

**TRACE ELEMENTS AND NATURALLY OCCURRING RADIOACTIVE
MATERIALS IN “NON-TRADITIONAL FERTILIZERS” USED IN GHANA**

A thesis presented to the

Department of NUCLEAR SCIENCES AND APPLICATION, GRADUATE
SCHOOL OF NUCLEAR AND ALLIED SCIENCES UNIVERSITY OF GHANA

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BSc. (KNUST), 2008

In partial fulfillment of the requirements for the degree of

MASTER OF PHILOSOPHY

In

NUCLEAR AND ENVIRONMENTAL PROTECTION

July, 2013

DECLARATION

This thesis is a result of research work undertaken by Ernest Osei Assibey in the Department of Nuclear Sciences and Application, School of Nuclear and Allied Sciences, University of Ghana, under the supervision of Prof. S. B. Dampare, Dr. Dickson Adomako and Mr. John Pwamang.

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DEDICATION

This work is dedicated to the Lord Almighty for his gift of life, manifold blessings bestowed on me and his protection all my life.

Secondly, I dedicate this work to my parents Mr. & Mrs. Osei Assibey for their guidance, love and direction through the way of the light. I will forever be indebted to them.

Finally, this study is dedicated to my fiancée, Ms. Ophelia Bema Kusi for being there for me when I needed her throughout the duration of this research work.



ACKNOWLEDGEMENT

Praise to the Lord God Almighty for bringing me this far in my life. It is by his grace and love that I am alive and able to function; it is in Him I find my strength.

My special thanks go to my supervisors; Prof. S.B. Dampare, Dr. Dickson Adomako and Mr. Pwamang for their constructive criticisms and contributions towards the completion of this research work.

I am very grateful to the West African Agricultural Productivity Programme (WAAPP) for co-sponsoring my studies in-part, without which this research would not have been possible. This same gratitude goes to the Environmental Protection Agency (EPA) for co-sponsoring my thesis work.

Many thanks also goes to the Director, Plant Protection and Regulatory Services Directorate (PPRSD), Mr. Jack-Vesper Suglo who has offered me countless advice and support. I am particularly grateful to my boss, Mrs. Felicia Ansah-Amprofi and colleagues at PPRSD; Eric Dzimado, Lawrence Alato and Gerald Mantey for their pieces of advice and encouragement in the course of this climb on the academic ladder.

I am also immensely grateful to the following personalities; Mr. Ekow Quagraine, Sheriff Enti-Brown, Mr. N. S. Opata all of NNRI-GAEC.

Finally my thanks go to my parents for their support in diverse ways. I love you mum and dad.

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ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectroscopy
AAPFCO	Association of American Plant Food Control
Al	Aluminium
As	Arsenic
Ba	Barium
Br	Bromine
CA	Cluster Analysis
Cd	Cadmium
CDFA	Canadian Department of Food and Agriculture
Co	Cobalt
Cu	Copper
Fe	Iron
GHARR-1	Ghana Research Reactor-1
Hg	Mercury
INAA	Instrumental Neutron Activation Analysis
K	Potassium
Ni	Nickel
Na	Sodium

A large, faint watermark of the University of Ghana crest is centered on the page. The crest features a shield with three golden wheat stalks at the top and a golden emblem with two scrolls at the bottom. Below the shield is a banner with the Latin motto "INTEGRI PROCEDAMUS".

Mn	Manganese
La	Lanthanum
Si	Silicon
MoFA	Ministry of Food and Agriculture
NPK	Fertilizers containing Nitrogen, Phosphorus and Potassium
NORM	Naturally Occurring Radioactive Material
Pb	Lead
P	Phosphorous
PPRSD	Plant Protection and Regulatory Services Directorate
PCA	Principal Component Analysis
S	Sulfur
TENORM	Technologically Enhanced Naturally Occurring Radioactive Material
UNSCEAR	United Nations Committee on Effects of Atomic Radiations
USEPA	United States Environmental Protection Agency
V	Vanadium
W	Washington State Department of Agriculture
Zn	Zinc

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ABSTRACT

Fertilizers have been implicated for being contaminated with toxic trace elements and naturally occurring radioactive materials (NORMs) even though they are an indispensable component of our agriculture. This phenomenon of contamination has been investigated and established world-wide in various forms of fertilizers (i.e., granular or “traditional” type and liquid/powder or “non-traditional type”). In Ghana, the crop sub-sector has seen a gradual rise in the importation and use of ‘non-traditional fertilizers’ which are applied to both the foliar parts and roots of plants.

This notwithstanding, research on fertilizers has been largely skewed towards the “traditional” types, focusing principally on the subjects of yield, effects of application and their quality. This study was, therefore, undertaken to bridge the knowledge gap by investigating the levels of trace elements and NORMs found in the ‘non-traditional’ fertilizers used in Ghana. The principal objective of the study was to investigate the suitability of the “non-traditional fertilizers” for agricultural purposes with respect to trace elements and NORMs contamination.

Atomic Absorption Spectrometry and Instrumental Neutron Activation Analysis were employed to determine the trace elements (Cu, Zn, Fe, Na, Al, Br, Ni, Cd, As, Hg, Co, Pb, La, Mn, Si, Ca, Cl, S, K, Ba and V) and NORMs (^{238}U , ^{232}Th and ^{40}K) concentrations in thirty-nine (39) fertilizer samples taken from two major agro-input hubs in the country (Kumasi-Kejetia and Accra). Multivariate statistical analyses (cluster analysis, principal component analysis and Pearson’s correlation) were applied to the data obtained in order to identify possible sources of contamination, investigate sample/parameter affinities and groupings and for fingerprinting.

The toxic trace element concentrations determined in all samples were found to be in the order $Fe > Cu > Co > Cd > Cr > Ni > Pb > As > Hg$. The study found most of the trace elements determined to be within limits set by international standards (Canada and Hungary and Washington State) except for Cu and Cd. However, all toxic trace elements were within allowable limits projected by the SUIT#25 model. Minimum guaranteed nutrients other than Nitrogen, Phosphorus and Potassium determined were largely found to be below levels set by the Part III of Act 803-Fertilizer Control and its Regulations even for the companies who declared the results on their labels. Generally, the activity concentrations in both the liquid and solid fertilizers were found to be in the order $K-40 > Th-232 > U-238$. The activity concentrations and hazard indices (Radium equivalent, Dose rate and Representative level) for the natural radionuclides U-238 and Th-232 were also found to be within safety limits and world average figures.

However, the activity concentrations and computed hazard indices for K-40 in some products such as SKMKi were higher than the world average and standards set by United Nations Scientific Committee for Effect of Atomic Radiations (UNSCEAR). It was found from the Multivariate analysis that the toxic element Cd clustered with nutrients Zn and Fe, indicating that Cd might have been introduced during the process of nutrient addition to the fertilizers in the form of chelates. The natural radionuclides, ^{232}Th and ^{238}U also largely grouped together indicating that they are from a common source rock. The naturally occurring radioactive material K-40 also groups with Na, Br and partially with K indicating their common origin. The results from the cluster analysis, principal component analysis and Pearson's correlation show good agreement and suggest that all the liquid fertilizers can be grouped into five major

groups with respect to their elemental contents. The CA, PCA and Pearson's correlation analysis for the solid samples also indicate similarities of 3 major clusters with sub-groupings and 5 components respectively.

In conclusion, the dangers associated with the use of "non-traditional" fertilizers in Ghana are low with respect to toxic trace elements since their concentrations in the fertilizers are low. The potential for trace element accumulation in soil has also been found to be low. Furthermore, the liquid fertilizers are not radiologically significant whereas some solid fertilizers are significant due to their high activity concentrations and hazard indices.

It is recommended that regulators continue to monitor imported fertilizers for toxic trace element content in order to ensure their safety for agriculture and environment at large. Further research and monitoring of trace elements and naturally occurring radioactive materials in other forms of fertilizers is required trace element and radiological data generation.

The study has indicated the usefulness of multivariate analysis in contamination source determination and finger printing that may play a significant role in fertilizer quality monitoring.

CHAPTER ONE

INTRODUCTION

1.1 Background

Fertilizers are essential component of agriculture because they are mostly the sole source of nutrients for cultivated crops aside what may be available in the soil. Fertilizers help to increase crop production and to improve the properties of the nutrient-deficient soils. Fertilizers may be organic, inorganic or biological in nature depending on the materials used in their manufacture. Inorganic fertilizers are mostly made of minerals mined from the earth such as phosphate or potassium bearing rocks, (Botezatu *et al*, 2003). Organic and biological fertilizers on the other hand are from organic matter and biological components respectively.

Inorganic fertilizers may be of compound (e.g., NPK) straight or single fertilizers in nature depending on the constituents and purpose of application. For the purpose of this study, the granular compound fertilizers will be tagged as 'traditional' because they are the type of fertilizers often used since commercial fertilizers were introduced into Ghana. The newer type will be referred to as 'non-traditional'. The 'non-traditional' fertilizers are either of powder or liquid form but mostly dissolved in water before application unto plant root and leaves.

In Ghana, the Ministry of Food and Agriculture puts import figures of solid fertilizers at 56,163 Mt in 1997, which increased to 669,550.80 Mt in 2012 and that of liquid fertilizers at 2,692,580.36 Lt in 2012, (PPRSD, 2013) With Government interventions, such as the Fertilizer Subsidy Program which seeks to increase application per acre from the current 10 kg to 20 kg by 2015, it is envisaged that imports will continue to rise. The Plants and Fertilizer Act (Act 803), passed in

September 2010, seeks to protect the Ghanaian environment and its populace against the potential dangers associated with fertilizer use as part of its purpose. The regulatory process is still at its early stages but there is the need for accurate baseline data on the potential risk associated with the use of non-traditional fertilizers as a result of heavy metal and natural radionuclide contamination.

According to US EPA (1999a), CDFA (2004) and WSDA (2007), the presence of heavy metals in inorganic fertilizers is well established. Analytical testing of a wide range of fertilizer products showed that some phosphate, potassium, micronutrient fertilizers, and liming materials contain elevated levels of arsenic, cadmium, and lead compared to other fertilizer types (e.g., nitrogen and gypsum). A few waste-derived fertilizer products have been shown to contain elevated (part per trillion) levels of dioxins (WDE, 1999; US EPA, 1999b).

1.2 Problem Statement

Over the years, fertilizers have become an indispensable part of agriculture generally due to the increasing populations that need to be fed, decreasing availability of farmlands and the depleted nature of arable lands. Through research, improved crop varieties and fertilizers have been combined to achieve this aim. However, with all the merits that come with these fertilizers for supplying plant with required nutrients, they have also been implicated for containing other non-essential elements such as heavy metals, naturally occurring radioactive materials (NORMs) and other contaminants together with the nutrients they supply (Schroeder and Balassa, 1963; Kongshaug *et al.*, 1992; Mortvedt and Beaton, 1992).

Also, fertilizers may contain elements such as manganese, molybdenum and copper that are beneficial to plants at trace levels but may be injurious or even toxic to them and those in the upper hierarchy of the food chain including humans at elevated levels (Addo *et al.*, 2006; Appiah *et al.*, 2000). To this end, a number of interventions have been instituted by the World Health Organization (WHO), United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) and United States Environmental Protection Agency (US EPA) since this discovery was made in 1963 by Shroeder and Ballassa; and subsequently studying the radiological hazards associated with fertilizers (Botezatu and Iacob, 2003). These interventions include accepted limits on contaminants to be found in the fertilizers and treatment of raw materials to reduce these contaminants.

However, in Ghana, research into this important field is limited and until now, the few studies on fertilizers have focused on the traditional fertilizers (granular fertilizers) only. For example, Addo *et al.* (2006) investigated the levels of heavy metals in granular fertilizers used in Ghana and observed that although fertilizers contained some heavy metals, the potential for metal accumulation was low over prolonged fertilizer application. Sheriff (2010) also did a quality control analysis on the traditionally known fertilizers to assess their nutrient contents in comparison with that guaranteed by importers. He found the primary macro-nutrients to be within accepted limits. However, most of the secondary macronutrients were not within the accepted limits.

Additionally, no research has been carried out to assess the radiological significance of fertilizers on the Ghanaian market. This phenomenon has become of much interest worldwide due to the possibility of fertilizers being contaminated with natural

radionuclides after processing from the source phosphate and/or potassium-bearing rocks.

This study, therefore, seeks to fill this knowledge gap by investigating “non-traditional fertilizers” used in Ghana for their trace element levels and naturally occurring radioactive materials (NORMs).

1.3 Justification

Part III of the Plants and Fertilizer Act, 2010 (Act 803) is on Fertilizer Control in Ghana. Its regulations have also been passed as Ghana’s Plant Fertilizer Regulations, 2012 (L.I. 2194). However, regulators mostly rely on data generated from research to act. Hence, this work would provide the regulatory bodies, users of fertilizers as well as the scientific community with good scientific reference and baseline information. In addition, the data generated will give a comprehensive account of the current market situation as far as contamination of non-traditional fertilizers are concerned.

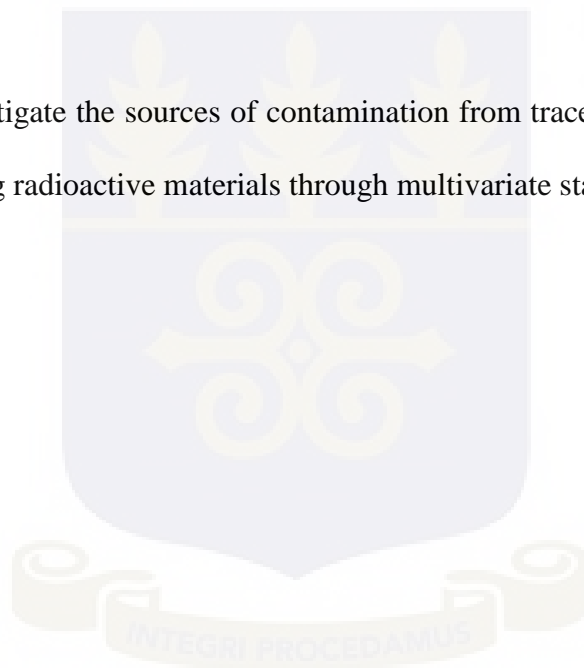
1.4 Objectives of the Study

The primary objective of this work is to investigate the suitability of “non-traditional fertilizers” for agriculture purposes with respect to trace elements and naturally occurring radioactive materials contamination.

The specific objectives of this project are to;

1. Determine the level of contamination and toxicological significance of non-traditional fertilizers due to levels of essential and non-essential trace elements in non-traditional fertilizers.

2. Determine the activity concentrations of ^{40}K , ^{238}U and ^{232}Th in different brands of non-traditional fertilizers in order to assess their radiological significance.
3. Assess the potential for toxic trace elements accumulation in soils over prolonged fertilizer application with reference to production and application patterns.
4. Generate a useful baseline data for assessing the radiological impact of the non-traditional fertilizers on the Ghanaian populace and the environment.
5. To investigate the sources of contamination from trace elements and naturally occurring radioactive materials through multivariate statistical analysis.



CHAPTER 2

LITERATURE REVIEW

2.1 Definition of Fertilizer

Generally, “Fertilizer” means any substance containing one or more recognized plant nutrient(s) that is used for its plant nutrient content and designed for use or has value in promoting plant growth (Ghana Fertilizer Policy Document, 2013).

Specifically:

- a) “Inorganic Fertilizers” are fertilizers produced by chemical processes or mined and derived from an inorganic substance or synthetic organic substance.
- b) “Organic Fertilizers” are fertilizers derived from non-synthetic organic material, including sewage sludge, animal manures, and plant residues produced through the process of drying, cooking, composting, chopping, grinding, fermenting or other methods.
- c) “Bio-fertilizers” refers to any substance which contains living micro-organisms which when applied to seed, plant surfaces or soil, colonizes the rhizosphere or the interior of the plant and promotes growth by increasing the supply or availability of primary nutrients to the host plant(s), (Ghana Fertilizer Policy Document, 2013).

According to the USEPA (1999), fertilizers may be composed of multiple fertilizer materials. In addition, fertilizers may contain additives which "alter transformation in the soil, maintain good physical condition, reduce corrosiveness and serve some purpose other than providing plant nutrients" (Meister, 1997).

2.2 Nutrients in Fertilizers

Primary nutrients are defined by the Association of American Plant Food Control (AAPFCO) as nitrogen (N), available phosphate (P_2O_5) and soluble potash (K_2O). The AAPFCO defines secondary and micronutrients as "those other than the primary nutrients that are essential for the normal growth of plants and that may need to be added to the growth medium.

Secondary plant nutrients include calcium, magnesium and sulfur whereas micro plant nutrients include boron, chlorine, cobalt, copper, iron, manganese, molybdenum, sodium and zinc." Calcium (liming materials and gypsum), magnesium (from dolomite limestone) and sulfur (in the form of inorganic sulfates and sulfur in organic matter) are used to aid in fruit and leaf development and leaf color.

2.2.1 Macro-nutrients

The macronutrients are consumed in larger quantities and are present in plant tissue in quantities from 0.15 % to 6.0 % on a dry matter (0% moisture; DM) basis. Micronutrients are consumed in smaller quantities and are present in plant tissue on the order of parts per million (ppm), ranging from 0.15 to 400 ppm dry matter, or less than 0.04 % dry matter. Only three other macronutrients are required by all plants: carbon, hydrogen and oxygen. These nutrients are supplied by water and carbon dioxide.

2.2.1.1 Primary Macro-nutrients

Nitrogen

Of the three major nutrients, plants require nitrogen in the largest amounts. Nitrogen promotes rapid growth, increases leaf size and quality, hastens crop maturity, and promotes fruit and seed development. Because nitrogen is a constituent of amino acids, which are required to synthesize proteins and other related compounds, it plays an important role in almost all plant metabolic processes. Nitrogen is an integral part of chlorophyll manufacture through photosynthesis (Turker, 1999).

Nitrogen fertilizer is available in both organic (manures) and inorganic forms. The amount of nitrogen in organic sources varies with source material and its state of decomposition. However, for commercial crop production, the following inorganic fertilizers are primarily used: ammonium nitrate (33.5 %N), potassium nitrate (13 % N), sodium nitrate (16 % N), calcium nitrate (15.5 % N), urea (46 % N), mono-ammonium phosphate (18 % N), di-ammonium phosphate (46 % N) and liquid nitrogen (30 % N and 10-34-0).

Nitrogen Deficiency

Nitrogen-deficient plants exhibit slow stunted growth, and their foliage is pale green. Deficiency symptoms generally appear on the bottom leaves first. In severe cases, the lower leaves have a “fired” appearance on the tips, turn brown, usually disintegrate, and fall off.

In contrast, too much nitrogen causes excessive vegetative growth, delays maturity, increases lodging, fosters disease, and poses an environmental threat to surface and ground water.

Nitrogen deficiency generally stems from inadequate fertilizer application, denitrification by soil microbes, or leaching loss due to excessive rainfall. Crop response to fertilization with nitrogen is generally very prompt, depending on the source of nitrogen, stage of plant growth, rainfall and temperature.

Phosphorus

Normal plant growth cannot be achieved without phosphorus. It is a constituent of nucleic acids, phospholipids, the coenzymes DNA and NADP, and most importantly ATP. It activates coenzymes for amino acid production used in protein synthesis; it decomposes carbohydrates produced in photosynthesis; and it is involved in many other metabolic processes required for normal growth, such as photosynthesis, glycolysis, respiration, and fatty acid synthesis. It enhances seed germination and early growth, stimulates blooming, enhances bud set, aids in seed formation, hastens maturity, and provides winter hardiness to crops planted in late fall and early spring.

Phosphorus Deficiency

Phosphorus deficient plants are characterized by stunted growth, dark green leaves with a leathery texture, and reddish purple leaf tips and margins. Reddish purple margins are characteristic of phosphorus deficiency on corn. Some corn growers apply a starter fertilizer containing phosphorus to offset the effects of cool weather during early season growth. Since phosphorus does not leach in mineral soils, any

problems associated with surface water contamination can be attributed to soil erosion (Turker, 1999).

Phosphorus deficiency symptoms generally occur in soils with low phosphorus content. An application of phosphate fertilizer based on rates recommended by a soil test will correct this problem. Phosphorus occurs in organic fertilizers (manures); inorganic blended fertilizers; and high phosphate materials such as mono and di-ammonium phosphate (11-48-0 & 18-46-0) representing the percentage ratios of nitrogen-phosphorus-potassium, triple superphosphate (0-46-0), and liquid mixes such as 10-34-0.

Potassium

Potassium has many functions in plant growth. These include: essential for photosynthesis, activation of enzymes to metabolize carbohydrates for the manufacture of amino acids and proteins, facilitation of cell division and growth by helping to move starches and sugars between plant parts, increasing of disease resistance, increasing of drought tolerance. Other functions include, regulating the opening and closing of stomata, improving the firmness, texture, size and color of fruit crops, and

Potassium Deficiency

Potassium-deficient plants exhibit chlorosis (loss of green color) along the leaf margins or tips starting with the bottom leaves and progressing up the plant. In severe cases, the whole plant turns yellow, and the lower leaves fall off. As with other nutrients, lack of potassium causes stunted plants with small branches and little vigor.

An application of potassium fertilizer will correct a deficiency and, if diagnosed early in the growing season, will benefit the current crop. Otherwise, the benefit of applying potassium will be for the following crop. Potassium can be obtained from fertilizers such as potassium nitrate (13-0-44), muriate of potash (0-0-60), potassium sulfate (0-0-50), or a mixture of potassium and magnesium sulfate.

2.2.1.2 Secondary Macro-Nutrients

Calcium

Calcium is a constituent of cell walls and is involved in production of new growing points and root tips. It provides elasticity and expansion of cell walls, which keeps growing points from becoming rigid and brittle. It is immobile within plants and remains in the older tissue throughout the growing season. It acts as a base for neutralizing organic acids generated during the growing process and aids in carbohydrate translocation and nitrogen absorption. Indeed, calcium might be considered the bricks in plant assembly, without which cell manufacture and development would not occur.

Calcium Deficiency

Calcium (Ca) deficiency symptoms appear in the meristem regions (new growth) of leaves, stems, buds, and roots. Younger leaves are affected first and are usually deformed. In extreme cases, the growing tips die. The leaves of some plants hook downward and exhibit marginal necrosis. Roots on calcium-deficient plants are short and stubby. Soil reserves are replenished and maintained with frequent applications of lime. Calcium can also be supplied by applying fertilizers such as calcium nitrate (19.4% Ca), calcium sulfate (22.5% Ca), and normal superphosphate (20.4% Ca).

Calcium deficiency is generally an indication of the need for lime. Soils that are properly limed will provide adequate calcium for several years. For crops like peanuts that require a high calcium concentration near the soil surface at pegging, a banded or broadcast application of gypsum (CaSO_4 , 22.5% Ca) will supply adequate calcium for normal crop production. For certain specialty crops, a foliar application of calcium nitrate is effective in correcting a deficiency.

Magnesium

Magnesium is a constituent of the chlorophyll molecule, which is the driving force of photosynthesis. It is also essential for the metabolism of carbohydrates (sugars). It is an enzyme activator in the synthesis of nucleic acids (DNA and RNA). It regulates uptake of the other essential elements, serves as a carrier of phosphate compounds throughout the plant, facilitates the translocation of carbohydrates (sugars and starches), and enhances the production of oils and fats. Magnesium deficiency is most prevalent on sandy coastal plain soils where the native magnesium content is low.

Magnesium Deficiency

The predominant symptom is interveinal chlorosis (dark green veins with yellow areas between the veins). The bottom leaves are always affected first. As the deficiency becomes more acute, the symptoms progress up the plant. Chlorotic leaves generally turn red and then develop spotted necrotic areas. In severe cases, the entire leaf turns yellow. Magnesium deficiency is the common cause of “grass tetany” in ruminant animals. In acute situations, the entire plant becomes chlorotic.

Sulfur

Sulfur is an essential component in the synthesis of amino acids required to manufacture proteins. Sulfur is also required for production of chlorophyll and utilization of phosphorus and other essential nutrients. Sulfur ranks equal to nitrogen for optimizing crop yield and quality. It increases the size and weight of grain crops and enhances the efficiency of nitrogen for protein manufacture. Crops that have a high nitrogen requirement must have adequate sulfur to optimize nitrogen utilization. Sulfur increases yield and protein quality of forage and grain crops along with production and quality of fiber crops.

Sulfur Deficiency

Sulfur deficiency is characterized by stunted growth, delayed maturity, and general yellowing of plants. Yellowed plants are also characteristic of nitrogen deficiency. However, unlike nitrogen deficiency which begins in the older leaves and progresses up the plant, sulfur deficiency symptoms begin in the young, upper leaves first. Sulfur deficiencies are often misdiagnosed as nitrogen problems, leaving growers to wonder why their nitrogen applications are ineffective. In many crops, an acute sulfur deficiency causes the entire plant to turn yellow.

2.2.2 Micronutrients

2.2.2.1 Micronutrients and Plant Growth

Nutrients which are needed in very minute quantities are: iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), molybdenum (Mo) and chlorine (Cl). There is no "most important element" since all are required for life, growth and reproduction. They are, therefore, called essential elements. Plant tissues also contain other

elements (Na, Se, Co, Si, Rb, Sr, F, I), which are not needed for the normal growth and development.

Manganese

Manganese (Mn) acts as an enzyme activator for nitrogen assimilation. It is essential for the manufacture of chlorophyll. Low plant manganese, therefore, reduces the chlorophyll content causing leaves to turn yellow (chlorosis).

Manganese Deficiency

Manganese deficiency is typically characterized by interveinal chlorosis (dark green veins with yellow discoloration between the veins), but symptoms vary depending on the crop. Small grain crops may have grey specks and stripes that run parallel to the leaf blade. Known as "grey speck," this symptom occurs at random across a field. Leaves of deficient corn plants have yellow stripes that run parallel to the blade.

Manganese deficiency is due to one of these factors: (1) the soil contains less than 4 ppm manganese; or (2) the soil contains more than 4 ppm manganese, but the pH is above 6.2.

Zinc

Zinc participates in chlorophyll formation and production of auxins, an essential growth hormone. It activates enzymes in protein synthesis, and it is involved in the regulation and consumption of sugars. It is also necessary for starch formation and proper root development. Zinc influences the rate of seed and stalk maturation.

Zinc Deficiency

Besides the soil's natural reserves, some liming materials contribute even more zinc to the soil. Application of zinc containing fungicides and animal and poultry waste products can also add zinc to the soil. The first obvious symptom of zinc deficiency is interveinal chlorosis of the upper (youngest) leaves. Afterwards, shoot growth slows down, causing the affected plant parts to have a rosette-like appearance. Zinc deficiencies in corn and sorghum are typified by a wide band of white tissue on each side of the leaf midrib. This symptom is known as "white bud". The "little leaf" symptom in cotton is also due to zinc deficiency.

Copper

Copper (Cu) is involved as an enzyme activator and is thought to be involved in chlorophyll formation although its specific role is still unclear. It is also thought to be involved in protein synthesis.

Copper Deficiency

The critical level required for normal crop production is about 0.5 ppm. Soils with Cu concentrations in excess of 20 ppm may occur in areas where copper fungicides or poultry and swine wastes have been applied. The first symptoms are yellowing of the youngest leaves accompanied by slightly stunted growth. In cases of severe deficiency, the younger leaves turn pale yellow. Then, leaf tips curl downward, eventually turn brown and die. This symptom is referred to as "leaf tip die back" and is most pronounced on small grains. In extreme cases, leaves become shriveled, twisted, broken and ragged, and ultimately the plant dies. Copper deficiency can be corrected by adding a small amount of copper fertilizer to the soil.

Granular copper sulfate (25 % Cu) and liquid copper (8 % Cu) are the most common sources of Cu used for blending. Maximum benefit is achieved by uniform application and incorporation into the soil. A single application will generally be adequate for several years.

Boron

Boron (B) is an enzyme activator and is involved in the production of starch required for production of cellulose. The major function of boron is in sugar transport to meristem regions of roots and tops. This is evidenced by the fact that transport of sugars is retarded in boron-deficient plants, resulting in reduced growth. Boron is also thought to be involved in cell formation and development; nitrogen metabolism; flower fertilization; active salt absorption; hormone, fat and phosphorus metabolism; and photosynthesis. However, the general consensus is that all of these metabolic processes benefit directly from the influence of boron in sugar transport throughout the plant.

Boron Deficiency

The first visible symptom of boron deficiency is death of the growing tips. This disorder is generally followed by growth of lateral shoots, the tips of which may also be deformed or die. The leaves of boron-deficient plants are usually thick, have a coppery texture, and become curled and brittle.

Other symptoms include stunted roots, failure to set flowers, or flower abortion. Boron deficiency causes internal tissues to disintegrate, causing abnormalities such as distorted, cracked or hollow stems.

Molybdenum

Molybdenum (Mo) is required for symbiotic nitrogen fixation (nodulation) by legumes and reduction of nitrates for protein synthesis. Plants require molybdenum levels of 0.1 to 2.5 ppm in their tissues for normal growth. Applying higher rates can create problems.

Over-application of molybdenum on forage crops can cause a disease called “molybdenosis”, heart disease, and scouring in ruminant animals. High molybdenum content in forage crops can also interfere with copper uptake in ruminant animals ultimately causing a copper deficiency. Therefore, caution is needed when applying molybdenum to crops scheduled for grazing or silage. Molybdenum availability varies with soil type, being highest on organic soils, less on clays and least of all on sandy-textured soils.

Molybdenum Deficiency

Molybdenum deficiency symptoms are very similar to those for nitrogen: pale-green to yellow leaves; yellow spots on leaves; marginal chlorosis along side and tip of blade; thick cupped leaves; reddish-brown coloration of stems and petioles; and whiptail leaves (narrow irregular growth). The marginal chlorosis exhibited by some plants looks similar to potassium deficiency. A low rate of foliar sprays can generally correct a deficiency.

2.3 Plants Nutrient Uptake by Leaves and Roots

Scientific research conducted in the 1950s by Dr. Turkey and associates at the Michigan State University led to the validation that nutrients can be absorbed by foliar application to the leaf. It was shown that the foliar applied nutrients mainly enter through the stomata of the leaf and in some cases through the cuticles.

Although the quantity of nutrients absorbed by the leaf during foliar application may be small, it is compensated by a higher efficiency of uptake than applying the same quantity of nutrients to the soil. This is due to specific soil conditions where the nutrients can be lost by leaching, negated by chemical reactions, incorporated into microbial bodies and affected by many other factors in the soil. These factors inhibit a portion, and in severely adverse soil conditions cause a majority of the nutrients to become unavailable to the plant roots.

There is a clear advantage of foliar application of nutrients in the case of adverse soil conditions, for the reason that one can overcome limitations of the soil and its ability to transfer nutrients into the plant. However, foliar application of nutrients is by no means a substitute for proper soil fertilizer management.

A range of other benefits are associated with foliar fertilization. These include rapid results, prolonged blooming, improved plant health, increased crop yields, reduced growth stress, growth during dry spells, better cold and heat tolerance and improved resistance to disease.

2.4 Trace Elements in Fertilizers

Schroeder and Balassa (1963) were the first to identify that fertilizers are implicated in raising some toxic trace elements concentrations in food crops, and since then much work has been performed to investigate the impact of impurities in fertilizers on crop uptake of potentially toxic elements. According to Allaway (1971), and Kpombrekou and Tabatabai (1994), the main source of fertilizer-derived toxic trace elements in soils is phosphatic fertilizers, manufactured from phosphate rocks (PRs) that contain various metals as minor constituents in the ores. Phosphate rock (PR) contains various toxic trace elements including radionuclides as minor constituents in the ores (Mortvedt *et al.*, 1992).

Varying amounts of these elements are transferred to fertilizers in production processes, and are later applied to soils with these fertilizers which can potentially enter the food chain. Several studies have shown that toxic trace elements in fertilizers can accumulate in soil and become readily available to plants (Sauerbeck, 1992; McLaughlin *et al.* 1996). Sauerbeck (1992) compiled a list of the concentration ranges of some elements present in phosphate rocks and compared them with their corresponding averages in the earth's crust. He concluded that, in terms of fertilizer use, elements which can be considered to have a potential risk of accumulation in soils are As, Cd, Cr, F, Sr, Th, U and Zn. In a more recent study, McLaughlin *et al.* (1996) assessed the potential for contamination by phosphate fertilizers and concluded that Cd and F would accumulate at faster rates than As, Pb or Hg.

The presence of toxic trace elements in inorganic fertilizers is well established (US EPA, 1999a; CDFA, 2004; WSDA, 2007). Analytical testing of a wide range of fertilizer products shows that some phosphate, potassium, micronutrient fertilizers and liming materials contain elevated levels of As, Cd and Pb compared to other fertilizer types (e.g., nitrogen, potash, gypsum). A few waste-derived fertilizer products also have been shown to contain elevated (part per trillion) levels of dioxins (US EPA, 1999).

Trace elements occur naturally in soils and in source materials used to manufacture fertilizers. In addition, heavy metals (and other hazardous constituents) occur in products from the addition of recycled industrial wastes (e.g., steel mill flue dust, mine tailings) to fertilizers. Federal statutes allow some reclassified industrial wastes to be used in the manufacture of fertilizers, provided that such use constitutes “beneficial recycling”, and that the concentrations of hazardous constituents in the resulting fertilizers do not exceed the treatment standards specified for wastes.

