UNIVERSITY OF NAIROBI

EFFECTS OF LONG TERM USE OF INORGANIC FERTILIZERS ON ACCUMULATION OF SELECTED HEAVY METALS AND PRIMARY MACRONUTRIENTS ON MAIZE FARM SOILS: CASE STUDY OF KERITA FARM IN TRANS NZIOA COUNTY, KENYA.

BY

KANANU JUDITH

I56/82398/2012

A thesis submitted for examination in partial fulfilment of the requirements for award of the degree of Master of Science in Chemistry of the University of Nairobi

2015

DECLARATION

I declare that this this thesis is my original work and has not been submitted elsewhere for examination, award of a degree or publication. Where other people's work or my own work has been used, this has probably been acknowledged and referenced in accordance with the University of Nairobi's requirements.

Signature..................................... Date....................................

Judith Kananu
I56/82398/2012
Department of chemistry
School of physical sciences
University of Nairobi

This thesis is submitted for examination with our approval as research supervisors

Prof. G.N. Kamau Signature Date
Department of chemistry
School of physical sciences ....
University of Nairobi
Box 30197-00100
Nairobi Kenya
gnkamau@uonbi.ac.ke

Dr. V.O Madadi Signature Date
Department of chemistry
School of physical sciences ....
University of Nairobi Box 30197-00100
Nairobi Kenya
vmadadi@uonbi.ac.ke

DEDICATION

This thesis is dedicated to the late Michael Mithika

ACKNOWLEDGEMENT

The completion of this thesis would not have been possible had it not been the contribution of many others who supported financially, critically, logistically and morally. First and foremost, I thank the Almighty God my creator for leading the way for me throughout the research thesis.

I acknowledge my supervisors Prof G.N Kamau from University of Nairobi, Department of Chemistry for his invaluable unrelenting professional support during research and thesis writing, Dr. V.O Madadi University of Nairobi, Department of Chemistry for his professional and academic input during research period. I also acknowledge my husband Mr. Solomon Namaswa for his understanding during the entire process when I had to spend several days collecting data.

I express my most sincere appreciations to the efforts and contribution of Kenya Agricultural Research Institute (KARI), Department of Geology and Mines and College of Agriculture and Veterinary Sciences for providing the instruments/equipment for data analysis.

The effort of every other person not mentioned and who has contributed in one way or the other to the success of this thesis is also appreciated.

ABSTRACT

Concern has been raised by researchers over toxic heavy metals which enter the human and animal food chain as a result of application of inorganic fertilizers for food production. The presence of heavy metals in some inorganic fertilizers has raised fears that long term use of these fertilizers could lead to accumulation of these metals to toxic levels that may eventually exceed natural levels in soils. Environmental problems related to fertilizers such as eutrophication, together with their potential bioaccumulation in the food chain have also been of concern. The aim of this research was to analyse and document the effect of long term use of inorganic fertilizers on the accumulation of selected heavy metals and macro-nutrients on maize farm soils in Trans Nzoia.

An Atomic Absorption Spectrophotometer (AAS) was used to determine the concentrations of heavy metals (Cd, Cr, Cu, Pb and Zn) in soil and fertilizer samples. Nitrogen (N), Phosphorus (P) and Potassium (K) in maize farm soils and frequently used fertilizer samples (DAP, Urea and CAN) were determined using Kjeldahl method for nitrogen analysis, UV-visible spectroscopy and flame photometry respectively. Soil characterization was performed to determine the soil pH using pH meter, soil texture using hygrometer method and the Total Organic Carbon using wet chemistry technique. Phosphorus retention capacity was determined using phosphorus adsorption isotherm method.

