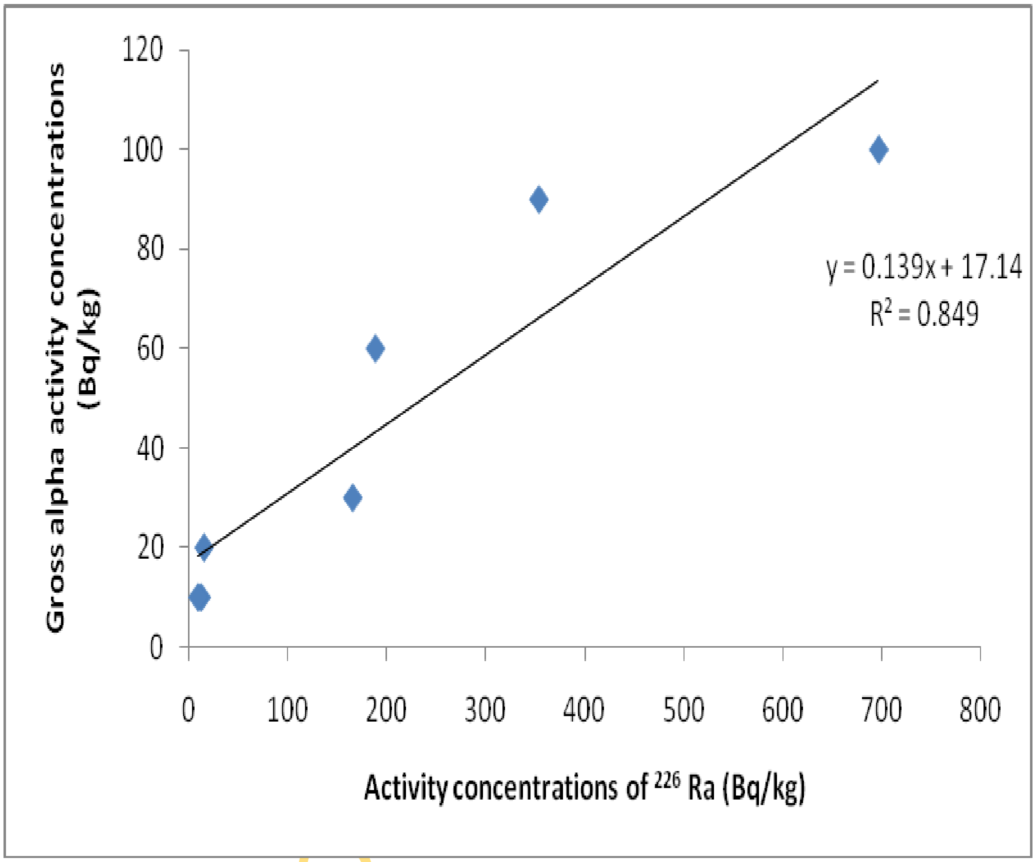

Figure 4.7: Correllation between the gamma activity concentration of ^{226}Ra and the gross alpha activity concentration in chemical fertilizers

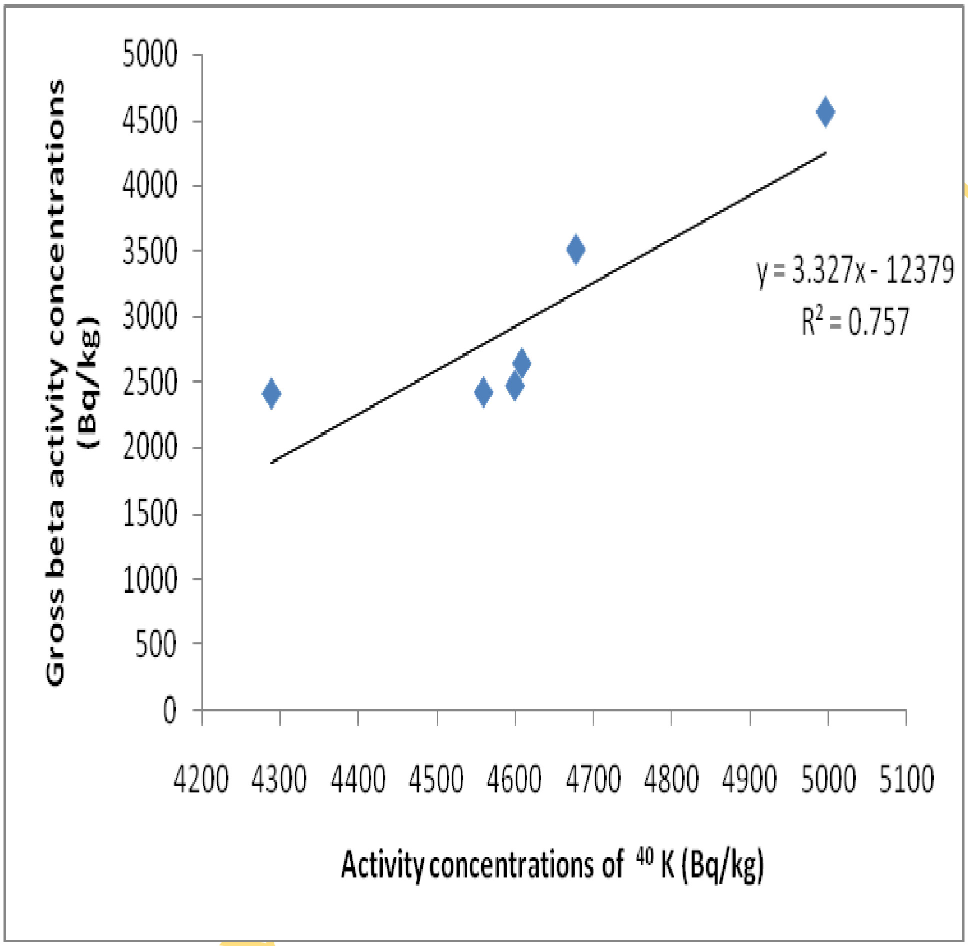

Figure 4.8: Correllation between the activity concentration of ^{40}K and the gross beta activity concentration in chemical fertilizers

Table 4.6: The Committed Effective Dose Due to Alpha, Beta and Gamma radiation from ingestion of fertilizer particles

Sample	Ingestion effective dose (μSv/y) Gross alpha	Ingestion effective dose (μSv/y) Gross Beta	Ingestion effective dose (μSv/y) gamma	Total Ingestion effective dose (μSv/y
Superphosphate SSP	0.51	0.12	0.56	1.190
NPK (15-15-15) GFCN	0.15	0.22	0.028	0.398
NPK (15-15-15) F&C	0.05	0.23	0.029	0.309
NPK(15-15-15) MAGIC	0.05	0.22	0.025	0.295
NPK(15-15-15) GFCN	0.46	0.42	0.027	0.907
NPK(15-15-15) F&C	0.31	0.32	0.028	0.658
NPK(15-15-15) ITL/TAK	0.10	0.24	0.028	0.600

4.4 The Radiation Hazard Parameters in Fertilizers Samples

The results of the activity concentrations of the chemical fertilizers were used to assess the potential radiological hazards associated with the fertilizers by estimating the radiological indices and compared with values obtained from other studies .

4.4.1 Radium Equivalent Activity

The Radium equivalent activity for the NPK fertilizers, Single Superphosphate fertilizer and Phosphate rocks were calculated using equation 3.5. The radium equivalent values are presented in Table 4.7.

4.4.2 Gamma Representative Index

The Gamma representative index for the NPK fertilizers, Single Superphosphate fertilizer and Phosphate rocks were calculated using equation 3.6. The values are presented in Table 4.8. The Radium equivalent activities and the Gamma representative index values obtained in this study compared well with values obtained in other countries of the world as presented in Table 4.9.

4.5.1 Activity Concentrations (Bq kg^{-1}) in Farm Soil Samples in the Nigerian Prison farm and School of Agriculture, Kaduna

The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in the farm soil samples from the Prison farm in the northern region of Nigeria are shown by the boxplot distribution in Figures. 4.9, 4.10 and 4.11 The results show that the mean activity concentration values of ^{40}K, in the SSP fertilized farm soil samples varied from 71 - 227 Bq kg^{-1}, with a mean value of 176.8 ± 42.3 Bq kg^{-1} . The activity concentration of ^{226}Ra ranged from 343.6 - 82.0 Bq kg^{-1}, with a mean value of 69.1± 9.1 Bq kg^{-1}, while the activity concentration of ^{232}Th ranged from 9.6 to 25.3 Bq kg^{-1} with a mean value of 19.0 ± 4.2 Bq kg^{-1}.

Table 4.7: Radium equivalent activity and Representative level index

Fertilizer Brand	No of Samples		Radium equivalent Activity. (Bq kg^{-1})	Representative gamma level index I_γ (Bq kg^{-1})
GFCN	20	Range	307.4 - 470.5	2.7 -4.0
		Mean	411.2 ± 18.5	3.5 ± 0.1
ITL/TAK	10	Range	599.8 - 940.1	4.6 – 7.1
		Mean	788.3 ± 30.1	6.0 ± 0.2
MAGIC	16	Range	252.9 - 438.6	2.2 – 3.7
		Mean	371.2 ± 17.2	3.2 ± 0.3
F & C	14	Range	501.2 – 858.1	4.0 – 6.5
		Mean	677.5 ± 22.7	5.2 ± 0.2
NAFCON	6	Range	381.0 – 450.0	3.3 – 3.8
		Mean	412.8 ± 13.3	3.5 ± 0.1

Table 4.8: Radium equivalent activity, Representative level index due to Single Superphosphate fertilizers and Phosphate rock.

Fertilizer Brand	No of Samples	City		Radium equivalent Act. (Bq kg^{-1})	Representative level index I_γ (Bq kg^{-1})
SSP	12	Kaduna	Range	454.2–852.3	3.1 – 5.8
			Mean	725.7±118.4	4.9 ± 0.8
Phosphate rock	13	Kaduna		1448.1 ±82.8	9.9 ± 0.6

Table 4.9: Radium equivalent activity, representative level index, $I_{\gamma r}$, of the present work and other studies

Country	Sample	Rad. equivalent (Bq/kg^{-1})	Level index ($I_{\gamma r}$)	References
Egypt	Super phosphate fertilizer	336	2.3	Hussein (1994)
Finland	Phosphate fertilizer	316		Mustonen (1985)
Pakistan	Super phosphate fertilizer	615		Khan et al.(1996)
Egypt (Qena)	Phosphate fertilizer	461.7	3.1	Nour et al (2005)
Germany	Phosphate fertilizer	597		Pfister et al (1976)
Germany	Phosphate fertilizer	597		Pfister et al (1976)
Nigeria	SSP	454-852		Present work
Italy	NPK	433		Righi et al (2005)
Egypt	NPK	197.77	1.47	El-Zakla et al (2007)
Egypt	NPK	160.88	1.25	El-Zakla et al (2007)
Nigeria	NPK	253-940	2.2 – 7.1	Present work
Tanzania (Arusha)	Phos. Rock	6069		Makweba and Holm(1993)
USA(Florida	Phos. Rock	1629.4		Guimond(1993)
Sudan(uro)	Phos. Rock	4147		Sam et al (1999)

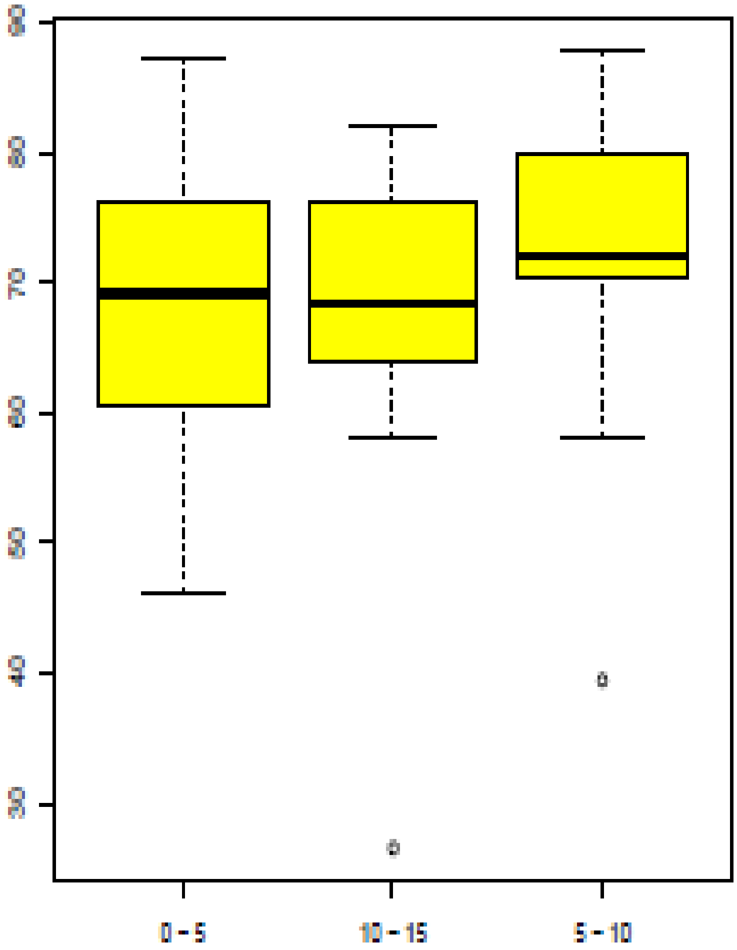

Fig. 4.9: The activity concentrations of ^{226}Ra in the farm soil from Nigerian Prison farm with respect to vertical profile

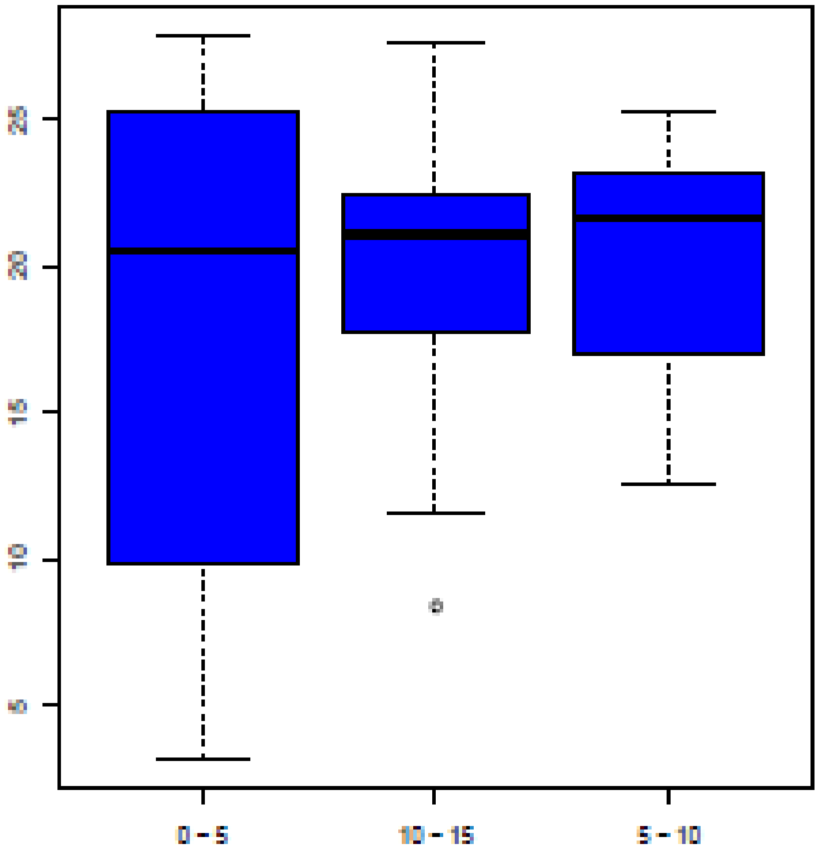

Fig. 4.10: The activity concentrations of ^{232}Th in the farm soil from Nigerian Prison farm with respect to vertical profile

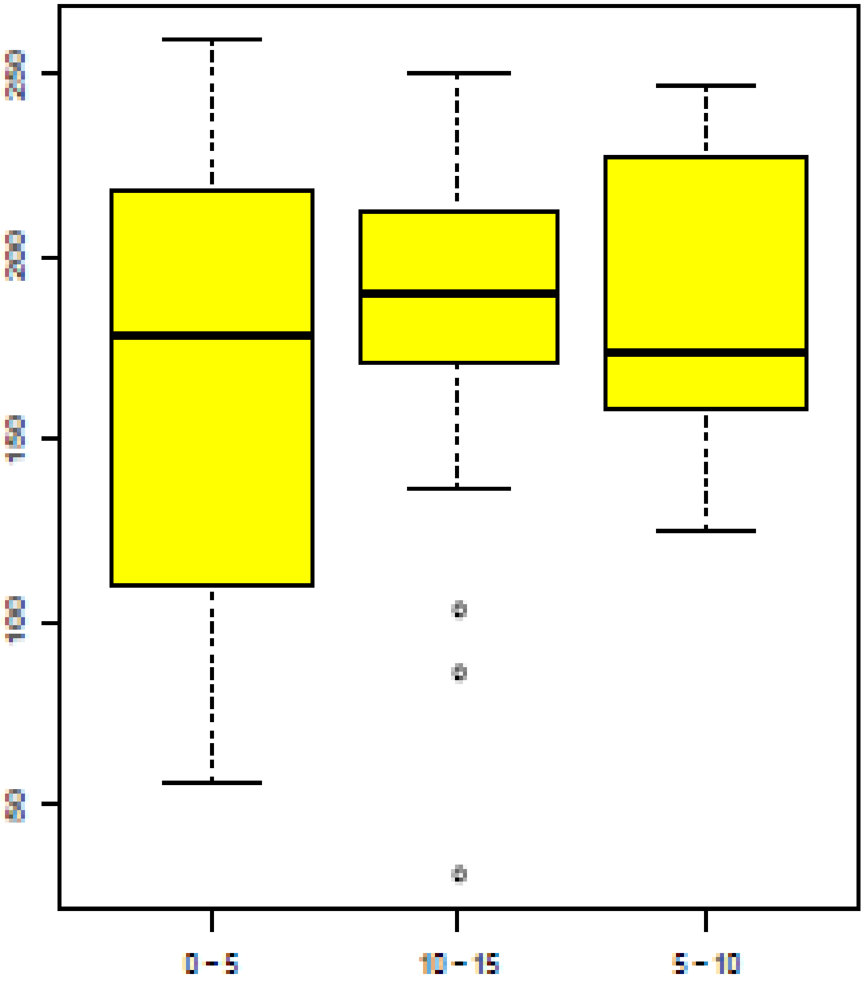

Fig. 4.11: The activity concentrations of ^{40}K in the farm soil from Nigerian Prison farm with respect to vertical profile

Using Analysis of Variance (ANOVA) of the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the cultivated farm soil from the Nigerian Prison farm, Kaduna, Kaduna state, the p-values are 0.439, 0.538 and 0.631 for 0-5 cm, 5-10 cm and 10-15 cm respectively. There were no significant differences ($P > 0.05$) in activity concentrations of the radionuclides within the same depth and across the vertical profile in the surface soil. This is suggestive of uniform or random distribution of radionuclides across the vertical profile in contrast to the report of Rodrıguez et al. (2012). However, further than 20.0 cm depth, his assertion that activity concentrations decreases with depth may be true, this study was based on the rooting zone of the experimental plants.

The activity concentrations of the radionuclides in the farm soil samples from the School of Agriculture, Kaduna in the northern region of Nigeria are shown in Figures 4.12, 4.13 and 4.14. The mean activity concentration values of these radionulclides in soil samples fertilized with both NPK(15-15-15) and SSP from the School of Agriculture, Kaduna varied from 234.0 Bq kg^{-1} to 373.7 Bq kg^{-1} with a mean value of 301.2 ± 42.5 Bq kg^{-1} for ^{40}K, 45.2 to 72.3 Bq kg^{-1} with a mean value of 61.4 ± 7.7 Bq kg^{-1} for ^{226}Ra and 12.1 to 32.7 Bq kg^{-1} with a mean value of 27.1± 6.2 Bq kg^{-1} for ^{232}Th. The activity concentration values of ^{40}K and ^{232}Th are higher in the second cultivated farm soil with mean values of 301.2 ± 42.5 Bq kg^{-1} and 27.1 ± 6.2 Bq kg^{-1} respectively. This may be attributed to the combination of the two fertilizers (NPK and SSP) used in School of Agriculture, Kaduna farm. However, the use of NPK fertilizer may be responsible for the higher activity concentration of ^{40}K in the farm soil since the activity concentrations of ^{40}K is relatively higher. In Nigerian Prison farm where only Single Superphosphate fertilizer was used, the activity concentration value of ^{226}Ra in the cultivated farm soil has the highest value of 69.1 ± 9.1 Bq kg^{-1}. This may further indicate that the use of Phosphate fertilizer elevated the concentration of ^{226}Ra in the cultivated farm soil more than other natural radionuclides of interest.

Using Analysis of Variance (ANOVA) of the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the cultivated farm soil from from the School of Agriculture farm, Kaduna, Kaduna state. The p-values are 0.82, 0.95 and 0.89 across the profile, there were no significant differences ($P > 0.05$) in the activity concentrations of the.

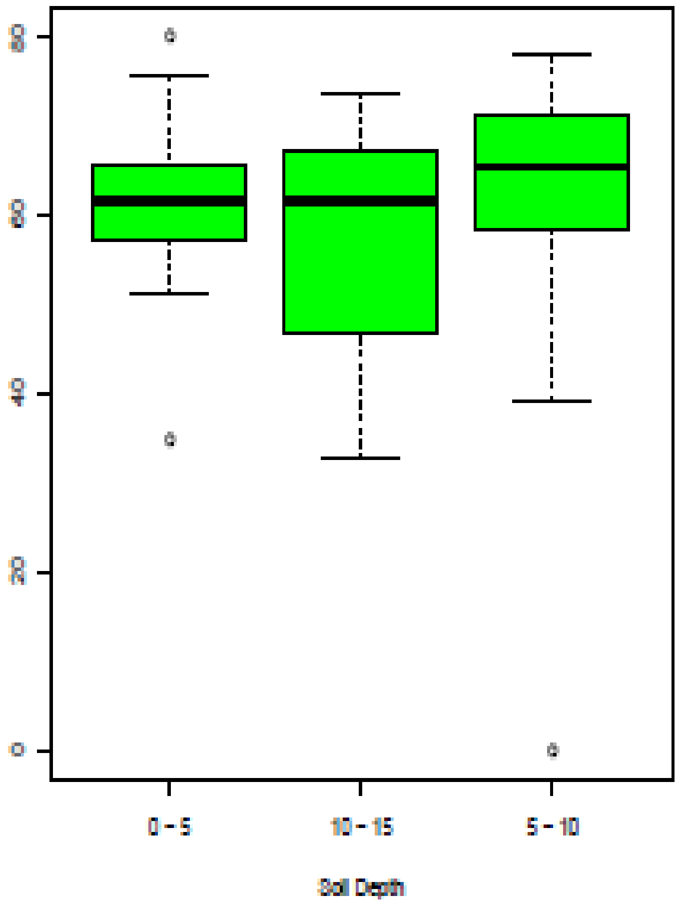

Fig. 4.12: The activity concentrations of ^{226}Ra in the farm soil from School of Agriculture farm, Kaduna with respect to vertical profile

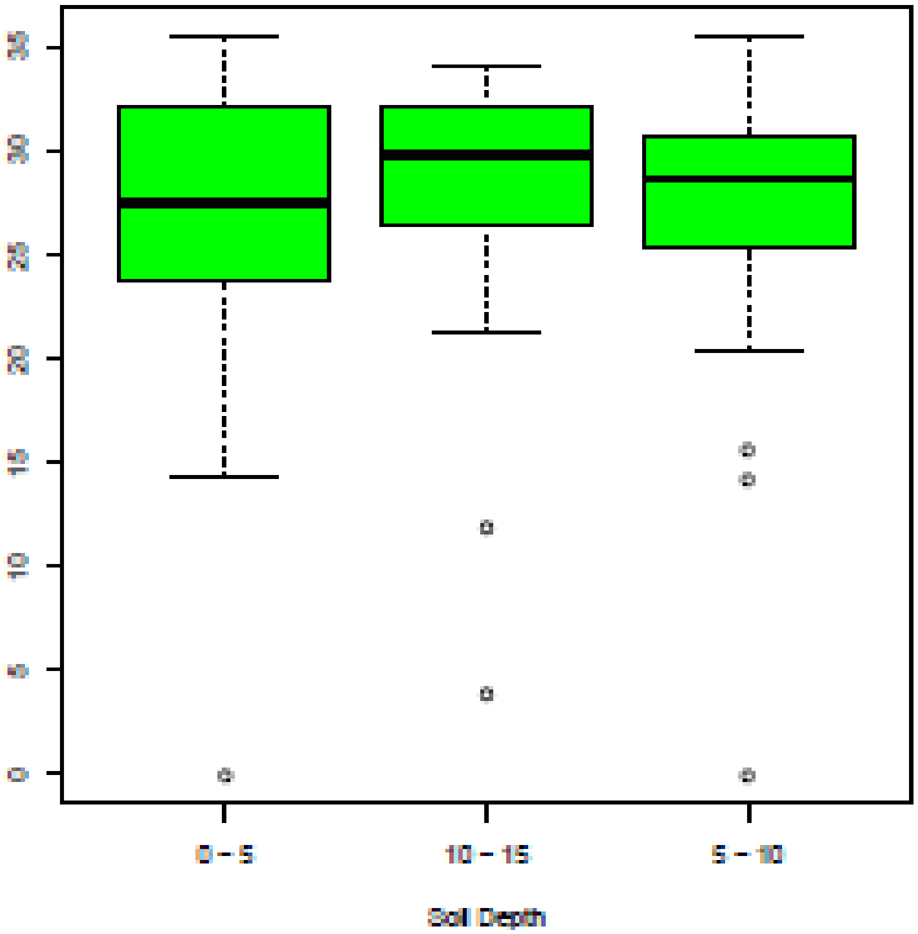

Fig. 4.13: The activity concentrations of ^{232}Th in the farm soil from School of Agriculture farm, Kaduna with respect to vertical profile `

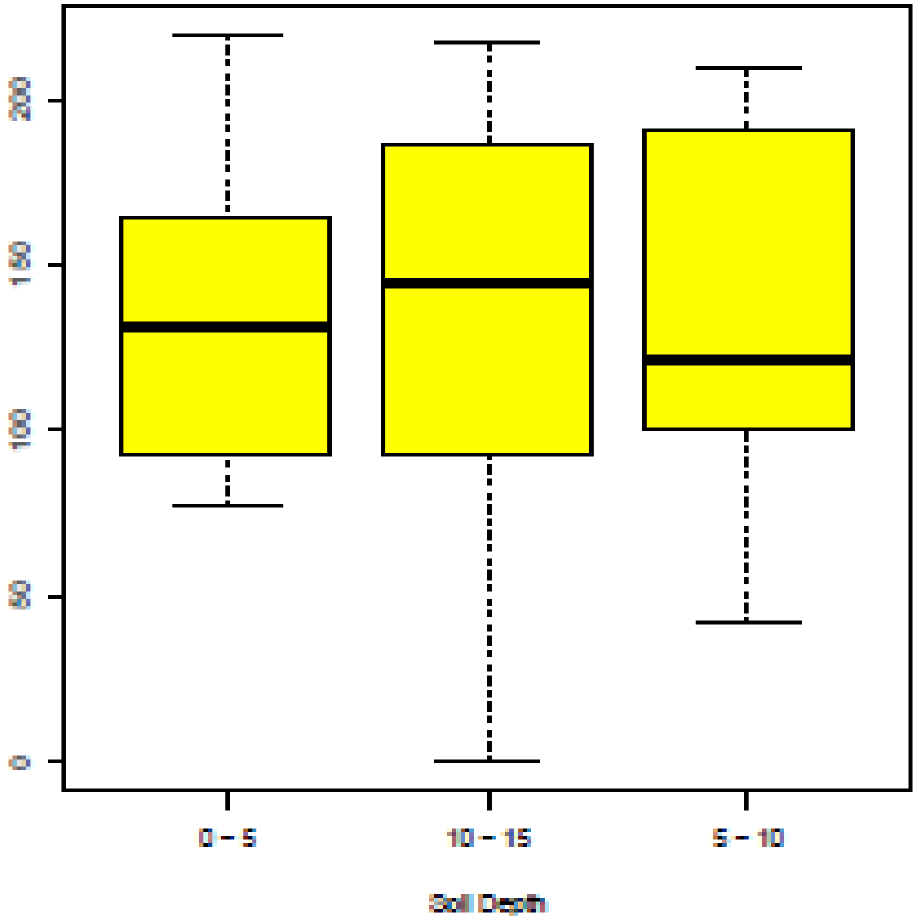

Fig. 4.14: The activity concentrations of ^{40}K in the farm soil from School of Agriculture farm, Kaduna with respect to vertical profile

radionuclides across the depths profile in the surface soil. The results also show that the activity concentrations of the radionuclides are uniformly distributed within the vertical profile observed in this study

4.5.2. The Radiation Harzard in Fertilized Cultivated Farm Soil Samples from Kaduna, Northern Nigeria

The activity concentrations of the primodial radionuclides ^{40}K, ^{226}Ra and ^{232}Th in fertilized farm soil were determined in order to evaluate the radiation hazard indices in cultivated farm soil due to the use of fertilizers. The chemical fertilizers investigated contain no artificial radionuclides in line with the research report of Ashraf et al. (2001) and Abbady, (2006). The external radiation hazard that can be incured by farmers and the workers in the farm is usually evaluated by some parameters discussed below. The mean activity concentration values in Tables 4.10 and 4.11 were used for the evaluation of the harzard indices.