Food production and fertilizer application are inextricably linked. With global population rising and many countries enjoying a long awaited economic growth, the demand for higher-quality, nutrient rich food is increasing. This long-term trend supports the continuing appetite for potash, nitrogen and phosphate to protect and restore the fertility of the world’s agricultural land (FAO, 2007).

With the increasing use of fertilizer products as projected by the Food and Agricultural Organization (FAO) for the sub-Saharan African region from 1.3 million tonnes from 1995 to 1997, increased to 1.7 million tonnes in 2015, with an increase of +0.4 % (The Soil Profile, Vol. 16-2006). It is important that the regulatory

framework in Ghana should be strengthened. Hence, there is the need to investigate the use of liquid fertilizers as well which happens to be flooding the Ghanaian market of late.

According to the Soil Profile (2006), for many years commercial fertilizers have been regulated to ensure that the product label provides accurate information on essential plant nutrient content. In recent years, however, concerns about quality in some fertilizer and liming products have extended beyond nutrient content to the potential presence of non nutrient toxic substances. The application of fertilizer products that have a high content of heavy metals results in the buildup of toxic trace elements in soil. This increases the potential for exposure of crops, animals and humans to toxic trace elements. Both organic and chemical fertilizer products may be at risk from heavy metal contamination. Generally, the most serious cause of trace element contamination results when industrial byproducts are recycled into fertilizers. Micronutrient fertilizers, for example, are frequently derived from recycled industrial wastes.

2.4.1 Health Effects from Exposure to Toxic Trace Elements

Health effects associated with exposures to lead, arsenic, cadmium, mercury, and several factors influence whether adverse health effects will occur from an exposure to a hazardous chemical. These factors include the dose (how much), the duration (how long), and how a person comes into contact with it. Additional factors include exposures to other chemicals, age, gender, diet, family traits, lifestyle, and state of health. Heavy metals have several different chemical forms (species and congeners, respectively) that influence their fate and transport in the environment, bioavailability,

and toxicity. Heavy metals and dioxins are relatively persistent in the environment, and they also bio-accumulate in the food chain.

The summary of the adverse health effects associated with exposures to some toxic elements determined is provided in the subsequent sections.

2.4.1.1 Arsenic

The US EPA (1999) and the US Public Health Service have identified arsenic as a known carcinogen (Group A). High arsenic exposures have also been shown to damage the nervous and gastrointestinal systems, and to cause developmental effects in laboratory animals (ATSDR, 2007a). Perhaps the single-most characteristic effect of long-term oral exposure to inorganic arsenic is a pattern of skin changes. These include patches of darkened skin and the appearance of small "corns" or "warts" on the palms, soles, and torso, and are often associated with changes in the blood vessels of the skin. Arsenic is naturally occurring in environmental media (e.g., air, water, soil), and found in some consumer products.

2.4.1.2 Cadmium

Exposures to high levels of cadmium in food or water severely irritate the stomach, and may lead to vomiting and diarrhea, and sometimes death. Consuming lower levels of cadmium over a long period of time can lead to a build-up of cadmium in the kidneys (ATSDR, 1999). If exposures reach a high level, cadmium may cause kidney damage, and also cause bones to become fragile and break easily. Cadmium naturally occurs in soil and in ore/rock (e.g., phosphates) and wastes used to make fertilizers,

and depending on the soil conditions, may be readily taken up by crops and other plants.

2.4.1.3 Lead

The main target for lead toxicity is the nervous system, both in adults and children.

Long-term exposure of adults to lead at work has resulted in decreased performance in some tests that measure functions of the nervous system (ATSDR, 2007b). Lead exposure also may cause weakness in fingers, wrists or ankles. Lead exposure also has been shown to cause small increases in blood pressure, particularly in middle-aged and older people. At high levels of exposure, lead can severely damage the brain and kidneys in adults or children and ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage. Children are more susceptible to lead toxicity than adults because of effects on nervous system development.

2.4.1.4 Mercury

The nervous system has been shown to be especially sensitive to methyl mercury found in fish and mercury vapour. However, the inorganic form of mercury that is likely to be found in inorganic fertilizers is considered to be less toxic because it does not pass easily from the blood into the brain. Ingestion of high levels of inorganic mercury causes damage to the kidneys and gastrointestinal effects (ulcers, stomach distress) (ATSDR, 2007b)). The health effects to human upon exposure to mercury and other trace elements of are summarized in Table 2.1

Table 2.1: The toxicity of certain trace elements to humans (Merian, 1984; Geldmacher *et al.*, 2004)

Heavy metals	The negative effect on human body
As, Bi, Cr, Cu Fe, Mn and Sb	Impair the function of liver
Au, Cd, Hg, Pb and U	Impair the function of kidney
As, Pb	Impair the function of hematopoiesis system
As, Bi, Pb	Cause illnesses of heart - circulation system or illnesses of the respiratory system with inhalation absorption
As, Hg, Mn, Pb, Ti	Cause damage of the central and peripheral nervous system
As, Cr, Hg	Cause mutagenicity
Pb, Hg	Cause teratogenicity
As, Be, Cd, Cr, Ni, U	Cause human carcinogens

2.5 Naturally Occurring Radioactive Materials (NORMs) in Fertilizers

2.5.1 Radioactivity in the Environment

Traces of radioactivity can be found in all materials alive or dead. These radionuclides are either of a natural or anthropogenic origin, and exist in different levels and chemical status in all environmental compartments (lithosphere, hydrosphere and atmosphere), which is known as environmental radioactivity or radioecology. Radioecology is an area of science that deals with the understanding of where radionuclides originate and how they migrate, react chemically and affect the ecospheres (Kopp and Burkart, 1989).

To assess these impacts of natural radioactivity quantitatively, it is necessary not only to define the sources of radioactivity and their environmental distribution but also to

understand the effect of the environmental parameters and how radionuclides are transferred between the ecological systems (IAEA, 1979). Sources of radiation definition and radioactivity measurements are significant to determine the environmental impacts and to estimate radiation doses. This data can then be linked to epidemiological studies that attempt to relate human health effects to the radiation exposures (Commission of the European Communities, 1993).

Environmental radioactivity has been an important area of research throughout the 20th century that has been promoted by two powerful stimuli, namely: (i) the remarkable power and sensitivity of radionuclides and their descendants as tracers of the rates and mechanisms of environmental and geological processes; and (ii) the introduction of man-made radionuclides and technologically enhanced natural occurring radioactive material (TENORM) as an important class of environmental contamination. Research involving natural radionuclides has contributed greatly to developing a quantitative understanding of the functioning of the environment. It is necessary to characterize not only the biogeochemical properties of the radionuclides, but also the biogeochemical processes occurring in the receiving environment in order to achieve an improved understanding of the environmental fate of contaminant radionuclides (MacKenzie, 2000).

2.5.2 Contamination of Fertilizers by Naturally Occurring Radioactive Materials

The concern of contamination of fertilizers by naturally occurring radioactive materials has arisen from research proving that radionuclides at trace levels can be concentrated during the processing of phosphate ores for production of fertilizers. Mortvedt and Beaton (1992) in their research study on “Heavy Metal and

Radionuclide Contaminants in Phosphate Fertilizers” concluded that phosphate rocks contain various metals and radionuclides as minor constituents in the ores. Phosphate rock varies considerably in the content of U, Ra and Th, depending on the geographical area from which it was mined (Kongshaug *et al.*, 1992).

The technological processes employed in the phosphate industry and during the production of energy from fossil fuels concentrate the natural radioactive elements in the products and in the wastes, sometimes resulting in higher levels of radiation than in the ore/raw materials (Elena *et al.*, 2003). Radiological impacts of phosphate rocks mining and manufacture could be significant due to the elevated radioactivity contents of the naturally occurring radioactive materials (NORM), such as U-238 series, Th-232 series and K-40, in some phosphate deposits (Khater *et al.*, 2007).. People who work in these industries are also potentially exposed to radioactivity from the products and waste sometimes much higher than in the ore/raw materials (Botezatu *et al.*, 2003).

2.5.3 Health Concerns from Exposure to Naturally Occurring Radioactive Materials

Application of fertilizers containing elevated levels of radionuclides has been shown to cause many-fold accumulative increases in the levels of such radionuclides in treated soils, including Ra-226, a precursor to radon gas, Rn-222 (Ioannides *et al.*, 1997). This accumulation constitutes a source of technologically enhanced natural radiation, increasing the total exposure of humans and other species from natural radionuclides.

Plants uptake of radionuclides from soil is a highly complex process and depends on many factors including the plant species, soil conditions and the concentration of radionuclides in the soil. In addition, concentrations of radionuclides taken up by plants can vary significantly between different parts of the plant (Mortvedt, 1994). Uranium presents both chemical and radiological hazards. The damage caused by exposure to low-dose exposure is invisible and not immediate. Uranium accumulates in kidneys, brain and other organs (Ioannides *et al.*, 1997).

The ionization radiation causes cellular toxicity, DNA damage, genetic damage such as blindness, deafness and chronic diseases and it induces cancer as well. Health effect will depend on the kind of radiation, absorbed radiation dose (dosimetry) and type of tissue. At lower level radiations, cells can be killed or be slightly damaged and left alive. If the cell is left alive, it can produce a cancer in addition to the damage that is caused. However, if such a damage occurs in the ovum or/and in the sperm then genes may be altered in future fetuses leading to deformed babies (Bertell, 1986; Sheppard *et al.*, 2005).

Furthermore, U has several radiotoxic decay products such as Ra-226. Radium-226 is considered as one of the most toxic radionuclides as it can be easily assimilated into bone because the metabolic behaviour of radium in the body is similar to that of calcium. Radium-226 decays slowly, producing radon (Rn-222) with a half-life of 3.8 days, an alpha emitter, which inhaled can cause lung cancer (Lloyd *et al.*, 1997).

2.6 Fertilizer Industry in Ghana

The expansion and liberalization of the agro-input industry has led to the influx of so many fertilizer products on the Ghanaian market, some of which are substandard. The

emerging market is that of the liquid and powdered fertilizers (non-traditional) which manufacturers purport to have an advantage over the granular fertilizers. According to Vister *et al.*, (1995), the ongoing World Bank-inspired structural adjustment programs in sub-Saharan African involve increased private sector participation in the key sectors of the economies of countries carrying out needed reforms. In West Africa, the programs have produced significant changes in the agricultural input procurement and distribution sector. For example, with the exemption of Niger and Nigeria, the task of fertilizer procurement and distribution in all the countries has shifted from the central government to the private sector. As expected, this seemingly positive development has not occurred without some problems.

In Ghana, the Economic Recovery Period saw the liberalization of the agri-input industry. This was manifested in the complete relinquishing of the importation and distribution of agro-input from the Ministry of Food and Agriculture of the government to the private sector directly. However, the government regulates the industry, and in 2010 passed the Plants and Fertilizer Act, (Act 803) by an act of parliament to oversee the implementation of this duty. Figure 2.1 shows the import trend of fertilizers from 1997 through 2012.

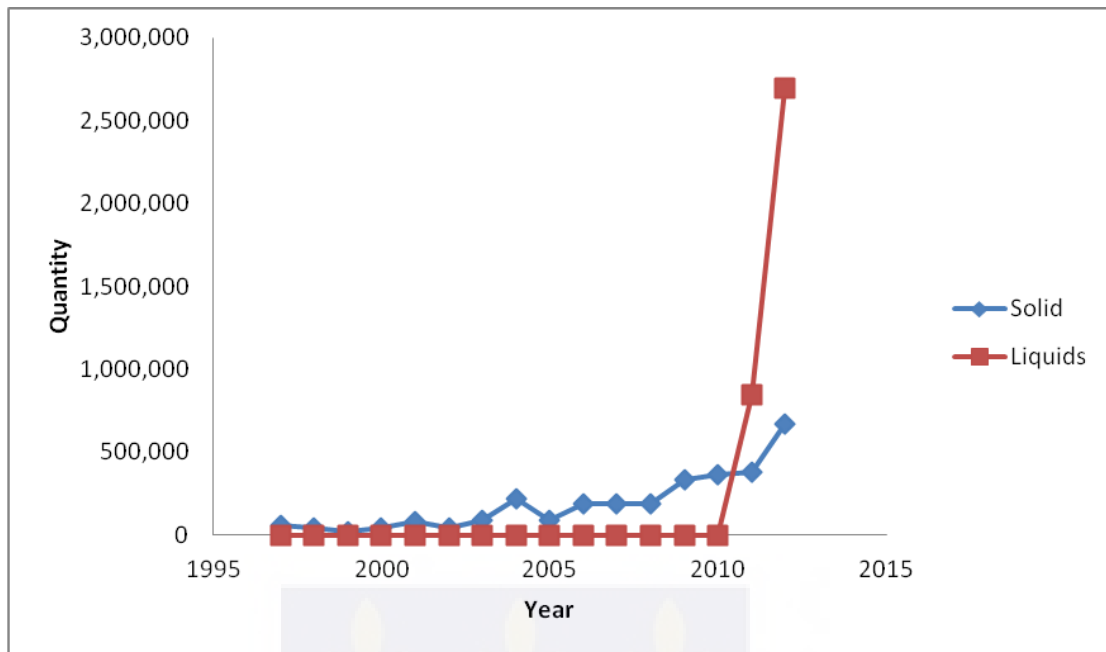


Fig 2.1: Fertilizer Imports from 1997 to 2012 (Source; Pesticide and Fertilizer Regulatory Division, MoFA)

2.6.1 The Plants and Fertilizer Act, 2010 (Act 803)

The Plants and Fertilizer Act, 2010 (Act 803) is the Eight Hundred and Third Act of the Parliament of the Republic of Ghana which was assented on 6th of September, 2010 and passed by Parliament on 10th of November, 2010. The Act is made up of three technical parts (i.e., Part I, II and III). Part I, deals with Plant Protection, whereas Parts II and III respectively deal with Seeds and Fertilizer Control.

2.6.1.1 Purpose of Part III of Act 803– Fertilizer Control

The third part of the Act 803 (Fertilizer Control) has 47 sections (from section 67 to section 114). For sustainable agricultural growth and development, there is the need for farmers to have access to quality agro-inputs including fertilizers. To this end the

Part III of Act 803 makes provisions for manufacturers, importers, distributors and retailers of fertilizers to be properly regulated to ensure that the interest of farmers and fertilizer enterprises are safeguarded, and the environment of Ghana protected against the potential dangers associated with fertilizer use.

2.6.2 Non-Traditional Fertilizers Import and Use in Ghana

The past few years has seen the introduction into the Ghanaian agro-input market, fertilizers that are meant for both foliar and root application, referred to as non-traditional (Fig. 2.3). Until now, the “non-traditional” fertilizers had been thought to be used for only supplementing the granular type (traditional fertilizers), as seen in figure 2.2 that was used on a larger scale in much bigger farms or just for vegetable farming. This, however, is not the case as these new products being introduced also contain the same or higher levels of both macro and micro-nutrients just as one would find in the granular type fertilizers.

The unique thing about these fertilizers is that they are mixed with water before they are applied to plants or to the soil. These fertilizers may either be made of NPK only, NPK in addition to secondary macro-nutrients and/or micro-nutrients or may entirely be a single nutrient/specialized fertilizer. The fertilizers are concentrates or water-soluble powders of synthetic chemicals that contain a mix of nitrogen, phosphorous, potassium and iron.



Fig. 2.2: The “Traditional” type of NPK fertilizer



Fig. 2.3: “Non-traditional” fertilizers (both powdered and liquid)

2.6.3 Comparison of Traditional and Non-traditional Fertilizers

2.6.3.1 Advantages of Non-Traditional Fertilizers Over Granular/Traditional Fertilizers

The non-traditional fertilizers are easy to apply to lawns and plants. After following the directions to dilute the concentrate or create a liquid solution from powder mix, one can apply liquid fertilizer using spray bottles or sprinkler attachments. The solution acts quickly to make nutrients available to plants. Some liquid fertilizers provide an immediate effect as leaves and roots absorb the mixture. Due to their smaller weights of 1litre for liquid or 5 kg for solid, there is less operational cost due

to handling by farmers. Less storage cost/problems associated with the products make them attractive because they require less storage space.

There is also more homogeneity in the application because the fertilizer is mixed with water and agitated to be evenly distributed. Another advantage is the relative accuracy in application since the farmer can easily measure what to use in order to give plants the required nutrients only.

2.6.3.2 Disadvantages of Non-Traditional Fertilizers Compared To Granular/Traditional Fertilizers

Severe damage to plants and lawns may occur to if the directions for mixing or applying non-traditional fertilizers are not followed. Too much liquid fertilizer can burn grass, leaving discolored streaks on the lawn, and damage plant foliage.

The solution can also leach deep into the soil, making it unavailable. Consequently, liquid fertilizer needs more frequent applications than other types of fertilizer. Liquid fertilizer may also contribute to water pollution if it seeps into storm drains.

2.6.3.3 Advantages of Granular Fertilizers

Gardeners work granular fertilizer into soil after sprinkling or spreading the granules into flower beds or grass. The effects of granular fertilizer last longer because the solid is absorbed at a slower rate. The release period of granules can vary from a month up to nine months. An advantage of slow-release granular fertilizer is that one does not have to apply it often. Organic granular fertilizer that does not contain

chemicals is also commercially available. Using slow-release organic granular fertilizer significantly decreases the chances of damaging lawns and plants.

2.6.3.4 Disadvantages of Granular Fertilizers

Nutrients from granular fertilizers are sometimes not readily available to plants.. Plants may not receive nutrients fast enough to help them recover from deficiencies. Granular fertilizers also need moisture and warm temperatures to act. The pH of soil may also adversely influence their effectiveness. As with foliar fertilizer, inappropriate application of granular fertilizer will leave telltale streaks and spots of burned grass on lawns.

2.7 Previous Work on Fertilizer Contamination in Ghana

Although research publications exist in this area of study, they have been largely skewed towards the traditional fertilizer types (granular). Until now these research studies have been largely skewed toward essential nutrients verifications, yields upon application and heavy metal determination in traditional type fertilizers.

Stephens in 1960 conducted experiments to determine the residual effects of single super on the yields of succeeding crops as well as summarized the evidence of S deficiency in Ghana soils. He recommended single super and $(\text{NH}_4)_2\text{SO}_4$ as the fertilizers for general use in Ghana, especially in the savanna zone, since residual effects of single super were large.

Others evaluated before carrying out the study include that by Appiah *et al.*, (2000) which was an evaluation of the effect of fertilizer application on some peasant cocoa

farms in Ghana. His major findings were that the gross yields of the fertilized plots exceeded those of unfertilized plots by 61.7% in the 1st year, 99.8% in the 2nd year, 116.0% in the 3rd year, and 106.0% in the 4th year. At the end of the 4th year, 75% of the farms had yields more than 1000 kg/ha. Addo *et al.*, (2006) analysed inorganic fertilizers used in Ghana for heavy metals and microelements. The conclusions drawn from his work indicate that although fertilizers analysed contained heavy metals, they were at levels that could not accumulate in the soil or cause health effects upon application. He however recommended for in-situ monitoring of the elements studied.

Sheriff in 2010 carried out a study to determine the heavy metals in 'granular fertilizer' (traditional). His major findings were that the heavy metal content of the fertilizers widely agreed with international and local standards.

Sheriff *et al.*, (2012) again in his research on "Quality control analysis of fertilizers in Ghana: the macronutrient perspective, concluded that most of the fertilizer samples in the country have macronutrient concentrations within recommended limits but micronutrients were lower than the guaranteed minimum.

2.8 Multivariate Statistical Analysis

The use of multivariate statistical analysis allows for the rigorous inspection and evaluation of variability present in the voluminous data produced by the chemical characterization of various samples. In order to process the variability between fertilizer samples, different methods were used. The elemental and activity concentration values were first transformed to log base 10(\log_{10}) values before performing multivariate statistical analysis on the data. This compensated for the differences in magnitude between major and trace elements, and normalized element

distribution. Cluster analysis (CA) and Principal component analysis (PCA) was thereafter employed using SPSS 20.0 statistical package.

2.8.1. Cluster Analysis

Cluster analysis is described as a group of multivariate techniques whose primary purpose is to accumulate objects based on the unique characteristics they possess. Cluster analysis classifies objects (variables), so that each object is analogous to the others in the cluster with regard to a predetermined selection criterion. The resulting clusters of objects are supposed to show high internal homogeneity and high external (between clusters) heterogeneity. Each cluster thus describes, in terms of the data collected, the class to which its members belong; and this description may be abstracted through use from the particular to the general class or type (Einax *et al.*, 1997). Hierarchical agglomerative clustering (HCA) is the most general approach, which presents perceptive similarity between any one sample and the entire data set, and is usually demonstrated by a dendrogram (tree diagram) (McKenna, 2003).

The dendrogram presents a vivid profile of the clustering processes, presenting a picture of various grouped variables and their proximity to each other, with a dramatic reduction in dimensionality of the original data. The Euclidean distance usually provides the similarity between two samples and a distance can be symbolized by the difference between analytical values from the samples (Otto, 1998).

In this study, HCA was presented on the normalized data set using the Ward's method as agglomeration technique and squared Euclidean distance as a measure of similarity. The Ward's method employs an analysis of variance approach to assess the distances

between clusters in an attempt to reduce the Sum of Squares (SS) of any two clusters that can be formed at each step.

2.8.2. Principal Component Analysis or Factor Analysis

Principal component analysis (PCA) is a powerful pattern recognition technique that attempts to explain the variance of a data set of intercorrelated variables with a smaller set of independent variables (principal component) (Boamponsem *et al.*, 2010). PCA is designed to transform the original variables into new, uncorrelated variables (axes), called the principal components. This process reduces the dimensionality of data by a linear combination of original data to generate new latent variables which are orthogonal and uncorrelated to each other (Nkansah *et al.*, 2010). The new axes lie along the directions of maximum variance. PCA provides an objective way of finding indices of this type so that the variation in the data can be accounted for as concisely as possible (Sarbu and Pop, 2005). The principal component (PC) provides information on the most meaningful parameters, which describe a whole data set affording data reduction with minimum loss of original information (Helena *et al.*, 2000).

The principal component can be expressed as:

$$z_{ij} = a_{i1}x_{1j} + a_{i2}x_{2j} + a_{i3}x_{3j} + \dots + a_{im}x_{mj} \quad (2.1)$$

where;

z is the component score, a is the component loading, x is the measured value of variable, i is the component number, j the sample number and m stands for the total number of variables.

Factor Analysis (FA) is similar to PCA except for the preparation of the observed correlation matrix for extraction and the underlying theory (Tabachnick and Fidell, 2007). The major objective of FA is to reduce the contribution of less significant variables to simplify even more of the data structure coming from PCA. This goal can be achieved by rotating the axis defined by PCA, according to well established rules, and constructing new variables, also called Varifactors (VF) (Shrestha and Kazama, 2007). In fact, PC is a linear combination of observable variables, whereas VF can include unobservable, hypothetical, latent variables (Vega *et al.*, 1998; Helena *et al.*, 2000).

PCA of the normalized variables was presented to extract significant PCs and to further decrease the contribution of variables with less significance; these PCs were subjected to varimax rotation (raw) generating VFs (Howitt and Cramer, 2005; Shrestha and Kazama, 2007 and references therein). Therefore, a small number of factors will generally explain the same amount of information as do the much larger set of original observations (Shrestha and Kazama, 2007). The FA can be expressed as:

$$Z_{ji} = af_1f_{1i} + af_2f_{2i} + af_3f_{3i} + \dots + af_mf_{mi} + e_{fi} \quad (2.2)$$

where,

z stands for the measured variable, a is the factor loading, f is the factor score, e is the residual term accounting for errors or other source of variation, i the sample number and m the total number of factors. The correlation coefficient matrix measures how well the variance of each constituent can be explained by relationship with each other (Liu *et al.*, 2003). The terms “strong”, “moderate”, and “weak” were applied to factor loadings and refer to absolute loading values as >0.75 , $0.75-0.50$ and $0.50-0.30$, respectively, following the approach of Liu *et al.* (2003).



CHAPTER 3

METHODOLOGY

3.1 Sample Collection

Twenty-nine (29) different fertilizer brands making thirty-nine samples were sampled from central commercial hubs of two areas in Ghana, Accra (Accra central and Tema) and Kumasi (Kejetia). This is because a larger percentage of the importers and retailers are situated in these locations. Efforts were made to sample all brands from both importers and retailers, but this was not possible for all the products as some products could only be sampled from the importer and vice versa due to their availability.

The samples were collected in their original containers and then given respective sample codes that comprised acronyms of the company name, product name and researcher's name before transportation to the laboratory.

3.2 Determination of Analytes of Interest Using Atomic Absorption Spectrometry

The trace elements, cobalt (Co), iron (Fe), lead (Pb), copper (Cu), cadmium (Cd), chromium (Cr), nickel (Ni) and zinc (Zn) were determined using flame atomic absorption spectrometry (FAAS) whereas arsenic (As) and mercury (Hg) were determined using the hydride generation atomic absorption spectrometry (HG-AAS).

3.2.1 Sample Preparation for AAS analysis

3.2.1.1 Instrumentation

- The Mettler Toledo XS603S digital analytical balance was used for the weighing of samples for digestion.
- Digestion of samples was performed in 100 mL polytetrafluoroethylene (PTFE) Teflon microwave digestion bombs (Parr Instrument Company) using a conventional microwave digester (ETHOS 900 Labstation, INST: MLS-1200 MEGA).

3.2.1.2 Chemicals

Digestion of fertilizer samples was achieved using a combination of 65 % nitric acid (HNO_3) and 98 % sulphuric acid (H_2SO_4).

3.2.1.3 Digestion Procedure

Fertilizer samples were prepared by weighing 0.5 grams of the fertilizer into PTFE tube. This was followed by the addition of 5 mL of 65% nitric acid (HNO_3) and 2.5 mL of 98% sulphuric acid (H_2SO_4). Digestion of the samples was done according to the protocol for digestion of fertilizers (Milestone Acid Digestion Cookbook, 1996; Jorham and Engman, 2000).

The PTFE tubes were then covered tightly, transferred into the microwave carousel. The carousel was then placed into the microwave chamber. The fertilizer samples were digested according to the procedure in Table 3.1.

Table 3.1: ETHOS 900 Microwave digestion scheme for fertilizer samples

DIGESTION STEP	Digestion Time (min)	Microwave Power (W)
1	2	250
2	2	0
3	6	250
4	5	400
5	5	600

The digestion process was completed after 20 minutes in the oven. This time is adequate to allow almost all solid fertilizers to be dissolved into solution. After digestion has taken place the microwave was vented for 5 minutes and then the samples were taken out and cooled before further work was carried out. The digested solution was then poured into a glass test tube and diluted with distilled water to the 20 mL mark and labelled appropriately.

The samples were then prepared in triplicates and taken to the AAS laboratory for the determination of analytes of interest.

3.2.2 Sample Analysis

Elements that were analyzed by the Flame AAS were cobalt (Co), iron (Fe), lead (Pb), copper (Cu), cadmium (Cd), chromium (Cr), nickel (Ni) and zinc (Zn) whereas arsenic (As) and mercury (Hg) were determined using hydride generation method.

3.2.2.1 Instrumentation

A Fast Sequential Atomic Absorption Spectrometer (VARIAN, AA 240 FS, Australia) equipped with a deuterium background corrector was used for all atomic absorption measurements.

3.2.2.2 Standards

The under-listed commercially available stock standard solutions of Cd, Cr, Cu, Pb, Fe, Ni, Co and Zn were used: 1000 ± 4 mg Cd L⁻¹ in 2% (w/w) HNO₃; 1000 ± 4 mg Cr L⁻¹ in 2% (w/w) HNO₃; 1000 ± 4 mg Cu L⁻¹ in 2% (w/w) HNO₃; 1000 ± 4 mg Fe L⁻¹ in 2% (w/w) HNO₃; 1000 ± 4 mg Pb L⁻¹ in 2% (w/w) HNO₃; 1000 ± 4 mg Zn L⁻¹ in 2% (w/w) HNO₃; 1000 ± 4 mg Ni L⁻¹ in 2% (w/w) HNO₃; 1000 ± 4 mg Co L⁻¹ in 2% (w/w) HNO₃ (Trace CERT[®], Fluka, Chemie, Switzerland).

3.2.2.3 Calibration of AAS

Standards (with known concentrations) for the various elements were prepared (Table 3.2) from the commercial stock standard solutions and used for the calibration of the atomic absorption spectrometer. The absorbances measured for each element's standard solutions were used to prepare a linear regression line (plot of absorbance against concentration) [Appendix 1]. The concentration of each element in the sample was deduced from the regression line of that element.

The equations relate absorbance to concentrations, and therefore enable quantitative analysis to be carried out. Three blank solutions were prepared exactly the same way the samples were prepared except that in this case, the sample was not included. The readings obtained from the blank solution were subtracted from the readings obtained

from the samples before actual calculations were done. The flame atomiser was made up of air (flow rate: 13.50 L/min) as oxidant and acetylene (flow rate: 2 L/min) as fuel. The experimental conditions for the atomic absorption measurement of the analytes are presented in Table 3.3.

Table 3.2. Prepared Standards for Calibration of AAS

Analyte	Concentration of calibration standard (mg/L)		
	Calibrant 1	Calibrant 2	Calibrant 3
Cd	0.5	2.00	5.00
Fe	2.00	5.00	10.00
Pb	2.00	5.00	10.00
Zn	0.25	0.5	0.75
Ni	2.00	5.00	10.00
Cr	1.00	2.00	5.00
Cu	2.00	5.00	8.00
Co	2.00	5.00	8.00

3.2.2.4 Atomic absorption measurement of fertilizer samples

Measurement of the atomic absorption of the digested fertilizer samples was done after the calibration. The concentrations were deduced from the respective regression lines, and the actual concentration was subsequently calculated.

Table 3.3: FAAS conditions used for determination of Cd, Cr, Cu, Pb, Fe, Ni, Co and Zn

Element	Hollow Cathode Lamp		
	Current (mA)	Wavelength (nm)	Slit width (nm)
Cd	4.0	228.8	0.1
Cr	7.0	357.9	0.2
Cu	4.0	324.7	0.5
Fe	5.0	248.3	0.2
Ni	4.0	232.0	0.2
Pb	5.0	217.0	1.0
Zn	5.0	213.9	1.0
Co	7.0	240.7	0.2

3.2.3 Calculation of Concentration

The actual concentration of the analyte in the sample was calculated using the relation:

$$C_{sam_actual} = \frac{C_{sam_Calib} \cdot D_f \cdot V_n}{M_{sam}} \quad (3.1)$$

Where;

C_{sam_actual} - Actual concentration of sample

C_{sam_Calib} - Sample concentration (calibration curve)

D_f - Dilution factor

V_n - Nominal volume

M_{sam} - mass of sample

3.2.4 Determination of As and Hg using HG AAS

3.2.4.1 Instrumentation

A Fast Sequential Atomic Absorption Spectrometer (VARIAN, AA 240 FS, Australia) equipped with a VGA-77 vapour generation system (VARIAN, Australia) fitted with a peristaltic pump for continuous gas flow (for hydride generation). However rather than a flame as in FAAS, an absorption cell is placed in the optical path of the atomic absorption spectrometer during the determination of Hg.

The radiation sources were the hollow cathode lamp of As (wavelength 193.7 nm; spectral slit width 0.5 nm; lamp current 10 mA), and the hollow cathode lamp of Hg (wavelength 253.7 nm; spectral slit width 0.5 nm; lamp current 4 mA) (VARIAN, Australia).

3.2.4.2 Chemicals and reagents

All solutions were prepared from analytical reagent grade chemicals:

Sodium borohydride (NaBH_4), Sodium hydroxide (NaOH), Hydrochloric acid (37% HCl), and Potassium iodide (KI). Hydride generation for Hg determination was performed using 0.3% (w/v) NaBH_4 in 5% (w/v) NaOH as reductive solution and 5 M HCl as carrier solution. For As determination, hydride generation was performed

with a 0.6% (w/v) NaBH_4 in 0.5% (w/v) NaOH as the reductive solution with 6 M HCl as the carrier solution.

3.2.4.3 Standards

Commercially available stock standard solution of concentration $1000 \text{ mg As L}^{-1}$ (Trace CERT[®], Fluka Chemie, Switzerland). Commercially-available stock standard solution of concentration $999 \text{ } \mu\text{g Hg/mL}$ (Spectrascan, Teknolab AB, Sweden),

3.2.4.4 Calibration of the HG-AAS

The Hg ($0.1, 0.25, 0.5 \text{ mg L}^{-1}$) and As ($0.2, 0.4, 0.6 \text{ mg L}^{-1}$) calibration standards were respectively prepared from the commercial stock standard solutions and used for calibration. A linear regression line was prepared (for each element) (Appendix 2) similar to that used in FAAS using the concentrations of the calibration standards and their corresponding absorbances. Determination of the Hg concentration in the samples was obtained from its regression line equation after measurement of the absorbance.

3.2.4.5 HG-AAS measurement of Hg

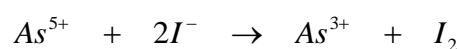
Absorbance measurement was done for Hg atoms in the vapour state which had been transferred to the absorption cell. No flame was used to atomise the Hg as it was already in the atomic form.

3.2.4.6 Atomic Absorption measurement of As in fertilizer samples

Prior to the determination of As by HG-AAS, As^{V} was reduced As^{III} with KI.

3.2.4.7 Reduction of As^V to As^{III}

To reduce all As^V to As^{III}, 4 mL of freshly prepared 5 M KI was added to the digested solution. This was followed by hydride generation and subsequently by atomic absorption measurement.