The study revealed that both the fertilizers and farm soil had significant amounts of chromium, cadmium, lead copper and zinc. DAP fertilizer recorded the highest levels of all the five metals with zinc levels being the highest among the three types of fertilizers as shown: 22.21±0.09 mg/kg, 1.67±0.0.00 mg/kg,16.38±0.06 mg/kg,301.53±0.59 mg/kg and 342.60±0.57 mg/kg for Cu, Cd, Pb, Cr, and Zn respectively. Metal concentrations obtained from the maize farm soils were higher than that of the control site. The mean concentration for Cu, Pb, Cr and Zn in maize farm soils was 8.52±1.56 mg/kg, 37.72±3.44 mg/kg, 42.11±3.25 mg/kg and 29.36±2.74 mg/kg, respectively while the mean concentration for Cu, Pb, Cr and Zn in the control soils was 5.12±0.71 mg/kg, 18.98±0.88 mg/kg, 19.15±1.56 mg/kg and 14.71±0.63 mg/kg respectively. However, the concentration of the toxic elements after long term use of chemical fertilizers did not exceed the internationally accepted concentration levels such as the USEPA and Department of Agriculture, Forestry and Fisheries (Kenya).

Nitrogen and phosphorus concentrations in major fertilizers investigated in this study were found not to be in agreement with labelled contents reported by manufacturers. The biggest variation was observed in phosphorus in Di-ammonium Phosphate (DAP) fertilizer which had very high concentration of 66.7% above the declared content of range 46 - 54%. The three fertilizers lacked potassium which was in agreement with the declared amount of 0 % on fertilizer label. Phosphorus was found to be sufficient with a mean concentration of 39.33±2.96 ppm above 35 ppm regarded minimum for maize production while Nitrogen and Potassium in maize farm soils were found to be deficient for maize production.

Soil characterization revealed that the maize farm soils had lower pH of 5.034±0.25 compared to that of control site of 6.35±0.21. The pH of both soils was less than 7.0 implying that they were acidic. The Total Organic Carbon in the soil under study was generally low but it was observed that clay textural class of soil had higher total organic carbon compared to sandy clay loam, silty clay loam soils and sandy clay textural classes. Soil texture was found to correlate with TOC. Soils under study portrayed an average soil phosphorus retention ability that highly correlated with soil texture.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AAS: Atomic Absorption Spectrophotometer

AD: Air Dry

AOAC: Association of Official Analytical Chemists

As: Arsenic

B: Boron

Ca: Calcium

CAN: Calcium of Ammonium Nitrate

CCE: Calcium Carbonate Equivalent

Cd: Cadmium

Cr: Chromium

CS: Control Site

Cu: Copper

DAP: Di-Ammonium Phosphate

FAS: Fertilizer Amended Site

Fe: Iron

Ha: Hectares

K: Potassium

M: Mean

MCF: Moisture Correction Factor

Mg: Magnesium

Mo: Molybdenum

N: Nitrogen

NG: Not Given

NH_3: Ammonia

Ni: Nickel

NO_3^-: Nitrate

OD: Oven Dry

P: Phosphorus

p: Significance

Pb: Lead

Po: Organic phosphorus

Pi: Inorganic phosphorus

PVC: Polyvinyl chloride

S: Sulphur

SD: Standard deviation

Sr: Strontium

Th: Thorium

TOC: Total Organic Carbon

TSP: Triple Super Phosphate

U: Uranium

USEPA: United States Environmental Protection Agency

Zn: Zinc

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Agricultural application of chemical fertilizers is increasing globally, due to depletion of soil nutrients. As human population continues to increase, putting pressure on food production systems, mainly crop and livestock production, the increase in the demand for food also raises but soil fertility deteriorates with time. This has led to substantial increase in application of plant nutrients, including inorganic fertilizers in the last 50 years to increase food production in order to satisfy human population demand [Ashraf, 2006]. More than 30 million metric tons of phosphate fertilizers are annually consumed worldwide to increase crop production and land reclamation [Khater and AL-Sewaidan, 2008]. Studies have shown that heavy metals in fertilizers can accumulate in soil and become readily available to plants [Modaihsh *et al.*, 2004]. Therefore, longterm application of fertilizers can redistribute and elevate toxic heavy metals such as As, Cd and Pb, in soil and consequently contribute to increased bioaccumulation of the heavy metals in the food chain.

