

ELEMENTAL AND RADIOLOGICAL ANALYSES OF SELECTED INORGANIC AND ORGANIC FERTILIZERS IN NIGERIA

The research consists of investigating the possible presence and concentrations of heavy metals and the concentration of natural radionuclides in inorganic and organic fertilizers in Nigeria. The ^{40}K activity mean concentrations of inorganic fertilizers was $566 \pm 0.36 \text{ Bqkg}^{-1}$ ranging from 101.45 to 1033.60 Bqkg^{-1} . ^{226}Ra activity concentrations range from 22.99 to 34.48 Bqkg^{-1} with a mean of $28.36 \pm 1.96 \text{ Bqkg}^{-1}$, ^{232}Th had a mean of $57.33 \pm 0.7 \text{ Bqkg}^{-1}$ ranging from 40.71 to 77.10 Bqkg^{-1} . The air absorbed dose rate ranged from 53.91 to 144.90 nGyh^{-1} with a mean of 72.31 nGy h^{-1} which is higher than the world average 51 nGyh^{-1} . The annual effective dose rate had an average of $88.37 \mu\text{Svy}^{-1}$ (0.088 mSvy^{-1}) ranging from 60.51 to $178.23 \mu\text{Svy}^{-1}$. The R_{aeq} averaged 134 Bqkg^{-1} ranging from 106 to 207 Bqkg^{-1} which is far below the 370 Bqkg^{-1} set for radiation hazard. The H_{ex} and H_{in} averaged 0.48 and 0.39 with ranges from 0.398 to 0.83 and 0.29 to 0.77 respectively. The ^{40}K average activity concentration of the organic fertilizers was $305.33 \pm 0.196 \text{ Bqkg}^{-1}$ with a range from 120 to 907 Bqkg^{-1} , ^{232}Th averaged 45.04 Bqkg^{-1} ranging from 14.66 to 60.20 Bqkg^{-1} . ^{226}Ra averaged $24.87 \pm 0.02 \text{ Bqkg}^{-1}$ with a range of 12.83 to 65.69 Bqkg^{-1} . The average air absorbed dose rate was 51.59 nGyh^{-1} it ranged from 30.33 to 101.23 nGyh^{-1} . The annual effective dose rate averaged $61.33 \mu\text{Svy}^{-1}$ (0.061) which is lower than the world average ($0.07 \mu\text{Svy}^{-1}$) it ranged from 33.39 to $124.51 \mu\text{Svy}^{-1}$. The R_{aeq} is 112.90 Bqkg^{-1} which is far below the 370 Bqkg^{-1} maximum. The H_{ex} and H_{in} averaged 0.31 and 0.37 respectively. From Radiological point, organic fertilizers do not impart significant radiological risk, because the radiological hazard indices are low compared to world averages. For the elemental analysis of inorganic fertilizer, nine fertilizers analyzed contain Cd 3.6 mg/kg, Cu 11 mg/kg, Fe 6,228 mg/kg, Zn 475 mg, Mn 4.42 mg/kg and Ti 631 mg/kg. Eight fertilizers contain, in addition to metals above Cr 34 mg/kg, Si 814 mg/kg and K 62,954 mg/kg. All except two contain Vanadium 25 mg/kg. Six contain Pb 1.2 mg/kg. All inorganic fertilizers contain at least 13 heavy metals in their composition. Nine of the organic fertilizers contain Cd 0.14 mg/kg, Cu 1.8 mg/kg, Fe 136 mg/kg, Ni 1.6 mg/kg, Zn 9.9 mg/kg and Mn 22.45 mg/kg. Eight organic fertilizers in addition to the metals listed above also contain, Cr 0.7 mg/kg, As 1.1 mg/kg, Co 2.7 mg/kg, Si 8130 mg/kg and Ti 298 mg/kg. Two organic fertilizers recorded the presence of Cs 0.18 mg/kg and Sb 0.06 mg/kg. The presence of the elements in the environment does not pose any immediate hazard to the environment because the concentrations are within those found in soils. However; constant monitoring of the environment should be done to avoid the accumulation of these elements in the environment.

CHAPTER ONE

1.0

INTRODUCTION

1.1 Background to Research

The application of plant nutrients, particularly those produced from phosphate raw materials has increased substantially in the past ten decades (Khater & AL-Sewaidan, 2008). Lambert, R., Grant, C. & Sauvé, C. (2007) noted that, the world consumes more than 30 million metric tons of phosphate fertilizers annually. The consumption of these products has resulted to increase in crop production and land reclamation. Nowadays, the application of fertilizers, phosphate fertilizers in particular and organic fertilizers is an essential part of activities in agriculture that helps to increase crop production and improve the properties of the nutrient-deficient or nutrient--depleted lands.

The supply of these plant nutrients that improve the properties of soil is limited and depleted with every harvest, through leaching and runoff water thus, causing further reduction in quantity and yield of plants. However, possible negative effects of phosphate fertilizer application to crop lands are the contamination of cultivated lands by heavy metals and naturally occurring radioactive materials (NORM) (Lambert *et al.*, 2007). It has been noted by Rossler, C.E., Smith, Z.A., Bolch, W.E. & Prince, R.J. (1979) and IAEA, (1994) that, generally Uranium (^{238}U) in phosphate rocks has concentrations ranging from 3–400 mg/kg which is equivalent to 37–4900 Bq/kg ^{238}U in terms of radioactivity measurement and for Radium (^{226}Ra) a range of 100–10,000 Bq/kg for the different phosphate rock deposits. The United Nations Scientific Committee on the Effects of Atomic Radiation noted that, the concentration of ^{238}U and its decay products tend to be higher in phosphate rock deposits of sedimentary origin where ^{238}U series have typical concentrations of about 1500 Bq/kg (UNSCEAR, 1993). Phosphate rock can be of sedimentary, volcanic or biological origin. It is the raw material for the production of all phosphate products including phosphate fertilizers. Rock Phosphate, it has

been observed (Santos, P.L., Gouvea, R. C., & Dutra, I.R. 1995), the manufacture and the use of its products can lead to environmental contamination with heavy metals and radioactive materials and therefore, intimated that, the use of phosphate fertilizers in agriculture could be potential source of radiation exposure to the farmers and public. Not only could harm come to human beings, but to organisms as well; when they are exposed to natural and anthropogenic radioactive agents that cause damage to the cells (GRPC, 1977). Heavy metals and radionuclides are harmful agents which affect many aspects of ageing and health and can also affect key components of the cell within the body (GRPC, 1977). Naturally Occurring Radioactive Materials (NORM) and technologically enhanced NORM are both ionizing radiation, while heavy metals /or trace elements can be toxic when their concentrations exceed their threshold levels in the environment.

The term NORM distinguishes naturally occurring radioactive materials from anthropogenic sources of radioactive materials, such as those produced by nuclear power installations or those used in nuclear medicine as in chemo therapy and X-ray spectrometry, where incidentally the radioactive properties of the material may be what make it useful. These two harmful agents ; ionizing radiation and heavy metals and the possible proliferation of their release due to anthropogenic activities into the environment is the primary concern of this work with particular focus on the use of inorganic, processed organic and naturally occurring organic fertilizers in Nigeria. It has been observed that, natural environmental radioactivity and the associated gamma radiation depend primarily on geological and geographical conditions, and these appear at different levels in the soil of each region of the world (UNSCEAR, 2000). In addition the sources of heavy metals and radioactive materials in the environment have been observed to be from anthropogenic activities such as mining, smelting, steel and iron industry, chemical industry, as well as from agricultural activities (Sucie, I. Cosma., Todica, M., Bolboaca, S.D. & Jantschi.L, L. 2008). It should be noted that, prolong use of phosphate

fertilizers increases the presence of heavy metals in the soil which can affect the quality of food, groundwater, microorganism' activity, and plant growth to mention but a few (Popescu, H.L., Hilt, M & Lancranjan, I. 2009).

1.2 Statement of problem

Fertilizers are used as plant nutrients, they contain heavy metals and radionuclides obtained from the phosphate raw material and recycled hazardous industrial wastes which are not degradable. The accumulation of these toxic materials in the soil above their threshold levels due to excessive use of phosphate fertilizers and organic fertilizers becomes an increased indestructible poison in the environment. Plants pick up these contaminants and when eaten by humans pose some health problems like cancer and autoimmunity.

The presence of radionuclides in the environment through the excessive use of phosphate and organic fertilizers (commercially available organic fertilizers and naturally occurring organic fertilizers) increases the level of naturally occurring radioactive materials (NORM) in the environment. The increase of these materials in the environment above threshold limits poses some health problems to humans, problems like cancer and genetic aberrations caused by gamma radiation emitted by elements like Uranium, Thorium and Potassium -40, therefore the concentrations of these materials in the environment must be monitored.

1.3 Aim and Objectives of the study

1.3.1 Aim of the study:

i. This research has the focus of investigating the possible presence and concentrations of heavy metals, other elements and radionuclides in inorganic and organic fertilizers (processed and naturally occurring organic fertilizers) in Sabon Gari Local Government Area, Kaduna State, Nigeria. This is to ascertain the elements and their concentrations added to the environment from the excessive use of fertilizers.

1.3.2 Objectives of the study:

- i. To determine the activity concentrations of naturally occurring radioactive materials (NORM) found in six different brands of NPK, (Nitrogen-Phosphorous-Potassium), Single Super phosphate, Diammonium Phosphate fertilizers and Cow dung, Sheep and chicken faecal droppings and in three different processed organic fertilizers.
- ii. To determine the concentrations of heavy metals and other elements in six different brands of NPK, Single Super phosphate, Diammonium Phosphate and in Cow dung, Sheep and chicken faecal droppings and in three processed organic fertilizers.

1.4 Justification of the study

The knowledge of activity concentrations and distribution of natural radionuclides in fertilizers can help gather information that would help in monitoring and controlling environmental contamination by natural radioactivity. The knowledge can be used to constantly monitor the environment for the accumulation of heavy /or trace elements found in inorganic and organic fertilizers in the Federal Republic of Nigeria. We can use the information in order to arrest land degradation by the accumulation of these elements in the soil. In addition, this knowledge will help the farmers be warned of the possible presence and quantity of toxic metals in fertilizers for best protection of the health of their families.

1.5 Scope of Study

The scope of this research is to ascertain the possible presence and concentrations of the following elements: As, Cd, Co, Cr, Cu, K, Fe, Mn, Ni, Pb, Sb, Si, Ti, V, Cs, and Zn in both inorganic and in organic fertilizers. The scope is also to determine the activity concentrations of Uranium, Thorium and Potassium in inorganic and organic fertilizers.

CHAPTER TWO

2.0

LITERATURE REVIEW

2.1 Heavy metals in fertilizers

Lide (1992) defined heavy metal as “chemical element with specific gravity that is at least five times the gravity of water, (specific gravity of water is 1 at 4°C). The Oxford Dictionary of Chemistry defines heavy metal as “A metal with high relative atomic mass”. Sometimes the term is loosely applied to common transition metals such as Cu, Pb, and Zn. These metals are the cause of environmental pollution from a number of sources, including fertilizers, lead industrial effluents and leaching of metal ions from the soil into lakes and rivers. When humans are exposed to high levels of Mercury, Gold, and Lead, this leads to the development of autoimmunity, a condition in which the body attacks its own cells mistaking them for foreign invaders (Janet Glover-Kervliant, 1995).

2.1.1 Beneficial heavy metals

It is not all doom with heavy metals because, heavy metals in small quantities referred to as trace elements are nutritionally essential for healthy life. For instance Fe, Cu, Mn and Zn or some form of these metals are commonly found in foodstuff, in fruits and in vegetables and in commercially available multivitamins National Institute of Safety and Health NIOSH, (1988b) Heavy metals also find industrial application in the manufacture of insecticides, batteries, and steel NIOSH, (1988b). However, heavy metals become toxic when not metabolized by the body and accumulate mostly in the soft tissues. They may enter the human body through food, water, air or may be absorbed through the skin when humans contact them in agriculture and in manufacturing, pharmaceutical and industrial settings NIOSH, (1988b).

2.1.2 Relationship of heavy metals to Organisms

For healthy life, organisms require varying amounts of heavy metals such as iron, Cobalt, Manganese, Copper, Molybdenum and Zinc. These are also required by humans in small amounts. Excessive levels can however, be damaging to the organism. Other heavy metals such as Mercury, Plutonium, and Lead are toxic metals which have no known beneficial effects on the organisms, while Vanadium, Tungsten and Cadmium are normally toxic however, for some organisms, they can be beneficial under certain conditions (Lane & More, 2010).

2.1.3 Principles of techniques used in measuring heavy metal concentrations

2.1.3.1 Atomic absorption spectroscopy

The technique makes use of absorption spectroscopy to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on Beer-Lambert Law. In order to analyze a sample for its atomic constituents, it has to be atomized. The atomizers most commonly used nowadays are flames and electro thermal (graphite tube) atomizers. The atoms are irradiated by optical radiation, and the radiation source could be an element-specific line radiation source or a continuum radiation source.

The radiation then passes through a monochrometers in order to separate the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by a detector. In short, the electrons of the atoms in the atomizer can be promoted to higher orbital (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength).

This amount of energy, for instance, wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm), which gives the technique its elemental selectivity. The radiation flux without a sample and with a sample in

the atomizer is measured using a detector, and the ratio between the two values (the absorbance) is converted to analyte concentration or mass using Beer-Lambert Law.

(Sucie, *et al.*, 2008).

2.1.3.2 X-Ray Fluorescence Spectrometry

The principle of XRF involves the excitation of inner shell electrons of an element. When incident photon in the X-ray region is impinged on the inner shell electron at high enough energy, the electron is ejected from the atom resulting in higher energy electrons moving to fill the vacancy. As the filling of the vacancy created by the electrons ejected from the inner shell occurs, the element fluoresces. The energy difference between the two electron shell levels is given off by the atom in the form of electromagnetic radiation called X-rays. The X-ray spectrum generated from the above processes gives a number of characteristic peaks whose energy leads to the identification of the element present, while the intensity of the peak gives the concentration of the elements present. It should however be noted that, the element to be excited depends on the voltage supplied to the system. (Sucie, *et al.*, 2008).

2.1.3.3 Instrumental Neutron Activation Analysis

Instrumental Neutron Activation Analysis is a technique that is used to determine large number of elements in different matrices (Munoz, L., Gras, N., Guzman, C., Thieck, M., & Vanska, L.1993). The principle involves the n-gamma reaction which is the fundamental reaction for neutron activation analysis (Elkhang, F.A., Abdalla, I.A & Ahmed, M. M.O. 1994).The gamma rays emitted during the decay of the nucleus have specific energies that are characteristic for the nuclide in question. The probability of a neutron interacting with a nucleus is a function of the neutron energy. This probability is referred to as the capture cross-section, and each nuclide has its own neutron energy—capture cross-section relationship. For many nuclides, the capture cross-section is greatest for low energy neutrons (referred to as thermal neutrons). Some nuclides have greater capture cross-sections for higher energy neutrons

(epithermal neutrons). For routine neutron activation analysis, we are generally looking at nuclides that are activated by thermal neutrons. The activity for a particular radionuclide, at any time t during an irradiation, can be calculated from the following equation

$$A_t = \sigma_{act} \phi N (1 - e^{-\lambda t})$$

Where A_t = the activity in number of decays per unit time, σ_{act} = the activation cross-section, ϕ = the neutron flux (usually given in number of neutrons $\text{cm}^{-2} \text{s}^{-1}$), N = the number of parent atoms,

λ = the decay constant (number of decays per unit time),

t = the irradiation time.

From this equation, we can see that the total activity for a particular nuclide is a function of the activation cross-section, the neutron flux, the number of parent atoms, and the irradiation time. The optimum irradiation time depends on the type of sample and the elements of interest. (Ogunleye, *et al.*, 2001).

After the sample has been activated, the resulting gamma ray energies and intensities are determined using a solid-state detector (usually Germanium). Gamma rays passing through the detector generate free-electrons. The number of electrons (current) is related to the energy of the gamma ray. Given the differences in half-lives for various nuclides, there are optimum times to count an activated sample. The Nigerian Research Reactor 1 (NIRR-1) installed and commission at the Centre for Energy Research and Training (CERT) Ahmadu Bello University Zaria, Nigeria was used to analyze twelve of the samples. The NIRR-1 is a Miniature Neutron Source Reactor (MNSR) which is a low- power nuclear reactor with highly enriched Uranium as fuel, light water as moderator and Beryllium as reflector was used for the analysis. The whole system consists of a horizontal dip-stick High Purity Germanium (HPGe) detector with a relative efficiency of 10% at 1332.5 KeV gamma ray line, MAESTRO emulation software compatible with the ADCAM ®Multi-Channel Analyzer (MCA) card and the associated

electronics modules all made by EG & ORTEC interfaced with a Personal Computer. The efficiency curves of the detector system at near and far source detector geometries were determined by standard gamma –ray sources in the range of 59.5-2254KeV and extended to 4000KeV. The WINSPAN 2004 software was used for data processing and the gamma-ray spectral analysis (Liyu, 2004). On the basis of the well known activation equation, the software requires that calibration factors be predetermined by a multi-element standard reference material for elements of interest using adopted irradiation and counting regimes as given in Table 2.2. Nuclear data and limits for the elements of interest using adopted experimental conditions are given in Table 2.1 below.

