Investigation of the Radiological Impact of Naturally Occurring Radionuclides from the usage of Phosphate and Organic Fertilizers on Farmlands in the New Juaben Municipality of Ghana

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DECLARATION

This thesis is the result of research work undertaken by John Andrew Gyenfie in the department of Nuclear Safety and Security, School of Nuclear and Allied Sciences, University of Ghana, under the supervision of Dr. Joseph Korbla Gbadago and Dr. Augustine Faanu.

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ABSTRACT

The radiological impact of naturally occurring radioactive materials (NORMs) from the usage of phosphate and organic fertilizers in the New Juaben Municipality of Ghana was investigated. The activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K were measured in seven (7) widely used phosphate and organic fertilizers using gamma spectroscopy. The activity concentrations were found to be 32.10±2.60 Bq/kg, 12.20±1.60 Bq/kg and 3005.50±68.80 Bq/kg respectively. The radioactivity level index ($I_\gamma$) which gives an estimate of the level of risk associated with natural radionuclides in specific material was found to be higher than the recommended limit of one (1) in some of the fertilizer samples collected from storage. The storage also recorded a relatively high dose rates (ranging from 96-624 µSv/a) compared to the surrounding background (ranging from 109-241 µSv/a) suggesting that the storage of large quantities of these fertilizers can lead to a possible increase in the dose rates. The mean activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K in cultivated (fertilized) soils were found to be 12.50±3.30 Bq/kg, 10.60 ± 2.80 Bq/kg and 206.0 ± 30.2 Bq/kg respectively. These values were relatively higher than those found in their respective virgin (unfertilized) soils ($^{226}$Ra- 9.0±1.7 Bq/kg; $^{232}$Th - 8.10±1.70 Bq/kg; and $^{40}$K-139.0±13.3 Bq/kg). This might be considered as an indication that the use of fertilizers to increase soil fertility enhances the level of $^{226}$Ra, $^{232}$Th and $^{40}$K in agricultural soils. The averages of other risk indices such as radium equivalent, the absorbed dose rate in air at 1m above the ground, the mean outdoor annual effective dose and the external hazard index estimated for the cultivated soils were found to be higher than their corresponding virgin soils but generally lower than the world averages. Therefore, the radiological impact associated with NORMs in the cultivated lands as a result of the application of fertilizers is expected to be low
however, the storage of large quantities of fertilizers in warehouses could be monitored for the long-term to establish exposure rates of the workers.
DEDICATION

This work is dedicated to the entire membership of my family including those who have passed away and more especially to my Grandparents, Mrs Agnes Aubyn and Mrs Elizabeth Gyenfie.
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LIST OF ABBREVIATIONS

UNSCEAR - United Nations Scientific Committee on the effects of atomic radiation
BSS - Basic Safety Standards
IAEA - International Atomic Energy Agency
G.A.E.C - Ghana Atomic Energy Commission
RPB - Radiation Protection Board
PPRD - Plant Protection and Regulatory Services Directorate
ICRP – International Commission for Radiological Protection
FAO – Food and Agricultural Organisation
MOFA - Ministry of Food and Agriculture
IFA - International Fertilizer Association
NJM - New Juaben Municipality
NORMs - Naturally Occurring Radioactive Materials
TENORM – Technologically Enhanced Naturally Occurring Radioactive Material
mSv – millisievert ($10^{-3}$ Sievert)
Bq – Becquerel
Bq/g – Becquerel per gram
Bq/kg – Becquerel per kilogram
µSv – microsievert
µSv/a – microsievert per annum
nGy/h – nano gray per hour
MCA – Multi Channel Analyser
MeV – mega electrovolt
keV – kilo electrovolt
NaI (TI) – Sodium Iodide (Thallium)
HPGe – High Purity Germanium
SSDL – Secondary Standard Dosimetry Laboratory
DCF – Dose Conversion Factor
ALARA – As Low as Reasonably Achievable
MDA – Minimum Detectable Activity
LLD – Lower Limit of Detection
BDL – Below Detection Limit
ASI – Asikasu
ASO – Asokore
BOR – Bornya
TRO – Trom
EFF – Effiduase
U – Uranium
Ra – Radium
Th – thorium
K – Potassium
Hex – External Hazard Index
Ra$_{eq}$ – Radium equivalent activity
NP: nitrogen–phosphorus
NPK: nitrogen–phosphorus–potassium
SSP: single superphosphate
TCP: tricalcium phosphate
TSP: triple superphosphate
MAP: monoammonium phosphate
DAP: diammonium phosphate
MCP: monocalcium phosphate
DCP: dicalcium phosphate
CHAPTER 1

INTRODUCTION

1.1 Background

Natural sources of exposure to ionizing radiation are unending and inevitable aspect of our lives on this earth. Human exposure to natural radiation has always existed. This exposure can exceed the exposure of all man-made sources put-together (UNSCEAR, 2010).

One of the main contributors of natural radiation exposure (terrestrial exposure) is from primordial radionuclides (UNSCEAR, 2010). Primordial radionuclides are defined as radionuclides that occur naturally on the earth in significant quantities. It is usually used to refer to $^{40}\text{K}$, $^{238}\text{U}$, $^{232}\text{Th}$ and their radioactive decay products (IAEA Safety Glossary, 2007). These radionuclides are of particular interest as they have half-lives comparable to the age of the earth and some are in significant quantities which could be of concern as they pose a potential risk to human health owing to the emission of ionising radiations. Moreover, these primordial radionuclides are present in various amounts in all environmental media including the human body (UNSCEAR, 2010 and Hamidalddin, 2014).

There were circumstances where the exposure of workers to natural sources of radiation was sufficiently higher to warrant management and control of radiation as an occupational hazard (UNSCEAR, 2010). According to UNSCEAR, 2010 report, exposure to natural background radiation forms the most important part of total
exposure for most individuals. The global average annual exposure to natural radiation sources remains approximately 2.4 mSv (UNSCEAR, 2000).

There are two exposure situations from primordial radionuclides which are external and internal radiation exposures. The main contributors to external exposures come from gamma emitting radionuclides present in trace amounts in the soil, mainly $^{40}$K, and the $^{238}$U and the $^{232}$Th families. Information on outdoor exposure comes from indirect measurements of radiation in soils. Internal exposures arise from the intake of terrestrial radionuclides by inhalation and ingestion irradiating various organs with alpha and beta particles, as well as gammas. The presence of dust particles containing radionuclides of $^{238}$U and $^{232}$Th decay chains results in doses from inhalation. The short-lived decay products of radon forms a major portion of exposure due to inhalation and are the most important among the inhalation of natural radiation (UNSCEAR, 2010).

The mining, extraction and processing of ores can lead to significant increase of levels of naturally occurring radioactive materials (NORMs) in products, by-products and wastes. Amongst these extractive and processing industries, is the phosphate industry which produces fertilizers for use in agriculture. The phosphate ores typically contains about 1500 Bq/kg of uranium including radium, whiles some phosphate rocks contain about 20,000 Bq/kg of $\text{U}_3\text{O}_8$. In most cases, 90% of the ore is treated with sulphuric acids leading to enriched concentrations up to 150% relative to the ore (UNSCEAR, 2010 and Gbadago et al, 2011). Fertilizer is any material containing one or more essential elements and is used in supplying nutrients to soils to promote plant growth. The primary nutrients namely nitrogen, phosphorus and potassium are required in macro quantities (Government of India, 2010). According to FAO (1985), it may be either a naturally occurring or an industrially produced
product. Fertilizers come in different forms; it can be solid, liquid or gaseous. It is important to note that fertilizers are only one of the inputs that lead to higher crop yields. With fertilizers, soils of low fertility (over-exploited soils) can regain their fertility for crop production (FAO & IFA, 2000).

There are two (2) basic types of fertilizers: Organic fertilizers (organic manure or organic matter) and Chemical fertilizers (inorganic or mineral fertilizers). Organic fertilizers are made from biological and organic materials such as cow dung, pig excreta, chicken droppings, vegetable wastes and others after it has been well-composted and well-decomposed before its application to soils. It is very beneficial as it helps to improve soil structure, reduces soil erosion, regulating effects on soil temperature, and helps the soil to store more moisture as well as providing food for soil organisms (FAO & IFA, 2000). Chemical fertilizers are manufactured through chemical means in special laboratories. Use is also made of natural deposits and ores by chemically processing them to extract essential nutrients needed for plant growth and higher yields (IAEA, 2013). According to FAO & IFA (2000), the combination of organic matter and mineral fertilizers provides the ideal environmental condition for crops, as the organic matter improves soil properties and mineral fertilizers supply the plant nutrients needed.

Due to the rapid increase in population of Ghana, there is high demand for increase in food production to support and sustain the growing population. Increased food production can largely be realized amongst other factors through the usage of fertilizers. It is projected that, there will be a 70% increase in demand for food by 2050 to feed the growing world population (IAEA, 2013).
Increased usage of fertilizers has its disadvantages since the elements such as heavy metals and NORMs, it contains may be introduced into agricultural soils and thereby contaminating these soils eventually.

The persistent and prolonged usage of the fertilizers can redistribute, restructure or elevate the level of primordial radionuclides in the soil profile (Khater, 2008 and Ahialel et al, 2014). Hence, the study, seeks to investigate the level of naturally occurring radionuclides in phosphate and organic fertilizers and their associated radiological impacts on agricultural farmlands in the New Juaben Municipality (NJM).

1.2 Statement of the Problem

The application of fertilizers to soils to improve soil fertility and crop yields have received significant interest in the 21st century becoming a global practice. According to Khater (2008), globally, more than 30 million metric tonnes of phosphate fertilizers are used every year to improve crop yields. MOFA (2013) revealed that about 3.4 million metric tonnes of all kinds of fertilizers were imported into the country in the year 2012. The radioactivity content of phosphate fertilizers varies according to the geological origin of the phosphate ore and on the method of production (Gbadago et al, 2011 and IAEA, 2003). There is a likely contamination of the environment through the application of fertilizers particularly the phosphate fertilizers as they might contain elevated levels of radionuclides of the $^{238}U$, $^{232}Th$ decay series as well as $^{40}K$ (Samad, Ali, Paul et al, 2012). Therefore, the persistent and prolonged usage of fertilizers can redistribute, restructure or elevate the level of primordial radionuclides in the soil profile (Khater, 2008). It is therefore possible that contact with elevated levels of these naturally occurring radionuclides materials
(NORMs) may lead to stochastic effects. It has been estimated that workers who do mishandle these fertilizers during packaging and transport are likely to receive additional external exposures at dose rates up to 0.8 mGy.hr$^{-1}$ (Alharbi, 2013).

Thus, the potential hazards associated with the level of NORMs in the phosphate fertilizers must be studied and documented. Furthermore, the storage of huge stockpiles of these phosphate fertilizers especially in warehouses may elevate the dose rates leading to higher exposures should the gamma indices indicate high levels.

Thus, this research work seeks to estimate the level of NORMs ($^{226}$Ra, $^{232}$Th and $^{40}$K) in phosphate and organic fertilizers as well as its radiological impacts in the New Juaben Municipality of the Eastern Region of Ghana.

1.3 General and Specific Objectives

The general objective of this proposed research is to investigate the radiological impact of NORMs (defined as $^{226}$Ra, $^{232}$Th and $^{40}$K in this work) in phosphate and organic fertilizers utilized in the NJM.