3.2.5 Validation of AAS technique

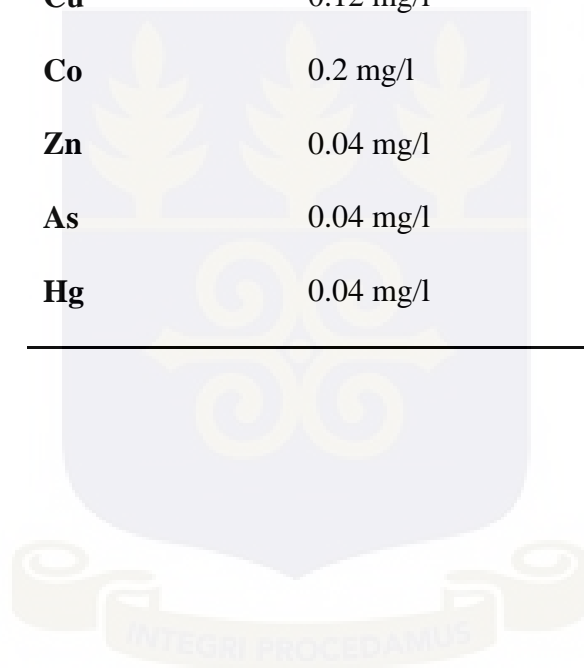
To determine the validity of the AAS technique, fertilizer products with certified concentrations of the various analytes were analyzed. Values obtained from the study and certified values are compared in Table 3.4. The detection limits for the AAS are also outlined in Table 3.5.

Table 3.4 Comparison of Measured and Certified Results

Certified Fertilizer	Element	Concentration (mg/L)		Recovery (%)
		Measured	Certified	
Multicote	Zn	1420	1500	94.6
	Fe	5600	6000	93.3
	Cu	8.9	10	89
	Co	0.378	0.388	97
Polyfeed	Zn	72.0	70.0	102
	Fe	500.0	500.0	100
	Cu	55.0	61.0	91.6
	Co	0.509	0.519	98
Plant Feed	Zn	0.155	0.171	90
	Fe	49.0	47.0	102
	Cu	0.155	0.171	90
	Co	0.219	0.229	96

Table 3.5: Detection Limits of elements determined by AAS

ELEMENT	DETECTION LIMIT
Pb	0.04 mg/l
Ni	0.04 mg/l
Fe	0.24 mg/l
Cd	0.08 mg/l
Cr	0.04 mg/l
Cu	0.12 mg/l
Co	0.2 mg/l
Zn	0.04 mg/l
As	0.04 mg/l
Hg	0.04 mg/l



3.3 Instrumental Neutron Activation Analysis

The following elements were determined by INAA; Br, Na, La, Al, Mn, Si, Ca, Cl, S, K, Ba and V.

3.3.1. Sample Preparation

3.3.1.1 Instrumentation

- The Mettler Toledo XS603S digital analytical balance was used for the weighing of samples for digestion.

3.3.1.2 Standard Reference Materials

- IAEA Soil-7 which is supplied by the International Atomic Energy Agency, Vienna.
- NIST SRM 1646a (Estuarine Sediment) from the National Institute of Standards and Technology.

3.3.1.3 Procedure for sample preparation

For the powdered samples, 200 mg of each was weighed onto a polyethylene foil, wrapped, thermally sealed, labeled and placed in a 9.8 cm³ plastic “rabbit” capsule and heat-sealed. 500 mg of the liquid samples was pipetted into a small capsule, covered and heat sealed before transfer into the “rabbit” for irradiation. A sample each was placed in the capsule for the short-lived radionuclides while 2-3 samples were placed in the capsule for medium-lived radionuclides. IAEA Soil-7 was used in the quantification of the analytes of interest. The validation of this technique (INAA) was carried out using Estuarine Sediment (SRM 1646a). The reference materials were

prepared in a similar way as the samples for irradiation. The analytical samples and reference materials were prepared in triplicates.

3.3.2. Irradiation, Counting and Analysis

3.3.2.1 Instrumentation

- Spectroscopy system, consisting of high purity Germanium (HPGe) N-type coaxial detector (model GR 2518), high voltage power supply (model 3105), and a spectroscopy amplifier (model 2020), manufactured by Canberra Industries Inc.
- The detector system at fixed geometry was coupled to an 8 k Ortec Multichannel Analyzer (MCA) emulation card and a microcomputer. The detector system operated at a bias voltage of (– ve)3000 V full width at half maximum, and resolution of 1.8 keV for ^{60}Co gamma ray energy of 1332 keV with 25% relative efficiency.
- MAESTRO-32 software was used for accumulation of gamma-ray spectrum.

3.3.2.2 Procedure for Irradiation

Before an irradiation scheme was established, preliminary studies were carried out in order to get an accurate irradiation scheme which included the right amount of sample to irradiate. Table 3.6 shows the irradiation schemes considered for short-lived radionuclides before arriving at a favourable scheme (scheme 3).

For medium-lived radionuclides, the same sample masses were used, and the irradiation, delay and counting times adopted were 1 hour, 24 hours and 10 minutes respectively.

Table 3.6: Irradiation and Counting Schemes

Scheme	Sample Mass (g)		Irradiation Time	Delay Time (min)	Counting Time (min)
	Solid	Liquid			
1	0.1	0.2	30 secs	5	10
2	0.2	0.2	1 min	2	10
3	0.2	0.5	1 min	5	10

The analytical samples and the standards were irradiated in the inner sites of the Ghana Research Reactor – 1 (GHARR–1) facility, installed at the Nuclear Reactors Research Centre (NRRC) of National Nuclear Research Institute (NNRI), Ghana Atomic Energy Commission (GAEC). The GHARR–1 was operated at half-full power of 15.0 kW at thermal neutron flux of $\sim 5.0 \times 10^{11} \text{ ncm}^{-2}\text{s}^{-1}$. The samples were sent into the reactor via the pneumatic transfer system operating at 25.0 atmospheres. The output spectral intensities of the analytical samples and the standards were processed by MCA software and card. The radioisotopes were identified by the spectral intensities. The areas under the photo-peaks of the elements were obtained by integration, and converted into levels of concentration by using comparator method of neutron activation analysis, (Ehman *et al.*, 1991).

3.3.3 Validation of INAA Technique using Estuarine Sediment 1646a

The reliability of the results obtained using the INAA technique was validated using NIST 164a (Estuarine Sediment). The values obtained showed good agreement with the certified values (Table 3.7). The detection limits of the INAA analysis carried out in this study are also shown in Table 3.8.

Table of 3.7: Comparison of Measured and Certified values

Element	Concentration		Recovery (%)
	Measured	Certified	
Ca (%)	0.511	0.519	98.4
K (%)	0.89	0.864	103
Na (%)	0.76	0.741	102
Al (%)	1.95	2.297	84
S (%)	0.317	0.352	90
Mn (mg/kg)	234	234.5	99
V (mg/kg)	40.3	44.84	89

Table 3.8: Detection Limits of elements determined by INAA.

ELEMENT	DETECTION LIMIT(mg/kg)
Br	1.00
Na	1.4
La	10.5
Al	10
Mn	0.45
Si	0.2
Ca	0.03
Cl	1.6
Ba	0.03
V	0.5
K	100

3.4 Determination of Naturally Occurring Radioactive Materials (NORMs)

3.4.1 Sample Preparation

3.4.1.2 Procedure

The fertilizer samples were bought directly from the market in their original containers (polypropylene bottles for the liquid and sachets for the powdered samples). For activity concentration measurement, the fertilizer samples were also transported to the laboratory and prepared into 1 litre Marinelli beakers as shown in Fig. 3.1. The masses of 1 kg for powdered and 1 litre for liquid samples were taken using a Mettler Toledo AG-BD 1201 balance. This mass would be later used in the calculation of the activity concentrations. The beakers were thick enough to prevent the permeation of radon.

The beakers were closed by screw caps, and plastic tape was wrapped over the caps and then stored for measurement as shown in Fig. 3.1. This step was necessary to ensure that radon gas was confined within the volume and that the daughters would also remain in the sample. The measurements were performed five weeks later to ensure the secular equilibrium to be established between the long-lived parent nuclides of Ra-226 (U-238) and Th-232, and their short-lived daughters (Hamby and Tynybekov, 2002; Vassas *et al.*, 2006; El-Zakla *et al.*, 2007).



Fig. 3.1 Samples prepared into 1litre Marinelli beakers

3.4.2 Calibration of gamma spectrometry system

3.4.2.1 Calibration Standard

Calibration standard (W 146) with approximate volume 1000 mL and density 1.0 g cm⁻³ in a 1.0 L Marinelli beaker, supplied by Deutscher Kalibrierdienst (DKD-3), QSA Global GmbH, Germany containing radionuclides with known energies.

3.4.2.2 Procedure for Calibration

Prior to the measurements, the detector and measuring assembly were calibrated for energy and efficiency to enable both qualitative and quantitative analysis of the samples to be performed. The energy and efficiency calibrations were performed using mixed radionuclide calibration standard homogeneously distributed in the form of solid water.

The standard containing radionuclides with known energies [²⁴¹Am (59.54 keV), ¹⁰⁹Cd (88.03 keV), ⁵⁷Co (122.06 keV), ¹³⁹Ce (165.86 keV), ²⁰³Hg (279.20 keV), ¹¹³Sn (391.69 keV), ⁸⁵Sr (514.01 keV), ¹³⁷Cs (661.66 keV), ⁶⁰Co (1173.2 keV and 1332.5 keV) and ⁸⁸Y (898.04 keV and 1836.1 keV)] and activities in a 1000 mL Marinelli beaker was used.

3.4.3 Energy Calibration

The energy calibration was performed by matching the principal gamma ray peaks observed in the spectrum of the standard (W 146) to the channel numbers. The formulae relating the energy and the channel number is expressed as;

$$E = A_0 + A_1 \cdot CN \quad (3.2)$$

where;

E - Energy,

CN - Channel number for a given radionuclide,

A_0 and A_1 - Calibration constants for a given geometry.

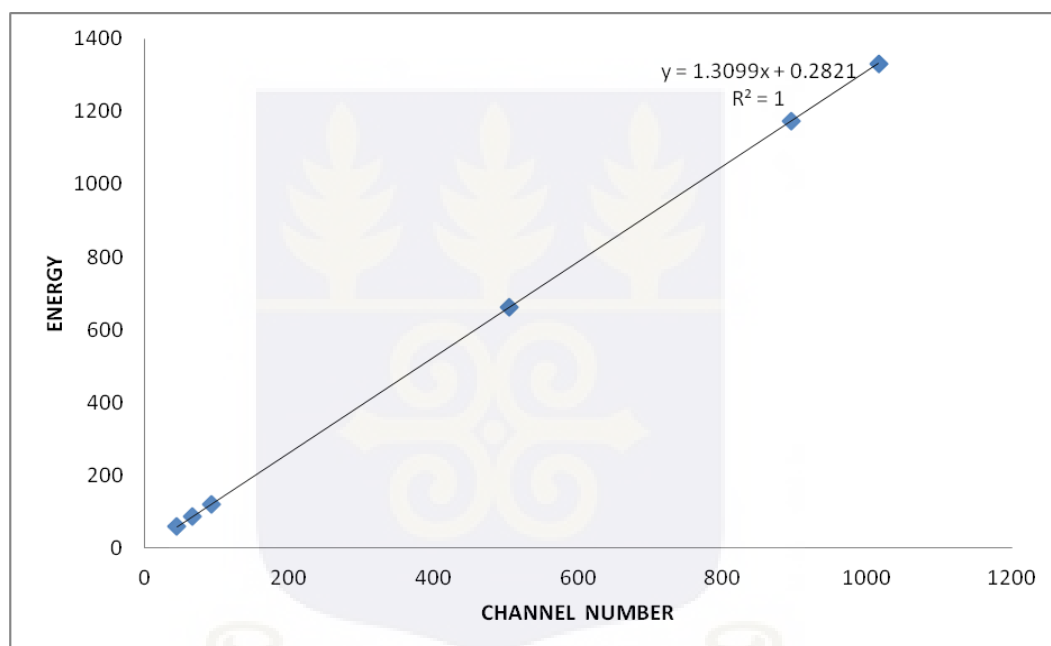


Figure 3.2: Energy calibration for 1L Marinelli geometry

3.4.4 Efficiency Calibration

The efficiency calibration was performed by acquiring a spectrum of the standard until the count rate of total absorption could be calculated. The net count rate was determined at the photo peaks for all the energies to be used for the calculation of the efficiency. The efficiency was then related to the count rate and the activity of the standard.

$$\eta = \frac{N_T - N_B}{P_E \cdot A_{STD} \cdot T_{STD}} \quad (3.3)$$

where,

P_E - Gamma ray emission probability for the energy E , η is the efficiency of the detector, N_T is the total count under a photopeak in a peak range, N_B is the background counts, A_{STD} is the activity of the calibration standard for a given radionuclide in Bq at the time of measurement and T_{STD} is the counting time.

The efficiency is related to the energy by the expression:

$$\ln \eta(E) = B_0 + B_1 \ln E + B_2 (\ln E)^2 \quad (3.4)$$

where,

B_0 , B_1 , B_2 are calibration constants for a given geometry. The efficiency calibration curve is shown in Fig. 3.5.

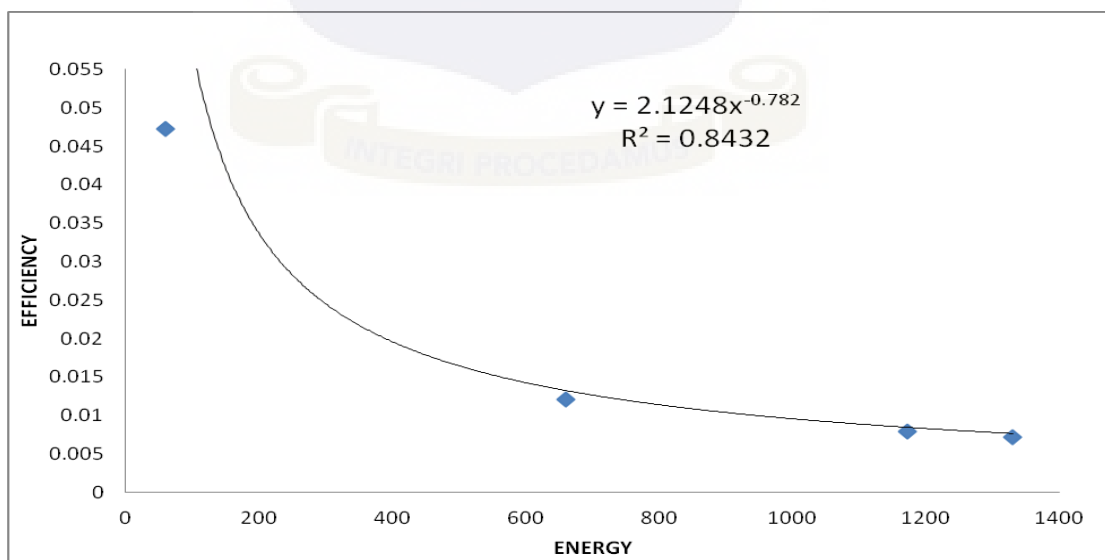


Figure 3.3: Efficiency calibration curve for 1 Litre geometry

3.4.5 Sample Measurement and Analysis of Spectra

3.4.5.1 Instrumentation

- γ -spectrum acquisition and evaluation software, MAESTRO-32.
- γ -spectrometric system, consisting of high purity Germanium (HPGe) N-type coaxial detector (model GR 2518), high voltage power supply (model 3105), and a spectroscopy amplifier (model 2020), manufactured by Canberra Industries Inc.
- The γ -ray detector system at fixed geometry was coupled to an 8 k Ortec Multichannel Analyzer (MCA) emulation card and a microcomputer. The detector system operated at a bias voltage of -3000V full width at half maximum, and resolution of 1.8 keV for ^{60}Co gamma ray energy of 1332 keV with 25% relative efficiency.

3.4.5.2 Standard Reference Material (SRM)

The standard (NW 146) with approximate volume 1000 mL and density 1.0 g cm^{-3} in a 1.0 L Marinelli beaker. The standard was supplied by Deutscher Kalibrierdienst (DKD-3), QSA Global GmbH, Germany.

3.4.5.3 Procedure

The activity concentrations of the fertilizer samples were determined by a non-destructive analysis using a computerized gamma ray spectrometry system with high purity germanium (HPGe). The relative efficiency of the detector system was 25%, and resolution of 1.8 keV at 1.33 MeV of ^{60}Co . The gamma spectrometer is coupled to conventional electronics connected to a multichannel analyzer card (MCA)

installed in a desk top computer. A software program called MAESTRO- 32 was used to accumulate and analyze the data manually using spread sheet (Microsoft Excel) to calculate the natural radioactivity concentrations in the samples. The detector is located inside a cylindrical lead shield of 5 cm thickness with internal diameter of 24 cm and height of 60 cm. The lead shield is lined with various layers of copper, cadmium and Plexiglas, each 3mm thick.

A counting time of 36,000 seconds (10 hrs) was used to acquire spectral data for each sample. In order to subtract the background from each measurement, an empty Marinelli beaker (with the same geometry) was measured. The activity concentrations of the uranium-series were determined using γ -ray emissions of ^{214}Pb at 351.9 keV (35.8 %) and ^{214}Bi at 609.3 keV (44.8 %) for ^{226}Ra . For the ^{232}Th -series, the emissions of ^{228}Ac at 911 keV (26.6 %), ^{212}Pb at 238.6 keV (43.3 %) and ^{208}Tl at 583 keV (30.1 %) were used. The ^{40}K activity concentration was determined directly from its emission line at 1460.8 keV (10.7 %). The information is further illustrated in Table 3.9.

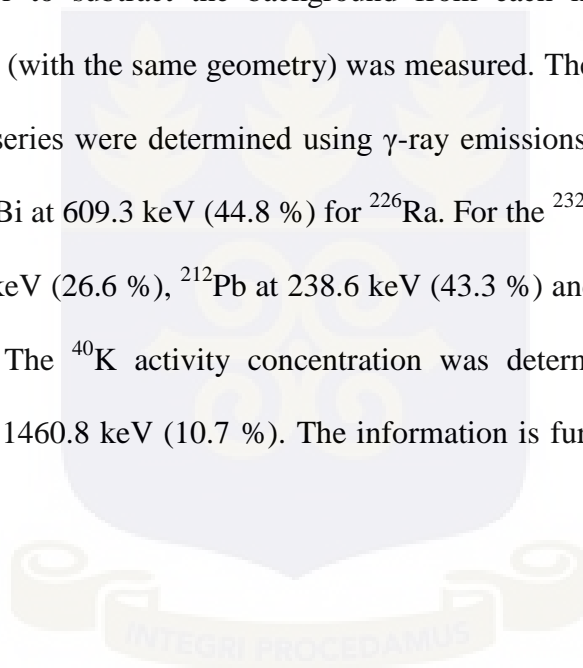


Table 3.9: The γ -ray Emissions Scheme of Daughters of Radionuclides (^{238}U , ^{232}Th and ^{40}K)

Radionuclide	Primary Gamma Rays			Secondary Gamma Rays		
	Daughter	E, keV	P_{γ}	Daughter	E, keV	P_{γ}
^{238}U	^{214}Pb	351.92	0.358	^{214}Pb	295.21	0.185
	^{214}Bi	609.31	0.4479	-	-	-
	^{214}Bi	1764.49	0.1536	-	-	-
^{232}Th	^{208}Tl	2614.53	0.3534	^{228}Ac	911.21	0.266
	^{212}Pb	238.63	0.433	-	-	-
	^{208}Tl	583.19	0.3011	-	-	-
^{40}K	-	1460.83	0.1067	-	-	-

3.4.6 Calculation of Activity Concentration

The specific activity concentrations (A_{sp}) of ^{238}U , ^{232}Th , ^{40}K and in Bq l^{-1} for the fertilizer samples were determined using equation 3.4.

$$A_{sp} = \frac{N_{sam}}{P_E \cdot \epsilon \cdot T_c \cdot M} \quad (3.5)$$

where;

- N_{sam} - net counts of the radionuclide in the sample
- P_E - gamma ray emission probability (gamma yield)
- ϵ - total counting efficiency of the detector system
- T_c - sample counting time
- M - mass of sample (kg) or volume (L)

The hazard indices of the naturally occurring radioactive elements were computed from the activity concentrations using Microsoft Excel 2007.

3.5 Statistical Analysis

The experimental data were subjected to statistical analysis using SPSS software (version 20.0 for Windows). Data comprising trace elements and naturally occurring radioactive materials in non-traditional fertilizers were subjected to multivariate analysis: Cluster Analysis (CA) and Principal Component Analysis (PCA)/Factor Analysis (FA) using SPSS 20.0 for windows. Prior to such analyses, the raw data were commonly normalized to avoid misclassifications due to the different order of magnitude and range of variation of the analytical parameters (Aruga *et al.*, 1995).

Principal component analysis (PCA) was used to infer the hypothetical source of heavy metals (natural or anthropogenic) and the natural radionuclides. Factor analysis (FA, the components of the PCA) was performed by varimax rotation, which minimized the number of variables with a high loading on each component, thereby facilitating the interpretation of PCA results. Cluster analysis (CA) was applied to identify groups of samples with similar heavy metal and natural radionuclide contents, clustering the samples with similar heavy metal contents and/or natural radionuclides. The CA was formulated according to the Ward-algorithmic method, and the squared Euclidean distance was employed for measuring the distance between clusters of similar metal/natural radionuclide contents. Pearson's product moment correlation matrix was used to identify the relationship among metals and/or natural radionuclides and support the results obtained by multivariate analysis.

CHAPTER 4

RESULTS

4.1 Chemical Analysis

Instrumental Neutron Activation Analysis (INAA) and Atomic Absorption Spectrometry (AAS) techniques were employed to determine elements in both solid and liquid fertilizer samples. Elements determined by the AAS technique are Cu, As, Pb, Co, Cr, Ni, Hg, Fe, Cd and Zn. Br, Mn, V, Na, La, Al, Si, Ca, Cl, K, Ba and S were determined by INAA. Results of the analysis are shown in Tables 4.1 and 4.2.

The highest concentration of Cu (216 mg/L) was found in NPK+ fertilizer (sample SFGHr) and the lowest of 0.16 mg/L was found in micronutrient fertilizer type of fertilizer (sample SKMBr). The concentration of Pb was highest in NPK only and lowest in micronutrient fertilizers, at 4.12 and 0.12 mg/L respectively. The highest concentration of Ni (7.84 mg/L) was found in sample SMAPr, a NPK only fertilizer at with the lowest concentration (0.28 mg/L) from sample SKPFGi. The values 393.12 mg/L and 13.4 mg/L were the highest and lowest concentrations recorded of Fe in samples SHSBr and SFGMi, respectively.

The highest and lowest values for Cd were 4.68 mg/L and 0.96 mg/L in samples SJFMr and SEMPIbi respectively. Mercury was, however, not detected in any of the samples. The highest and lowest concentrations of As were 42.6 mg/L (NPK+ sample) and 0.36 mg/L (Secondary nutrient fertilizers). Cobalt was detected in only 8 of the samples analyzed (mostly NPK fertilizers). Zinc was detected in its highest and lowest concentrations of 54.0 mg/L and 0.44 mg/L in samples SKMBi and SKPFGi respectively. The highest concentration measured for Cr (14.92 mg/L) in the liquid fertilizer sample SKMSi (NPK only). The highest concentration of V

(990 mg/kg) was determined in sample SKPGi which is a NPK with micronutrients while the lowest value of 0.6 occurred in SGAr also an NPK fertilizer. micronutrient only fertilizer. From the data generated above, possible toxic elements accumulation is in the order $Fe > Cu > Co > Cd > Cr > Ni > Pb > As > Hg$.

4.2 Naturally Occurring Radioactive Materials

The activity concentrations were determined using N-type coaxial high purity germanium(HPGe) γ -ray semiconductor detector(Canberra) connected to a multi-channel analyzer. The measured activity concentrations of the natural radionuclides ^{238}U , ^{232}Th and ^{40}K are presented in Tables 4.1 and 4.2. The concentration of ^{238}U varied from 1.7 to 16.3 Bq/kg with a mean of 8.86 Bq/kg. The concentration of ^{232}Th varied from 2.1 to 30.8 Bq/kg with a mean of 14.34 Bq/kg, whereas ^{40}K has a concentration of 0.1–19,710 Bq/kg with a mean concentration of 3695.8 Bq/kg.

The mean specific activities of U (Ra-226), Th-232 and K-40 in solid fertilizers were 8.24, 12.36 and 8510.31 Bq/kg respectively, and in liquid fertilizers were 9.19, 15.46 and 1,103.37 Bq/L respectively. The activity concentrations of the measured natural radionuclides are further illustrated in Fig. 4.1 to Fig. 4.8.

The solid fertilizers had relatively low concentrations for U-238 (figure 4.1). The highest concentrations however, can be seen in samples SJFMr, SKPFGGr, SKPFRr and SKPFRr. These samples are all NPKs and most have other micronutrients as additives. Their concentrations are greater than 12 Bq/kg.



Table 4.1- Elemental (mg/kg) and Activity Concentrations (Bq/kg) quantified in solid fertilizer samples.

	SMAPr	SFHMi	SFHMr	SJFMi	SJFMr	SJRDi	SJSMi	SKPFGi	SKPFGr	SKPFRr	SKPFRi	SKMKi	SKMKr
	NPK ONLY	NPK+	NPK+	NPK+	NPK+	NPK+	NPK+	NPK+	NPK+	NPK+	NPK+	NK	NK
Cu ^a	8.36	114.84	94.44	1.92	<0.12	<0.12	1.2	<0.12	6.52	12.8	18.16	<0.12	<0.12
Pb ^a	2.36	4.12	0.48	<0.04	<0.04	<0.04	0.72	<0.04	2.76	3.36	<0.04	<0.04	1.84
Ni ^a	7.84	<0.04	<0.04	<0.04	1.32	4.16	<0.04	<0.04	0.8	0.28	0.52	0.44	<0.04
Fe ^a	153.44	29.6	28.96	37.2	77.84	121.92	61.28	<0.24	127.48	159.12	176.96	24.28	30.12
Cd ^a	3.96	3.64	3.56	2.84	4.28	3.08	3.44	<0.08	2.28	4	3.84	2.76	3.68
Cr ^a	0.32	0.64	<0.04	0.36	0.88	0.96	<0.04	<0.04	0.08	0.2	0.16	0.44	0.8
Zn ^a	8.48	21.8	20.72	10.8	6.16	21.08	4.6	0.04	18.72	11.92	9.88	15.72	6.2
Co ^a	<0.2	<0.2	<0.2	0.84	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	2.12	2.96	0.84
As ^a	0.16	0.08	<0.04	<0.04	<0.04	<0.04	<0.04	0.2	0.24	0.12	0.24	<0.04	0.12
Hg ^a	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Br ^b	3.2	6.4	11.77	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	19.25	32.61
Na ^b	6.5	<1.4	1384	2581	2220	814.5	1871	946.7	<1.4	<1.4	<1.4	6839	8324
La ^b	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5
Al ^b	54	21.89	117.4	98.2	151.7	214	<10	113.1	157.2	157.2	125.3	<10	<10
Mn ^b	45	3.8	5.03	51.28	23.34	34.8	<0.45	95.51	225.1	225.1	296	<0.45	<0.45
Si ^b	32	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	9511	<0.2	<0.2	<0.2	<0.2	<0.2
Ca ^b	233	<0.03	1487	788.1	1088	<0.03	<0.03	800.1	1100	1100	828.1	<0.03	240.9
Cl ^b	320	<1.6	<1.6	251.1	221.2	<1.6	<1.6	629.2	6563	6563	6858	<1.6	1359
S ^b	<5.0	<5.0	<5.0	5508	5239	<5.0	<5.0	11830	<5.0	<5.0	<5.0	<5.0	29330
K ^b	197653	30630	55890	255300	265437	68660	14830	65370	98706	188348	187547	289868	289768
Ba ^b	<0.03	<0.03	<0.03	125.8	127.3	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	167.07	0.03
V ^b	<0.5	19.0	<0.5	0.83	0.15	<0.5	<0.5	990	<0.5	<0.5	<0.5	<0.5	<0.5
U-238	2.1	7.5	8.5	5.9	14.4	12.4	2.9	14.7	11.8	13.8	1.7	5.5	5.5
Th-232	6.1	11.5	11.4	8.1	27.9	17.6	4.9	11.9	22	25	7.1	4.9	4.2
K-40	4576.2	4801.2	4826.2	16156.2	9082.5	8765	8245.1	4893.33	4532.4	5262.4	4857.6	18710	19710

^a-Concentration determined by AAS technique;^b-Concentration determined by INAA technique

Table 4.2- Elemental (mg/l) and Activity Concentrations (Bq/l) quantified in liquid fertilizer samples

	SKMSi	SCSIIr	SCSIIIr	SBBXi	SBBXr	SGAi	SGAr	SKFDi	SFGHr	SADGi	SEMPr	SEMPIbi	SIPMr
	NPK ONLY	NPK ONLY	NPK ONLY	NPK+	NPK+	NPK+	NPK+	NPK+	NPK+	NPK+	NPK+	NPK+	NPK+
Cu^a	<0.12	7.16	34.72	212.6	183.68	<0.12	<0.12	<0.12	216.36	0.4	52.16	2.24	<0.12
Pb^a	3.76	2.12	0.76	<0.04	1.56	<0.04	2.28	3.16	0.72	<0.04	<0.04	1.6	<0.04
Ni^a	<0.04	<0.04	<0.04	0.36	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Fe^a	357.48	45.76	138.52	375.9	349.68	<0.24	28.68	55.92	352	28.08	47.28	16.76	16.48
Cd^a	4.12	3.0	3.0	1.92	3.16	<0.08	2.44	2.08	2.88	2.04	2.24	0.96	1.84
Cr^a	14.92	<0.04	0.2	<0.04	<0.04	<0.04	<0.04	0.16	0.52	<0.04	<0.04	<0.04	<0.04
Zn^a	23	6	4.64	30.88	18.48	<0.04	12.52	3.88	48	9.92	6.52	8.92	8.92
Co^a	1.16	<0.2	1.00	<0.2	<0.2	<0.2	<0.2	<0.2	42.6	<0.2	<0.2	<0.2	<0.2
As^a	0.56	<0.04	0.08	0.52	0.36	<0.04	<0.04	0.12	<0.04	<0.04	<0.04	<0.04	<0.04
Hg^a	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Br^b	4.7	<1.00	<1.00	190	210	<1.00	3.0	6.1	6.4	3.6	4.6	<1.00	6.4
Na^b	1192	<1.4	867.4	398	3554	304.8	<1.4	2583	<1.4	470.7	<1.4	<1.4	<1.4
La^b	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5
Al^b	1119	72.5	<10	53	66.12	54.04	27.66	117.6	21.9	38.64	33.35	19.35	21.9
Mn^b	7.46	160.8	<0.45	465	456.9	90.81	1.11	7.24	87	1.5	76.7	725.7	56
Si^b	<0.2	<0.2	<0.2	33.0	<0.2	<0.2	<0.2	9897	<0.2	5056	<0.2	<0.2	<0.2
Ca^b	303.7	8703	<0.03	234	365.2	298.9	601.2	517.2	<0.03	320.2	654	2176	<0.03
Cl^b	388.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	1160	<1.6	<1.6	<1.6	<1.6	<1.6
S^b	1253	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
K^b	95666	34445	47260	187653	188653	<100	87965	98763	12340	19050	<100	<100	<100
Ba^b	45.81	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	322.6	<0.03	<0.03	<0.03	<0.03	<0.03
V^b	17.9	0.64	<0.5	<0.5	<0.5	<0.5	0.6	37.14	0.19	14.0	<0.5	<0.5	91.0
U-238	3.7	13.6	7.0	13.3	10.7	14.5	14.1	1.6	12.5	2.1	16.3	16.3	3.4
Th-232	14.4	11.9	15.4	25.9	13.4	25.1	24.1	2.1	12.8	16.1	22	22	5.6
K-40	4294	1234.4	2048.3	2660.3	2674	2967	2497	35	765.3	74.2	1078.3	1078.3	64

^a-Concentration determined by AAS technique. ^b-Concentration determined by INAA technique

Table 4.2 Cont'd

	SLAPr	SHSBi	SHSBr	SCSiR	SKMBi	SKMBr	SKAMi	SKPKi	SKFSi	SEP	SDGGi	SFTCi	SFTCr
	NPK+	NK	NK	NK	Others	Others	Others	Others	Others	Others	Others	Others	Others
Cu^a	<0.12	<0.12	<0.12	33.16	0.2	0.16	360	0.6	1.04	<0.12	0.28	600	600
Pb^a	<0.04	<0.04	0.28	1.44	<0.04	<0.04	<0.04	1.92	1.28	<0.04	0.24	0.12	3.32
Ni^a	0.52	<0.04	0.28	BDL	<0.04	<0.04	1.44	<0.04	1.08	<0.04	<0.04	<0.04	<0.04
Fe^a	19.2	400	393.12	13.52	78.28	82.48	560	19.84	178	<0.24	14.6	41.6	46.56
Cd^a	1.16	2.52	2.56	2.24	1.76	2.52	2.24	2.48	2.48	<0.08	1.4	2	2.32
Cr^a	<0.04	<0.04	0.28	<0.04	<0.04	0.24	0.2	0.44	<0.04	<0.04	<0.04	0.12	<0.04
Zn^a	14.8	37	31.88	23.64	54	52	44	11.64	17.28	<0.04	40.24	6.8	16.64
Co^a	<0.2	<0.2	0.76	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
As^a	<0.04	<0.04	0.44	<0.04	<0.04	0.16	<0.04	<0.04	0.4	<0.04	<0.04	<0.04	<0.04
Hg^a	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Br^b	3.89	7.3	7.1	27.1	11.34	<1.00	<1.00	<1.00	19.25	<1.00	<1.00	<1.00	1.8
Na^b	<1.4	208	212	2274	2086	<1.4	23	30	6839	<1.4	<1.4	1350	3668
La^b	<10.5	<10.5	<10.5	<10.5	19.1	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5	<10.5
Al^b	44	129.6	135.6	31.65	31.76	<10	47	32	<10	19.35	20.95	38.83	<10
Mn^b	25	19.8	21.34	5.25	2815	<.45	<.45	<.45	<.45	725.7	13	86.42	14
Si^b	42	<0.2	<0.2	<0.2	<0.2	627.9	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ca^b	133	959.5	961.5	360.2	1626	<0.03	11	7.3	<0.03	2176	427.1	569.9	35.1
Cl^b	412	5846	5852	<1.6	390.7	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6
S^b	<5.0	<5.0	<5.0	<5.0	1749	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
K^b	<100	3428	3456	98670	245	252.5	<100	<100	<100	<100	<100	<100	<100
Ba^b	<10	<10	<10	<10	160.5	48.14	<10	<10	177.07	<10	<10	<10	<10
V^b	<0.5	0.98	0.98	<0.5	169.9	<0.5	<0.5	<0.5	<0.5	<0.5	6.8	<0.5	<0.5
U-238	2.1	10.2	13	13	11.9	8.9	3.2	3.2	3.2	14.8	12	1.8	12.5
Th-232	56.1	8.4	26.1	21.2	24.6	10.1	6.8	5.8	3.8	16.9	21.2	2.1	10.1
K-40	123.2	553.2	531.6	3992	314.1	266.8	423	323	23	306	307.2	54.2	0.1

^a-Concentration determined by AAS technique. ^b-Concentration determined by INAA technique

The liquid fertilizers plots are shown in Fig. 4.2 and indicates fertilizers with concentrations greater than 12Bq/L are SEMPr, SEMPIbi, SGAi, SGAr, SCSII, SEP, SFTCr, SFTCi and SCSi, whereas SKMSi, SKFDi, SADGi, SLAPr, SKAMi, SKPKi, SKFSi and SFTCi have concentrations below 5 Bq/L.