The risks of heavy metal accumulation through agricultural activities and the problems posed by heavy metals by fertilizers and other soil inputs have increasingly drawn the attention of farmers, environmental organizations, consumers, and public policymakers worldwide [USEPA, 1999]. Adverse health effects that results upon consumption of contaminated food stuff have also received much attention [Singh, 1991; 1994]. Even though heavy metals occur naturally in all soils, they are in minute quantities, but they can accumulate in agricultural soils from various sources, such as fertilizers, organic supplements, atmospheric deposition and urban and industrial activities. Some of these metals are not essential nutrients for plants and animals. However, sufficiently high concentrations can become toxic and constitute serious health problems whenever they enter into the human food chain [Modaihsh *et al*. 2004].

The key heavy metals released from fertilizer used include As, Cd, Cr, Fe, Sr, Th, U and Zn [Modaihsh *et al*., 2004]. Therefore, elements have a potential risk of accumulation in soil with repeated fertilizer application. Rothbaum *et al.*, [1986] indicated that differences in accumulation of heavy metals in soils is related to pH differences and/or organic matter content as well as the interplay of these two factors with adsorption and desorption of heavy metals, and that the interaction of the applied Cd with soil organic matter apparently affects its mobility in soils.

The addition of large quantities of phosphorus to agricultural land through the use of fertilizers can also result in serious environmental impacts such as eutrophication. Eutrophication occurs when surface waters become over-enriched with nutrients such as N and P. This stimulates plant and algal growth, which subsequently die and decompose. This reduces dissolved oxygen concentrations in water columns, which is detrimental to aquatic life [Jeffrey, 1998]. Following addition of fertilizer to land, phosphate can leach from the land into the surrounding environment, resulting in high phosphate levels in receiving water bodies such as rivers and seas. These elevated nutrient levels can cause excessive algal blooms of the water body, with severe impacts on the aquatic environment [Brigden *et al*., 2002].

Continuous application of Phosphorus to soil either as inorganic or organic amendment results in the buildup of soil Phosphorus. However, Ige *et al*., [2005] indicated that a large build-up of soil Phosphorus is often agronomically beneficial and may not be environmentally harmful, provided the soil has an adequate capacity to retain added Phosphorus. Therefore, knowledge of the capacity of soil to retain Phosphorus is essential in the proper management of phosphorus additions to soils. Phosphorus sorption capacity is generally different under different soil conditions [Li *et al.*, 1972]. To manage phosphorus addition to soil in a way that ensures the integrity of the adjacent environment, there is a need to assess the risk of phosphorus loss of soils in the Kenyan farms. An important factor in assessing such a risk is the capacity of these soils to accommodate the added phosphorus.

1.2 Macro-Nutrients

Macronutrients are major nutrients that are required by plants in large quantities for growth. They include: nitrogen, phosphorus, potassium, hydrogen, calcium and oxygen. These elements are further divided into fertilizer and liming agents. Fertilizer elements are nitrogen, phosphorus and potassium while liming elements are calcium, magnesium and sulphur.

Maize yield and farmers' benefit depend on soil fertility. Soil fertility depends on the status of soil nutrients such as total amount of N, P, and K, their capacity to produce nutrients in the form that can be easily taken up by the crops, toxic substances, soil erosion, being washed out and other ways of loss. Soil fertility can be reduced, especially under humid tropical conditions in less developed and developing countries because of deduction of nutrients from soil stock and less returns back to the soil [Lieu, *et al*., 2010]. Mineral fertilizer inputs have dominant factors of the overall nutrient balance, but their use is often imbalance and their efficiency remains below optimum levels. Therefore, managing the variability in soil nutrient supply that has resulted from intensive maize cropping is one of the major challenges to sustaining and increasing maize yields in the Kenyan maize farm soils. This study was aimed at determining heavy metal concentrations, alteration of primary macronutrients and soil pH. It is also aimed at determining the impact of fertilizers on soil with respect to heavy metal concentration levels, primary nutrients, soil pH and soil phosphorus retention capacity in Kerita maize farms where inorganic fertilizers are used extensively used for maize production. The control site was at Kiptuimet Primary School football pitch which lies within the same geographical region as Kerita farm and also has the same type of soil but no fertilizers have been applied to this pitch for a long period of time.