To achieve the general objective, the proposed study aims to address the following specific objectives:

i. To determine the activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K in different brands of fertilizers available and widely used in the New Juaben Municipality.

ii. To estimate the level of NORMs on agricultural lands where these fertilizers are applied for agricultural purposes.
iii. To estimate the radiological hazards associated with the storage and use of the fertilizers.

iv. To compare the estimated activity concentrations and the radiological hazard indices with international recommended dose limits as well as similar studies carried out in other countries.

1.4 Relevance and Justification

Almost all fertilizers used in Ghana are imported from other countries. Inorganic fertilizers especially the phosphate fertilizers are produced from phosphate ores and these ores depending on its geological origin may contribute significantly to the level of NORMs in phosphate fertilizers.

Out of the nearly 3.4 million metric tonnes of fertilizers imported in 2012, 2,923,304 metric tonnes were NPK fertilizer, 43,384 metric tonnes were muriate of potash whilst 78,355 metric tonnes were SSP and TSP (all containing some amount of phosphorus). These brands constitute a very significant portion of the fertilizers used in Ghana (MOFA, 2013). There is therefore the need to evaluate the level of NORMs in the various brands of fertilizer being used as well as assessing the radiological implications.

The results of this study will add up to the general body of knowledge and research work of natural radioactivity in fertilizers as well as providing baseline data for observing possible future anthropomorphic impact or associated radiological risks through fertilizer use. In addition, it will open up the path for extensive studies leading to formulation of guidelines on import, storage and use of fertilizers in Ghana.
1.5 Scope of Work and Delimitations

A survey was undertaken to identify the most widely used phosphate and organic fertilizers in the agrochemical industry in the New Juaben Municipality. The fertilizer sampling was centred in Koforidua which is the municipality capital. It is the central supplying channel of fertilizers to its villages and other districts famous in agricultural production in the Eastern Region.

The chemical fertilizers were selected based on whether there was a phosphorus or phosphate component. Therefore, only the phosphorus or phosphate fertilizers available on the market were sampled on the part of chemical fertilizers. The organic fertilizers are sparingly used by farmers in the whole country so only the frequently used organic fertilizer types available on the local market were sampled.

Soil samples from selected agricultural farmlands that extensively use phosphate and organic fertilizers at five different communities in the municipality were collected to assess the level of impact of fertilizers on the radiological profile of the agricultural soils. The farmlands were selected to include those on which cash crops are grown. Samples collected were sent to the gamma-ray spectrometry laboratory of the Ghana Atomic Energy Commission (G.A.E.C) in Accra for preparation and analysis.
1.6 Structure of the dissertation

The work is organised into five (5) chapters:

Chapter 1 is the introduction which comprises of the background, statement of the problem being investigated, justification and relevance of this work, the objectives and scope of the work.

Chapter 2 contains a literature review on fertilizers, natural radioactivity, NORMs and their decay modes, radioactivity in soils, phosphate and organic fertilizers, the radiological impact from use of these fertilizers, works already done and gaps being filled by this research work.

Chapter 3 describes the study area, sampling and analytical methods for the determination of the concentration of NORMs in the samples. Gamma spectrometry (High purity Germanium detector) is used for counting of the gamma emitting radionuclides.

Chapter 4 presents the results and discussions on the results. The possible radiological impact from the use of the phosphate and organic fertilizers are assessed by using various radiological parameters including radium equivalent activity ($Ra_{eq}$), outdoor absorbed dose ($D$ (nGy/hr)), effective Dose, ($Deff$ (mSv)), external radiation hazard ($Hex$) and radioactivity level index ($I_\gamma$).

Finally, in chapter 5, conclusions are drawn on the discussion of the results to determine the radiological impact associated with the use of phosphate and organic fertilizers in the New Juaben Municipality.
CHAPTER 2

LITERATURE REVIEW

2.1 Definition of Fertilizers and its types

Fertilizers are substances that are used to improve the levels of available plant nutrients and/or the chemical and physical properties of soil, thereby directly or indirectly enhancing plant growth, yield, and quality (Ullmann’s Agrochemicals, 2007). According to FAO (2000), any natural or manufactured material which contains at least 5% of one or more of the three primary nutrients (N, P₂O₅, K₂O) can be called a fertilizer. Fertilizers next to water contribute largely to increasing agricultural production (FAO, 1984). Fertilizers are classified in terms of their composition as follows:

1. Mineral fertilizers: They consist of inorganic or synthetically produced organic compounds essential to normal plant growth and development. It can be natural or manufactured.

2. Organic fertilizers: They are well-decomposed waste products from animal husbandry such as farmyard manure, plant decomposition products, vegetable waste and cow dung. They contain small amounts of nutrients but their main importance lies in their supply of organic matter to soils to promote microbial growth in soils, improving soil physical properties such as its water holding capacity, aeration, erosion reduction, buffering, soil surface temperature, improvement of chemical properties (supply of nutrients in balanced ratios, slow release of soil nutrients and so on). To use organic fertilizers in
supplying vital nutrients for plant growth implies, very large quantities of it has to be applied which is unadvisable because of their bulky nature.

In terms of its nutrient content, fertilizers can be classified as (Ullmann’s Agrochemicals, 2007; Fertilizer Manual-RB209, 2010; FAO, 2000 and FAO 1984):

- Straight fertilizers (single nutrient fertilizers): They are fertilizers that contain only one primary nutrient. E.g. Urea and ammonium salts.
- Compound fertilizers: They are fertilizers that contain several primary nutrients and sometimes micronutrients as well. E.g. NP, NPK and PK fertilizers.
- Micronutrients fertilizers: They are fertilizers that contain nutrients required in small amounts by plants. E.g. Boron, copper and iron.

The particles of fertilizers can be of different sizes and shapes depending on its process of manufacture. It can be in the form of solids: granules, pellets, crystals or powdery and liquids (FAO, 2000).

2.2 Radioactivity in Phosphate and Organic Fertilizers

The starting material for the production of all phosphate products including phosphorus for fertilizers is the phosphate rock. In many parts of the world, the phosphate rock is applied directly on farmlands as a source of phosphorus for soils at rates ranging from 300-600 kg/ha (Khater et al, 2001 and LeMone et al, 2009). Depending on the origin of the phosphate rock, the radionuclide activity concentrations in phosphate rock products such as phosphate fertilizers may vary. Phosphate mining provides about 80% of all exploitable P₂O₅ meant for use in fertilizer (IAEA, 2013). The radioactivity level of U in phosphate rock originating
from sedimentary deposits is generally found to be within the range of 0.2 -2.5 Bq/kg. $^{238}$U concentrations are significantly lower in phosphate rocks of igneous origin as reported in IAEA safety report series No. 78. Meanwhile the $^{232}$Th concentration in products of sedimentary origin as well as in igneous products from Kola, Russian federation, generally falls between 0.01 to 0.1 Bq/g. $^{232}$Th in igneous products from Saudi Arabia also falls within the range of 0.3 - 0.4 Bq/g which is slightly higher than levels found in most sedimentary products. Most notably, the concentration of other radionuclides in the $^{238}$U and $^{232}$Th decay series is comparable to that found in the original phosphate ore as they appear to be in close radioactive equilibrium (UNSCEAR, 1988 and UNSCEAR, 1993).

By addition of acids such as sulphuric or phosphoric acids to ground or pulverised rocks, phosphate fertilizers are then manufactured (Figure 2.1) (Cooper, 2005; Righi, 2005 and US-EPA, 1999). 90 – 95% of the uranium in the phosphate rock migrates into the phosphate acid during sulphuric acid digestion process, existing in the form of uranyl phosphate complexes (IAEA, 2013). The $^{238}$U concentration in the phosphoric acids varies in the range of 0.14 – 2.6 Bq/kg depending on the geological characteristics of the ores and the variations of the process used for its production. Some studies have also found that, up to 75% of the $^{232}$Th migrates into the phosphoric acid (IAEA, 2013). Therefore, the production of phosphoric acid results in the redistribution of huge amounts of natural radioactivity from the ores into the acids which is then carried into the fertilizer products.
2.2.1 Work done on fertilizers

The level of NORMs in fertilizers and their radiological impacts have been studied all around the world. Activity concentrations of NORMs in phosphate fertilizers have been reviewed in both UNSCEAR 1988 and UNSCEAR 1993 where it was concluded that the concentrations of $^{40}$K and $^{232}$Th and its decay products are always low but the concentrations of the radionuclides of $^{238}$U decay series are 5 - 50 times higher than in normal soils with typical values of 4000 and 1000 Bq/kg of $\text{P}_2\text{O}_5$ for $^{238}$U and $^{226}$Ra respectively.

Abbady (2005) used gamma ray spectroscopy (High purity germanium detector) to assess the natural radioactivity and its radiological hazards in some Egyptian rock phosphates. The mean activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K were determined to be $410\pm39$ Bq/kg, $7.9\pm0.95$ Bq/kg and $37.6\pm4$ Bq/kg respectively.
whiles the mean absorbed dose rate, the radium equivalent and the external hazard index were found to be 181.9±20 nGy.hr⁻¹, 317-520 Bq/kg and 0.4-0.7 respectively. It was found that the radionuclide concentration varied with locations as a result of varying geological characteristics and processes used in phosphate rock mining.

Sahu et al (2014) reported high concentrations of $^{238}$U and $^{226}$Ra (1.34 Bq/g and 1.29 Bq/g) and significantly lower activity concentrations of $^{232}$Th and $^{40}$K in phosphate rocks used in a phosphate fertilizer plant in India.

Khater and Al-Sewaidan (2008) assessed the level of NORMs in both local and imported phosphate fertilizers in the city of Riyadh in Saudi Arabia finding the average activity of $^{238}$U to be 1017 Bq/kg which was elevated in phosphate deposits of sedimentary origin.

El-Taher and Abdelhalm (2013) using a NaI(Tl) detector reported the average radioactivity level of $^{226}$Ra, $^{232}$Th and $^{40}$K to be in the ranges of 9.0±1.3 to 55±4.9 Bq/kg, 8.86±1.80 to 42.0±8.0 Bq/kg and 2700.0±4.9 Bq/kg respectively for phosphate fertilizers used in the Qassim region of Saudi Arabia. Except for $^{40}$K in NPK fertilizers with a mean value of 2700 Bq/kg, $^{40}$K in other fertilizers was within world’s average values.

Elisha et al (2013) analysed some selected organic fertilizers in Zaria area council in Nigeria for their level of NORMs. The results showed a $^{40}$K mean activity concentration of 305.33±0.20 Bq/kg, a $^{226}$Ra mean activity concentration of 24.87±0.02 Bq/kg and a $^{232}$Th mean activity concentration of 45.04±0.04 Bq/kg. From the calculated radiological hazard indices, it indicated that organic fertilizers do not pose any significant radiological hazard to the environment.
Alhardi (2013) assessed the level of NORMs as well as its doses in both chemical and organic fertilizers used in the Al-Taif city of Saudi Arabia using a NaI detector. A total of 45 samples of nine (9) brands of fertilizers were analysed with the results showing a mean specific activities of $^{226}$Ra, $^{232}$Th and $^{40}$K of 64 Bq/kg, 17 Bq/kg and 2453 Bq/kg respectively which was within the range of values reported in several other countries. The Radium equivalent (Ra$_{eq}$) did not exceed the maximum permissible level of 370 Bq/kg. Also found in this study was the fact that there was higher level of NORMs in chemical fertilizers than in organic fertilizers.