4.5.3 The Radiation Hazard Parameters in Nigerian Prison and School of Agriculture, Kaduna Farm Soil Samples

The radiation hazard parameters obtained for farm soil samples were obtained using the equations 3.5, 3.6, 3.7 and 3.8. The radiation hazard indices; radium equivalent activity (Bq kg^{-1}), representative gamma level index, the total absorbed dose rate in air due to gamma radiation, as well as the outdoor effective dose assessment are presented in Tables 4.12 and 4.13.

The dose rate values ranged from 32.2 to 59.3 nGyh^{-1} with an average value of 49.9 ± 7.3 nGyh^{-1} which corresponds to an annual effective dose rate of 61.2 ± 12.7 µSvy^{-1}. The value for radium equivalent R_{eq} ranged from 71.4 to 130.7 Bq kg^{-1} with an average value of 109.9 ± 15.7 Bq kg^{-1}. The calculated annual effective dose lies within the world wide average values reported by UNSCEAR, and it remains in the dose criterion of 1 mSv/y recommended by ICRP, (2000). The gamma radiation level index, $I_{\gamma r}$ values ranged from 0.50 to 0.92 with an average value of 0.77 ± 0.11. The calculated I_y values for all the samples were lower than the international values $I_y < 1$. It was observed that for all the farm soil samples from this farm analyzed , the radium

Table 4.10: Mean Activity Concentration (Bq/kg) of ^{40}K , ^{226}Ra and ^{232}Th in Soil samples from the Nigerian Prison farm in the northern part of Nigeria

Location	No of samples	Activity concentrations (Bq/ kg)		
		^{40}K	^{226}Ra	^{232}Th
1	3	113.3 ± 33.1	72.8 ± 14.2	9.6 ± 3.9
2	3	71.0 ± 32.9	43.6 ± 14.0	15.6 ± 2.8
3	3	193.8 ± 32.7	69.7 ± 14.1	19.7 ± 3.8
4	3	194.5 ± 32.7	79.5 ± 14.0	21.2 ± 3.8
5	3	188.9 ± 32.4	76.4 ± 14.0	20.3 ± 3.8
6	3	187.9 ± 32.6	66.2 ± 13.8	20.0 ± 3.8
7	3	145.9 ± 32.8	56.9 ± 14.1	18.0 ± 3.9
8	3	113.8 ± 32.6	63.9 ± 14.0	12.0 ± 3.9
9	3	162.5 ± 32.6	65.6 ± 14.0	14.7 ± 3.8
10	3	205.8 ± 32.8	76.3 ± 13.9	21.1 ± 3.8
11	3	185.4 ± 32.1	71.1 ± 14.0	22.7 ± 4.0
12	3	198.7 ± 32.7	66.7 ± 14.0	22.6 ± 3.8
13	3	191.5 ± 31.0	67.4 ± 13.6	21.2 ± 3.9
14	3	227.2 ± 33.0	74.9 ± 14.2	25.3 ± 3.9
15	3	204.8 ± 32.9	82.0 ± 14.2	23.0 ± 3.8
16	3	200.9 ± 32.9	75.6 ± 14.0	19.9 ± 3.9
17	3	219.7 ± 34.5	66.4 ± 13.3	15.8 ± 3.4
Mean		***176.8 ± 42.3***	***69.1 ± 9.1***	***19.0 ± 4.2***
Range		***(71.0 - 227.2)***	***(43.6 – 82.0)***	***(9.6 – 25.3)***

Table 4.11: Mean Activity Concentration (Bq/kg) of ^{40}K , ^{226}Ra and ^{232}Th in Soil samples from the School of Agriculture farm in the northern part of Nigeria

Sample	No of Samples	Activity Concentration (Bq/kg)		
		^{40}K	^{226}Ra	^{232}Th
1	3	349.8 ± 33.1	65.2 ± 13.7	26.0 ± 3.7
2	3	348.6 ± 33.3	64.1 ± 13.9	25.5 ± 3.9
3	3	373.4 ± 34.0	70.4 ± 14.2	25.7 ± 4.0
4	3	234.0 ± 33.5	45.2 ± 13.8	12.1 ± 3.3
5	3	373.7 ± 33.6	72.3 ± 14.1	25.8 ± 3.9
6	3	315.2 ± 32.9	59.0 ± 13.7	20.5 ± 3.9
7	3	338.2 ± 33.7	50.3 ± 13.9	18.2 ± 3.9
8	3	264.4 ± 32.0	50.8 ± 13.7	20.5 ± 3.3
9	3	286.2 ± 30.1	55.7 ± 13.9	32.7 ± 4.0
10	3	303.9 ± 30.3	70.9 ± 14.2	32.4 ± 4.1
11	3	284.7 ± 30.2	60.0 ± 14.1	32.7 ± 3.7
12	3	280.3 ± 30.5	64.0 ± 14.1	31.9 ± 4.1
13	3	299.9 ± 31.2	68.9 ± 14.1	32.2 ± 4.1
14	3	246.0 ± 30.0	63.4 ± 13.9	31.1 ± 4.1
15	3	287.2 ± 30.3	63.3 ± 14.1	32.5 ± 4.1
16	3	265.6 ± 30.2	56.4 ± 14,1	31.0 ± 4.1
17	3	269.7 ± 31.0	63.0 ± 15.7	30.6 ± 4.1
Mean		301.2 ± 42.5	61.4 ± 7.7	27.1 ± 6.2
Range		(234.0- 373.7)	(45.2 72.3)	12.1 –32.7)

Table 4.12: Radiation Hazard Parameters in Farm Soil Samples of the Nigerian Prison farm, Kaduna

Sample	Rad. equivalent(Bq/kg^{-1})	Level index ($I_{\gamma r}$)	Dose rate (nGy/h)	Annual eff Dose μSv/y
1	95.3 ± 22.3	0.65 ± 0.16	42.5 ± 10.1	52.2 ± 12.4
2	71.4 ± 20.5	0.50 ± 0.14	32.2 ± 9.3	39.5 ± 11.4
3	112.8±22.1	0.79 ± 0.15	51.4 ± 10.0	63.0 ± 12.3
4	124.8±22.0	0.87 ± 0.15	56.6 ± 10.0	69.5 ± 12.2
5	120.0±21.9	0.84 ± 0.15	54.4 ± 9.9	66.8 ± 12.2
6	109.3±21.7	0.77 ± 0.15	49.8 ± 9.9	61.1 ± 12.1
7	93.9 ±22.2	0.66 ±0.16	42.7 ± 10.1	52.4 ±12.3
8	89.8 ±22.1	0.62 ± 0.15	40.3 ± 10.0	49.5 ±12.3
9	99.1 ± 21.9	0.70 ± 0.15	44.9 ± 9.9	55.1 ±12.2
10	122.3±21.9	0.86 ± 0.15	55.7 ± 9.9	68.3 ± 12.2
11	117.9±22.2	0.83 ± 0.16	53.6 ± 10.1	65.8 ± 12.4
12	114.3±22.0	0.81 ± 0.15	52.2 ± 9.9	64.1 ± 12.2
13	112.5±21.6	0.79 ± 0.15	51.3 ± 9.8	62.9 ± 12.0
14	128.6±22.3	0.91 ± 0.16	58.8 ± 10.1	72.1 ± 12.4
15	130.7±22.2	0.92 ± 0.16	59.3 ±10.0	72.8 ± 12.3
16	119.5±22.1	0.84 ± 0.15	54.3 ± 10.0	66.7 ± 12.3
17	105.9±20.8	0.75 ± 0.15	48.5 ± 9.5	59.5 ± 11.6
Mean	109.9±15.7	0.77 ±0.11	49.9 ±7.3	61.2 ± 12.7
Range	71.4– 130.7	0.50 – 0.92	32.2 – 59.3	39.5 – 72.8

Table 4.13: Radiation Hazard Parameters in Farm Soil Samples of the School of Agriculture, Kaduna

Sample	**Rad. Equivalent (Bq/kg^{-})**	**Gamma Level index ($I_{\gamma r}$)**	**Dose rate (nGy h^{-1})**	**Annual eff Dose (µSv y^{-1})**
1	129.3± 21.5	0.93 ± 0.15	60.4 ± 9.8	74.1 ± 12.0
2	127.4 ± 22.0	0.92 ± 0.15	59.5 ± 10.0	73.0 ± 12.3
3	135.9 ± 22.5	0.98 ± 0.16	63.4 ± 10.2	77.8 ± 12.5
4	80.5 ± 21.1	0.58 ± 0.15	37.5 ± 9.6	46.0 ± 11.7
5	138.0 ± 22.3	0.99 ± 0.16	64.3 ± 10.1	78.9 ± 12.4
6	112.6 ± 21.8	0.81 ± 0.15	52.5 ± 9.9	64.5 ± 12.1
7	102.4 ± 22.1	0.75 ± 0.15	48.3 ± 10.0	59.2 ± 12.3
8	100.5 ± 20.9	0.72 ± 0.15	46.8 ± 9.5	57.5 ±11.6
9	124.5 ± 21.9	0.89 ± 0.15	58.0 ± 9.9	71.2 ± 12.2
10	140.6 ± 22.4	1.00 ± 0.16	65.1 ± 10.1	80.0 ± 12.4
11	128.7 ± 21.7	0.92 ± 0.15	59.8 ± 9.8	73.4 ± 12.0
12	131.2 ±22.3	0.94 ± 0.16	60.8 ± 10.1	74.6 ± 12.4
13	138.0 ± 22.4	0.98 ± 0.16	63.9 ± 10.1	78.5 ± 12.4
14	126.8 ± 22.1	0.90 ± 0.15	58.5 ± 10.0	71.8 ± 12.3
15	131.9 ± 22.3	0.94 ± 0.16	61.2 ± 10.1	75.1 ± 12.4
16	121.2 ± 22.3	0.87± 0.16	56.3 ± 10.1	69.1 ± 12.4
17	127.5 ± 24.0	0.91 ± 0.17	59.0 ± 10.8	72.4 ± 13.3
Mean	123.4±15.9	0.88 ± 0.11	57.4±7.3	70.4 ±12.8
Range	80.5 – 140.6	0.58 -1.00	37.5 – 65.1	46.0 – 80.0

equivalent activity values are well within and less the permissible limit of 370 Bq kg^{-1} despite the use of chemical farm fertilizer. The calculated absorbed dose rate are within the world average outdoor exposure due to terrestrial gamma radiation 55 nGy y^{-1}, according to UNSCEAR, (2000). The calculated radiation hazard indices values in the School of Agriculture Farm Soil samples from the northern part of Nigeria are presented in Table 4.13. The dose rate values ranged from 37.5 to 65.1 nGyh^{-1} with an average value of 57.4 ± 7.3 nGyh^{-1} which corresponds to an annual effective dose rate of 70.4 ± 12.8 µSvy^{-1}. The value for radium equivalent R_{eq} ranged from 80.5 to 140.6 Bq kg^{-1} with an average value of 123.4 ± 15.9 Bq kg^{-1}. The gamma radiation level index, $I_{\gamma r}$ values ranges from 0.58 to 1.0 with an average value of 0.88 ± 0.11. . The calculated I_y values for all the samples were lower than the international values $I_y < 1$ It was observed that for all the farm soil samples from this farm analyzed , the radium equivalent activity values are well within and less the permissible limit of 370 Bq kg^{-1} despite the use of chemical farm fertilizer. The calculated absorbed dose rate are within the world average outdoor exposure due to terrestrial gamma radiation 55 nGy y^{-1}, according to UNSCEAR, (2000).

4.5.4: Activity Concentrations (Bq kg^{-1}) in Farm Soil Samples at Onne, Rivers State in the Southern Region

The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in the farm soil samples from Onne, Rivers State in the southern region of Nigeria are shown in the boxplot distribution in Figures 4.15, 4.16 and 4.17. The activity concentrations vary from 83.7 to 202.2 Bq kg^{-1} with an average value of 134.4 ± 43.5 Bq kg^{-1} for ^{40}K, 9.4 to 38.8 Bq kg^{-1} with an average value of 30.2 ± 8.0 Bq kg^{-1} for ^{226}Ra and 7.4 to 20.6 Bq kg^{-1} with an average value of 12.7 ± 3.2 Bq kg^{-1} for ^{232}Th. The average values are lower than the values obtained in the northern region of Nigeria; this may be attributable to the constant or heavy use of both NPK and SSP fertilizers to maintain soil fertility in the northern part of Nigeria. The reduced soil fertility in the northern part is due to soil degradation, nutrient mining, erosion and desertification (Yusuf, and Yusuf, 2008) which are not common in the southwestern and southern part of Nigeria.

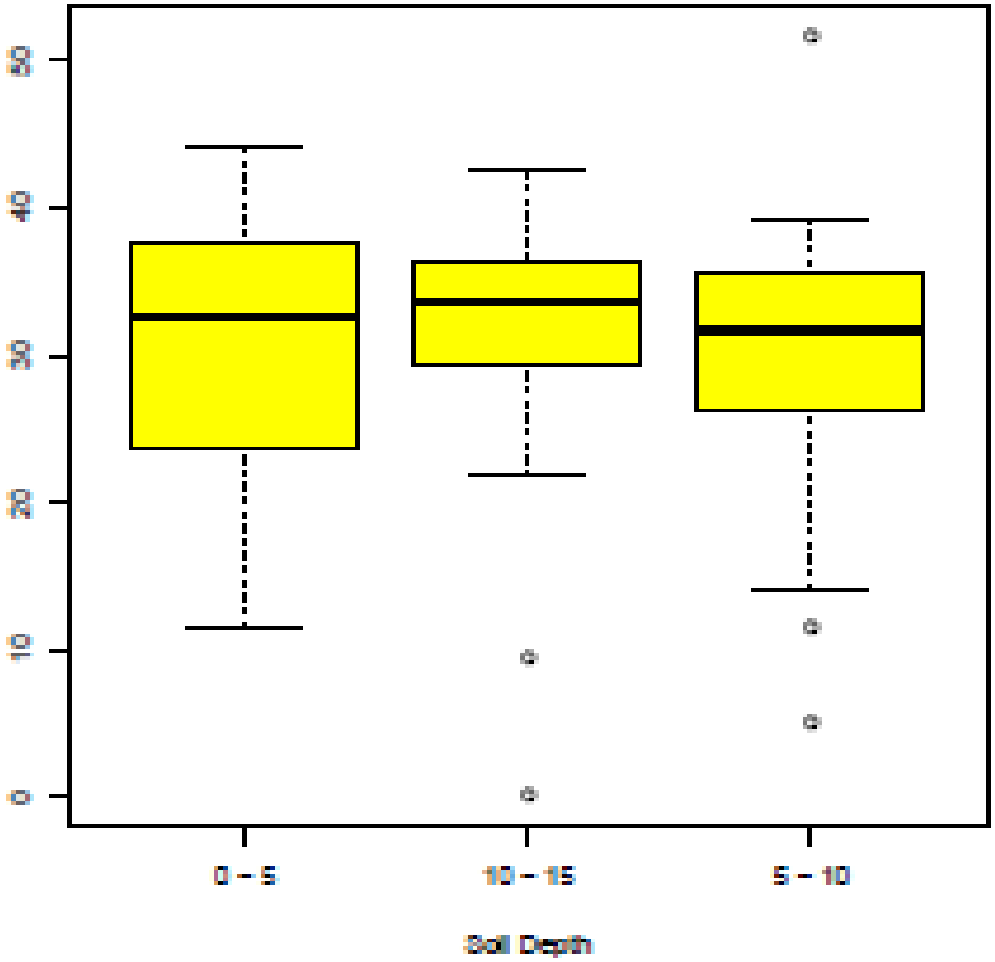

Fig. 4.15: The activity concentrations (Bq/ kg) of ^{226}Ra in the farm soil from Onne, with respect to vertical profile

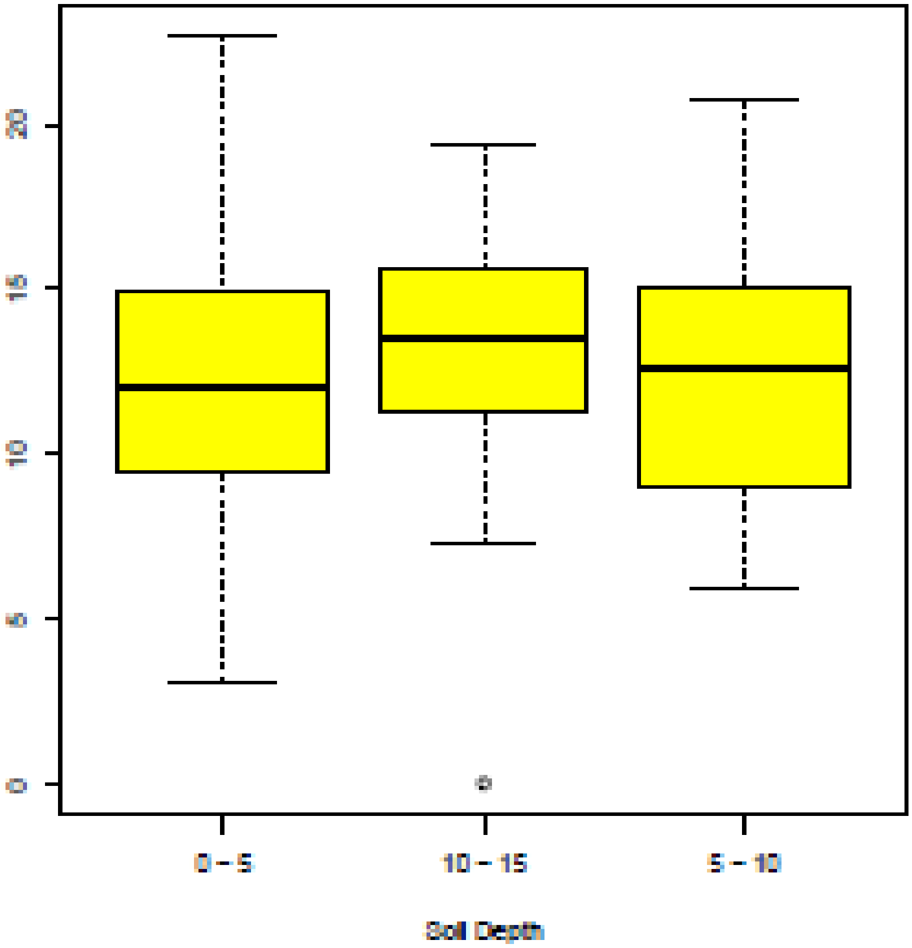

Fig. 4.16: The activity concentrations of ^{232}Th in the farm soil from Onne, Rivers state with respect to vertical profile

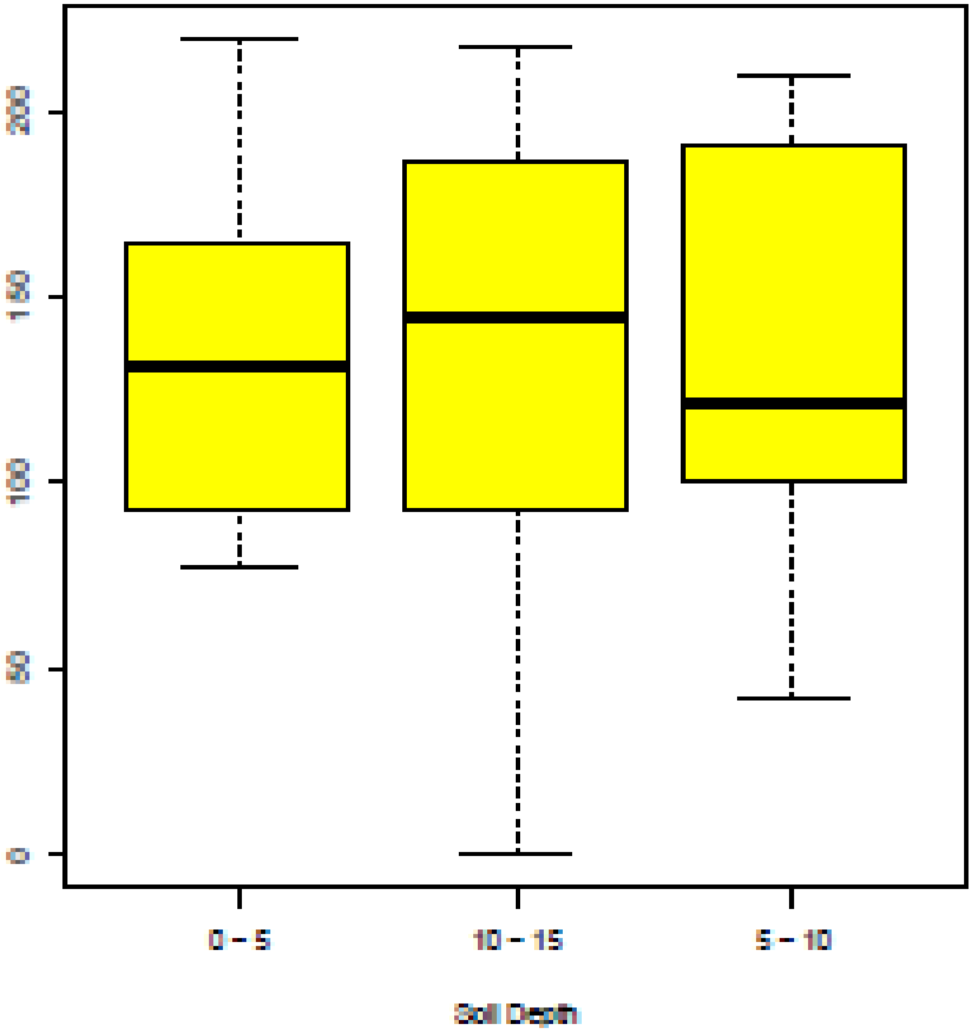

Fig. 4.17: The activity concentrations of ^{40}K in the farm soil from Onne, with respect to vertical profile

Using Analysis of Variance (ANOVA) of the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the cultivated farm soil from from the cultivated farm around National Fertilizer Company Nigeria (NAFCON) Onne, southern, Nigeria, the p-values are 0.97, 0.86 and 2.0×10^{-16} respectively. There were no significant differences ($p > 0.05$) in the activity concentrations ^{226}Ra and ^{232}Th. There were significant differences ($p < 0.05$) in the activity concentrations of ^{40}K across the vertical profile. This is similar to what was obtained in the northern region, hence, it can be concluded that radionuclides are uniformly distributed across the vertical profile, 0 – 15 cm depth; this is within the rooting zone of the plants used in the experimental farm

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4.5.5: Radiation hazard parameters in onne, southern region farm soil samples

Using equations 3.5, 3.6, 3.7 and 3.8, and the values in Table 4.14, the calculated values of the radiation hazard indices in the farm soil samples from Onne, Rivers State, southern part of Nigeria are presented in Table 4.15 . The dose rate values ranged from 17.0 to 31.1 nGyh^{-1} with an average value of 27.2 ± 3.9 nGyh^{-1} which corresponds to mean annual effective dose of 33.4 ± 4.8 µSv y^{-1}. The value for radium equivalent R_{eq} ranges from 36.2 to 67.8 Bq kg^{-1} with an average value of 58.7 ± 8.6 Bq kg^{-1}. The gamma radiation level index, $I_{\gamma r}$ values ranges from 0.26 to 0.49 with an average value of 0.42 ± 0.06. The calculated I_y values for all the samples were lower than the international values $I_y < 1$ It was observed that for all the farm soil samples from this farm analyzed , the radium equivalent activity values are well within and less the permissible limit of 370 Bq kg^{-1} despite the use of chemical farm fertilizer. The calculated absorbed dose rate are within the world average outdoor exposure due to terrestrial gamma radiation 55 nGy y^{-1}, stated by UNSCEAR (2000).

Table 4.14: Mean Activity Concentrations (Bq kg^{-1}) in Farm Soil Samples at Onne, Rivers State in the Southern Region

Location	No of Samples	Activity Concentration (Bq/kg)		
		^{40}K	^{226}Ra	^{232}Th
1	3	108.3 ±30.0	25.1± 15.4	13.4 ±3.6
2	3	95.5 ± 29.2	32.4 ±13.8	12.7 ±3.7
3	3	127.4 ±29.8	33.5 ±15.1	9.9 ± 3.6
4	3	136.5 ±27.1	34.9 ±13.7	14.0 ±3.7
5	3	202.2 ±30.8	31.0 ±14.5	7.4 ± 3.6
6	3	117.9 ±29.0	35.9 ±15.5	10.0 ±4.0
7	3	198.9 ±30.2	33.7 ±14.7	12.2 ±3.7
8	3	139.5 ±27.2	34.0 ±13.7	11.6 ±3.8
9	3	193.0 ±31.2	35.5 ±13.9	12.2 ±3.7
10	3	191.1 ±28.1	32.5 ±13.4	12.3 ±3.7
11	3	183.7 ±29.8	35.1 ±13.5	11.7 ±3.7
12	3	83.7 ± 29.9	38.8 ±15.4	14.6 ±3.7
13	3	102.0 ±29.7	31.7 ±15.4	14.1 ±3.8
14	3	124.0 ±29.0	26.8 ±15.6	20.6 ±3.9
15	3	108.4 ±28.9	23.8 ±15.4	11.0 ±3.9
16	3	117.9 ±29.0	35.9 ±15.5	10.0 ±4.0
17	3	90.3 ± 25.5	12.8 ±15.4	11.5 ±4.7
18	3	98.1 ± 28.9	9.4 ± 14.6	19.5 ±4.0
Mean		134.4 ± 40.8	30.2 ± 8.0	12.7 ± 3.2
Range		(83.7-202.2)	(9.4 -38.8)	(7.4-20.6)

Table 4.15: Radiation Hazard Parameters in Farm Soil Samples of Onne, Southern Region

Sample	Rad. equivalent (Bq/kg $^{-1}$)	Level index ($I_{\gamma r}$)	Dose rate (nGy h^{-1})	Annual eff dose (µSv y^{-1})
1	52.6 ± 22.9	0.37 ± 0.16	24.4 ±10.3	29.9 ± 12.6
2	57.9 ± 21.3	0.41 ± 0.15	26.5 ± 9.6	32.5 ± 11.8
3	57.5 ± 22.5	0.41 ± 0.16	26.5 ±10.2	32.5 ± 12.5
4	65.4 ± 21.1	0.47 ± 0.15	30.2 ± 9.5	37.0 ± 11.7
5	57.2 ± 22.0	0.42 ± 0.15	26.9 ± 9.9	33.0 ± 12.2
6	59.3 ±23.5	0.42 ± 0.16	27.1 ±10.6	33.3 ± 13.0
7	66.5 ± 22.3	0.48 ± 0.16	31.1 ±10.1	38.2 ± 12.4
8	61.3 ± 21.2	0.44 ± 0.15	28.3 ± 9.6	34.8 ±11.8
9	67.8 ± 21.6	0.49 ± 0.15	31.7 ± 9.8	38.9 ± 12.0
10	64.8 ± 20.9	0.47 ± 0.15	30.4 ± 9.4	37.3 ±11.6
11	66.0 ± 21.1	0.48 ± 0.15	30.8 ± 9.5	37.7 ± 11.7
12	66.1 ± 23.0	0.46 ± 0.16	30.0 ±10.4	36.8 ±12.7
13	59.7 ± 23.1	0.42 ± 0.16	27.4 ±10.4	33.6 ± 12.8
14	65.8 ± 23.4	0.47 ± 0.16	30.6 ±10.5	37.5 ± 12.9
15	47.9 ± 23.2	0.34 ± 0.16	22.2 ±10.5	27.3 ± 12.8
16	59.3 ± 23.5	0.42 ± 0.16	27.1 ±10.6	33.3 ± 13.0
17	36.2 ± 24.1	0.26 ± 0.17	17.0 ±10.8	20.9 ± 13.3
18	44.8 ± 22.5	0.32 ± 0.16	21.3 ±10.2	26.1 ± 12.5
Mean	58.7 ± 8.6	0.42 ± 0.06	27.2 ± 3.9	33.4 ± 4.8
Range	36.2 – 67.8	0.26 – 0.49	17.0 –31.1	20.9 – 38.9

4.5.6 Vertical distribution of radionuclides in the farm soil samples

The study of the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th is important in order to evaluate the external irradiation from gamma vertical distribution of the radionuclides -emitters in soil and to estimate the plant root uptake. The concentration of radionuclides: ^{40}K and ^{226}Ra in the farm soil vertical profile samples in the northern Nigeria increased with depth down to the highest value at a depth of 10.0 cm as shown in Figures 4.18 and 4.19. Also beyond the depth of 10.0 cm the activity concentrations decreases, this is an indication that the radionuclides are available for plant roots within this depth, similar to the observation of Boris Faybishenko (2013).