1.3 Statement of the Research Problem

Heavy metals in fertilizers can accumulate in soil and become readily available to plants. Also long term continued application of fertilizers can redistribute and elevate toxic heavy metals in soil profiles and consequently their transfer to the food chain. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Some people cannot excrete them efficiently enough and a build-up in their bodies occurs.

Though presence of toxic elements in fertilizers poses environmental and health concerns, there is no indication on fertilizer labels to inform users about the presence and quantity of toxic metals. This is because fertilizer labeling laws only require the name and address of manufacturer/packer, name of the fertilizer, guaranteed percentages of the main nutrient elements, net weight of the material in the package and the handling instructions to be enlisted [Ukpabi *et al*. 2012], hence the need for data.

There is also no data on the impact of extended use of fertilizer in Trans Nzoia maize farm soils and the phosphorus retention capacity of these soils. Therefore, there is need to undertake research to provide more information on the phosphorus retention capacity of these soils.

1.4 Objectives

1.4.1 Overall Objective

The main objective was to analyse the effect of continued application of inorganic fertilizers on the accumulation of selected heavy metals, primary nutrients and soil phosphorus retention capacity of Kerita maize farm soil.

1.4.2 Specific Objectives

I. To characterize Kerita maize farm soil and Kiptuimet primary school football pitch soil

II. To analyse nitrogen, phosphorus, potassium and selected heavy metals (Cd, Cr, Cu, Zn and Pb) content in the major fertilizers used in Kerita farm

III. To analyse nitrogen, phosphorus, potassium and selected heavy metals (Cd, Cr, Cu, Zn and Pb) content in Kerita farm and Kiptuimet primary school soils

IV. Determine the effect of different soil fertilization on phosphorus retention capacity of Kerita maize farm soil

1.5 Justification of the Study

Kenyan farmers apply large amount of fertilizers in their soils to achieve high yields. This trend has been practised in Trans Nzoia since the colonial period. Unfortunately, not many people are aware of the effects associated with the long term use of the chemical fertilisers. The findings of this research work shall be helpful to the stakeholders involved in agriculture such as farmers, environmental organizations, consumers, and public policymakers in order to understand the effect of continuous application of large amounts of inorganic fertilizer in the soil. In this way relevant measures can be put in place.

1.6 Alternative Hypothesis

Levels of heavy metals, primary macronutrients, soil characteristics and phosphorus retention capacity differ significantly in the two study sites constituting the fertilizer amended soil and the control site soil.

CHAPTER TWO

LITERATURE REVIEW

2.1 General Overview

Schroeder and Balassa [1963] were the first to identify that fertilizers were implicated in raising some heavy metal concentrations in food crops due to their accumulation in the soil. Since then much work has been performed to investigate the impact of impurities in fertilizers on soil after long term use.

2.2 Sources of Heavy Metals in Soils and Fertilizers

Some fertilizers and amendments may contain concentrations of trace elements and heavy metals due to the mineralogy and manufacturing processes of the material or the addition of waste-derived material. Waste-derived material refers to recyclable materials used for alternative purposes. The presence of metals in fertilizers is of concern as it can potentially lead to the accumulation of toxic metals in fertilized soils resulting to adverse effect on livestock and human health. Metals of concern in fertilizers include arsenic (As), cadmium (Cd), lead (Pb), nickel (Ni) and zinc (Zn). The first three are considered non-nutritive metals as they provide no nutritional value for plants. The latter two metals are essential plant and animal micronutrients and high levels may not necessarily be toxic. Fertilizer products containing phosphorous inherently contain heavy metals particularly Cd. Manufacturing processes only remove a small percentage of heavy metals while the majority remains in the final product. Micronutrient sources may also contain naturally occurring amounts of heavy metals from the raw ore source and extraction processes. Simple Nitrogen and Potassium fertilizer materials have relatively low heavy metal concentrations [Mortvedt, 1981].