Table 2.1: Nuclear data and limits for the elements of interest using adopted experimental conditions

Target isotope	Product isotope by (n, γ) reaction	Half -life	Gamma-energy (KeV)	LOD(mg/kg)
²³ Na	²⁴ Na	14.96hr	1368.60	40(L1)
²⁶ Mg	²⁷ Mg	9.46min	1014.4	7250(S1)
²⁷ Al	²⁸ Al	2.24min	1778.99	17(S1)
³⁷ Cl	³⁸ Cl	37.24min	1624.7	2900(S1)
⁴¹ K	⁴² K	12.36hr	1524.58	2400(S2)
⁴⁵ Sc	⁴⁴ Sc	83.81d	889.28	0.2(L2)
⁴⁸ Ca	⁴⁸ Ca	8.72min	3084.54	6600(S1)
⁵⁰ Ti	⁵¹ Ti	5.72min	329.08	2500(S1)
⁵⁰ Cr	⁵¹ Cr	27.7d	320.98	23(L1)
⁵¹ V	⁵² V	3.75min	1434.08	15(S1)
⁵⁵ Mn	⁵⁶ Mn	2.58hr	846.76	0.9(S2)
⁵⁸ Fe	⁵⁹ Fe	44.5d	1099.25	829(L2)
⁵⁹ Co	⁶⁰ Co	5.27y	1173.2	3.0(L2)
⁶⁵ Cu	⁶⁶ Cu	5.10min	1039.2	172(S1)
⁶⁴ Zn	⁶⁵ Zn	243.9d	1115.55	120(L2)
⁷¹ Ga	⁷² Ga	14.1hr	834.1	1.0(L1)
⁷⁵ As	⁷⁶ As	26.32hr	559.10	1.2(L1)
⁸¹ Br	⁸² Br	35.3hr	776.5	3.0(L1)
⁸⁵ Rb	⁸⁶ Rb	18.8d	1076.60	3.0(L2)
¹¹⁵ In	^{116m} In	54.15min	1097.3	0.5(S1)
¹²¹ Sb	¹²² Sb	64.8hr	564.24	0.5(L2)
¹³³ Cs	¹³⁴ Cs	2.06y	795.85	1.7(L2)
¹³⁰ Ba	¹³¹ Ba	11.8d	496.3	264(L2)
¹³⁹ La	¹⁴⁰ La	40.3hr	1596.21	0.2(L1)
¹⁴⁰ Ce	¹⁴¹ Ce	32.5d	145.44	14(L2)
¹⁵¹ Eu	¹⁵² Eu	13.3y	1408.5	0.6(L2)
¹⁵² Sm	¹⁵³ Sm	46.27hr	103.18	0.1(L10)
¹⁵⁹ Tb	¹⁶⁰ Tb	72.3d	879.38	1.1(L2)
¹⁶⁴ Dy	¹⁶⁵ Dy	2.33hr	94.70	0.7(LS1)
¹⁷⁴ Yb	¹⁷⁵ Yb	4.19d	396.33	0.9(L1)
¹⁷⁶ Lu	¹⁷⁷ Lu	6.71d	208.36	0.1(L2)
¹⁸⁰ Hf	¹⁸¹ Hf	42.4d	482.2	1.1(L2)
¹⁸¹ Ta	¹⁸² Ta	115d	1221.4	1.0(L2)
¹⁹⁷ Au	¹⁹⁸ Au	2.7d	411.8	0.02(L1)

Table 2.2: Routine irradiation and measuring regimes for NIRR-1

Neutron flux/irradiation channel	Procedure	Tir	Td	Tc	Activation products
1×10 ¹¹ n/cms/outer irradiation channel(B4,A2)	S1	2min	2-15min	10min	²⁸ Al, ²⁷ Mg, ³⁸ Cl, ⁴⁹ Ca, ⁶⁶ Cu, ⁵¹ Ti, ⁵² V, ^{116m} In
	S2	2min	3-4h	10min	²⁴ Na, ⁴² K, ¹⁶⁵ Dy, ⁵⁶ Mm, ^{152m} Eu,
5×10 ¹¹ n/cms/inner irradiation channels(B1,B2,B3,L2and A1)	L1	6h	4-5d	30min	²³⁹ Np(U), ⁷² Ga, ¹²² Sb
	L2	6h	10-15d	60min	⁴⁶ Sc, ¹⁴¹ Ce, ⁶⁰ Co, ⁵¹ Cr, ¹³⁴ Cs, ¹⁵² Eu, ¹⁷⁷ Lu, ¹³¹ Ba, ⁸⁶ Rb, ¹⁸² Tb, ¹⁷⁵ Yb, ²³³ Pa(Th), ⁶⁵ Zn, ⁵⁹ Fe, ¹⁸¹ Hf

Key

Tir=irradiation time, Td= decay time, Tc= counting time

2.2 Relationship of radionuclides to organism

Phosphate rock constitutes the bulk of the raw materials used in the manufacture of inorganic fertilizer. It has been shown that, phosphate rock contains stable and radioactive elements and heavy metals that could be of environmental concern to the public (Ogunleye, P.O., Mayaki, M.C., & Amapu, I.Y. 2001). It has also been noted by the above researchers that, the product, tailing, and effluent of phosphate rock processing may contain not only toxic elements such as Arsenic, Lead, Chromium, Copper and Zinc but also radioactive elements such as Uranium, Thorium and Potassium-40. Guimond & Hardin, (1989) have reported that phosphate rocks have, in addition to heavy metals, high concentrations of Radium-226 (^{226}Ra) a progeny of Thorium. The assessment of radionuclides from waste streams of phosphate processing plants in the soils and rocks in many parts of the world have increased in the past two decades, because of their hazard on the health of the populace (Belivermis, M., Onder, K., Yavuz, C. V. & Sayhan, T. 2009).

While this is the case, the research into natural radionuclides and heavy metals in inorganic, processed organic and naturally occurring organic fertilizers in Nigeria is grossly inadequate. To focus on this area, heavy metal contents and a number of radiological activities such as the Radium equivalent activity which is employed in comparing the activity concentrations of samples are determined. Radium equivalent is used as a common index which takes into account the radiation hazard associated with ^{226}Ra , ^{232}Th , and ^{40}K . Radium equivalent activity provides a useful guideline in regulating safety standards on radiation protection for the public. It is defined based on the assumption that 10BqKg-1 of ^{226}Ra , 7 BqKg-1 of ^{232}Th and 130Bqkg-1 ^{40}K produce the same gamma dose rate. It is calculated by use of the following equation: $\text{Raeq} = \text{ARa} + 1.43\text{ATh} + 0.077\text{AK}$ (Beretka & Mathew, 1985).

The letters ARa, ATh and AK are activity concentrations of Radium, Thorium and Potassium respectively. The recommended value of radium equivalent is 370Bq kg-1 as stated by Beretka

&Mathew, (1985). The decay of naturally occurring radionuclides in the soils produces a radiation field that transcends the soil-air interface to produce significant human exposure. The quantification of this exposure factor is done by external hazard index, H_{ex} which is given by the expression;

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \leq 1 \text{ (UNSCEAR, 2000).}$$

Taking into consideration the hazardous effects of Radon a progeny of Radium to the respiratory organs, its internal exposure is quantified by the internal hazard index which is given by the expression;

$$H_{in} = \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \leq 1$$

The absorbed dose rate (D) due to gamma radiation in air at 1m above the ground surface for uniform distribution of naturally occurring radionuclide was calculated for both inorganic and organic fertilizers by use of the expression:

$$D \text{ (nGyh}^{-1}\text{)} = 0.0461A_{Ra} + 0.623A_{Th} + 0.0417A_K \text{ (UNSCEAR, 2000).}$$

These radiological hazard indices are measured for both inorganic and organic fertilizers, (processed organic and naturally occurring organic fertilizers) since these fertilizers are spread on our farms and gardens and are used by plants as source of energy and growth which could affect humans through the food chain. Plants, like all living organisms are made up of cells. Within these cells occur numerous metabolic reactions that are responsible for growth and reproduction. Plants depend upon chemical nutrients in the soil to provide the basic metabolic reactions (Mills & Jones, 1996). The supply of plant nutrients is limited and depleted with every harvest, thus causing further reduction in quality and yield in crop plants. The depletion of these plant nutrients is exacerbated by leaching and runoff during raining season. If the yield of plants is to improve or maintained, macro and micronutrients that have been depleted from the soil must be replenished by adding fertilizers.

2.3 Fertilizers as source of plant nutrients

Fertilizers are complex chemical compounds that are necessary for proper growth and development of plants. These are either added to the soil or applied on the leaves of the plants in the liquefied form. Fertilizers can be broadly categorized into two different types - organic fertilizers and inorganic fertilizers. Organic fertilizers are usually composed of enriched organic matter of plant or animal origins such as sludge, bone meal, blood meal, chicken litter, Cow dung, Sheep droppings (<http://www.madehow.com/vol-3/fertilizer.html>, 2012).

The inorganic fertilizers on the other hand are chemical substances that are prepared specifically to suit a particular purpose. They are also known as chemical fertilizers and are usually available in powdered, granular (pikes and pellets) and liquid forms. Inorganic fertilizers of different formulations are composed of six different macronutrients; Nitrogen, Phosphorus, Potassium, Calcium, Magnesium, and Sulphur and seven micronutrients: Boron, Chlorine, Copper, Iron, Manganese, Molybdenum, and Zinc (Wikipedia, the free encyclopaedia, September 2011).

The American Heritage Dictionary defines fertilizer as “any of large materials, including manure and nitrogen, phosphorus and potassium compounds spread or worked into the soil to support plant growth”. The Britannica concise encyclopaedia defines fertilizer as “natural or artificial substances containing the chemical elements that improve growth and production of plants.” Fertilizer overuse can contaminate soil through accumulation of impurities, which come from the raw materials used in their manufacture. Mixed fertilizers contain ammonium nitrate, (NH_4NO_3), phosphorus (P_2O_5), potassium (K_2O). In addition, present in trace amounts are As, Pb, and Cd, found in rock phosphate mineral that are transferred into the phosphate fertilizer.

2.4 Effects of heavy metals and radionuclides on the environment

The raw material used in the production of inorganic fertilizers is phosphate ore, which is a rich source of phosphorus, a component of chemical fertilizer, has in it heavy metals and other elements that are toxic. These toxic substances are further increased by the recycling of hazardous industrial waste into fertilizer which introduces toxic materials and chemicals into our farmlands (Boukhenfouf, & Boucenna, 2011). Even though fertilizers are important in our daily life for agricultural community, because they replenish the depleted nutrients found in the soil, farmers are however oblivious of the possibilities of contamination of farmlands with heavy metals and ionizing radiation and the relative degree of absorption by plants and the subsequent impact on human health.

Furthermore, underground water / or surface water can be contaminated through leaching and runoff water with heavy metals and radionuclides. This problem has two angles to it, both toxicological and radiological. The prolonged use of fertilizers on our farm lands can increase the degradation of the farmland and cause pollution by radionuclide found in phosphate fertilizers, which are potential sources of radiation hazards through soil, underground water, and runoff water. Heavy metals associated with fertilizers can percolate into underground water due to rainwater or disperse as particles through runoff water during raining season causing algal bloom and eutrophication of water bodies thus, affecting aquatic life. These could constitute serious radiological and toxicological hazards. The pathways of radiation exposure and heavy metal contamination are numerous, including water, air and through the food chain. (Boukhenfouf, & Boucenna, 2011)

2.5 Chemical Fertilizer production process

Phosphate ores contain phosphorous in mineral forms that are primarily calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$). Phosphate ores can be divided into two types, sedimentary and igneous (Kroschwitz & Howe-Grant, 1995). In addition to the phosphate minerals, these ores can

contain a wide range of impurities. The composition of the ores can vary considerably with their origin, with sedimentary ores typically containing significantly higher concentrations of impurities; which include a range of heavy metals as well as naturally occurring radionuclides (Coward & Burnett, 1994). The production of superphosphate fertilizers involves processes where the phosphate ore is reacted with acid. Single super phosphate (SSP) fertilizers are produced using sulphuric acid. Triple superphosphate (TSP) fertilizers are produced with the use of phosphoric acid, which is produced from the phosphate ore in a separate process. The production of fertilizers through these processes results in the production of large quantities of solid waste, which is primarily calcium sulphate, commonly known as phosphogypsum (Kroschwitz & Howe-Grant, 1995). In the production processes, substantial amounts of the impurities present in the ore can be transferred to the fertilizers and phosphoric acid produced. The other impurities are present in various production waste streams, mainly in the phosphogypsum solid waste (Erdem E., Tinkilic N., Yilmaz V.T. & Uyaink Olmez H. 1996)

One form of ore, the Apatite (which occurs in several different forms) is the basic Phosphorous compound in commercially important deposits of phosphate rock. Phosphorus in apatite minerals is only slightly soluble in water and of limited availability to crops. However, reactive phosphate rock and partially acidulated phosphate rocks are satisfactory sources of Phosphorous for crops grown on some acid tropical soils. Acidulation or heat treatment of phosphate rock are the two processes of producing phosphorous and acidulation is the most commonly used technique for improving the agronomic suitability of phosphate rock. The majority of finished Phosphorous containing materials used in agriculture are made from wet process phosphoric acid.

2.6 Natural radioactivity

Radioactivity is the spontaneous emission of energy from unstable atoms as they decay. These unstable atoms are said to be 'radioactive', because they emit radioactivity from the nucleus as they decay. Radioactive elements, such as Uranium, Thorium and Potassium decay readily to form lighter atoms. The energy that is released in the process is made up of small, fast-moving particles and high-energy waves as in alpha and gamma radiation. These particles and waves are invisible and the intensity of radioactivity of an element varies according to the stability of atoms. Examples of elements with naturally occurring radioactive isotopes are Carbon, Bismuth, Radon, and Strontium. The length of time that is taken for half of the nuclei in an element to decay is called its 'half-life'. A half-life can be very short (milliseconds to hours) or very long (hundreds of thousands of years). Radiation also arises from nuclear fission. Fission can be spontaneous but is usually initiated and controlled in a nuclear reactor, it releases energy as the heavy nucleus is split into two to produce radioisotopes that are commonly used in medicine, industry, science and agriculture (Ogunleye, *et al.*, 2001).

2.6.1 Natural radioactivity in phosphate rock

Natural radioactivity of phosphate rocks has been determined by many researchers, for instance, Ogunleye *et al.*, (2001) determined the radioactivity and heavy metal composition of Nigerian phosphate rock collected from the Sokoto basin, using Instrumental Neutron Activation Analysis (INAA) and X-ray Fluorescence Spectrometry (XRF) techniques. The natural activity concentrations due to ^{238}U , ^{232}Th and ^{40}K were determined by gamma ray spectrometry using Hyper- Pure Germanium (HPGe) detector. Their results showed that the average concentration of some toxic elements (As, Sb, Cr, and Zn) in phosphate rocks showed no appreciable difference from that in agricultural soils but, that the Uranium and Thorium contents were enriched significantly. A similar work was carried out by Saueia and Mazzilli, (2006) on the distribution of natural radionuclides in the production and use of phosphate

fertilizers in Brazil. They characterized the phosphate rocks and the fertilizers produced from the phosphate rocks using alpha and gamma ray spectrometry by measuring the activity concentration of ^{226}Ra , ^{228}Ra and ^{210}Pb . They found that the radioactive series of U (^{238}U , ^{234}U , ^{230}Th , ^{226}Ra and ^{210}Pb) and the series of Th (^{232}Th , ^{228}Ra and ^{228}Th) were at equilibrium in the phosphate rock but, they observed that after acidulation of the phosphate rock, there was a redistribution of the radionuclides which migrated according to their chemical properties, Uranium isotopes (^{238}U and ^{234}U) were found in the fertilizers TSP(Triple Super Phosphate) and SSP(Single Super Phosphate), whereas Thorium isotopes(^{232}Th , ^{228}Th and ^{230}Th), Radium isotopes (^{226}Ra and ^{228}Ra) and ^{210}Pb were redistributed uniformly in the fertilizers TSP and SSP and in phosphogypsum. Their results are in agreement with Mazzilli, B.P., & Palmiro, V. (2000), who found enrichment factors from phosphate rock to phosphogypsum of 90% for ^{226}Ra , 80% for ^{232}Th and ^{230}Th and 100% for ^{210}Pb .

2.6.2 Radioactive materials in fertilizers

Radiation is a fact of life, we cannot escape it. Every form of life on earth is exposed to radiation either from cosmogenic or terrestrial sources. We are exposed to radiation from naturally occurring radioactive materials present in the earth, the houses we live in, the food and drinks we consume. Even the air we breathe in contains radioactive aerosols. We are also exposed to anthropogenic radiation, for example X-ray, fallout from nuclear explosive testing and small quantities of radioactive materials allowed to escape to the environment in course of normal operations of nuclear installations (IAEA, 2005). The term radiation sometimes means, “Ionizing” radiation, (radiation which changes the physical state of atoms when it strikes, causing them to be ionized that is, causing them to be electrically charged). In some cases, the presence of such ions can disrupt normal biological processes.

There are different types of radiations i.e. alpha, beta, X-ray and gamma radiations. Unstable naturally occurring and man-made atoms that emit these kinds of radiation are said to be

radioactive in nature. Radioactivity is the spontaneous emission of energy from unstable atoms, a random process that happens naturally as isotopes of particular element decay. Man's bodily exposure to natural radiation originates mainly from terrestrial background radiation; For instance, terrestrial sources of geological origin (presence of Uranium, Thorium and Potassium in rocks and soil) and cosmic (cosmogenic radionuclides).

According to Santos, (2005), concerns that relate to exposures resulting from natural radiation emerged in the 1970s, and became the cause of intense research, which resulted in the publication of several standards and guidelines by regulatory organizations worldwide. People now have growing interest in determining the levels of radiation to which the population of a given region is exposed. In this context, exposure to environmental radioactivity is one of the basic objectives of any environmental monitoring program. It is known that, in the environment, on the average, the rate of ionizing radiation exposure is 2.4 mSv /year (UNSCEAR, 2000) yet mankind survives it. Therefore, it is very likely, there is threshold of radiation dose below which there is no permanent damage to the human body, due to the body's ability to recover and heal (UNSCEAR, 2000). However, scientifically any dose level of radiation can be harmful to human body.

High doses of ionizing radiation can destroy the cells of organisms; induce cancer or genetic defects by altering the characteristics of the cells. Therefore, measuring radioactivity in the environment is of great importance to monitor and control the levels of radiation to which man is exposed directly or indirectly because , man is continuously being exposed to ionizing radiation from Naturally Occurring Radioactive Materials (NORM). Before the 1960s, the control of natural radiation by man was deemed as unnecessary because, it was considered almost constant and equal to 1milli Sievert/year (UNSCEAR, 2000). Since the Chernobyl accident and the recent accident in Fukushima, the fear and concern of the population are concentrated on technologically enhanced NORM radiation sources, particularly nuclear

facilities. However, most of the average collective exposure to ionizing radiation of the world population is due to natural cause.

The origin of these materials is the Earth's crust and the cosmos, but they find their way into fertilizers, water, food and the human body. Generally, phosphate fertilizers contain some of these materials and the materials reflect the geology of their site of origin. The average activity concentrations of these materials; ^{226}Ra , ^{232}Th and ^{40}K in the Earth's crust are 35, 30 and 400 Bq/kg respectively (UNSCEAR, 2000). As noted above, the United Nations Scientific Committee on Effects of Atomic Radiation (UNSCEAR, 2000) estimated the annual human exposure from natural sources to be 2.4mSv/yr. However, elevated levels of natural radionuclides causing annual doses of several milli Sievert (mSv) have been identified in Brazil, France, India, Nigeria and Iran (UNSCEAR, 2000). The phosphate rock deposit areas normally show high natural radioactivity and since, chemical phosphate fertilizers are produced from phosphate rock, they also contain radioactive elements and thus show natural radioactivity. This is why the phosphorus constituents contribute towards most of the radioactivity associated with Radium in soil (IAEA, 1990). The use of different types of phosphate fertilizers on our crop lands for enhancing crop yield has become very common nowadays.