Fasae and Jibiri (2011) investigated the natural radioactivity level in brands of fertilizers used in some commercial cities in South Western Nigeria using gamma ray spectroscopy. The results of the measurement showed that the average activity concentrations of $^{40}$K, $^{226}$Ra and $^{232}$Th ranged from 3972.0±416.9 Bq/kg to 5089±111.3 Bq/Kg, 9.9±7.3 Bq/kg to 450.6±14.3 Bq/kg and <5.1 Bq/kg to 15.1±2.8 Bq/kg respectively. Except $^{40}$K which exceeded the permissible limit, all the activities of the natural radionuclides in the fertilizers investigated were within range as reported in other parts of the world.

Research on fertilizers in Ghana has been largely skewed towards estimation of the level of heavy metals in fertilizers and their environmental impacts. Addo et al (2006) determined the concentration of heavy metals and other toxic elements in nine (9) brands of inorganic fertilizers used in Ghana using Instrumental Neutron Activation Analysis. Only Co and Sc occurred in all the brands, with concentrations ranging from 0.44 mg/kg to 5.02 ± 0.02 mg/kg for Co and 0.10 mg/kg to 2.60 ± 0.01 mg/kg for Sc. Narstey et al (2012) studied the contribution of heavy metal levels (Cu, Pb, Mn, Zn, Ni, Cd, Cr, and Fe) in some fertilizers to soils and cocoa in some cocoa farms in the Western region of Ghana. Iron (Fe) occurred as the highest metal in all
cases whiles Zn was the least recorded metal in the fertilizers. In general, contributions from the fertilizers to the elemental concentrations in the soil and also in cocoa beans were found to be minimal and fell within acceptable limits. These works dealt extensively with the level of heavy metals in fertilizers and the resulting pollution of soils and high concentrations in plants. Ahialey et al (2014) determined the concentrations of the metals; Cd, Co Cr, Cu, Mg, Mn, Pb and Zn in phosphate fertilizers by flame atomic absorption spectrometry (FAAS) in Ghana and found their levels to be within limits required for most field crops. Adjirackor (2010) assessed the level of NORMs in five (5) inorganic fertilizers which included three (3) non-phosphatic fertilizers in the Greater Accra Region of Ghana. The specific activities of $^{226}\text{Ra}$, $^{232}\text{Th}$ and $^{40}\text{K}$ in the five (5) brands of fertilizers were found to be in the range of 1.30- 150.52 Bq/kg, 13.89- 51.39 Bq/kg and 38.33- 8390.17 Bq/kg respectively.

In Ghana, phosphate and organic fertilizers are widely used and apart from studies done on the heavy metal contents of these fertilizers, not much study has been carried out in establishing the radionuclide contents of these fertilizers. It is also possible for high radioactivity content in fertilizers to give off high dose rates in an enclosed storage. This study was therefore focused on the determination of the NORMs content of the phosphate and organic fertilizers, and the dose rates at storage places in order to assess the radiological impact on the usage.
2.3 Radioactivity in Soils

Apart from the documented high content of naturally occurring radionuclides in phosphate ores/rocks used in the production of phosphate fertilizers, other reasons have led researchers to study NORMs in phosphate fertilizers and its environmental impacts. One of such reasons is the continued application of fertilizers to agricultural farm soils over long periods (years) which could eventually increase the NORMs content of soils resulting in increasing public exposure.

Hameed et al (2014) determined the impact of phosphate fertilizers on the radiological profile of cultivated soils in Sriranyam, India. From the data obtained, it was found that $^{238}$U in cultivated soils were 25% higher than that of virgin soils whereas $^{232}$Th activity was 12.4% higher in cultivated soils than virgin soils concluding that intense use of phosphate rich fertilisers was responsible for the enhanced levels of NORMs in cultivated soils. The Ra$_{eq}$ for both the cultivated and virgin soils was found to be 164.5 Bq/kg and 181.7 Bq/kg respectively hence does not pose any significant radiological risks as they were below the recommended limit of 370 Bq/kg.

Natural radioactivity in cultivated and reclaimed soils in Upper Egypt was reported by Abbady et al (1998) using a NaI (Tl) detector. The activity concentrations obtained fell within the lowest range of the world average values of 30 Bq/Kg, 35 Bq/Kg and 400 Bq/kg for $^{226}$Ra, $^{232}$Th and $^{40}$K respectively.

Kant et al (2006) assessed the radiological risks associated with the use of phosphate fertilizers in soils in the Mathura district in India using a high purity germanium detector. It was found that the activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K as well as the absorbed dose rate in air were found to increase substantially in soils on which
phosphate fertilizers were used thereby clearly indicating that the farmers were exposed to higher levels of radiation when applying the fertilizers and from the fertilized soils. The $Ra_{eq}$ in all the soil samples were below the 370 Bq/Kg limit whiles the equivalent dose was within the safe limit of 1mSv/yr.

Al-Saif (2009) reported the activity concentrations of $^{226}$Ra, $^{228}$Ra, $^{40}$K and $^{137}$Cs to be slightly higher in cultivated soils as compared to uncultivated soils due to the use or application of phosphate fertilizers in the Hail province in Saudi Arabia.

Gross alpha and beta activity levels in chemical fertilizers applied in agricultural farm soils in Nigeria was investigated by Jibiri and Fasae (2013). The alpha and beta activities in NPK (15-15-15) fertilizers were found to be in the range of 20.0±10.0 to 90.0±20.0 Bq/kg and 2410.0±80.0 to 4560.0±140.0 Bq/kg respectively whiles the alpha and beta activity concentrations in the cultivated soils ranged from 2.0 to 30.0 Bq/kg and 150.0 to 620 Bq/kg respectively. There were more beta emitters in the NPK fertilizers than in the SSP fertilizers whiles the vice versa holds for alpha emitters.

Hamidalddin (2014) determined the agricultural primordial radionuclide concentrations in Um Hablayn, Saudi Arabia finding the radium, thorium and potassium contents exceeding world average values. The $Ra_{eq}$ value did not exceed the permissible limit of 370 Bq/kg but the absorbed dose rate in air (169.7 nGy/hr) was higher than the world’s average of 60 nGy/hr. The result above was attributed to the excessive use of phosphate fertilizers in the Kingdom of Saudi Arabia.

Akhtar et al (2005) conducted a study to investigate the amount of radioactivity in both barren and cultivated soils of the Bio- Saline Research Station in Pakistan where the variation in activity concentrations of $^{226}$Ra, $^{228}$Ra and $^{40}$K fell within the world
range of values but with an absorbed dose rate in air higher than the world’s average. Moreover the higher value of dose in fertilized soils as compared to barren lands was attributed to the use of fertilizers for cultivation.

2.4 Natural Radioactivity

Natural radioactivity is the spontaneous disintegration or transformation of naturally occurring unstable nucleus (radionuclides) into a stable nucleus with the emission of alpha and beta particles and/or gamma radiations. Gamma radiation is not a mode of radioactive decay but a mechanism by which certain radionuclides (excited nuclei) get rid of excess energy without affecting the atomic mass or the atomic mass number (Cember et al., 2009; Santawamaitre, 2012 and Tetteh-Larbi, 2012). These radionuclides occur in nature in significant quantities in dead materials, the air we breathe, in soils, in foods, in water, in the human body amongst others. Therefore, human exposure to environmental radiation has been with us since the creation of the earth originating from extra-terrestrial sources and radioactive elements in the earth’s crust. Human exposure to natural radiation is the main contributor to population collective doses resulting from external exposure from cosmic rays and radioactive substances in the earth’s crust or ground, building materials as well as internal radiation from inhalation and ingestion of natural radionuclides in air and diet. Internal radiation for most people is the highest contributor to annual dose. Some human practices modify radiation exposure to humans, especially releasing natural radionuclides to the environment during minerals or ores processing e.g. during phosphate fertilizer production and use. The worldwide annual average effective dose equivalent from natural sources is estimated to be 2.4 mSv for adult population (Table 2.1) (UNSCEAR, 1988 and UNSCEAR, 1993).
Table 2.1: Annual effective doses to adults from natural sources (UNSCEAR, 1993).

<table>
<thead>
<tr>
<th>Source of exposure</th>
<th>Annual Effective Dose (mSv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cosmic rays</td>
<td>0.39</td>
</tr>
<tr>
<td>Terrestrial gamma rays</td>
<td>0.46</td>
</tr>
<tr>
<td>Radionuclides in the body (except radon)</td>
<td>0.23</td>
</tr>
<tr>
<td>Radon and its decay products</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>Total (rounded)</strong></td>
<td><strong>2.4</strong></td>
</tr>
</tbody>
</table>

Natural sources of radiation are from cosmic rays, cosmogenic radionuclides, terrestrial (primordial) radionuclides, and anthropogenic sources (UNSCEAR, 1988; UNSCEAR, 1993 and UNSCEAR, 2000).

2.4.1 Cosmic Radiation and Cosmic Radionuclides

Continual bombardment of the earth by high energy particles (mostly alpha particles and protons) originating from space (the sun or beyond our solar system) results in the production of cosmic radiation or rays. These high energy particles interact with nuclei of atoms present in the atmosphere (nitrogen, oxygen, argon) producing neutrons, protons, pions, and kaons (secondary cosmic radiation) having sufficient energy to penetrate into the ground and sea as well as a variety of reaction products known as cosmogenic radionuclides such as $^3$H, $^7$Be, $^{10}$Be, $^{14}$C, $^{22}$Na and $^{24}$Na (UNSCEAR 1988; UNSCEAR, 1993 and UNSCEAR, 2000).

The dose rate in air from the directly ionising component of cosmic radiation is established to be 32 nGy/hr at sea level whiles the neutron component results in an
effective dose rate of 3.6 nGy/hr with both components intensity increasing with altitude (UNSCEAR, 1993 and Cember et al, 2009).

The most significant among the cosmogenic radionuclides are $^3$H and $^{14}$C used for the derivation of doses from man-made environmental releases. Production of cosmogenic radionuclides is greatest in the upper stratosphere, i.e. it is altitude and latitude dependent. Annual effective doses from cosmogenic radionuclides are estimated to be 12 μSv from $^{14}$C, 0.15 μSv from $^{22}$Na, 0.01 μSv from $^3$H and 0.03 μSv from $^7$Be (UNSCEAR, 1993 and UNSCEAR, 2010). Therefore, doses from these four (4) radionuclides as a contributor to the total radiation exposure from natural sources is considered insignificant in the Health physics context.

2.4.2 Terrestrial Radionuclides

Terrestrial radionuclides also known as Primordial radionuclides are very long lived radionuclides and their decay products that have been in existence since the creation of the earth about 4.5 billion years ago and have not significantly decayed. They typically have half-lives of the order of millions of years. The terrestrial radionuclides of interest in terms of doses are the $^{40}$K (Half-life = $1.28\times10^9$ yrs.), $^{232}$Th (Half-life = $1.14\times10^{10}$ yrs.), $^{238}$U (Half-life = $4.47\times10^9$ yrs.) and $^{235}$U (Half-life= $7.04\times10^8$ yrs.) (Tetteh-Larbi, 2012; USCEAR, 1988; USCEAR, 1993 and UNSCEAR, 2010). Several radionuclides that contributes significantly to human exposures results from the decay of Th and U radionuclides.