Studies have shown that the main source of fertilizer - derived heavy metals in soils is phosphatic fertilizers, manufactured from phosphate rocks that contain various metals as minor constituents in the ores [Kpomblekou and Tabatabai, 1994]. Analysis of fertilizers commercially manufactured in Lebanon revealed the presence of heavy metals in the fertilizers at elevated concentrations being persistent in the environment, and continuous addition of fertilizers containing these metals to the soil can result in their accumulation over time. The presence of cadmium in the fertilizers at elevated concentration is of most concern as a result of the toxicity of this metal and its ability to accumulate in soils, and bioaccumulation in plants and animals. According to the study by Semu and Singh [1995] in Tanzania, they showed that there was a significant amount of heavy metal enrichment of soils receiving the high fertilizer and Copper fungicide inputs relative to virgin or low input soils. This resulted in higher concentrations of the metals in the leaves of tobacco grown in these soils. Although the magnitudes were not big, therefore probably posing no immediate danger, greater risks could arise in the future due to the observed increasing trend.

In Kenya, Omwoma *et al*. [2010] analysed heavy metals in top soil samples from Nzoia sugarcane farms in Western Kenya and found elevated levels of heavy metals in the soils compared with a control soil sample from an adjacent field where fertilizers were not applied. The heavy metal loads in the sugarcane farms were above international standards. The levels of the same metals in the fertilizers used in the sugarcane farms were within acceptable international standards. A risk assessment of the continued use of phosphate fertilizer (DAP) in the farms based on a 50-year period, did not exceed international threshold. The soil pH value was low compared to the control site a situation that could accelerate heavy metal solubility and mobility in the farm soil. Lowering of soil pH was attributed mainly to fertilizer application and partly to increased organic matter content as shown by the high mean total organic carbon content values in comparison with a control soil meant total organic carbon content value.

Fertilizer grade is generally indicated as a three number code of the three primary macronutrients: nitrogen (N), phosphorus (P) and potassium (K). The first value corresponds to total nitrogen content, the second to available phosphorus (P_2O_5), and the third to water soluble potash (K_2O) content. Each value represents a percentage of nutrient content by weight. Total Nitrogen content is represented as elemental N and may be further split into four N forms which include: nitrate nitrogen, ammoniacal nitrogen, water soluble organic nitrogen (and/or urea), and water insoluble nitrogen. Knowing which N form is present in a fertilizer is important in determining the availability of N in the soil [Brady and Weil, 1999].

On top of primary macronutrients fertilizers may contain other nutrients such as sulphur (S), iron (Fe), boron (B), zinc (Zn), and molybdenum (Mo). These nutrients may be added as additional nutrients or may be impurities remaining in the fertilizer material following mining and manufacturing processes. If present as additional nutrients it will be listed on the fertilizer label on an elemental basis, similar to N. Forms and solubility's may also be listed. If a significant source of a particular nutrient, other than N, P, or K, is present in the fertilizer, it is typically labelled as a fourth value in the fertilizer grade. This is most often seen with fertilizers containing Sulphur [Havlin *et al*., 1999]. However, the quality of fertilizers in terms of guaranteed percentages of nutrient elements as labelled by the manufacturer has been questioned. In a study conducted by Sheriff *et al*. [2012] to validate specifications indicated by manufacturers on their fertilizer products in Ghana from five major fertilizer importing companies for macronutrient analysis to determine the fertilizer quality revealed a 98% agreements between the measured values and the certified values for the primary macronutrients nitrogen, phosphorus and potassium (N, P and K). Primary macronutrients were valid. However, most of them fell short of the requirements for secondary macronutrient concentration. Therefore, the need for a good quality control system to undertake periodic quality monitoring of the chemical compositions of fertilizers imported into the country was emphasized since they may directly or indirectly have impacts on the environment.