In Nigeria, just as everywhere else, farmers use fertilizers to replenish the natural nutrients depleted from soil due to continual cultivation of crops, weathering and erosion of land (Jibiri & Fasea, 2009). The raw material used in the production of inorganic fertilizers is phosphate ore. It is present normally in the form of calcium phosphates $\text{Ca}_3(\text{PO}_4)_2$ which are very old marine deposits associated with fossils (sedimentary phosphates). This form represents 85 % of the worldwide production. The materials are often heated to 950°C to decompose calcium carbonate and organic matter. The second type of phosphate material is apatite, $\text{Ca}_5[(\text{PO}_4)_3(\text{F})]$, that is of igneous origin, phosphate rocks are used extensively, mainly as a source of

phosphorus for inorganic fertilizers and for the production of phosphoric acid and other special chemicals (Jibiri & Fasea, 2009).

Chemical fertilizers are mainly composed of nitrogen, phosphorus and potassium (NPK); the phosphorus portion has its source in the phosphate rocks, which contain enhanced concentration of natural radionuclides. The mining and processing of phosphate ores may redistribute ^{226}Ra and its progenies among the products, by-products and wastes of the phosphate industry (Pantelica, 1997). It is known that humans can be exposed to hazards that arise from industrial plants using phosphate rock as raw material to manufacture fertilizers due to the release of dust in the environment (Pantelica, 1997). The ore contains radioactive Potassium (^{40}K); (^{238}U) and Thorium (^{232}Th) series, their decay products and these are mainly natural primordial radionuclides that are redistributed during mining and processing of the phosphate ore.

Despite the beneficial influence of phosphate fertilizers on the soil and agricultural plants, it is of uttermost interest to estimate their hazardous effects on the environment because, they become a source of radioactivity by redistributing naturally occurring radionuclides at trace levels throughout the environment. The radioactivity of naturally occurring radionuclides redistributed by the overuse of NPK fertilizers has been found to reduce quantity of vegetables and crops grown on soil over the years (Tutor vista, 2012). It has been found to reduce the protein content of wheat, maize and corn grown on that soil. The carbohydrate quality of such crops also gets degraded. Excess potassium content in soil decreases Vitamin C and carotene content in vegetables and fruits. The vegetables and fruits grown on over-fertilized soil are more prone to attacks by insects and disease (Tutor vista, 2012).

The intensive use of chemical fertilizers can pollute underground water, destroy microorganisms and insects, make plants more susceptible to the attack of diseases and reduce soil fertility. This phenomenon may result in potential radiological risks owing to external

exposure during resident time in the farms, internal exposure through ingestion of food grown on such soils and through direct inhalation of suspended dusts from air and farm machinery (Abdelaziz, M. E., Hanafy A. H., Ahmed, M. M., & Shaaban, R. P. 2007). For these reasons, the knowledge of the activity concentrations and distributions of the natural radionuclides in fertilizer materials are very important since, it provides useful information in monitoring environmental contamination by natural radioactivity. As a result of these potential risks, many researchers have given attention to the negative effects of using phosphorous based chemical fertilizers in agriculture, which affect both agriculture itself and human beings as well (Abdelaziz *et al.*, 2007).

Therefore, for this reason, the development of satisfactory alternatives for supplying the nutrients needed by crops (processed organic and naturally occurring organic fertilizers) may decrease the risk and problems associated with conventional NPK chemical fertilizers and thereby protect both the environment and human health (Abdelaziz *et al.*, 2007). With this background information, the review in this work is focused broadly on some selected works done on heavy metals and radiological assessment of phosphate rock and on different types of fertilizers to justify the concept of this study which is assessing the chemical and radiological status of chemical fertilizers, processed and naturally occurring organic fertilizers.

2.6.3 Method of determining natural radioactivity

2.6.3.1. Gamma –ray spectrometry using NaI (TI) detector

The use of gamma- ray spectrometry in the analysis of bulk samples requires that, the emitted characteristic gamma rays from the sample be assessed either directly or indirectly to quantify the amount of the particular radionuclide or element of interest. The process of gamma spectrometry involves the measurement of gamma spectra from natural samples by the use of detectors to determine the bulk Uranium, Thorium and Potassium content of the samples in question. For this analysis, the detector used is the Thallium doped Sodium Iodide, (NaI (TI))

detector. Gamma spectrometry is a widely used analytical technique with many applications in natural environmental studies. The technique has the advantages of; cheapness, relative ease of sample preparation and the simplicity of the procedures for data analysis (Ibeanu, 1999)

2.6.3.2 Instrumentation

The instruments for measuring gamma radiation operate on the principle of converting characteristic photon energy into electrical energy which is then, detected and measured by the analogue or digital device. The intensity of the electrical pulse is used to quantify the different radionuclides. This is done by recording the count rate in distinct energy windows specified for the gamma energy of particular radionuclide. The widely used instruments are solid state detectors and scintillation counters such as NaI (Tl) detector that has very wide acceptance. The instrument used for measuring the gamma radiation in this work is a Multi Channel Analyzer system (MCA). The MCA consists of 7.62cm by 7.62cm NaI (Tl) detector which is optically coupled to photomultiplier tube (PMT) with preamplifiers and amplifiers fully incorporated. In the MCA, high energy photons are converted to low energy photons which are then converted to electrical pulses by the PMT. The intensity of each pulse is proportional to the quantity of the nuclide characterized by the particular gamma energy. The most commonly used scintillation materials are the high density Thallium-activated Sodium Iodide, NaI (Tl) which has the advantage of high atomic number that increases the probability of interactions between the nuclide and the detector. Ibeanu (1999) stated that, spectral analysis for the discrimination needed for the quantitative and qualitative analysis can be achieved in two ways. These are through integral and differential spectrometry. The integral spectrometry records the whole spectrum from a predetermined low position that covers the energy peaks of interest. While the differential spectrometry involves the acquisition of information on the energy peaks with an energy window set about the peak of interest. Differential spectrometry employing three channels is used for this work. The channels used are the ^{40}K channel which

is determined from the single 1460KeV gamma line, the ^{238}U channel of 1764keV energy peak and the ^{226}Th channel with energy peak of 2614KeV. Details are stated in Table 3.2

Table 2.3: Spectral energy windows used in analysis using NaI (Tl) gamma spectroscopy system

Element	Isotope used	γ -ray energy(KeV)	Energy window (KeV)	Calibration factor CPS/BqKg ⁻¹)	Detection limits BqKg ⁻¹
^{226}Ra	Bi	1764.00	1620-1820	8.632	3.84
^{232}Th	Tl	2614.50	2480-2820	8.768	9.08
^{40}K	K	1460.00	1380-1550	6.451	14.54

All the raw data obtained were converted to conventional units by use of calibration factors to determine the activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K .

2.6.3.3 System Calibration

The calibration of the Multi Channel Analyzer (MCA) is necessary, because it provides a means for finding an expression that relates particle energy to the channel number that is the particle-energy storage. The MCA housing a Maestro (a version of software analyzer) was used. The calibration of the NaI (Tl) (Sodium Iodide Thallium detector) involves the setting of amplification system steadily and gradually to 900V along with the routine procedure for initialing readings. The calibrating standard Sources Ce-137 and Co-60 were placed inside the detector, one after the other and counted for 100 seconds to give amplifier gain of 72% resolution of 66.16KeV for Ce-137.

2.6.3.4 Evaluation of Specific Activity of the samples

All the fertilizer samples were analyzed using a 7.6×7.6 cm NaI (TI) detector crystal enclosed in a graded 6cm-thick Canberra lead shield and lined with cadmium and copper sheets to assist in the reduction of background radiation. The samples were measured after calibration with standards for a period of 29,000 seconds, after which the net area under the corresponding

gamma ray peaks in the energy spectrum were used to compute the activity concentrations in the samples through the equation

$$C [Bq/Kg] = \frac{Cn}{Cfk} \dots\dots\dots (3.1) \text{ (Ibeanu, 1999)}$$

Where,

C= the activity concentration of the radionuclide in the sample given in Bqkg⁻¹

Cn =the count rate (counts per second)

Cfk= the calibration factor for the detecting system

The required energy peaks of interest in this observation are from ²³⁸U, ²³²Th and ⁴⁰K. The resulting data for the analysis were converted to conventional units of radioactivity by the use of calibration factors for the determination of activity concentrations. The detection limit of a measuring system describes its operation capability without the influence of the sample. Values below these numbers will be taken as below detection limit (BDL)

2.6.3.5 Calibration Factors

The calibration factors for each standard radionuclide used in the analysis were determined using the method described by Ibeanu, (1999).

Where;

$$CF, {}^{40}\text{K} = \frac{cps(K-40)}{ppm(K-40)} \quad \text{or} \quad \frac{cps(K-40)}{Bq(K-40)}$$

$$CF, {}^{266}\text{Ra} = \frac{cps(Ra-226)}{ppm(Ra-226)} \quad \text{or} \quad \frac{cps(Ra-226)}{Bq(Ra-226)}$$

$$CF, {}^{232}\text{Th} = \frac{cps(Th-232)}{ppm(Th-232)} \quad \text{or} \quad \frac{Cps(Th-232)}{Bq(Th-232)}$$

For the estimation of the concentration of the radionuclides in the samples, the counting rate (cps) and calibration factors obtained from above were substituted into equation 3.1 above.

2.6.4 Natural radioactivity in fertilizers

Similar work has been done on fertilizers by Boukhenfouf & Boucenna, (2011), who evaluated the fluxes of natural radionuclides in local production of phosphate fertilizers and determined the content of radioactivity in several commercial fertilizers produced in Algeria.

They used gamma spectrometry to determine activity concentration due to naturally occurring ^{226}Ra , ^{232}Th and ^{40}K in five types of samples. The results show that these radionuclides were present in an average concentration of 134.7 ± 24.1 ^{226}Ra , 131.8 ± 16.7 ^{232}Th , 11644 ± 550 ^{40}K Bq/kg for the first fertilizer NPK and 190.3 ± 30 ^{226}Ra , 117.2 ± 10.3 ^{232}Th , 5312 ± 249 ^{40}K Bq/kg for the second fertilizer (NPKs). For the virgin and the fertilized soils, the corresponding values were 47.01 ± 7.3 , 33 ± 7 , 329.4 ± 19.7 Bq/kg and 53.2 ± 10.6 , 50.0 ± 7 , 311.4 ± 18.7 Bq/kg respectively. For well water, the values were 1.93 and 0.12 Bq/kg; however, they found that the third value was below the Minimum Detectable Activity (MDA). They noted that, the Radium and Thorium values in the soil increased with the addition of NPK fertilizers.

In a related work conducted by Jibiri & Fasea, (2009) the activity concentration of naturally occurring radionuclides ^{40}K , ^{226}Ra and ^{232}Th were measured in different brands of fertilizer samples sold to farmers in retail markets in six commercial cities in south-western Nigeria. Gamma ray spectrometry was employed in measuring background radiation of ^{234}U , ^{232}Th and ^{40}K radionuclides. The results of measurements showed that the average activity concentration of ^{40}K in the nitrogen, phosphorus and potassium fertilizers 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) fertilizers and phosphate rocks were also determined. However, high activity concentrations of ^{226}Ra were obtained in the SSP fertilizer and phosphate rocks and in two other brands of fertilizers. They concluded that, the values of the activity concentration of the radionuclides in the brands of fertilizers used in

Nigeria are within the range of values reported in several other countries except ^{40}K concentration which was higher.

A group of researchers from Brazil analyzed the rate of natural and artificial radiation from radionuclides present in cement, soil and fertilizers used in Sergipe State – Brazil. In the samples analyzed, Be-7 and Cs-137 were detected in organic fertilizers within the brewing processes before its use in agriculture. ^{231}Th was also found in samples of soil and cement in the state of Sergipe, while the activity concentrations of ^{238}U , ^{234}U , ^{226}Ra , ^{232}Th and ^{40}K (Potassium) and Radium equivalent Raeq were also determined (Cardoso, L.X., Souza, O.S., Ferreira, L.C.F., Ferrira, C.O., Barboza, E., & Alhanti, E.C. 2011).

2.7 Pathways of Radioactive Materials into the Human Body

Radioactive materials release into the environment can affect human body through a number of pathways which is characterized as complete or potential. These pathways include air, water, food and direct irradiation of the body. For a complete exposure to occur the following must be in place:

A source of chemical or radioactive contamination

A medium through which contamination is accomplished

A point of exposure or place where human exposure is likely to occur

A route of human exposure for instance, eating or breathing and there has to be an exposed population (McCluggage, 1991).

2.7.1 Water pathway (ingestion)

There are several ways through which radionuclides can contact with water; either through percolation, runoff or deposition through air. Exposure by ingestion occurs when someone

swallows radioactive material and the danger comes when the ingested material emits alpha radiation that disrupts proper cell functions (McCluggage, 1991).

2.7.2 Soil pathway (through food chain)

Radionuclides get into the soil through air deposition, water used for irrigation and fertilizers used as plant nutrients to add to the amount naturally found in soils. The radionuclides in the soils get into the food chain through plants. Just as other minerals in the soil are absorbed by plants so are radioactive elements and when these plants are eaten by humans the radionuclides enter into the human body and become a radiological risk (McCluggage, 1991).

2.8 Toxicity of heavy metals

Heavy metals can affect both plant and animal health when they exceed the biological recommended limits. The bio-toxic effects of heavy metals are felt when these elements are ingested or inhaled above their recommended limits, these effects could be acute, or chronic. The general signs of the effects of the toxicity of Cd, Cr, Pb, As, Cu, and Zn have been reported to include the following: diarrhoea, stomatitis, gastrointestinal disorders, paralysis, vomiting, depression and convulsion with radioactive elements being neurotoxic, carcinogenic, mutagenic or teratogenic (McCluggage, 1991).

Cadmium finds its way into the body through food, water, air, or smoking cigarettes. Children in particular, because of the mouthing habits can be exposed to Cadmium toxicity by ingesting contaminated soil. Gastrointestinal absorption from food or water is the principal source of internally deposited cadmium in the population. Thirty percent of Cadmium that reaches the blood deposits in the liver, another 30% deposits in the kidneys, and the rest distributes throughout all other organs and tissues of the body, the absorbed cadmium is excreted primarily in the urine. Cadmium-113m induces cancer from the beta particles associated with its radioactive decay when it is taken into the body.

The chemical toxicity of Cadmium includes the damage done to the respiratory system, headache, chest pains, muscular weakness, pulmonary oedema, and death (McCluggage, 1991). Lead is also one of the significant toxic metals; it gets into the body through ingestion or breathing and can also be absorbed through the skin with the concomitant effect of the inhibition of haemoglobin synthesis, thus can affect almost every organ and system in the body, including the gastrointestinal tract, the hematopoietic system (blood-forming tissues), cardiovascular system, central and peripheral nervous systems, kidneys, immune system, and reproductive system. Exposure of pregnant women to high levels of lead can result in premature births and smaller babies. Young children exposed to lead poisoning do suffer from learning difficulties and reduced growth. Carcinogenic effects are associated with lead-210 which is radioactive ((McCluggage, 1991).

2.9 Toxicity of radioactive materials

According to the Organic Consumers Association, phosphate rock is the major source of 'yellow cake' (uranium oxide) for nuclear weapons and the nuclear power industry, and may contain as much as 200mg/kg of uranium. The phosphate fertilizer may contain radioactive lead, radon, polonium and other radioactive materials. These radioactive molecules can cause bone cancer, lung cancer and many other types of cancer. The risk is most serious to growers working with phosphate fertilizer. Fertilizer containing radioactive substances may also be a high risk for you if you have indoor plants fertilized with phosphate fertilizers.

Caesium is a metal that may be stable (non radioactive) or unstable (radioactive). The most common form of Caesium is Cs-137 which is produced when Uranium and Plutonium absorb neutrons and undergo fission. It has a half life of 30 yrs and decays by emission of beta and gamma radiation to Barium -137(Ba-137). Caesium -137 is much more significant environmental contaminant than Cesium-134. Cattle bio-accumulate Cs in milk, meat, urine and faeces. Arsenic is a toxic metal known to cause cancer in humans it is released from both

anthropogenic activities and naturally from the crust. Anthropogenic sources include the use and manufacture of pesticides and mining activities. Background concentration in soils is 1mg/kg to 40mg/kg.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Sample collection

3.1.1 Inorganic Fertilizer Samples

Nine samples of inorganic fertilizers were purchased from Samaru market in Sabon Gari Zaria Local Area, Kaduna State, Nigeria. These samples are as seen in Table3.1 below.

Table3.1inorganic fertilizer brands

s/n	Brand name	brand
1	Sambuka four corner vital	NPK
2	Golden (15-15-15)	NPK
3	AFCUTT(15-15-15)	NPK
4	Tak(20-10-10)	NPK
5	Maishaho(20-10-10)	NPK
6	Golden (20-10-10)	NPK
7	Diammonium phosphate (DAP)	DAP
8	Tak Agro	SSSP 18%
9	FSFC	SSSP 18%

The samples were transferred into polythene bags, labelled and taken to the laboratory for heavy metal and naturally occurring radioactive material analysis.

3.1.2 Processed commercial organic fertilizer sample collection

Three processed commercial organic fertilizers (Royal fertilizer plus, Crystallizer and Mega green) commercially available were obtained from IAR (Institute for Agricultural Research) Ahmadu Bello University Zaria, Kaduna State, Nigeria and taken to the laboratory for analysis.

3.1.3 Naturally occurring organic fertilizer sample collection

Two Cow dung (white Fulani- open-field herd and white Fulani-milk-shade herd), one Sheep dropping hay flock and one Layers litter Shika brown were collected from NAPRI (National Animal Production Research Institute), while one Layers litter coded Layers litter BZ farm was obtained from Abulude's poultry farm and one Sheep dropping grazing flock was obtained from Mamuda's pen in Samaru; these nine samples were transferred into polythene bags, labelled and taken to the laboratory for analysis

3.2 Sample preparation for gamma spectrometry

The fertilizer samples were crushed into fine powder by use of an agate mortar and pestle. Three hundred grams (300g) were weighed and packaged into Radon-impermeable cylindrical plastic containers, selected to fit the space allocated to the detector vessel. A triple-stage sealing system was made for each packaging to avoid Radon-222 from escaping. The inner rims of each container lid were smeared with Vaseline wax; the lid was filled with candle wax to block the gap between lid and container, and finally tight –sealing lid container with a masking adhesive tape. The prepared samples were left alone for thirty days to enable Radon and its progenies to reach secular radioactive equilibrium prior to the laboratory analysis (Ibeanu, 1999).