$^{238}$U and $^{232}$Th head series of decays and are known as parent radionuclides consisting of 14 and 11 significant radionuclides respectively. Radionuclides present in the $^{235}$U decay series are ignored as they contribute insignificantly to total dose
from background radiation. Therefore, the ever presence of these terrestrial radionuclides results in external irradiation of the human body by gamma radiation and internal irradiation by alpha, beta particles and gamma radiations. These radionuclides are present to varying degrees in all media in the environment; in air, in water, in organic materials, living organisms, building materials, rocks and soils (UNSCEAR, 1993; UNSCEAR, 2000 and UNSCEAR, 2010).

Table 2.2 contains the list of primordial radionuclides. The most important radionuclides among the set of non-serieted terrestrial radionuclides are $^{40}$K, $^{50}$V, $^{87}$Rb, $^{113}$Cd and $^{115}$In with $^{40}$K and $^{87}$Rb been the most significant in terms of population dose (Al-Saif, 2009 and Santawamaitre, 2012).
2.4.3 Uranium-238 Series

Uranium-238 is among the three (3) radioisotopes of uranium with a percentage natural abundance of 99.3%. Uranium is present everywhere in the environment at very low concentrations, found in soils with an average concentration of 3ppm corresponding to approximately 74 mBq/g. In its pure form; it is a silvered coloured heavy metal, twice as dense as lead and occurring as an oxide, U₃O₈ in its natural
state. Its half-life is about 4.5 billion years (Argonne National lab., 2005 and Cember et al, 2009).

$^{238}\text{U}$ is the parent radionuclide in this series, decaying by an alpha emission into $^{234}\text{Th}$; with $^{206}\text{Pb}$ been the stable product of this series, normally reached after eight (8) alpha and six (6) beta decay steps (Figure 2.2). $^{226}\text{Ra}$, a member of the $^{238}\text{U}$ decay series with a half-life of 1600 years is amongst the most toxic long-lived alpha emitters present in the environment. It dissolves readily and is chemically similar to calcium. It decays to gaseous radon radionuclide, $^{222}\text{Rn}$ with a half-life of only a few days but two (2) longer-lived decay products $^{210}\text{Pb}$ and $^{210}\text{Po}$ which are very significant contributors to human exposure from natural sources of radiation and providing the main pathway for radiation exposure to the lungs. Inhalation of $^{222}\text{Rn}$ has been associated with increased risk of lung cancers (Faanu et al., 2011 and Righi et al., 2005).

$^{238}\text{U}$ is the first member of the $^{238}\text{U}$ series, which also consists of radionuclides whose mass numbers are divisible by four (4) and leaves a remainder of two (2); thus also called the 4n + 2 series (Cember et al, 2009; El-Sayed, 2014; Contemporary Physics Education Project, 2003 and Argonne National lab., 2005). It should be noted that a steady state equilibrium is achieved between the $^{238}\text{U}$ and its progenies where for a given sample, each member of the series has the same activity as a result of the $^{238}\text{U}$ having a half-life that is hundred times or more greater than any of its progenies (Santawamaitre, 2012; Al-Marzooqi, 2009; Contemporary Physics Education Project, 2003 and El-Sayed, 2014).
Figure 2.2: Natural Decay Series: Uranium-238 (Argonne National lab., 2005).

$^{214}\text{Pb}$ and $^{214}\text{Bi}$ from the $^{238}\text{U}$ decay series and $^{228}\text{Ac}$, $^{212}\text{Pb}$ and $^{208}\text{Tl}$ from the $^{232}\text{Th}$ decay series are the main radionuclides contributing to gamma exposure. $^{208}\text{Tl}$ has the highest gamma energy at 2614 keV. The main interest from radiation protection point of view in the phosphate industry is exposure to gamma radiation from radionuclides in the $^{238}\text{U}$ decay series (IAEA, 2013).
2.4.4 Thorium-232 Series

Thorium is about four (4) times more abundant in nature than uranium. $^{232}\text{Th}$ is the most abundant among the Th isotopes, and is the first element or parent radionuclide in the Th series. It is a radioactive metal found in low levels in soils, rocks, water, plants and animals (US-EPA, 2002). The mass numbers of all members in this series is divisible by four (4) as all decays in this series is by alpha particle emission or beta particle emission. Thus, the $^{232}\text{Th}$ decay series is also known as the $4n$ series. In this series is $^{208}\text{Pb}$ which is the stable product reached after six (6) alpha and five (5) beta decays with $^{220}\text{Rn}$ been the gaseous component of this series (Figure 2.3) (Cember et al, 2009 and El-Sayed, 2014).

In this series too, a steady state equilibrium is achieved between $^{232}\text{Th}$ and its progenies (Santawamaitre, 2012; Al-Marzooqi, 2009 and El-Sayed, 2014).
2.4.5 Actinium-235 Series

The first member of this series is the uranium isotope, $^{235}\text{U}$ with a percentage natural abundance of 0.7% and a very long half-life of $7.13 \times 10^8$ yrs., ending with a stable isotope of $^{207}\text{Pb}$ (Figure 2.4). The mass numbers of radionuclides in this series are all
divisible by four (4) leaving a remainder of three (3), thus this series been known as the $4n + 3$ series. The gaseous radon radionuclide of this series is $^{219}$Rn.

![Natural Decay Series: Uranium-235](http://ugspace.ug.edu.gh)

**Figure 2.4: Natural Decay Series: Uranium-235 (Argonne National lab., 2005)**

**NOTES:**
The symbols $\alpha$ and $\beta$ indicate alpha and beta decay, and the times shown are half-lives.

An asterisk indicates that the isotope is also a significant gamma emitter.
2.4.6 Potassium-40

Potassium is a soft, silver-white metal present everywhere in nature; in soils, plants and animals. It is extensively distributed in crustal rocks at about 27g/kg and in humans at about 1.7g/kg, as such is very important from the health physics point of view. There are three (3) common naturally occurring isotopes of potassium; $^{39}$K, $^{40}$K and $^{41}$K. Non-radioactive $^{39}$K constitutes about 93% of naturally occurring potassium; radioactive $^{40}$K comprises a very small fraction, about 0.012% of naturally occurring potassium whiles the rest is made up by stable $^{41}$K. Though, there are several other radioactive isotopes of potassium in addition to $^{40}$K, they have their half-lives to be less than a day as such they are not considered from the radiation point of view (Argonne National lab., 2005). $^{40}$K has a half-life of 1.3 billion years; decaying to $^{40}$Ca by beta particle emission (no gamma emission) and to $^{40}$Ar by electron capture (gamma emission); both $^{40}$Ca and $^{40}$Ar are stable nuclides (Argonne National lab., 2005).

Potassium is a major constituent of soil and as such together with nitrogen and phosphorus are extensively supplied to farm soils through the application of fertilizers for proper plant growth. It is the most common natural radioactive radionuclide in soils, in human tissues and in most foods especially bananas (Tetteh-Larbi, 2012).
2.5 Radiological impact of use of phosphate and organic fertilizers

The main pathway by which radionuclides in fertilizers are introduced into the environment is through its use in agriculture. Fertilizers are extensively applied to agricultural farm soils to improve soil fertility ensuring proper growth and improved crop yields.

The extensive use of fertilizers especially the phosphate fertilizers is likely to result in an increase in the radium and uranium content of soils leading to a corresponding increase of doses to the public through external exposures from fertilized soils and internal exposures from eating of foods cultivated on such soils. $^{226}$Ra, a member of the $^{238}$U decay series with a half-life of 1600 years is among the most toxic long-lived alpha emitters present in the environment. Inhalation of $^{222}$Rn produced through the radioactive decay of $^{226}$Ra from dust particles from the application of granular fertilizers to farm soils has been associated with increased risk of lung cancers (Faanu et al., 2011 and Righi et al., 2005).

Migration and leaching of soluble NORMs and their decay products from fertilized farms through run offs after rains into surface and underground waters might increase their natural radionuclides concentrations leading to increased doses from drinking of such waters as well as contamination of fishes.

Therefore, it is worthy to note that prolonged use of fertilizers that contains NORMs might result in significant radiological risks to the environment. The radiological impact from application of fertilizers on the agricultural lands and the environment will be estimated using the following radiological parameters: Radium Equivalent Activity ($Ra_{eq}$), Outdoor Absorbed rate, ($D$ (nGy/hr)), Effective Dose, ($Def$ (mSv)), External Radiation Hazard ($Hex$) and Radioactivity Level Index ($I_γ$).
CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Materials used in this research work included:

- Polyethylene bags
- Hand trowel
- Weighing balance
- Drying trays
- Oven
- Grinders and Sieves
- Marinelli Beakers
- Survey meter (RADOS-200)
- High purity germanium (HPGe) detector
- Software programmes: GENIE 2000, Origin Pro 8.5 and Microsoft Excel.

3.2 Description of the New-Juaben Municipality

The Legislative Instrument (LI) 1426 of 1988 established the New Juaben Municipal Assembly comprising of 52 communities with Koforidua as its capital (Fig. 3.1.). New Juaben covers an area size of 159 km$^2$ among the 21 administrative districts in the Eastern region of Ghana (Ghana Statistical Service, 2014). The Municipality lies between longitudes 1030’ West and 0030’ East and latitudes 60 and 70 North. On the north-east, it shares a boundary with East Akim district, to the South-East with Akwapem North, Yilo Krobo on the East and Suhum Kraboa Coaltar district on the West (Ghana Statistical Service, 2014 and The Composite Budget, 2012). The year 2010 Population and Housing Census put the population of the Municipality at 183,727 (Ghana Statistical Service, 2014).
Its rural fertile lands are very much adapted for small to medium scale farming, cattle rearing and poultry (Information on the New Juaben Municipality, 2014). The underlying rock formation is metamorphic known as the Akwapim-Togo rocks. The main source of drinking water in the Municipal is the Densu River Basin and its tributaries which are dammed close to the Municipality capital, Koforidua. The Densu River is one of the most-exploited rivers in Ghana and provides also for industrial and agricultural purposes.

The climatic zone of the Municipality falls within the semi-deciduous rain forest whiles its vegetation is typified by tall trees with evergreen undergrowth consisting of some commercial trees such as Odum, Onyina, Kyenkyen, Wawa and others (Ghana Statistical Service, 2014).
Figure 3.1: Map of New Juaben Municipality (Ghana Statistical Service, 2014).
3.3 Sample Collection

The fertilizer sampling took place in Koforidua which is the municipality capital and as such is the central supplying channel of fertilizers to its villages and other districts famous in agricultural production in the Eastern Region.

The chemical fertilizers were selected based on whether there was a phosphorus or phosphate component based on their labels. Therefore, only the phosphorus or phosphate fertilizers available on the New Juaben market were sampled on the part of chemical fertilizers. The organic fertilizers are sparingly used by farmers in the whole country so only the frequently used organic fertilizer types available on the local market were sampled. Below is a table displaying the various brands of phosphate and organic fertilizers sold in Koforidua.

Table 3.1: Phosphate and organic fertilizers sold in the New Juaben Municipality.