2.3 Role of Macro-Nutrients in the Soil and Plants

2.3.1 Nitrogen

Nitrogen can only be absorbed by plants in ionic form either inform of nitrate ions or ammonium ions. Nitrate is soluble in water and readily leached during heavy rains and it plays an important role in protein formation. It forms part of the chlorophyll molecule and makes plant succulent with green colour, regulates the availability of potassium and phosphorus in plants and it also increases the size of grains and their protein content. The deficiency of nitrogen can result to the yellowing of the leaves (chlorosis), stunted growth whereby the plants become dwarfs with roots being extremely short and the leaves turn brown and fall prematurely (Hue and Silvia, 2000).

2.3.2 Phosphorus

Phosphorus exists in the soil either in inorganic or organic form and the action of microorganisms convert organic phosphorus into phosphates which can be easily absorbed by plants. Phosphates are relatively insoluble in soil water and therefore not easily leached. It is essential nutrient in plants for root development whereby it encourages establishment of roots and nodule formation, it is essential for flowering, fruits and seed formation and also ripening of fruits. It also strengthens the plant stems hence preventing logging. Its deficiency results to symptoms such as increase in production of anthocyanin, the pigment that gives plants a purplish colour, stunted growth of the green parts and poor development of the metabolizing organs of the plant.

2.3.3 Potassium

It is abundantly found in clay soils as it is a constituent element of clay particles. It is readily leached in sandy soils and its roles in plants include: carbohydrates formation and translocation, it is a component of chlorophyll molecule and it is also necessary for the neutralization of organic acids in plants. Its deficiency results to premature leaf fall, leaf curling, leaf surfaces loose chlorophyll and become yellowish hence become chlorotic [Hue and Silvia, 2000].

2.4 Effects of Cultivation on the Organic Carbon in the Soil

Organic carbon in the soil is a major factor contributing to aggregation of soil particles and improves soil structure by increasing total porosity and percent of macro-pores. It also decreases crust formation and reduces susceptibility to erosion [Sanchez, 1997]. The amount of organic carbon in the soil varies and it is mostly affected by climate and vegetation under natural conditions [Stevenson, 1974]. Organic carbon in tropical soils under forest is delicately balanced due to the continuous addition of fresh material being offset by decomposition. Exposure of soil due to removal of vegetation reduces organic carbon. The decrease can greatly be attributed to two cases. First, clearing and cultivation of land results in reduced rate of addition of vegetation organic material [Cunningham *et al.*, 1963] and secondly, the rate of decomposition of the soils organic carbon is accelerated as a result of a combination of factors favouring increased mineralization after clearing and cultivation [Lal *et al.*, 1979]. It has been established that sites with abundant vegetation have relatively more organic matter. Also trees/bush sites have consistently higher organic content, while bare ground has the least amount of organic carbon [Kironchi, 1992].

2.5 Transport and Fate of Heavy Metals in Agricultural Soils

Primary determinants of transport and fate of heavy metals applied to soil through fertilizers and related products are the soil physical processes which include erosion, leaching, export in harvested plants, and volatilization. These processes are major potential pathways for loss from soil at an application site. Heavy metals are not subject to chemical degradation that plays an important role in fate of organic compounds. Therefore, chemical conditions in soil are important secondary determinants of heavy metal transport and fate. These chemical factors affect the interactions between metals and solid phases of soils, soil water, and air within and above soil. There are four general classes of these interactions which include specific adsorption, co-precipitation, cation exchange, and organic complexation. Specific adsorption involves partly covalent bonds of the heavy metal with lattice ions on soil particle surfaces. Co-precipitation involves formation of water insoluble precipitates from metal ions (cations) and anions such as carbonate, sulfide, or phosphate. Cation exchange is non-specific interaction of metals with negative surface charges on soils minerals, such as clay. Lastly, soil organic matter (e.g., humus) adsorbs metals by forming chelate complexes, with carboxyl groups playing a predominant role. The most important chemical determinant that limits mobility in soils is the absorption of metals from soil water to soil particles. Another chemical factor that influences heavy metal transport and fate especially mobility in soil water is the soil pH. It begins with the ionization of metals which increases at low pH thereby increasing water solubility and mobility followed by hydronium ions displacing most other cations on negative surface charges. This reduces metal absorption by cation exchange and organic complexation [Alloway, 1995].