The activity concentrations of ^{232}Th in northern and southern farm soil is approximately constant across the vertical profile, this may suggest that there is a uniform distribution of ^{232}Th due to its solubility this agrees with Sheppard and Evenden (1988) observation. In contrast, the activity concentrations of the radionuclides: ^{40}K and ^{226}Ra in the cultivated farm soil samples from the southern Nigeria exhibits the highest value within the 10 – 15 cm depth as shown in Figure 4.20. The activity concentrations of the radionuclides: ^{40}K and ^{226}Ra increases beyond 10.0 cm. There seems also to be a downward positive distribution trend of ^{40}K and ^{226}Ra in the cultivated farm soil samples.

4.5.7 Comparison of the cultivated farm soil samples

Comparing the northern and southern farm soil samples, the multivariate ANOVA presents p-values of 0.00, 0.00 and 0.00, There were significant differences ($p < 0.05$) in the activity concentrations of the radionuclides. The application of SSP fertilizer in the northern region may contribute more to the activity concentrations of the primordial radionuclides.

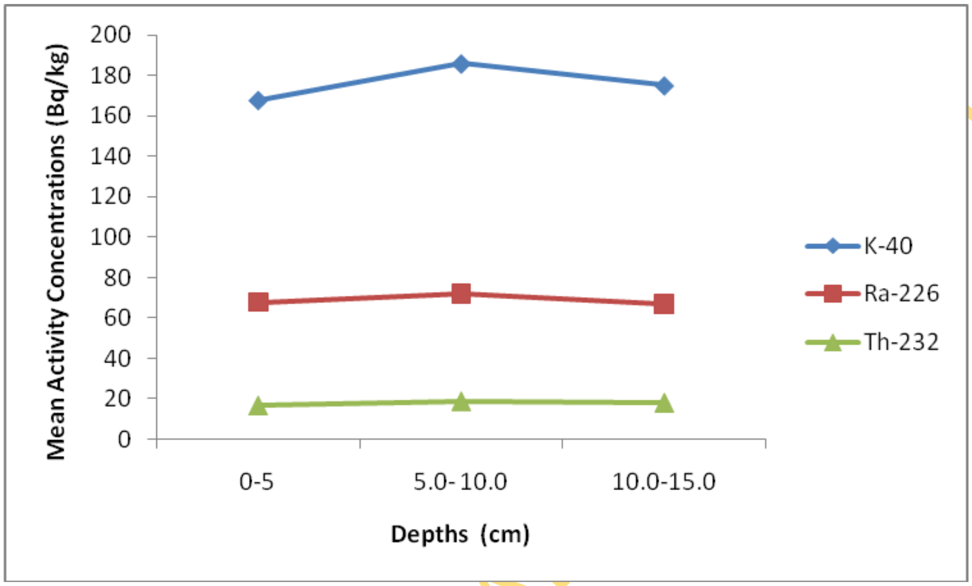

Figure 4.18 Radionuclide Vertical Distribution in Northern Nigeria Prison farm soil

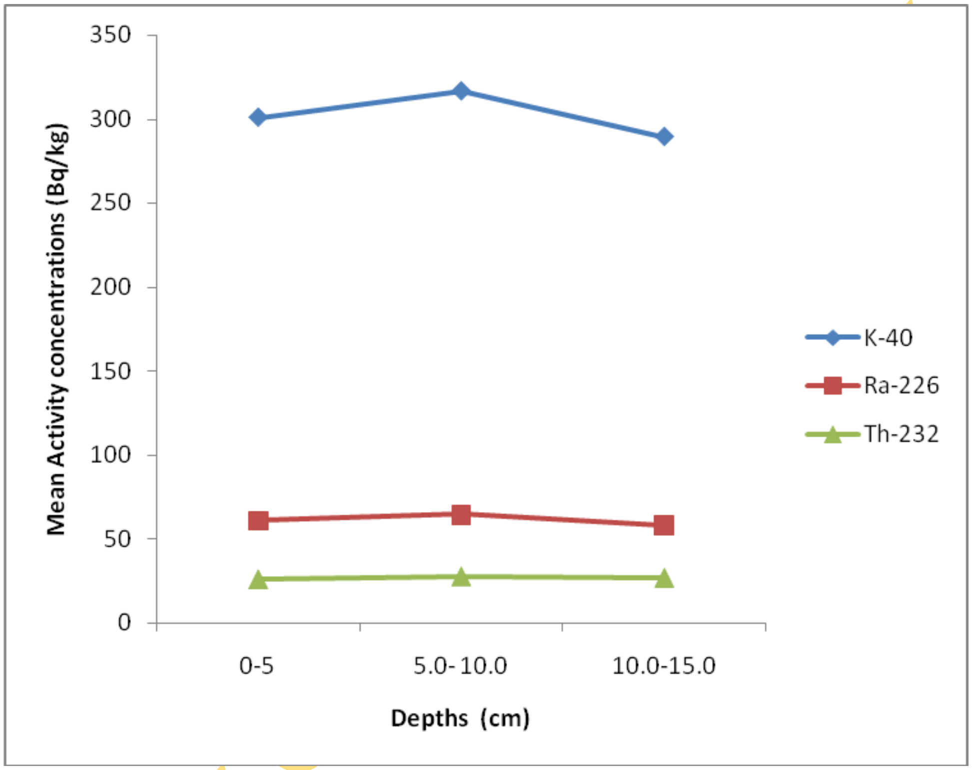

Figure 4.19 Radionuclide Vertical Distribution in Northern Nigeria School of Agriculture farm soil

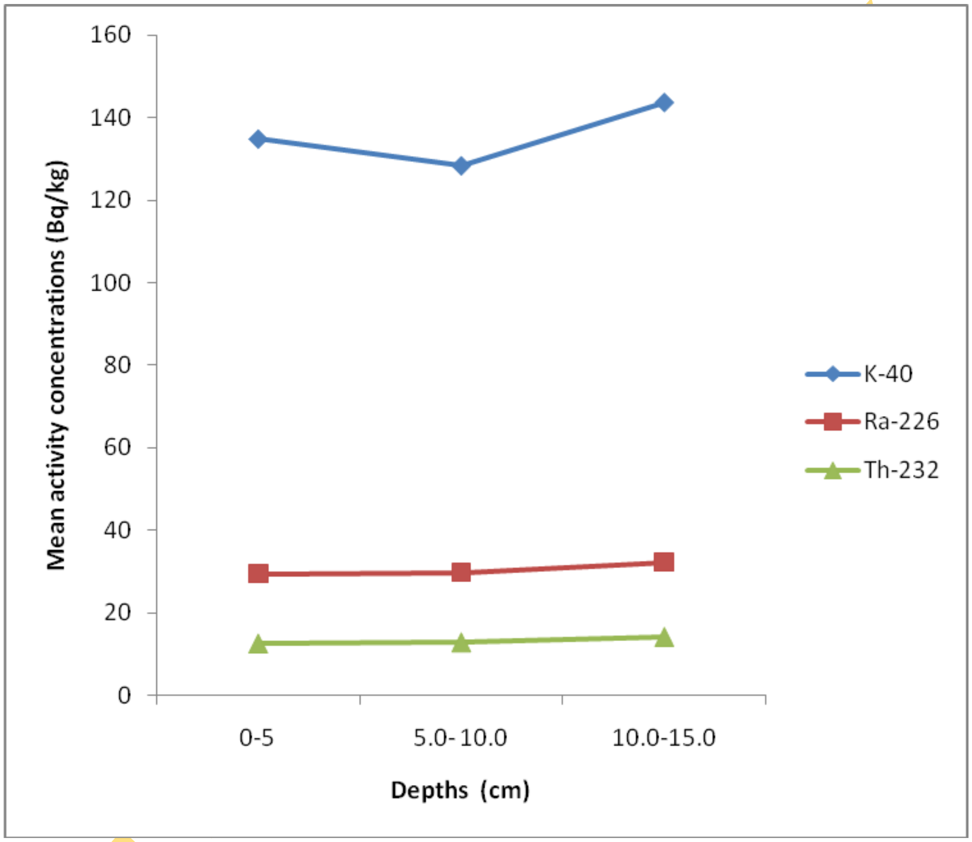

Figure 4.20 Radionuclide Vertical Distribution in cultivated farm soil in Onne

The average activity concentration values obtained in the southern region are lower than the values obtained in the northern region of Nigeria. This may be.attributed to heavy use of both NPK and SSP fertilizers to maintain soil fertility in the northern region of Nigeria.

The p-values of 0.000, 0.000 and 0.000 were obtained for the multivariate ANOVA analysis of the activity concentrations of the radionuclides ^{40}K, ^{226}Ra and ^{232}Th in the cultivated farm soil from the northern region and southern region. There were significant differences ($p < 0.05$) in the activity concentrations of the radionuclides. This also indicates that the differences in the activitiy concentrations of the radionuclides are significant across the two regions, this may be attributed to the variations in the geographical and soil formations of the two regions.

The results of the activity concentrations of the radionuclides ^{40}K, ^{226}Ra and ^{232}Th in the cultivated farm soil from the northern region were correllated with the activity concentrations in the cultivated farm soil from the southern region as presented in Figsures 4.21 – 4.23. The correlation coefficients (R^2) obtained are 0.04, 0.07 and 0.01 for ^{40}K, ^{226}Ra and ^{232}Th respectively. The correlation give a low correlation coefficients which shows a low positive relationship between the activity concentrations of the radionuclides in the two regions. However the additional use of single superphosphate fertilizer(SSP) may account for the variations in the determined values coupled with the geological formations. Comparing the northern, southern farm soils and the virgin soil, multivariate ANOVA, p-values of 0.00, 0.00 and 0.00 , there were significant differences ($p < 0.05$) in the activity concentrations. The activity concentrations of the ^{40}K, ^{226}Ra and ^{232}Th in the virgin soil are lower compare to the northern and southern farm soil, since there have been no farming activities and contamination due to application of chemical fertilizer. Moreso leaching, run-off and cultivation do not occur in the forest.

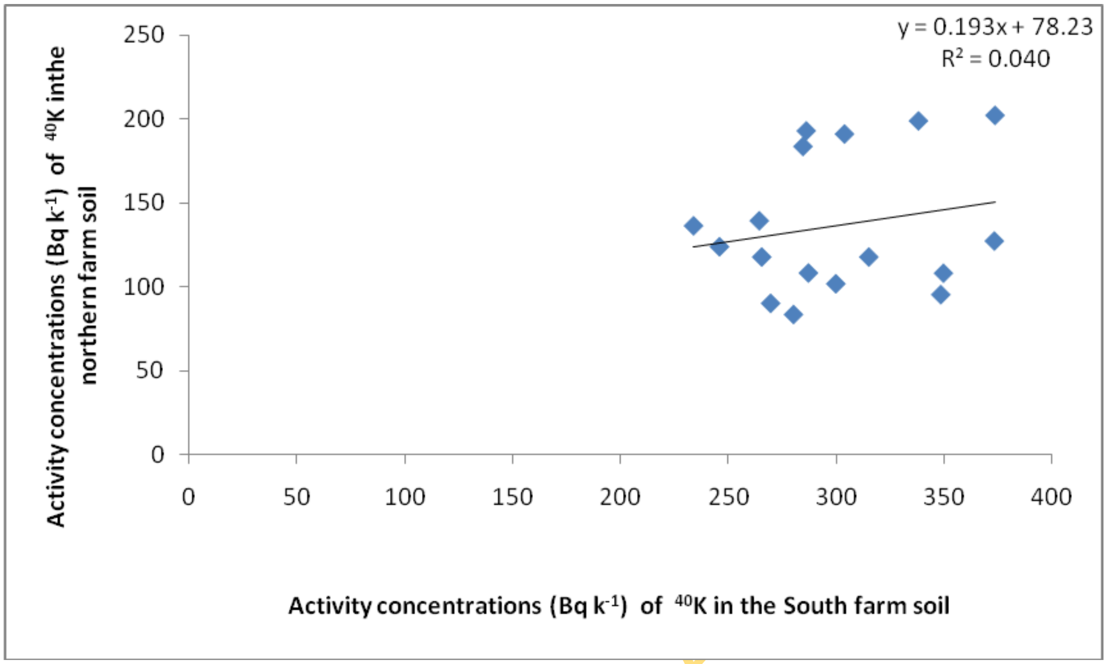

Fig. 4.21: Northern farm soil with SSP and NPK correlated with southern farm soil with NPK

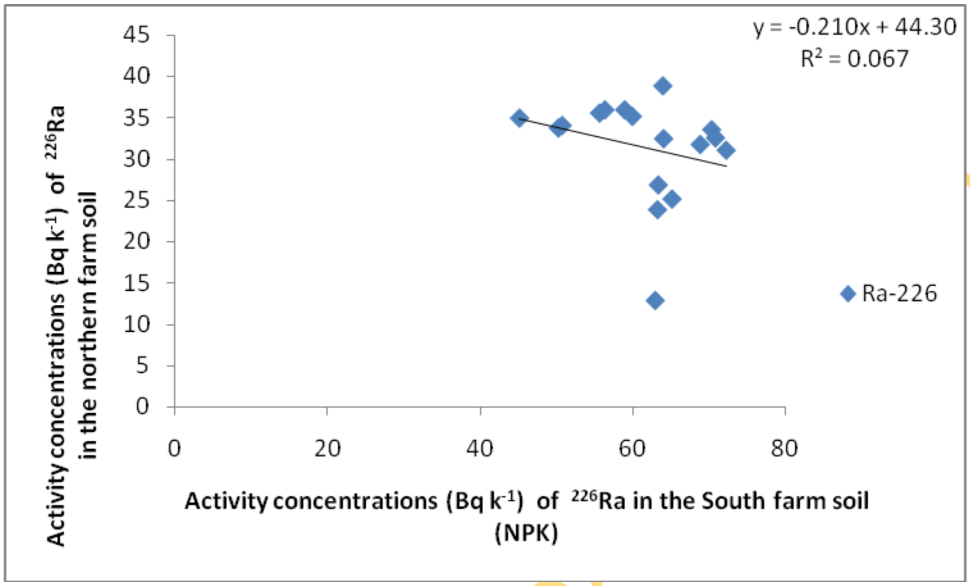

Fig. 4.22: Northern farm soil with SSP and NPK correlated with southern farm soil with NPK

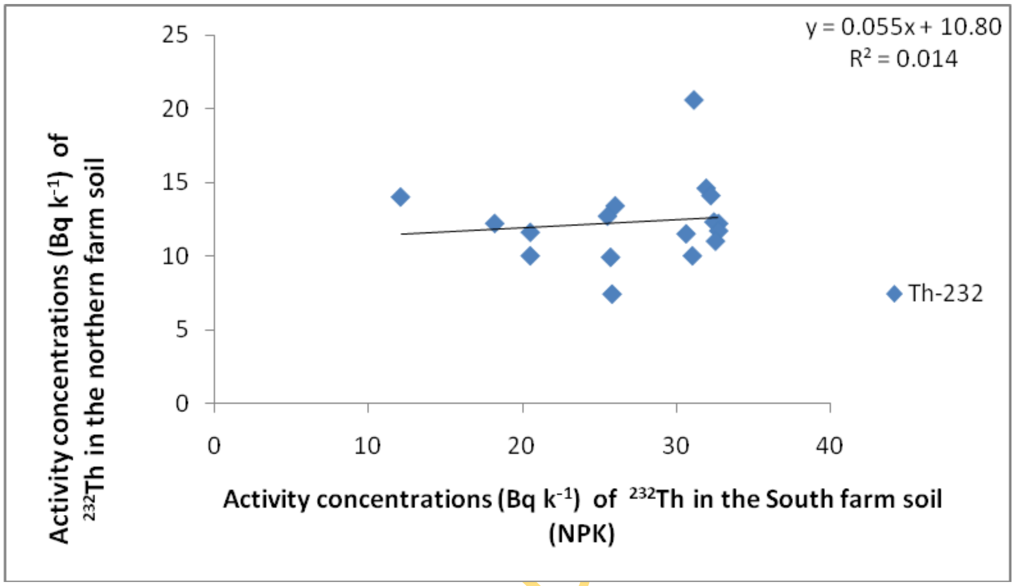

Fig. 4.23: **Northern farm soil with SSP and NPK correlated with southern farm soil with NPK**

4.5.8: Activity Concentrations (Bq kg^{-1}) of ^{40}K, ^{226}Ra and ^{232}Th in Virgin Soil (VS) Samples

The range and mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in virgin soil samples at the Government Reserved forest in Ikere- Ekiti, Ado-Ekiti and Egbe-Ekiti are presented in Table 4.16. The activity concentrations values in the samples from Ikere – Ekiti ranged between 198 - 241 Bq kg^{-1}, 44 - to 61 Bq kg^{-1} and 15 - to 22 Bq kg^{-1} with a mean values of 217 ± 13 Bq kg^{-1}, 53 ± 5.2 Bq kg^{-1} and 18 ± 2.6 Bq kg^{-1} for ^{40}K, ^{226}Ra and ^{232}Th respectively.

At the Government Reserved forest in Ado –Ekiti, the activity concentration values ranged between 189 - 208 Bq kg^{-1}, 30 - 50 Bq kg^{-1} and 13 - 18 Bq kg^{-1} with a mean values of 200 ± 10.1 Bq kg^{-1}, 40 ± 3.7 Bq kg^{-1} and 15 ± 3.0 Bq kg^{-1} for ^{40}K, ^{226}Ra and ^{232}Th respectively. The activity concentrations values of ^{40}K, ^{226}Ra and ^{232}Th in a virgin soil at the Government Reserved forest, Egbe - Ekiti ranged between 240 - 260 Bq kg^{-1}, 50.4 - 60.3 Bq kg^{-1} and 18 - 26.5 Bq kg^{-1} with a mean values of 249 ± 12.7 Bq kg^{-1}, 56.3 ± 1.2 Bq kg^{-1} and 22 ± 2.9 Bq kg^{-1} for ^{40}K, ^{226}Ra and ^{232}Th respectively.

The activity concentration values of ^{40}K, ^{226}Ra and ^{232}Th in the Virgin soil samples from the study areas are lower than the activity concentration values obtained from the farm locations earlier studied. This may be attributable to no farming activities, degradation, nutrient mining, erosion, desertification and application of chemical fertilizer in the study areas. These activities characterize cultivated farm soils (Yusuf, and Yusuf, 2008).

The p-value, 0.93 was obtained from the ANOVA analysis shows There were no significant differences ($p > 0.05$) in the activity concentrations of ^{226}Ra in the samples collected from Ado – Ekiti and Ikere – Ekiti locations. The p-value, 0.00 obtained for ^{40}K and ^{232}Th There were significant differences ($P < 0.05$) in the activity concentrations of the samples collected from the locations.

Table 4.16: Range and mean activity concentrations (Bq kg^{-1})of ^{40}K, ^{226}Ra and ^{232}Th in virgin soil from Government Reserved forest locations in Ekiti

S/N	No of Samples	Activity concentrations (Bq kg^{-1})		
		^{40}K	^{226}Ra	^{232}Th
Ikere - Ekiti	20	(235 – 264)	(43 – 56)	(11 – 22)
		240 ± 20.8	51 ± 13.1	18 ± 3.1
Ado – Ekiti	20	(189 – 208)	(31 – 50)	(13– 18)
		204 ± 10.1	40 ± 3.7	15 ± 3.0
Egbe - Ekiti	20	(240-260)	(50.4 – 60.3)	(18 – 26.5)
		249 ± 12.7	56.3 ± 1.2	22 ± 2.9

4.6 Mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in experimental farm soil, tomatoes and vegetable samples

4.6.1 Experimental soil samples (VS)

The results of the mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the experimental farm soil samples (VS_{C}, VS_{SSP} and VS_{NPK}), in tomato (*Lycopersicum esculentum* K. Karsten) and Vegetable (*Amaranthus hybridus* Linnaeus) samples are presented in Tables 4.17, 4.18, 4.19, 4.20, 4.21 and 4.22. The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the experimental farm soil samples treated with single superphosphate fertilizer (VS_{SSP}) are 285.0 ± 3.3 Bq kg^{-1}, 66.0 ± 2.0 Bq kg^{-1} and 10.0 ± 1.4 Bq kg^{-1} respectively.

The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the control experimental farm soil samples (VS_{C}) are 204 ± 2.4 Bq kg^{-1}, 43.0 ± 2.3 Bq kg^{-1} and 7.0 ± 1.7 Bq kg^{-1} respectively. The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the experimental farm soil samples treated with Nitrogen-Phosphorus-Potassium (VS_{NPK}) are 352.0 ± 1.9 Bq kg^{-1}, 62.0 ± 1.7 Bq kg^{-1} and 8.0 ± 1.9 Bq kg^{-1} respectively.

Results presented in Table 4.23 showed that the application of SSP and NPK fertilizers contributed to the activities of ^{40}K, ^{226}Ra and ^{232}Th in the experimental farm soil samples (VS_{SSP}) compared to the control farm. Geological formation may also contribute to farm soil radioactivity, since soils of intrusive and metamorphic origin present a major contribution by 32 - 45%, 22- 25% and 30 - 46% for thorium series, uranium series and potassium series respectively (Amaral, et al, 1992). However, disregarding the contribution of geological formations, SSP fertilizer contributed to the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th by 40%, 53% and 43% respectively, while NPK fertilizer contributed to the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th by 72%, 44% and 14% respectively. Table 4.24 shows that the results obtained in this study compared well with the values obtained in other studies in literature.

Table 4.17: Activity concentrations of ^{40}K, ^{226}Ra and ^{232} Th in SSP farm Soil and Tomato samples

S/N	Activity conc. ^{40}K (Bq kg^{-1})			Activity conc. ^{226}Ra (Bq kg^{-1})			Activity conc. ^{232}Th (Bq kg^{-1})		
	Soil	Tomato	TF	Soil	Tomato	TF	Soil	Tomato	TF
1	280 ± 21	120 ± 18	0.429	65 ± 10	50 ± 12	0.769	22 ± 7	8 ± 2	0.363
2	290 ± 22	125 ± 19	0.431	66 ± 12	51 ± 10	0.773	24 ± 9	10 ± 3	0.417
3	285 ± 19	122 ± 17	0.428	67 ± 10	52 ± 14	0.776	23 ± 6	9 ± 2	0.391
4	286 ± 20	123 ± 18	0.430	69 ± 11	53 ± 11	0.768	25 ± 7	11 ± 3	0.440
5	283 ± 20	121 ± 16	0.428	63 ± 14	49 ± 14	0.777	26 ± 8	12 ± 4	0.462
Range	283-290	120-125		63-69	49-53		22-26	8-12	
Mean	285 ± 3.3	122 ± 1.7	0.428	66 ± 2	51 ± 1.4	0.773	24 ± 1.4	10 ± 1.4	0.417

Table 4.18: Activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in SSP farm Soil and Vegetable samples

S/N	Activity conc. ^{40}K (Bq kg^{-1})			Activity conc. ^{226}Ra (Bq kg^{-1})			Activity conc. ^{232}Th (Bq kg^{-1})		
	Soil	Vegetable	TF	Soil	Vegetable	TF	Soil	Vegetable	TF
1	280 ± 20	140 ± 30	0.500	70 ± 19	55 ± 14	0.786	25 ± 10	10 ± 2	0.40
2	281 ± 21	139 ± 26	0.495	72 ± 18	56 ± 15	0.777	27 ± 13	12 ± 5	0.44
3	282 ± 20	142 ± 24	0.504	74 ± 21	57 ± 15	0.770	28 ± 11	13 ± 3	0.46
4	284 ± 19	144 ± 27	0.507	76 ± 20	58 ± 17	0.763	29 ± 12	15 ± 1	0.51
5	285 ± 22	145 ± 26	0.509	77 ± 19	60 ± 14	0.779	30 ± 9	16 ± 4	0.53
Range	281-285	139-145		70-77	54-60		25-30	10-16	
Mean	282 ± 1.9	142 ± 2.3	0.504	74 ± 2.6	57 ± 1.7	0.770	27 ± 1.8	13 ± 2.1	0.48

Table 4.19: Activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in Control farm Soil and Tomato samples

S/N	Activity conc. ^{40}K (Bq kg^{-1})			Activity conc. ^{226}Ra (Bq kg^{-1})			Activity conc. ^{232}Th (Bq kg^{-1})		
	Soil	Tomato	TF	Soil	Tomato	TF	Soil	Tomato	TF
1	200 ± 28	60 ± 15	0.300	40 ± 10	15 ± 3	0.375	10 ± 2	5 ± 2	0.500
2	202 ± 26	63 ± 12	0.311	41 ± 11	16 ± 2	0.390	11 ± 4	6 ± 1	0.545
3	204 ± 30	65 ± 17	0.318	43 ± 19	18 ± 4	0.418	12 ± 3	7 ± 3	0.583
4	206 ± 28	66 ± 12	0.320	45 ± 12	19 ± 3	0.422	14 ± 2	8 ± 2	0.571
5	208 ± 29	68 ± 13	0.327	46 ± 11	20 ± 6	0.435	15 ± 4	10 ± 3	0.666
Range	200-208	60-68		40-46	15-20		10 - 15	5 - 10	
Mean	204 ± 2.4	64 ± 1.4	0.314	43 ± 2.3	18 ± 1.7	0.419	12 ± 1.9	7 ± 1.7	0.583

Table 4.20: Activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in Control farm Soil and Vegetable samples

S/N	Activity conc. ^{40}K (Bq kg^{-1})			Activity conc. ^{226}Ra (Bq kg^{-1})			Activity conc. ^{232}Th (Bq kg^{-1})		
	Soil	Vegetable	TF	Soil	Vegetable	TF	Soil	Vegetable	TF
1	200 ± 20	70 ± 24	0.350	40 ± 13	20 ± 9	0.500	10 ± 2	6 ± 2	0.600
2	202 ± 22	71 ± 18	0.351	41 ± 12	22 ± 10	0.537	11 ± 4	5 ± 1	0.454
3	204 ± 20	72 ± 19	0.353	43 ± 10	24 ± 11	0.558	12 ± 3	7 ± 3	0.583
4	205 ± 21	73 ± 21	0.356	45 ± 11	21 ± 9	0.467	14 ± 2	10 ± 2	0.714
5	207 ± 19	74 ± 20	0.357	46 ± 14	25 ± 11	0.543	15 ± 4	12 ± 4	0.800
Range	200 -207	70-74		40-46	20 - 25		10 - 15	6 - 12	
Mean	204 ± 2.4	72 ± 1.4	0.353	43 ± 2.3	22 ± 1.7	0.512	12 ± 1.9	8 ± 2.6	0.666