<table>
<thead>
<tr>
<th>BRAND</th>
<th>ORIGIN</th>
<th>FORM</th>
<th>MAIN COMPONENTS (%)</th>
<th>NITROGEN</th>
<th>PHOSPHORUS</th>
<th>POTASSIUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAIFA MAP</td>
<td>ISRAEL</td>
<td>GRANULATED</td>
<td>12</td>
<td>12</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>SUPER MASTER</td>
<td>USA</td>
<td>GRANULATED</td>
<td>15</td>
<td>5</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>POLY FEED</td>
<td>ISRAEL</td>
<td>POWDERED</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>ACARP ORGANIC COMPOST</td>
<td>GHANA</td>
<td>POWDERED</td>
<td>UNKNOWN</td>
<td>UNKNOWN</td>
<td>UNKNOWN</td>
<td>UNKNOWN</td>
</tr>
<tr>
<td>N.P.K 23.10.10+3S</td>
<td>BELGIUM</td>
<td>GRANULATED</td>
<td>23</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>N.P.K 15.15.15</td>
<td>RUSSIA</td>
<td>GRANULATED</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>N.P.K 15.15.15</td>
<td>GHANA</td>
<td>GRANULATED</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>
Six (6) brands of both granular and foliar phosphate fertilizers and one (1) brand of organic fertilizer available on the New Juaben Municipality market were collected from different fertilizer retail shops between the months of November (2014) and January (2015). Four (4) samples (0.5kg each) of each fertilizer brand were collected in the markets and transferred into labelled polyethylene bags and sent to the G.A.E.C laboratory for preparation and analysis. In addition, seven (7) agricultural farms in different communities (Asokore, Effiduase, Asikasu, Bornya and Trom) in the Municipality that extensively use fertilizers were identified with the help of MOFA extension officers. Soil samples were taken from seven (7) farms to assess the radiological impact of NORMs from the application of fertilizers to the agricultural soils. Three (3) virgin soil samples (soils on which no fertilizers are applied) from the towns where sampling were done were also taken as control samples for analysis. A standard random sampling method was used in the soil sampling at a depth 5-15 cm where fertilizers applied are concentrated, avoiding locations such as old roadways, field edges, water channels and manure piles (IAEA, 2004).

3.4 Sample preparation and analysis

The solid samples upon reaching the Radiation Protection Institute’s gamma-ray spectrometry laboratory of G.A.E.C were air-dried for 7 days, and then oven heated at a temperature of 105°C for about 3-4 hours to completely remove moisture. The samples were ground into fine powder using a ball mill and sieved through a 500 µm mesh size pore into one (1) litre Marinelli beakers, weighed and then sealed for one (1) month for secular equilibrium to be achieved between short-lived daughters of $^{238}$U and $^{232}$Th decay series and their long-lived parent radionuclides before counting.
Each sample was counted using a high purity germanium detector for a period of 36000 seconds to acquire a spectral data.

### 3.5 Description of the Gamma Spectrometry System

The PC-based gamma ray spectrometer used consists of an extended range coaxial germanium detector (XtRa) (Model Number: GX4020), a high voltage power supply, a preamplifier (Model Number: 2002CSL), an ultra-low background cryostat: U-style integral (Model Number: 7500SL), a multichannel analyser (MCA) and a GENIE 2000 analytical software (for data acquisition, manipulation and analysis of spectra on a computer). The detector crystal is cooled by liquid nitrogen at a temperature of 77K or -196°C, provided in a 30litre Dewar.

The relative efficiency of the detector is 40% with energy resolutions of 1.10KeV and 2.0KeV at gamma ray energies of 0.122MeV and 1.332MeV of $^{57}$Co and $^{60}$Co respectively.

The detector functions in a recommended bias voltage of (+) 4500V, a depletion voltage of (+) 4000V, a leakage current at recommended bias of 0.01nA and a preamplifier test point voltage at a recommended voltage of (-) 0.8V.

Below is a block diagram (Figure 3.2) and a pictorial view (Figure 3.3) of the gamma spectrometry system used in this study.
Figure 3.2: Block diagram of the gamma ray spectrometry used (Reguigui, 2006).

Figure 3.3: A pictorial view of the Gamma Spectrometry System used.
3.5.1 Calibration of the Gamma Spectrometer

The determination of an instrument’s response or reading relative to a series of known radiation values (from a standard radiation source) covering the range of the instrument, and adjusting the instrument to provide a correct response is known as its calibration (Martin, 2006). The energy and efficiency calibrations are the parameters most significant in gamma spectroscopy. They form an integral part of this analytical technique for both qualitative and quantitative analysis of radionuclides in the samples.

Certified standard radioactive sources were used for the calibrations. The standard source used was suitable for this purpose as it had been prepared in such a way to have identical shape and density as the samples that are to be compared with so to minimize the deviations in the activities to be measured (Lordford, 2012 and Gilmore, 2008).

For the energy and efficiency calibrations, it was necessary that the energies of the gamma rays of the radionuclides in the standard source be accurately known as well as their gamma ray emission probabilities and activities (Gilmore, 2008).

The energy and efficiency calibrations were done prior to measurements using a multinuclide reference standard supplied by the Czech Metrology Institute Inspectorate for Ionizing Radiation of mass and density, 0.980 kg and 0.98 g/cm\(^3\) respectively. The standard consists of a matrix of nine (9) artificial radionuclides homogeneously dispersed in silicon resin into a 1L Marilleni beaker. It consists of the following radionuclides with their corresponding energies (energy range of 60 keV to ~2000 keV):
Am-241(59.54 keV), Cd-109(88.03 keV), Ce-139(165.86 keV), Co-57(122.06 keV), Co-60(1173.2 keV and 1332.5 keV), Cs-137(661.66 keV), Sn-113(391.69 keV), Sr-85(514.01 keV) and Y-88(898.04 keV and 1836.1 keV).

The spectrum of the standard source was obtained by counting it for 36000 s via the XtRa detector.

### 3.5.2 Energy Calibration

To obtain a relationship between peak position (channel number) in the spectrum and the corresponding gamma energy, the energy calibration is performed even before measurements start. The standard source was described earlier was counted for 36000 s, long enough for a good statistical precision for the peaks.

The true positions (channel numbers) of every full energy peak was determined accurately, and the energy of the photon (gamma ray) plotted against the channel number to obtain a curve that is used to determine the energy of a photon that is responsible for an unknown peak in the spectrum (Gilmore, 2008 and Reguigui, 2006).

The graph obtained generates a linear relationship, relating the energy of a gamma ray to the channel number in the form of an expression below:

\[ E \ (keV) = I \ (keV) + G \times C \ (Channels) \]

Where,

I and G are the intercepts (which is usually set as close as possible to zero) and the gradient (linear energy scale (keV/channel number) of the MCA) of the calibration line and C, the channel position.
3.5.3 Efficiency Calibration

The main aim in gamma spectroscopy is to relate the peak area of a spectrum to the amount of radioactivity it represents defined in terms of the absolute full energy peak efficiency. Thus, it relates the peak area, at a particular energy, to the number of gamma rays emitted by the source (Martin, 2006).

Reguigui (2006) defined the full-energy peak efficiency as the “the fraction of photons of a particular energy emitted by a source, that contributes to the corresponding full energy peak observed in the pulse height spectrum”. It is dependent on the geometry of the sample like the size, density and the distance from the detector and is given in the following equation as (Lordford, 2012; Reguigui, 2006 and Khandaker et al, 2012):

$$\varepsilon_\gamma = \frac{C_\gamma}{A \times P_\gamma \times T_c}$$

Where, 

$\varepsilon_\gamma$ is the counting efficiency

$C_\gamma$ is the net gamma ray count of the full energy peak observed in the pulse height spectrum

$P_\gamma$ is the gamma yield (gamma emission probability)

$A$ is the activity of the source in Bq at the time of counting

$T_c$ is the counting time

Efficiency calibration improves the sensitivity of the detection as well as the reliability of the results of analysis. The efficiency calibration was performed using the same spectrum obtained in the energy calibration for the standard source.
The present activity of each nuclide’s photo peak in the standard source matrix was found using information on the Standard certificate provided and by utilizing Ms Excel. Their activities were calculated using the following equation:

\[ A = A_0 e^{-\lambda t} \]

Where,

A is the present activity calculated

\( A_0 \) is the activity of nuclide at the time prepared

\( t \) is the time elapsed since its preparation

\( \lambda \) is the decay constant

The GENIE 2000 spectrum analytical software was then used to find the net gamma ray count of each nuclide at their corresponding energies.

Knowing the \( P_\gamma \) and the \( T_c \) (36000 s), the \( \varepsilon_\gamma \) was calculated for each radionuclide in the standard source at the photo peaks for all the energies to be used.

The efficiency, \( \varepsilon_\gamma \) at each energy as a function of the peak energy, \( E \) was plotted on a log-log scale yielding the polynomial in the form of (Gbado et al, 2011 and Reguigui, 2006):

\[ \ln \varepsilon = a_0 + a_1 (\ln E) + a_2 ((\ln E)^2) + a_3 ((\ln E)^3) \]

Where,

\( a_0, a_1, a_2 \) and \( a_3 \) are calibration constants for a given geometry.
3.5.4 Lower Limit of Detection and Minimum Detectable Activity of the Gamma Spectrometry System

In measuring low-level activity samples, the Lower Limit of Detection (LLD) and the Minimum Detectable Activity (MDA) are often used as detection limits in determining the sensitivity of the measurement at or near background level. The LLD is defined as the smallest amount of sample activity that yields a net count above the background at a prevailing condition of a confidence level of 95% (Martin, 2006). The LLD is considered an index that takes into account the statistical variation in measured counts of both the sample and the background. Thus, it is related only to the observed counts produced by the detector system and not dependent on other factors involved in the method of measurement or sample characteristics (Gilmore, 2008 and Martin, 2006).

The LLD in counts for a total background, B, for equal count times for both background and sample measurements at a 95% confidence level is given by the equation (Lordford, 2012 and Gilmore, 2008):

\[ LLD = 2.706 + 4.653\sqrt{B} \]

\[ \sqrt{B} = \sigma_B \], represent the standard deviation of the background in the region of interest and B is the number of counts for the background spectrum of the sample.

The LLD determined above is then used to derive the MDA, a priori activity level that the detector can detect and report correctly 95% of the time. The MDA determined is the least amount of activity that can be confidently measured (Gilmore, 2008; Reguigui, 2006 and Martin, 2006). The LLD from which the MDA is derived is obtained through measurements on a “blank” (with no activity), counted for the same time period as would be the samples, taking into consideration all the necessary
factors like the instrument’s characteristics (background and efficiency), sample size, counting time and any other factors that can influence the measurement (e.g. gamma emission probability etc.).

As such an empty, clean and dry 1L Marinelli beaker was counted for the same period of time as would be for the samples to obtain the background spectrum to be used in deriving the LLD and the MDA using their respective equations (Gilmore, 2008 and Martin, 2006).

$$MDA = \frac{LLD}{m \times T_c \times \varepsilon \times P_\gamma}$$

Where,

LLD is the Lower Limit of Detection

m is the sample mass

T_c is the count period

P_\gamma is the gamma emission probability

\varepsilon is the detector efficiency.

The gamma ray energies of the gamma emitting radionuclides within the uranium and thorium series are used to quantify the activity concentrations of the parent radionuclides which cannot be measured directly as listed in Table 3.2.
Table 3.2: Primary and Secondary gamma ray energy lines and their associate emission probability for $^{238}$U, $^{232}$Th and $^{40}$K (IAEA, 2007).