The rates of metal absorption and desorption from soil particle surfaces differ greatly. Absorption includes initial fast reactions, followed by slow reactions. The four general classes of absorption interactions constitute fast reactions. The mechanistic basis for slow reactions involves at least two processes:

(a) Sorption to soil particle surfaces is fast, diffusion into pores and subsequent sorption at these sites is time-dependent.

(b) Sorbed complexes may undergo subsequent reactions to form more stable structures. Desorption of metals deep in pores or complexed in stable “aged” structures is much slower than initial sorption.

The basis for explaining the capacity of chromium, cadmium, lead, zinc, and copper to accumulate in agricultural soils and in plants that grow on the soils depends on the transport and fate of these metals. This partially explains the “irreversible” sorption that is often reported. For example, desorption of lead from three soils with different organic matter content in stirred-flow reactors varies from 32 to 76%. These data do not reflect truly irreversible sorption, however. Slow desorption is not resolved in the design of most experiments due to the short times of typical experiments. Lead continues to desorb from these soils as more water volume washes through it. There is a progressive decline in the percentage desorbed with cumulative washes. The slow reactions for desorption are much slower than the slow reactions for sorption. Classical chemical descriptions for chemical sorption/desorption assume equilibrium conditions [Strawn and Sparks, 2000].

2.6 Healthy Risks Associated With Selected Heavy Metals Contamination

2.6.1 Chromium (Cr)

Chromium appears most commonly in the environment as a trivalent salt Cr^{3+}. It is found in air, water, soil and some foods which is an essential trace element aiding in the metabolism of carbohydrates (Chromium; http//www.atsdr.cdc.gov.tfacts7.html). It is found in foods such as brewer's yeast and cereal grains. Hexavalent Chromium (Cr^{6+}) may originate from industrial applications such as steel making, tanning, plating, and textiles. Hexavalent chromium is considered by the USEPA to be a carcinogen and can be easily absorbed by the body leading to ulceration of the liver and nasal septum. The process that take place in the stomach during digestion tend to change Cr^{6+} to Cr^{3+}, but Cr^{6+} is a strong oxidizer agent and can destroy cell walls easily. Sources of Cr^{6+} in the fertilizer stream include: steel manufacturing, tannery wastes, leather by-product, and sewage sludge [Parnes, 1986]. Chromium attaches tightly to soil particles and the usual exposure pathways are due to exposure to dusts and sediments.

2.6.2 Copper

Copper is an essential micro element that is also applied as a fungicide, algaecide, and molluscicide and to control crustaceans. Environmental contamination from copper generally originates from mining and smelting operations. Copper is allowed in organic farming with restrictions on its use to reduce copper accumulation [Savits *et al.*, 1995]. Accumulation of copper in the soil can result from contaminated soil amendments as well as from pesticide application. In order to monitor and prevent copper accumulation in soil there in a need restrict its presence in inorganic fertilizers as well as in pesticides.