Fig. 4.3 shows Th-232 activity concentrations in solid fertilizers. Samples SJFMr, SKPFgr and SKPFRr have concentrations above 20 Bq/kg. SJSMi, SKMKi and SKMKr have concentrations below 5 Bq/kg.

Samples SBBXi, SGAi, SGAr, SEMPi, SEMPIbi, SKMBi, SHSBr, SFTCi AND SCII have concentrations above 20Bq/L (Fig. 4.4). Low concentrations were however obtained in SKFDi, SIPM, SLAPr, SKAMi and SKPKi and SFTCi.

The concentrations for the K-40 were higher than the concentrations of U-238 and Th-232, especially for solid fertilizers. However the concentrations for the liquid samples are lower comparatively. The K-40 activity concentrations for solid samples are illustrated in Fig. 4.5. Low concentrations were obtained in SMAPr, SFHMi, SFHMr, SKPFGi, SKFgr, SKPFRr and SKPFri (lower than 500 Bq/kg comparatively). However, much higher concentrations (over 1500 Bq/kg) were obtained in three samples; SJFMi, SKMKi and SKMKr. Fig. 4.6 details activity concentrations for liquid fertilizer samples and have concentrations below 5 Bq/L SKFDi, SEMPIbi, SLAPr, SFTCi and SKPKi. However, samples SBBXi, SGAi, SGAr, SKMBi, SHSBr AND SKFSi have higher concentrations above 20 Bq/L. Generally, the activity concentrations in both the liquid and solid fertilizers are in the order K-40 > Th-232 > U-238 (Figs. 4.7 and 4.8).

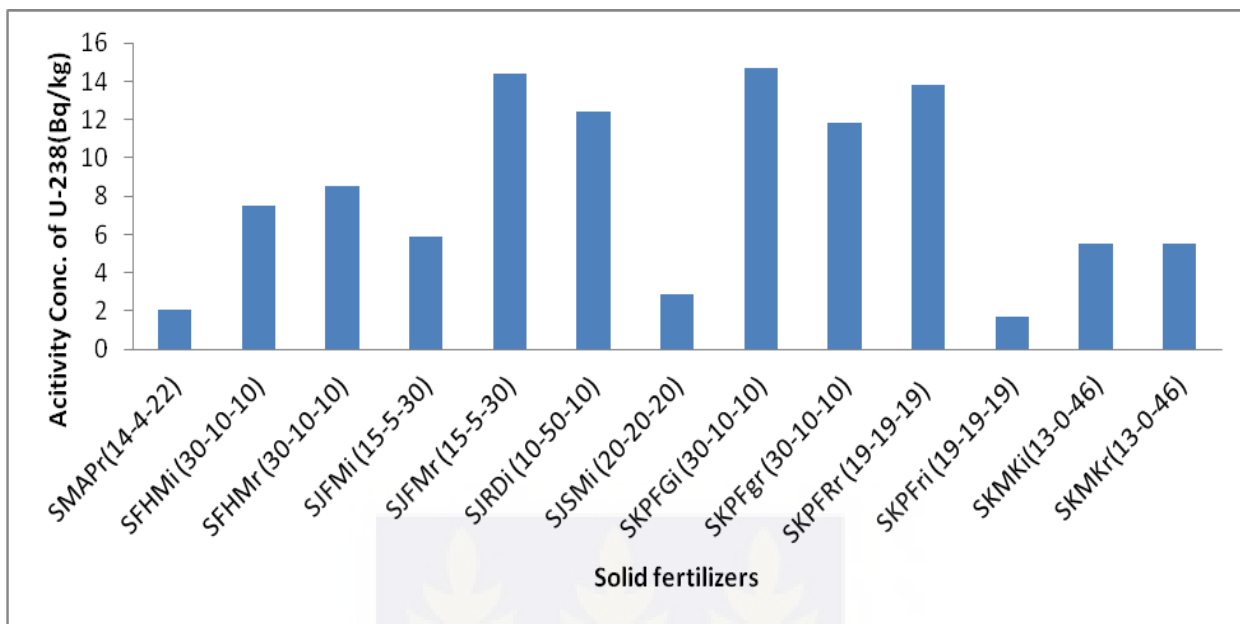


Figure 4. 1 Activity concentration of U-238 in solid fertilizers

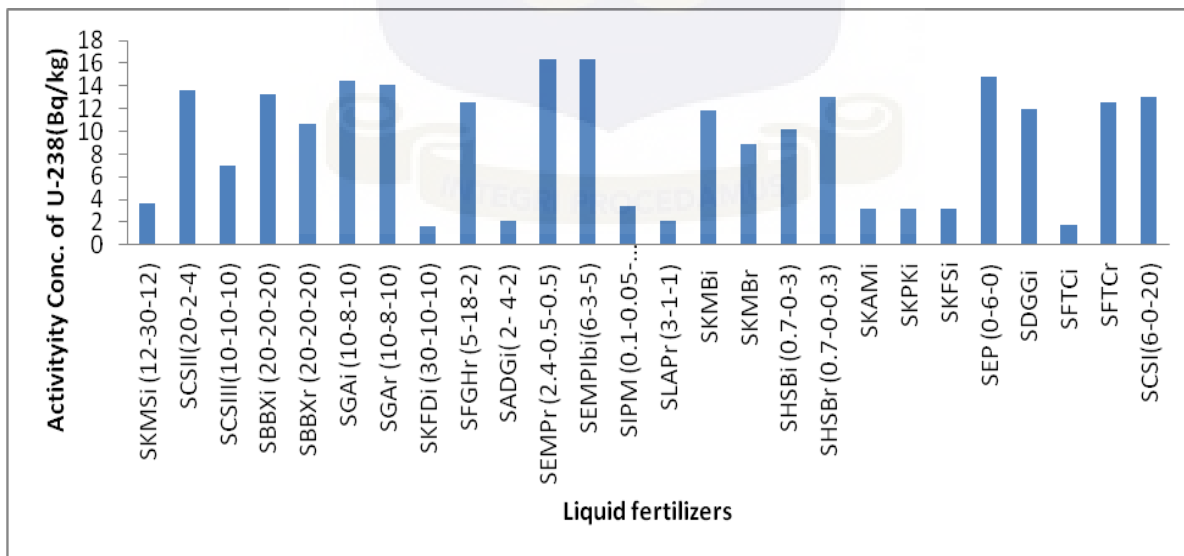


Figure 4.2 Activity concentration of U-238(Ra-226) in liquid fertilizers

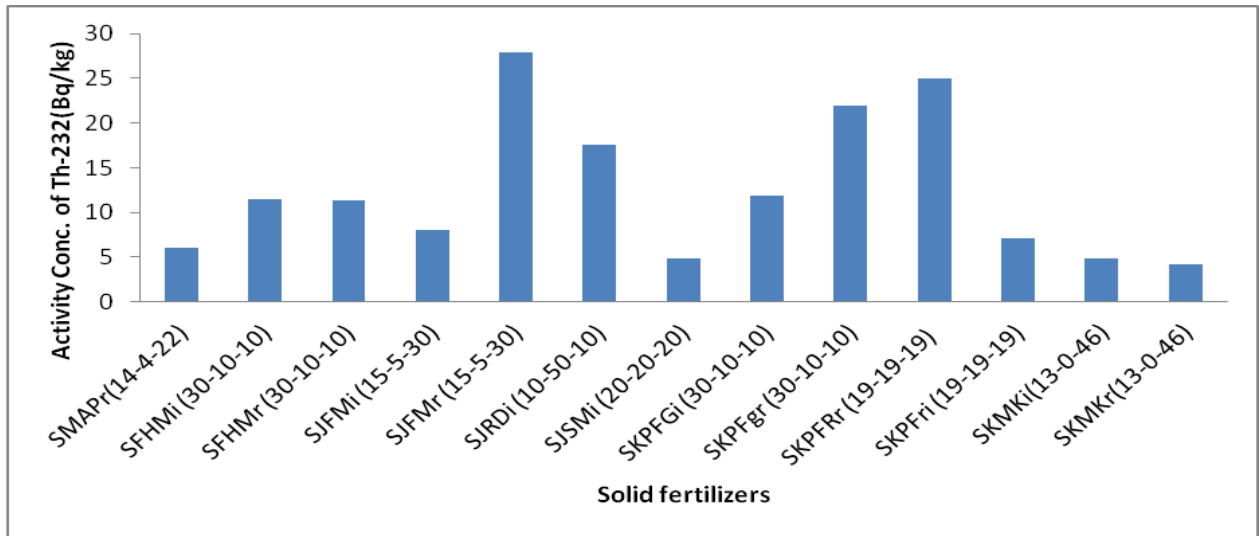


Figure 4.3 Activity concentration of Th-232 in solid fertilizers

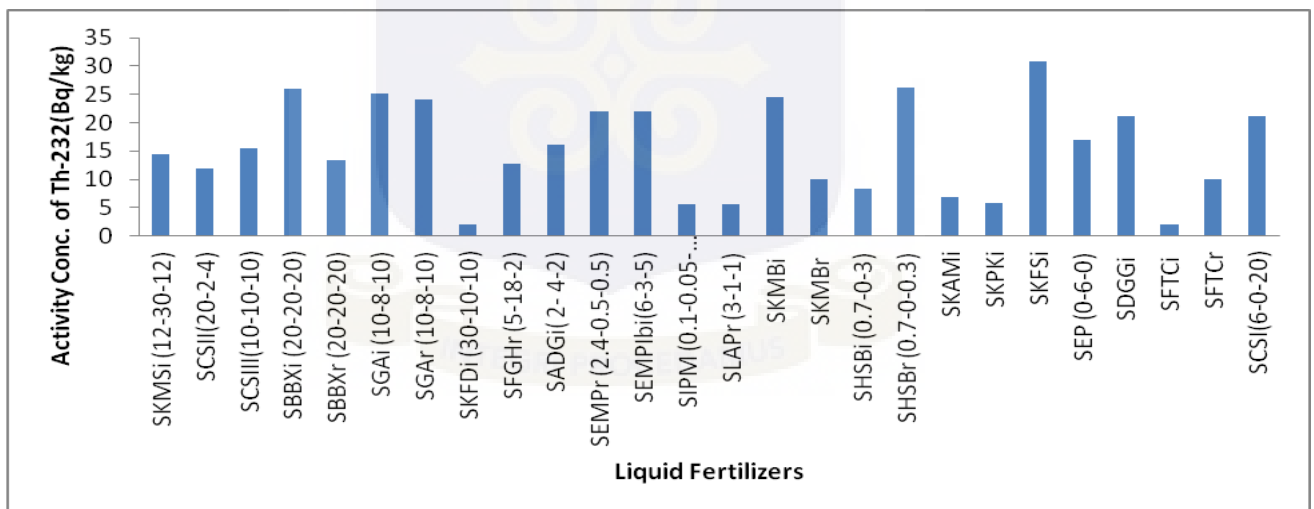


Figure 4.4 Activity concentration of Th-232 in liquid fertilizers

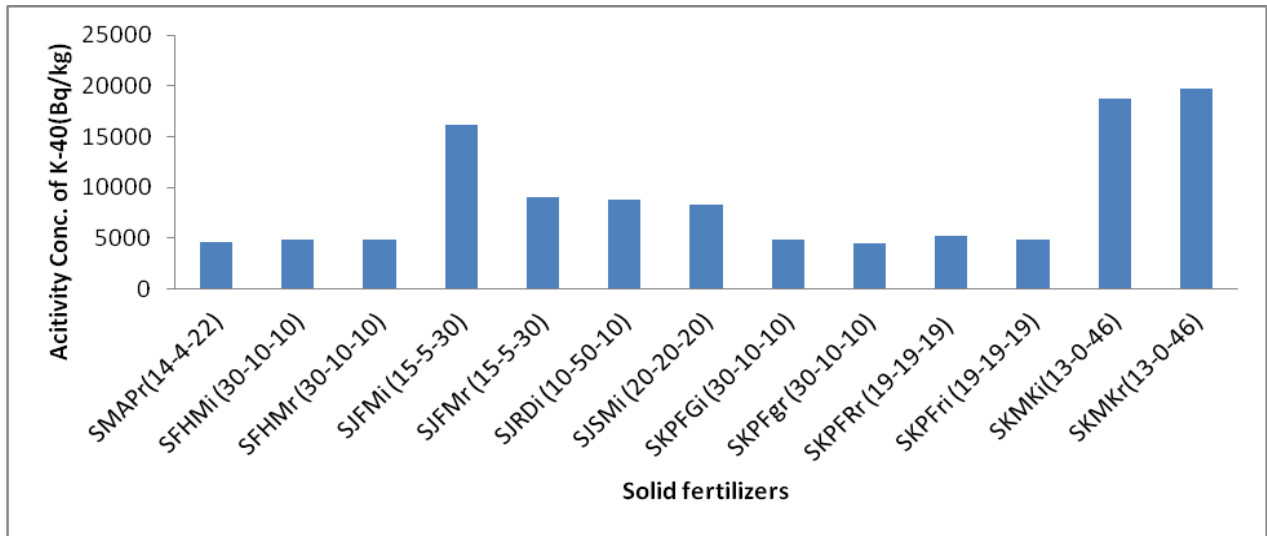


Figure 4.5 Activity concentration of K-40 in Solid fertilizers

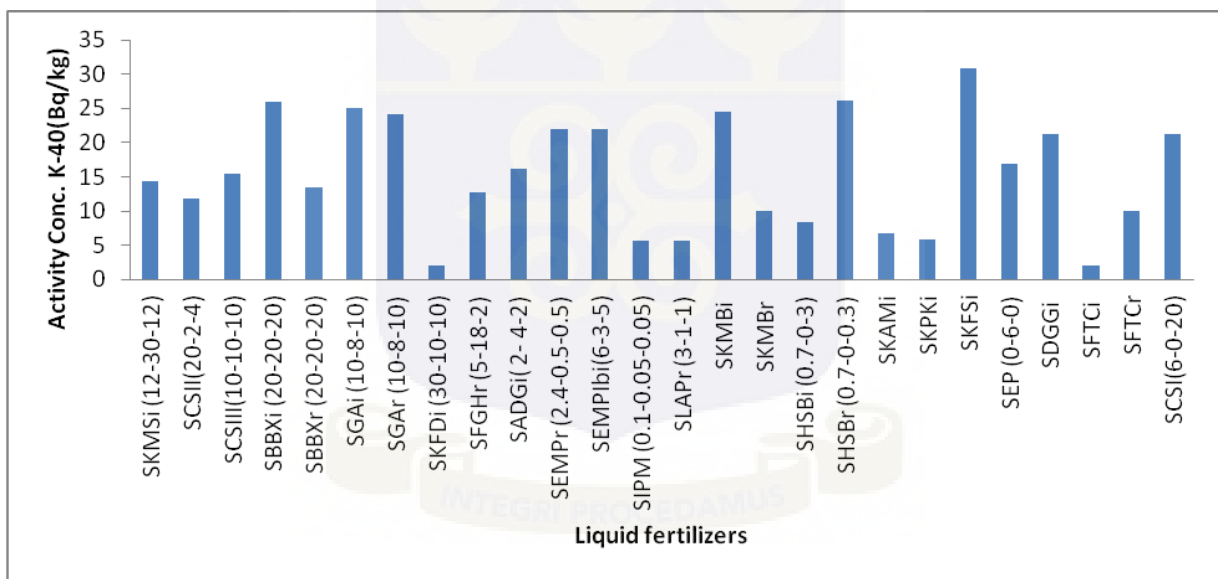


Figure 4.6 Activity concentration of K-40 in Solid fertilizers

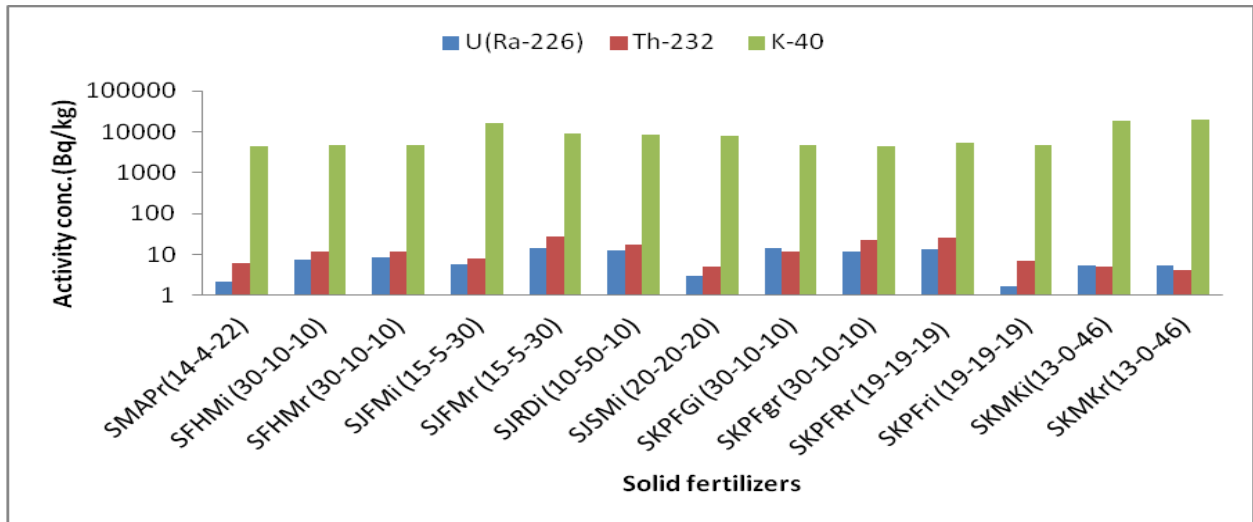


Figure 4.7 Activity concentrations of K-40, Th-232 and K-40 in solid fertilizers

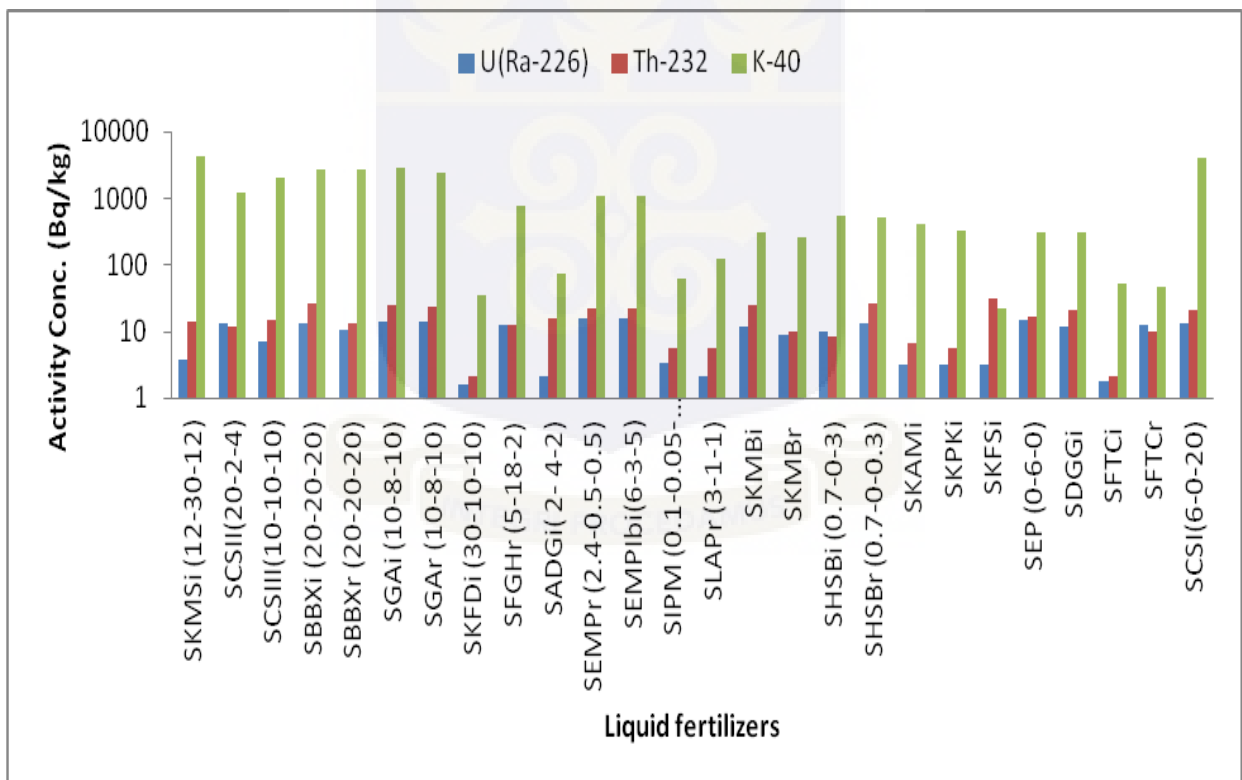


Figure 4.8 Activity concentrations of K-40, Th-232 and K-40 in liquid fertilizers

4.3 Statistical Analysis

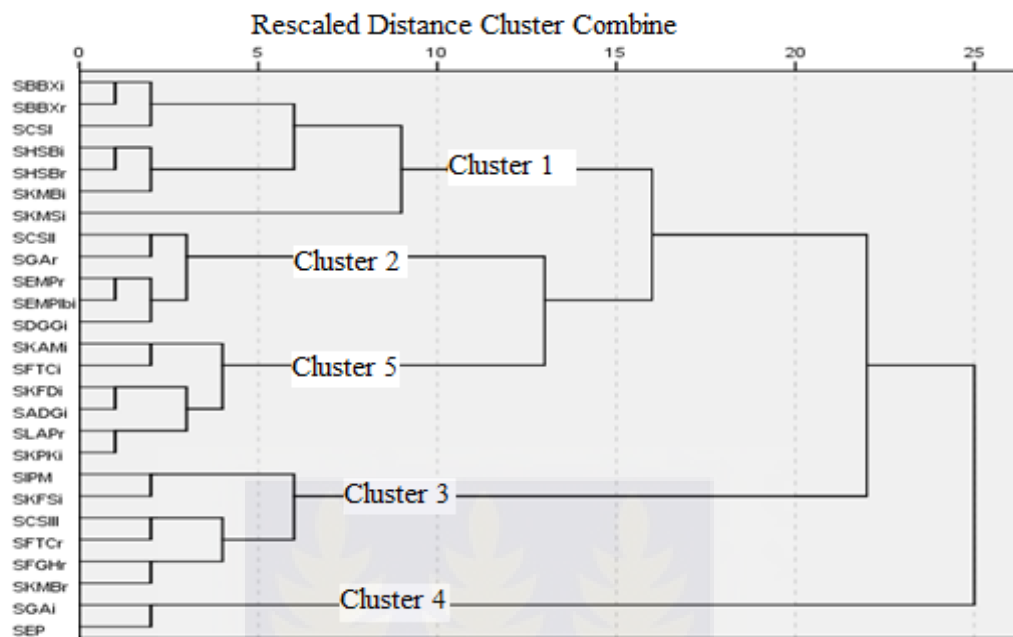
The multivariate statistical analysis was applied to allow a comprehensive inspection and evaluation of variability present in the data obtained. R- and Q-mode cluster analysis and R-mode principal component analysis were employed on the fertilizer samples and parameter data to determine their groupings and affinities as well as to trace the possible sources of contamination of the fertilizer samples.

4.2.1 Cluster Analysis

Cluster analysis was performed on the log-transformed variables using Euclidean distance and Ward's linkage method and the data standardized by Z-score approach. The Q-mode cluster analysis suggests 5 clusters for the liquid fertilizer samples considered (Fig. 4.9A) and 3 clusters for the solid fertilizers (Fig. 4.9B). The R-mode also clusters the variables under the liquid samples into 2 main clusters (Figure 4.10A) and those under the solid samples into 3 clusters (4.10B).

R-mode cluster analysis for the variables generated 2 major clusters for the liquid samples. Cluster 1 consists of elements Cu, Cd, Zn, Cr, Fe, K, K-40, Br and Na with Cd, Fe, Zn, Cu and Cr forming a sub-cluster, and Br, Na, K and K-40 forming another sub-cluster. Cluster 2 consists of Th-232, U-238, Ca, Mn, Al with U-238 and Th-232, and Al, Ca and Mn forming sub-clusters. For the solid samples, the R-mode cluster analysis yielded 3 clusters with cluster 1 grouping Cu, Cd, Zn, Cr and Fe together. Cluster 2 consists of K, K-40, Na, Br and Cr, whereas Cluster 3 contains a group of elements (Al, Ca and Mn) and radionuclides (U-238 and Th-232).

(A)



(B)

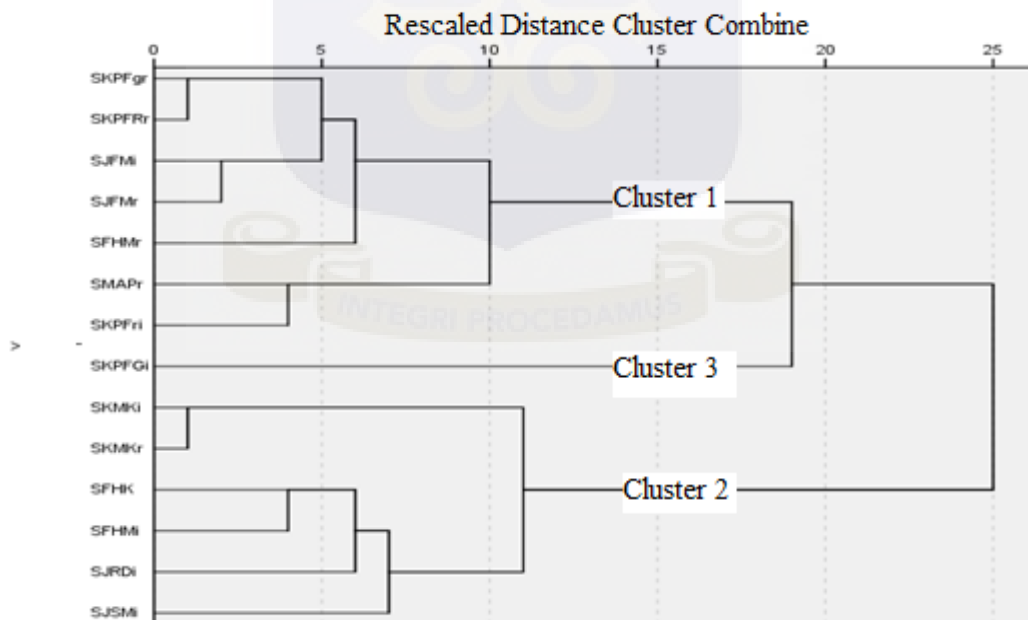
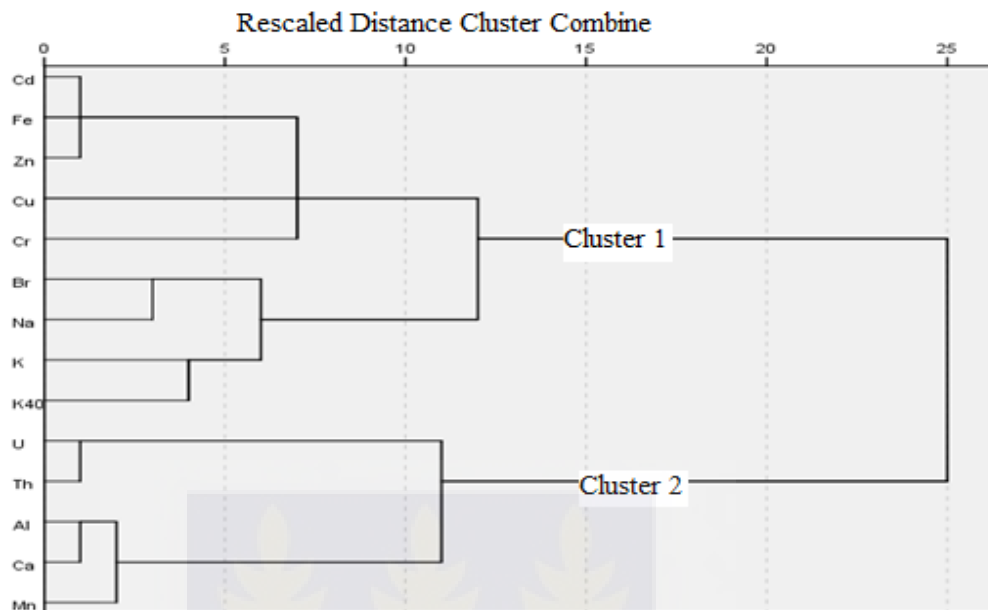


Fig.4.9 Dendrogram showing the clustering of liquid (A) and solid (B) non-traditional fertilizer samples.

(A)



(B)

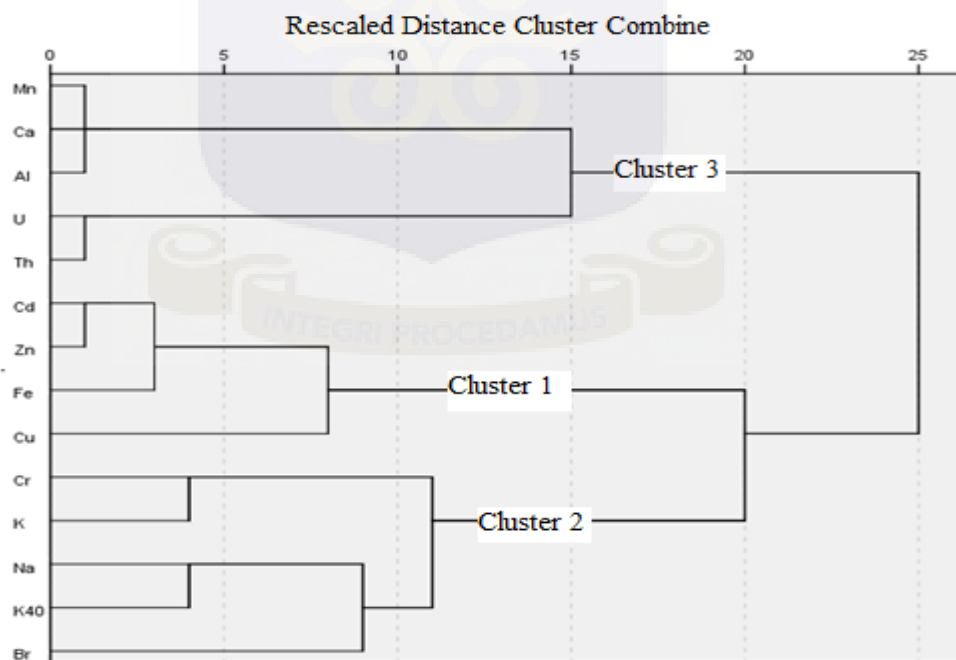


Fig. 4.10 Dendrogram showing clustering of measured parameters in liquid (A) and solid(B) non-traditional fertilizers.