<table>
<thead>
<tr>
<th>Parent Radionuclide</th>
<th>Primary Gamma Rays</th>
<th>Secondary Gamma Rays</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-238</td>
<td>Pb-214*</td>
<td>351.93</td>
</tr>
<tr>
<td></td>
<td>Bi-214*</td>
<td>609.32</td>
</tr>
<tr>
<td></td>
<td>Bi-214*</td>
<td>1764.54</td>
</tr>
<tr>
<td>Th-232</td>
<td>Tl-208*</td>
<td>2614.51</td>
</tr>
<tr>
<td></td>
<td>Pb-212*</td>
<td>238.63</td>
</tr>
<tr>
<td></td>
<td>Tl-208*</td>
<td>583.19</td>
</tr>
<tr>
<td>K-40</td>
<td>-</td>
<td>1460.82</td>
</tr>
</tbody>
</table>

Asterisk (*) commonly used energy lines

3.6 Calculation of Activity concentrations

The specific activity concentration of NORMs in both the fertilizer and soil samples were calculated using the analytical expression:

$$A_{sp}(E,i) = \frac{N_{sam(E,i)}}{\epsilon_{\gamma}(E) \cdot T_c \cdot P_{\gamma(E,i)} \cdot M_{sam}}$$

Where,

$A_{sp}$ is the specific activities in Bq/kg of the radionuclides in a sample

$N_{sam(E,i)}$ is the net counts for the radionuclide, $i$ at energy $E$
M_{sam} \text{ is the dry-weight of sample (kg)}

\varepsilon_{\gamma} \text{ is the photopeak efficiency}

P_{\gamma(E,i)} \text{ is the gamma emission probability of the radionuclide, } i \text{ for a transition at energy } E

T_c \text{ is the counting time}

By ignoring the uncertainties in both the counting time and the gamma emission probabilities, the overall uncertainty or error in the activity calculations is given as (Faanu et al., 2011):

\[ dA_{sp} = A_{sp} \sqrt{\left(\frac{dN}{N}\right)^2 + \left(\frac{d\varepsilon}{\varepsilon}\right)^2 + \left(\frac{dM}{M}\right)^2} \]

\( dN \) is the uncertainty in the integration of the peak area of each full energy event.

\( dM \) is the standard uncertainty on the weighing balance used to weigh the samples which was 0.0001 kg.

\( d\varepsilon \) is the uncertainty in the efficiency at each energy used.

### 3.7 Ambient Gamma Dose rate in the Fertilizer Storage Rooms

During the fertilizer sampling, the ambient gamma dose rates were measured in the fertilizer storage rooms using a digital survey meter, RADOS RDS-200 (Serial No.:241041) which is a multi-purpose radiation meter useful for low dose rate measurements. The dose rate meter was calibrated at the Radiation Protection Institutes’ Secondary Standard Dosimetry laboratory of the Ghana Atomic Energy Commission with a calibration factor provided. At each fertilizer storage room, ten
(10) measurements were made at 1 meter above ground and the average value taken in µSv/h.

3.8 Calculation of Radiological Effects

The expected radiological impact from utilization of fertilizers on the agricultural lands and the environment are estimated using the following indices:

3.8.1 Radium Equivalent Activity (Ra\textsubscript{eq})

Ra\textsubscript{eq} is a single radiological indicator used to collectively estimate the radiological hazard posed by the activity concentrations or levels of $^{226}$Ra, $^{232}$Th and $^{40}$K due to non-uniform radiation exposure (El-Fiki et al., 2008; Issa et al., 2012; Gbadago et al., 2011) which is given as:

$$R_{eq} = C_{Ra} + \frac{10}{7} C_{Th} + \frac{10}{130} C_{K} \ldots \ldots eqn(1)$$

Where,

$C_{Ra}$, $C_{Th}$ and $C_{K}$ are activities or concentrations in Bq/kg for $^{226}$Ra, $^{232}$Th and $^{40}$K respectively. It is assumed that 1 Bq/kg of $^{226}$Ra, 0.7 Bq/kg of $^{232}$Th and 13 Bq/kg of $^{40}$K produce equal gamma ray dose rate. The maximum value of $R_{eq}$ should not exceed 370 Bq/kg to limit exposures to 1.5 mGy$^{-1}$ (Gbadago et al., 2011).
3.8.2 Outdoor Gamma Absorbed dose rate and Outdoor Annual Effective Dose for Soil

Using the conversion factors 0.0417 nGy.hr\(^{-1}\) for \(^{40}\text{K}\), 0.462 nGy.hr\(^{-1}\) for \(^{226}\text{Ra}\) and 0.604 nGy.hr\(^{-1}\) for \(^{232}\text{Th}\), the total air absorbed dose rate (nGy.hr\(^{-1}\)) in the outdoor air at 1m above the ground due to the activity concentrations of \(^{40}\text{K}\), \(^{226}\text{Ra}\) and \(^{232}\text{Th}\) (Bq/kg) from fertilizer applications on agricultural soils is calculated using equation 2, (Alharbi, 2013; UNSCAER, 2010 and Gbadago et al. 2011).

\[
\text{Outdoor Gamma Absorbed dose, } D(n\text{Gy. hr}^{-1}) = 0.462C_{\text{Ra}} + 0.604C_{\text{Th}} + 0.0417C_{K} \quad \ldots \quad \text{eqn}(2)
\]

\(C_{\text{Ra}}, C_{\text{Th}}\) and \(C_{K}\) have the same meaning as eqn. (1)

To estimate the annual effective dose equivalent, \(D_{\text{eff}}\), the following equation is used (Issa et al, 2008):

\[
\text{Outdoor Annual effective dose rate, } Deff(\text{mSv}) = D \times T \times F \quad \ldots \quad \text{eqn}(3)
\]

Where,

\(D\) (nGy/hr) – Calculated outdoor absorbed dose rate in air at 1m height

\(T\)- Outdoor occupancy factor (0.2\times24\times365.25)

\(F\)- Conversion factor (0.7\times10^{-6}\) Sv/Gy

3.8.3 External Radiation Hazard (Hex)

\[
Hex = \frac{C_{\text{Ra}}}{370} + \frac{C_{\text{Th}}}{259} + \frac{C_{K}}{4810} \quad \ldots \quad \text{eqn}(4)
\]

Where,

\(C_{\text{Ra}}, C_{\text{Th}}\) and \(C_{K}\) are the same as defined before (Hameed, Pillai & Mathiyarasu, 2014). The decay of naturally occurring radionuclides in 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 the external hazard index (Elisha, et al, 2013 and Samad et al, 2012).

To keep the external radiation hazard insignificant, it should always be less than unity i.e. limiting the radiation exposure attributable to NORMs in the samples to permissible dose equivalent of 1mSv.

### 3.8.4 Radioactivity Level Index ($I_\gamma$)

This is used to estimate the level of risk coupled with $\gamma$- radiation associated with NORMs in specific investigated samples which is given as (El-Zakla et al, 2007; Gbadago et al, 2011 and El-Taher et al.s, 2013):

$$I_\gamma = \frac{C_{Ra}}{150} + \frac{C_{Th}}{100} + \frac{C_{K}}{1500} \leq 1 \quad eqn(5)$$

Where, $C_{Ra}$, $C_{Th}$ and $C_{K}$ are the same as defined before.
CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Energy and Efficiency Calibrations

The energy and efficiency calibrations done prior to measurements using a multinuclide reference standard in a 1L Marilleni beaker supplied by the Czech Metrology Institute Inspectorate for Ionizing Radiation are shown in figures 4.1 and 4.2 respectively. The standard radionuclides that were used for the energy and efficiency calibrations are shown in the Appendix 1.

The Minimum Detectable Activities (MDA) calculated for $^{226}$Ra, $^{232}$Th and $^{40}$K as described in section 3.5.4 and are shown in table 4.1 with estimated values of 0.14, 0.12 and 4.70 Bq/kg respectively.

![Energy Calibration](image)

$y = 0.093 + 0.244x$

$R^2 = 1$

Figure 4.1: Energy calibration curve using mixed standard radionuclides in a one litre Marinelli beaker.
Efficiency Calibration

\[ \text{In Eff} = -40.88 + 19.20 \text{ In E} - 3.13 \text{ In E}^2 + 0.16 \text{ In E}^3 \]

\[ R^2 = 0.98 \]

Figure 4.2: Efficiency calibration curve as a function of energy for mixed radionuclides standard in a one litre Marinelli beaker.

Table 4.1: The Minimum Detectable Activities of $^{226}$Ra, $^{232}$Th and $^{40}$K.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>MDA(Bq/kg) ± Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{226}$Ra</td>
<td>0.14 ± 0.01</td>
</tr>
<tr>
<td>$^{232}$Th</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>$^{40}$K</td>
<td>4.70 ± 0.20</td>
</tr>
</tbody>
</table>
4.2 Activity Concentration in the Fertilizers

The estimated activity concentrations of $^{226}\text{Ra}$, $^{232}\text{Th}$ and $^{40}\text{K}$ and the radioactivity level index in the fertilizers are shown in Table 4.2. In addition, the external gamma dose rates at 1m above ground in the fertilizer storage rooms measured is also shown in Table 4.3. The activity concentration of $^{226}\text{Ra}$ in the fertilizers ranged from $<0.14$ to $117.20$ Bq/kg with an average value of $32.10\pm2.60$ Bq/kg. The highest activity concentration of $^{226}\text{Ra}$ occurred in FT5 whiles FT1, FT2 and F6 had their $^{226}\text{Ra}$ activities below detection limit (BDL). For the $^{232}\text{Th}$, it varied from $<0.12$ to $44.70$ Bq/kg with an average value of $12.20\pm1.60$ Bq/kg. The $^{232}\text{Th}$ activity concentration was below the detection limit in F2 and F3 whiles F7 had the highest $^{232}\text{Th}$ activity of $37.20\pm7.50$ Bq/kg. However, the activity of $^{40}\text{K}$ was recorded in all the fertilizers and fluctuated from 4.90 to 5592 Bq/kg with an average concentration of $3005.50 \pm 68.80$ Bq/kg. The highest $^{40}\text{K}$ activity ($5325.20 \pm 266.80$ Bq/kg) was recorded in F6 whiles the lowest $^{40}\text{K}$ was in FT1 ($5.40 \pm 0.50$ Bq/kg).

The Table 4.2 reveals great variations especially in the $^{226}\text{Ra}$ and $^{232}\text{Th}$ activity concentrations. The wider variation of the primordial radionuclides in the fertilizers is probably as a result of the geological origin of its components especially the phosphate component which can be of sedimentary or of igneous origin. Moreover, the method of chemical processing of the phosphate ores (either by the ‘wet’ process or ‘thermal’ process) in the manufacture of the phosphate in the phosphate fertilizers can also be the reason.

The radioactivity level index, $I_\gamma$ is widely used to estimate the level of risk coupled with $\gamma$- radiation associated with $^{226}\text{Ra}$, $^{232}\text{Th}$ and $^{40}\text{K}$ in fertilizers which is calculated and shown in Table 4.2. For the level of risk to be insignificant, the $I_\gamma$
should be less than or equal to one (1) but it was found to be higher than the recommended value of 1 in all the fertilizer samples except FT1 and FT4. This suggests that the storage of large quantities of fertilizers can lead to an increase in the effective annual gamma dose rate. It must be emphasised that the higher $I\gamma$ values was primarily due the high activity concentrations of $^{40}\text{K}$ in these fertilizers in the order of thousands. Therefore, the storage of large quantities of fertilizers in warehouses might be a source of concern from the radiation point of view in terms of external gamma dose rates as well as in the build-up of indoor radon concentrations (in highly enclosed and poorly ventilated warehouses).