Table 4.21: Activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in NPK farm Soil and Tomato samples

S/N	Activity conc. ^{40}K (Bq kg^{-1})			Activity conc. ^{226}Ra (Bq kg^{-1})			Activity conc. ^{232}Th (Bq kg^{-1})		
	Soil	Tomato	TF	Soil	Tomato	TF	Soil	Tomato	TF
1	350 ± 31	122 ± 20	0.349	60 ± 15	30 ± 13	0.500	15 ± 7	6 ± 2	0.400
2	351 ± 40	124 ± 18	0.353	61 ± 12	32 ± 12	0.525	16 ± 5	8 ± 3	0.500
3	352 ± 35	125 ± 21	0.355	62 ± 14	33 ± 15	0.532	18 ± 7	7 ± 2	0.390
4	354 ± 32	127 ± 23	0.358	63 ± 16	34 ± 12	0.540	20 ± 8	9 ± 4	0.450
5	355 ± 36	128 ± 19	0.360	65 ± 15	36 ± 11	0.554	21 ± 10	10 ± 2	0.480
Range	350 - 355	122 -128		60 -65	30 - 36		15-21	6-10	
Mean	352 ± 1.9	125 ± 2.1	0.355	62 ± 1.7	33 ± 2.0	0.532	18 ± 1.7	8 ± 1.9	0.44

Table 4.22: Activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in NPK farm and Vegetable samples

S/N	Activity conc. ^{40}K (Bq kg^{-1})			Activity conc. ^{226}Ra (Bq kg^{-1})			Activity conc. ^{232}Th (Bq kg^{-1})		
	Soil	Vegetable	TF	Soil	Vegetable	TF	Soil	Vegetable	TF
1	350 ± 19	130 ± 22	0.371	60 ± 15	42 ± 13	0.700	15 ± 6	8 ± 3	0.533
2	351 ± 21	132 ± 21	0.376	61 ± 23	43 ± 12	0.705	16 ± 4	9 ± 2	0.563
3	352 ± 19	133 ± 23	0.378	62 ± 22	45 ± 15	0.726	18 ± 6	10 ± 4	0.555
4	354 ± 23	134 ± 25	0.379	63 ± 14	46 ± 12	0.730	19 ± 3	12 ± 2	0.632
5	355 ± 26	135 ± 18	0.380	65 ± 17	47 ± 16	0.723	20 ± 8	13 ± 1	0.650
Range	350 - 355	130 -135		60 - 65	42 - 47		15 - 20	8 - 13	
Mean	352 ± 1.9	133 ± 1.7	0.378	62 ± 1.7	45 ± 1.9	0.726	18 ± 1.9	10 ± 1.9	0.555

Table 4.23: Mean activity concentrations (Bq kg^{-1}) of ^{40}K, ^{226}Ra and ^{232}Th in the Chemical Fertilizer, Farm soil and Experimental Soil samples

Sample	**Activity concetrations (Bq kg^{-1})**		
	^{40}K	**^{226}Ra**	**^{232}Th**
SSP Fertilizer	301±36	694±113	15±2
NPK Fertilizer	4542±408	330±135	BDL
Virgin Soil (VS_C)	204±2	43±2	7±2
Soil fertilized with SSP (VS_{SSP})	285±3	66±2	10±1
Soil fertilized with NPK (VS_{NPK})	352±2	62±2	8±2
Northern Farm soil fertilized with SSP	177±42	69±9	19±4
Northern Farm soil fertilized with SSP and NPK	301±43	69±8	27±6
Southern Farm soil with NPK	134±41	30±8	13±3

Table 4.24: Comparison of average activity in (Bq kg^{-1}) with published results in soil from different areas in Nigeria and other countries

Country	Note	Activity Concentration (Bq kg^{-1})			References
		^{40}K	^{226}Ra	^{232}Th	
Yugoslavia (Vojvodina)	Agricultural Soil	454.0	39.0	53.0	Bikit et al., 2005
Egypt (El-Gharbia and El-Menoufia)	Cultivated areas	654.0	32.0	32.0	Sharshar and Elnimr, 1998
Upper Egypt	Cultivated Soil	181.1	13.2	13	Abbady *et al* ., 2006
Nigeria, Jos Plateau	Farm Soil	836	134	251	Jibiri *et a*., 2009*
Nigeria, Abeokuta	Farm Soil	411	65	184	Jibiri et al., 2009**
Egypt	Farm soil	140.1	14.0	13.8	Diab, 1999
Egypt, Cairo	Cultivated Soil	264.1	31.12	10.96	Diab et al., 2008
Nigeria, Nothern Region	Farm Soil	301.2	61.4	27.1	Present study
Nigeria, Southern Region	Farm Soil	134.4	30.2	12.7	Present study
Nigeria	Farm Soil (Control)	204	43	7	Present study
World average		140-850	17 – 60	11 - 64	UNSCEAR, 2000

*** Some farm soil samples had traces of tin spoil known for high contents of ^{226}Ra and ^{232}Th.**

**** From elevated radiation area of Nigeria.**

The activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K in the experimental farm soil were compared using ANOVA analysis at $\alpha_{0.05}$, the p-values are 2.9×10^{-16}, 0.0678 and 2.07×10^{-7} respectively. There were significant differences ($p < 0.05$) in the activity concentrations of ^{226}Ra and ^{40}K, while there were no significant differences ($p > 0.05$) in the activity concentrations of ^{232}Th.

The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in the fertilized experimental farm soil (SSP) and control farm soil samples were correlated as shown in Appendix 4.15, 4.16 and 4.17. The correlations coefficients (R^2) of 0.48, 0.93 and 0.78 were estimated for the ^{40}K, ^{226}Ra and ^{232}Th respectively.The correlation coefficients of ^{226}Ra and ^{232}Th are close to unity, this shows a positive relationship between the activity of the radionuclides in the farm soil with SSP fertilizer (VS_{SSP}) and the farm soil without any fertilizer (control).

The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in the fertilized experimental farm soil (NPK) samples and the control farm soil samples were correllated as shown in Appendix 4.18, 4.19 and 4.20.

The correlations coefficients (R^2) of 0.79, 0.52 and 0.77 were estimated for the ^{40}K, ^{226}Ra and ^{232}Th respectively.The correllation coefficients are close to unity, these shows positive relationship between the activity of the radionuclides in the farm soil with NPK fertilizer and the farm soil without any fertilizer (control). This implies that for an activity concentration of the chemical fertilizer introduced to the soil, there is a corresponding increase in the activity concentration of the primordial radionuclide in the soil.

The correlations coefficients (R^2) of 0.79, 0.78 and 0.98 were estimated for the ^{40}K, ^{226}Ra and ^{232}Th respectively in the experimental farm soil samples and the SSP fertilizer samples as shown in Appendix 4.21, 4.22 and 4.23. These shows positive relationship between the activity of the radionuclides in the farm soil with SSP fertilizer and the activity concentrations of the SSP fertilizer. This is also an indication that the activity concentration of the chemical fertilizer introduced to the soil, there is a corresponding increase in the activity concentration of the primordial radionuclide in the agricultural farm soil.

The correlations coefficients (R^2) of 0.97, 0.93 and 0.0000 were estimated for the ^{40}K, ^{226}Ra and ^{232}Th respectively in the experimental farm soil samples and the NPK fertilizer samples as shown in Appendix 4.24, 4.25 and 4.26. The correllation coefficients are very close to unity except ^{232}Th, these shows positive relationship between the activity of ^{40}K and ^{226}Ra in the farm soil with NPK fertilizer and the activity concentrations of the NPK fertilizer. The linear mathematical model may be used to predict contribution of chemical fertilizer to farm soil radioactivity.

4.6.2: Activity concentrations in tomatoes (*Lycopersicum esculentum* K. Karsten) and vegetable (*Amaranthus hybridus* Linnaeus) samples

The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the tomatoes samples from the farm soil fertilized with single superphosphate fertilizer (SSP) are 122 ± 1.7 Bq kg^{-1}, 51 ± 1.4 Bq kg^{-1} and 10 ± 1.4 Bq kg^{-1} respectively as presented in Tables 4.17, 4.19 and 4.21.

The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the control experimental farm tomatoes samples are 64 ± 1.4 Bq kg^{-1}, 18 ± 1.7 Bq kg^{-1} and 7 ± 1.7 Bq kg^{-1} respectively. The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the experimental farm tomatoes in soil samples treated with Nitrogen-phosphorus-potassium (NPK) are 125 ± 2.1 Bq kg^{-1}, 33 ± 2.0 Bq kg^{-1} and 8 ± 1.9 Bq kg^{-1} respectively. The application of NPK fertilizer elevated the activities of ^{40}K, ^{226}Ra and ^{232}Th in the tomato plant samples when compared to the Control farm. The SSP fertilizer contributed to the activities concentrations of ^{40}K, ^{226}Ra and ^{232}Th in tomato plant by 91%, 183% and 43% respectively. This further confirms that SSP is rich in uranium and its decay products (Pfister et al. 1976). The results also show that NPK fertilizer contributed to the activities concentrations of ^{40}K, ^{226}Ra and ^{232}Th in tomato plants by 95%, 83% and 14% respectively.

The p-value of the test on the activity concentrations of ^{226}Ra ^{232}Th and ^{40}K are 7.2×10^{-12}, 1.05×10^{-5} and 2.1×10^{-4} respectively. There were significant differences ($P < 0.05$) in the activity concentrations of ^{226}Ra ^{232}Th and ^{40}K.

The results for tomato samples were significantly different with the different experimental soil conditions. Tomato samples in the NPK fertilized soil exhibit highest mean value of the activity concentration of ^{226}Ra, while the tomato samples in the Control soil has the least mean value. Also, tomatoes in the SSP fertilized soil exhibit highest mean value of the activity concentration of ^{232}Th and ^{40}K, while the Tomatoes in the Control soil have the least mean value. The statistical analysis also suggest that the use of the chemical fertilizers may enhance the activity concentrations of the naturally occuring radionuclides in farm soil and in the plants in the cultivated farm.

The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the vegetable (*Amaranthus hybridus* Linnaeus) in the farm soil samples treated with single superphosphate fertilizer (SSP) are 142 ± 2.3 Bq kg^{-1}, 57 ± 1.7 Bq kg^{-1} and 13 ± 2.1 Bq kg^{-1} respectively as presented in Tables 4.18, 4.20 and 4.22.

The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the control experimental farm vegetables samples are 72 ± 1.4 Bq kg^{-1}, 22 ± 1.7 Bq kg^{-1} and 8 ± 2.6 Bq kg^{-1} respectively. The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the experimental farm Vegetables in soil samples treated with nitrogen-phosphorus-potassium (NPK) are 133 ± 1.7 Bq kg^{-1}, 45 ± 1.9 Bq kg^{-1} and 10 ± 1.9 Bq kg^{-1} respectively. Also, results show that the application of NPK fertilizer elevated the activities of ^{40}K, ^{226}Ra and ^{232}Th in the experimental farm soil samples compared to the control farm. The SSP fertilizer contributed to the activities concentrations of ^{40}K, ^{226}Ra and ^{232}Th in Vegetables (*Amaranthus hybridus* Linnaeus) by 97%, 159% and 63% respectively. The results also show that NPK fertilizer contributed to the activities concentrations of ^{40}K, ^{226}Ra and ^{232}Th by 85 %, 105% and 28% respectively. This may be attributable to the rooting depth of the vegetable plant 5 – 10 cm. It follows that both chemical fertilizers enhanced the activity concentrations of ^{226}Ra, this may be due to the phosphorus obtained from phosphate rock, a raw material used for the production of SSP and NPK fertilizer. It was also noted that SSP fertilizer enhanced the activity concentrations of ^{226}Ra more than NPK fertilizer.

The p-value of the test on the activity concentrations of ^{226}Ra ^{232}Th and ^{40}K are 1.14×10^{-12},0.42 and 0.33 respectively. There were significant differences ($p < 0.05$) in the activity concentrations of ^{226}Ra , while There were no significant differences ($p > 0.05$) in the activity concentrations of ^{232}Th and ^{40}K.

The activity concentration values for the control farm soil compare well with the values obtained in other parts of the world as presented in Table 4.24. The variation among the levels in soils of different countries may be attributed to the wide variations in geological formations of different types of soil. However, it is not yet known which long-term consequences might stem from the release of these small amounts of natural radioactivity. Eisenbud and Gesell (1997) pointed out that continued application of phosphate fertilizers to soil over a period of many years could eventually increase the radium and uranium concentrations in the soil, which would result in a corresponding increase in the population dose. The prolonged use of phosphate fertilizers might also induce, in specific situations, a remarkable increase in natural radionuclides concentrations in surface and/or underground waters by migration of soluble compounds of uranium and its decay products, an event that has already occurred and has been widely documented (Spalding and Sackett, 1972; Zielinski *et al*., 1997). Therefore, it is not possible to exclude that, over the long period; a prolonged use of fertilizers containing natural radionuclides might induce significant radiological impacts on the environment (Eisenbud and Gesell, 1997; Ioannides *et al*., 1997; Sam *et al*., 1999). It is underlined how chemical fertilizer application for long periods might induce an increase in natural radioactivity concentration in soils, thus entailing a possible dose increase to the population.

4.6.3 Radionuclide transfer factor

Transfer factor values in excess of unity imply active bioaccumulation of activity. Values less than unity imply either strong binding of the radioactivity to the soil or that the plant is not accumulating radioactivity (Twining1 *et al*, 2006).

Using the equation 3.9 and the activity concentration values in Tables 4.19, 4.20, 4.21, 4.22, 4.23 and 4.24 the Transfer factors the radionuclides ^{40}K, ^{226}Ra and ^{232}Th from the fertilized farm soil to the Tomato and Vegetable plants were obtained and are presented in Tables 4.25 and 4.26. The Vegetable plant samples have higher mean transfer factors compared to Tomato (*Lycopersicum esculentum* K. Karsten) samples in the experimental farm this is in good agreement with Saleh et al, (2007). This may be attributable to the variation in growth rate and root surface area.

Results also show that Radium has highest TF. This may be due to the fact that radium is more soluble than other primordial radionuclide of interest. Potassium is an important element to fertile the crop. Even though potassium is the radioactive element but it does not harm in aquatic system. Potassium is important for plant grow in order to adapt to the environmental stress.

These values are less than unity (< 1); this may imply that the plant is not accumulating that material. This is an indication that the transferred radionuclides to the soil due to the application of chemical fertilizer are available for uptake by plants.

4.6.4 Committed Effective Doses

The annual committed effective dose values due to intake of the experimental plants were estimated using equation 3.10. The values obtained are presented in Tables 4.27 and 4.28.

The annual effective committed dose due to intake of the tomatoes (*Lycopersicum esculentum* K. Karsten) in SSP, NPK fertilized farms and Control farm are 0.332 µSv y^{-1}, 0.222 µSv y^{-1} and 0.144 µSv y^{-1} respectively. The SSP fertilizer contributed to the annual effective committed dose due to Tomatoes by 130% while NPK fertilizer contributed to the annual effective committed dose by 54%. The annual effective

Table 4.25 The Mean and Range of the Transfer factors of the radionuclides ^{40}K, ^{226}Ra and ^{232}Th in the Tomatoes (*Lycopersicum esculentum* K. Karsten) samples from the experimental farm

Plant sample	Transfer Factor		
	^{40}K	^{226}Ra	^{232}Th
Tomatoes in VS_{SSP}	0.428 (0.428 – 0.430)	0.773 (0.773 – 0.777)	0.417 (0.383 – 0.462)
Tomatoes in VS_{NPK}	0.355 (0.349 – 0.360)	0.532 (0.500 – 0.558)	0.440 (0.390 – 0.500)
Tomatoes in Control	0.314 (0.300 – 0.327)	0.419 (0.375 – 0.435)	0.583 (0.500 – 0.666)

Table 4.26 The Mean and Range of the Transfer factors of the radionuclides ^{40}K, ^{226}Ra and ^{232}Th in the Vegetable (*Amaranthus hybridus* Linnaeus) samples from the experimental farm soil

Plant sample	Transfer Factor		
	^{40}K	^{226}Ra	^{232}Th
Vegetable in VS_{SSP}	0.504 (0.495 – 0.509)	0.770 (0.763 – 0.786)	0.481 (0.400 – 0.533)
Vegetable in VS_{NPK}	0.378 (0.371 – 0.380)	0.726 (0.700 – 0.730)	0.440 (0.390 – 0.500)
Vegetable in Control	0.353 (0.350 – 0.357)	0.512 (0.467 – 0.558)	0.600 (0.454 – 0.860)

Table 4.27: The Mean activity concentrations (Bq kg^{-1}) and Committed effective dose (mSv y^{-1}) in the Tomatoes (*Lycopersicum esculentum* K. Karsten) samples from the experimental farm

S/N	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{232}Th (Bq kg^{-1})	Committed effective dose due to ^{226}Ra (μSv y^{-1})	Committed effective dose due to ^{232}Th (μSv y^{-1})	Committed effective dose due to ^{226}Ra & ^{232}Th (μSv y^{-1})
SSP	122 ± 1.7	51 ± 1.4	10.1 ± 1.4	0.286	0.046	0.332
NPK	125 ± 2.1	33 ± 2.0	8 ± 1.9	0.185	0..037	0.222
Control	64 ± 1.4	20 ± 1.7	7 ± 1.7	0.112	0.032	0.144

Table 4.28: The Mean activity concentrations (Bq kg^{-1}) and Committed effective dose (mSv y^{-1}) in Vegetable (*Amaranthus hybridus* Linnaeus)

S/N	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{232}Th (Bq kg^{-1})	Committed effective dose due to ^{226}Ra (μSv y^{-1})	Committed effective dose due to ^{232}Th (μSv y^{-1})	Committed effective dose due to ^{226}Ra & ^{232}Th (μSv y^{-1})
SSP	142 ± 2.3	57 ± 1.7	13 ± 2.1	0.115	0.022	0.137
NPK	133 ± 1.7	45 ± 1.9	10 ± 1.9	0.091	0.017	0.108
Control	72 ± 1.4	33 ± 1.7	8 ± 2.6	0.066	0.013	0..079

committed dose due to intake of the vegetable plant in SSP, NPK fertilized farms and Control farm are 0.137 µSv y^{-1} , 0.108 µSv y^{-1} and 0.079 µSv y^{-1} respectively. The SSP fertilizer contributed to the annual effective committed dose due to intake of vegetable by 71% while NPK fertilizer contributed to the annual effective committed dose by 35%.

4.6.5 Correlation between the activity concentrations of the radionuclides in the experimental farm soils and the plants

There is a significant positive correlation with correlation coefficients (R^2) values of 0.98, 0.92 and 0.96 between the activity concentration of ^{40}K in the SSP, Control and NPK fertilized farm soil, and the activity concentration of ^{40}K in the tomatoes (*Lycopersicum esculentum* K. Karsten) (Figure 4.24).

The correlation coefficients (R^2) values of 0.98, 0.94 and 1.0 between the activity concentration of ^{226}Ra in the SSP, Control and NPK fertilized farm soil, and the activity concentration of ^{226}Ra in the tomatoes are shown in Figure 4.25. There is a significant positive correllation.

The correlation coefficients (R^2) values of 1.0, 0.82 and 1.0 between the activity concentration of ^{232}Th in the SSP, Control and NPK fertilized farm soil, and the activity concentration of ^{226}Th in the tomatoes are shown in Figure 4.26. There is a significant positive correllation.

There is a significant positive correlation with correlation coefficients (R^2) values of 0.93, 0.98 and 0.89 between the activity concentration of ^{40}K in the SSP, Control and NPK fertilized farm soil, and the activity concentration of ^{40}K in the vegetable plant (Figure 4.27).

There is a significant positive correlation with correlation coefficients (R^2) values of 0.92, 0.42 and 0.98 between the activity concentration of ^{226}Ra in the VS_{SSP}, control and VS_{NPK} fertilized farm soil respectively, and the activity concentration of ^{226}Ra in the vegetables (Figure 4.28).

There is a significant positive correlation with correlation coefficients (R^2) values of 0.98, 0.93 and 0.72 between the activity concentration of ^{232}Th in the VS_{SSP}, control

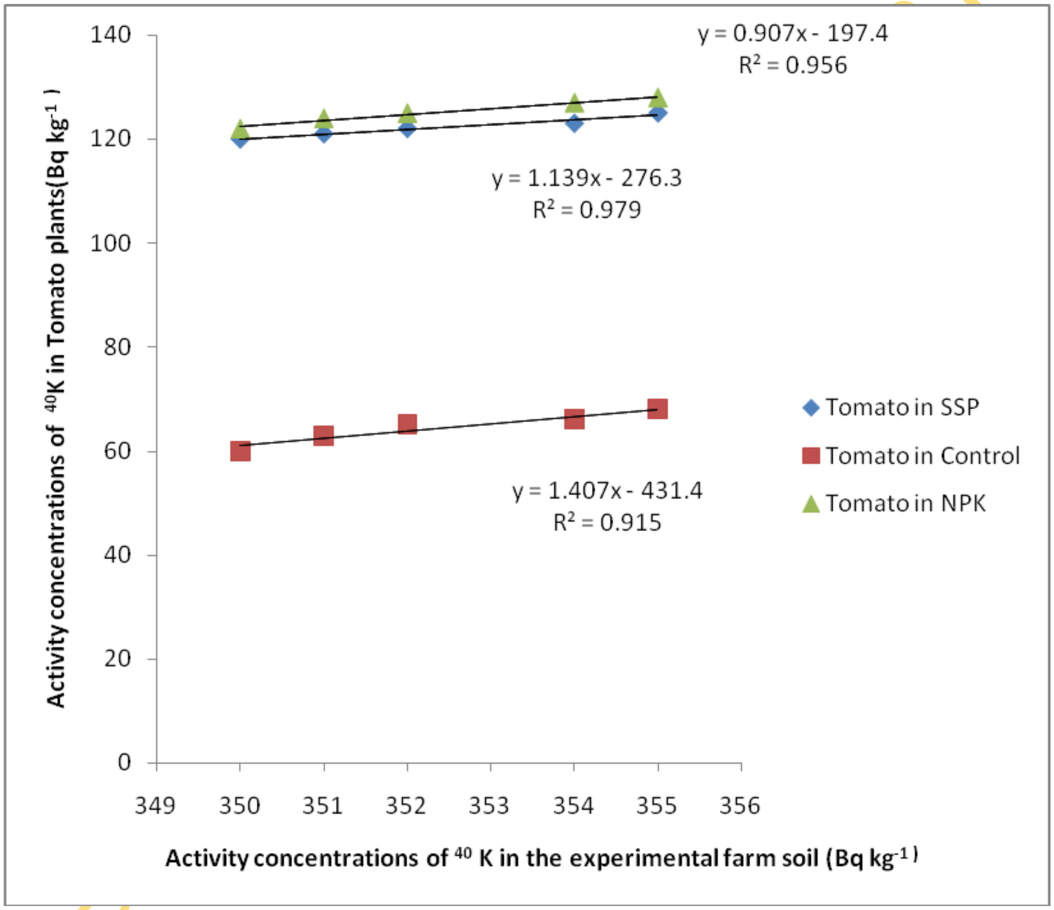

Fig. 4.24: **The activity concentrations of ^{40}K in tomatoes in the experimental farm soil**

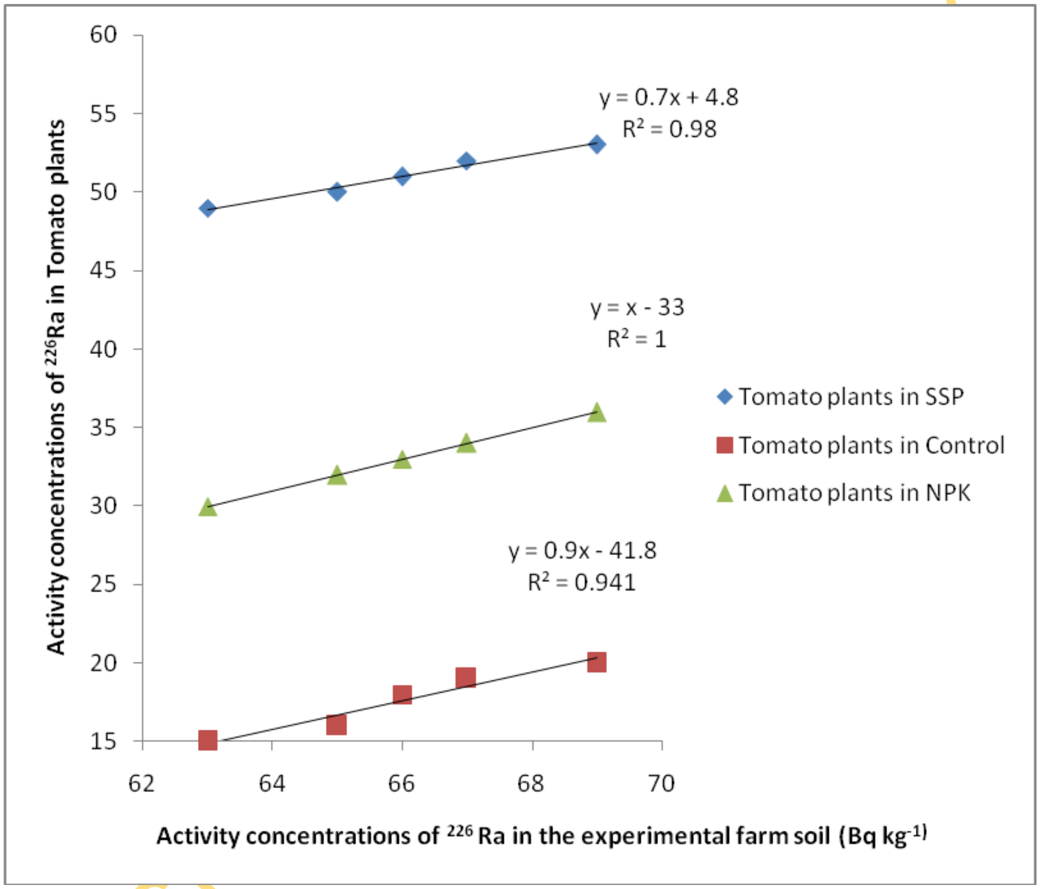

Fig. 4.25: **The mean activity concentration ^{226} Ra of Tomatoes in experimental farm soil**

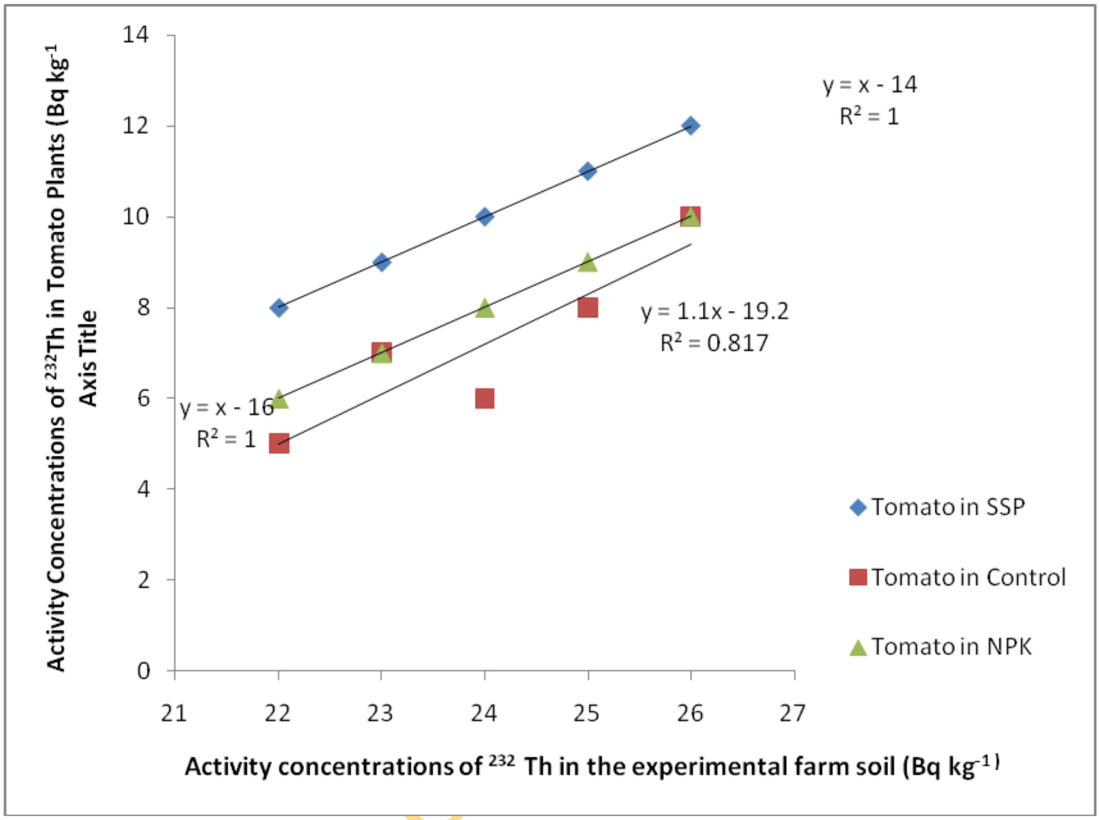

Fig. 4.26: The mean activity concentration of ^{232}Th in Tomatoes in experimental farm soil

and VS_{NPK} fertilized farm soil respectively, and the activity concentration of ^{232}Th in the vegetables (Figure 4.29). It is apparent that there is tendency for the vegetable to take up ^{226}Ra more readily than Tomato (Lycopersicum esculentus) as presented in Tables 4.27, and 4.28. It may be attributable to the rooting zone of the two plants, the rooting zone of tomato is deeper than vegetable (Jones, 2015). The rooting zone of vegetable is within the 5 – 10 cm depth in the surface layer where ^{226}Ra has the highest activity concentration of as discussed earlier.