4.2.2. Principal Component Analysis (PCA)

The relationship between the fertilizers and their chemical compositions was investigated by factor analysis (FA). Factor Analysis was also used to determine the structure in the data set. Factor analysis was conducted by the use of extraction method of principal component analysis (PCA) and the Varimax method was used in rotating the principal components together with Kaiser Normalization. Results of the Varifactor (VF) from the Varimax rotation for solid fertilizers are displayed in Tables 4.3 and 4.4. The results of the solid fertilizers dataset indicate five main factors controlling the variables of the samples under study. Eigen values are normally used in principal component analysis to ascertain the number of principal components (PCs) which can be retained for further studies. Eigen values give a measure of significance of the PCs and the factor with the highest eigen values is the most significant. Eigen values greater than 1 are usually considered as significant (Vega et al., 1998).

The scree plot gives an idea of the number of PCs that can be retained in order to appreciate the data structure of the study. The two scree plots shown in Appendix 2 indicate a pronounced change in the slope after the 5th eigen values of 1.501 and 1.555 for solid and liquid fertilizer samples respectively. The five (PCs) for both solid and liquid have eigen values greater than unity thereby making them significant. The eigen values explain for 84.91 % and 80.1 % of the total variance information contained in the original data for solid and liquid non-traditional fertilizers respectively.

The component loadings express the correlation between the original variables and the newly formed components and are linear combinations for each principal component. They can be used to determine the relative importance of a variable as compared to other variables in a PC and does not reflect the importance of the component itself.

With respect to the solid samples (Table 4.3), PC 1 explains 23.37 % of the total variance and is positively and largely contributed by Al, Mn, Ca and K. PC 2 explains 19.03 % of the total variance and is both positively and negatively largely contributed by Ca, Na and K-40. PC 5 contributes 10.7 % to the total variance and is positively contributed by Br.

Table 4.3: Rotated component matrix of 5 factor model explaining 84.9 % of the total variance for solid fertilizers

Variable log-transformed	COMPONENT					CUMMUNALITIES
	PC 1	PC 2	PC 3	PC 4	PC 5	
Cu	0.185	0.813	0.014	-0.129	-0.011	0.712
Cd	-0.312	0.381	0.717	-0.044	0.318	0.86
Zn	-0.402	0.474	0.536	0.239	0.439	0.923
Cr	0.028	-0.352	0.778	0.005	-0.013	0.73
Fe	0.004	0.409	0.830	-0.124	-0.234	0.927
Br	-0.206	-0.081	0.000	-0.228	0.909	0.928
Na	-0.035	-0.810	-0.104	-0.172	0.041	0.7
Al	0.868	0.365	-0.173	0.133	-0.074	0.94
Mn	0.903	0.132	-0.039	-0.066	-0.333	0.949
Ca	0.941	0.069	-0.029	0.098	-0.082	0.907
K	0.629	-0.348	0.551	-0.014	0.300	0.911
U	0.013	-0.236	-0.172	0.932	0.006	0.955
Th	0.190	0.212	0.107	0.872	-0.323	0.957
K40	-0.220	-0.550	0.035	0.364	0.075	0.49
Eigenvalues	3.271	2.664	2.485	1.967	1.501	
% variance	23.367	19.026	17.747	14.048	10.720	
Cummulative %	23.367	42.393	60.140	74.189	84.909	

Significant values are in bold type face.

Values in Italic indicate significant negative loadings.

Table 4.4: Varimax rotation factor scores for 5 factor model for the analyzed solid fertilizers

SAMPLE ID	VF 1	VF 2	VF 3	VF 4	VF 5
SMAPr	<i>0.782</i>	0.969	0.458	-1.857	0.012
SFHK	-1.173	<i>0.719</i>	-0.418	0.773	1.451
SFHMi	-1.261	1.040	-0.151	0.323	0.393
SFHMr	0.379	0.932	-0.935	0.316	1.365
SJFMi	0.802	-0.597	0.483	-0.156	-0.162
SJFMr	0.835	-0.934	0.962	1.166	-0.585
SJRDi	-1.687	-0.810	1.001	<i>0.785</i>	-1.213
SJSMi	-1.555	0.122	-0.826	-1.369	-1.508
SKPFGi	0.873	-1.164	-2.783	0.331	-0.749
SKPFgr	0.603	0.998	0.114	1.041	-0.468
SKPFRr	0.837	<i>0.766</i>	0.589	1.156	-0.448
SKPFri	<i>0.797</i>	0.812	0.597	-1.221	-0.667
SKMKi	-0.424	-1.299	0.409	-0.533	1.226

Significant values are in bold type face.

Values in Italic indicate moderately significant loadings.

Similarly, for the liquid samples, PC 1 accounts for 20.1 % and is positively and largely contributed by Cd, Zn and Fe. PC 2 makes up 17.7 % of total variance and is positively and largely contributed by Al, Mn and Ca while PC 5 which accounts for 11.1% of variance is contributed largely by K-40 and Cr.

For the solid fertilizer samples, the significant scores for PC1 are observed in SMAPr, SJFMi, SJFMr, SKPFGi, SKPFRr and SKPFRr (Table 4.4), indicating that elements Al, Mn, Ca and K are significant in these samples. Significant scores for PC 2 are seen in SKPFGr, SKPFRr, SMAPr, SKPFri, SFHK, SFHMi AND SFHMr, indicating that Ca, Na and K-40 are significant in these samples and so on.

Table 4.5: Rotated component matrix of 5 factor model explaining 80.1% of the total variance for liquid fertilizers

Variable log-transformed	COMPONENT(LIQUIDS)					CUMMUNALITIES
	PC 1	PC 2	PC 3	PC 4	PC 5	
Cu	0.393	-0.233	0.153	0.353	-0.277	0.433
Cd	0.872	-0.128	-0.177	0.148	0.172	0.859
Zn	0.909	-0.048	0.005	-0.004	0.016	0.83
Cr	0.244	-0.041	-0.212	-0.053	0.839	0.813
Fe	0.869	-0.028	-0.118	0.296	0.164	0.885
Br	0.308	0.112	0.03	0.695	-0.179	0.624
Na	-0.011	0.058	-0.192	0.89	0.034	0.833
Al	0.001	0.886	-0.008	0.06	0.363	0.921
Mn	-0.152	0.805	0.222	0.167	-0.284	0.829
Ca	-0.094	0.938	0.199	-0.048	-0.071	0.936
K	0.327	-0.011	0.214	0.622	0.369	0.675
U	-0.067	0.075	0.903	-0.123	-0.267	0.912
Th	-0.078	0.235	0.879	0	-0.016	0.833
K40	-0.102	0.11	0.595	0.438	0.509	0.828
Eigenvalues	2.812	2.477	2.228	2.139	1.555	
% of variance	20.084	17.695	15.912	15.277	11.11	
Cumulative %	20.084	37.778	53.69	68.967	80.077	

Significant values are in bold type face.

Values in Italic indicate significant negative loadings.

Table 4.6: Varimax rotation factor scores for 5 factor model for the analyzed liquid fertilizers

SAMPLE ID	VF 1	VF 2	VF 3	VF 4	VF 5
SKMSi	0.268	0.830	-0.109	0.658	3.649
SCSII	0.256	0.860	0.470	-0.569	-0.183
SCSIII	-0.378	-1.946	0.321	0.827	0.900
SBBXi	0.861	0.459	1.342	1.596	-0.646
SBBXr	0.612	0.589	0.338	2.052	-0.638
SGAi	-3.221	0.067	1.032	0.335	0.368
SGAr	-0.005	-0.181	1.505	-0.952	0.974
SKFDi	-0.601	0.638	-1.833	0.903	0.679
SFGHr	1.257	-1.853	0.698	-0.454	0.568
SADGi	-0.267	0.160	-0.812	0.510	-0.105
SEMPr	0.351	0.368	1.018	-0.683	-0.995
SEMPIbi	-0.076	0.661	1.016	-1.188	-0.813
SIPM	-0.425	-1.513	-1.035	-0.701	-0.322
SLAPr	-0.316	0.542	-1.466	-0.410	-0.581
SKMBi	0.659	1.465	0.305	0.307	-1.144
SKMBr	0.633	-1.522	-0.012	-1.231	0.456
SHSBi	0.827	0.876	-0.494	0.217	-0.429
SHSBr	0.879	0.865	0.567	-0.177	0.615
SKAMi	1.129	0.534	-0.982	-0.899	-0.106
SKPKi	0.046	0.499	-1.205	-1.432	0.952
SKFSi	-0.024	-1.376	-1.451	0.873	-1.145
SEP	-2.651	0.533	0.304	-0.838	-0.682
SDGGi	0.378	0.052	0.526	-1.634	-0.446
SFTCi	-0.172	0.415	-1.498	0.660	-0.168
SFTCr	0.126	-1.803	0.105	0.692	-0.996
SCSI	-0.145	-0.221	1.350	1.537	0.238

Significant values are in bold type face.

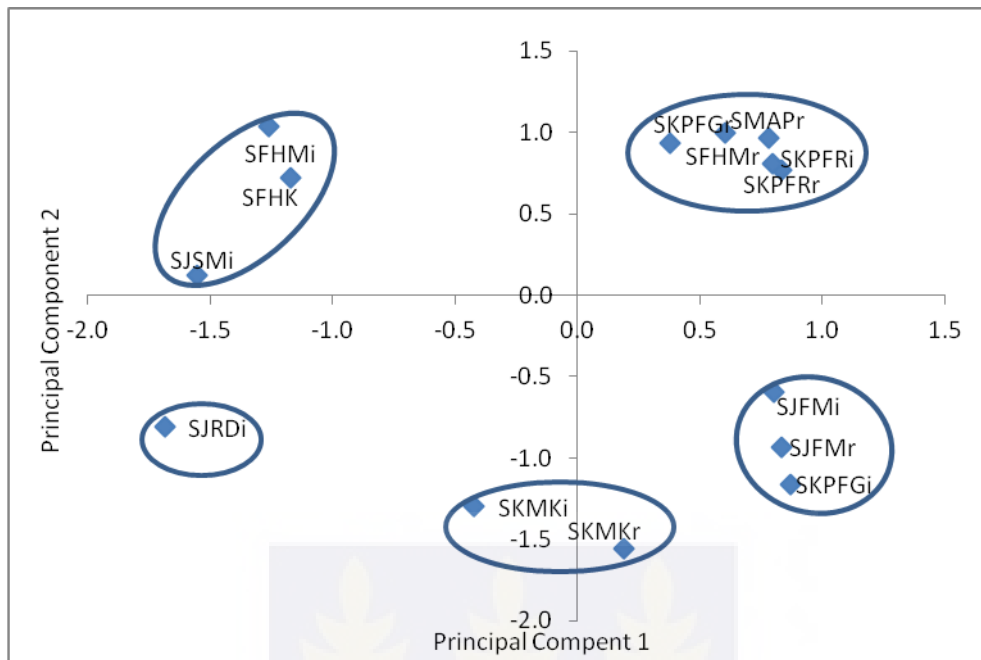
In the case of the liquid fertilizer samples, PC 1 has significant scores in sample SBBXi, SFGHr, SHSBi, SHSBr and SKAMi, suggesting that Cd, Zn and Fe are significant in these samples. PC 2 has significant scores in sample SKMSi, SCSII, SKMBi and SHSBr which have U, Th and K-40 being significant in them.

The first three VFs for both solid and liquid fertilizers have been plotted to further establish the special relationship between analyzed samples and their variables. This further gives an indication of how the measured variables have influenced the sample variability. The variable groupings are also explored further in plots of the first three principal components generated.

Fig. 4.11 shows a plot of the first three Varimax factors for solid samples and indicates for the various groupings ; SKMKi and SKMKr group together, SFHMi, SFHMr and SJSMi are clustered together; SJFMi, SJFMr and SKPFGi also move closely together whereas SJRDi is more of an outlier. There is a lot of similarity between the first and second graphs but for SKPGi which also dissociates from the group and samples SKMKr, SKMKi, SMAPr, SJFMr, SKPFRi, SKPFGr and SFHMr which cluster together. This indicates that these samples have some similarities in terms of their source or constituents.

Fig. 4.12 indicates plots that are similar to the cluster groupings in the cluster analysis. Parameters with high affinities among themselves group as; Zn, Cd, Fe, Th and Cu cluster together; Al, Mn and Ca cluster together; U, Cr, K-40, Na and Br also cluster together while K does not cluster with any of the parameters. However U in the second plot clustered with Th, K-40, Na and K-40 instead of Zn, Cd, Fe and Cu.

(A)



(B)

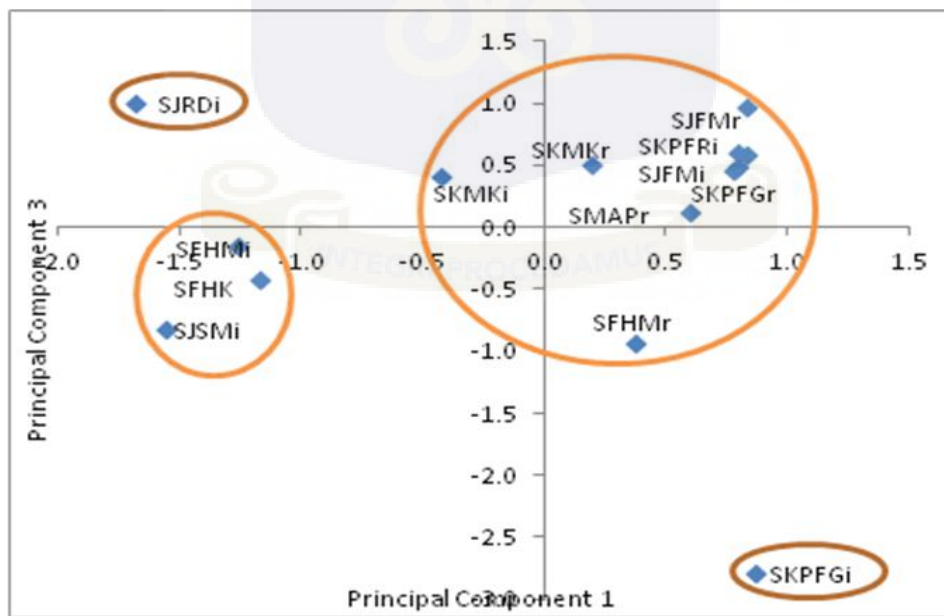
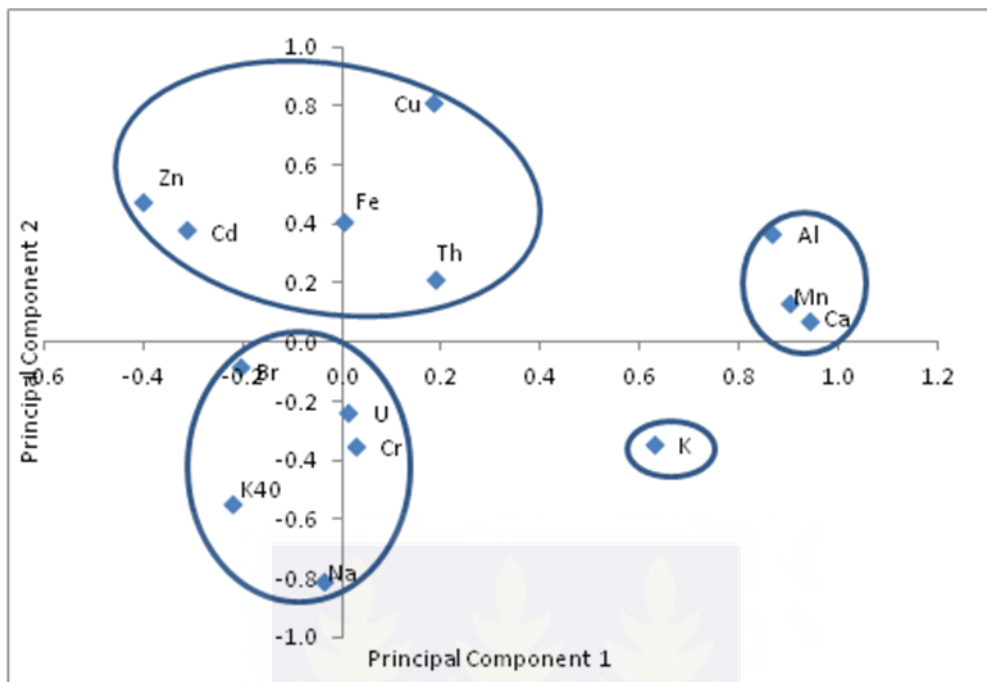


Fig.4.11 PC 1 against PC 2 in (A) and PC 1 against PC 3 in (B) for solid samples

(A)



(B)

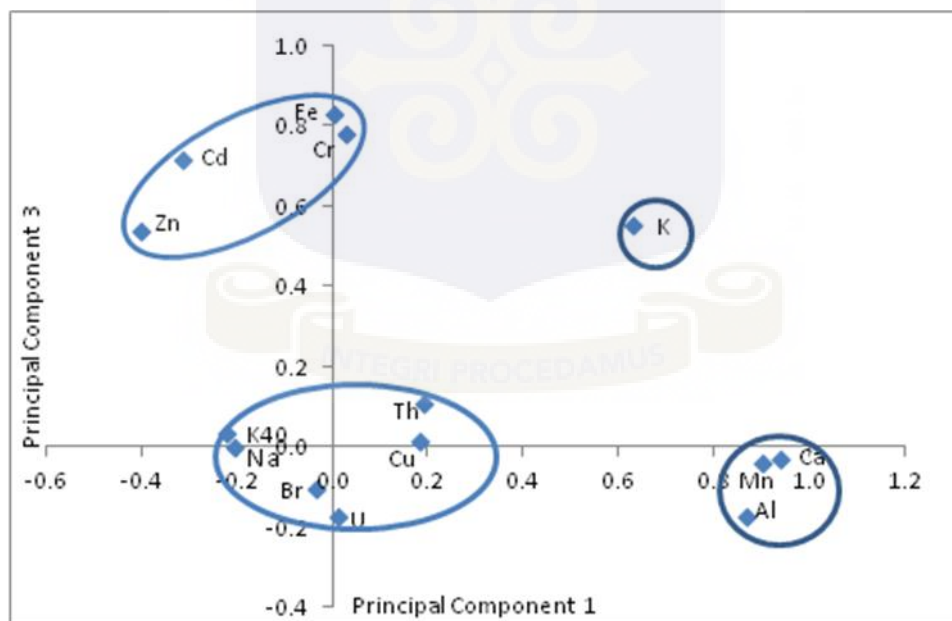
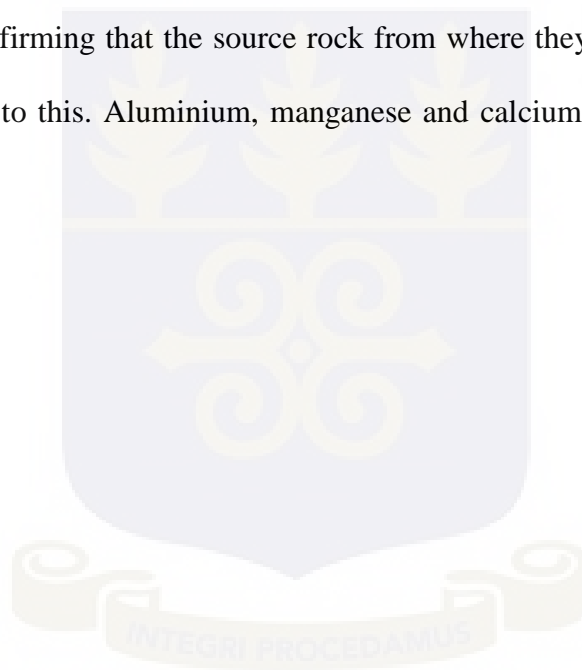


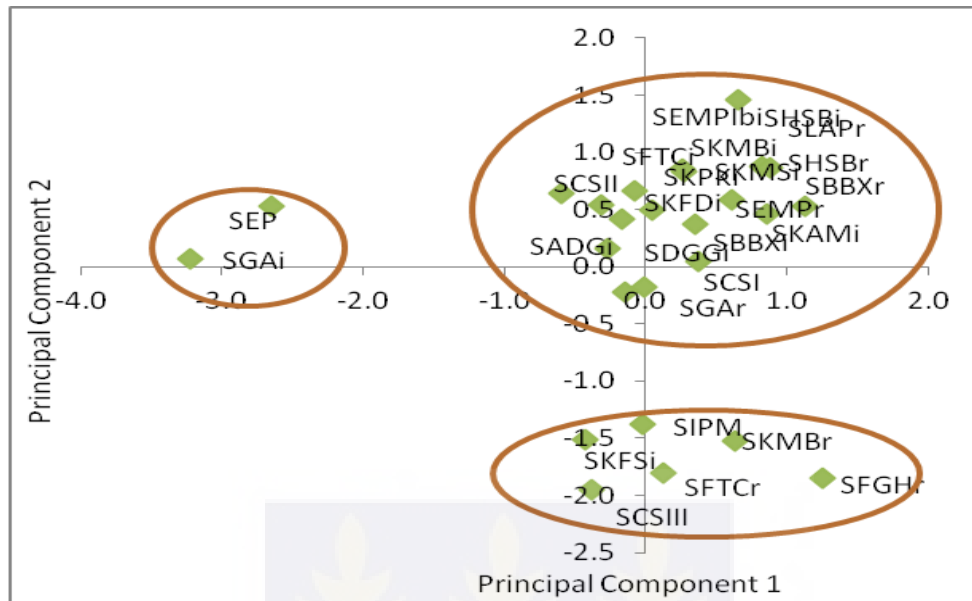
Fig. 4.12 PC 1 against PC2 in (A) and PC 1 against PC 3 in (B) for solid sample variables

Fig. 4.13 shows the plot of the first three varimax factors for the liquid fertilizers. The groupings are as follows; SEP and SGAI; SEMPIbi, SCSII, SADGi, SDGGi, SCSi, SGAr, SBBXr, SKAMi, SHSBr, SLAPr, SHSbi,SKFDi and SKMBi; SIPM, SKMBr, SKFSi, SFTCr, SCSIII and SFGHr. The second plot (Fig.4.13B) indicates a general affinity among samples as seen in Fig. 4.13B except for SLAP and SKFDi.

For the liquid sample parameters, the plots in Fig. 4.14 shows a greater affinity between Fe, Cd and Zn for both plots confirming their common origin. The natural radioactive materials also group together confirming that the source rock from where they have been mined from could have contributed to this. Aluminium, manganese and calcium also group together for both plots.



(A)



(B)

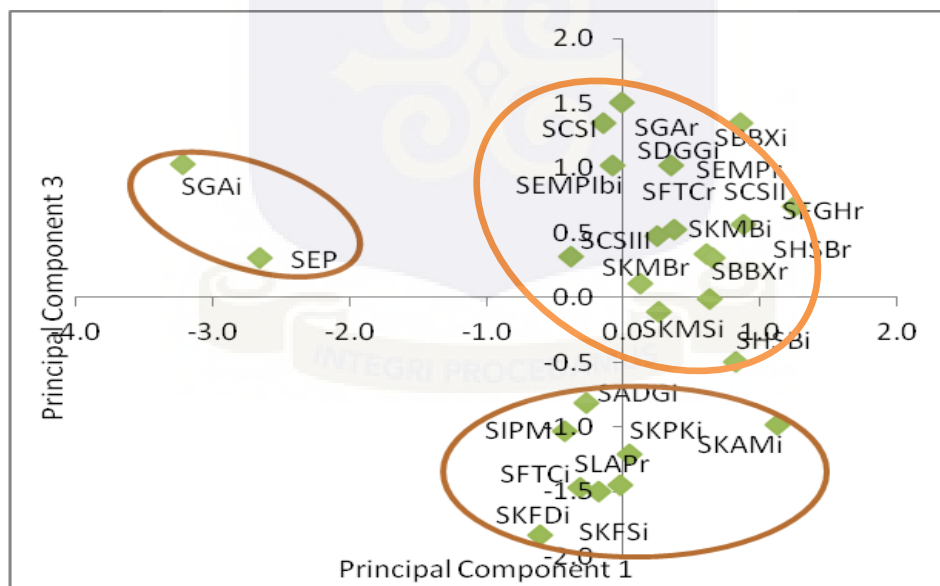
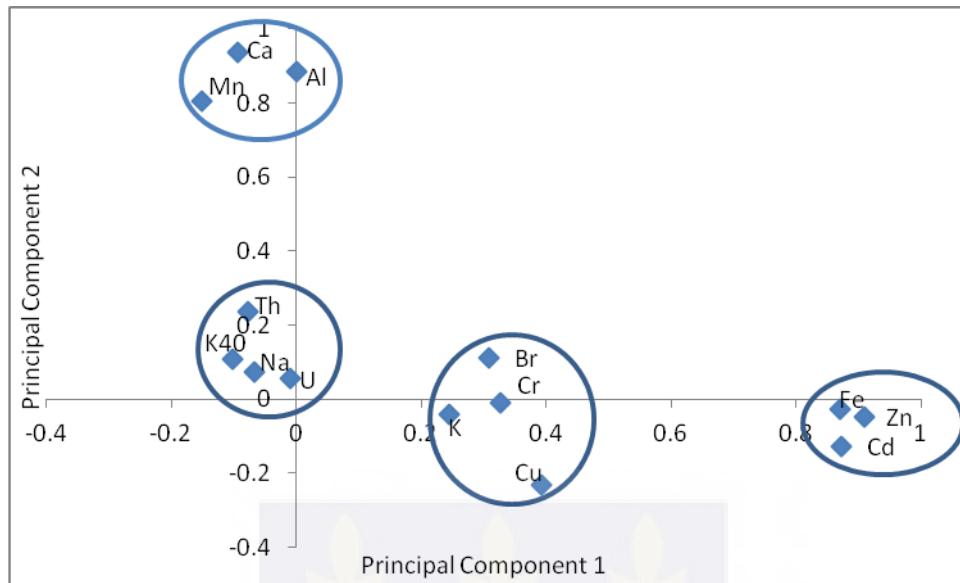


Fig. 4.13 PC 1 against PC 2 in (A) and PC 1 against PC 3 in (B) for liquid samples

(A)



(B)

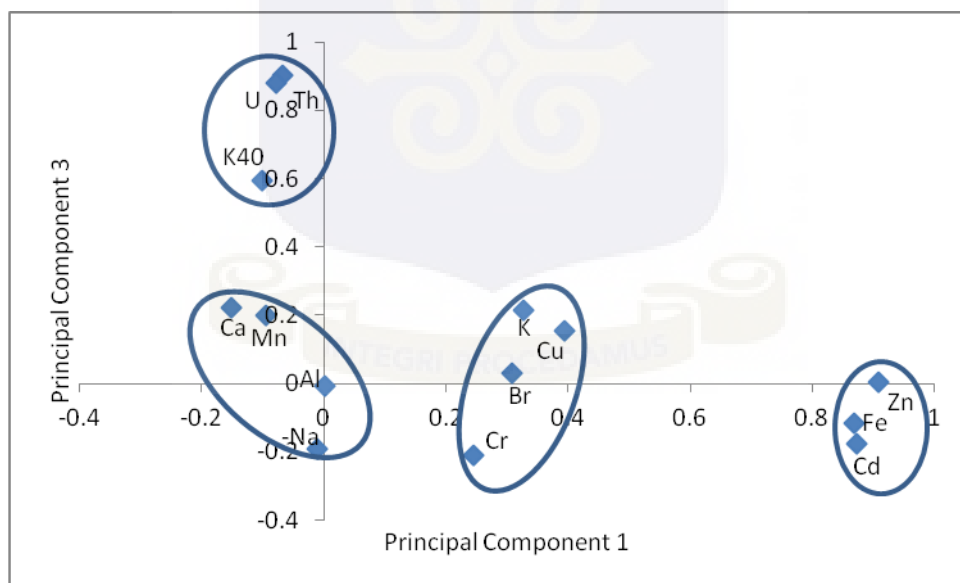


Figure 4.14 PC 1 against PC 2 in (A) and PC 1 against PC 3(B) for liquid sample variables

4.2.3 Pearson Correlation

Liquid Fertilizer Samples

The Pearson's correlation coefficient matrix for analyzed fertilizer parameters are displayed in Table 4.7. The relationships between the parameters have been further confirmed by the correlations. The correlations exhibited by the parameters in the liquid fertilizers generally agree with that shown by both the CA and PCA. According to the values of the Pearson correlation coefficients, a strong positive significant correlation ($p < 0.01$) exists between Cd vs. Zn ($r = 0.746$, $p < 0.01$), Fe vs. Zn ($r = 0.748$, $p < 0.01$), Cd vs. Fe ($r = 0.802$, $p < 0.01$). These named associations with very correlations are confirmed both by the CA and PCA. Other strong positive significant correlations that exhibit very affinities are Na vs. Br ($r = 0.51$, $p < 0.01$), Al vs. Mn ($r = 0.542$, $p < 0.01$) and Th vs. U ($r = 0.769$, $p < 0.01$).

Other parameters also exhibited a weak positive correlation namely; K40 vs. Th ($r = 0.486$, $p < 0.05$), K vs. K40 ($r = 0.426$, $p < 0.05$), Na vs. K ($r = 0.483$, $p < 0.05$), Fe vs. K ($r = 0.465$, $p < 0.05$) and Br vs. Fe ($r = 0.4260$, $p < 0.05$). These weak correlations are also supported in the CA and PCA as most of the parameter like Br and Fe, Cd and K, Fe and K and Na and K, do not display strong affinities in either CA nor PCA as well.

Table 4.7: Pearson's correlation matrix among studied liquid fertilizer samples

	Cu	Cd	Zn	Cr	Fe	Br	Na	Al	Mn	Ca	K	U	Th	K40
Cu	1													
Cd	0.324	1												
Zn	0.214	0.746**	1											
Cr	-0.043	0.298	0.214	1										
Fe	0.384	0.802**	0.748**	0.409*	1									
Br	0.161	0.275	0.329	-0.118	0.426*	1								
Na	0.186	0.143	0.06	0.041	0.292	0.510**	1							
Al	-0.235	-0.041	-0.049	0.232	0.032	0.128	0.072	1						
Mn	0.036	-0.34	-0.216	-0.256	-0.114	0.136	0.141	0.542**	1					
Ca	-0.169	-0.21	-0.155	-0.193	-0.199	-0.036	-0.011	0.800**	0.794**	1				
K	0.27	0.459*	0.23	0.227	.465*	0.334	.483*	0.137	-0.043	0.039	1			
U	0.116	-0.314	-0.092	-0.384	-0.22	-0.019	-0.275	-0.048	0.33	0.289	0.029	1		
Th	-0.092	-0.264	-0.017	-0.224	-0.173	0.081	-0.065	0.172	0.364	0.381	0.097	0.769**	1	
K40	0.095	-0.028	-0.064	0.197	0.034	0.24	0.242	0.333	0.183	0.145	0.428*	0.311	0.486*	1

*Correlation is significant at 0.05 level

**Correlation is significant at 0.01 level

Solid Fertilizer Samples

The Pearson's correlation coefficient matrix for analyzed solid sample parameters are displayed in Table 4.8. The relationships between the parameters have been further confirmed by the correlations and new associations have also been revealed. The correlations exhibited by the parameters in the solid fertilizers generally agree with that shown by both the CA and PCA. According to the values of the Pearson correlation coefficients, a strong positive significant correlation ($p < 0.01$) exists between Cd vs. Zn ($r = 0.81$, $p < 0.01$), Fe vs Cd ($r = 0.874$, $p < 0.01$), Fe vs. Zn ($r = 0.707$, $p < 0.01$), Na vs. Cu ($r = 0.695$, $p < 0.01$), Ca vs. Al ($r = 0.861$, $p < 0.010$) and Th vs. U ($r = 0.767$, $p < 0.01$). These strong affinities among the parameters all confirms except for Na and Cu which indicates a potential relationship between the two elements. Weak positive significant correlations exists among K vs. Cr ($r = 0.555$, $p < 0.05$), a phenomenon confirmed by the PCA.