3.3 Laboratory Analysis

For the analysis of specific activity concentrations of natural radioactive substances in the fertilizers, gamma –ray spectrometer with NaI (TI) detector, Canberra type at the Centre for Energy Research and Training, Ahmadu Bello University was used.

3.4 Instrumental Neutron Activation Analysis (INAA)

Instrumental neutron activation was done using NIRR-1(Nigeria Research Reactor -1) at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria. The certified reference material IAEA-Coal fly ash was used to determine the calibration factors for all the elements. For the determination of calibration factors, sample aliquots of the standard of approximately 150mg were weighed and wrapped into polyethylene films. The polyethylene films and the rabbit capsules were cleaned by soaking in 1.1HNO₃ for 3 days and washed with de-ionized water. Blank concentrations of all the elements were investigated using adopted procedures given in Table 2.1 and were found to be below the limits of detection for the setup for the polyethylene films.

3.5 X-Ray Fluorescence spectrometry (XRF)

3.5.1 Procedure for sample preparation and analysis

The sample for analysis was weighed and ground in agate mortar and a binder (PVC dissolved in Toluene) was added to the sample, carefully mixed and pressed in a hydraulic press into a pellet. The pellet was loaded into the sample chamber of the X-ray spectrometer Mini Pal 4 model PW4030 at the Centre for Energy Research, and Training, Ahmadu Bello University, Zaria. A voltage (30 Kv maximum) and a current (1mA maximum) were applied to produce the X-rays that excited the sample for a preset time (10minutes in this case). The spectrum from the sample was analyzed to determine the concentration of the elements in the sample.

3.6 Atomic Absorption Spectroscopy

3.6.1 Sample Preparation for heavy metal analysis

The samples were crushed using a pestle and mortar until they pass through 1.2 mesh and one gram aliquot was separately weighed by difference into a 100 ml glass-boiling tube, to this de-ionized water was added, followed by concentrated Hydrochloric acid, and concentrated Nitric acid. The samples were digested at 80°C and gradually heated to boil for four hours. The heated mixture was then allowed to cool and was filtered. The filtrate was finally diluted to volume of 100ml with de-ionized water. It was then aspirated into the Variant AA240FS (Fast Sequential Atomic Absorption Spectrometer) in the Multi-User laboratory in Ahmadu Bello University, Zaria and the results were acquired by use of spectra AA software

CHAPTER FOUR

4.0

RESULTS AND DISCUSSION

4.1 Elemental Assessment of Inorganic and Organic Fertilizer Samples by AAS

The analyses of inorganic and organic fertilizers for the possible presence and quantities of metal pollutants were carried out by Atomic Absorption Spectroscopy (AAS) and complemented by X-Ray Fluorescence (XRF) and Instrumental Neutron Activation Analysis (INAA) methods to get a better picture of their composition in the selected fertilizers.

The results of AAS analysis of inorganic fertilizers are presented in Tables 4.1. From Table 4.1, the results of Cd in inorganic fertilizers ranged from 1.0 mg/kg to 15.9 mg/kg with a mean of 3.6 mg/kg. Cu concentration ranged from 5.0 mg/kg to 32.0 mg/kg with a mean value of 11.04 mg/kg. There was appreciable difference in the copper concentrations. Pb was not detected in Tak (20-10-10) NPK, Golden (20-10-10) NPK and DAP it ranged from BDL to 5.0 mg/kg. The mean concentration was 1.16 mg/kg. The Fe concentrations of the fertilizers ranged from 1,263 mg/kg - 9,924 mg/kg with a mean of 6,228 mg/kg. Ni concentrations ranged from 5.8 mg/kg to 127.3 mg/kg. Ni had a mean of 31.0 mg/kg. The highest Ni concentration 127.3 mg/kg was recorded for Sambuka (15-15-15) NPK followed by DAP at 62.2 mg/kg.

The Mn concentration in the analyzed fertilizers had a range of 177.2 mg/kg to 1,702 mg/kg and a mean of 442.4 mg/kg. FSFC SSP 18% fertilizer recorded the highest concentration of Mn. The concentration of Zn in the inorganic fertilizers ranged from 15.8 mg/kg to 3900 mg/kg. DAP fertilizer recorded the highest of 3900 mg/kg.

Table 4.1: Elemental Composition of Inorganic Fertilizer Samples in mg/kg by AAS

S/N	Sample	Cd	Cu	Fe	Ni	Mn	Pb	Zn
1	CRP1	10.7	13.0	549.0	127.3	299.2	1.0	153.9
2	CRP2	1.0	5.6	1,263.0	8.7	258.6	1.0	32.1
3	CRP3	5.0	12.1	4,247.0	5.8	335.8	5.0	20.7
4	CRP4	3.0	7.2	6,515.0	15.3	206.6	BDL	25.7
5	CRP5	5.0	5.3	5,992.0	10.3	177.2	0.012	15.8
6	CRP6	4.0	6.7	7,412.0	12.2	246.2	BDL	19.2
7	CRP7	15.9	32.0	6,440.0	62.2	475.3	BDL	3900
8	CRP8	3.0	8.6	8,713.0	16.7	282.3	2.0	20.5
9	CRP9	3.7	8.9	9,924.0	20.9	170.2	3.2	106.5
	Mean	3.6	11.0	6,228.0	31.0	442.4	1.2	474.9
	Range	1.0-15.9	5.3 32.0	1,263.0- 9,924.0	5.8-127.3	177.2- 1,702.0	BDL 5.0	15.8- 3900.0
10	CRS12	0.633	11.2	1,6028.0	12.3	11,866.0	16.3	39.7
11	CRS13	0.621	52.9	5,626.0	36.1	410.8	11.8	244.4
	rock mean	0.627	30.3	10,827.0	24.2	6,138.4	14.14	142.05

Key:

CRP1= Sambuka four corner vital (15-15-15) NPKCRP2 Golden (15-15-15) = NPK

CRP3= AFCUTT (15-15-15) NPKCRP4= Tak (20-10-10) NPK CRP5= Maishaho (20-10-0) NPKCRP6= Golden (20-10-10) NPK CRP7= DAP (Diammonium phosphate)

CRP8= Tak Agro (Single superphosphate 18%), CRP9= FSFC (Single super phosphate 18%), CRS 12 Sokoto phosphate rock, CRS 13 Togo phosphate rock

The results from Table 4.2 for organic fertilizers show that the concentrations of Cd ranged from 0.02 mg/kg to 0.28 mg/kg and it had a mean of 0.14 mg/kg. The Mn concentrations range from 35.7mg/kg to 1,157.8 mg/kg and the mean was 224.5 mg/kg. The highest concentration of 1,157.8 mg/kg was recorded for Crystallizer. For the naturally occurring fertilizers, the Layers litter Shika brown recorded the highest Mn concentration of 137.0 mg/kg. All others have concentrations below 100.0 mg/kg. The Ni concentrations in the organic fertilizers ranged from 0.64 mg/kg to 5.26 mg/kg and the mean was 1.62 mg/kg. The Fe concentrations in the organic fertilizers had a ranged of 7.69 mg/kg to 5000 mg/kg and the mean was 1,365.47 mg/kg. The processed organic fertilizers recorded Fe concentrations in the order Crystallizer> Royal fertilizer plus >Mega green; 4,368.0 mg/kg>1343.6 mg/kg>216.6 mg/kg respectively. The concentration of Pb in the organic fertilizer samples ranged from BDL to 1.34 mg/kg and the mean was 42.0 mg/kg. The highest concentration 1.34 mg/kg was recorded by Cow dung of the open milking herd. The concentration of Cu in the organic fertilizers ranged from 1.10 mg/kg to 3.57 mg /kg with Cow dung milking herd recording the highest concentration of 3.57mg/kg. The organic fertilizers have mean Cu concentration of 1.83 mg/kg. Zn concentration in the organic fertilizers ranged from 7.67 mg/kg to 16.29 mg/kg the mean of Zn concentrations was 9.94 mg/kg. Layers litter Shika brown recorded the highest concentration of 16.29 mg/kg.

Table4.2: Elemental composition of organic fertilizer samples in mg/kg by AAS method

S/N	SAMPLE ID	Cd	Cu	Fe	Ni	Mn	Pb	Zn
1	CRC14	0.22	1.28	1,343.60	0.219	331.00	1.04	7.67
2	CRC15B	0.28	1.10	4,368.00	0.526	1,157.80	1.17	6.92
3	CRC 15	0.13	1.17	216.60	0.118	159.00	BDL	8.11
4	CRNL16	0.17	1.78	101.20	0.074	137.00	0.16	8.35
5	CRNL17	0.14	2.03	742.00	0.158	50.82	0.03	16.29
6	CRND18	0.12	1.25	453.70	0.078	66.74	0.03	8.65
7	CRND19	0.10	3.57	7.69	0.140	40.32	1.34	8.36
8	CRNS20	0.02	2.65	56.44	0.078	35.37	BDL	12.21
9	CRNS21	0.04	1.63	5000.0	0.064	42.57	0.03	12.91
	Mean	0.14	1.83	1,365.50	0.162	224.51	0.42	9.94
	Range	0.02- 0.28	1.10- 3.57	7.69- 500.0	0.064- 0.526	35.37- 1,157.8	BDL- 1.34	7.67-16.29
10	CRC12	63.3	1.12	160.280	0.123	1,186.6	1.63	3.97
11	CRC13	62.1	5.29	56.260	0.361	41.08	1.18	24.44
	Mean	62.7	3.21	108.270	0.242	613.8	1.41	14.21

KEY:

CRC14 =Royal fertilizer plus, CRC15b= Mega Green, CRNL16= Layers litter (Shika brown), CRNL17= Layers litter (BZ farm) CRND18= Cow dung (open grazing herd), CRND19= Cow dung (milking herd non-grazing), CRNS20=Sheep dropping (open grazing flock), CRNS21= Sheep dropping (open hay flock), CRC12=Sokoto phosphate rock, CRC 13= Togo phosphate rock

Table 4.3 shows the elemental composition of inorganic fertilizers by X-ray fluorescence method. The mean concentration of Potassium was 62,954 mg/kg with a range of BDL mg/kg to 142,462 mg/kg. The highest concentration 142,462mg/kg was recorded for Golden (20-210-10) NPK it was not detected in FSFC SSP 18%. Silicon recorded a mean of 8,148 mg/kg with the highest value of 20,400 mg/kg recorded for Tak Agro SSSP18%. It was not detected in Golden (15-15-15) NPK. Vanadium recorded a mean of 29.0 mg/kg the highest concentration was recorded for Tak Agro SSP 18% at 58mg/kg. Vanadium was not detected in FSFC SSP18% and AFCUTT (15-15-15) NPK. Chromium was not detected in FSFC SSP18%. The mean concentration was 34.0 mg/kg with the highest concentration recorded for Sambuka (15-15-15) NPK at 72.0 mg/kg.

Titanium was also detected in all the inorganic sample fertilizer at a mean of 631mg/kg. The highest concentration was recorded for Tak Agro SSP 18% at 1,897 mg/kg.

Table4.3: Elemental Composition of Inorganic Fertilizer samples in mg/kg by XRF

SAMPLE CODE	method					
	Al	Ca	Cr	Si	Ti	V
CRP1	BDL	BDL	72.0	288.0	62	24.0
CRP2	BDL	BDL	32.0	BDL	113	2.0
CRP3	110,400	9,401	31.0	9,630	335	BDL
CRP4	79,580	BDL	24.0	17,640	1,773	33.0
CRP5	65,320	2,761	26.0	15,840	1,773	45.0
CRP6	59,800	BDL	40.0	7,110	1,327	51.0
CRP7	BDL	6,378.4	47.0	816	119	52.0
CRP8	77,280	1,426	37.0	20,400	1,897	58.0
CRP9	5,520	84,799	BDL	1,608	55	BDL
Mean	44,211	11,641	34.0	8,148	631	29.0
Range	0- 110,400	0- 84,799	0- 72.0	0- 20,400	55- 1,897	0- 58.0

BDL=Bellow detectable limit

Key:

CRP1= Sambuka four corner vital (15-15-15) NPK

CRP2 Golden (15-15-15) = NPK

CRP3= AFCUTT (15-15-15) NPK

CRP4= Tak (20-10-10) NPK

CRP5= Maishaho (20-10-10) NPK

CRP6= Golden (20-10-10) NPK

CRP7= DAP (Diammonium phosphate)

CRP8= Tak Agro (Single superphosphate 18%)

CRP9= FSFC (Single superphosphate 18%)

From results of Table 4.4 the mean concentration of Chromium in the organic fertilizers was 0.72 mg/kg with a range of 0.17 mg/kg to 2.53 mg/kg. The highest concentration was recorded for Mega green fertilizer at 2.53 mg/kg, all the rest have concentrations slightly above 0.10 mg/kg.

The mean concentration of Potassium in organic fertilizer is 11,724 mg/kg with a range of 5,266.8 mg/kg to 23,708 mg/kg. The highest concentration (23,708 mg/kg) was recorded for Cow dung grazing herd followed by Cow dung milking herd at 23,254 mg/kg. Silicon recorded a mean of 8,215.9 mg/kg with the highest value of 12,570 mg/kg recorded for Layers litter BZ farm followed by Sheep dropping grazing flock. Vanadium recorded a mean concentration of 7.6 mg/kg. The concentration ranged from below instrument detection limit to 24.4 mg/kg, with the highest concentration recorded for Cow dung milking herd at 18.3 mg/kg. Titanium in organic fertilizers recorded a mean of 1,176 mg/kg. The range was below detection limit to 4,836 mg/kg. The highest concentration was recorded for Mega green processed organic fertilizer. Its detection was below instrument detection limit for Sheep dropping hay flock.

Table4.4: Results of elemental composition of Organic Fertilizer samples by XR method

SAMPL E CODE	Al	Ca	Cr	Si	Ti	V
CRC14	32,200	17,802	0.3	8,130.0	372.0	BDL
CRC15B	3,634	11,084	2.5	6,960.0	4,836. 0	6.1
CRNL16	BDL	19,174	1.0	2,157.0	516.0	BDL
CRNL17	19,780	7,567	0.2	12,570. 0	797.30	12.0
CRND18	28,520	5,436	0.3	8,910.0	669.60	BDL
CRND19	BDL	7,668	1.0	6,750.0	670.0	18.3
CRNS20	21,160	5,292	0.4	10,860. 0	1,550. 0	24.4
CRNS21	8,740	11,956	0.2	9,390.0	BDL	BDL
MEAN	14,254	10,747	0.7	8,215.9	1176.0	7.6
RANGE	0- 28,520	5,292- 19,174	0.2-2.5	2,157.0 - 12,570. 0	0- 4,836. 0	0-24.4

KEY:

CRC14 =Royal fertilizer plus

CRC15b= Mega Green

CRNL16= Layers litter (Shika brown)

CRNL17= Layers litter (BZ farm)

CRND18= Cow dung (open grazing herd)

CRND19= Cow dung (milking herd non-grazing)

CRNS20=Sheep dropping (open grazing flock)

CRNS21= Sheep dropping (open hay flock)

Table 4.5 shows that, Cs was detected in all the four selected inorganic fertilizers analyzed using NIRR-1 facilities.

The mean concentration of Cs in the inorganic fertilizers was 3.3 ± 0.3 mg/kg with a range of 1.2-5.4 mg/kg. Tak Agro SSP 18% recorded the highest concentration of 5.4 mg/kg. Arsenic was not detected in Sambuka (15-15-15) NPK. The highest concentration was recorded for DAP fertilizer at 18.1 mg/kg. The mean was 4.98 mg/kg and the range was BDL- 18 mg/kg.

Cobalt was detected in all the inorganic fertilizers at a mean concentration of 4.3 mg/kg and at a range of 2.8-6.5 mg/kg. The highest concentration was recorded for Tak Agro SSP 18%, while DAP recorded the lowest concentration. Antimony in the Table 4.5 had a mean value of 0.99 ± 0.1 mg/kg. The highest concentration was recorded for DAP fertilizer at 36.0 ± 0.2 mg/kg. Antimony was not detected in AFCUTT (15-15-15) NPK and in Maishaho (15-15-15) NPK.

Table4.5: Results showing elemental composition of inorganic fertilizers using NIR-1

Sample Code	Cs	Co	Sb	As
CRP3	4.30	3.30	BDL	BDL
CRP5	2.40	4.50	BDL	0.700
CRP7	1.20	2.80	3.60	18.10
CRP8	5.40	6.50	0.36	1.10
Mean	3.33	4.30	0.99	4.98
Range	1.20-5.40	2.80-6.50	BDL-3.60	BDL-18.10

Key:

CRP3= AFCUTT (15-15-15) NPK,

CRP4= Tak (20-10-10) NPK

CRP5= Maishaho (20-10-10) NPK,

CRP7= DAP (Diammonium phosphate),

CRP8= Tak Agro (Single superphosphate 18%)

From Table 4.6, Cs was detected in only Layers litter Shika brown at 0.3 ± 0.1 mg/kg and in Layers litter BZ farm at 1.13 ± 0.114 mg/kg. The mean concentration was 0.18 ± 0.03 mg/kg. All the other samples recorded BDL using NIRR-1 facilities.

The mean Cobalt concentration in the soil is 12 mg/kg, ranging from 0.1 – 70 mg/kg. Cobalt was detected in all the organic fertilizers at a mean concentration of 2.68 ± 0.14 mg/kg and at a range of 1.1 mg/kg -9.7 mg/kg; the highest concentration was recorded for Royal fertilizer plus which is a processed organic fertilizer. Crystallizer recorded 1.7 mg/kg. The naturally occurring fertilizers were led by Layers litter Shika brown /BZ farm at 2.4 ± 0.2 mg/kg and 2.2 ± 0.1 mg/kg respectively. All the others fertilizers recorded concentration > 1.0 mg/kg. The recommended human health screening level is 660 mg/kg.