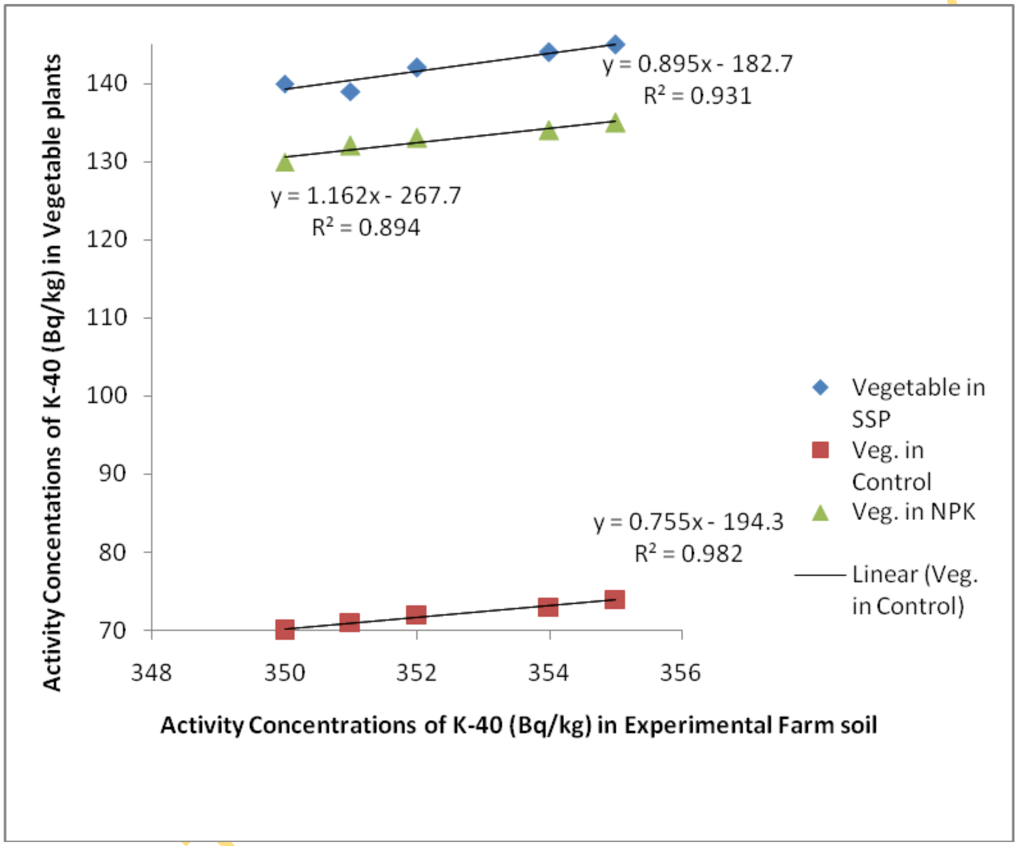

Fig. 4.27: The mean activity concentration of ^{40}K in Vegetable (*Amaranthus hybridus* Linnaeus) in the experimental farm soil

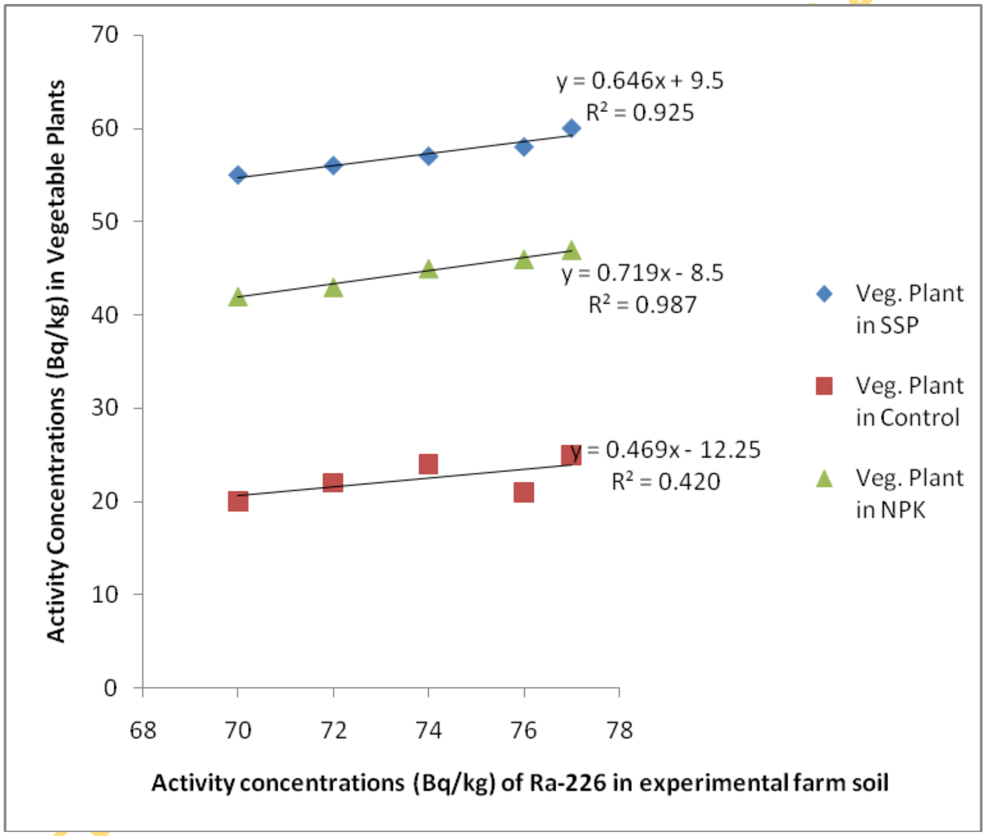

Fig. 4.28: The mean activity concentration of ^{226}Ra in Vegetable (*Amaranthus hybridus* Linnaeus) in the experimental farm soil

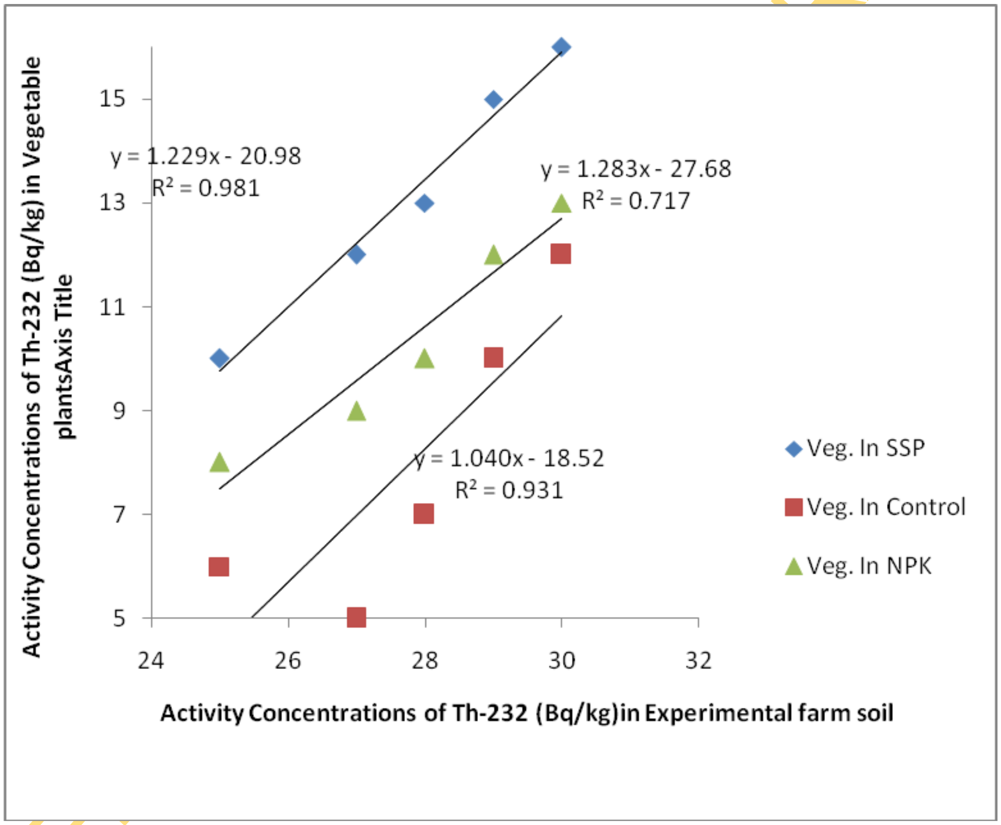

Fig. 4.29: The mean activity concentration of ^{232}Th in Vegetable (*Amaranthus hybridus* Linnaeus) the experimental farm soil

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMENDATIONS

5.1 Summary

The activity concentrations of the natural radionuclides ^{40}K, ^{226}Ra and ^{232}Th in different brands of chemical fertilizer samples (Single superphosphate SSP, nitrogen-phosphorous-potasium NPK) sold in Nigeria, fertilized farm soil samples from the northern and southern Nigeria were measured using gamma-ray spectroscopy. The gross alpha and gross beta activity concentrations were measured using AN EURISYS MEASURE- IN- 20, a gas flow proportional counter. The mean activity concentrations of the farm soil and plants samples in the experimental farm have been measured, hence, the contributions of fertilizers to farm soil radioactivity, transfer ratio and committed effective doses were determined. The results obtained could be summarized as follows:

1. The results showed that the means of the activity concentrations due to ^{40}K, ^{226}Ra and ^{232}Th in NPK fertilizer samples studied ranged between 3284.0 - 5279.9 Bq kg^{-1}, < LLD - 532.1 Bq kg^{-1} and < LLD – 19.7 Bq kg^{-1} respectively. The mean of the activity concentrations due to ^{40}K, ^{226}Ra and ^{232}Th in single superphosphate fertilizer samples studied ranged between 221.3 – 352.9 Bq kg^{-1}, 437.2 – 813.7 Bq kg^{-1} and < LLD – 8.0 Bq kg^{-1} respectively. Results further showed that NPK fertilizer produced by ITL/TAK and F & C fertilizer companies have the highest mean activity concentration of 451 ± 14 Bq kg^{-1} and 337 ± 91 Bq kg-1 for ^{226}Ra in the cities of Ibadan and Lagos respectively while the least mean value of 9.9 ± 7.3 Bq kg^{-1} was obtained in NPK produced by Magic Premium Fertilizer Company, Osogbo.
2. The gross alpha activity concentrations in NPK fertilizers varied from 2.0 – 90 Bq kg^{-1} while the value 100.0 ± 20.0 B kg^{-1} was obtained for single superphosphate fertilizer. This correlates with the higher gamma activity concentration value of ^{226}Ra compared to ^{232}Th. The GFCN, F&C and ITL/TAK fertilizer companies exhibit high gross alpha activity values of 90 Bq/kg^{-1}, 60 Bq/ kg^{-1} and 30 Bq/ kg^{-1}

respectively. These values correlates with the activity concentration values obtained for ^{226}Ra which could be the major contributor to the alpha activity values. The NPK fertilizer brands have higher values of gross beta activity concentration in the range of 2410 ± 80.0 to 4560.0 ±140.0 Bq kg^{-1} compared to 1440.0 ± 70 Bq kg^{-1} value obtained for SSP.

3. The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in fertilized cultivated soil samples from the two farms in Kaduna, in the northern Nigeria were 71.0 to 373.7 Bq kg^{-1}, 43.6 to 82.0 Bq kg^{-1} and 9.6 to 32.7 Bq kg^{-1} respectively. Also, the mean radioactivity concentrations due to ^{40}K, ^{226}Ra and ^{232}Th in cultivated soil samples from the southern Nigeria studied was in the range of 83.7 to 202.2 Bq kg^{-1}, 9.4 to 38.8 Bq kg^{-1} and 7.4 to 20.6 Bq kg^{-1} respectively. The average outdoor effective dose rates calculated in the farm locations from the northern part of Nigeria ranged from 61.2 µSv y^{-1} to 70.4 µSv y^{-1} while the calculated values for the southern part of Nigeria farm locations ranged from 32.8 µSv y^{-1} to 49.7 µSv y^{-1}. The calculated absorbed dose rates are within the world average outdoor exposure due to terrestrial gamma radiation 55 nGy y^{-1} (UNSCEAR, 2000).

4. The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the Control (Virgin) experimental farm soil (VS_C) samples were 204 ± 2.4 Bq kg^{-1}, 43 ± 2.3 Bq kg^{-1} and 7.0 ± 1.7 Bq kg^{-1} respectively. The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the experimental farm soil samples treated with single superphosphate fertilizer (VS_{SSP}) were 285 ± 3.3 Bq kg^{-1}, 66 ± 2.0 Bq kg^{-1} and 10 ± 1.4 Bq kg^{-1} respectively. The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th radionuclides in the experimental farm soil samples treated with nitrogen-phosphorus-potassium (VS_{NPK}) are 352 ± 1.9 Bq kg^{-1}, 62 ± 1.7 Bq kg^{-1} and 8 ± 1.9 Bq kg^{-1} respectively. Single superphosphate fertilizer contributed to the activities concentrations of ^{40}K, ^{226}Ra and ^{232}Th in the experimental farm soil by 40%, 53% and 43% respectively while NPK fertilizer contributed to the activities concentrations of ^{40}K, ^{226}Ra and ^{232}Th by 72%, 44% and 14% respectively.

5. The use of the chemical fertilizers enhanced the activity concentrations of the radionuclides in the vegetable (*Amaranthus hybridus* Linnaeus) via the uptake of the radionuclides from the soil. This is an indication that the application of chemical fertilizer for long periods might increase the natural radioactivity concentration in farm soils and plants, with consequet increase in dose to the population.
6. The SSP fertilizer contributed to the activities concentrations of ^{40}K, ^{226}Ra and ^{232}Th in tomatoes (*Lycopersicum esculentum* K. Karsten) by 90%, 183% and 43% respectively. This further confirms that SSP is rich in uranium and its decay products (Pfister *et al*. 1976). The results also showed that NPK fertilizer contributed to the activities concentrations of ^{40}K, ^{226}Ra and ^{232}Th in tomatoes by 95%, 83% and 14% respectively.
7. The SSP fertilizer contributed to the activities concentrations of ^{40}K, ^{226}Ra and ^{232}Th in vegetables by 97%, 159% and 63% respectively. The results also showed that NPK fertilizer contributed to the activities concentrations of ^{40}K, ^{226}Ra and ^{232}Th by 85 %, 104% and 25% respectively. The results clearly indicate that the farmers are exposed to higher levels of radiation during application of chemical fertilizers to the field and afterwards from the fertilizer mixed soil.
8. The vegetables samples have higher mean transfer factors compared to Tomatoes samples in the experimental farm. This could be attributed to the variation in growth rate and root surface area. Radium is more soluble than other primordial radionuclide of interest, this may account for the highest TF.
9. SSP fertilizer contributed to the annual effective committed dose in to Tomatoes by 130% while NPK fertilizer contributed by 54%. Also SSP fertilizer contributed the annual effective committed dose in vegetable plant by 71% while NPK fertilizer increased dose by 35%.
10. The committed effective dose (CEDs) due to consumption of tomatoes and vegetables of VS_{NPK} and VS_{SSP} were 0.22 and $0.33 \mu Sv/y$; 0.11 and

$0.14 \mu Sv/y$, respectively, which are lower than the recommended CED of $0.1 mSv/y$ by International Commission on Radiological Protection (ICRP).

5.2 Conclusion

It is therefore concluded that chemical fertilizers contribute to farm soil radioactivity and the committed effective doses to human is elevated more by single superphosphate fertilizer.

5.3 Recommendations

In this study only the contribution of NPK (15-15-15) and Single Superphosphate fertilizers (SSP) were considered. The following recommendations may be considered for further studies. Other chemical fertilizers with different elemental ratios such as NPK (10-10-10), NPK (20-10-10), NPK (16-16-16) might be very useful in future research on this topic. This will access the radionuclide contribution to cultivated farm soil due to the different types of chemical fertilizer. The results of this study have provided a preliminary information that can be further investigated or studied in the future. However, ^{40}K, ^{226}Ra and ^{232}Th migration were not considered, the migration is affected by a number of factors like the type of soil, its chemical properties and organic matter content. ^{40}K, ^{226}Ra and ^{232}Th mobility in soil also depends on climatic conditions such as rainfall, temperature or humidity and biological activity of microorganisms in soil (Ajayi, 2010).

Efforts should be made at national and international level to reduce Ra-226 activity in the fertilizers, like extracting uranium from phosphoric acid by solvent extraction method, so that the fertilizers are more ecofriendly.

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APPENDIX 4.1

NPK(15-15-15) Samples From GFCN

	Activity Concentrations (Bq/kg)		
S/N	^{40}K	^{226}Ra	^{232}Th
1	4663.51 ± 65.10	18.86 ± 13.23	12.22 ± 3.52
2	5184.22 ± 16.25	26.29 ± 13.18	7.57 ± 3.46
3	4694.48 ± 52.59	19.07 ± 13.24	10.64 ± 3.41
4	4643.45 ± 52.14	10.52 ± 13.11	6.08 ± 3.52
5	4945.18 ± 48.95	2.66 ± 12.49	9.05 ± 3.47
6	3991.65 ± 52.62	4.21 ± 13.16	10.84 ± 3.51
7	5051.08 ± 50.84	20.75 ± 12.87	6.37 ± 3.48
8	5015.16 ± 50.74	14.86 ± 12.77	12.63 ± 3.47
9	5279.94 ± 57.81	24.82 ± 5.62	-0.80 ± 3.50
10	4987.17 ± 52.16	14.58 ± 12.89	1.86 ± 3.56
11	4853.28 ± 49.12	20.68 ± 12.97	11.19 ± 3.79
12	347.73 ± 16.96	19.84 ± 12.80	16.56 ± 3.75
13	5019.45 ± 50.57	6.03 ± 12.97	17.70 ± 3.69
14	5195.69 ± 51.60	10.59 ± 12.81	19.67 ± 3.76
15	5025.98 ± 51.26	6.59 ± 12.90	12.43 ± 3.77
16	5084.01 ± 51.37	8.06 ±12.87	17.30 ± 3.72
17	5252.88 ± 51.86	6.45 ± 12.86	12.85 ± 3.73
18	5148.95 ± 51.08	8.13 ± 12.92	13.81 ± 3.78
19	5052.94 ± 50.84	14.86 ± 12.99	12.87 ± 3.76
20	5111.44 ± 52.11	18.30 ± 13.05	16.72 ±3.84

APPENDIX 4.2

NPK(15-15-15) samples from ITL/TAK

	Activity Concentrations (Bq/kg)		
S/N	**^{40}K**	**^{226}Ra**	**^{232}Th**
1	4039.14 ± 57.60	435.25 ± 21.08	-1.34 ±3.50
2	4505.46 ± 75.47	467.50 ± 20.58	6.39 ± 4.48
3	4490.06 ± 62.92	456.70 ± 21.00	-0.36 ± 3.36
4	4845.16 ± 54.59	442.75 ±20.41	-3.13 ± 3.50
5	5018.51 ± 55.91	304.73 ± 19.13	3.39 ± 3.43
6	5168.82 ± 56.47	329.33 ± 18.69	-1.29 ± 3.52
7	5074.40 ± 57.67	434.83 ± 20.65	1.57 ± 3.48
8	4624.69 ± 54.25	288.81 ± 17.80	1.36 ± 3.29
9	4712.12 ± 56.69	427.26 ± 19.67	-5.76 ± 2.91
10	5047.16 ± 59.36	532.13 ± 21.67	6.97 ± 3.96

APPENDIX 4.3

NPK(15-15-15) samples from Magic

	Activity Concentrations (Bq/kg)		
S/N	^{40}K	^{226}Ra	^{232}Th
1	3283.97 ± 48.01	2.38 ± 11.64	-1.63 ± 3.83
2	4070.68 ± 47.91	13.46 ±11.59	-9.29 ± 3.39
3	4160.90 ± 47.10	12.97 ±11.64	-2.30 ±3.39
4	3952.47 ± 47.44	8.62 ± 11.70	-8.34 ± 3.39
5	4391.72 ± 47.81	27.62 ± 11.78	1.59 ±3.41
6	5050.8 ± 50.8	7.0 ± 2.0	5.0 ± 3.5
7	4623.34 ± 50.31	1.96 ± 11.76	5.00 ± 3.35
8	4815.21 ± 49.95	14.30 ± 11.98	0.58 ± 3.32
9	4888.83 ± 49.98	9.46 ± 12.00	9.54 ± 3.60
10	4950.50 ± 49.94	26.29 ± 11.91	8.72 ± 3.61
11	4679.84 ± 49.71	-0.49 ± 11.84	9.97 ± 3.61
12	4415.05 ± 49.70	7.57 ± 11.85	10.95 ±3.55
13	4953.76 ± 50.06	11.78 ± 11.91	11.08 ± 3.57
14	5131.78 ± 50.77	7.29 ± 12.05	4.24 ± 3.68
15	4754.20 ± 50.20	8.20 ± 11.83	10.66 ± 3.59
16	3568.82 ± 49.34	0.21 ± 11.63	7.17 ± 3.51

APPENDIX 4.4

NPK(15-15-15) Samples From Fertilizer and Chemical (F & C)

	Activity Concentrations (Bq/kg)		
S/N	^{40}K	^{226}Ra	^{232}Th
1	4244.31 ± 53.81	283.98 ±18.22	-9.76 ± 3.46
2	4553.88 ± 53.25	203.36 ± 16.96	-7.98 ± 3.44
3	4513.01 ±54.85	329.96 ±18.83	-9.14 ± 3.53
4	4751.96 ±54.90	387.51 ± 18.78	-2.84 ± 3.51
5	4975.04 ± 56.17	377.07 ± 19.15	0.11 ± 3.49
6	4829.40 ± 55.87	403.15 ± 19.38	-6.12 ± 3.54
7	3867.38 ± 52.94	226.49 ± 17.76	-12.24 ± 3.41
8	4542.87 ± 54.72	391.02 ± 19.18	-5.21 ± 3.50
9	4583.18 ± 56.01	286.85 ± 18.69	-13.05 ± 3.46
10	4213.90 ± 54.10	287.55 ± 17.77	-8.38 ± 3.41
11	4010.78 ± 51.96	209.18 ± 16.89	-9.56 ± 3.47
12	4950.59 ± 56.62	471.91 ± 20.13	-4.45 ± 3.54
13	4637.01 ± 53.92	332.20 ± 18.10	0.29 ± 3.50
14	4916.54 ± 56.42	422.77 ± 19.65	-2.08 ± 3.47

APPENDIX 4.5

Single Super Phosphate Fertilizer(SSP)

	Activity Concentrations (Bq/kg)		
S/N	^{40}K	^{226}Ra	^{232}Th
1	283.82 ± 36.01	566.90 ± 22.90	7.98 ± 3.89
2	221.31 ± 34.10	437.21 ± 21.10	6.25 ± 3.75
3	289.60 ± 37.23	629.78 ± 23.84	2.23 ± 3.91
4	267.68 ± 36.89	625.28 ± 23.84	4.71 ± 3.90
5	320.77 ± 39.98	804.26 ± 26.37	0.96 ± 3.99
6	298.93 ± 39.45	733.95 ± 26.15	-1.12 ± 3.97
7	343.06 ± 38.70	733.74 ± 25.23	2.19 ± 4.02
8	286.24 ± 36.95	654.03 ± 23.96	5.76 ± 3.95
9	316.29 ± 40.04	794.65 ± 26.35	3.64 ± 4.12
10	337.56 ± 39.13	813.72 ± 25.54	-0.94 ± 4.00
11	352.86 ± 38.97	779.86 ± 25.51	4.69 ± 4.05
12	294.27 ± 39.40	749.16 ± 25.90	-1.74 ± 3.94

APPENDIX 4.6

NPK(15-15-15) Samples From OYO-STATE

	Activity Concentrations (Bq/kg)		
S/N	**^{40}K**	**^{226}Ra**	**^{232}Th**
1	4663.51 ± 65.10	18.86 ± 13.23	12.22 ± 3.52
2	5184.22 ± 16.25	26.29 ± 13.18	7.57 ± 3.46
3	4694.48 ± 52.59	19.07 ± 13.24	10.64 ± 3.41
4	4643.45 ± 52.14	10.52 ± 13.11	6.08 ± 3.52
5	4945.18 ± 48.95	2.66 ± 12.49	9.05 ± 3.47
6	4039.14 ± 57.60	435.25 ± 21.08	-1.34 ±3.50
7	4505.46 ± 75.47	467.50 ± 20.58	6.39 ± 4.48
8	4490.06 ± 62.92	456.70 ± 21.00	-0.36 ± 3.36
9	3991.65 ± 52.62	4.21 ± 13.16	10.84 ± 3.51
10	4845.16 ± 54.59	442.75 ±20.41	-3.13 ± 3.50
Mean	4600.2 ± 53.8	188.4 ± 16.1	5.8 ± 3.6
Range	3991.65 – 5184.22	2.66 – 467.50	6.08 – 12.22

APPENDIX 4.7

NPK(15-15-15) Samples From Ekiti-State

	Activity Concentrations (Bq/kg)		
S/N	**^{40}K**	**^{226}Ra**	**^{232}Th**
1	5051.08 ± 50.84	20.75 ± 12.87	6.37 ± 3.48
2	5015.16 ± 50.74	14.86 ± 12.77	12.63 ± 3.47
3	5279.94 ± 57.81	24.82 ± 5.62	-0.80 ± 3.50
4	5018.51 ± 55.91	304.73 ± 19.13	3.39 ± 3.43
5	5168.82 ± 56.47	329.33 ± 18.69	-1.29 ± 3.52
6	5074.40 ± 57.67	434.83 ± 20.65	1.57 ± 3.48
7	4987.17 ± 52.16	14.58 ± 12.89	1.86 ± 3.56
8	4624.69 ± 54.25	288.81 ± 17.80	1.36 ± 3.29
9	4712.12 ± 56.69	427.26 ± 19.67	-5.76 ± 2.91
10	5047.16 ± 59.36	532.13 ± 21.67	6.97 ± 3.96
Mean	4997.904 ± 194.8387	239.2092 ± 202.4259	2.63174 ± 5.100913
Range	4624.69 – 5279.94	14.58 – 532.13	1.36 – 12.63