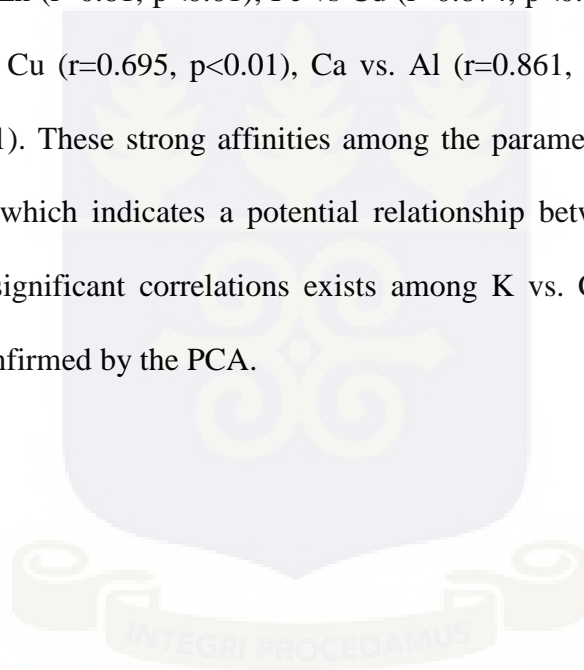


Table 4.8: Pearson's correlation matrix among studied solid fertilizer samples

	Cu	Cd	Zn	Cr	Fe	Br	Na	Al	Mn	Ca	K	U	Th	K40
Cu	1													
Cd	0.343	1												
Zn	0.465	0.810**	1											
Cr	-0.276	0.473	0.409	1										
Fe	0.344	0.874**	0.707**	0.39	1									
Br	0.043	0.223	0.264	0.205	-0.15	1								
Na	-.695**	-0.168	-0.303	-0.002	-0.429	0.267	1							
Al	0.42	-0.19	-0.211	-0.355	-0.041	-0.311	-0.378	1						
Mn	0.172	-0.231	-0.323	-0.343	0.049	-0.457	-0.335	0.880**	1					
Ca	0.179	-0.174	-0.247	-0.224	-0.023	-0.219	-0.171	0.861**	0.843**	1				
K	-0.305	0.176	0.067	.555*	0.194	0.154	0.087	0.282	0.428	0.474	1			
U	-0.273	-0.343	-0.062	0.041	-0.327	-0.182	0.121	0.07	-0.049	0.145	-0.027	1		
Th	0.09	-0.064	0.139	0.066	0.15	-0.533	-0.35	0.363	0.242	0.322	-0.01	0.767**	1	
K40	-0.395	-0.017	0.032	0.095	-0.227	0.019	0.445	-0.303	-0.273	-0.18	0.023	0.374	0.026	1

*Correlation is significant at 0.05 level

**Correlation is significant at 0.01 level

CHAPTER 5

DISCUSSION

5.1. Minimum guarantee of nutrients other than Nitrogen, Phosphorus and Potassium

For this particular discussion, results obtained from the analysis in milligram per kilogram (mg/kg) or milligram per litre (mg/l) for selected essential elements were converted to percentages (%) since elemental concentrations in commercial fertilizers are declared in percentages. This was done in order to determine whether trace nutrients analyzed satisfied conditions of Section 93 (1 –3) of the Plants and Fertilizer Act, 2010 (Act 803), which stipulates the minimum concentrations in percentage (%), where other plant nutrients are guaranteed in addition to nitrogen, phosphorus and potassium. Hence, the objective was to find out whether these essential elements met the minimum standards for addition to the fertilizers. Results obtained are converted to percentages using the formula;

$$(\%) \text{ Elemental conc.} = \frac{\text{Calculated concentration (mg/kg)}}{10,000} \quad (5.1)$$

Table 5.1 shows details of the minimum nutrient concentrations that can be guaranteed in percentage according to Section 93 (1 –3) of the Plants and Fertilizer Act, 2010 (Act 803). The results obtained for each element [in percentage using the expression (5.1)] are compared with the minimum percentage that may be guaranteed according to the Plants and Fertilizer Act, 2010 (Act 803), and presented in Figures 5.1 to 5.6. The minimum guaranteed level for each element is highlighted.

Table 5.1 Minimum Guarantee for fertilizers(Plants and Fertilizer Act, 2010-Act 803)

Element	Percent (%)
Calcium (Ca)	1.0000
Magnesium (Mg)	0.5000
Sulfur (S)	1.0000
Boron (B)	0.0200
Chlorine (Cl)	0.1000
Cobalt (Co)	0.0005
Copper (Cu)	0.0500
Iron (Fe)	0.1000
Manganese (Mn)	0.0500
Molybdenum (Mo)	0.0005
Sodium (Na)	0.1000
Zinc (Zn)	0.0500

Fourteen (14) samples had values above the minimum guaranteed level of 0.1 % for sodium (Na) (Fig. 5.1). It can be inferred from the results generated from the analysis that only two products (SFTCi and SFTCr), out of the forty products had values above the minimum required concentrations for copper (Cu) (Fig. 5.2). Only one sample had a value above the minimum guarantee level for calcium (Ca) (Fig. 5.3). Five products had their Mn content above the minimum guaranteed level of 0.05 % (Fig. 5.4). For chlorine, seven samples had their results greater than the guaranteed level (Fig. 5.5).

None of the products analyzed had their zinc concentrations above minimum the required percentage mark; all the various types of fertilizers fell short of the required minimum concentration of 0.05 %. Only one product registered an acceptable level of minimum required percentage for cobalt (Co). No product met the minimum percentage mark for iron (Fe). Only few samples have their concentrations above the minimum guaranteed level 1.0 % (Fig. 5.6).

This signifies a shortfall even amongst the fertilizer products which guaranteed their products to have these nutrients in them.

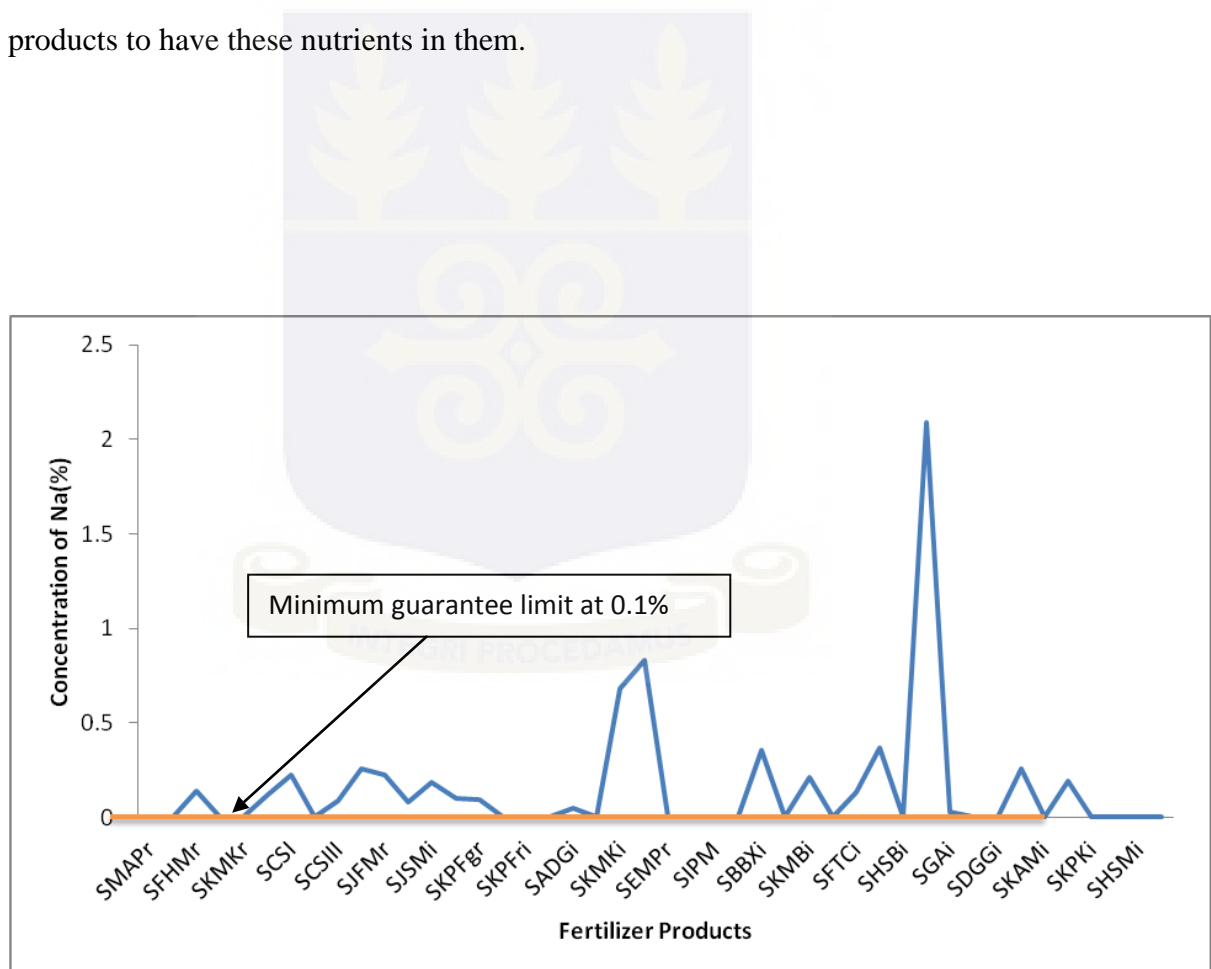


Fig 5.1 Graph showing the calculated concentration (%) of Na in relation to the minimum guaranteed.

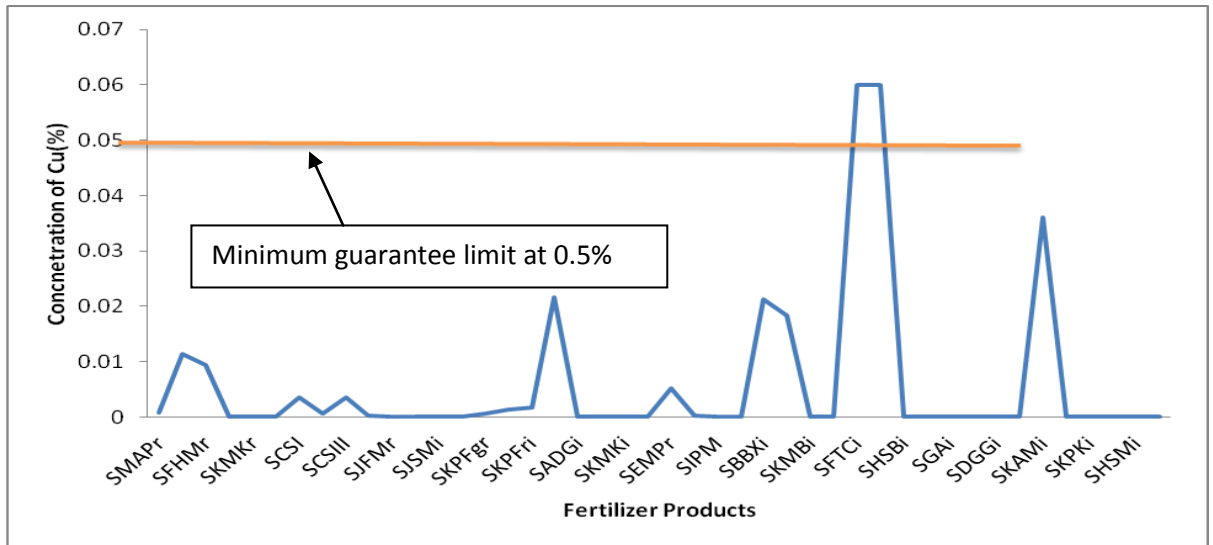


Fig 5.2 Graph showing the calculated concentration (%) of Cu in relation to the minimum guaranteed.

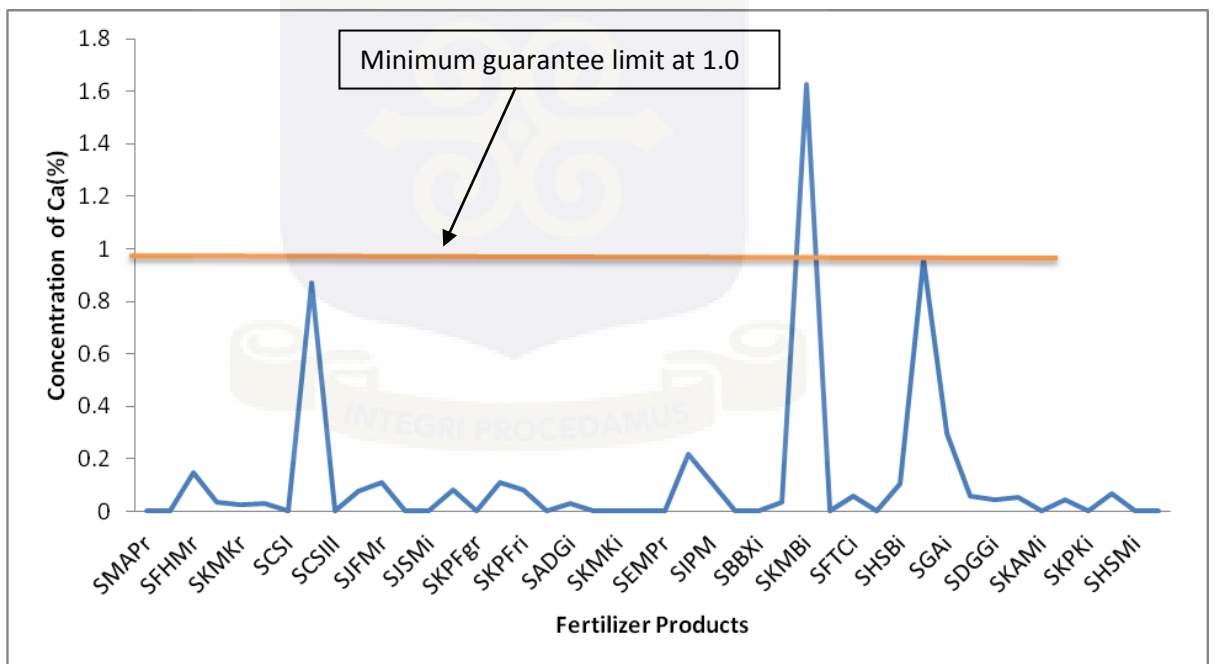


Fig 5.3 Graph showing the calculated concentration (%) of Ca in relation to the minimum guaranteed.

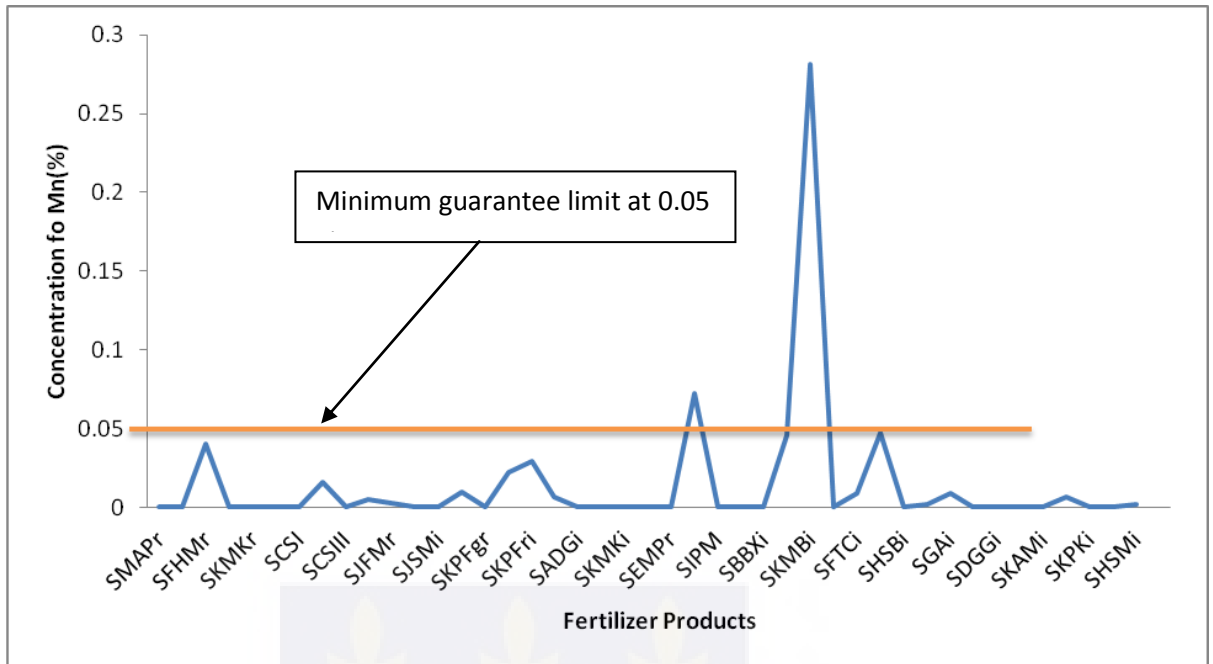


Fig 5.4 Graph showing the calculated concentration (%) of Mn in relation to the minimum guaranteed.

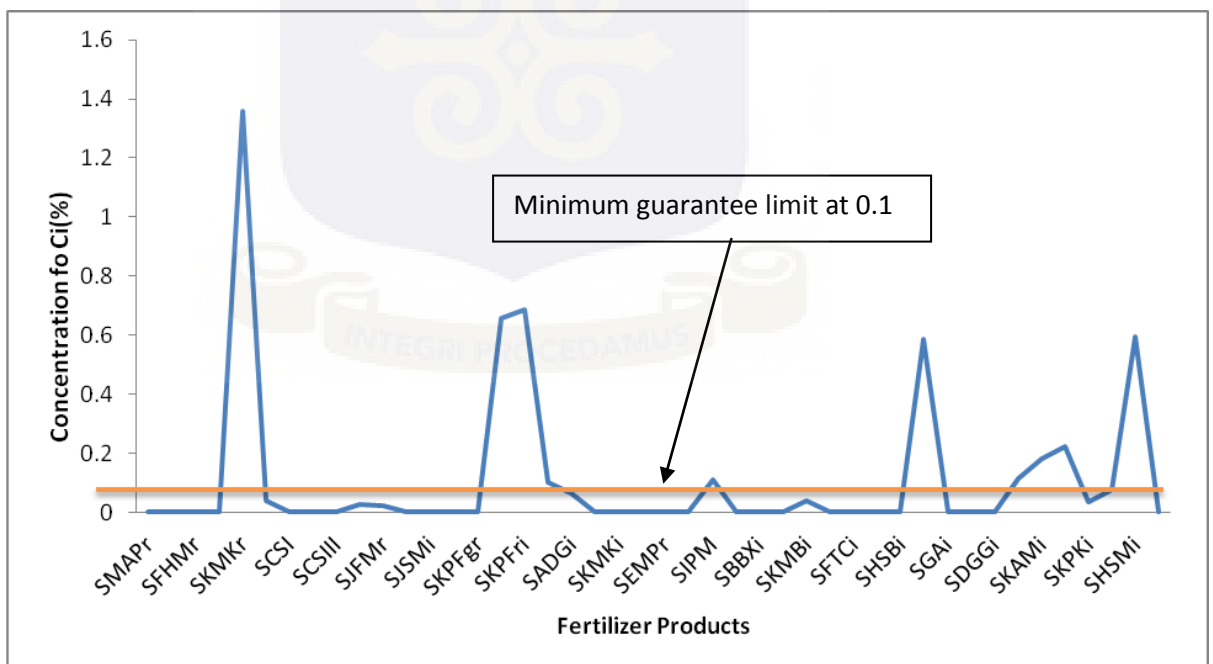


Fig 5.5 Graph showing the calculated concentration (%) of Cl in relation to the minimum guaranteed.

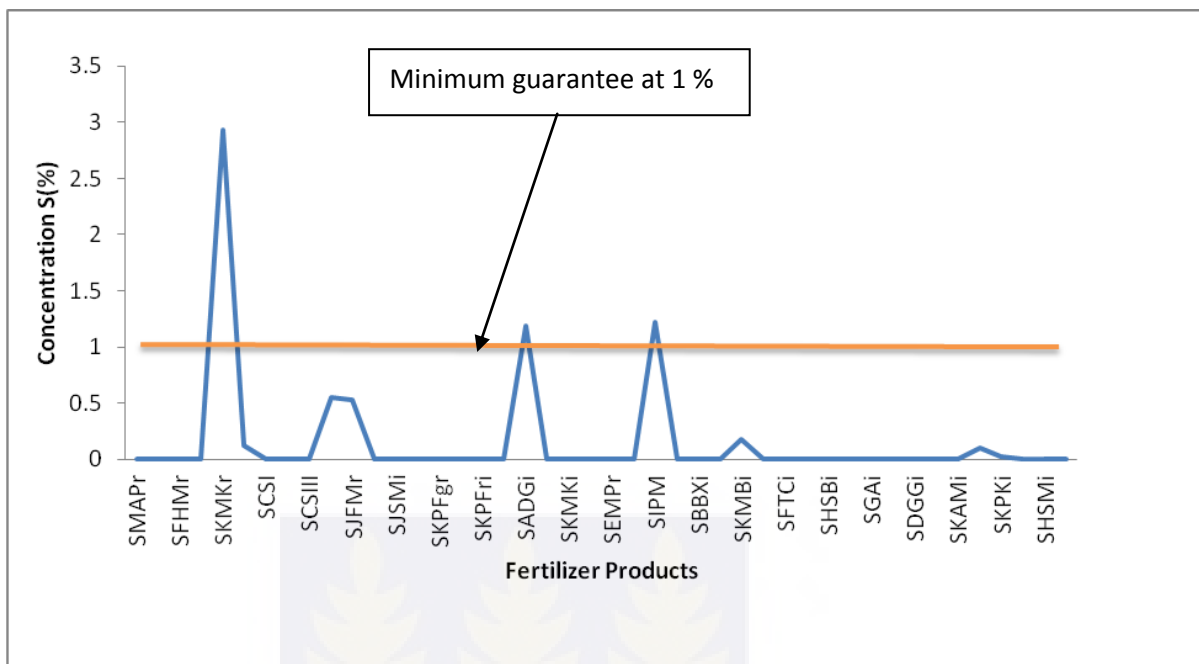


Fig 5.6 Graph showing the calculated concentration (%) of S in relation to the minimum guaranteed.

5.2 Contamination of Fertilizers by Trace Elements and NORMs

5.2.1 Trace Elements

Fertilizers contain both essential and non-essential elements. Trace elements which may be needed in minute quantities (micronutrients) can be toxic if their levels become elevated in the fertilizers. On the other hand, there are elements which are classified as toxins in the fertilizers such as As, Hg, Cd and Pb. All these elements should conform to safety limits determined.

In order to assess the toxicity or otherwise of these fertilizers, comparison was made with both local and international standards. The following standards were used in this study.

Washington State Regulatory Standard for Trace Elements in Fertilizers

Washington State Regulatory Standard on acceptable annual addition of elements to the soil is based on a combination of fertilizer contents and application rates. In order to determine whether a fertilizer is up to standard, concentration value (mgkg^{-1}) was divided by a factor of 1.0×10^6 , and then multiplied by the maximum number of applications per year and maximum application amount.

$$\frac{\text{Concentration}(\text{ppm})}{1,000,000} \times \text{application rate per year} \quad (5.2)$$

The results should not exceed the values assigned for the elements in Table 4.2. Therefore, the assumption made in computing the standard is by using a higher application rate of 200 kg ha^{-1} of fertilizer two times a year (depending on crop type, soil type or agronomic practices). From the formula above, As, Cd and Co would constitute 0.0252 , 0.01 and 0.256 kg ha^{-1} respectively, considering the highest concentrations among each of the fertilizer samples analyzed. All the concentrations fall short of the maximum allowable level under the Washington State Standards.

Table 5.2: Washington State standards for some heavy metals in fertilizers

Elements	As	Cd	Co	Hg	Se
Maximum Allowable Level	0.359	0.096	0.719	0.023	0.067

Canadian and Hungary Standards for Trace Elements in Fertilizers

The results obtained were also compared with standards from Canada and Hungary. The levels of trace elements in the fertilizer samples analyzed were found to be lower than the standards set by Hungarian and Canadian Regulators (Table 4.3), except for Cu and Cd. Cadmium concentrations for the NPK and NPK+ samples were generally at par or higher than these standard values of 3.0 and 4.0 for Hungarian fertilizers and Canadian compost respectively. This could be as a result of their transfer from the potassium and phosphate bearing rocks from which they are mined and produced from. However, the other toxic trace elements are within range comparatively, indicating that the non-traditional fertilizers analyzed are generally safe for use according to the standards.

Table 5.3 Limiting concentrations of trace elements in Hungarian fertilizers and Canadian compost (mg kg⁻¹)

Elements/conc.	As	Cd	Co	Cr	Cu	Hg	Se
Hungarian Fertilizers	10.0	4.0	50.0	100.0	-	1.0	-
Canadian Compost	13.0	3.0	34.0	210.0	100.0	0.8	2.0

SUIP #25 for Fertilizer Regulation of Trace Elements

SUIP 25 is a software program widely used to calculate the allowable trace metal concentrations for the fertilizers with guaranteed P_2O_5 and/or selected micronutrients contents. The software is, however, based on the content of P_2O_5 and/or selected micronutrients and hence fertilizer samples which did not contain either of these elements could not be evaluated. Concentrations of the oxide and micronutrients are inputted into special columns of software which then generate an estimated allowable heavy metal that can be in that particular fertilizer. The software has been adopted locally in the Fertilizer Regulations thereby binding the local fertilizer industry in Ghana in terms of heavy metals allowance by Regulators.

Upon evaluation using this software, the analyzed samples were found to be generally safe for use since the concentrations derived are within the levels from the software (Table 5.4). However, the limitation to this model is that it is not able to compute for samples that do not contain Phosphorus (P_2O_5) or declared micronutrients, hence making comparison of results from such fertilizers impossible.

Table 5.4: Permissible Trace Element Limit (ppm) in Fertilizer Samples using SUIP #25 for Fertilizer Regulation in Ghana

SAMPLE CODE	As ^s	As*	Cd ^s	Cd*	Co ^s	Co*	Pb ^s	Pb*	Hg ^s	Hg*	Ni ^s	Ni*	Zn ^s	Zn*
SMAPr	195	0.16	150	3.96	2050	BDL	915	2.36	10	BDL	2300	7.84	2345	8.48
SFHM_i	130	0.08	100	3.64	324	BDL	610	4.12	10	BDL	2,500	BDL	354	21.8
SFHM_r	130	BDL	100	3.56	324	BDL	610	0.48	10	BDL	2,500	BDL	354	20.72
SKMK_i	78	BDL	60	2.76	816	2.96	366	BDL	6	BDL	4566	0.44	254	15.72
SKMK_r	78	0.12	60	3.68	816	0.84	366	1.84	6	BDL	4566	BDL	254	6.2
SKMS_i	271	0.56	209	4.12	2,842	1.16	1274	3.76	20	BDL	5225	BDL	8778	23
SCS_{II}	78	BDL	60	3.00	816	BDL	366	2.12	6	BDL	1,500	BDL	2,520	6.0
SCS_{III}	130	0.08	100	3.00	1,360	1.00	610	0.76	10	BDL	2,500	BDL	4,200	4.64
SBBX_i	260	0.52	200	1.92	2,720	BDL	1,220	BDL	20	BDL	5,000	0.36	8,400	30.88
SBBX_r	260	0.36	200	3.16	2,720	BDL	1,220	1.56	20	BDL	5,000	BDL	8,400	18.48
SGA_i	112	BDL	83	BDL	2,228	BDL	488	BDL	8	BDL	2,000	BDL	n/a	BDL
SGAR	112	BDL	83	2.44	2,228	BDL	488	2.28	8	BDL	2,000	BDL	n/a	12.52
SKFD_i	n/a	0.12	n/a	2.08	n/a	BDL	n/a	3.16	n/a	BDL	n/a	BDL	n/a	3.88
SJFM_i	78	BDL	60	2.84	816	0.84	366	BDL	6	BDL	1,500	BDL	2,520	10.8
SJFM_r	78	BDL	60	4.28	816	BDL	366	BDL	6	BDL	1,500	1.32	2,520	6.16
SJRD_i	650	BDL	500	3.08	6,800	BDL	3,050	BDL	50	BDL	12,500	4.16	21,00	21.08
SJSM_i	260	BDL	200	3.44	2,720	BDL	1,220	0.72	20	BDL	5,000	BDL	432	4.6
SKPF_{Gi}	130	0.2	100	BDL	2,228	BDL	610	BDL	10	BDL	2,500	BDL	4,200	BDL
SKPF_{Gr}	130	0.24	100	2.28	2,228	BDL	610	2.76	10	BDL	2,500	0.8	4,200	18.72

n/a- sample does not contain Phosphorus(P₂O₅) or micronutrients.

*-Concentration determined from this study.

^s- Concentration determined by SUIP# 25 Software

Table 5.4 cont'd

SAMPLE CODE	As ^s	As*	Cd ^s	Cd*	Co ^s	Co*	Pb ^s	Pb*	Hg ^s	Hg*	Ni ^s	Ni*	Zn ^s	Zn*
SKPFRr	247	0.12	190	4	2,548	BDL	1,159	3.36	19	BDL	4,750	0.28	7,980	11.92
SKPFri	247	0.24	190	3.84	2,548	2.12	1,159	BDL	19	BDL	4,750	0.52	7,980	9.88
SFGHr	234	BDL	180	2.88	2,448	42.6	1,098	0.72	18	BDL	4,500	BDL	7,560	48
SADGi	112	BDL	83	2.04	2,228	BDL	463	BDL	6	BDL	1,900	BDL	n/a	9.92
SEMPr	112	BDL	83	2.24	2,228	BDL	463	BDL	6	BDL	1,900	BDL	n/a	6.52
SEMPIbi	112	BDL	83	0.96	2,228	BDL	463	1.6	6	BDL	1,900	BDL	n/a	8.92
SIPM	78	BDL	60	1.84	816	BDL	366	BDL	6	BDL	1,500	BDL	2,520	8.92
SLAPr	112	BDL	83	1.16	2,228	BDL	463	BDL	6	BDL	1,900	0.52	2,900	14.8
SHSBi	n/a	BDL	n/a	2.52	n/a	BDL	n/a	BDL	n/a	BDL	n/a	BDL	n/a	37
SHSBr	n/a	0.44	n/a	2.56	n/a	0.76	n/a	0.28	n/a	BDL	n/a	0.28	n/a	31.88
SCSI	234	BDL	180	2.24	2,448	BDL	1,098	1.44	18	BDL	4,500	BDL	7,560	23.64
SKMBi	216	BDL	160	1.76	4,300	BDL	893	BDL	11	BDL	3,667	BDL	n/a	54
SKMBr	216	0.16	160	2.52	4,300	0.36	893	0.84	11	BDL	3,667	BDL	n/a	52
SKFSi	n/a	0.4	n/a	2.48	n/a	BDL	n/a	1.28	n/a	BDL	n/a	1.08	n/a	17.28
SEP	78	BDL	60	BDL	816	BDL	366	BDL	6	BDL	1,500	BDL	2,520	BDL
SDGGi	n/a	BDL	n/a	1.4	n/a	BDL	n/a	0.24	n/a	BDL	n/a	BDL	n/a	40.24
SFTCi	n/a	BDL	n/a	2	n/a	BDL	n/a	0.12	n/a	BDL	n/a	BDL	n/a	6.8
SFTCr	n/a	BDL	n/a	2.32	n/a	BDL	n/a	3.32	n/a	BDL	n/a	BDL	n/a	16.64

n/a- sample does not contain Phosphorus(P₂O₅) or micronutrients.

*- Concentration determined from this study.

^s- Concentration determined by SUT# 25 software

5.2.2 Naturally Occurring Radioactive Materials

The measured activity concentrations of the natural radionuclides ^{238}U , ^{232}Th and ^{40}K are shown in Table 4.1 and 4.2. Samples produced from different sources showed activity concentrations that were lower than the permissible levels for ^{238}U and ^{232}Th of 41.0 Bqkg^{-1} and 52.2 Bqkg^{-1} but higher for ^{40}K at 230 Bqkg^{-1} . The results show that the liquid fertilizers emit a slightly higher radiation than the solids due to ^{238}U and ^{232}Th whilst the solid fertilizers have a much higher radioactivity from ^{40}K . In order to investigate the radiological significance of these concentrations, the concentrations have been compared with the hazard indices (Radium Equivalent, Dose rate, Representative level index) instituted by the United Nations Scientific Committee on Effects of Atomic Radiations and the Nuclear Energy Agency of the Organization of Economic Co-operation and Development (NAE-OECD). The activity concentrations have also been compared with world average values.

Radium Equivalent (Raeq)

The radiation equivalent activity is a weighted sum of activities of the three natural radionuclides ^{238}U , ^{232}Th and ^{40}K based on the estimation that 10 Bq/kg of ^{238}U (^{226}Ra), 7 Bq/kg of ^{232}Th and 130 Bq/kg of ^{40}K produce the same gamma ray dose rate (Beretka and Matthew, 1985). The variations of these ratios may be due to the different origins of the phosphate and potassium ores and/or on the chemical processing of the ore during fertilizer manufacture. The radium equivalent activity was calculated by using the following relation;

$$Raeq = U + (1.43Th) + (0.077K) \quad (5.3)$$

where;

Raeq –Radium equivalent

U – Activity concentration of U-238 (Bq/kg)

Th – Activity concentration of Th-232 (Bq/kg)

K- Activity concentration of K-40 (Bq/kg)

From the data generated from the analysis, the range value of all samples for *Raeq* varied from 7.3 Bq/kg to 1,529 Bq/kg. However, mean values for solid and liquid fertilizers are respectively 681.21 Bq/kg and 116.18 Bq/l. Therefore, the radium equivalent activity for the liquid fertilizers did not exceed 370 Bq/kg, the maximum permissible limit for radiation dose for all samples while that of the solid far exceeds it.

The hazard associated with the use and handling of the solid fertilizers should, therefore, be an issue of great concern. From the radiation point of view, a high content of natural radionuclides in the fertilizer would be significant in the accumulation of radon gas due to the large quantities of chemical fertilizers in the warehouse or storage area.

As shown in Appendix 3, the *Raeq* ranged between 10.41 Bq/kg to as high as 1529.18 Bq/kg. The large variations in *Raeq* can be attributed to the high content of ^{40}K as compared to ^{238}U and ^{232}Th . Most of the fertilizers are NPKs and generally do not have high levels of ^{238}U and ^{232}Th as associated with single superphosphate and triple superphosphate fertilizers due to the production mechanism. The variations in *Raeq* among the analysed solid and liquid fertilizers are presented in Figures 5.7 and

5.8. The minimum value is determined in liquid fertilizer (SKFDi; Fig. 5.8) fertilizer and the maximum was determined in powdered fertilizer (SKMK; Fig. 5.7). The relatively high radium equivalent activities found to exceed 370 Bq/kg, the maximum permissible limit for radiation dose, were found in the powdered samples, due to the relatively high content of ^{40}K .