Arsenic is a toxic metal known to cause cancer to humans. It is released into the environment through anthropogenic activities such as mining. Background concentration in soils is 1 mg/kg to 40 mg/kg. The highest concentration was recorded for Royal fertilizer plus at 5.7 ± 0.2 mg/kg. Naturally occurring fertilizers recorded concentration < 1 mg/kg. Arsenic is used as a growth promoter in poultry and pigs and in the preservation of wood. The concentration of Arsenic in feeds ranges from 10-50 mg/kg.

Antimony in the organic fertilizers recorded a mean 0.06 ± 0.028 mg/kg. Antimony was detected in only two fertilizers, Royal fertilizer plus and Layers litter Shika brown at concentrations of 0.27 ± 0.08 mg/kg and 0.24 ± 0.06 mg/kg respectively. Antimony background concentration in soil is 0.3 mg/kg-8.6 mg/kg

Table4.6: Results showing elemental composition of organic fertilizers by using NIRR-1

SAMPLE CODE	Cs	Co	Sb	As
CRC14	BDL	9.70	0.27	5.70
CRC15B	BDL	1.70	BDL	0.34
CRNL16	0.30	2.40	0.24	0.72
CRNL17	1.13	2.20	BDL	0.60
CRND18	BDL	1.30	BDL	0.30
CRND19	BDL	1.20	BDL	0.40
CRNS20	BDL	1.80	BDL	0.70
CRNS21	BDL	1.10	BDL	0.20
MEAN	0.18	2.68	0.06	1.12
RANGE	BDL-1.13	1.10-9.70	BDL-0.27	0.20-5.70

KEY:

CRC14 =Royal fertilizer plus, CRC15= Crystallizer, CRC15b= Mega Green, CRNL16= Layers litter (Shika brown), CRNL17= Layers litter (BZ farm), CRND18= Cow dung (open grazing herd), CRND19= Cow dung (milking herd non-grazing), RNS20=Sheep dropping (open grazing flock) CRNS21= Sheep dropping (open hay flock).

For Table 4.7 the concentrations of Cr, Co and Cs in the organic fertilizers were significantly different from those found in the inorganic fertilizers ($P < 0.05$).

But the result shows that there was no significant variability in the, K, As, Fe, Zn, and Sb concentrations in the organic and inorganic fertilizers ($P < 0.05$).

Table4.7 the metal concentrations in the selected organic and inorganic fertilizers were compared with the Student t-test.

Metals	Types	Mean	Std. Deviation	Std. Error	t-value	DF	P
Ti	Organic	353.75	550.846	159.016	0.913	22	.371
	Inorganic	848.42	1794.357	517.986			
V	Organic	7.80	9.636	2.782	2.044	22	.053
	Inorganic	51.88	74.087	21.387			
Mn	Organic	323.108	119.8967	34.6112	0.595	22	.558
	Inorganic	394.417	397.5277	114.7564			
K	Organic	20800	10833.292	3127.302	0.986	22	.335
	Inorganic	29000	28446.045	8211.666			
As	Organic	.5267	.21719	.06270	1.969	22	.062
	Inorganic	4.3867	6.78643	1.95907			
Cr	Organic	8.642	4.4059	1.2719	2.256	22	.034
	Inorganic	56.292	73.0420	21.0854			
Fe	Organic	5121.83	2690.748	776.752	1.800	22	.086
	Inorganic	8308.25	5510.901	1590.860			
Co	Organic	1.733	.5348	.1544	3.792	22	.001
	Inorganic	4.858	2.8044	.8096			
Zn	Organic	80.25	33.276	9.606	.494	22	.627
	Inorganic	64.50	105.413	30.430			
Sb	Organic	.0450	.10587	.03056	1.705	22	.102
	Inorganic	.7342	1.39616	.40304			
Cs	Organic	.258	.4611	.1331	3.126	22	.005
	Inorganic	2.308	2.2244	.6421			

Note $P \leq 0.05$ significant difference in concentration

$P > 0.05$ no significant difference in concentration

For Mg, V, Dy, Sm, Sc, Cr, Co and Cs the concentrations in the organic fertilizers were significantly different from those found in the inorganic fertilizers ($P < 0.05$). But there was no significant variability in the Al, Ca, Na, and K, As, La, Unp, Fe, Zn, and Br, Rb, and Sb concentrations in the organic and inorganic fertilizers ($P > 0.05$).

The variability in the concentrations of the metals in the different fertilizers as branded in their respective sources was tested with the analysis of variance. The result used here are those tested with the instrumental neutron activation analysis for the twelve samples.

Table 4.8 shows the means were ranked using the Duncan Multiple Range Test. The concentrations of the individual metal and significant difference are indicated by letters along the mean scores.

Only AAS detected Cd and Pb in the fertilizer samples. Zn was detected by all the techniques. The XRF technique was significantly different in its detection of the metal concentration in the fertilizers from the AAS and the INAA. Between the AAS and the INAA, no significant difference was observed in their detection levels.

Table4.8 Statistical mean concentration of heavy metals in mg/kg detected by the different techniques

Techniques	Cd	Cu	Fe	Ni	Mn	Pb
	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E
AAS	0.18±0.03a	0.22±0.02b	115.58±20.79b	0.38±0.05b	35.58±6.09b	0.07±0.01a
XRF	BDL	4.32±0.51a	4,954.6±718.34a	2.70±7.36a	133.47±18.47ab	BDL
INAA	BDL	BDL	BDL	BDL	202.01±45.45a	BDL
Total	0.06±0.01	1.52±0.25	1,690.1±318.14	14.4±3.05	123.69±17.50	0.02±0.00

Techniques	Zn	Cr	Si	Ti	V
	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E
AAS	007.01±1.50b	BDL	BDL	BDL	BDL
XRF	361.0±62.07a	23.65±4.00a	9,386.1±1199.1a	1,418.2±278.42a	22.83±3.86a
INAA	44.92±11.23b	09.52±1.99b	BDL	360.65±167.35b	17.88±7.22a
Total	137.64±25.43	11.06±1.73	3,128.7±567.08	592.95±120.71	13.57±2.85

Technique	K	As	Co	Sb	Cs
	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E
AAS	BDL	BDL	BDL	BDL	BDL
XRF	50,532.7±8699.6a	BDL	BDL	BDL	BDL
INAA	29,834.60±16394.a	1.48±0.65	1.98±0.40a	0.23±0.13a	0.73±0.25a
Total	26,789.10±6422.17	0.49±0.22	0.66±0.16	0.08±0.04	0.24±0.09

Note: Means with the same letter are not significantly different at 0.05

In Table 4.9, the activity concentrations were in this order $^{40}\text{K} > ^{232}\text{Th} > ^{226}\text{Ra}$. The ^{40}K has a mean activity of $566.32 \pm 0.36 \text{Bqkg}^{-1}$ ranging from 101.45 to 1033.60Bqkg^{-1} . The ^{226}Ra activity concentration ranges from 22.99 to 34.48Bqkg^{-1} with a mean activity of $28.36 \pm 1.96 \text{Bqkg}^{-1}$. ^{232}Th has mean activity concentration of $57.33 \pm 0.74 \text{Bqkg}^{-1}$ ranging from 40.71 to 77.10Bqkg^{-1} . The Raeq (Radium equivalent) ranges from 113.06 to 207.69Bqkg^{-1} with a mean activity of $134.84 \pm 3.130 \text{Bqkg}^{-1}$.

Tables 4.9: Specific activity concentrations in Bq/kg of radionuclides in inorganic fertilizers

Inorganic Fertilizer.	K-40	error ±	Ra-226	error±	Th-232	error ±	Raeq Bq/kg
CRP1	198.590	0.129	30.269	2.734	50.966	1.178	118.442±4.04
CRP2	2,481.600	1.594	22.987	10.094	49.601	2.057	113.059±13.7
CRP3	317.850	0.204	23.754	1.425	40.707	1.482	106.440±3.112
CRP4	356.140	0.229	24.773	0.359	60.905	0.551	139.290±1.755
CRP5	198.590	0.128	30.269	2.734	50.966	1.178	118.442±4.04
CRP6	1,033.620	0.665	26.187	0.226	71.266	0.063	207.686±0.95
CRP7	101.450	0.065	38.476	0.033	77.101	0.068	156.540±0.166
CRP8	227.010	0.149	23.335	0.020	54.457	0.048	118.690±0.217
CRP9	179.440	0.115	35.226	0.030	60.000	0.053	134.840±0.198
Mean	566.032	0.364	28.364	1.962	57.329	0.742	134.826±3.130
Range	101.450- 2,481.600	0.065- 1.596	22.990- 38.480	0.020- 10.100	40.710- 77.100	0.040- 1.482	113.060- 207.690

Key:

CRP1= Sambuka four corner vital (15-15-15) NPK, CRP2 Golden (15-15-15) = NPK

CRP3= AFCUTT (15-15-15) NPK, CRP4= Tak (20-10-10) NPK, CRP5= Maishaho (20-10-10) NPK, CRP6= Golden (20-10-10) NPK, CRP7= DAP (Diammonium phosphate), CRP8= Tak Agro (Single superphosphate 18%), CRP9= FSFC (Single superphosphate 18%)

Statistically the means with the same letter are not significantly different at $P > 0.05$

The mean Radium -226 activity concentration of AFCUTT (15-15-15) NPK and Maishaho (15-15-15) NPK are not significantly different at $24.467 \pm 0.713d$ and $24.953 \pm 0.180cd$ $Bqkg^{-1}$.

Sambuka (15-15-15) NPK and CP2 have mean Thorium activity at $51.6 \pm 0.59e$ and $50.63 \pm 1.03e$ $Bqkg^{-1}$ which are not significantly different at 0.05.

Table 4.10: The Results of Statistical comparison of activity concentration of inorganic fertilizer samples

Types of Fertilizers	K-40	Bqkg ⁻¹	Ra-226	Bqkg ⁻¹	Th-232	Bqkg ⁻¹
	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E
CRP1	0.128±0.0003f	199.050±0.457f	0.027±0.001abc	31.640±1.37abc	0.0452±0.001e	51.600±0.59e
CRP2	1.598±0.0018a	2,488.400±6.838a	0.024±0.004bcd	28.034±5.05bcd	0.0444±0.001e	50.630±1.03e
CRP3	0.207±0.002d	321.120±3.266d	0.021±0.001d	24.467±0.713d	0.0364±0.007e	41.450±0.74f
CRP4	0.231±0.002c	358.850±2.708c	0.022±0.0002cd	24.953±0.180cd	0.0537±0.0003c	61.180±0.28c
CRP5	0.128±0.0003f	199.050±0.457f	0.027±0.0012abc	31.640±1.37abc	0.0452±0.0005e	51.60±0.59e
CRP6	0.662±0.0025b	1,029.800±3.810b	0.022±0.0011cd	24.971±1.217cd	0.062±0.001b	70.070±1.20b
CRP7	0.064±0.001h	99.305±2.145h	0.032±0.0015a	36.739±1.737a	0.0674±0.0002a	76.870±0.23a
CRP8	0.148±0.0015e	227.210±0.241	0.019±0.0005d	22.836±0.50d	0.048±0.0003d	54.180±0.28d
CRP9	0.115±0.0008g	178.280±1.166g	0.029±0.0011ab	34.010±1.22ab	0.0518±0.0009c	59.020±0.98c
mean	0.364±0.113	566.790±176.5	0.025±0.0011	28.809±1.217	0.0503±0.0022	57.390±2.48

Note: Means with the same letter are not significantly different at 0.05

Key:

CRP1= Sambuka four corner vital (15-15-15) NPK

CRP2 Golden (15-15-15) = NPK

CRP3= AFCUTT (15-15-15) NPK

CRP4= Tak (20-10-10) NPK

CRP5= Maishaho (20-10-10) NPK

CRP6= Golden (20-10-10) NPK

CRP7= DAP (Diammonium phosphate)

CRP8= Tak Agro (Single superphosphate 18%)

CRP9= FSFC (Single superphosphate 18%)

Table 4.11 shows the ^{40}K specific activity concentration of organic fertilizers ranging from 120.16 to 907.98Bqkg⁻¹ with a mean of 305.33 ±0.20 Bqkg⁻¹.

The ^{226}Ra activity concentration in the organic fertilizer has a mean of 24.8749±0.02 Bqkg⁻¹ with a range of 121.83 to 65.68Bqkg⁻¹.

^{232}Th has mean activity concentrations of 45.04±0.05Bq kg⁻¹ with a range of 14.66 to 60.21Bqkg⁻¹. Royal fertilizer plus recorded the highest concentration activity of ^{40}K at 907.98±0.58Bqkg⁻¹. The organic fertilizers show no significant difference in the Raeq values.

Tables 4.11: The Results of the Specific activities of radionuclide in organic fertilizers

Organic fertilizer	K-40	error±	Ra-226	error±2	Th-232	error±3	Raeq. Bq/kg
CRC14	907.98	0.59	65.68	0.06	53.01	0.04	212.34±0.68
CRC15	142.84	0.09	12.83	0.01	48.19	0.04	92.74±0.15
CRNL16	227.01	0.15	25.18	0.02	42.19	0.04	102.99±0.20
CRNL17	361.56	0.23	24.18	0.02	43.19	0.04	113.79±0.29
CRND18	207.88	0.13	20.22	0.02	14.67	0.01	57.19±0.164
CRND19	244.70	0.16	18.77	0.02	52.11	0.05	112.13±0.22
CRNS20	120.16	0.08	18.66	0.02	52.59	0.05	103.12±0.14
CRNS21	139.34	0.09	13.67	0.01	39.22	0.03	80.49±0.14
CRCD22	396.52	0.26	24.68	0.02	60.21	0.05	141.32±0.33
MEAN	305.33	0.19	24.87	0.02	45.04	0.04	112.90±0.26

KEY:

CRC14 =Royal fertilizer plus, CRC15b= Mega Green, CRNL16= Layers litter (Shika brown), CRNL17= Layers litter (BZ farm),

CRND18= Cow dung (open grazing herd), CRND19= Cow dung (milking herd non-grazing), CRNS20=Sheep dropping (open grazing flock)

CRNS21= Sheep dropping (open hay flock), CRCD22= food concentrate for Cows

From Table 4.12 means with the same letters are not significantly different at $P < 0.05$.

Mega green and Sheep dropping hay flock have Potassium activity at 142.09Bq/kg and 137.64Bq/kg which is not significantly different. Layers litter Shika brown and Layers litter BZ farm have ^{226}Ra activity that is not significantly different at $P < 0.05$.

Cow dung milking herd and Sheep dropping hay flock have ^{232}Th activity that is not significantly different.

Table4.12: The Results of Statistical comparison of activity concentrations of organic fertilizer samples

Types of Fertilizers	K-40	Bqkg ⁻¹	Ra-226	Bqkg ⁻¹	Th-232	Bqkg ⁻¹
	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E
CRC14	0.580±0.004a	902.38±5.61a	0.06±0.0007a	64.890.789a	0.046±0.001b	52.12±0.89b
CRC15B	0.091±0.001g	142.09±0.75g	0.01±0.0001d	12.69±0.140d	0.042±0.0003c	47.73±0.35c
CRNL16	0.144±0.003e	223.14±3.87e	0.02±0.0016b	24.47±0.713b	0.036±0.0007d	41.45±0.74d
CRNL17	0.231±0.002c	358.85±2.71c	0.02±0.0002b	22.82±1.797b	0.037±0.0011d	41.97±1.22d
CRND18	0.132±0.002f	205.36±2.50f	0.02±0.0015c	18.46±1.758c	0.013±0.0002f	14.47±0.20f
CRND19	0.156±0.002d	241.85±2.85d	0.02±0.0009c	17.73±1.043d	0.045±0.0008b	51.25±0.86b
CRNS20	0.076±0.001h	118.61±1.56h	0.02±0.0003c	18.36±0.300c	0.046±0.0003b	52.25±0.35b
CRNS21	0.089±0.001g	137.64±1.71g	0.01±0.001d	12.98±0.695d	0.034±0.0004e	38.77±0.46e
CRCD22	0.253±0.002b	392.86±3.65b	0.02±0.001b	23.87±0.811b	0.052±0.001a	59.12±1.08a
Mean	0.195±0.036	302.53±55.86	0.02±0.003	24.039±3.647	0.039±0.003	44.348±2.96

Note: Means with the same letter are not significantly different at P<0. 05

KEY:

CRC14 =Royal fertilizer plus,

CRC15b= Mega Green,

CRNL16= Layers litter (Shika brown),

CRNL17= Layers litter (BZ farm),

CRND18= Cow dung (open grazing herd),

CRND19= Cow dung (milking herd non-grazing),

CRNS20=Sheep dropping (open grazing flock)

CRNS21= Sheep dropping (open hay flock),

CRCD22= food concentrate for Cows

Table 4.13 shows the Radium equivalent of inorganic fertilizers having a mean of 134.82Bq/kg. Dap fertilizer has the highest value of 207.69Bq/kg. The lowest value is recorded for AFCUTT (15-15-15) NPK

Table4.13: The Results of Radium equivalent (R_{aeq}) activity of inorganic fertilizers

s/n	Fertilizer type	Raeq Bq/kg
1	CRP1	118.44
2	CRP2	113.06
3	CRP3	106.44
4	CRP4	139.29
5	CRP5	118.44
6	CRP6	207.69
7	CRP7	156.54
8	CRP8	118.69
9	CRP9	134.84
	MEAN	134.82

Key:

CRP1= Sambuka four corner vital (15-15-15) NPK

CRP2 Golden (15-15-15) = NPK

CRP3= AFCUTT (15-15-15) NPK

CRP4= Tak (20-10-10) NPK

CRP5= Maishaho (20-10-10) NPK

CRP6= Golden (20-10-10) NPK

CRP7= DAP (Diammonium phosphate)

CRP8= Tak Agro (Single superphosphate 18%)

CRP9= FSFC (Single superphosphate 18%)

Table 4.14 shows the Radium equivalent (R_{aeq}) activity of organic fertilizers. The mean is 112.34Bq/kg. The highest value of 212.34 Bq/kg was recorded for Royal fertilizer plus. The lowest at 57.19Bq/kg is recorded for Cow dung open grazing herd.

Table4.14: The Results of Radium equivalent (Raeq) activity of organic fertilizers

s/n	Fertilizer	Raeq Bq/kg
1	CRC14	212.34
2	CRC15	92.74
3	CRNL16	102.99
4	CRNL17	113.79
5	CRND18	57.19
6	CRND19	112.13
7	CRNS20	103.12
8	CRNS21	80.49
9	CRCD22	141.32
	MEAN	112.90

KEY:

CRC14 =Royal fertilizer plus,

CRC15= Crystallizer,

CRNL16= Layers litter (Shika brown),

CRNL17= Layers litter (BZ farm),

CRND18= Cow dung (open grazing herd),

CRND19= Cow dung (milking herd non-grazing),

CRNS20=Sheep dropping (open grazing flock)

CRNS21= Sheep dropping (open hay flock),

CRCD22= food concentrate for Cows

Table 4.15 presents the results of the specific activity of ^{226}Ra , ^{232}Th and ^{40}K in phosphate fertilizers from different countries.