APPENDIX 4.8

NPK(15-15-15) Samples From Ondo –State

	Activity Concentrations (Bq/kg)		
S/N	^{40}K	^{226}Ra	^{232}Th
1	4853.28 ± 49.12	20.68 ± 12.97	11.19 ± 3.79
2	347.73 ± 16.96	19.84 ± 12.80	16.56 ± 3.75
3	5019.45 ± 50.57	6.03 ± 12.97	17.70 ± 3.69
4	5195.69 ± 51.60	10.59 ± 12.81	19.67 ± 3.76
5	5025.98 ± 51.26	6.59 ± 12.90	12.43 ± 3.77
6	5084.01 ± 51.37	8.06 ±12.87	17.30 ± 3.72
7	5252.88 ± 51.86	6.45 ± 12.86	12.85 ± 3.73
8	5148.95 ± 51.08	8.13 ± 12.92	13.81 ± 3.78
9	5052.94 ± 50.84	14.86 ± 12.99	12.87 ± 3.76
10	5111.44 ± 52.11	18.30 ± 13.05	16.72 ±3.84
Mean	4609.235 ± 1501.33	11.95205 ± 5.895373	15.11169 ± 2.817592
Range	347.73 – 5252.88	6.03 – 20.68	11.19 – 19.67

APPENDIX 4.9

NPK(15-15-15) Samples From Osun –State

S/N	Activity Concentrations (Bq/kg)		
	^{40}K	^{226}Ra	^{232}Th
1	4623.34 ± 50.31	1.96 ± 11.76	5.00 ± 3.35
2	4815.21 ± 49.95	14.30 ± 11.98	0.58 ± 3.32
3	4888.83 ± 49.98	9.46 ± 12.00	9.54 ± 3.60
4	4950.50 ± 49.94	26.29 ± 11.91	8.72 ± 3.61
5	4679.84 ± 49.71	-0.49 ± 11.84	9.97 ± 3.61
6	4415.05 ± 49.70	7.57 ± 11.85	10.95 ±3.55
7	4953.76 ± 50.06	11.78 ± 11.91	11.08 ± 3.57
8	5131.78 ± 50.77	7.29 ± 12.05	4.24 ± 3.68
9	4754.20 ± 50.20	8.20 ± 11.83	10.66 ± 3.59
10	3568.82 ± 49.34	0.21 ± 11.63	7.17 ± 3.51
Mean	4678.137 ± 438.1413	8.65735 ± 7.861017	7.79024 ± 3.504917
Range	3568.82 – 4953.76	0.21 – 26.29	0.58 – 11.08

APPENDIX 4.10

NPK (15-15-15) Samples From Ogun – State

	Activity Concentrations (Bq/kg)		
S/N	**^{40}K**	**^{226}Ra**	**^{232}Th**
1	3283.97 ± 48.01	2.38 ± 11.64	-1.63 ± 3.83
2	4070.68 ± 47.91	13.46 ±11.59	-9.29 ± 3.39
3	4160.90 ± 47.10	12.97 ±11.64	-2.30 ±3.39
4	3952.47 ± 47.44	8.62 ± 11.70	-8.34 ± 3.39
5	4391.72 ± 47.81	27.62 ± 11.78	1.59 ±3.41
6	4244.31 ± 53.81	283.98 ±18.22	-9.76 ± 3.46
7	4553.88 ± 53.25	203.36 ± 16.96	-7.98 ± 3.44
8	4513.01 ±54.85	329.96 ±18.83	-9.14 ± 3.53
9	4751.96 ±54.90	387.51 ± 18.78	-2.84 ± 3.51
10	4975.04 ± 56.17	377.07 ± 19.15	0.11 ± 3.49
Mean	4289.794 ± 472.0247	164.6929 ± 167.7207	
Range	3283.97 – 4975.04	2.38 – 387.51	

APPENDIX 4.11

NPK (15-15-15) Samples From Lagos –State

	Activity Concentrations (Bq/kg)		
S/N	**^{40}K**	**^{226}Ra**	**^{232}Th**
1	4829.40 ± 55.87	403.15 ± 19.38	-6.12 ± 3.54
2	3867.38 ± 52.94	226.49 ± 17.76	-12.24 ± 3.41
3	4542.87 ± 54.72	391.02 ± 19.18	-5.21 ± 3.50
4	4583.18 ± 56.01	286.85 ± 18.69	-13.05 ± 3.46
5	5050.80 ± 50.84	7.01 ± 11.81	5.03 ± 3.52
6	4213.90 ± 54.10	287.55 ± 17.77	-8.38 ± 3.41
7	4010.78 ± 51.96	209.18 ± 16.89	-9.56 ± 3.47
8	4950.59 ± 56.62	471.91 ± 20.13	-4.45 ± 3.54
9	4637.01 ± 53.92	332.20 ± 18.10	0.29 ± 3.50
10	4916.54 ± 56.42	422.77 ± 19.65	-2.08 ± 3.47
Mean	4560.243 ± 408.3912	303.8134 ± 135.0988	
Range	3867.38 – 5050.80	7.01 – 471.91	

APPENDIX 4.12

Activity concentrations (Bq kg^{-1}) of ^{40}K, ^{226}Ra and ^{232}Th in Virgin soil from Government Reserved forest in Ikere-Ekiti

S/N	^{40}K (Bq/kg)	^{226}Ra (Bq/kg)	^{232}Th (Bq/kg)
1	220 ± 6.5	53.0 ± 6.1	18.0 ± 34.2
2	210 ± 6.8	51.0 ± 4.5	17.0± 25.8
3	230 ± 6.8	52.0 ± 5.9	19.0 ± 24.9
4	240 ± 6.6	54.0 ± 6.2	20.0 ± 25.8
5	200 ± 6.5	49.0 ± 6.5	16.0± 32.2
6	215 ± 6.7	55.0 ± 4.5	14.0 ± 21.8
7	205 ± 6.6	50.4 ± 6.0	15.0 ± 24.7
8	212 ± 6.8	57.0 ± 5.9	22.0 ± 25.7
9	198 ± 6.9	48.0 ± 6.4	21.0 ± 28.5
10	205 ± 6.5	56.0 ± 6.5	23.0 ± 32.2
11	216 ± 6.8	50.0 ± 6.5	13.0 ± 26.8
12	214 ± 7.0	59.0 ± 6.5	18.5 ± 26.6
13	236 ± 6.9	49.0 ± 5.8	17.5 ± 25.6
14	213 ± 6.5	45.0 ± 6.2	16.8 ± 26.8
15	207 ± 6.5	58.0 ± 6.5	19.2 ± 32.2
16	233 ± 6.7	44.0 ± 4.5	18.7 ± 21.8
17	241 ± 6.8	59.0 ± 4.6	20.5 ± 28.6
18	210 ± 6.8	60.0 ± 5.7	16.5 ± 30.8
19	211 ± 6.5	46.0 ± 6.5	18.9 ± 32.2
20	229 ± 6.7	61.0 ± 4.5	17.1 ± 21.8

APPENDIX 4.13

Activity concentrations (Bq kg^{-1}) of ^{40}K, ^{226}Ra and ^{232}Th, in Virgin soil from Government Reserved forest in Ado – Ekiti

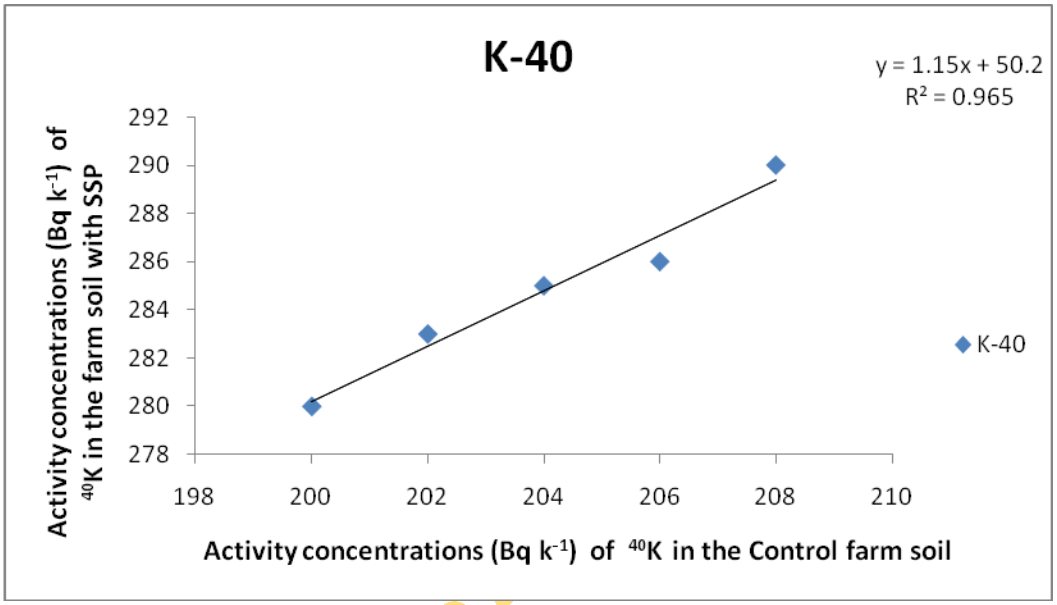
S/N	^{40}K (Bq/kg)	^{226}Ra (Bq/kg)	^{232}Th (Bq/kg)
1	200.0 ± 5.2	40.0 ± 5.8	15.0 ± 35.5
2	204.0 ± 5.5	42.0 ± 5.2	14.0 ± 19.9
3	201.0 ± 5.2	41.0 ± 5.7	13.0 ± 20.6
4	198.0 ± 5.9	37.0 ± 6.3	16.0 ± 32.6
5	199.0 ± 5.2	45.0 ± 5.8	15.8 ± 35.6
6	196.0 ± 5.5	35.0 ± 5.3	14.9 ± 19.6
7	202.0 ± 5.4	44.0 ± 5.6	15.2 ± 20.9
8	203.0 ± 5.8	36.0 ± 5.3	14.7 ± 34.5
9	189.0 ± 5.7	47.0 ± 5.4	15.4 ± 32.6
10	205.0 ± 5.2	33.0 ± 5.8	14.7 ± 35.5
11	193.0 ± 5.3	43.0 ± 5.3	15.1 ± 19.8
12	210.0 ± 5.7	32.0 ± 5.4	15.3 ± 34.7
13	190.0 ± 5.2	46.0 ± 5.5	14.8 ± 30.5
14	206.0 ± 5.8	38.0 ± 5.7	15.6 ± 35.3
15	208.0 ± 5.2	46.0 ± 5.8	14.2 ± 35.5
16	203.0 ± 5.4	50.0 ± 5.0	15.9 ± 19.7
17	197.0 ± 5.2	48.0 ± 5.4	14.5 ± 34.9
18	204.0 ± 5.3	31.0 ± 5.2	15.8± 33.8
19	198.0 ± 5.2	49.0 ± 5.8	15.6 ± 35.5
20	201.0 ± 5.3	30.0 ± 5.4	14.1 ± 19.8
Range	(189 – 208)	(30 – 50)	(13 – 18)
Mean	200 ± 10.1	40 ± 3.7	15 ± 3.0

APPENDIX 4.14

Activity concentrations (Bq kg^{-1}) of ^{40}K, ^{226}Ra and ^{232}Th in Virgin soil from Government Reserved forest in Egbe-Ekiti

S/N	^{40}K (Bq/kg)	^{226}Ra (Bq/kg)	^{232}Th (Bq/kg)
1	256.0 ± 7.2	55.9 ± 4.5	22.0 ± 17.6
2	260.0 ± 7.2	56.3 ± 4.5	23.0 ± 16.9
3	240.0 ± 7.2	57.4 ± 4.2	21.0 ± 17.5
4	252.0 ± 7.3	58.3 ± 4.7	24.0 ± 16.7
5	248.0 ± 7.1	54.5 ± 4.3	20.0 ± 16.4
6	230.0 ± 7.2	56.4 ± 4.3	26.0 ± 17.3
7	231.0 ± 7.2	57.7 ± 4.3	18.0 ± 16.6
8	232.0 ± 7.1	52.5 ± 4.5	28.0 ± 17.4
9	278.0 ± 7.4	56.1 ± 4.4	16.0 ± 17.6
10	270.0 ± 7.5	51.4 ± 4.5	24.5 ± 16.9
11	234.0 ± 7.3	50.7 ± 4.3	20.5 ± 16.7
12	255.0 ± 7.2	50.4 ± 4.4	26.5 ± 16.5
13	245.0 ± 7.2	53.5 ± 4.2	18.5 ± 17.4
14	257.0 ± 7.2	60.3 ± 4.3	23.5 ± 16.6
15	243.0 ± 7.4	54.9 ± 4.4	21.5 ± 17.8
16	258.0 ± 7.6	55.3 ± 4.6	22.5 ± 16.9
17	242.0 ± 7.3	56.4 ± 4.4	22.7 ± 17.6
18	251.0 ± 7.5	57.3 ± 4.6	23.7 ± 16.8
19	249.0 ± 7.4	60.0 ± 4.4	22.9 ± 16.6
20	253.0 ± 7.3	56.7 ± 4.4	22.3 ± 17.5

APPENDIX 4.15



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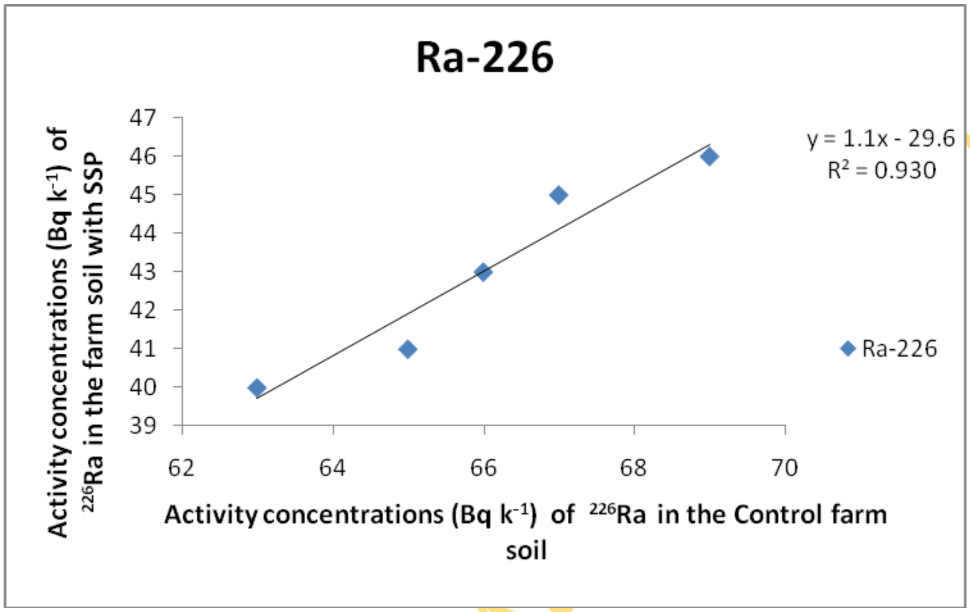

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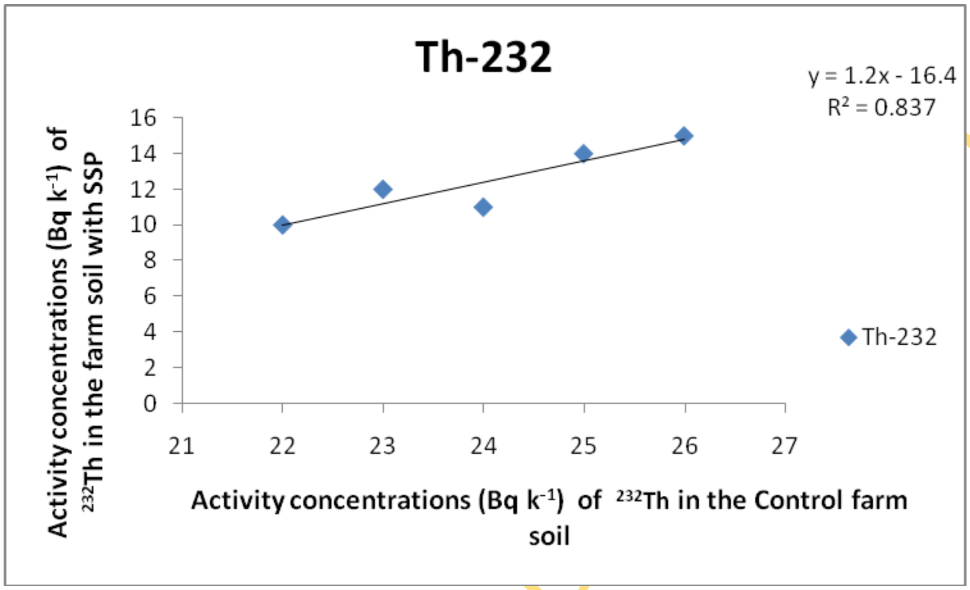

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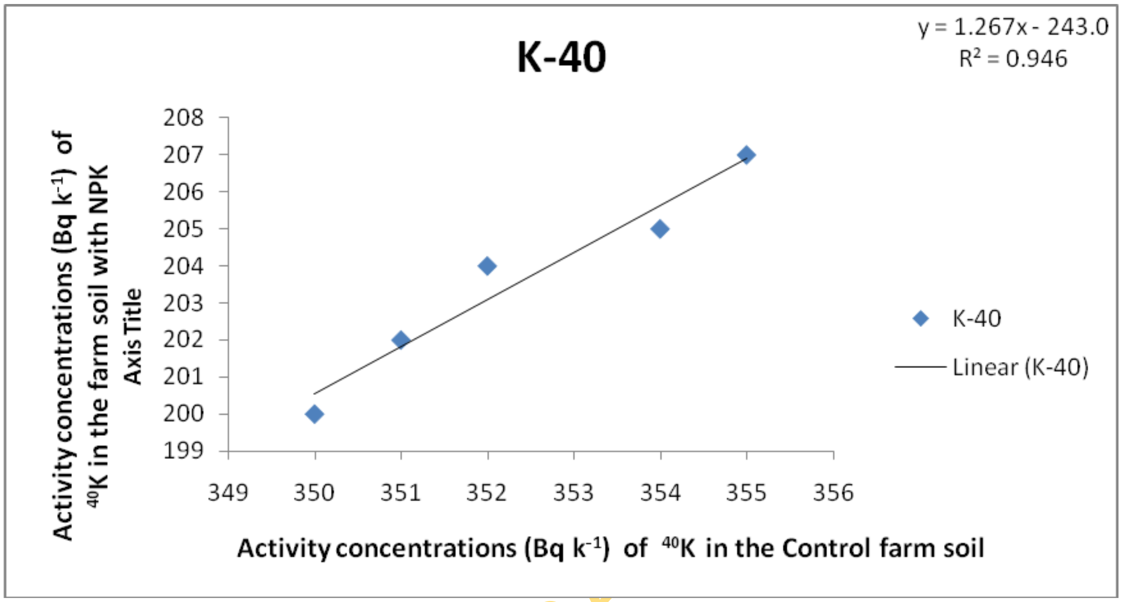

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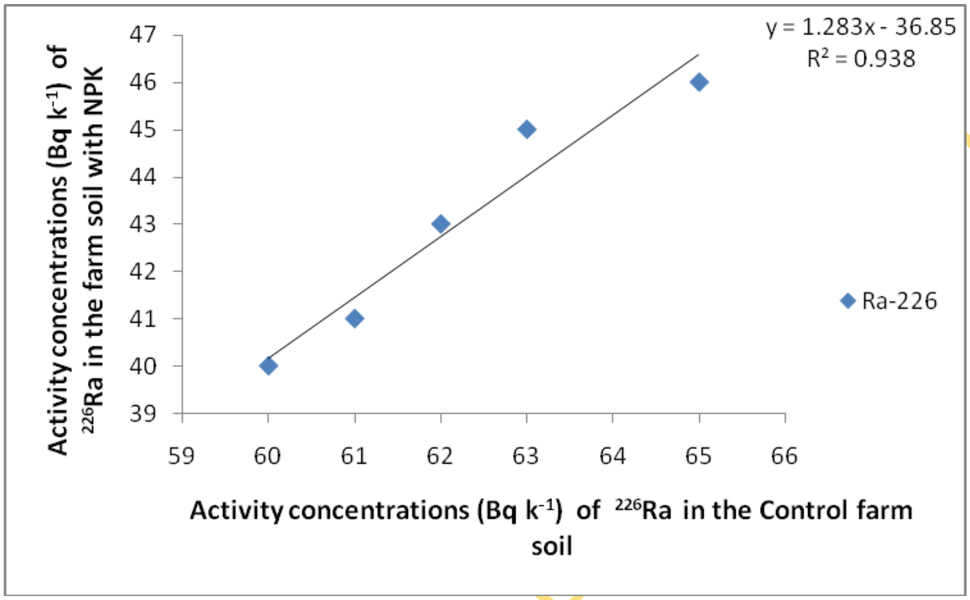

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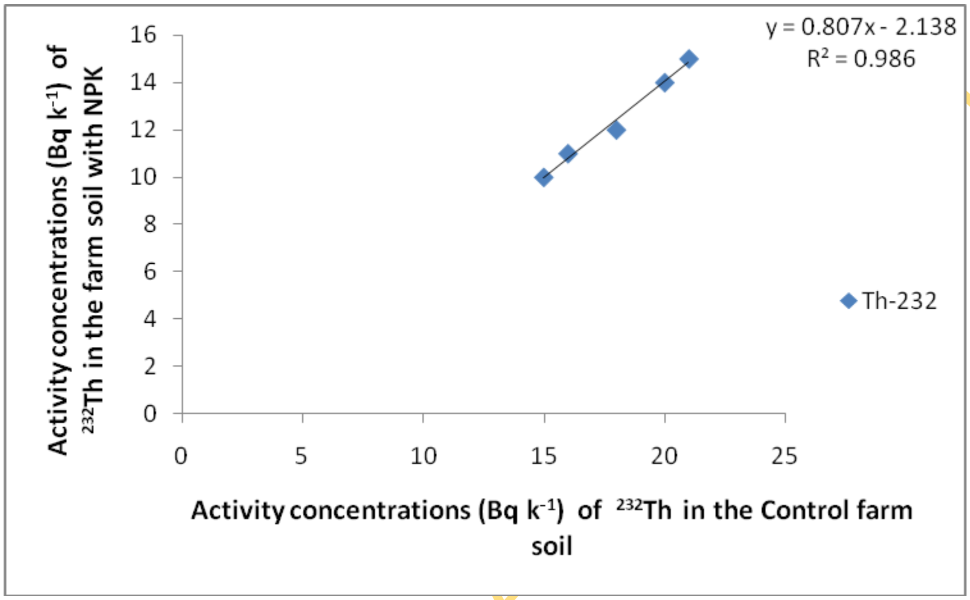

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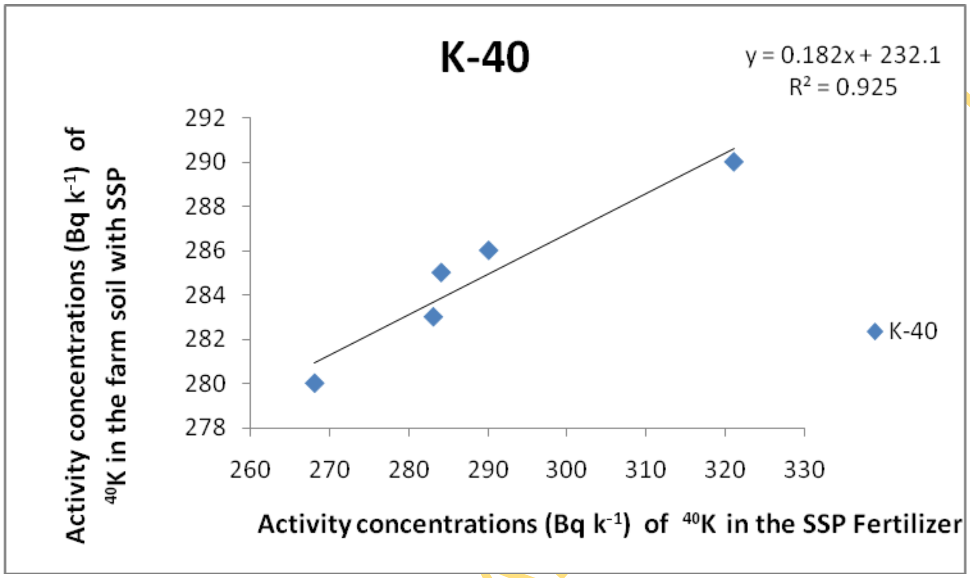

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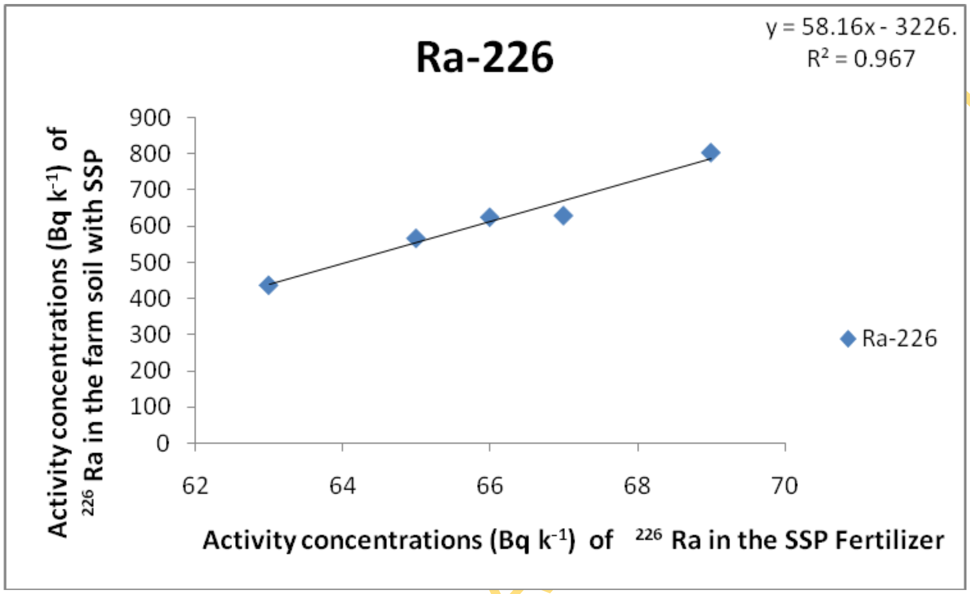

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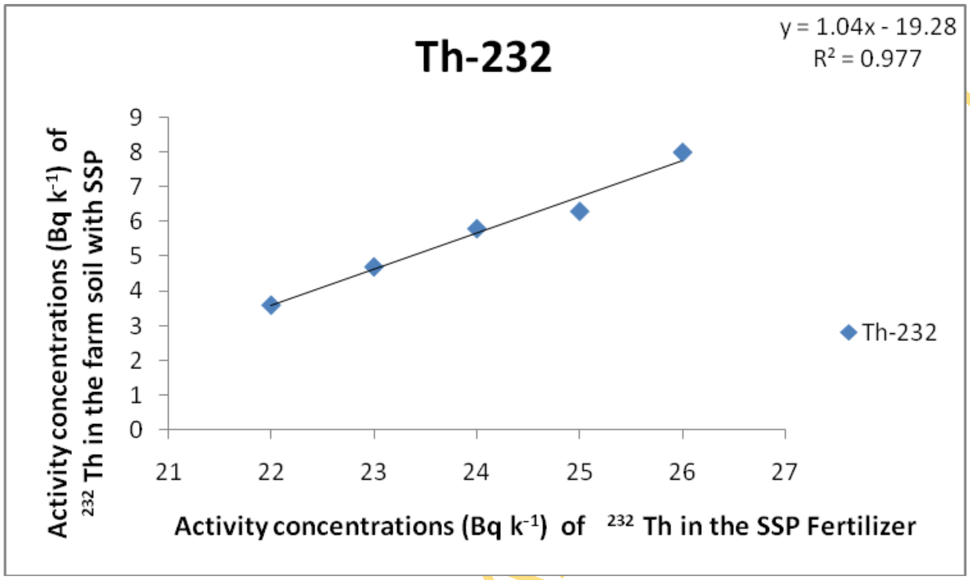