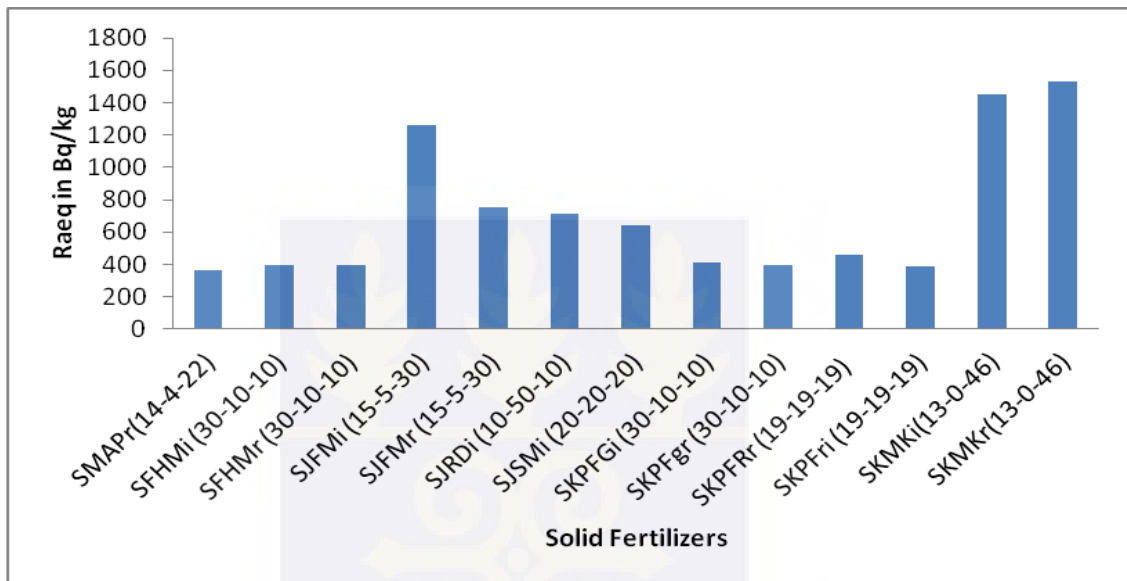


Figure 5.7 Ra_{eq} of Solid Fertilizer Samples

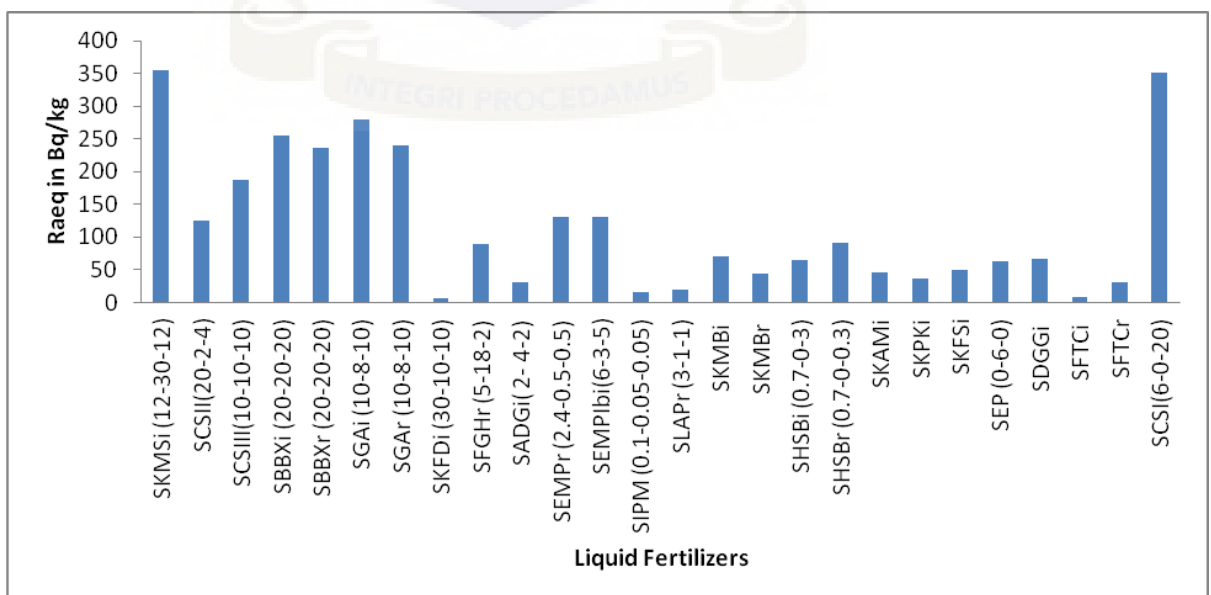


Figure 5.8 Ra_{eq} of Liquid Fertilizer Samples

Dose rate (D)

The average absorbed dose rate in air from terrestrial sources of gamma radiation in soil is estimated as 55 nGy^{-1} . Conversion factors to convert the specific activities A_U , A_{Th} and A_K of U, Th and K respectively, in absorbed dose rate at 1 m above the ground are outlined. The corresponding values relative to different types of fertilizer are calculated using the following relation;

$$D = 0.42C_U + 0.662C_{Th} + 0.043C_K \quad (5.4)$$

where D is the dose rate in nGy^{-1} and C_U , C_{Th} and C_K are the activity concentrations values of uranium, thorium and potassium in Bqkg^{-1} , respectively. The dose rates computed for the solid and liquid fertilizer samples are shown in Figures 5.9 and 5.10, respectively. The absorbed dose rates vary from 7 nGy^{-1} to 1453 nGy^{-1} with 1453 nGy^{-1} being on a higher side due to the exceptionally high K content in SKMK samples. The normal range of the sample would have been 7 nGy^{-1} to 644 nGy^{-1} .

The minimum and maximum absorbed doses were found to vary from 3.47 to 826 nGy/h with an average value of 166.46 nGy/h for all samples; but solid fertilizers range from 195.48 to 826 nGy/h (mean, 366.15 nGy/h) whereas the liquid fertilizers range from 3.47 to 189 nGy/h with a mean of 58.93 nGy/h .

UNSCEAR (2000) gave the absorbed dose a wide range (18–93 nGy/h) with an average value of 59 nGy/h . The results show that the absorbed dose rate for both the solid and liquid fertilizers are much higher than the world average. This gives an

indication that the dose associated with some of the fertilizer samples are much higher than are allowed and may be potentially dangerous upon exposure to them.

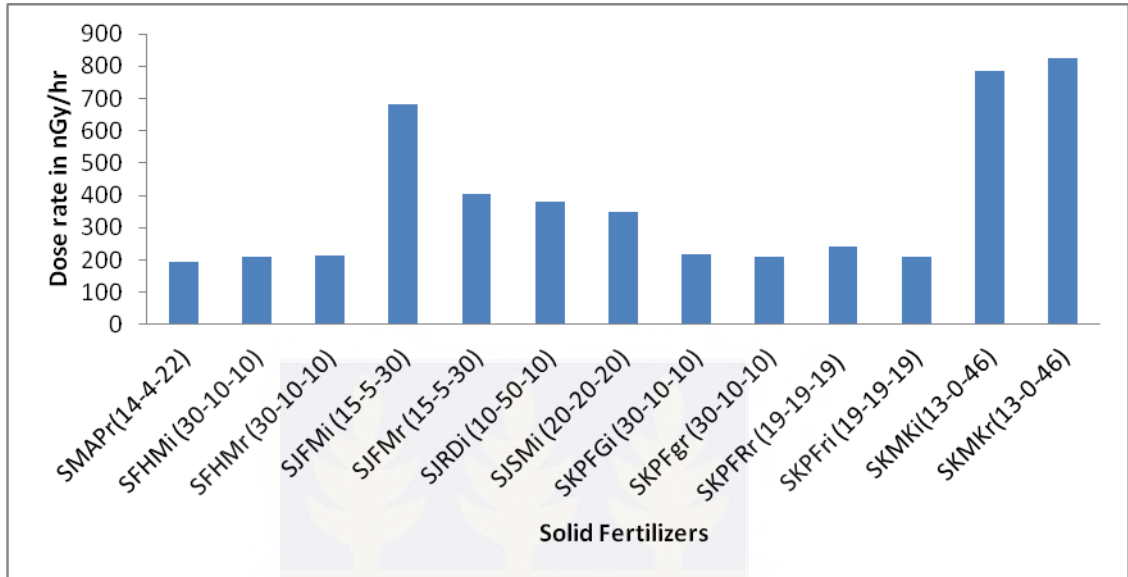


Fig. 5.9 Dose rate of Solid Fertilizer Samples

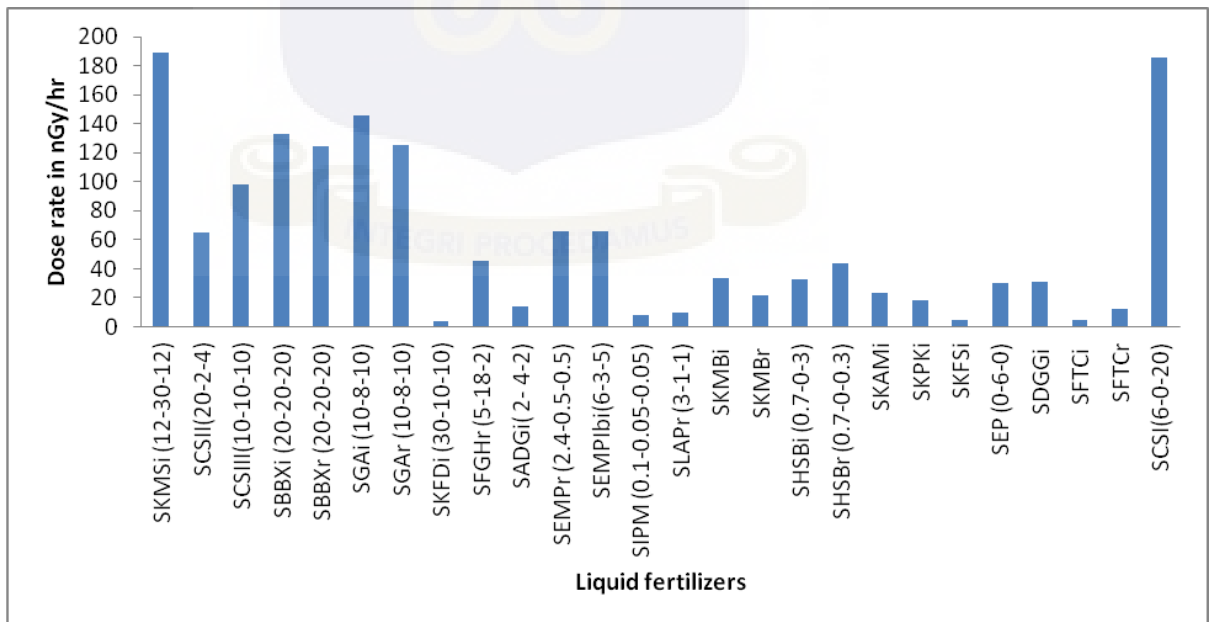


Fig. 5.10 Dose rate of Liquid Fertilizer Samples

Representative Level Index (Iyr)

This index is used in estimating the level of gamma-radiation hazard associated with the exposure to the natural radionuclides in fertilizers. For representative level index (*Iyr*), the maximum suggested value is 1. The value is calculated using the formula derived by the Nuclear Energy Agency of the Organization of Economic Co-operation and Development (NAE-OECD) in 1979;

$$Iyr = \frac{CU}{150} + \frac{CTh}{100} + \frac{CK}{1500} < 1 \quad (5.5)$$

where *CU*, *CTh* and *CK* (in Bq/kg) are the activity concentrations of ²³⁸U, ²³²Th, and ⁴⁰K, respectively. The upper limit for significance used by regulators is unity for this index.

Any value less than 1 shows that the external radiation dose given off is less than the maximum suggested dose. The representative index values obtained from this study range from 0.0043 to 1.01 (Table 5.6). However, only product SKMKi registered a value of 1.01, making its gamma radiation emitted significant. All other fertilizer products (liquid and solid) are within the safe upper limit of unity. Therefore, the non-traditional fertilizers studied are safe except one product (SKMKi) which should be monitored. The variations in the representative level indices with respect to the solid and liquid samples are respectively displayed in Figures 5.11 and 5.12.

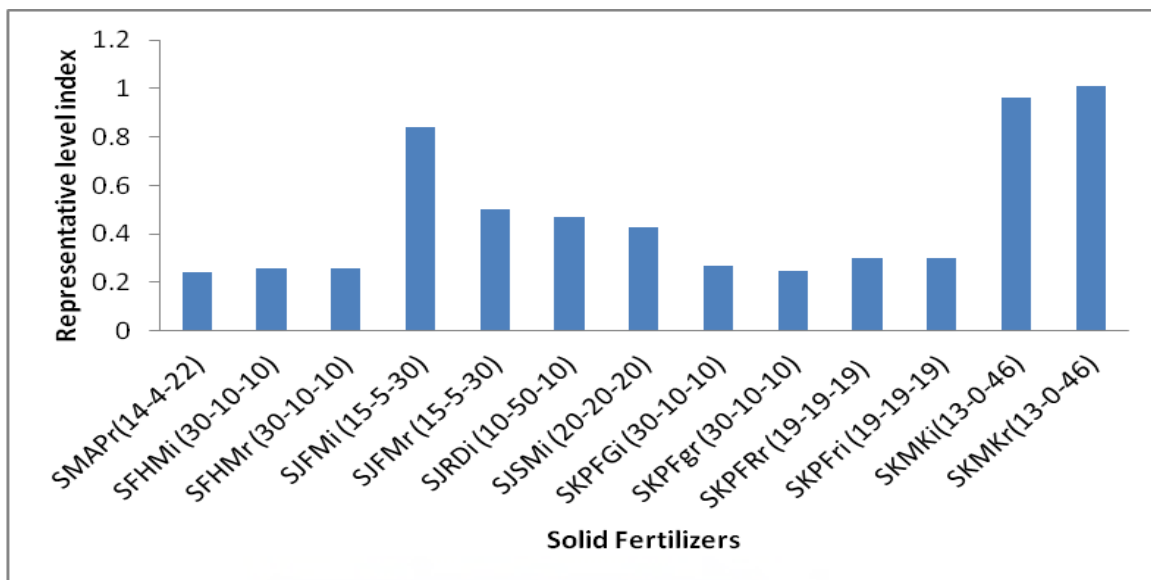


Figure 5.11 Representative Level for Solid Fertilizer Samples

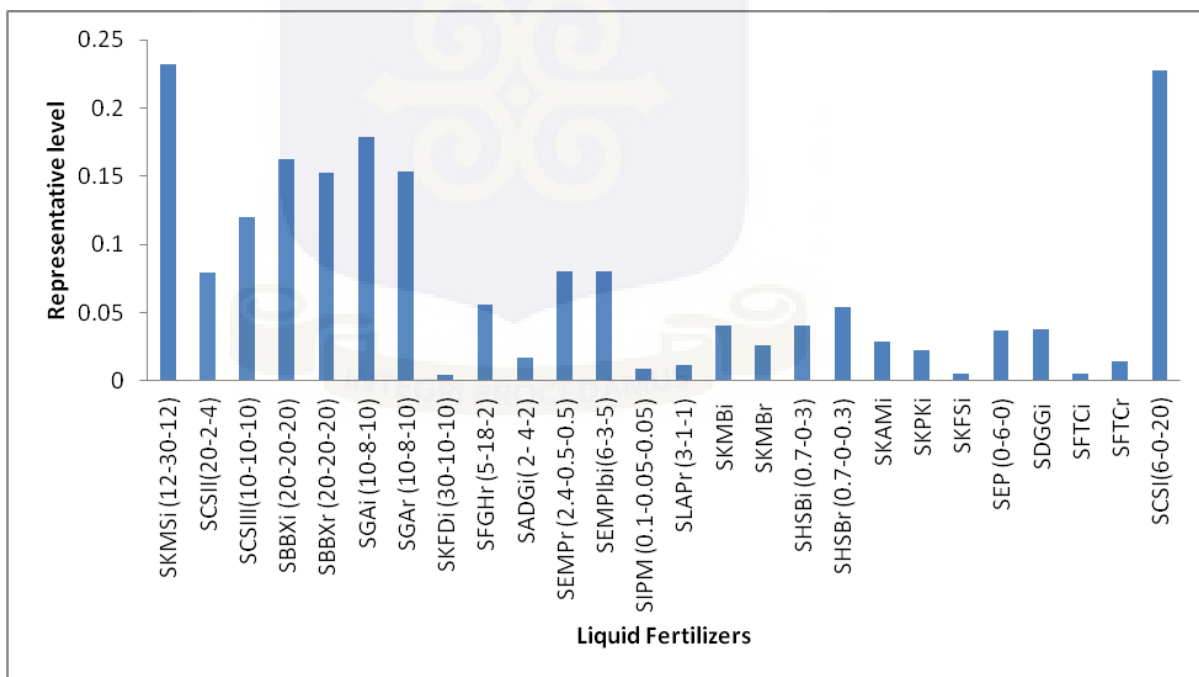


Figure 5.12 Representative Level for Liquid Fertilizer Samples

Comparison of Activity Concentrations with other Countries

The given data indicate little variations in the NORMs specific activities in NPK fertilizers from different countries in literature data, but without any clear trends due to the different sources of phosphate and potassium ore and/or chemical processing. The activity concentrations have been compared with others from other countries as compiled by Jibiri and Fasae (2011) and presented in Table 5.5 and further illustrated by Figures 5.13–5.16.

Table 5.5 Activity Concentration of ^{238}U , ^{232}Th and ^{40}K in other Countries

Countries	Samples	Activity Concentrations			References
		^{40}K	^{238}U	^{232}Th	
Pakistan	NPK	885	386	38	Gulmond and Windham (1975)
USA	NPK	200	780	49	Khan et al. (1996)
Germany	NPK	720	520	15	Ashraf and Al-Sewaidan (2007)
Saudi Arabia	NPK	2818	75	23	Mustonen (1985)
Finland	NPK	3200	54	11	Mustonen (1985)
Nigeria	NPK	4729	143	9	Jibiri and Fasae (2011)
Ghana	NPK (Solid)	6727	8.7	13.7	Present Study
Ghana	NPK (liquid)	1542.4	9.3	15.5	Present Study
Egypt	SSP	446-882	301	125-239	El-Bahi et al. (2004)
Egypt	SSP	4	66	366	Ahmed and Abdel (2005)
Nigeria	SSP	301	695.8	4.7	Jibiri and Fasae (2011)
Nigeria	Phosphate Rock (Sokoto)	536.2	1038.8	257.9	Jibiri and Fasae (2011)
Nigeria	Phosphate Rock (Togo)	871	1801.4	15.6	Jibiri and Fasae (2011)

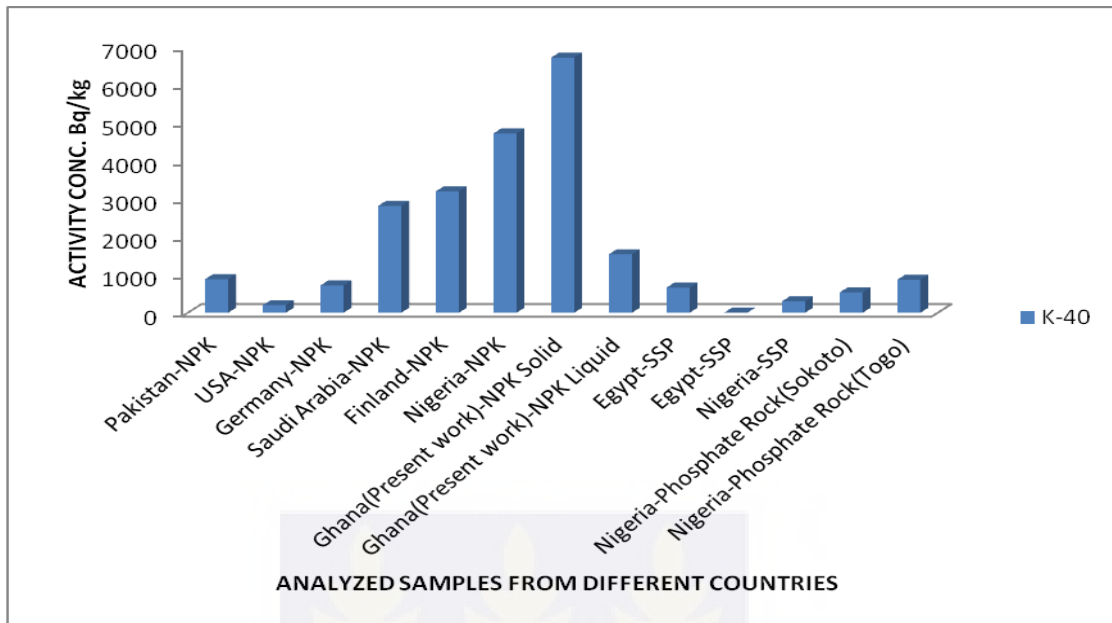


Fig. 5.13 Comparison K-40 World Average with Present Work

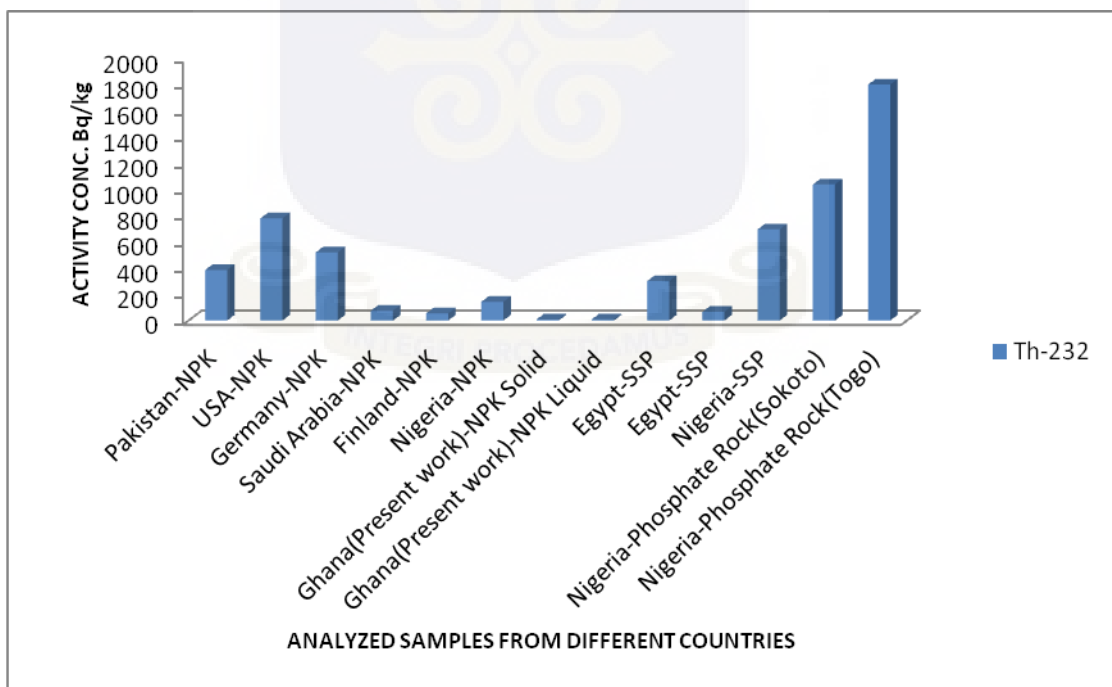


Fig. 5.14 Comparison Th-232 World Average with Present Work

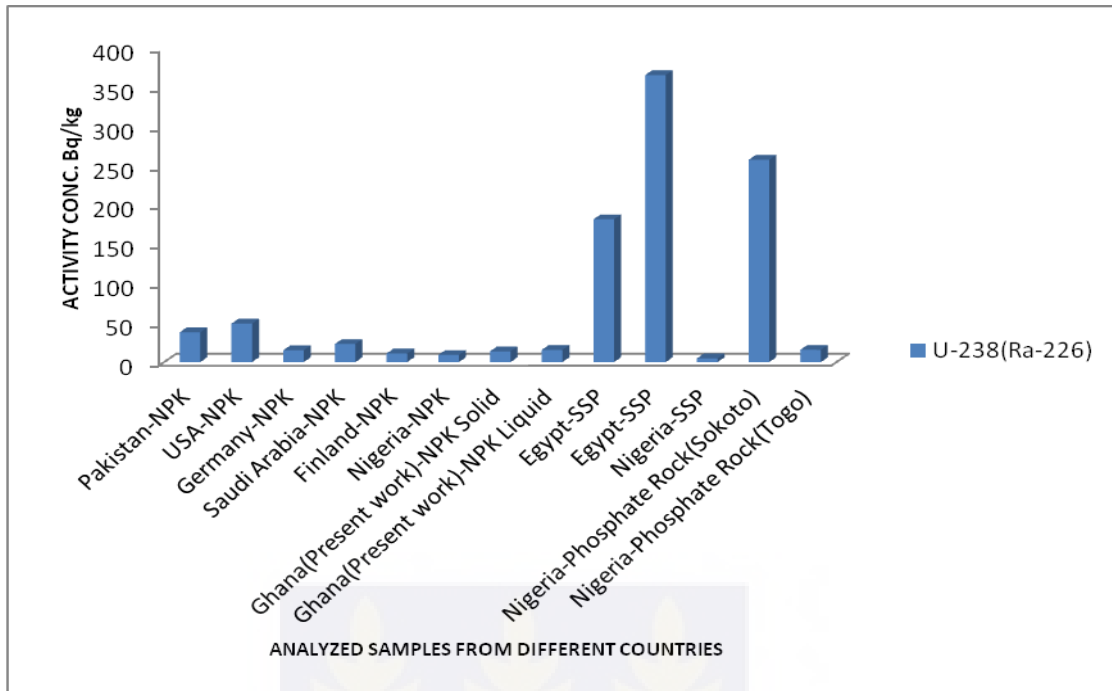


Fig 5.15 Comparison U-238(Ra-226) World Average with Present Work

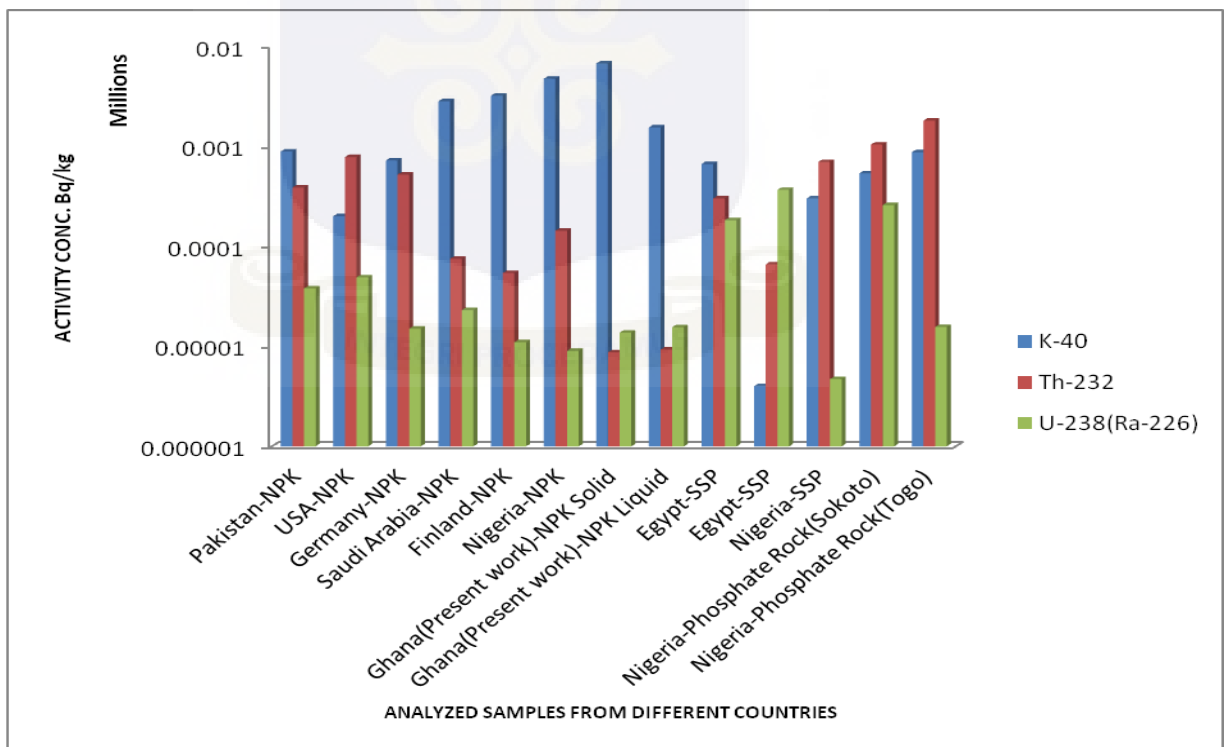


Fig 5.16 Comparison K-40, Th-232 and U-238 World Average with Present Work

The mean activity concentration values for solid NPK fertilizers are compared with the range of activity concentrations around the world and reported in scientific literature with respect to ^{40}K , ^{238}U and ^{232}Th , which are 4–4729 Bq/kg, 54–1801 Bq/kg and 9–366 Bq/kg, respectively. In this study, the activity concentrations for the ^{238}U and ^{232}Th are found to be within their respective world ranges, but the mean value of ^{40}K (6,727 Bq/kg) is above the values reported for other countries. The liquid fertilizer values, however, are found to be within range for all the natural radionuclides determined.

Phosphate and potassium are used in the production of some chemical fertilizers including NPK. Since phosphate and potassium contain some natural radionuclides such as ^{238}U , ^{232}Th and ^{40}K , fertilizers have become a major contributor to outdoor terrestrial natural radiations. Among the constituents of agricultural NPK fertilizers are potassium ores (potassium sulphate, potassium chloride) (Conceição and Bonotto, 2006). Hence, the measured activity concentrations are likely from the rock ores from which these fertilizers are produced. The location and geological formation are major contributory factors for the levels of radioactivity obtained.

Investigation of gamma radiation activity in the chemical fertilizers has been performed in order to determine the effect of the use of chemical fertilizers on human health. A possible negative effect of chemical fertilizers is contaminating the cultivated lands and uptake by plants of the trace metals and some naturally occurring radioactive materials (NORM) (Lambert *et al.*, 2007). Radionuclides present in the fertilizers affect the common people and farmers immensely (Ghosh *et al.*, 2008). The large concentration of natural radionuclides in the fertilizers contaminates the

environment and agricultural field. Direct inhalation of dust of such fertilizers could also affect the farmers on agricultural land (Pfister *et al*, 1976; Scholten and Timmermans, 1996).

Exposure to ionizing radiation is generally considered undesirable at all levels. The energy of gamma radiation emitted from ^{238}U , ^{232}Th and ^{40}K is greater than 1.022 MeV which is the threshold of pair production (electron-positron). So the dangerous damage of this kind of radiation must be taken into count. Chemical fertilizers are considered one of a possible additive of natural radionuclides, especially ^{40}K in the environment.

Potassium found in the human bodies is mostly acquired through the ingestion of food, which irradiates the cells. The natural ionizing radiation represents 10 % of the average annual dose to the human body from all types of radiation (UNSCEAR, 1993). The environmental impact of chemical fertilizer production depends on the raw materials, production processes and the status of the pollution control equipment (Bhatti and Malik, 1994). Exposure of workers and the public to radiation from fertilizers is, therefore, not unlikely (Diab *et al*, 2008). Higher radiation levels are associated with the chemical fertilizers. Therefore, the study of natural activity in artificial fertilizers is of great interest in environmental pollution field.

For ^{238}U radionuclide, the values obtained for NPK fertilizers are lower than the world average of 41 Bq/kg (UNSCEAR, 1983), as the highest activity concentration obtained was 16.3 Bq/kg. The NPK values obtained for Th-232 (with 27.9 Bq/kg being the highest) are also lower than the world average of 52.2 Bq/kg (UNSCEAR,

1983). The highest value for K-40 was 19710 Bq/kg while the lowest was 0.1 Bq/kg. A significant number of the samples had their activity concentrations (K-40) higher than the world average of 230 Bq/kg for (UNSCEAR, 1983). This indicates that the material source or ore from which these fertilizers were produced have high levels of ^{40}K or that the production process did not take into consideration the tendency for this sort of contamination. This contamination is a source of concern and is further discussed in the next section.

5.3 Contamination Source Identification

R-mode cluster analysis for the variable generated 2 major clusters for the liquid samples. Cluster 1 consists of elements Cu, Cd, Zn, Cr and Fe as the first group. Most of these elements, apart of toxic elements, are added to the fertilizers as incorporated EDTA chelates. The micronutrients are also mostly derived from waste materials hence their possible contamination with non-essential elements. This assertion is further confirmed by the Pearson's correlation that shows a strong positive significant correlation between Cd and Zn, Cd and Fe and then Zn and Fe.

Potassium (K), K-40, Br and Na found as a sub-cluster indicates that they are from a common raw material source. This sub-group, however, may not have originated from a different source from the other subgroup consisting of Cu, Cd, Fe, Zn and Cr. Cadmium and Cr are contaminants which might have been introduced during the incorporation of the micronutrients. Cluster 2 consists of, Th-232, U-238, Ca, Mn, Al which indicate they are from a common source or raw material used in manufacturing the fertilizers.

For the solid samples, R-mode cluster analysis for variables gave 3 clusters with cluster 1 grouping the chelated elements together. Cluster 2 consists of K, K-40, Na, Br and Cr which is as a result of the raw material or source rock from which the potassium is mined. The affinity between K and Na is further confirmed by the Pearson's correlation indicating their strong positive correlation. Cluster 3 also contains a group of elements and radionuclides. The silicate minerals Al, Mn and Ca from which the essential elements are mined can be said to be contaminated with the radionuclides U and Th. The grouping of the silicate minerals and radionuclides, Th and U are also confirmed by the correlation analysis indicating their common origin in nature.