Table4.15: The Results of the Specific activity of ^{226}Ra , ^{232}Th and ^{40}K in phosphate fertilizers from different countries (Bqkg^{-1})

Country	^{226}Ra	^{232}Th	^{40}K	Raeq	Ref
Egypt	301	24	3	336	Hussein(1994)
	366	66.7	4	462	Khalifa and El-Arabi (2005)
USA	780	49	200	865	Guimond and Hardin (1989)
Finland	54	11	3200	316	Mustonen(1985)
Pakistan	526	50	221	615	Khan <i>et al</i> (1998)
Italy	120	3.5	4000	433	Right <i>et al</i> (2005)
Nigeria	28	57	566	134	Present study for inorganic fertilizers
	24	45	305	112	Present study for organic fertilizers

Table 4.16 presents the values of Hex (external radiation hazard) and Hin (internal radiation hazard) expressing radiation hazard in inorganic fertilizers.

Golden (15-15-15) NPK has the highest Hex (external radiation hazard) and the highest Hin (internal radiation hazard) at 0.83 and 0.77. AFCUTT recorded the lowest external and internal radiation hazards at 0.77 and 0.35 respectively.

Table4.16: The Values of Hex and Hin expressing radiation hazard in inorganic fertilizers

s/n	fertilizer type	Hex	Hin
1	CRP1	0.39	0.32
2	CRP2	0.83	0.77
3	CRP3	0.35	0.29
4	CRP4	0.44	0.29
5	CRP5	0.39	0.32
6	CRP6	0.55	0.48
7	CRP7	0.53	0.42
8	CRP8	0.38	0.32
9	CRP9	0.46	0.36
	Mean	0.48	0.39

Key:

CRP1= Sambuka four corner vital (15-15-15) NPK

CRP2 Golden (15-15-15) = NPK

CRP3= AFCUTT (15-15-15) NPK

CRP4= Tak (20-10-10) NPK

CRP5= Maishaho (20-10-10) NPK

CRP6= Golden (20-10-10) NPK

CRP7= DAP (Diammonium phosphate)

CRP8= Tak Agro (Single superphosphate 18%)

CRP9= FSFC (Single superphosphate 18%)

Table 4.17 shows the values of Hex (external radiation hazard) and Hin (internal radiation hazard) expressing radiation hazard in organic fertilizers. The mean Hex and Hin values are 0.30 and 0.37 respectively. The highest value of Hex and Hin are 0.57 and 0.75 respectively and are recorded for Royal fertilizer plus. The lowest value of Hex is 0.22 and is recorded for Sheep dropping hay flock. The lowest Hin value is 0.21 and is recorded for Cow dung grazing herd.

**Table4.17: The values of Hex and Hin expressing radiation hazard
organic fertilizers**

s/n	Fertilizer	Hex	Hin
1	CRC14	0.57	0.75
2	CRC15	0.25	0.29
3	CRNL16	0.28	0.35
4	CRNL17	0.31	0.37
5	CRND18	0.15	0.21
6	CRND19	0.30	0.36
7	CRNS20	0.28	0.33
8	CRNS21	0.22	0.25
9	CRCD22	0.38	0.45
	mean	0.31	0.37

KEY:

CRC14 =Royal fertilizer plus,

CRC15= Crystallizer,

CRNL16= Layers litter (Shika brown),

CRNL17= Layers litter (BZ farm),

CRND18= Cow dung (open grazing herd),

CRND19= Cow dung (milking herd non-grazing),

CRNS20=Sheep dropping (open grazing flock)

CRNS21= Sheep dropping (open hay flock),

CRCD22= food concentrate for Cows

The mean absorbed air-dose rate for inorganic fertilizers is 72.31nGyh^{-1} with contributions of 23.60, 13.03 and 35.1 nGyh^{-1} from ^{40}K , ^{226}Ra and ^{232}Th respectively are shown in Table 4.18. The range of dose rate for Potassium (^{40}K) was 7.48 to 103.48nGyh^{-1} with the highest dose rate recorded for Golden (15-15-15) NPK. The range for Radium (^{226}Ra) was $10.97\text{-}17.78\text{nGyh}^{-1}$ with the highest dose rate recorded for DAP fertilizer at 17.78nGyh^{-1} .

Table4.18: The Air absorbed dose rates of inorganic fertilizers

s/n	fertilizer type	K-40 nGyh ⁻¹	Ra-226 nGyh ⁻¹	Th-232 nGyh ⁻¹	Total nGyh ⁻¹
1	CRP1	8.28	13.98	31.65	53.91
2	CRP2	103.48	10.97	30.80	144.90
3	CRP3	13.25	10.97	25.28	49.50
4	CRP4	14.85	11.45	37.82	64.12
5	CRP5	8.28	13.98	31.65	53.91
6	CRP6	43.10	12.099	44.26	99.46
7	CRP7	4.23	17.78	47.88	69.89
8	CRP8	9.47	10.78	33.82	54.07
9	CRP9	7.48	16.27	37.26	61.01
	Mean	23.60	13.033	35.60	72.31
	Range	7.48- 103.48	10.97- 17.78	25.28- 37.26	53.91- 144.90

Key:

CRP1= Sambuka four corner vital (15-15-15) NPK

CRP2 Golden (15-15-15) = NPK

CRP3= AFCUTT (15-15-15) NPK

CRP4= Tak (20-10-10) NPK

CRP5= Maishaho (20-10-10) NPK

CRP6= Golden (20-10-10) NPK

CRP7= DAP (Diammonium phosphate)

CRP8= Tak Agro (Single superphosphate 18%)

CRP9= FSFC (Single superphosphate 18%)

In Table 4.18 the organic fertilizers recorded mean of air-absorbed dose rate of $51.59 \text{ n Gy h}^{-1}$. The order was Thorium>Potassium>Radium. Royal fertilizer plus has the highest value 101.23 nGy/h and lowest value 27.1523 nGy/h was recorded by Cow dung grazing herd.

Table4.19: Air- absorbed dose rates of organic fertilizers

s/n	fertilizer type	K-40 nGy/h	Ra-226 nGy/h	Th-232 nGy/h	total nGy/h
1	CRC14	37.86	30.34	34.1	101.23
2	CRC15	5.96	5.93	30.02	41.9
3	CRNL16	9.47	11.63	26.28	47.38
4	CRNL17	15.08	11.17	26.9	53.16
5	CRND18	8.67	9.34	9.37	27.15
6	CRND19	10.2	8.67	32.46	51.34
7	CRNS20	5.01	8.62	32.77	46.4
8	CRNS21	5.81	6.31	18.21	30.33
9	CRCD22	16.53	11.4	37.51	65.45
	Mean	12.73	11.49	27.51	51.59

KEY:

CRC14 =Royal fertilizer plus,

CRC15= Crystallizer,

, CRNL16= Layers litter (Shika brown),

CRNL17= Layers litter (BZ farm),

CRND18= Cow dung (open grazing herd),

CRND19= Cow dung (milking herd non-grazing),

CRNS20=Sheep dropping (open grazing flock)

CRNS21= Sheep dropping (open hay flock),

CRCD22= food concentrate for Cows

Table 4.20 is the Summary of inorganic/ organic fertilizer dose rates and radiation hazard indices. For the inorganic fertilizers the mean air absorbed dose rate is 72.31 nGy/h. Golden (15-15-15) recorded the highest at 144.9 nGy/h. The lowest air absorbed dose rate 49.5 nGy/h was recorded by AFCUTT (15-15-15) NPK. The inorganic fertilizers recorded mean annual effective dose rates 88.37 μ Sv/y. AFCUTT has the highest value 178.23 μ Sv/y; the lowest value 60.51 μ Sv/y was recorded by Tak Agro SSP 18%. The inorganic fertilizers have Raeq mean 134.83 μ Sv/y. Golden (15-15-15) NPK have the value of 207.67 μ Sv/y which is the highest value.

Organic fertilizers have air absorbed dose rate mean 51.59 nGy/h and the highest value 101.23 nGy/h was recorded for Royal fertilizer plus. Cow dung open grazing herd has the lowest value 27.15 nGy/h. The value of mean annual absorbed dose rate of the organic fertilizers was 61.33 μ Sv/y. The sample coded Royal fertilizer plus recorded the highest value 124.51 μ Sv/y while the lowest value 37.30 μ Sv/y was recorded by Sheep dropping hay flock. The Raeq was 112.90 with the highest value 212.34 recorded for Royal fertilizer Plus.

Table4.20: The Summary of inorganic/ organic fertilizer dose rates and radiation hazard indices

s/n	Sample Code	Air absorbed Dose rate nGy/h	Annual effective dose μ Sv/y	Raeq	Hex	Hin
inorganic fertilizers						
1	CRP1	53.91	66.15	118.442	0.398	0.316
2	CRP2	144.9	178.23	113.059	0.832	0.77
3	CRP3	49.5	60.89	106.44	0.542	0.287
4	CRP4	64.12	79.87	139.29	0.443	0.29
5	CRP5	53.91	66.31	118.442	0.398	0.316
6	CRP6	99.46	122.34	207.686	0.549	0.478
7	CRP7	69.89	85.96	156.54	0.527	0.423
8	CRP8	54.07	60.51	118.69	0.384	0.321
9	CRP9	61.01	75.04	134.84	0.459	0.364
	Mean	72..31	88.37	134.83	0.504	0.396
Organic fertilizers						
10	CRC14	101.23	124.513	212.343	0.571	0.749
11	CRC15	41.9	51.54	92.737	0.251	0.285
12	CRNL16	47.38	58.28	102.989	0.278	0.346
13	CRNL17	53.16	65.39	113.786	0.307	0.372
14	CRND18	27.15	33.39	57.198	0.154	0.209
15	CRND19	51.34	63.15	112.13	0.303	0.359
16	CRNS20	46.4	57.07	103.124	0.282	0.329
17	CRNS21	30.33	37.30	80.493	0.217	0.254
18	CRC22	65.45	80.50	141.317	0.383	0.448
	Mean	51.59	61.33	112.90	0.305	0.372

4.2

Discussion

4.2.1 Atomic Absorption

Table 4.1 presents the results of the seven heavy metals analyzed in the fertilizers samples using AAS. Pb was not detected in Tak (20-10-10) NPK, Golden (20-10-10) NPK and DAP. The concentration of Pb in the other samples ranged from 0.1 mg/kg -5.0 mg/kg with a mean of 1.16 mg/kg. The highest concentration of 5.0 mg/kg was recorded for AFCUTT (15-15-15) NPK. This value falls below 10-30mg/kg range in soil (ATSDR Tox. Profile, 2007) or 3-5 mg/kg found in sedimentary rocks (Munkholm, 1992)

The presence of Cadmium in the fertilizers is of great importance because of its toxicity and its ability to accumulate in soil and bio-accumulate in plants and animals (Alloway, 1990). It accumulates in the kidney (WHO, 1992) and it is considered a carcinogen (IARC, 1994).

The range of Cd concentration in the inorganic fertilizers was 0.1 mg/kg -15.9 mg/kg with a mean of 3.6 mg/kg, this value falls within the range of uncontaminated soil (Alloway, 1990). Sambuka (15-15-15) NPK and DAP recorded higher Cd concentration of 10.7 mg/kg and 15.9 mg/kg than all other inorganic fertilizers whose Cd concentration is not significantly different from one another.

The higher Cd concentrations recorded by the two fertilizers could be due to the origin of the raw material from which they were produced and the process of production which may have allowed the transfer of Cadmium into the fertilizer from the rock used in their production as noted by (Brigden, K., Stringer, R.& Santillo ,D. 2002).

Note that, Cd concentration of the phosphate rock samples CRC12 and CRC13 in table4.1 above is high and that fertilizers use phosphate rock as raw material in their manufacture.

The DAP fertilizer showed the highest Cd concentration of 15.9 mg/kg which is not up to the tentative critical phytotoxic level of total Cd which is in the range of 3-8 mg/kg as reported by Kabata-Pendias & Pendias, (1984).

The range of Cu concentration in the inorganic fertilizers was 5.3 mg/kg -32.0 mg/kg with a mean of 11.20 mg/kg. DAP fertilizer recorded the highest Cu concentration of 32.0 mg/kg followed by Sambuka (15-15-15) NPK and AFCUTT (15-15-15) NPK with concentrations of 13.0 and 12.1mg/kg respectively. The other fertilizers analyzed showed no significant difference in the copper concentration. Copper is an essential micronutrient, but it is a potential pollutant when it accumulates in the soil above its threshold level 2-100mg/kg as reported by Munkholm, (1992). The difference in copper concentrations within the fertilizer samples could be due to the amount allowed or added to the fertilizer by the manufacturers as an essential micronutrient for both plants and animals.

The Fe concentrations in the inorganic fertilizers ranged from 12.63 mg /kg- 99. 24 mg /kg and it had the mean of 62.28 mg/kg. The highest concentration of 99.24mg/kg Fe was recorded by FSFC SSP 18% followed by Tak Agro SSP 18%. The DAP and Tak (20-10-10) NPK showed no significant difference in their Fe concentrations. Iron is recognized as beneficial to the growth of plants and crops and to quality of soil (Shaffer, 2001).

Ni had a range of concentrations from 5.8 mg/kg to 127.3mg/kg with mean concentration of 31.0 mg/kg. The highest Ni concentration 127.3mg/kg is recorded in Sambuka (15-15-15) NPK followed by DAP at 62.2mg/kg. .Ni is not a micronutrient, but at high concentration, it could be a pollutant. The abundance of Nickel in rocks and soils is 5 mg/kg to 20mg/kg and 2 mg/kg to 750 mg/kg respectively. The maximum value for Nickel obtained from the inorganic fertilizers analyzed is far below its minimum in soils as reported by (Munkholm, 1992). Kabata- Pendias

&Pendias, (1984) estimated the phytotoxic level of total Nickel in surface soils to be 100mg/kg.

Mn is also recognized as beneficial to plant growth and crops and to the quality of soil. The range of 177.2 mg/kg to 1702.0 mg/kg and a mean of 442.4 mg/kg respectively were recorded for Mn in the inorganic fertilizers analyzed. FSFC SSP 18% fertilizer recorded the highest concentration of Mn followed by DAP fertilizer which recorded a concentration of 475.3 mg/kg.

The range of concentrations of Zn in the inorganic fertilizers was 0.0158 to 39.0mg/kg and a mean concentration of 474.9 mg/kg. DAP fertilizer recorded the highest value of 3900.0 mg/kg followed by Sambuka (15-15-15) NPK 1.539 mg/kg and by FSFC super phosphate 18% fertilizer 1.07 mg/kg. Ogunyele *et al.*, (2001) quoted Reilly (1980) as stating the maximum permissible concentration in food stuff as 40-50mg/kg and the concentration in uncultivated soil of north Guinea Savannah as 31.5 to 402mg/kg. Note that maximum concentration recorded by DAP fertilizer falls within the values obtained in the soils of North Guinea Savannah.

Table 4.2 presents the results of nine organic fertilizer samples analysed using AAS technique. Their Cd concentrations ranged from 0.1 mg/kg to 2.8mg/kg. The mean was 1.4 mg/kg which is 38% less than the concentration of Cd in inorganic fertilizers. The processed organic fertilizers; Royal fertilizer plus, Crystallizer and Mega green showed no significant difference in Cd concentration from naturally occurring fertilizers; Layers litter Shika brown, Layers litter BZ farm, and Cow dung grazing herd. The mean Cd concentration in the organic fertilizers is within the range in soil, 0.01 -2.0 mg/kg (Munkholm, 1992)

The Mn concentration is about 507% its concentration in inorganic fertilizers which ranged from 35.4 mg/kg to 1157.8 mg/kg with a mean of 224.5mg/kg. The value of Mn concentrations of 1,157.8 mg/kg in the samples was the highest and was recorded for Crystallizer followed by Royal fertilizer plus at 33.10mg/kg) and Mega green fertilizers 159.0mg/kg these are all processed

organic fertilizers.

Among the naturally occurring fertilizers the Layers litter Shika brown recorded the highest Mn concentration of 137.0 mg/kg. All others have concentrations below 100.0 mg/kg. Mn is also recognized as beneficial to plant growth and crops and to the quality of soil (Shaffer, 2001).

Ni concentrations in the organic fertilizers ranged from 0.64 mg/kg to 5.26 mg/kg and its mean of 1.62 mg/kg is 38% less than concentration in inorganic fertilizers. The highest concentration was recorded for Crystallizer 5.26 mg/kg followed by Royal fertilizer plus 2.19mg/kg and lastly by Mega green 1.18mg/kg processed organic fertilizers. The difference in concentrations in the processed organic fertilizers could be due to the source and type of raw materials used in their manufacture. Among the naturally occurring fertilizers the Layers litter Shika brown has the highest concentration of 1.59 mg/kg Ni, followed by Cow dung milking herd 1.40 mg/kg) this high concentration of Ni in animal faeces could be because of metallic contamination during the milling of the feeds.

Fe concentrations in the organic fertilizers ranged from 7.69 mg/kg to 5000.0 mg/kg with mean concentration of 1,365.5 mg/kg. The mean Fe concentration in inorganic fertilizer is 219% more than the concentration in organic fertilizers. The processed organic fertilizers recorded Fe concentrations in the order Crystallizer> Royal fertilizer plus >Mega green; 4,368.0 mg/kg>1,343.6 mg/kg>216.6 mg/kg respectively. This difference in concentrations within the fertilizer samples could be deliberate addition by manufacturers since Fe is micronutrient that helps in plant growth.

The mean concentration of Lead (Pb) in the organic fertilizer samples is 0.422mg/kg which is 365% the concentration in inorganic fertilizers. The Lead concentration ranged from BDL to 1.34 mg/kg. Lead was not detected in Mega green and in Sheep dropping of the grazing flock. The

highest concentration 1.34 mg/kg was recorded in Cow dung of the open milking herd, followed by Crystallizer then, Royal fertilizer plus with concentrations of 1.17 mg/kg and 1.04mg/kg respectively. The highest Pb concentration of 1.34 mg/kg is by far less than the concentration in the soil which ranges from 10-30 mg/kg. Lead is a toxic metal that has no known benefits either to humans or to plants.