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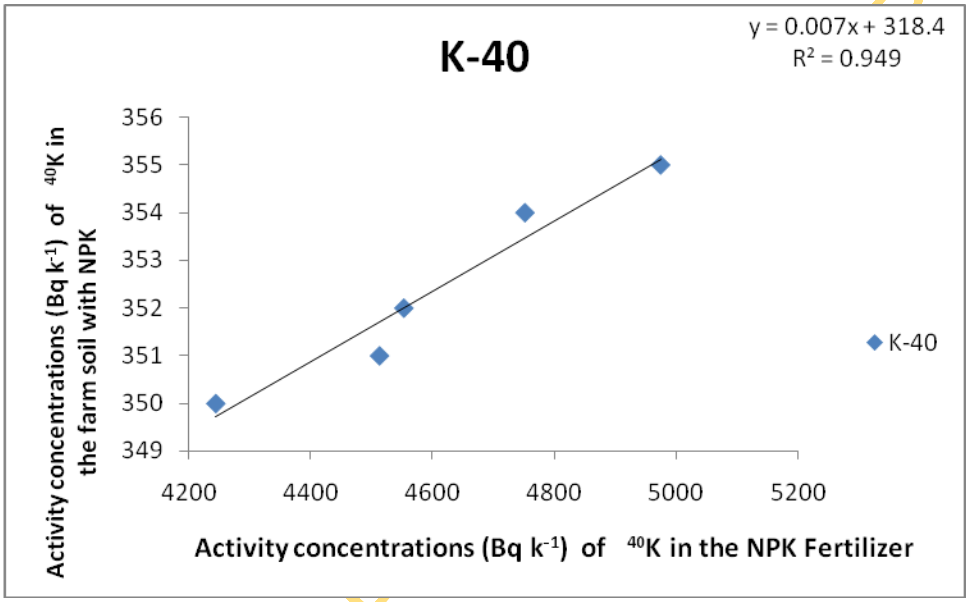

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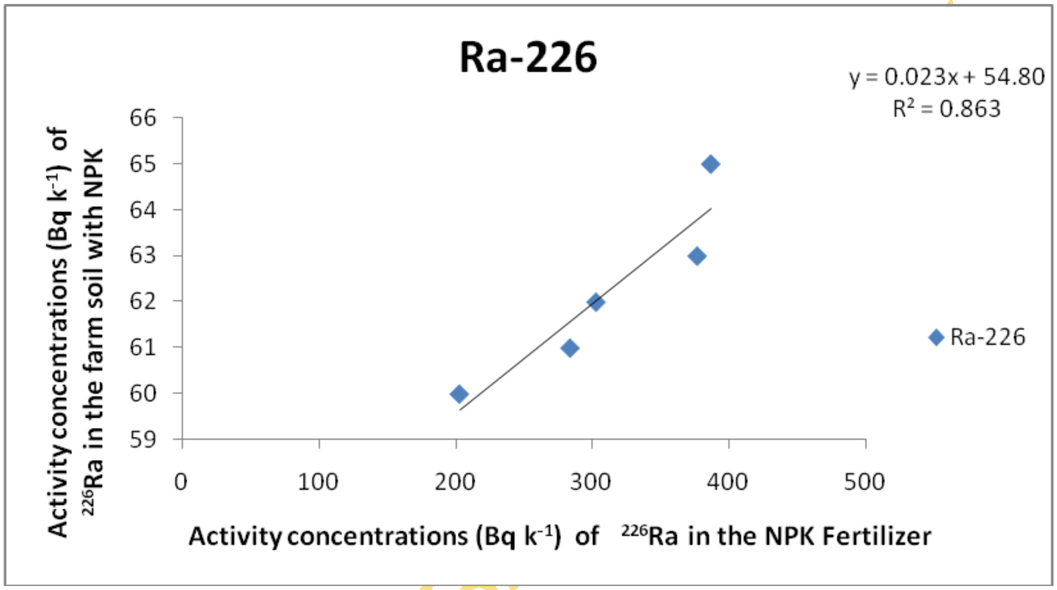

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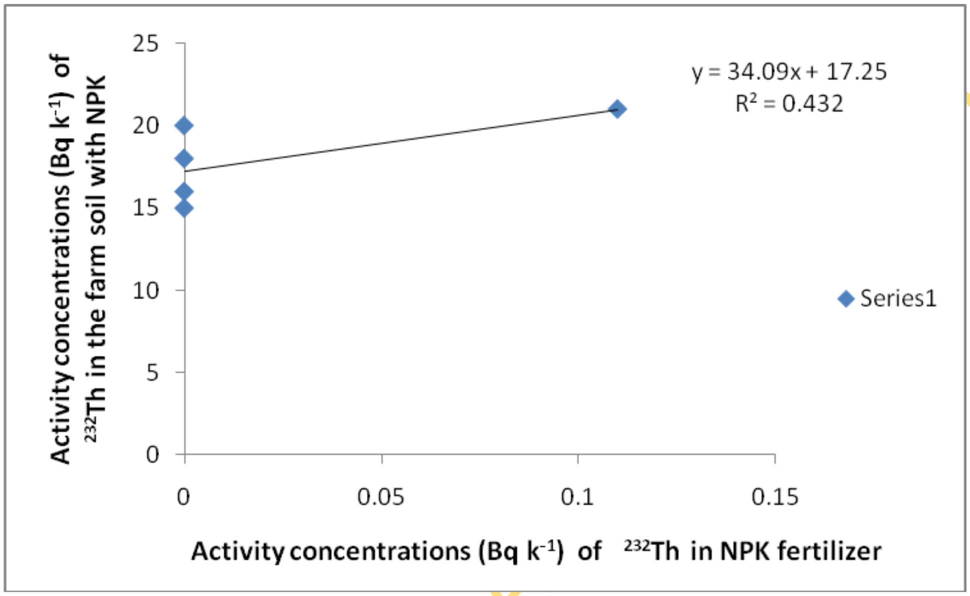

Table 4.17: Activity concentrations of ^{40}K, ^{226}Ra and ^{232} Th in SSP farm Soil and Tomato samples

	Activity concentrations (Bq kg^{-1})								
	^{40}K			^{226}Ra			^{232}Th		
Sample	Soil	Tomato	TF	Soil	Tomato	TF	Soil	Tomato	TF
1	280 ± 21	120 ± 18	0.429	65 ± 10	50 ± 12	0.769	22 ± 7	8 ± 2	0.363
2	290 ± 22	125 ± 19	0.431	66 ± 12	51 ± 10	0.773	24 ± 9	10 ± 3	0.417
3	285 ± 19	122 ± 17	0.428	67 ± 10	52 ± 14	0.776	23 ± 6	9 ± 2	0.391
4	286 ± 20	123 ± 18	0.430	69 ± 11	53 ± 11	0.768	25 ± 7	11 ± 3	0.440
5	283 ± 20	121 ± 16	0.428	63 ± 14	49 ± 14	0.777	26 ± 8	12 ± 4	0.462
Range	283-290	120-125		63-69	49-53		22-26	8-12	
Mean	285 ±3.3	122 ± 1.7	0.428	66 ± 2	51 ± 1.4	0.773	24 ± 1.4	10 ± 1.4	0.417

Table 4.18: Activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in SSP farm Soil and Vegetables samples

	Activity concentrations (Bq kg^{-1})								
	^{40}K			^{226}Ra			^{232}Th		
Samples	Soil	Vegetable	TF	Soil	Vegetable	TF	Soil	Vegetable	TF
1	280 ± 20	140 ± 30	0.500	70 ± 19	55 ± 14	0.786	25 ± 10	10 ± 2	0.400
2	281 ± 21	139 ± 26	0.495	72 ± 18	56 ± 15	0.777	27 ± 13	12 ± 5	0.444
3	282 ± 20	142 ± 24	0.504	74 ± 21	57 ± 15	0.770	28 ± 11	13 ± 3	0.464
4	284 ± 19	144 ± 27	0.507	76 ± 20	58 ± 17	0.763	29 ± 12	15 ± 1	0.517
5	285 ± 22	145 ± 26	0.509	77 ± 19	60 ± 14	0.779	30 ± 9	16 ± 4	0.533
Range	281-285	139-145		70-77	54-60		25-30	10-16	
Mean	282 ±1.9	142 ± 2.3	0.504	74 ± 2.6	57 ± 1.7	0.770	27 ± 1.8	13 ± 2.1	0.481

Table 4.19: Activity concentrations of ^{40}K, ^{226}Ra and ^{232} Th in Control farm Soil and Tomato samples

Activity concentrations (Bq kg^{-1})									
	^{40}K			^{226}Ra			^{232}Th		
Samples	Soil	Vegetable	TF	Soil	Vegetable	TF	Soil	Vegetable	TF
1	200 ± 28	60 ± 15	0.300	40 ± 10	15 ± 3	0.375	10 ± 2	5 ± 2	0.500
2	202 ± 26	63 ± 12	0.311	41 ± 11	16 ± 2	0.390	11 ± 4	6 ± 1	0.545
3	204 ± 30	65 ± 17	0.318	43 ± 19	18 ± 4	0.418	12 ± 3	7 ± 3	0.583
4	206 ± 28	66 ± 12	0.320	45 ± 12	19 ± 3	0.422	14 ± 2	8 ± 2	0.571
5	208 ± 29	68 ± 13	0.327	46 ± 11	20 ± 6	0.435	15 ± 4	10 ± 3	0.666
Range	200-208	60 - 68		40-46	15-20		10 - 15	5 - 10	
Mean	204 ± 2.4	64 ± 1.4	0.314	43 ± 2.3	18 ± 1.7	0.419	12 ± 1.9	7 ± 1.7	0.583

Table 4.20: Activity concentrations of ^{40}K, ^{226}Ra and ^{232} Th in Cotrol farm Soil and Vegetables samples

Activity concentrations (Bq kg^{-1})									
	^{40}K			^{226}Ra			^{232}Th		
Samples	Soil	Vegetable	TF	Soil	Vegetable	TF	Soil	Vegetable	TF
1	200 ± 20	70 ± 24	0.350	40 ± 13	20 ± 9	0.500	10 ± 2	6 ± 2	0.600
2	202 ± 22	71 ± 18	0.351	41 ± 12	22 ± 10	0.537	11 ± 4	5 ± 1	0.454
3	204 ± 20	72 ± 19	0.353	43 ± 10	24 ± 11	0.558	12 ± 3	7 ± 3	0.583
4	205 ± 21	73 ± 21	0.356	45 ± 11	21 ± 9	0.467	14 ± 2	10 ± 2	0.714
5	207 ± 19	74 ± 20	0.357	46 ± 14	25 ± 11	0.543	15 ± 4	12 ± 4	0.800
Range	200 -207	70-74		40-46	20 - 25		10 - 15	6 - 12	
Mean	204 ± 2.4	72 ± 1.4	0.353	43 ± 2.3	22 ± 1.7	0.512	12 ± 1.9	8 ± 2.6	0.666

Table 4.21: Activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in NPK farm Soil and Tomatoes samples

Activity concentrations (Bq kg^{-1})									
	^{40}K			^{226}Ra			^{232}Th		
Samples	Soil	Tomatoes	TF	Soil	Tomatoes	TF	Soil	Tomatoes	TF
1	350 ± 31	122 ± 20	0.349	60 ± 15	30 ± 13	0.500	15 ± 7	6 ± 2	0.400
2	351 ± 40	124 ± 18	0.353	61 ± 12	32 ± 12	0.525	16 ± 5	8 ± 3	0.500
3	352 ± 35	125 ± 21	0.355	62 ± 14	33 ± 15	0.532	18 ± 7	7 ± 2	0.390
4	354 ± 32	127 ± 23	0.358	63 ± 16	34 ± 12	0.540	20 ± 8	9 ± 4	0.450
5	355 ± 36	128 ± 19	0.360	65 ± 15	36 ± 11	0.554	21 ± 10	10 ± 2	0.480
Range	350 - 355	122 -128		60 -65	30 - 36		15-21	6-10	
Mean	352 ± 1.9	125 ± 2.1	0.355	62 ± 1.7	33 ± 2.0	0.532	18 ± 1.7	8 ± 1.9	0.44

Table 4.22: Activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in NPK farm Soil and Vegetables samples

Activity concentrations (Bq kg^{-1})									
	^{40}K			**^{226}Ra**			**^{232}Th**		
Samples	Soil	Tomatoes	TF	Soil	Tomatoes	TF	Soil	Tomatoes	TF
1	350 ± 19	130 ± 22	0.371	60 ± 15	42 ± 13	0.700	15 ± 6	8 ± 3	0.533
2	351 ± 21	132 ± 21	0.376	61 ± 23	43 ± 12	0.705	16 ± 4	9 ± 2	0.563
3	352 ± 19	133 ± 23	0.378	62 ± 22	45 ± 15	0.726	18 ± 6	10 ± 4	0.555
4	354 ± 23	134 ± 25	0.379	63 ± 14	46 ± 12	0.730	19 ± 3	12 ± 2	0.632
5	355 ± 26	135 ± 18	0.380	65 ± 17	47 ± 16	0.723	20 ± 8	13 ± 1	0.650
Range	350 - 355	130 -135		60 - 65	42 - 47		15 - 20	8 - 13	
Mean	352 ± 1.9	133 ± 1.7	0.378	62 ± 1.7	45 ± 1.9	0.726	18 ± 1.9	10 ± 1.9	0.555

Table 4.27:The Mean activity concentrations (Bq kg^{-1}) and Committed effective dose (μSv y^{-1}) in Tomatoes(*Lycopersicum esculentum* K. Karsten)

S/N	Activity concentrations (Bq kg^{-1})			Committed effective dose(μSv y^{-1})		
	^{40}K	^{226}Ra	^{232}Th	^{226}Ra	^{232}Th	Total
SSP	122 ± 1.7	51 ± 1.4	10.1 ± 1.4	0.286	0.046	01332
NPK	125 ± 2.1	33 ± 2.0	8 ± 1.9	0.185	0.037	0.222
Control	64 ± 1.4	20 ± 1.7	7 ± 1.7	0.112	0.032	0.144

Table 4.28:The Mean activity concentrations (Bq kg^{-1}) and Committed effective dose (μSv y^{-1}) in Vegetables(*Amaranthus hybridus* Linnaeus)

S/N	Activity concentrations (Bq kg^{-1})			Committed effective dose(μSv y^{-1})		
	^{40}K	^{226}Ra	^{232}Th	^{226}Ra	^{232}Th	Total
SSP	142 ± 2.3	57 ± 1.7	13 ± 2.1	0.115	0.022	0.137
NPK	133 ± 1.7	45 ± 1.9	10 ± 1.9	0.091	0.017	0.108
Control	72 ± 1.4	33 ± 1.7	8 ± 2.6	0.066	0.013	0..079

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ACTIVITY CONCENTRATIONS OF ^{226}Ra, ^{232}Th AND ^{40}K IN BRANDS OF FERTILISERS USED IN NIGERIA

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The activity concentration of naturally occurring radionuclides ^{40}K, ^{226}Ra and ^{232}Th have been measured in different brands of fertiliser samples sold to farmers in retail markets in six commercial cities in southwestern Nigeria. Gamma ray spectroscopy was employed in the measurements of these radionuclides. The results of measurements showed that the average activity concentration of ^{40}K in the nitrogen, phosphorus and potassium fertilisers across the cities varied from 3972.0 ± 416.9 to 5089.3 ± 111.3 Bq kg^{-1}, 9.9 ± 7.3 to 450.6 ± 14.3 Bq kg^{-1} for ^{226}Ra, while for ^{232}Th it varied from less than lower limit of detection to 15.1 ± 2.8 Bq kg^{-1}. The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in single super phosphate (SSP) fertilisers and phosphate rocks were also determined. However, high activity concentrations of ^{226}Ra were obtained in the SSP fertiliser and phosphate rocks and in particular, two brands of fertilisers from ITL/TAK and F & C companies. The values of the activity concentration of the radionuclides in the brands of fertilisers used in Nigeria are within the range of values reported in several other countries except ^{40}K.

INTRODUCTION

The use of different types of fertilisers in the agricultural sector for enhancing crop yield has become very common nowadays. In Nigeria, farmers make use of fertilisers to replenish the natural nutrients depleted from soil due to overcultivation of crops, weathering and erosion of land. The raw material used in the production of fertilisers is phosphate ore. It is present normally in the form of calcium phosphates $Ca_3(PO_4)$ which are very old marine deposits associated with fossils. This form represents 85 % of the worldwide production. The materials are often calcined by heating to 950°C before dispatch in order to decompose calcium carbonate and organic matter. The second type of phosphate material is apatite, $Ca_5[(PO_4)_3(F)]$, that is of igneous origin(1–3).

Phosphate rocks are used extensively, mainly as a source of phosphorus for fertilisers and further for phosphoric acid and other special chemicals. Chemical fertilisers are mainly composed of nitrogen, phosphorus and potassium (NPK); the phosphorus portion is taken from phosphate rocks, which contain enhanced concentration of natural radionuclides. Mining, milling, transporting of phosphate ores and manufacturing of phosphate fertilisers containing uranium are ways in which the workers, public and the environment are exposed to enhanced doses of radiation. During handling, packing and transporting fertilisers, some workers can receive additional external exposure at dose rates up to 0.8 μGy h^{-1}(3). The primary potential environmental radiation problem associated with phosphate rock mining and processing is related to mining debris and waste products. The typical concentration of uranium in phosphate rocks is between 30 and 260 ppm which by far exceeds its average abundance in the Earth's crust, which is ~4 ppm(3). Application of chemical fertilisers, therefore, may increase the phosphate and uranium concentrations in soils, resulting in impacts on natural systems, such as increasing in concentrations in nutrient and uranium concentration in surface waters, soils and sediments. However, mining and processing of phosphate ores may redistribute ^{226}Ra and its decay products among the various products, by-products and wastes of the phosphate industry(4, 5). Fertilisers redistribute naturally occurring radionuclides at trace levels throughout the environment and become a source of radioactivity. This phenomenon may result in potential radiological risks owing to external exposure during resident time in the farms and internal exposure through ingestion of food grown on such soils and through direct inhalation of suspended dusts from farm machinery and wind. Furthermore, the knowledge of the activity concentrations and distributions of the natural radionuclides in fertiliser materials are of interest since it provides useful information in the monitoring of environmental contamination by natural radioactivity. The aim of this study is therefore to (i) determine the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in the different brands of NPK fertiliser and single super phosphate (SSP) fertiliser sold in Nigeria and (ii) provide radiometric data that will enhance sparse environmental radioactivity data in the country that may be relevant for designing local rules and regulations for radiation protection and safety purposes by the Nigerian Nuclear Regulatory Authority in line with the provisions of International Atomic Energy Agency.

MATERIALS AND METHODS

Sample collection

In Nigeria, very few local fertiliser companies exist and as such fertilisers are produced in one location and distributed in different cities. These fertiliser products can easily be adulterated and the farmers are normally unable to check the quality. The quality and labelling of fertilisers is carefully regulated in the developed countries and the regulations are enforced. In developing countries such as Nigeria, even where regulations exist, they are rarely enforced adequately due to the lack of will and/or means. In order to ensure adequate and proper sample collection of brands of fertilisers that are available in the markets, initial information was obtained on the brands sold to farmers in different parts of the country.

In this study, sample of different brands of NPK (15-15-15) fertilisers were collected from the local retail markets in the commercial city centres in six states in the southwestern part of Nigeria. Samples of fertilisers were also collected directly from the abandoned stock piles of the two old and famous fertiliser producing companies in Nigeria: the National Fertilizer Company (NAFCON), Onne, Port-Harcourt, Rivers-State Nigeria and the National Superphosphate Fertiliser Company, Kaduna, Kaduna-State, Nigeria (NSPFC). Although these two companies are no longer producing fertilisers in the country, their products were very dominant in the Nigerian markets and were widely sold across all the regions of the country for more than two decades. The samples from these companies were collected in order to determine the concentration levels of natural radionuclides in their products and compare with the present common products in the Nigerian markets available to the farmers. Samples of SSP fertiliser and phosphate rocks were also collected from the National Superphosphate Fertilizer Company, while samples of NPK (15-15-15) were collected from NAFCON. In Nigeria, the SSP type of fertilisers are only used in the northern region of Nigeria because of the low fertility of farmland in that region, while NPK is widely used in the southwestern region, where the soil fertility is relatively good for agricultural practices. The four fertiliser companies whose products are the common type in the southwestern region of the country that were collected from retail markets outlets for the present study are as follows:

GFCN	Golden Fertilizer Company, Nigeria
ITL/TAK	ITL/TAK Fertilizer Company, Nigeria
MAGIC	Magic Premium Fertilizer Company, Nigeria
F & C	Fertilizer and Chemical Ltd., Kaduna, Nigeria

Sample preparation

The fertiliser samples were dried at 80°C in a temperature-controlled oven until there was no detectable change in the mass of the sample. It takes ~1 h per sample to remove all the moisture content from the sample in order that no detectable change in the mass of the sample was achieved. The dried samples were thoroughly crushed, grounded and pulverised to fine powder. The powder was passed through a 2-mm sieve. To avoid distribution of the gamma radiation emitting decay products in the gas room on top of the sample masses, the sample counting containers of uniform size (60-mm height by 65-mm diameter) were filled up almost totally (filling height 60 mm). With this filling height, the sample masses after corrections were ~200 g corresponding to the sample size limit capacity of the detector. The samples were sealed and left to cure for a period of ~30 d. This was done in order to allow for radon and its short-lived progenies to reach secular radioactive equilibrium prior to gamma spectroscopy. The reference soil was also transferred to a container of the same material and dimensions were as those used for the fertiliser samples. This was to ensure that the geometric configuration remained the same.

The variations of the effective sample density caused by this are seen not to affect the activity results within the experimental error of the measurement technique employed in this work. Differences between the effective atomic numbers in the chemical composition of the fertilisers and the standard samples would not affect the results since the mass attenuation co-efficient does not depend on the atomic number in the energy range under consideration to a very good approximation up to an atomic number of 40 (Zr)(6). Thus, self-absorption correction could be neglected. From the relative photon emission intensities and from the energy peak efficiencies, the activities of the gamma emitting decay products could be calculated, which equal the activities of the parent nuclides under the conditions of radioactive equilibrium. The standard reference soil sample used was prepared from Rocketdyne Laboratories, California, USA and a National Institute of Standards and Technology certified mixed standard gamma source (Ref. No. 48722-356) from Analytic Inc., Atlanta, GA, USA.

Measurement technique

A 10-cm Canberra lead-shielded 76 mm × 76 mm NaI(TI) detector crystal (Model No. 802 series, Canberra Inc.) coupled to a Canberra Series 10 plus multichannel analyser (MCA) (Model No. 1104) through a photomultiplier tube/preamplifier/amplifier was used for the radioactivity measurements. The detector has a resolution of 8 % full-width at half-maximum at ^{137}Cs energy of 0.662 MeV. This was good enough to distinguish the gamma ray energies of interest in the present study. The energy-channels relationship (Figure 1) did not deviate from linearity in the energy range within the limits of accuracy given by the energy resolving power of the detector. The full energy peak efficiencies, in dependence on photon energy and geometry, were evaluated from the full energy peak counting rate using the firm-ware algorithm of the MCA. The efficiency calibration data of the detector are presented in Table 1, while the efficiency curve of the detector is shown in Figure 2. The detailed calibration of the detector and procedures can be found in our earlier publications(7–10).

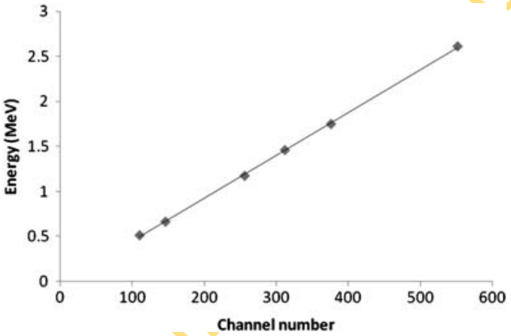

Figure 1. The energy calibration curve of the detector.

The choice of radionuclides to be detected as a reference was made based on the fact that the NaI(TI) detector used in this study had a modest energy resolution. Hence, the photons emitted by them would be sufficiently discriminated if their emission probability and their energy were high enough and the surrounding background continuum low enough. Therefore, the activity concentration of ^{214}Bi (determined from its 1.760 MeV gamma ray peak) was chosen to provide an estimate of ^{226}Ra in the fertiliser samples, while that of the daughter radionuclide ^{208}TI (determined from its 2.615 MeV gamma ray peak) was chosen as an indicator of ^{232}Th, because the secular equilibrium was achieved between the daughter nuclides and their parent nuclides. ^{40}K was determined by measuring the 1.460 MeV gamma rays emitted during the decay of ^{40}K.

The samples were placed symmetrically on top of the detector and measured for a counting period of 10 h. The net area under the corresponding peaks in the energy spectrum was computed by subtracting counts due to Compton scattering of higher peaks and other background sources from the total area of the peaks. Measurement of each sample was repeated three times and the mean net area was determined. The overall experimental error of the results caused by statistical counting error, area determination, calibration etc, was generally less than ±10 %. From the net area, the activity concentrations of the radionuclides in the samples were obtained using the equation(11):

$$C = kC_n \tag{1}$$

where C is the activity concentration of the radionuclide in the sample given in Bq kg^{-1}, $k = 1/\varepsilon P_\gamma M_s$, C_n is the count rate under the corresponding peak, ε is the detector efficiency at the specific gamma ray, P_γ is the absolute transition probability of the specific gamma ray and M_s is

Table 1. The calibration parameters of the detector at different gamma energies.

Radionuclide	Activity A of the reference source(7, 8) (Bq kg^{-1})	Energy (MeV)	Gamma yield	Peak net area (counts)	Photo peak efficiency (10^{-2})
^{137}Cs	7.24	0.662	0.852	2476	5.57
^{40}K	578.40	1.460	0.107	8342	1.87
^{226}Ra	20.90	1.760	0.159	400	1.67
^{232}Th	10.47	2.614	0.358	364	1.35

the mass of the sample (in kg). The detection limit (DL) of a measuring system describes its operating capability without the influence of the sample. The lower limit of detection (LLD) (given in Bq kg^{-1}), which is required to estimate the minimum detectable activity in a sample, was obtained using the equation$^{(11)}$

$$\mathrm{DL} = 4.65\frac{\sqrt{C_b}}{t_b}k \tag{2}$$

where C_b is the net background count in the corresponding peak, t_b is the background counting time (s) and k is the factor that converts counts per second (cps) to activity concentration (Bq kg^{-1}) as given in Equation (1). With the measurement system used in this work, DLs obtained were 17.3, 4.2 and 5.1 Bq kg^{-1} for ^{40}K, ^{226}Ra and ^{232}Th, respectively. Values below these numbers were taken in this work as being below the LLD of the detector.

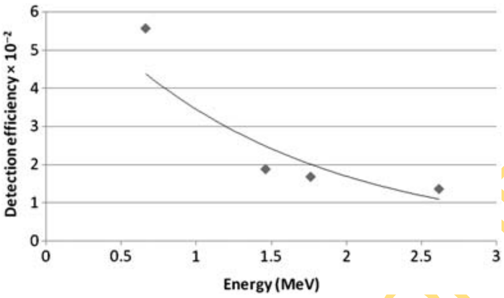

Figure 2. Detection efficiency (photo peak efficiency) curve of the detector at different gamma radiation energies.

RESULTS AND DISCUSSION

Activity concentrations of the radionuclides

The average activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in NPK (15-15-15) fertiliser samples commonly used by farmers in Nigeria are presented in Table 2 while those measured in phosphate rocks and SSP fertilisers are presented in Table 3. Table 4 presents the average activity concentration of the radionuclides in different brands of NPK fertiliser in the region under consideration. The quoted errors in the mean values in the tables are the arithmetic standard deviations at 95 % confidence interval and hence they represent the spread in the values in each city, except in cases where only one sample was analysed. For these cases, the reported error terms represent measurement uncertainty. As could be observed from Table 2, the NPK fertiliser produced by Golden Fertilizer Company Nigeria has the highest mean activity concentration of 5089.3 ± 111.3 Bq kg^{-1} for ^{40}K in the city of Akure, while the least mean value of 3972.0 ± 416.9 Bq kg^{-1} was obtained in Abeokuta from the NPK produced by Magic Premium Fertilizer Company. Also the NPK fertiliser produced by ITL/TAK and F & C fertiliser companies has the highest mean activity concentration of 450.6 ± 14.3 and 336.8 ± 91.1 Bq kg^{-1} for ^{226}Ra in the cities of Ibadan and Lagos, respectively, while the least mean value of 9.9 ± 7.3

Table 2. The range and mean concentrations of the radionuclides in the different samples of fertiliser produced by different companies and sold in retail markets in southwestern Nigeria.