Table 4.2: Activity concentrations of $^{226}\text{Ra}$, $^{232}\text{Th}$ and $^{40}\text{K}$ and the Radioactivity Level Index in the fertilizers.

<table>
<thead>
<tr>
<th>Fertilizers ID</th>
<th>Activity Concentration (Bq/kg)</th>
<th>$I\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{226}\text{Ra}$</td>
<td>$^{232}\text{Th}$</td>
</tr>
<tr>
<td>FT1</td>
<td>&lt;0.14</td>
<td>0.20±0.04</td>
</tr>
<tr>
<td>FT2</td>
<td>&lt;0.14</td>
<td>&lt;0.12</td>
</tr>
<tr>
<td>FT3</td>
<td>1.70±0.60</td>
<td>&lt;0.12</td>
</tr>
<tr>
<td>FT4(Organic)</td>
<td>8.70±0.80</td>
<td>7.90±0.90</td>
</tr>
<tr>
<td>FT5</td>
<td>107.60±9.60</td>
<td>9.40±1.30</td>
</tr>
<tr>
<td>FT6</td>
<td>&lt;0.14</td>
<td>6.20±1.00</td>
</tr>
<tr>
<td>FT7</td>
<td>10.50±3.40</td>
<td>37.20±7.50</td>
</tr>
<tr>
<td><strong>AVERAGE</strong></td>
<td>32.10±2.60</td>
<td>12.20±1.60</td>
</tr>
<tr>
<td><strong>RANGE</strong></td>
<td>&lt;0.14-117.20</td>
<td>&lt;0.12-44.70</td>
</tr>
</tbody>
</table>
Table 4.3 shows the ambient gamma dose rates to be greater than their respective background measurements in all the fertilizer storage rooms except S4. For S8, it was 3.3 times higher than its background measurement whiles it was 2.5 times and 2.6 times higher than the respective background measurements in S6 and S7 respectively. Therefore, it suggests that the storage of fertilizers elevates the ambient gamma dose rates above background measurements. The type of fertilizers as well as the number of fertilizers stored in the storage rooms can be factors in contributing to the ambient gamma dose rates in the storage rooms been higher their background measurements.

In only three of the locations were the fertilizer storage rooms separated from the offices and show rooms. Therefore, the fertilizer sellers and works may receive higher external radiation exposure if they work around the huge fertilizer stockpiles for longer periods. Though, the average ambient gamma dose rates in the storage rooms were higher than their background measurements, they were still below the annual exposure limit of 1mSv (1000 µSv) averaged.
Table 4.3: Annual Average Effective Gamma dose rates in the various fertilizer storage rooms.

<table>
<thead>
<tr>
<th>Location</th>
<th>Effective Dose Rates (µSv/a)</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Background</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>153±15</td>
<td>340± 34</td>
</tr>
<tr>
<td></td>
<td>Background</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>159±16</td>
<td>233±23</td>
</tr>
<tr>
<td></td>
<td>Background</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>170±17</td>
<td>252±25</td>
</tr>
<tr>
<td></td>
<td>Background</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td>137±14</td>
<td>107±11</td>
</tr>
<tr>
<td></td>
<td>Background</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>137±14</td>
<td>211±21</td>
</tr>
<tr>
<td></td>
<td>Background</td>
<td></td>
</tr>
<tr>
<td>S6</td>
<td>153±15</td>
<td>384±38</td>
</tr>
<tr>
<td></td>
<td>Background</td>
<td></td>
</tr>
<tr>
<td>S7</td>
<td>219±22</td>
<td>567±57</td>
</tr>
<tr>
<td></td>
<td>Background</td>
<td></td>
</tr>
<tr>
<td>S8</td>
<td>121±12</td>
<td>403±40</td>
</tr>
</tbody>
</table>

It is observed in Table 4.4 that the average activity concentration of $^{226}$Ra of the fertilizers in this study is less than other published works except in Nigeria (Elisha et al, 2013). The average activity concentration of $^{232}$Th was also found to be higher than reported activity concentrations from Serbia (BDL), Italy (3.5 Bq/kg), Finland (11 Bq/kg) but was lower than reported works in Nigeria (45.04±0.04 Bq/kg), India (25.2 Bq/kg) and Saudi Arabia (17 Bq/kg). The $^{40}$K activity concentration of the fertilizers in this present work compared well with other published data in other countries and was within the world mean range. Table 4.4 shows the mean $^{40}$K in fertilizers in this present study to be about 10 times higher than the mean $^{40}$K activity...
concentration in Nigeria, but it was found to be lower than the means obtained in Italy, Serbia and Finland.

Table 4.4: Mean Activity concentration of $^{226}$Ra, $^{232}$Th and $^{40}$K in the fertilizers compared to other published works

<table>
<thead>
<tr>
<th>Country</th>
<th>$^{226}$Ra (Bq/kg)</th>
<th>$^{232}$Th (Bq/kg)</th>
<th>$^{40}$K (Bq/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ghana</td>
<td>32.10±2.60</td>
<td>12.20±1.60</td>
<td>3005.50±68.80</td>
<td>Present Work</td>
</tr>
<tr>
<td>Italy</td>
<td>120</td>
<td>3.5</td>
<td>4000</td>
<td>Righi, S. et al (2005)</td>
</tr>
<tr>
<td>Nigeria</td>
<td>24.87±0.02</td>
<td>45.04±0.04</td>
<td>305.33±0.19</td>
<td>Elisha, J.J. et al (2013)</td>
</tr>
<tr>
<td>India</td>
<td>340</td>
<td>25.2</td>
<td>906.5</td>
<td>Hameed et al (2014)</td>
</tr>
<tr>
<td>Finland</td>
<td>54</td>
<td>11</td>
<td>3200</td>
<td>Mustonen (1985)</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>64</td>
<td>17</td>
<td>2453</td>
<td>Alharbi (2013)</td>
</tr>
</tbody>
</table>

NB: This activity concentration values represented in Table 4.4 above are for the localities from which the samples were taken but not representative for their respective countries. BDL means below detection Limit.

4.3 Activity concentration in the farm soils

Table 4.5 shows the activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K in cultivated soils in the various communities namely, Asikasu, Asokore, Bornya, Trom and Effiduase together with their respective virgin soils. The activity concentration of $^{40}$K was an order of magnitude higher than the activity levels of $^{226}$Ra and $^{232}$Th in both soils studied. Generally, except in some few cases, the results in table 4.5 shows the
average activity concentration of $^{226}$Ra, $^{232}$Th and $^{40}$K in the cultivated soils are higher than in the virgin (uncultivated) soils. This suggests that the use of phosphate fertilizers (mostly the NPK fertilizers) to enhance soil fertility in the New Juaben Municipality might be largely responsible for the enhanced level of $^{226}$Ra, $^{232}$Th and $^{40}$K in the cultivated soils as compared to the virgin soils.

Table 4.5: Results of the activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K in the cultivated farm soils and virgin soils.

<table>
<thead>
<tr>
<th>Soil ID</th>
<th>Activity Concentration(Bq/kg)</th>
<th>$^{226}$Ra</th>
<th>$^{232}$Th</th>
<th>$^{40}$K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$^{226}$Ra</td>
<td>$^{232}$Th</td>
<td>$^{40}$K</td>
</tr>
<tr>
<td>ASI VIRGIN</td>
<td></td>
<td>13.30± 1.40</td>
<td>10.90± 1.40</td>
<td>207.50± 10.80</td>
</tr>
<tr>
<td>ASO-EFF VIRGIN</td>
<td></td>
<td>7.20± 0.80</td>
<td>6.70± 0.70</td>
<td>86.50± 4.50</td>
</tr>
<tr>
<td>BOR- TRO VIRGIN</td>
<td></td>
<td>6.40± 0.70</td>
<td>6.60± 0.70</td>
<td>123.0± 6.30</td>
</tr>
<tr>
<td>AVERAGE</td>
<td></td>
<td>9.0±1.7</td>
<td>8.10±1.70</td>
<td>139.0±13.3</td>
</tr>
<tr>
<td>TRO</td>
<td></td>
<td>10.90± 1.10</td>
<td>8.90± 0.90</td>
<td>186.30± 9.50</td>
</tr>
<tr>
<td>ASI</td>
<td></td>
<td>18.40± 1.80</td>
<td>16.90± 1.60</td>
<td>333.60± 16.90</td>
</tr>
<tr>
<td>ASO 1</td>
<td></td>
<td>14.40± 1.40</td>
<td>6.80± 0.70</td>
<td>191.50± 9.80</td>
</tr>
<tr>
<td>ASO 2</td>
<td></td>
<td>8.20± 0.90</td>
<td>5.60± 0.60</td>
<td>148.20± 7.60</td>
</tr>
<tr>
<td>BOR 1</td>
<td></td>
<td>12.00± 1.20</td>
<td>10.2± 1.0</td>
<td>109.60± 5.70</td>
</tr>
<tr>
<td>BOR 2</td>
<td></td>
<td>12.80± 1.20</td>
<td>12.10± 1.10</td>
<td>129.0± 6.6</td>
</tr>
<tr>
<td>EFF</td>
<td></td>
<td>11.0± 1.1</td>
<td>13.80± 1.30</td>
<td>344.10± 17.40</td>
</tr>
<tr>
<td>AVERAGE</td>
<td></td>
<td>12.50±3.30</td>
<td>10.60±2.80</td>
<td>206.0± 30.2</td>
</tr>
</tbody>
</table>

Towns : ASI- Asikasu, ASO- Asokore, BOR- Bornya, TRO- Trom, EFF- Effiduase

According to UNSCEAR (2000) report, the world average value of the activity concentration of $^{226}$Ra in soils is 35 Bq/kg, for $^{232}$Th is 30 Bq/kg and for $^{40}$K is 400 Bq/kg. The mean activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K in both the virgin
and cultivated soil samples in this present study were far below the world average values as well as other similar studies in other countries shown in table 4.6.

Table 4.6: Comparison of mean activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K in soils in the study area and published data.