5.4 Sample Similarities and Groupings with CA and PCA

Sample clusters for liquid are as follows; cluster 1 consists of samples with nitrogen and potassium but no phosphates as well as no micronutrient additives. Cluster 2 consists of samples which contain some form of organic extracts and are mostly non-NPK, while cluster 3 is composed of samples with micronutrients and organic extracts. Cluster 4 consists of non-NPK fertilizers with no micronutrients while cluster 5 is made of liquid NPK samples with micronutrients. Clusters under the solid are as follows; cluster 1 consists of NPK solid samples which have micronutrients Cu and Zn. Cluster 2 consists of NPK solid samples with Fe as an additive.

The results from the cluster analysis and principal component analysis suggest that all the liquid fertilizers can be grouped into five major groups with respect to their

elemental contents. The CA and PC analysis for the solid samples also indicate similarities of 3 major clusters with sub-groupings and 5 components respectively.

5.5 Groupings and Affinity among Parameters

In terms of the variables, there is a clear indication of the following groupings for both solid and liquid; Al, Mn, Ca, U-238 and Th-232 which are likely from a similar raw material source or origin; Fe, Cu, Cd, Zn which may have also been grouped together likely due to their addition to the fertilizers as micro-nutrient in chelated form. The naturally occurring radioactive material K-40 has also grouped with Na and Br indicating their common origin.

From the principal component analysis, it can be inferred that some elements are characteristic of some fertilizers as depicted in Tables 5.6 and 5.7. This can be used in finger-printing of the various fertilizers types found on the market. Tables 5.6 and 5.7 depict that sample SJRD_i has the most parameters that are significant in it. Upon inspection in the data, it can be found that variable concentrations for this sample are high from the results table. Samples SKMK_i and SKMK_r, which also have Br being significant, have comparatively higher Br levels than most other samples. SHS_{Bi} and SHS_{Br} are also significant as far as Cd, Zn, Fe, Al, Mn and Ca are concerned, and upon inspection it can be seen that their concentrations almost similar. This technique can be used to identify the elements associated with certain products and can be very useful for regulatory purposes.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6.1. Conclusion

The trace elements in non-traditional fertilizers have been determined using the Atomic Absorption Spectrometry (AAS) and Instrumental Neutron Activation Analysis (INAA) techniques. The study found most of the trace elements analyzed to be within limits set by international standards (Canada and Hungary and Washington State) except for Cu and Cd. However all trace elements were within allowable limits projected by the SUI#25 model. The levels of trace elements were also found to be below levels capable of accumulating in soils after computing and comparing with international standards. The toxic trace element concentrations determined in all samples were found to be in the order $Fe > Cu > Co > Cd > Cr > Ni > Pb > As > Hg$.

The activity concentrations and hazard indices (Raeq, Dose rate and representative level) for the natural radionuclides U-238 and Th-232 were also found to be generally within safety limits and world average figures. However, the activity concentrations and computed hazard indices for K-40 in some products such as SKMKi are higher than the world average and standards set by UNSCEAR.

The Raeq was also found to be high among some of the products meaning that they should be monitored for their radon levels. Generally, the activity concentrations in both the liquid and solid fertilizers were found to be in order $K-40 > Th-232 > U-238$.

Minimum guaranteed other than Nitrogen, Phosphorus and Potassium which were analyzed were largely found to be below that set by the regulators even for the

companies who declared the results on their labels. This shows that plants will not get the required amount of nutrients.

The results from the cluster analysis, principal component analysis and Pearson's correlation showed good agreement and suggest that all the liquid fertilizers can be grouped into five major groups with respect to their elemental contents. The CA, PCA and Pearson's correlation analysis for the solid samples also indicate similarities of 3 major clusters with sub-groupings and 5 components respectively. Pairings that have been confirmed for both CA and PCA are for both solid and liquid among the parameters as; Al, Mn, Ca, U-238 and Th-232 which are likely from a similar raw material source or origin; Fe, Cu, Cd, Zn which may have also been grouped together likely due to their addition to the fertilizers as micro-nutrient in chelated form. The naturally occurring radioactive material K-40 also grouped with Na, Br and partially with K indicating their common origin.

In conclusion, the dangers associated with the use of "non-traditional" fertilizers in Ghana are low with respect to toxic trace elements since their concentrations in the fertilizers are low. The potential for trace element accumulation in soil has also been found to be low. Furthermore, the liquid fertilizers are not radiologically significant whereas some solid fertilizers are significant due to their high activity concentrations and hazard indices.

6.2. Recommendations

Further research and monitoring of trace elements and naturally occurring radioactive materials in other forms of fertilizers should be carried out in order to generate the

necessary trace elements and radiological data for regulators to act. The phosphate and potash fertilizers have been reported world-wide to contain high levels of radioactivity and hence should be investigated in Ghana.

An analytical laboratory dedicated to fertilizers and soil health should be set up and well equipped with the necessary equipments such as AAS, X-Ray fluorescence, Spectrophotometer, flame photometer, Kjeldahl apparatus and UV-Visible spectrophotometer to ensure quality monitoring of fertilizers on the Ghanaian market.

It is recommended that regulators continue to check imported fertilizers for heavy metals in order to ensure that they are safe for agriculture use and would not accumulate in the soils or be found in the food chain.

The study has indicated the usefulness of multivariate analysis in contamination source determination and finger printing that may play a significant role in fertilizer quality monitoring. It is therefore recommended that multivariate analysis be integrated into future research into fertilizer contamination studies.



CHAPTER 7

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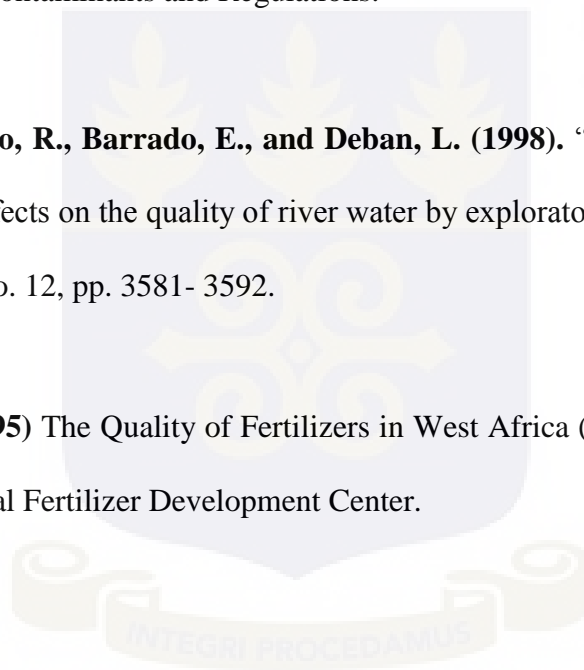
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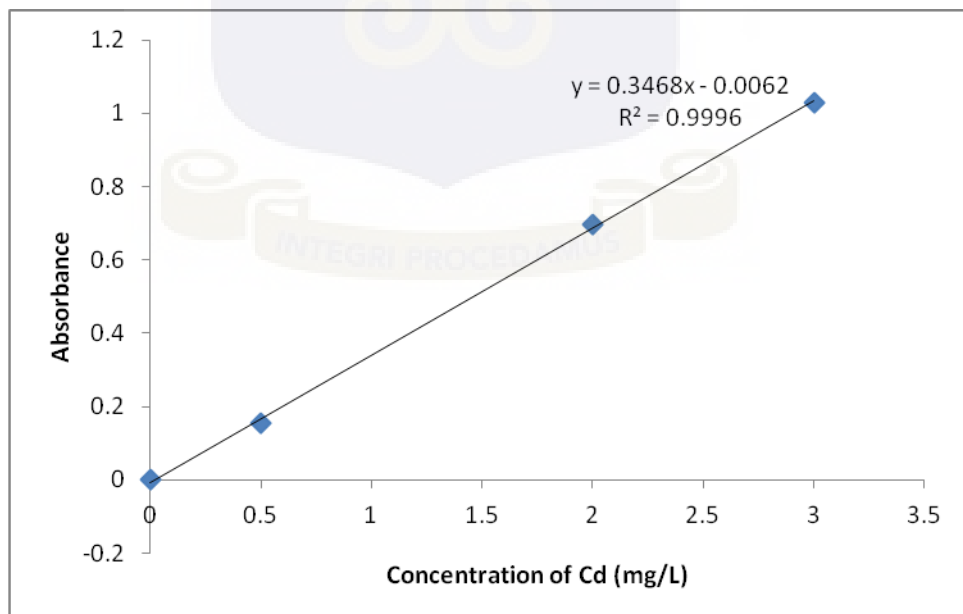
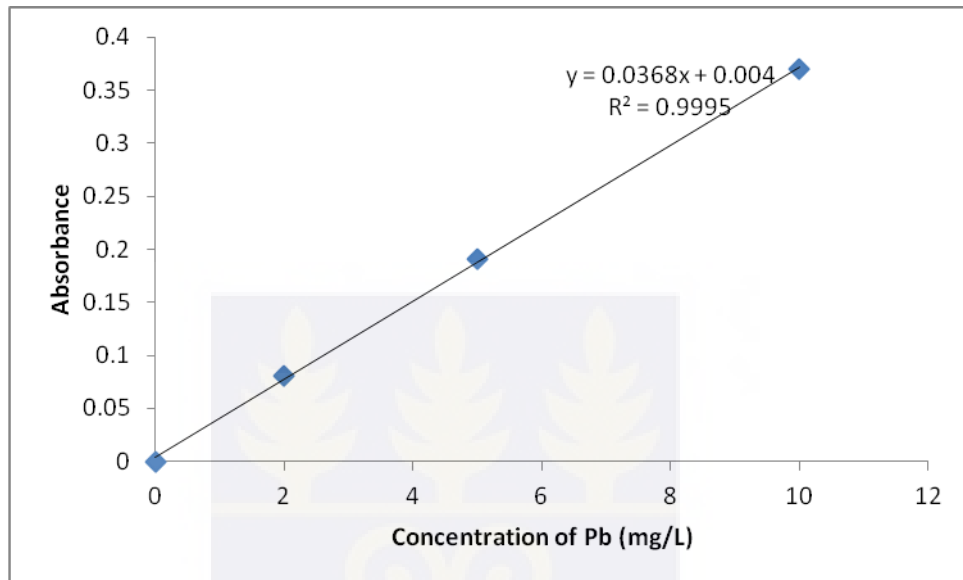
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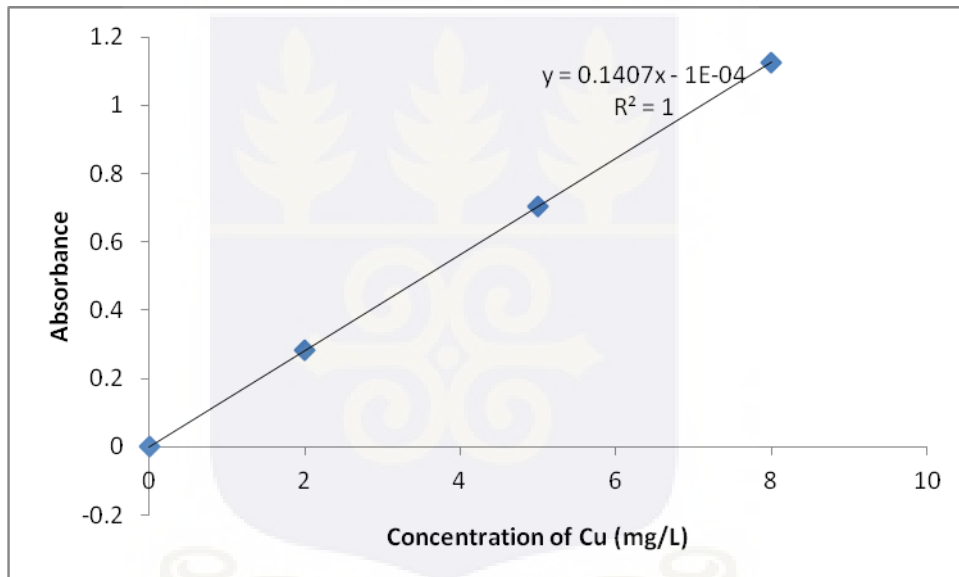
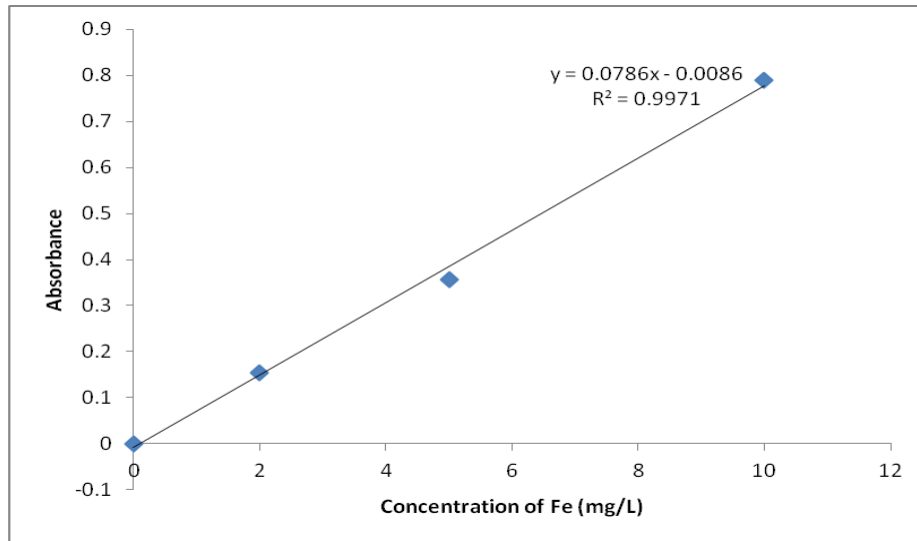
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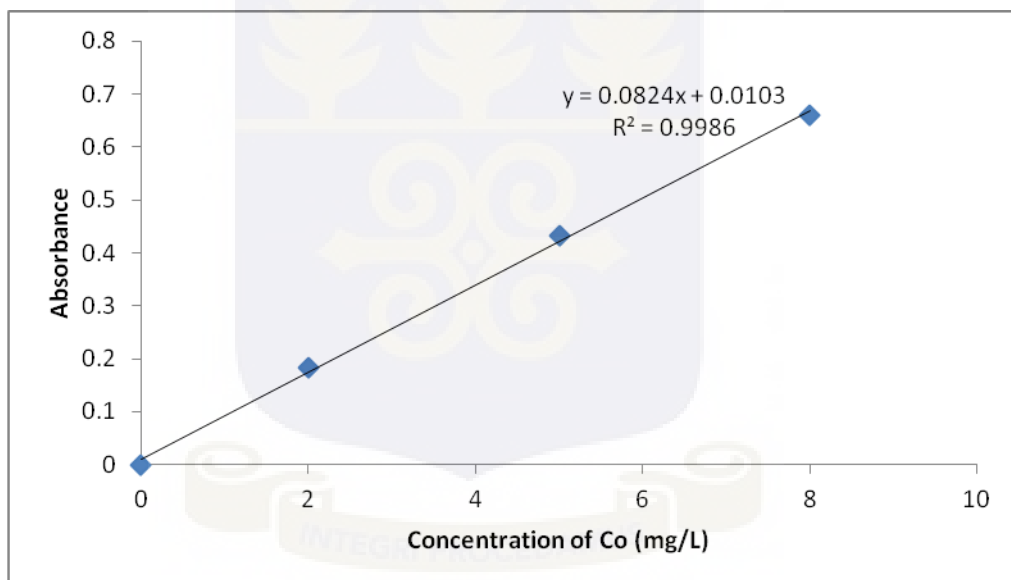
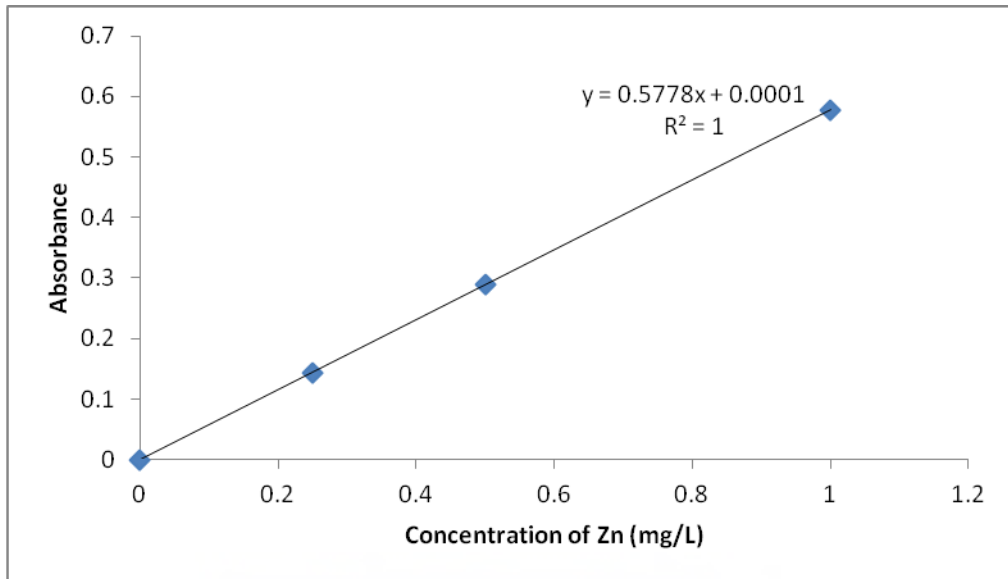
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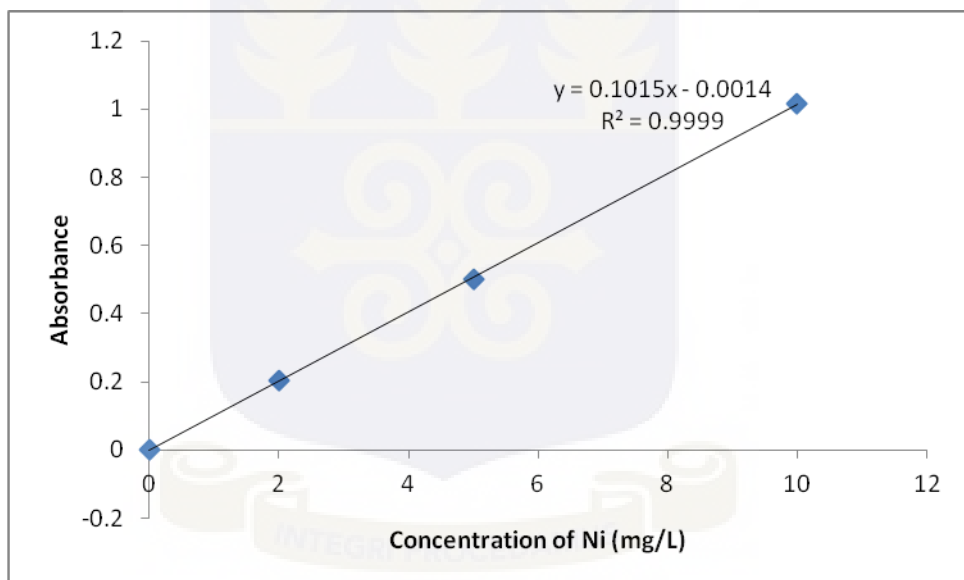
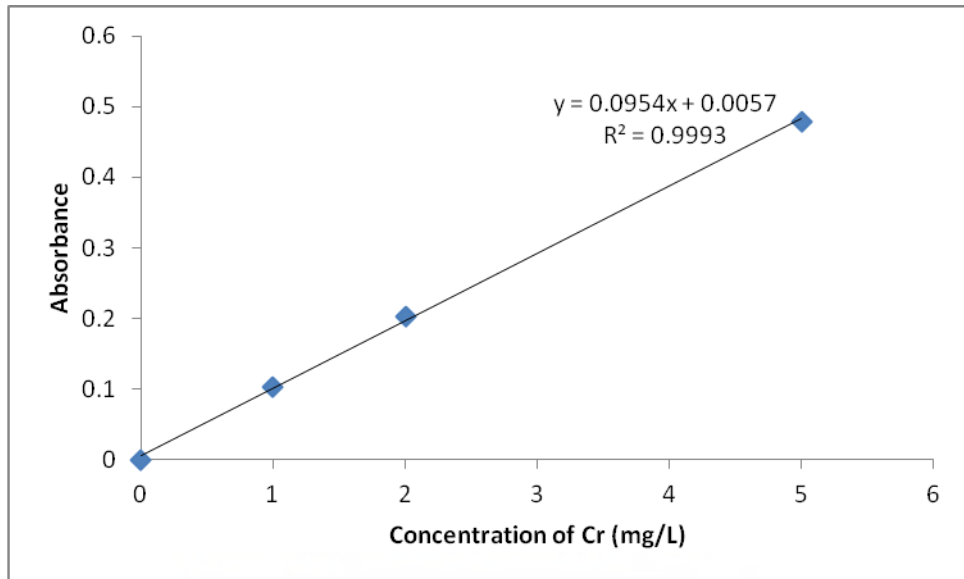
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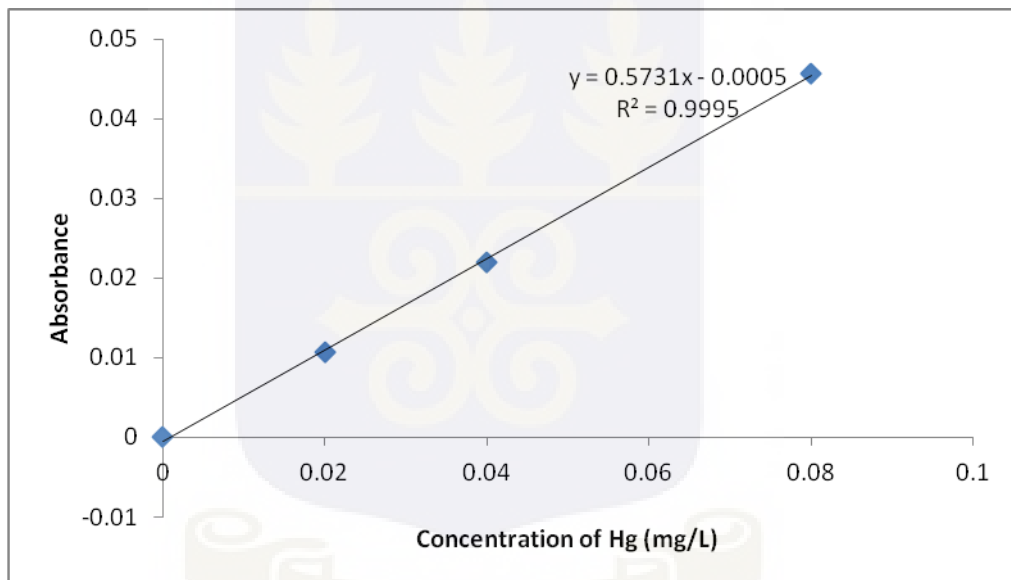
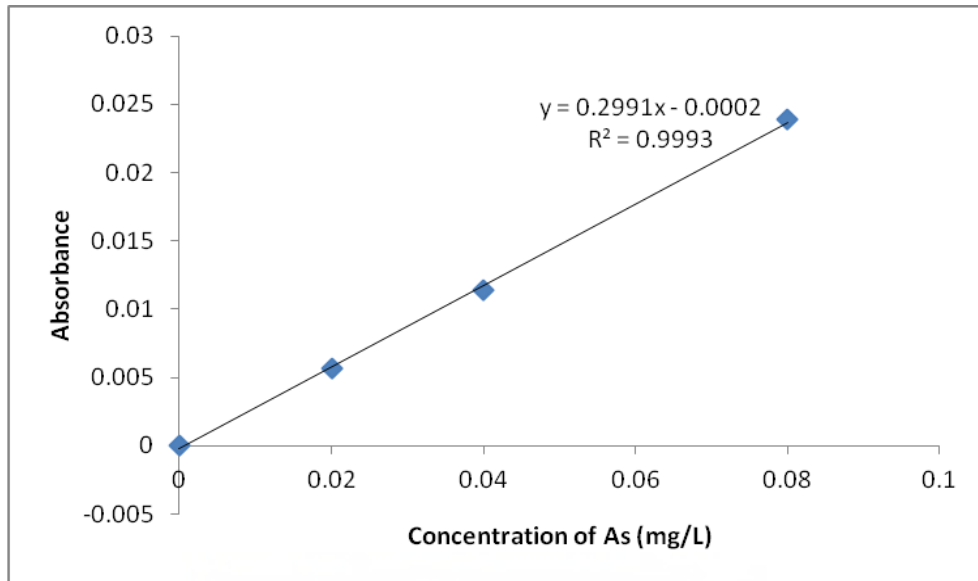


APPENDICES**APPENDIX 1****Linear Regression Lines for Calibration (FAAS and HG-AAS)**



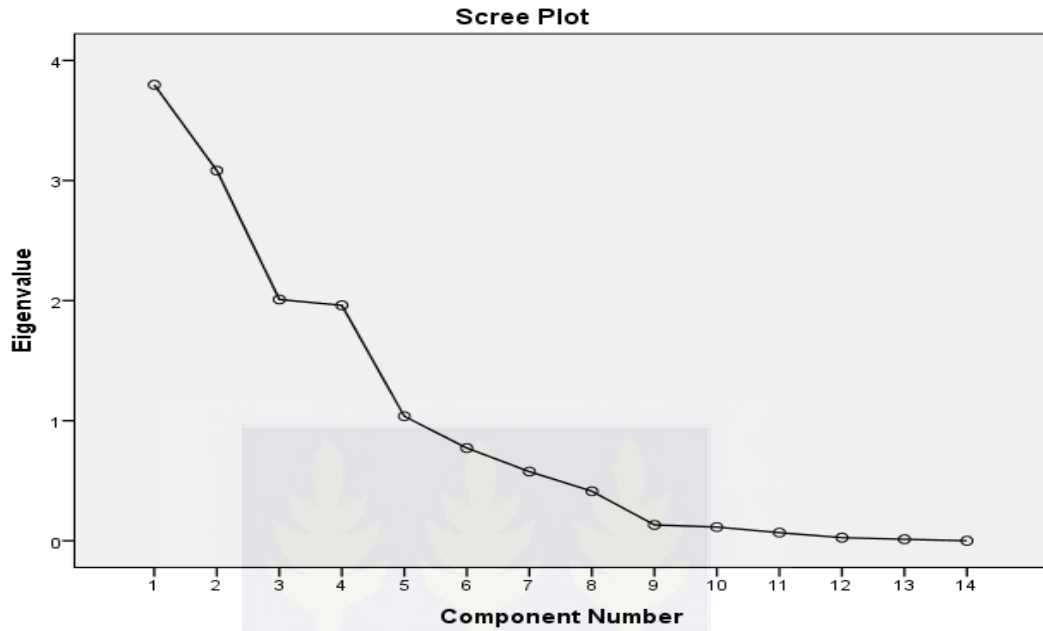




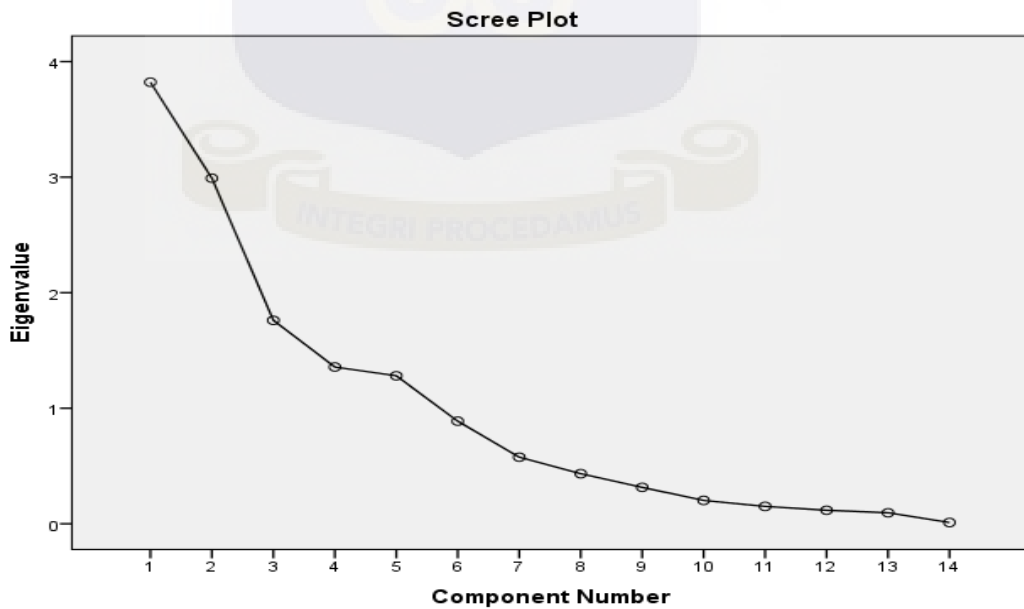


APPENDIX 2

Scree Plots for Principal Component Analysis of Studied Fertilizer Samples



Scree plot for the rotated component matrix of solid fertilizers



Scree plot for the rotated component matrix of liquid fertilizers

APPENDIX 3

Computed Radiation Hazard Indices for Fertilizer Samples

Sample I.D	Raeq	D (nGy h-1)	Representative level index(Iyr)
SMAPr	363.19	195.48	0.23
SKMSi	354.93	189.46	0.23
SCSIr	125.66	64.94	0.07
SCSIr	186.74	97.94	0.12
SFHM _i	387.48	207.38	0.25
SBBX _i	255.18	132.72	0.16
SBBX _r	235.76	124.54	0.15
SGA _i	278.85	145.58	0.17
SGA _r	240.83	125.19	0.15
SKFD _i	7.298	3.4671	0.004
SFHM _i	393.63	210.62	0.25
SFHM _r	396.41	212.06	0.26
SJFM _i	1261.51	681.3	0.83
SJFM _r	753.64	402.24	0.49
SJRD _i	712.47	381.85	0.46
SJSM _i	644.77	348.12	0.42
SKPF _{gi}	408.50	218.03	0.26
SKPF _{gr}	392.25	207.74	0.25
SKPF _{Rr}	454.75	240.91	0.29
SKPF _{ri}	385.88	207.63	0.25
SFGH _r	89.73	45.41	0.05
SADG _i	30.83	13.78	0.01
SEMP _r	130.78	65.78	0.08
SEMPI _{Bi}	130.78	65.78	0.08
SIPM _r	16.33	7.62	0.01
SLAP _r	91.81	39.99	0.05
SKMB _i	71.26	33.45	0.04
SKMB _r	43.88	21.33	0.03
SHS _{Bi}	64.81	32.85	0.04
SHS _{Br}	91.25	43.93	0.05
SKAM _i	45.49	23.22	0.03

SKPKi	36.36	18.45	0.02
SKFSi	10.41	4.73	0.01
SEPi	62.52	29.81	0.04
SDGGi	65.97	31.15	0.04
SFTCi	8.97	4.36	0.01
SFTCr	26.95	11.87	0.015
SKMKi	1453.17	785.71	0.96
SKMKr	1529.17	826.98	1.01
SCSIr	350.7	185.27	0.22



APPENDIX 4 – PRODUCT INFORMATION

Product Name	Product Code	Type Of Product	Net Content	Use
Gotta Grow	SDGG	Liquid	1 Litre	Foliar and soil applied
Plant Master	SIPM	Liquid	1litre	Foliar applied
Microbe Plus(Blue)	SEMPI	Liquid		Soil, foliar and drip
Microbe Plus(Phoscal)	SEMPII	Liquid	1litre	Foliar and drip
Profert-Premium Liquid Fertilizer	SEP	Liquid	1litre	Foliar
Di-GROW GREEN	SADG	Liquid	1litre	Foliar
Sino-Booster	SHSB	Liquid	1 or 500ml	Foliar and soil applied
Sidalco Npk(6:0:20)	SCSI	Liquid	1litre	Foliar
Sidalco Npk(20:2:4)	SCSII	Liquid	1litre	Foliar
Sidalco Npk(10:10;10)	SCSIII	Liquid	1litre	Foliar
Algua	SGA	Liquid	500ml	Foliar
Top Cop	SFTC	Liquid	1litre	Foliar
Golden Harvest	SFGH	Liquid	1litre	Foliar

Boost Xtra Npk	SBBX	Liquid	1litre	Foliar
Mango Boost	SKMB	Liquid	1litre	Foliar
Maize Starter	SKMS	Liquid	500ml	
All Plants	SLAP	Liquid	200ml	Foliar
Fruit Set	SKFS	Liquid	1litre	Foliar
Fruit Developer	SKFD	Liquid	1litre	Foliar
Pk	SKPK	Liquid	1litre	Foliar
Amino Mix	SKAM	Liquid	1litre	Foliar
Multi-K	SKMK	Solid	1kg	Foliar and drip
Poly Feed(Million More)	SKPFr	Solid	1kg	Foliar
Poly Feed	SKPFg	Solid	1kg	Foliar
Super-Master(20-20-20)	SJSM	Solid	1kg	Foliar
Root Development	SJRD	Solid	1kg	Foliar
Fruit Master	SJFM	Solid	1kg	Foliar
Harvest More	SFHM	Solid	1kg	Foliar
All Purpose Plant Food	SMAP	Solid	1kg	Foliar