Fertiliser companies	Cities	No. of samples		^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{232}Th (Bq kg^{-1})
(GFCN)	Ibadan	6	Mean	4687.1 ± 400.0	13.6 ± 9.3	9.4 ± 2.3
			Range	(3991.7–5184.2)	(2.7–26.3)	(6.1–12.2)
(ITL/TAK)	Ibadan	4	Mean	4470.0 ± 330.7	450.6 ± 14.3	
			Range	(4039.1–4845.1)	(435.3–467.5)	<LLD
(GFCN)	Ado-Ekiti	4	Mean	5083.4 ± 133.6	18.8 ± 4.9	7.0 ± 5.4
			Range	(4987.2–5279.9)	(14.6–24.8)	(<LLD −12.6)
(ITL/TAK)	Ado-Ekiti	6	Mean	4941.0 ± 218.8	386.2 ± 94.6	3.4 ± 2.6
			Range	(4624.7–5168.8)	(288.8–532.1)	(<LLD −13.5)
(MAGIC)	Abeokuta	5	Mean	3972.0 ± 416.9	13.0 ± 9.3	
			Range	(3284.0–4391.7)	(<LLD −27.6)	<LLD
(F & C)	Abeokuta	5	Mean	4607.6 ± 273.7	316.4 ± 75.4	
			Range	(4244.3–4975.0)	(203.4–87.5)	<LLD
(GFCN)	Akure	10	Mean	5089.3 ± 111.3	12.0 ± 5.9	15.1 ± 2.8
			Range	(4853.3–5195.5)	(6.0–20.7)	(11.2–19.7)
(F & C)	Lagos	9	Mean	4505.7 ± 392.7	336.8 ± 91.1	
			Range	(3867.4–4950.6)	(209.2–71.9)	<LLD
(MAGIC)	Osogbo	10	Mean	4678.1 ± 438.2	9.9 ± 7.3	8.3 ± 2.6
			Range	(3568.8–5131.8)	(<LLD −26.3)	(<LLD −11.1)

Table 3. The range and mean activity concentrations of the radionuclides in SSP fertiliser and the phosphate rocks.

Samples[a]	No. of samples	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{232}Th (Bq kg^{-1})
SSP	12	301.0 ± 36.4	695.8 ± 112.7	4.7 ± 2.0
Range		221.3–352.9	437.2–813.7	<LLD −8.0
Phosphate rock (Sokoto)	1	536.2 ± 45.3	1038.8 ± 28.4	257.9 ± 35.6
Phosphate rock (Togo)	1	871.0 ± 54.7	1801.4 ± 37.6	15.6 ± 5.1

[a]Samples were collected from NSPFC.

Table 4. Average activity concentrations (Bq kg^{-1}) of ^{40}K, ^{226}Ra and ^{232}Th in different brands of NPK fertilisers for the region under study.

Brands of fertiliser	No. of samples	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{232}Th (Bq kg^{-1})
GFCN	20	4953.3 ± 49.5 (3991.7–5279.9)	14.8 ± 10.0 (<LLD−26.3)	10.5 ± 3.3 (<LLD−19.7)
ITL/TAK	10	4705.5 ± 59.8 (4039.1–5168.8)	418.4 ± 20.2 (288.8–532.1)	5.3 ± 3.7 <LLD−7.0
MAGIC	15	4567.0 ± 50.0 (3284.0–5131.8)	10.0 ± 8.3 (<LLD−27.6)	6.7 ± 3.5 (<LLD−11.1)
F & C	14	4557.0 ± 54.7 (3867.4–4950.6)	326.6 ± 18.5 (203.4–471.9)	<LLD
NAFCON	6	4935.1 ± 49.0 (4649.1–5249.1)	11.3 ± 4.4 (7.0–18.2)	15.0 ± 3.6 (11.2–19.0)

Table 5. Comparison of activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in Nigerian samples and other countries.

Countries	Samples	Activity concentration (Bq kg^{-1})			References
		^{40}K	^{226}Ra	^{232}Th	
Pakistan	NPK	885	386	38	Tahir *et al.*(12)
USA	NPK	200	780	49	Gulmond and Windham(13)
Germany	NPK	720	520	15	Khan *et al.*(14)
Saudi Arabia	NPK	2818	75	23	Ashraf and Al-Sewaidan(15)
Finland	NPK	3200	54	11	Mustonen(16)
Nigeria	NPK	4729	143	9	Present work
Egypt	SSP	446–882	301	125–239	El-Bahi *et al.*(17)
Egypt	SSP	4	66	366	Ahmed and Abdel(18)
Nigeria	SSP	301	695.8	4.7	Present work
Nigeria	Phosphate rock (Sokoto)	536.2	1038.8	257.9	Present work
Nigeria	Phosphate rock (Togo)	871	1801.4	15.6	Present work

Bq kg^{-1} was obtained in Osogbo from the NPK produced by Magic Premium Fertilizer Company. The NPK fertiliser produced by GFCN fertiliser company has the highest mean activity concentration of 15.1 ± 2.8 Bq kg^{-1} for ^{232}Th in the city of Akure while the least mean value of 3.4 ± 2.6 Bq kg^{-1} was obtained in Ado-Ekiti from the NPK produced by ITL/TAK Fertilizer Company. Potassium concentration was found to be exceptionally high in all the fertiliser samples, which may be due to its importance in crop production for the farmlands in the region. From Table 3, the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th obtained for phosphate rock from Sokoto are 536.2 ± 45.3, 1038 ± 28.4 and 257.9 ± 35.6 Bq kg^{-1}, respectively, while the values obtained for phosphate rock from Togo (a neighbouring country of Nigeria) were 871.0 ± 54.7, 1801.4 ± 37.6 and 15.6 ± 5.1 Bq kg^{-1} for ^{40}K, ^{226}Ra and ^{232}Th, respectively. These results show that the activity concentrations of ^{40}K and ^{226}Ra are higher in the phosphate rock from Togo than the activity concentrations in the phosphate rock samples from Sokoto, Nigeria. This may be attributed to the geological and geographical differences in the two locations. The activity concentration of ^{232}Th was higher in samples from Sokoto than samples from Togo. However, ^{226}Ra had the highest activity concentration values in the samples from both locations in comparison with other radionuclides, though the reported values are within the range of values from other countries (Table 5). It was observed that activity concentration of ^{226}Ra in phosphate fertiliser and phosphate rocks are higher than the activity concentrations of ^{40}K and ^{232}Th, confirming that the main radioactivity content of phosphate rocks and phosphate fertilisers is due to ^{226}Ra and its decay products(3). And of particular interest is that the ^{226}Ra activity concentrations in two brands of fertilisers from ITL/TAK and F & C companies were 10 orders of magnitude higher than in other products in the region.

CONCLUSION

The activity concentration of ^{40}K, ^{226}Ra and ^{232}Th were measured in different brands of fertiliser sold in retail markets and available to farmers in southwestern region of Nigeria. The average of the activity concentration of ^{40}K in the samples varied from 3972.0 $\pm$ 416.9 to 5089.3 $\pm$ 111.3 Bq kg^{-1}, ^{226}Ra concentration varied from 9.9 $\pm$ 7.3 to 450.6 $\pm$ 14.3 Bq kg^{-1} while that of ^{232}Th varied from $<$LLD to 15.1 $\pm$ 2.8 Bq kg^{-1}. The activity concentration of ^{40}K, ^{226}Ra and ^{232}Th in SSP fertilisers varied from 221.3 to 352, 437.2 to 813.7 and $<$LLD to 8.0 Bq kg^{-1}, respectively, while in the phosphate rock samples, the concentration values of these radionuclides were 10 orders of magnitude higher. ^{226}Ra concentration was higher in two particular brands of fertiliser from ITL/TAK and F & C companies, while ^{40}K was exceptionally high across all the brands typically greater than 4000 Bq kg^{-1}.

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Natural Science

Gross alpha and beta activities and trace heavy elemental concentration levels in chemical fertilizers and agricultural farm soils in Nigeria

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ABSTRACT

The gross alpha (α) and beta (β) activities and trace heavy elemental concentrations have been determined in Single Super Phosphate (SSP) and Nitrogen Phosphorous Potassium (NPK) fertilizers samples used for agricultural purposes in Nigeria. Cultivated farm soil samples from two regions (north and south) in the country and samples of phosphate rocks were also analyzed for gross α and β radioactivity and elemental concentrations. The beta activity concentration in the NPK (15-15-15) fertilizers was found to vary from 2410.0 ± 80.0 Bq·kg^{-1} to 4560 ± 140.0 Bq·kg^{-1}, between 1340.0 ± 70.0 Bq·kg^{-1} and 1440.0 ± 70.0 Bq·kg^{-1} in the Single Super phosphate fertilizers while in the farm soil it ranged between 360.0 ± 40.0 Bq·kg^{-1} to 570.0 ± 50.0 for the north samples and 200.0 ± 50.0 to 230.0 ± 20 Bq·kg^{-1} for the south samples. The alpha activities in the NPK fertilizers was found to vary from 20.0 ± 10.0 to 90.0 ± 20.0 Bq·kg^{-1}, in the SSP it varied from 60.0 ± 20.0 to 100.0 ± 20.0 Bq·kg^{-1} while in the soil samples it varied from 8.0 ± 6.0 to 40.0 ± 10.0 Bq·kg^{-1} (north) and 10.0 ± 10.0 to 20.0 ± 10.0 Bq·kg^{-1} (south). The trace heavy metal concentration in Phosphate rock samples, SSP and the NPK (15-15-15) fertilizers samples were lower than the safety limits, however, the heavy elements were all detected in NPK fertilizers samples including Hg.

Keywords: Chemical Fertilizers; Gross Alpha Activity; Gross Beta Activity; Trace Heavy Elements; Farm Soil; Nigeria

1. INTRODUCTION

The addition of inorganic phosphate fertilizers to soil for agricultural crop growth and production is a common practice worldwide because they are sources of macronutrient (N, P, K, Ca, Mg and S) and micronutrients (B, Cl, Co, Cu, Fe, Mn, Mo, Ni, Se, Si and Zn) to the crops especially when they are deficient in the soils [1]. Inorganic fertilizers may contain radionuclides, heavy metals and fluorine, heavy metal micro-nutrients (Co, Cu, Fe, Mn, Mo, Ni, Zn) and heavy metals (As, Al, Cd, Pb and Hg) considered toxic when their concentrations exceed safety limits and importantly when they find their way into human systems through eco-systemic mechanisms [2]. For a plant to grow properly, it needs close to 60 chemical elements, the key elements accounting for 90% of a plant's dry weight are carbon, oxygen and hydrogen while some 8% to 9% of nitrogen, phosphorus, magnesium, sulphur, calcium and potassium. The remaining elements amount to a mere 1% or 2%; these include the important elements; boron, iron, copper, manganese, zinc and cobalt [3]. Fertilizer effects on crops are classified as either direct or indirect based on the plant need for the fertilizer. They have direct effects if they supply nutrients for plants directly and indirect if they serve to improve the soil's physical chemical and biological properties so as to mobilize the nutrients present in the soil and to neutralize the soil's acidity. There are multi-nutrient fertilizers which contain two or more macronutrients such as N-P, P-K, or N-K (double-nutrients) while N-P-K is termed tripled-nutrient fertilizers referred to as complete fertilizers. Phosphorus is one of the limiting elements to plant growth and development because lack of available phosphorus in soils limits the growth of both cultivated and uncultivated plants. Today, the only important source of fertilizer and industrial phosphorus is phosphate rock [4]. The phosphate rocks are also rich in uranium, thorium and their daughters, deposited as calcium phosphate minerals [2]. Contamination of soil and water bodies by major and trace elements may be caused by natural processes or through human activities in the environment [5].

The long-continued application of fertilizers and their by products can redistribute and elevate heavy metal and radionuclide concentrations in soil profiles. Research has shown that uranium concentrations in phosphate rock samples (a raw material for phosphate fertilizer) are enhanced by a factor of more than 10 above background uranium in soil. The ingestion of radionuclides through food intake via the soil treated with fertilizer accounts for a substantial part of average radiation doses to various organs of the body and also represents one of the important pathways for long term health considerations [6-9]. The heavy use of NPK fertilizers by farmers to improve crop yield following impoverishment of the soil has been attributed to be responsible for their elevated concentrations in food crops [6]. Despite the wide application of fertilizers in farming in the country and the different brands used by farmers, the much needed research has not been carried out in brands of fertilizers available to farmers. Until recently the level of natural radionuclide concentration levels (^{226}Ra, ^{232}Th and ^{40}K) in brands of fertilizer used in some part of Nigeria was determined by Jibiri and Fasae [7] by gamma ray spectrometry. As a further step to this initial research effort, the gross alpha and beta radioactivity levels in both farm soil and fertilizer samples in the country are investigated in this study. In view of the contribution of fertilizer to natural radiation exposures through their applications in farming activities and by crop uptake to food ingestions, the present study aims are as follows: 1) determine the level of radioactivity in the brand of fertilizers sold in Nigeria through their alpha and beta emissions and also in different farm soils where they have been applied for agricultural purpose; 2) determine the trace heavy elemental compositions in the fertilizer brands; and finally, 3) provide requisite radiometric data that may be useful in policy formulation and implementation on fertilizer safety and standards in the agricultural sector in Nigeria.

2. MATERIALS AND METHODS

2.1. Sampling

In the collection of samples of fertilizers in this study consideration was given to the two fertilizer manufacturing companies in the country; the Federal Superphosphate Fertilizer Company Ltd. (FSFC), located in Kaduna State in the Northern part of the country and National Fertilizer Company of Nigeria (NAFCON) in Port-Harcourt located in the southern part. Fertilizer samples from these two companies were collected and also the phosphate rocks, the raw materials (the Sokoto and Togo types) used by the companies in the manufacturing of fertilizers. Two samples of single super phosphate fertilizers were collected from FSFC marked SSP_1 and SSP_2 while NPK fertilizer brand were collected from markets outlets in six major commercial cities located in six states in southwestern Nigeria. This is because the markets represent the distribution channel of brands of fertilizers to the farmers and are centers of commerce in the region which are easily accessible by all strata of farmers. The markets in the city centers from where samples were collected in the southern states are: Oyo, Ogun, Osun, Ondo, Lagos and Ekiti and samples from each state was labeled NPK_{oy}, NPK_{og}, NPK_{os}, NPK_{od}, NPK_{La}, and NPK_{Ek}, respectively. Majorly, farmers from the southern part of the country use the NPK brand because of the fertile soil type while the north uses the SSP brand because it is an arid zone. Furthermore, samples of farm soil treated with SSP fertilizer were collected from School of Agriculture Kaduna farm and the Prison farm of the Nigerian Prison Services labeled $Soil_{North}$ while those treated with NPK were collected from farmlands around NAFCON labeled $Soil_{South}$. However, these sampling approaches were premised on the assumption that the farm soil samples from the farmlands in each of the region were treated with fertilizer types produced in that region. The validity of this assumption was however not investigated in this study.

2.2. Gross Alpha and Beta Counting Procedure

AN EURISYS MEASURE IN 20 a low background multiple (eight) channel alpha and beta counter was used for the measurements of the gross alpha and beta in the fertilizer and the farm soil samples. It is a gas flow proportional counter with 450 μg/cm^3 thick window of diameter 60 mm. The counting gas is an argon-methane mixture at the ratio of 90% and 10% respectively. The counting system incorporates an anti-coincident guard counters used to eliminate the influence of high energy cosmic radiation that would enter the measuring environment. The background radiation level within the measuring environment was estimated to be less than 1.0 μSv/hr. The chambers were covered with 10 cm thick lead and the inside dimensions are 480 × 280 × 105 mm^3. The system was connected to a micro-processor IN-SYST, a spreadsheet programmed QUARTTRO-PRO and a graphic programmer. For the alpha activity measurements the standard used is ^{239}Pu α-sources with activity ranging from 133.3 Bq to 185.8 Bq for the eight channels at 2π-stearadians. The radionuclide impurity in each of them varied from 0.74% - 0.82% [10]. For the beta activity measurements the standard used are ^{90}Sr β sources of diameter 38 mm and an active film of 12 mg·cm^{-3} thick. For the eight channels, eight sources of activities varied from 105.1 Bq to 117.7 Bq at 4π-stearadians. The radionuclide impurity in each of them was less than 0.1%. Cerca and LEA Laboratories in France certified all measurements with certificate No. CT001271/00/1778-1783

[10].

The beta and alpha specific activities were calculated using the expression in **Eq.1.** [10]:

$$\text{Specific Activity}(\alpha,\beta)\,\text{Bq/kg} = \frac{\text{Counting Rate }(\alpha,\beta) - \text{Background counting rate }(\alpha,\beta)}{\text{Sample Efficiency} \times \text{Channel Efficiency} \times \text{Weight of sample}} \qquad (1)$$

2.3. Trace Heavy Metal Determination

A one gram aliquot of each sample of the fertilizers was transferred into a conical flask. A 10.0 ml of the digestion solution containing a mixture of concentrated HNO_3 and HCL mixed in ratio 3:1 was added to each sample in the flask for digestion procedure as described by Rowel [11]. The mixture was heated until digestion was complete, that is, when the samples became whitish and brown fumes of HNO_3 seized to appear. The residue was diluted with deionized water, filtered and the filtrate was further diluted to make 100.0 ml using deionized water in a standard flask. Series of standard solution of each metal were prepared and run along with each sample at the respective wavelength for maximum absorption of each metal. The metal concentrations were thereafter determined using Atomic Absorption Spectrophotometer (AAS) (Buck Scientific Model 200A (AOAC, 1990).

3. RESULTS AND DISCUSSION

3.1. Gross Alpha and Beta Activities in the Fertilizer and Farm Soil Samples

Table 1. The gross alpha and beta activity concentrations in super phosphate and NPK fertilizer samples.

Samples	Alpha Activity (Bq·kg^{-1})	Beta Activity (Bq·kg^{-1})
Super phosphate SSP$_1$	100.0 ± 20.0	1340.0 ± 70.0
Super phosphate SSP$_2$	60.0 ± 20.0	1440.0 ± 70.0
NPK$_{\text{Oy}}$ (15-15-15)	3.0 ± 5.0	2410.0 ± 80.0
NPK$_{\text{Og}}$ (15-15-15)	10.0 ± 10.0	2470.0 ± 80.0
NPK$_{\text{Os}}$ (15-15-15)	10.0 ± 10.0	2420.0 ± 80.0
NPK$_{\text{Od}}$ (15-15-15)	90.0 ± 20.0	4560.0 ± 140.0
NPK$_{\text{La}}$ (15-15-15)	60.0 ± 20.0	3510.0 ± 100.0
NPK$_{\text{Ek}}$ (15-15-15)	2.0 ± 10.0	2640.0 ± 80.0

Table 2. The Gross alpha and beta activity concentrations in farm soil samples from two regions of Nigeria.

Sample	Alpha Activity (Bq·kg^{-1})	Beta Activity (Bq·kg^{-1})
Soil$_{\text{North 1}}$	8.0 ± 6.0	360.0 ± 40.0
Soil$_{\text{North 1}}$	30.0 ± 10.0	450.0 ± 50.0
Soil$_{\text{North 2}}$	30.0 ± 20.0	570.0 ± 50.0
Soil$_{\text{North 2}}$	40.0 ± 10.0	450.0 ± 40.0
Soil$_{\text{South 1}}$	10.0 ± 10.0	200.0 ± 50.0
Soil$_{\text{South 2}}$	20.0 ± 10.0	230.0 ± 20.0

The gross alpha and beta activity concentrations in the single superphosphate and NPK fertilizers are presented in **Table 1** while the concentrations in the farm soil samples from the two regions is presented in **Table 2**. As could be seen from **Table 1** the gross beta activity concentration varied from 2410.0 Bq·kg^{-1} (Oy) to 4560 Bq·kg^{-1} (Od) in the NPK (15-15-15) while in the SSP fertilizers it varied from 1340.0 Bq·kg^{-1} to 1440.0 Bq·kg^{-1}. This shows that there are more beta emitters in the NPK fertilizers than in the SSP fertilizers. This trend was a direct opposite on gross alpha activities in the sample. This shows that the gross alpha activities are higher in the SSP fertilizers (60.0 Bq·kg^{-1} and 100.0 Bq·kg^{-1}) than in NPK fertilizers with the range of values (2.0 Bq·kg^{-1} to 90.0 Bq·kg^{-1}). This observation was in agreement with the study by Jibiri and Fasae [7], that low activity concentration of ^{40}K is associated SSP and high values with NPK fertilizers. It could also be observed that the highest value of the gross beta activity concentrations in NPK fertilizers was from Ondo State (Od) samples (90.0 Bq·kg^{-1}) and the lowest was obtained in Ogun state (Og) samples. Hence, from the previous work by Jibiri and Fasae [7] and confirmed in this study showed that there is a direct relationship between the gross beta and alpha activities with the radionuclide contents in the samples. High ^{226}Ra and ^{40}K concentrations will indicate high gross alpha and beta activities in the samples. This is in agreement with the study by Aytas *et al.*, [12]. Generally we observed that there are mixes of fertilizer products sold in a particular State with varying radionuclide contents hence they will present different radioactivity scenario to natural radioactivity in farmlands in the States where they will be used for agricultural purposes. From **Table 2**, the gross beta activity concentration for farm soil samples from the northern part of Nigeria varied from 360.0 Bq·kg^{-1} to 570.0 Bq·kg^{-1} while for the alpha activities it varied from 8.0 Bq·kg^{-1} to 40.0 Bq·kg^{-1}. The gross beta activity concentrations for farm soil samples from the southern part of Nigeria varied from 200.0 Bq·kg^{-1} to 230.0 Bq·kg^{-1} while the gross alpha activity concentrations varied from 10.0 Bq·kg^{-1} to 20.0 Bq·kg^{-1}. The results show that the gross activity concentrations in farm soil samples in the northern part of the country are higher than the values obtained in the southern part of the country. It could also be observed that the introduction of fertilizer into the farm soil may have elevated the concentration of radionuclides in the northern part of the country more than in the southern part of the country, thereby elevating the concentration of radionuclides in food stuff possibly from the northern region of the country. As reported by Jibiri *et al.*, [6], fertilizer largely used to improve soil fertility is seen to have enhanced the quantity of natural radionuclides in the soil and consequently through uptake are made available to the plants. However, the gross alpha and beta activity concentrations values obtained in this study were lower than the range of values 141 $Bq \cdot kg^{-1}$ to 2589 $Bq \cdot kg^{-1}$ for beta activity concentrations and 109 $Bq \cdot kg^{-1}$ to 660 $Bq \cdot kg^{-1}$ for gross alpha activity concentrations obtained in West Bengal [13,14].

3.2. Trace Heavy Elemental Concentration in Super Phosphate Fertilizer, N-P-K (15-15-15) and Phosphate Rock Samples

The results of the elemental analysis for the soil samples are presented in **Table 3**. It could be observed that the elemental concentrations were higher in phosphate rock samples followed by SSP. The values were relatively low in the NPK samples. However, while heavy elements were not detectable in the phosphate rocks of different origins and in the SSP they were detected in the NPK fertilizer samples. Micronutrients such as Cu, Ni and Zn are essential for plant life while Cd, Cr and Pb are not essential elements but can be classified as toxic to plants. When these heavy metal concentration is compared with the mean concentration in the Earth's crust (Cd, 0.5 ppm; Cr, 200 ppm; Cu, 100 ppm; Ni, 80 ppm; Pb,16 ppm; Zn, 50 ppm, as reported by Sauerbeck [15], it may be observed that the analysed samples are enriched in Cd, Ni, Pb and Zn since under natural conditions, Pb occurs in the soil at 5 to 20 ppm, cadmium at 0.05 to 0.5 ppm, and arsenic at 1 to 5 ppm. In highly urbanized areas, Pb occurs in the soil at 100 to 200 ppm, cadmium at 1 to 5 ppm, and arsenic at 10 to 20 ppm. Threshold levels where these elements could be harmful by direct ingestion are generally higher than levels commonly found in urban soils. For example, US government threshold levels for Pb in the soil are greater than 500 ppm and greater than 20 ppm of cadmium [16] if the comparison is performed with the world range for phosphate rocks, *i.e.* Cd, 1 - 100 ppm; Cr, 7 - 500 ppm; Cu, 1 - 1000 ppm; Ni, 0 - 100 ppm; Pb, 0 - 10 ppm; Zn, 4 - 1000 ppm [5] and lesser in the Tokyo region (0.05 ppm of cadmium and 0.5 ppm of lead and zinc) [17] and in Europe [18]. From the values obtained in **Table 3**, the concentrations of heavy metals considered generally to be toxic varied from BDL to 3.73 $mg \cdot kg^{-1}$. These values were less than the values obtained internationally for which Cd ranged from <1 to 36.8 $mg \cdot kg^{-1}$, with a median of 33.2 $mg \cdot kg^{-1}$ for phosphatic fertilizers [19]. This may be an indication that suggests that the addition of heavy metals into the soil through the application of inorganic fertilizer do not significantly raise their concentration in soils to harmful levels. This assertion was supported by various international studies that the entry of heavy metals, especially Cd, Pb and Ni, into the human food chain may not be associated with inorganic fertilizers but to other anthropogenic sources, domestic and industrial residues/wastes and pesticides [20]. It is likely that the continued long use of fertilizer may elevate the concentrations of these elements in the farm soil if no reduction and remediation procedures are considered.

Table 3. Elemental concentrations in Super Phosphate fertilizers, N-P-K (15-15-15) fertilizers and Phosphate rock samples.

ELEMENT	Super phosphate Fertilizer SSP_1	Super phosphate Fertilizer SSP_2	N-P-K* Fertilizers	Phosphate rock (Togo)	Phosphate rock (Sokoto, Nigeria)
Mg ($mg \cdot kg^{-1}$)	3.68	1.12	13.17 ± 0.882	0.39	3.70
Mn ($mg \cdot kg^{-1}$)	3.64	24.60	1.067 ± 0.145	1.28	19.44
Fe ($mg \cdot kg^{-1}$)	37.40	450.70	15.25 ± 4.394	BDL	450.70
Pb ($mg \cdot kg^{-1}$)	13.80	BDL	0.60 ± 0.010	18.14	20.20
As ($mg \cdot kg^{-1}$)	0.30	BDL	BDL	0.20	0.50
Ni ($mg \cdot kg^{-1}$)	0.70	0.30	0.62 ± 0.624	BDL	0.80
Co ($mg \cdot kg^{-1}$)	0.11	BDL	0.03 ± 0.013	0.07	0.20
Cu ($mg \cdot kg^{-1}$)	5.27	14.78	18.03 ± 1.55	16.93	11.96
Cd ($mg \cdot kg^{-1}$)	0.77	0.62	1.475 ± 0.079	0.86	0.94
Ca ($mg \cdot kg^{-1}$)	2.25	0.14	0.142 ± 0.042	3.67	8.98
Se ($mg \cdot kg^{-1}$)	1.95	BDL	BDL	2.95	3.73
Zn ($mg \cdot kg^{-1}$)	BDL	BDL	0.033 ± 0.024	BDL	BDL
Cr ($mg \cdot kg^{-1}$)	BDL	BDL	0.147 ± 0.046	BDL	0.10
Hg ($mg \cdot kg^{-1}$)	BDL	BDL	1.43 ± 1.264	BDL	BDL

*± in NPK indicates the standard deviation value of the six samples analyzed.

4. CONCULSION

The gross beta and alpha activity concentrations and trace heavy elemental levels in the fertilizer samples used in Nigeria have been determined. NPK fertilizers were found to exhibit high gross beta activity concentrations while SSP exhibit high gross alpha activity concentrations. The farm soil samples from the northern part of the country exhibited high gross alpha and beta activities compared to farm soil samples from the Southern parts of Nigeria. The gross alpha and beta in the samples were good indicators for the presence of the natural radionuclide contents in the fertilizer samples. Though the concentrations of the heavy metals were very low in the fertilizer samples analyzed in this work compared to literature values it is anticipated that continually long use of the fertilizers in the farm soil may elevate their concentrations to toxic levels which may pose a health risk to the population if remedial actions are not considered.

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