<table>
<thead>
<tr>
<th>Country</th>
<th>Concentration in soil, Bq/kg</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{226}$Ra</td>
<td>$^{232}$Th</td>
</tr>
<tr>
<td>Ghana, Virgin soil</td>
<td>9.0±1.7</td>
<td>8.10±1.70</td>
</tr>
<tr>
<td>Ghana, Cultivated Soil</td>
<td>12.52±3.33</td>
<td>10.62±2.81</td>
</tr>
<tr>
<td>India, Virgin soil</td>
<td>6.8±3.2</td>
<td>87.5±63.5</td>
</tr>
<tr>
<td>India, Cultivated soil</td>
<td>8.4±4.5</td>
<td>98.4±63.6</td>
</tr>
<tr>
<td>India, Barren Land</td>
<td>9.1 ± 0.13</td>
<td>59.4 ± 1.45</td>
</tr>
<tr>
<td>India, Cultivated land</td>
<td>16.2 ± 0.22</td>
<td>68.1±1.44</td>
</tr>
<tr>
<td>India, Cultivated land</td>
<td>44.87 ±0.16</td>
<td>54.59± 0.08</td>
</tr>
<tr>
<td>Egypt, Cultivated land</td>
<td>16.43 ± 2.89</td>
<td>18.31 ± 5.25</td>
</tr>
<tr>
<td>Serbia, Cultivated land</td>
<td>51 ± 5</td>
<td>50 ± 4</td>
</tr>
<tr>
<td>Serbia, Uncultivated land</td>
<td>48 ± 2</td>
<td>47 ± 2</td>
</tr>
<tr>
<td>Worldwide</td>
<td>35</td>
<td>30</td>
</tr>
</tbody>
</table>

4.4 **Hazard Assessment of the soils**

The results of the outdoor absorbed and effective dose rates, radium equivalent activity and external hazard indices in both the cultivated and virgin soils in the cultivated farm soils and virgin soils are shown in Table 4.7.
The maximum value of Ra$_{eq}$ should not exceed 370 Bq/kg to limit the annual exposure to 1.5 m Gya$^{-1}$ (Gbadago et al., 2011). In the present study, the mean Ra$_{eq}$ value for cultivated soil samples (43.60 Bq/kg) was found to be higher than that of the virgin soil samples (31.20 Bq/kg); however, both are well below the permissible limit of 370 Bq/kg. Even though this difference in the Ra$_{eq}$ value in both soils may be attributed to the use of phosphate and organic fertilizers, possible exposure of farmers is expected to be very low.

The mean absorbed dose rate in air at 1 m above the ground calculated from the soil activity concentrations of both the virgin and cultivated lands were found to be 14.8 nGy/h (in a range of 12 - 21.40 nGy/h) and 20.80 nGy/h (in a range of 13.30-32.60 nGy/h) respectively. These values were found to be comparable with the world’s reported ranges of 18-93 nGy/h and mean of 59 nGy/h. In the UNSCEAR 2000 report, the worldwide average of the outdoor annual effective dose is 0.07 mSv. The mean outdoor annual effective dose results in this study are much lower than the world average value.

To limit the radiation exposure attributable to NORMs in a sample to permissible dose equivalent of 1 mSv, the external hazard index should be less than unity. Indications from Table 4.7 shows that the external hazard index estimated for both the virgin and cultivated soil samples were less than one.
Table 4.7: Results of the outdoor absorbed dose rate, outdoor annual effective dose, radium equivalent activity and external hazard indices in both the cultivated and virgin soils in the cultivated farm soils and virgin soils

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\text{Ra}_{eq}$, Bq/kg</th>
<th>Outdoor absorbed dose rate, $D$ (nGy/h)</th>
<th>Outdoor annual effective dose, $D_{eff}$ (mSv)</th>
<th>External (Hex)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASI VIRGIN</td>
<td>44.80</td>
<td>21.40</td>
<td>0.03</td>
<td>0.12</td>
</tr>
<tr>
<td>ASO-EFF VIRGIN</td>
<td>23.50</td>
<td>11</td>
<td>0.014</td>
<td>0.06</td>
</tr>
<tr>
<td>BOR- TRO VIRGIN</td>
<td>25.20</td>
<td>12</td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td><strong>AVERAGE</strong></td>
<td><strong>31.20</strong></td>
<td><strong>14.80</strong></td>
<td><strong>0.02</strong></td>
<td><strong>0.08</strong></td>
</tr>
<tr>
<td>TRO</td>
<td>37.90</td>
<td>18.20</td>
<td>0.022</td>
<td>0.102</td>
</tr>
<tr>
<td>ASI</td>
<td>68.30</td>
<td>32.60</td>
<td>0.040</td>
<td>0.184</td>
</tr>
<tr>
<td>ASO 1</td>
<td>38.90</td>
<td>18.70</td>
<td>0.023</td>
<td>0.105</td>
</tr>
<tr>
<td>ASO 2</td>
<td>27.60</td>
<td>13.30</td>
<td>0.016</td>
<td>0.074</td>
</tr>
<tr>
<td>BOR 1</td>
<td>35</td>
<td>16.30</td>
<td>0.020</td>
<td>0.094</td>
</tr>
<tr>
<td>BOR 2</td>
<td>40</td>
<td>18.60</td>
<td>0.023</td>
<td>0.108</td>
</tr>
<tr>
<td>EFF</td>
<td>57.20</td>
<td>27.80</td>
<td>0.034</td>
<td>0.154</td>
</tr>
<tr>
<td><strong>AVERAGE</strong></td>
<td><strong>43.60</strong></td>
<td><strong>20.80</strong></td>
<td><strong>0.03</strong></td>
<td><strong>0.12</strong></td>
</tr>
</tbody>
</table>
CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K in phosphate and organic fertilizers applied on farms in the New Juaben Municipality were measured using gamma ray spectrometry. The radiological impact of NORMs in the fertilizers applied on farmlands in the Municipality was evaluated.

The activity concentration of $^{226}$Ra, $^{232}$Th and $^{40}$K in the fertilizers averaged at 32.10±2.60 Bq/kg, 12.20±1.60 Bq/kg and 3005.50±68.80 Bq/kg respectively. $^{40}$K was the dominating radionuclide in the fertilizers having activity concentrations of the order of 1000’s of Bq/kg. The wider variation of the primordial radionuclides in the fertilizers might be attributed to the geological origin of its components and the method of chemical processing. These results indicate that fertilizers can be rich source of supply of $^{226}$Ra, $^{232}$Th and $^{40}$K to agricultural soils if they are continuously applied year after year.

The radioactivity level index, $I_\gamma$ was found to be higher than the permissible limit of one (1) in all the fertilizer samples except FT1 and FT4 (Table 4.2). Ambient dose rates measured in the storage rooms were relatively higher than that obtained for the background (Table 4.3). It is therefore possible that the storage of large quantities of fertilizers in closed warehouses may lead to the accumulation of high gamma radiation doses.
The average activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K were generally higher in the cultivated soils than that of the virgin soils. However, apart from $^{226}$Ra activity concentrations which were higher in all the cultivated soils, $^{232}$Th and $^{40}$K activity concentrations were lower in the virgin soils of Asokore (ASO1 and ASO2) and BOR 1 respectively. Even though relatively high activity concentrations were recorded in cultivated soils compared to the virgin soils, these values were far below that of world averages given in UNSCEAR, 2000.

The mean Ra$_{eq}$ value estimated for cultivated soil samples (43.60 Bq/kg) was found to be higher than that of the virgin soil samples (31.20 Bq/kg), though both are well below the recommended limit of 370 Bq/kg. The measured values suggest that the use of these fertilisers do not pose any serious radiological risk to the farmers.

The mean absorbed dose rate in air at 1m above the ground, the mean outdoor annual effective dose and the external hazard index estimated for both the virgin and cultivated soil samples were also found to be much lower than the world average permissible limits. This implies that the radiological hazard associated with the enhanced level of NORMs in cultivated soils through the application of fertilizers may be insignificant.
5.2 RECOMMENDATIONS

The following are some recommendations to relevant stakeholders based on the results of my study.

5.2.1 Scientific Community

There is the need for continuous study to establish the effects of seasonal variations on the concentrations of the radionuclides. The study could also be extended to estimate the radiological impact from other fertilizer types other than those investigated in this research work. This study could be extended to study internal dosimetry through inhalation of $^{220}\text{Rn}$, $^{210}\text{Po}$ and $^{210}\text{Pb}$ during fertilizer applications.

A lot of agricultural activities that use agrochemicals and fertilizers take place along the Densu river, as such, it is recommended that further studies should be undertaken to ascertain the level of radiological pollution of the river through such activities.

This study could also be extended to study the radiological impact of phosphate and organic fertilizers on plantations in other districts in Ghana that extensively use fertilizers to improve soil fertility and improve crop yields as well as establishing the transfer ratios from the fertilizers applied on the farmlands to the crops grown on them.

5.2.2 Regulatory body

It is recommended that upon further studies, results from this study could be used by regulatory bodies such as the Radiation Protection Board (RPB) of the G.A.E.C and the Plant Protection and Regulatory Services Directorate (PPRD) of MOFA in Ghana.
as baseline values in drawing up effective radiation protection programmes and regulatory procedures for monitoring of external radiation levels as well as radon concentrations in fertilizer storage facilities including ports. PPRD could carry out education through the farmers’ association for farmers that are directly involved in the extensive application of fertilizers on the need to wear protective gears such as mouth and nose masks to avoid inhalation of dust particles that may contain radionuclides.
REFERENCES


Al-Saif, A.S. (2009), Radioecological Aspects of Hail Region: Behaviour of Some Radionuclides in Soil, Thesis in the Department of Physics and Astronomy, College of Science, King Saud University.


University of Ghana  http://ugspace.ug.edu.gh


APPENDICIES

APPENDIX 1: Mixed Radionuclide Standard Certificate

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Half life (days)</th>
<th>Activity (kBq)</th>
<th>Combined standard uncertainty, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am-241</td>
<td>157800</td>
<td>4,694</td>
<td>1.1</td>
</tr>
<tr>
<td>Cd-109</td>
<td>462,6</td>
<td>14,54</td>
<td>1.4</td>
</tr>
<tr>
<td>Ce-139</td>
<td>137,5</td>
<td>1,355</td>
<td>1.1</td>
</tr>
<tr>
<td>Co-57</td>
<td>271,26</td>
<td>1,156</td>
<td>1.1</td>
</tr>
<tr>
<td>Co-60</td>
<td>1925,4</td>
<td>2,697</td>
<td>1.1</td>
</tr>
<tr>
<td>Cs-137</td>
<td>11019</td>
<td>2,689</td>
<td>1.3</td>
</tr>
<tr>
<td>Sr-113</td>
<td>115,1</td>
<td>4,000</td>
<td>2.2</td>
</tr>
<tr>
<td>Sr-85</td>
<td>64,78</td>
<td>4,570</td>
<td>1.5</td>
</tr>
<tr>
<td>Y-88</td>
<td>106,6</td>
<td>5,323</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Mass: 980.0 g  Density: 0.98 g/cm³  Volume: 1000 cm³  Reference date: 20.3.2014  Homogeneity better than: 1%

Description:
Radioactive material is homogeneously dispersed in silicone resin. Composition of the matrix: C - 0.324  H - 0.0816  O - 0.216  Si - 0.379 (mass ratio).

Measuring method:
Preparation issues from standard ER solutions whose activities were determined by suitable absolute method. Final control is based on gamma spectrometry on HPGe detector.

Note:
As the criterion of homogeneity standard deviation of the activity value of 1 cm³ element was chosen (n=10). The volume is calculated from the mass and the density.

Date of the certificate issue: 25.2.2014  Validity: 3 years

Customer:
CANBERRA-PACKARD CENTRAL EUROPE
Wienersiedlung 6
A-2432 Schwadorf
Austria

Control: RNDr. Richard Bludovský, CSc, RNDr. Pavol Dryák, CSc

Tel.: +420 266 020 497  Fax: +420 266 020 466

Ing. Jiří Suráň, MBA  director
APPENDIX 2: Sampling of the soil samples from some of the cultivated lands.
APPENDIX 3: Sample preparations at the Gamma ray Spectrometry laboratory of the Environmental Protection and Waste Management Centre.