Copper (Cu) is an essential micronutrient which does not bio-magnify in food. The National Institute for occupational Safety and Health, (1988b) has recommended 2 to 5mg of copper as adequate and safe quantity to be taken by adults on daily basis because it is good for human health (NIOSH,1988b); however, it is a potential pollutant when it accumulates in the soil above its threshold level 2-100mg/kg (Munkholm, 1992). Table 4.2 shows that Cu concentration in organic fertilizers is 165% greater than its concentrations in inorganic fertilizers. The concentration ranged from 1.10 mg/kg to 3.57mg/kg with Cow dung milking herd recording the highest concentration of 3.57mg/kg followed by Sheep dropping grazing flock 2.65mg/kg then Layers litter BZ farm with a concentration of 2.03mg/kg. The other fertilizers recorded concentrations lower than 2.0 mg/kg. The concentrations were below the threshold level of 2-100mg/kg level (Munkholm, 1992) and thus constitute no immediate potential hazard.

Zn is a micronutrient. Its concentration in the organic fertilizer ranged from 7.6mg/kg to 16.29 mg/kg and the mean was 9.9411mg/kg which is 477% less than the concentration in inorganic fertilizers. The Layers litter Shika brown recorded the highest concentration of 16.29mg/kg followed by Sheep droppings of both the open grazing flock and open hay flock. Zinc, just as copper does not bio-accumulate in plants. Its concentration is higher in inorganic fertilizers because it is most associated with ores and soils. Its concentration in USA soils is 10-300mg/kg (Alloway, 1990)

4.2.2 Elemental Analysis of Fertilizers by XRF

X-ray fluorescence analysis was carried out on both inorganic and organic samples for the following elements (Al, Ca, Cr, Ni, Si, Ti, and V.). The results are presented in Tables 4.3 and 4.4 below. The idea of running the XRF was to capture those heavy metals that were not captured by AAS to give a fuller picture of the presence and concentrations of the heavy metal profile in the fertilizers, therefore only metals not captured by AAS technique are discussed.

Table 4.3 shows the results of nine inorganic fertilizer samples that were analyzed by XRF for six elements Al, Ca, Cr, Ni, Si, Ti, and V. Al was not detected in Sambuka (15-15-15) NPK, Golden (15-15-15) NPK and in DAP. The range was BDL to 110,400 mg/kg. The mean concentration of Al in the inorganic fertilizer samples was 44,221mg/kg. The AFCUTT (15-15-15) NPK recorded the highest Al concentration of 110,400 mg/kg.

The range of BDL-84,799 mg/kg Ca was recorded by the inorganic fertilizer samples. Apart from Al and Ca, the other metals that showed any appreciable quantities compared to the above mentioned elements and worthy of analytical discussion is Silicon. Silicon recorded the highest value of 20,400mg/kg for Tak Agro SSSP18%. It was not detected in Golden (15-15-15) NPK. The range was BDL-20,400 mg/kg and the mean was 8.15×10^3 mg/kg

Vanadium recorded a mean of 29 mg/kg with the highest concentration recorded for Tak Agro SSP 18% at 58mg/kg. The lowest concentration was recorded for Golden (15-15-15) NPK. Vanadium was not detected in FSFC SSP18% and AFCUTT (15-15-15) NPK. The Vanadium concentration ranged from BDL to 58 mg/kg with a mean of 29 mg/kg. The highest Vanadium concentration was recorded by Tak Agro ssp18% fertilizer sample.

Chromium (Cr) was also detected in all the fertilizer samples except in FSFC SSP18%. The mean concentration was 34mg/kg with the highest concentration recorded for Sambuka (15-15-15) NPK

at 72 mg/kg all the rest recorded concentrations below 50.0 mg/kg.

The concentration of chromium in the soil is 2-60 mg/kg (Kabata- Pendias & Pendias, 1984). The concentration found in Sambuka 2 mg/kg is higher than the maximum concentration in soils. This fertilizer should not be chosen for soils recording maximum concentration to avoid its build up in the soil.

Titanium was also detected in all the inorganic sample fertilizer at a mean of 631mg/kg. The highest concentration was recorded for Tak Agro SSP 18% at 1,897mg/kg

Table 4.4 presents the results of the determination of five elements (Al, Ca, Cr, Ni, Si, Ti, and V) in eight organic fertilizers samples using XRF. The Cr concentration in the organic fertilizers ranged from 0.17-2.53 mg/kg and the mean was 0.72mg/kg. The highest Cr concentration was recorded by Mega green fertilizer at 2.53mg/kg. All the rest have concentrations slightly above 0.10mg/kg. The concentration of chromium in the soil is in the range of 2-60mg/kg. All the organic fertilizers have Chromium concentration far below the minimum in soil (Kabata- Pendias & Pendias, 1984).

Table 4.4 shows the range of Silicon concentrations in the organic fertilizers as 2,157mg/kg-1, 2570 mg/kg with mean value of 8,215.9 mg/kg. The highest value of 12,570mg/kg recorded for Layers litter BZ farm followed by Sheep dropping grazing flock. All fertilizers except Layers litter Shika brown recorded concentrations greater than 5000 mg/kg.

Vanadium concentrations as seen in Table4.4 ranged from BDL to 24.4 mg/kg with a mean value of 7.6 mg/kg which is lower than the mean value in inorganic fertilizers. The highest concentration was observed in Cow dung milking herd at 18.3 mg/kg. Layers litter BZ farm recorded concentration of 12.0 mg/kg. Royal fertilizer plus one of the two processed organic fertilizers recorded concentration of 61.0 mg/kg. The other fertilizers have BDL Vanadium concentration in

soils is 10-220 mg/kg as reported by Kabata –Pendias & Pendias, (1984).

Titanium in organic fertilizers recorded a mean of 117,600 mg/kg. The range was below detection limit to 483,600 mg/kg. The highest concentration was recorded for Mega green processed organic fertilizer. Royal fertilizer plus recorded a concentration of 372 mg/kg. For the naturally occurring fertilizers the highest concentration was recorded for Sheep dropping grazing flock at 155,000 mg/kg followed by Layers litter Shika brown at 79,730 mg/kg. Its detection was below instrument detection limit for Sheep dropping hay flock.

4.2.3 Instrumental Neutron Activation Analysis of Fertilizers by use of NIRR-1

Table 4.5 presents the result of the determination of four elements in four inorganic fertilizer samples by instrumental neutron activation analysis using The Nigeria Research Reactor-1(NIRR-1).Cs as seen from Table4.5 was detected in all the four selected inorganic fertilizers analyzed using NIRR-1 facilities. The range was from 1.2 mg/kg -5.4mg/kg. The value of the mean concentration of Cs in the inorganic fertilizers was 3.3 ± 0.3 mg/kg. Tak Agro SSP 18% recorded the highest concentration of 5.4mg/kg followed by AFCUTT (15-15-15) NPK at 4.3mg/kg. Arsenic as presented in Table 4.5 had concentration range from BDL- 18mg/kg with a mean of 4.98 mg/kg. Arsenic was not detected in Sambuka (15-15-15) NPK. The highest concentration of Arsenic was recorded for DAP fertilizer at 18.1mg/kg. The highest concentration was within the background concentration in soils. Cobalt is one of the metals essential in small but critical concentrations for the normal growth of plants and animals, but toxic at high concentrations. The mean Cobalt concentration in the soil is 12 mg/kg, ranging from 0.1 – 70 mg/kg. Cobalt concentration in Table4.5 had concentration values ranging from 2.8-6.5 mg/kg with a mean value of 4.3 mg/kg. Cobalt was detected in all the inorganic fertilizers. The highest concentration of

6.5mg/kg was recorded for Tak Agro SSP 18 %. DAP recorded the lowest concentration 2.8mg/kg. The recommended human health screening level is 660 mg/kg. The presence of Cobalt in the fertilizers could be a deliberate action by manufacturers to boost the micronutrient level of the fertilizers.

Antimony in the inorganic fertilizers recorded a mean of 0.99 ± 0.1 mg/kg. The highest concentration was recorded for DAP fertilizer at 36.0 ± 0.2 mg/kg and it was ten times the concentration in Tak Agro SSP 18%. Antimony was not detected in AFCUTT(15-15-15) NPK and in Maishaho (15-15-15)NPK. Antimony background concentration in soil is 0.3-8.6 mg/kg. (Harmsen, K., & Velk, P.L.G. 1985). The concentration of Antimony in the DAP fertilizer is about four times the maximum in soils.

Table 4.6 presents the result of the determination of four elements in eight organic fertilizer samples by instrumental neutron activation analysis using The Nigeria Research Reactor-1(NIRR-1) Cs was detected in only Layers litter Shika brown at 0.3 ± 0.1 mg/kg and in Layers litter BZ farm at 1.13 ± 0.114 mg/kg. All the other samples recorded BDL using NIRR-1 facilities. The mean concentration was 0.18 ± 0.03 mg/kg; this could be from the recent Fukushima accident.

Cobalt is one of the metals essential in small but critical concentrations for the normal growth of plants and animals, but toxic at high concentrations. The Cobalt concentration values in Table 4.6 ranged from a range of 1.1-9.7 mg/kg. Cobalt mean concentration in the soil is 12 mg/kg, ranging from 0.1 – 70 mg/kg. Cobalt was detected in all the organic fertilizers at a mean concentration of 2.68 ± 0.14 mg/kg. The highest concentration was recorded for Royal fertilizer plus which is a processed organic fertilizer. Crystallizer recorded 1.7mg/kg. The naturally occurring fertilizers were led by Layers litter Shika brown /BZ farm at 2.4 ± 0.2 mg/kg and 2.2 ± 0.1 mg/kg respectively. All other fertilizers recorded concentration. >1.0 mg/kg. The recommended human health

screening level is 660 mg/kg.

Arsenic is a toxic metal known to cause cancer to humans. It is released into the environment through anthropogenic activities such as mining. Background concentration in soils is 1 mg/kg to 40 mg/kg. The highest concentration was recorded for Royal fertilizer plus at 5.7 ± 0.2 mg/kg. Naturally occurring fertilizers recorded concentration <1 mg/kg. Arsenic is used as a growth promoter in poultry and pigs and in the preservation of wood. The concentration of Arsenic in feeds ranges from 10-50mg/kg.

Antimony in the organic fertilizers recorded a mean 0.06 ± 0.028 mg/kg. Antimony was detected in only two fertilizers, Royal fertilizer plus and Layers litter Shika brown at concentrations of 0.27 ± 0.08 mg/kg and 0.24 ± 0.06 mg/kg respectively. Antimony background concentration in soil is 0.3-8.6mg/kg.

4.2.4 Comparison of the techniques used for the detection of the metal concentrations in the fertilizers.

Three techniques were used for the detection of the metals in the different fertilizers. The result of the analysis of variance models used to compare their efficacy in detecting the metals are presented in Appendix II. The mean concentration of each of the metals detected by the respective technique is presented in Table 4.8. The means were ranked using the Duncan Multiple Range Test to determine the technique that was more efficient in detecting the concentrations of the individual metal and significant difference is indicated by letters along the mean scores.

The AAS was the only technique that was able to detect the concentration of Cd and Pb in the fertilizer samples. Cd and Pb concentrations were BDL for XRF and the INAA. Zn was detected by all the techniques. The XRF technique was found to detect more concentration of Zn and was significantly different in its detection of the metal concentration in the fertilizers from the AAS

and the INAA. Between the AAS and the INAA, no significant difference was observed in their detection levels of the metal in the fertilizers. Analysis of elements in fertilizers is better performed using either the XRF or the INAA techniques because of their sensitivities and the number of elements they can detect.

The metal concentrations in the selected organic and inorganic fertilizers were compared with the Student t-test. The results presented in Table 4.7 show that the concentration of Ti in both the inorganic and organic fertilizers is significantly different at $P > 0.05$

Cr concentration is significantly different in the two fertilizers at $P < 0.05$. Therefore, in soils where Cr concentrations are high, the used of inorganic fertilizers is not recommended because of their higher concentration of Cr.

4.3 Radiological analysis of fertilizers

The activity concentrations of the naturally occurring radionuclides in all the fertilizer samples were determined by gamma spectrometry using Thallium doped Sodium Iodide (Na (TI)) detector.

The results are presented in Table 4.9 and Table 4.10

Table 4.8 presents the activity concentration of the naturally occurring radionuclides in the fertilizer samples, and it shows that $^{40}\text{K} > ^{232}\text{Th} > ^{226}\text{Ra}$. The ^{232}Th activity concentration is about twice the concentration of ^{226}Ra . The ^{40}K has a mean activity of $566.322 \pm 0.3643 \text{ Bq kg}^{-1}$ ranging from 101.45 to 2,481 Bq kg^{-1} . The ^{226}Ra activity concentration ranges from 22.99 Bq/kg to 34.48 Bq kg^{-1} with a mean activity of $28.3641 \pm 1.9619 \text{ Bq kg}^{-1}$. ^{232}Th has mean activity concentration of $57.3298 \pm 0.7418 \text{ Bq kg}^{-1}$ ranging from 40.71 to 77.10 Bq kg^{-1} . The R_{eq} ranges from 113.06 to 207.69 Bq kg^{-1} with a mean activity of $134.826 \pm 3.130 \text{ Bq kg}^{-1}$.

As can be seen from Table 4.9 for inorganic fertilizers the ^{40}K activity for Golden (15-15-15) NPK

was the highest at $2,481.6 \pm 1.5959$ Bq kg⁻¹ followed by the activity concentration of Golden (20-10-10) NPK at $1,033.62 \pm 0.66473$ Bq kg⁻¹. This was expected due to the potassium composition of their makeup, this is due to the fact that potassium is the most abundant element in the soil (Okeyode, 2010). Sambuka (15-15-15) NPK and Maishaho (20-10-10) NPK recorded the same ⁴⁰K activity at 198.59 ± 0.1277 Bqkg⁻¹ these fertilizers show the same elemental and radiological compositions: they may be the same fertilizers. Even though all fertilizers show abundance of ⁴⁰K activity the lowest activity was recorded for DAP fertilizer at 101.45 ± 0.0653 Bqkg⁻¹. All the fertilizers show ⁴⁰K activity concentrations are within the world average in soil 140.0 to 850.0 Bqkg⁻¹ (UNSCEAR, 2000).

Thorium (²³²Th) was detected in all the fertilizers at >50 Bqkg⁻¹ Table 4.9. The highest ²³²Th activity was recorded for DAP fertilizer at 77.101 ± 0.0676 Bqkg⁻¹ followed by the activity concentration of Golden (20-10-10) NPK at 71.2655 ± 0.0625 Bqkg⁻¹. The ²³²Th in DAP and Golden (20-10-10) NPK exceeded the world average in soil 11.0 -64.0 Bq kg⁻¹ (UNSCEAR, 2000). The higher than world values of ²³²Th displayed by DAP and Golden (20-210-10) NPK fertilizers means that the raw material from which this fertilizers were produced had high concentration of ²³²Th that was transferred to the fertilizers during the production process.

²²⁶Ra was detected in all the fertilizers at $>22.987 \pm 10.094$ Bq kg⁻¹. The highest activity was recorded for DAP fertilizer at 38.4765 ± 0.033 BqKg⁻¹ followed by FSFC SSP 18% at $35.269 \pm 0.2264 \pm 0.0304$ Bqkg⁻¹. The ²²⁶Ra activity concentration is within the world average in soil 17.0-60 BqKg⁻¹ (UNSCEAR, 2000).

Table 4.9 paints a similar scenario with the ⁴⁰K activity concentration for the organic fertilizers ranging from 120.16 to 907.98 Bqkg⁻¹ with a mean of 305.33 ± 0.1963 Bqkg⁻¹. The ²²⁶Ra activity concentration in the organic fertilizer has a mean of 24.8749 ± 0.02140 Bqkg⁻¹ with a range of

121.8257 to 65.6829Bqkg-1. ²³²Th has mean activity concentrations of 45.0425±0.0528Bqkg-1 with a range of 14.662 to 60.2057Bq kg-1. Even though the inorganic fertilizers show slightly higher mean activity concentrations for the three radionuclides; ⁴⁰K, ²²⁶Ra and ²³²Th than in organic fertilizers, they however show no significant difference in the Raeq values. The radium equivalent of the two types of fertilizers, 134 and 112Bqkg-1 for inorganic and organic fertilizers respectively, falls within the permissible limit of 370Bqkg-1 OECD, (1979).

Royal fertilizer plus recorded the highest concentration activity of ⁴⁰K at 907.98±0.5839 Bqkg-1 as seen in Table4.9 this exceeded the world average in soil at 140.0-850.0 Bqkg-1 followed by the activity concentration of Layers litter Shika brown at 361.56±0.2325Bqkg-1. The food concentrate was included to ascertain how much radioactivity was in the feeds, it recorded 396.52±0.255Bqkg-1.

All the organic fertilizers recorded potassium activity above 100Bqkg-1.

The processed organic fertilizers recorded highest and lowest ²²⁶Ra activity which was higher for Royal fertilizer plus at 65.68±0.05567Bqkg-1 this exceeded the world average in soil (17.0-60.0Bqkg-1) and lowest for Crystallizer at 12.83±0.011Bqkg-1. The naturally occurring organic fertilizers recorded highest activity for Layers litter Shika brown at 25.18±0.0212 Bqkg-1 followed by the food concentrate which recorded 24.68±0.0213Bqkg-1. All the other organic fertilizers recorded ²²⁶Ra activity concentrations > 10Bqkg-1 but <60Bqkg-1 which is within the world average in soil of 17.0- 60.0Bqkg-1.

Royal fertilizer plus has the highest activity concentration of 53.008±0.0422Bqkg-1 followed by Cow dung grazing herd and Sheep dropping grazing flock at 52.109±0.045Bqkg-1 and 52.597±0.461Bqkg-1 these fall within the world average (11.0-64.0Bqkg-1).(UNSCEAR,2000).

Table4.13 and 4.14 show the radium equivalent activities in Bq kg-1 for different brands of

inorganic and organic fertilizers. As can be seen from Tables 4.13 and 4.14 the mean radium equivalent activity for both inorganic and organic fertilizers are $134.826 \pm 3.130 \text{ Bq kg}^{-1}$ and $112.902 \pm 0.256 \text{ Bq kg}^{-1}$ respectively, the radium equivalent of organic fertilizers are lower than those of inorganic fertilizers. The R_{aeq} values for both inorganic and organic fertilizers are well below the maximum limit of 370 Bq kg^{-1} . The radium equivalent of 370 Bq kg^{-1} corresponds to the dose rate limit of 1 mSv of radiation for the public (Jibiri *et al.*, 2009).

The R_{aeq} values were used in calculating the radiological hazard indices. The calculated values of the external hazard (Hex) index are found in Table 4.16 and 4.17 with the corresponding values of the internal radiation exposure index (Hin).

For radiation hazard to be negligible, the Hex and Hin values must be less or equal to unity as (UNSCEAR, 2000). The Hex and Hin values for inorganic fertilizers range from 0.398 to 0.832 with a mean of 0.482 for Hex and 0.29 to 0.77 with a mean of 0.395 for Hin respectively, see Table 4.16 and 4.17. All these values for both inorganic and organic fertilizers are less than unity, signifying that the use of these fertilizers may constitute no radiological hazard.

The absorbed dose rate is the energy impacted by ionizing radiation per unit mass of irradiated material; it has the units of Gray or Rad.

The results are tabulated in Tables 4.18 and 4.19. The mean absorbed air-dose rate for inorganic fertilizers was 72.31 nGy h^{-1} with contributions of 23.60, 13.03 and 35.1 nGy h^{-1} from ^{40}K , ^{226}Ra and ^{232}Th respectively. The mean air-dose rate of the fertilizers is slightly higher than the world average 51 nGy h^{-1} (UNSCEAR, 2000). The absorbed air dose rate is higher than the world average due to the probable presence of radioactive materials in the fertilizers either the naturally occurring radioactive materials or those obtained from recycling of hazardous waste.

The range of dose rate for Potassium (^{40}K) was 7.48 to 103.48 nGy h^{-1} with the highest dose rate recorded for Golden (15-15-15) NPK followed by Golden (20-10-10) NPK at 43.10 nGy h^{-1} . The range for Radium (^{226}Ra) was 10.97-17.78 nGy h^{-1} with the highest dose rate recorded for DAP fertilizer at 17.78 nGy h^{-1} followed by FSFC SSP 18% at 16.27 nGy h^{-1} . The highest dose rate for the Thorium (^{232}Th) was recorded for DAP at 47.83 nGy h^{-1} followed by the dose rate of Golden (20-10-10) NPK at 44.26 nGy h^{-1} .

The organic fertilizers recorded mean of air-absorbed dose rate of 51.59 nGy h^{-1} the world average value (51 nGy h^{-1}). The order of the air-absorbed dose rate was Thorium > Potassium > Radium with Thorium recording about two times the value for Radium. Royal fertilizer plus exceeded the world average at 101 nGy h^{-1} followed by food concentrate at 65 nGy h^{-1} .

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

It is now known that the specific activity distribution of K-40 for both inorganic and organic fertilizers are 566 and 305 Bq/kg are higher than those obtained in Pakistan 221 Bq/kg (Righi, S., Luciallib, P. & Bruzzia, L., (2005). Bq/kg () except for activity concentration recorded for Royal fertilizer plus at 907 Bq/kg. All are within regulatory benchmark of 140-850 Bq/kg (UNSCEAR, 2007). Therefore Royal fertilizer plus is not recommended to farmers and its use should be monitored to control environmental degradation. Ra-226 values for both types of fertilizers are higher than those obtained in Italy at 120 Bq/kg, but are within the world benchmark 17.0-

60.0Bq/kg(UNSCEAR,2000).Royal fertilizer plus has higher value , its use should be monitored.Th-232 specific activities for both types of fertilizers are 57.39 and 45Bq/kg, are higher than in Pakistan at 50Bq/kg(Khan *et al.*, 1998) but within word benchmark 11.0-60Bq/kg. It is now known that inorganic fertilizers contain up to sixteen elements in their composition. While organic fertilizers contain up to thirteen elements in their composition and may be safer for use by farmers than inorganic fertilizers

5.2 Recommendations

To protect the end users from toxic substances in fertilizers the following need to be done

- I. The use of the following fertilizers: Golden (15-15-15), Golden (20-10-10), FSFC (SSP18%), DAP, and Tak (15-15-15) should be monitored because of the energy impacted by ionizing radiation per unit mass.
- II. From the elemental analysis, only Tak Agro contains all the elements analyzed for at varying concentrations.
- III. All the fertilizers except Crystallizer and Mega green contain the following elements: Cr, Cd, Pb, Co and As. These fertilizers should be monitored in order to arrest land degradation when they accumulation in the soil above threshold levels.

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APPENDIX I:

ANALYSIS OF VARIANCE MODELS FOR THE DIFFERENT TEST

Variables	source	Sum of Squares	DF	Mean Square	F	Sig.
K-40	Between Groups	3.928	8	.491	102810.329	.000
	Within Groups	.000	9	.000		
	Total	3.928	17			
Bq_Kg	Between Groups	9531969.339	8	1191496.167	62562.265	.000
	Within Groups	171.405	9	19.045		
	Total	9532140.744	17			
Ra-226	Between Groups	.000	8	.000	5.931	.008
	Within Groups	.000	9	.000		
	Total	.000	17			
Bq_Kg	Between Groups	381.327	8	47.666	5.962	.007
	Within Groups	71.957	9	7.995		
	Total	453.284	17			
Th-232	Between Groups	.001	8	.000	217.307	.000
	Within Groups	.000	9	.000		
	Total	.001	17			
Bq_Kg	Between Groups	1870.700	8	233.838	214.644	.000
	Within Groups	9.805	9	1.089		
	Total	1880.505	17			

A FERTILIZER = INORGANIC

ANOVA (a)

Variables	source	Sum of Squares	DF	Mean Square	F	Sig.
K-40	Between Groups	.395	8	.049	6159.409	.000
	Within Groups	.000	9	.000		
	Total	.395	17			
Bq/_Kg	Between Groups	954667.290	8	119333.411	6141.685	.000
	Within Groups	174.871	9	19.430		
	Total	954842.160	17			
Ra-226	Between Groups	.003	8	.000	246.267	.000
	Within Groups	.000	9	.000		
	Total	.003	17			
Bq_Kg	Between Groups	4050.504	8	506.313	232.745	.000
	Within Groups	19.579	9	2.175		
	Total	4070.082	17			
Th-232	Between Groups	.002	8	.000	290.612	.000
	Within Groups	.000	9	.000		
	Total	.002	17			
Bq_Kg	Between Groups	2676.397	8	334.550	288.004	.000
	Within Groups	10.455	9	1.162		

	Total	2686.852	17			
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A

FERTILIZER = ORGANIC

Appendix ii

The ANOVA Procedure

Class Level Information

Class Levels Values

TYPE 12 CR7 CR8 CRC14 CRC15B CRND18 CRND19 CRNL16 CRNL17 CRNS20 CRNS21 CRP3 CRP5

Number of observations 24
3

The ANOVA Procedure

Dependent Variable: Mg

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Type	11	104857235.5	9532476.0	227.06	<.0001
Error	12	503785.5	41982.1		
Corrected Total	23	105361021.0			

R-Square	CoeffVar	Root MSE	Mg Mean
0.995218	9.624209	204.8954	2128.958

Dependent Variable: Al

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Type	11	14167306670	1287936970	7535.98	<.0001
Error	12	2050859	170905		
Corrected Total	23	14169357530			

R-Square	CoeffVar	Root MSE	Al Mean
0.999855	2.813478	413.4065	14693.79

Dependent Variable: Ca

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Type	11	26493919847	2408538168	5196.65	<.0001
Error	12	5561745	463479		
Corrected Total	23	26499481592			

R-Square	CoeffVar	Root MSE	Ca Mean
0.999790	3.292738	680.7927	20675.58

The ANOVA Procedure

Dependent Variable: Ti

Source	DF	Sum of Squares	Mean Square	F Value	Pr> F
Type	11	40125008.83	3647728.08	447.55	<.0001
Error	12	97805.00	8150.42		
Corrected Total	23	40222813.83			

R-Square	CoeffVar	Root MSE	Ti Mean
0.997568	15.01949	90.27966	601.0833

Dependent Variable: V

Source	DF	Sum of Squares	Mean Square	F Value	Pr> F
Type	11	73022.27125	6638.38830	2416.52	<.0001
Error	12	32.96500	2.74708		
Corrected Total	23	73055.23625			

R-Square	CoeffVar	Root MSE	V Mean
0.999549	5.554865	1.657433	29.83750

Dependent Variable: Mn

Source	DF	Sum of Squares	Mean Square	F Value	Pr> F
Type	11	1926920.491	175174.590	77496.6	<.0001
Error	12	27.125	2.260		
Corrected Total	23	1926947.616			

R-Square	CoeffVar	Root MSE	Mn Mean
0.999986	0.419071	1.503468	358.7625

Dependent Variable: Dy

Source	DF	Sum of Squares	Mean Square	F Value	Pr> F
Type	11	1301.463646	118.314877	1132.70	<.0001
Error	12	1.253450	0.104454		
Corrected Total	23	1302.717096			

R-Square	CoeffVar	Root MSE	Dy Mean
0.999038	6.991121	0.323194	4.622917

Dependent Variable: Na

Source	DF	Sum of Squares	Mean Square	F Value	Pr> F
Type	11	21817087.46	1983371.59	5861.46	<.0001
Error	12	4060.50	338.37		
Corrected Total	23	21821147.96			

R-Square	Coeff Var	Root MSE	Na Mean
0.999814	0.912694	18.39497	2015.458

Dependent Variable: K

Source	DF	Sum of Squares	Mean Square	F Value	Pr> F
Type	11	10637827929	967075266	2397.70	<.0001
Error	12	4840008	403334		
Corrected Total	23	10642667937			

R-Square	Coeff Var	Root MSE	K Mean
0.999545	2.531517	635.0858	25087.17

Dependent Variable: As

Source	DF	Sum of Squares	Mean Square	F Value	Pr> F
Type	11	596.4312333	54.2210212	6728.57	<.0001
Error	12	0.0967000	0.0080583		
Corrected Total	23	596.5279333			

R-Square	CoeffVar	Root MSE	As Mean
0.999838	3.654066	0.089768	2.456667

Dependent Variable: La

Source	DF	Sum of Squares	Mean Square	F Value	Pr> F
Type	11	302966.8892	27542.4445	555571	<.0001
Error	12	0.5949	0.0496		
Corrected Total	23	302967.4841			

R-Square	CoeffVar	Root MSE	La Mean
0.999998	0.408228	0.222654	54.54167

Dependent Variable: Sm

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Type	11	2923.310083	265.755462	151141	<.0001
Error	12	0.021100	0.001758		
Corrected Total	23	2923.331183			

R-Square	CoeffVar	Root MSE	Sm Mean
0.999993	0.499742	0.041932	8.390833

Dependent Variable: Unp

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Type	11	39472.87095	3588.44281	60229.8	<.0001
Error	12	0.71495	0.05958		
Corrected Total	23	39473.58590			

R-Square	CoeffVar	Root MSE	Unp Mean
0.999982	1.675329	0.244088	14.56958

Dependent Variable: Sc

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Type	11	287.4990125	26.1362739	17185.5	<.0001
Error	12	0.0182500	0.0015208		
Corrected Total	23	287.5172625			

R-Square	CoeffVar	Root MSE	Sc Mean
0.999937	1.222025	0.038998	3.191250

The ANOVA Procedure

Dependent Variable: Cr

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Type	11	72501.08333	6591.00758	3577.21	<.0001

Error	12	22.11000	1.84250
Corrected Total	23	72523.19333	

R-Square	CoeffVar	Root MSE	Cr Mean
0.999695	4.180864	1.357387	32.46667

Dependent Variable: Fe

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Type	11	474487011.5	43135182.9	3589.03	<.0001
Error	12	144223.5	12018.6		
Corrected Total	23	474631235.0			

R-Square	CoeffVar	Root MSE	Fe Mean
0.999696	1.632596	109.6295	6715.042

Dependent Variable: Co

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Type	11	148.0345833	13.4576894	751.13	<.0001
Error	12	0.2150000	0.0179167		
Corrected Total	23	148.2495833			

R-Square	CoeffVar	Root MSE	Co Mean
0.998550	4.061284	0.133853	3.295833

Dependent Variable: Zn

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Type	11	135797.1250	12345.1932	1445.29	<.0001
Error	12	102.5000	8.5417		
Corrected Total	23	135899.6250			

R-Square	CoeffVar	Root MSE	Zn Mean
0.999246	4.038153	2.922613	72.37500

Dependent Variable: Br

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Type	11	8145.184400	740.471309	13325.8	<.0001

Error	12	0.666800	0.055567	
Corrected Total	23	8145.851200		
R-Square	CoeffVar	Root MSE	Br Mean	
0.999918	1.966020	0.235726	11.99000	

Dependent Variable: Rb

Source	DF	Sum of Squares	Mean Square	F Value	Pr> F
Type	11	15281.12500	1389.19318	254.51	<.0001
Error	12	65.50000	5.45833		
Corrected Total	23	15346.62500			
R-Square	CoeffVar	Root MSE	Rb Mean		
0.995732	4.880016	2.336308	47.87500		

Dependent Variable: Sb

Source	DF	Sum of Squares	Mean Square	F Value	Pr> F
Type	11	24.38744583	2.21704053	969.20	<.0001
Error	12	0.02745000	0.00228750		
Corrected Total	23	24.41489583			
R-Square	CoeffVar	Root MSE	Sb Mean		
0.998876	12.27666	0.047828	0.389583		

Dependent Variable: Cs

Source	DF	Sum of Squares	Mean Square	F Value	Pr> F
Type	11	81.80333333	7.43666667	496.33	<.0001
Error	12	0.17980000	0.01498333		
Corrected Total	23	81.98313333			
R-Square	CoeffVar	Root MSE	Cs Mean		
0.997807	9.538163	0.122406	1.283333		

ANOVA

		Sum of Squares	DF	Mean Square	F	Sig.
Cd	Between Groups	.862	2	.431	29.244	.000

	Within Groups	1.723	117	.015		
	Total	2.585	119			
Cu	Between Groups	473.711	2	236.856	67.826	.000
	Within Groups	408.575	117	3.492		
	Total	882.286	119			
Fe	Between Groups	639689119.194	2	319844559.597	46.450	.000
	Within Groups	805635857.101	117	6885776.556		
	Total	1445324976.295	119			
Ni	Between Groups	48173.435	2	24086.718	33.355	.000
	Within Groups	84488.338	117	722.123		
	Total	132661.774	119			
Mn	Between Groups	559740.207	2	279870.104	8.587	.000
	Within Groups	3813110.395	117	32590.687		
	Total	4372850.602	119			
Pb	Between Groups	.117	2	.058	47.272	.000
	Within Groups	.145	117	.001		
	Total	.261	119			
Zn	Between Groups	3021950.701	2	1510975.351	28.471	.000
	Within Groups	6209362.141	117	53071.471		
	Total	9231312.842	119			
Cr	Between Groups	11330.148	2	5665.074	21.226	.000
	Within Groups	31226.460	117	266.893		
	Total	42556.608	119			
Si	Between Groups	2349276194.600	2	1174638097.300	61.275	.000
	Within Groups	2242897188.310	117	19170061.439		
	Total	4592173382.910	119			
Ti	Between Groups	43463723.401	2	21731861.700	15.446	.000
	Within Groups	164616412.059	117	1406977.881		
	Total	208080135.460	119			
V	Between Groups	11541.944	2	5770.972	6.448	.002
	Within Groups	104717.609	117	895.022		
	Total	116259.553	119			
K	Between Groups	51627578280.817	2	25813789140.409	5.621	.005
	Within Groups	537339982489.676	117	4592649422.989		
	Total	588967560770.493	119			
As	Between Groups	58.036	2	29.018	5.175	.007
	Within Groups	656.013	117	5.607		
	Total	714.049	119			
Co	Between Groups	104.412	2	52.206	24.186	.000
	Within Groups	252.548	117	2.159		
	Total	356.960	119			
Sb	Between Groups	1.457	2	.729	3.295	.041
	Within Groups	25.865	117	.221		

	Total	27.322	119			
Cs	Between Groups	14.162	2	7.081	8.410	.000
	Within Groups	98.506	117	.842		
	Total	112.668	119			

B ANOVA

		Sum of Squares	DF	Mean Square	F	Sig.
Cd	Between Groups	.455	19	.024	1.124	.340
	Within Groups	2.130	100	.021		
	Total	2.585	119			
Cu	Between Groups	117.427	19	6.180	.808	.693
	Within Groups	764.859	100	7.649		
	Total	882.286	119			
Fe	Between Groups	227392089.828	19	11968004.728	.983	.487
	Within Groups	1217932886.467	100	12179328.865		
	Total	1445324976.295	119			
Ni	Between Groups	24441.804	19	1286.411	1.189	.282
	Within Groups	108219.970	100	1082.200		
	Total	132661.774	119			
Mn	Between Groups	1252752.858	19	65934.361	2.113	.009
	Within Groups	3120097.744	100	31200.977		
	Total	4372850.602	119			
Pb	Between Groups	.038	19	.002	.899	.585
	Within Groups	.223	100	.002		
	Total	.261	119			
Zn	Between Groups	2098701.809	19	110457.990	1.549	.085
	Within Groups	7132611.033	100	71326.110		
	Total	9231312.842	119			
Cr	Between Groups	10662.684	19	561.194	1.760	.038
	Within Groups	31893.924	100	318.939		
	Total	42556.608	119			
Si	Between Groups	646245694.926	19	34012931.312	.862	.629
	Within Groups	3945927687.984	100	39459276.880		
	Total	4592173382.910	119			
Ti	Between Groups	56262494.244	19	2961183.908	1.950	.018
	Within Groups	151817641.216	100	1518176.412		
	Total	208080135.460	119			
V	Between Groups	47446.534	19	2497.186	3.629	.000
	Within Groups	68813.019	100	688.130		
	Total	116259.553	119			
K	Between Groups	137200137314.714	19	7221059858.670	1.598	.071
	Within Groups	451767423455.780	100	4517674234.558		
	Total					

	Total	5889675607 70.493	119			
As	Between Groups	218.633	19	11.507	2.323	.004
	Within Groups	495.416	100	4.954		
	Total	714.049	119			
Co	Between Groups	84.110	19	4.427	1.622	.065
	Within Groups	272.850	100	2.729		
	Total	356.960	119			
Sb	Between Groups	8.615	19	.453	2.424	.002
	Within Groups	18.707	100	.187		
	Total	27.322	119			
Cs	Between Groups	17.597	19	.926	.974	.497
	Within Groups	95.071	100	.951		
	Total	112.668	119			