2.6.3 Lead (Pb)

Lead is prone to accumulate in surface horizons of soil because of its low water solubility within an environmentally relevant pH range which results in very low mobility [Davies *et al.*, 1995]. Soil water contains only about 0.05-0.13% of the total soil lead concentration. Lead speciation is simple and Pb^{2+} is the dominant soluble form. It forms a number of highly insoluble precipitates including $Pb(OH)_2$, $Pb_3(PO_2)_2$, and $Pb(CO_3)$. Due to past uses of lead in industrial processes and consumer products (e.g. paint and gasoline), urban soils often contain high lead concentrations, up to 1,840 mg/kg. Lead easily accumulates on soil surface because of its low solubility in typical environmental contexts, and plant absorption factors are low (0.01-0.1). The tolerable level for lead in children’s daily diet load is 6 mg and it follows calcium and iron pathways when there are deficiencies in those metals in their body systems. The major sources of lead pollution include gasoline, lead-acid batteries, old paint, pesticides, inorganic fertilizers and industrial applications. Also demolition waste processed into wood products can be a source of lead found in fertilizer [Lepp, 2001]. In children, several neurologic problems are the principal concern for chronic lead exposure [Goyer and Clarkson, 2001]. Past uses of lead solder in food and beverage cans lead to significant human exposures to lead.

2.6.4 Zinc (Zn)

Zinc is an essential trace element that can be toxic to plants in excess. Much zinc bearing fertilizers are highly insoluble, and crops amended with these materials can show noticeable zinc deficiencies. Insoluble zinc materials do not appear to become significantly more soluble over long periods of time [Schreder, 2001].

2.6.5 Cadmium (Cd)

Cadmium is generally present at very low levels (0.1 to 0.5 ppm) in soils. Higher levels are present in sedimentary soils (0.1 to 25 ppm) and some volcanic shields. Typical daily national intake of Cd through diet is 20-40 µg Cd/day and World Health Organisation (WHO) sets a daily intake limit of 70 µg per day. Human implications associated with cadmium uptake include ingestion, inhalation and absorption [Wong and Lai, 2001]. Cadmium tends to be highly mobile in soil systems and therefore more available to plants than many other heavy metals [Alloway, 1995]. Cd^{2+} is the principal species in soil solution and its accumulation in food crops at soil concentrations that are not phytotoxic is a significant worry. Plant species vary widely in their tendency to accumulate cadmium. Crops that are of concern for cadmium uptake include green crops including lettuce, spinach, celery and Cole crops (heavy accumulators) and some root crops including potatoes and the carrot family (moderate accumulators). Sources of cadmium include bio solids, some phosphate ores, some micronutrient ores, and some industrial wastes. Available zinc level affect cadmium uptake; cadmium complexes with zinc and becomes technically insoluble when there is excess zinc in the soil [Lepp, 2001].

Phosphate fertilizers can contain significant cadmium concentrations and it can accumulate in crops and human health problems can result from crop cadmium contamination. Chronic cadmium exposures result in kidney damage, bone deformities, and cardiovascular problems [Goyer and Clarkson, 2001].

2.7 Effects of Fertilizer Reactions on Soil pH

Soil pH can be affected by certain fertilizer applications and generally, soil pH is optimum between pH 6.5 and 7.5. Some fertilizers may have long-term effect on soil pH after years of application while others have a more short-term and microsite effect. Microsite is defined as the area directly surrounding the fertilizer material and extends approximately 1 inch from the site of placement [Rachhpal *et al.* 1984].

Ammmonia (NH_3) based fertilizers such as urea can cause soil pH to temporarily increase, that is become more alkaline as a result of H^+ being taken out of solution to form NH_4^+ and this reaction occurs relatively quickly. Volatilization of NH_3 is a potential concern associated with increase in pH following the application of NH_3 fertilizers especially urea applied on the surface. Increase in pH promotes the formation of NH_3 in the soil, hence leading to greater NH_3 volatilization at high pH levels. Several studies have shown the loss of N from volatilization to be greatest under high rates of urea applied at the soil surface and to be substantially reduced with the incorporation of urea into the soil either mechanically or by rain or irrigation water [Fenn and Miyamoto, 1981].

In addition, studies suggest effects are highest on soils with low buffering capacities and not prevalent on well-buffered soils, although NH_3 losses up to 60% have been recorded in some calcareous soils from surface applied urea that was not immediately watered. In a number of Montana field trials, broadcast application rates of up to 150 lb N/ac as either urea or ammonium nitrate over summer, winter, and spring did not show any significant differences in yield or protein in spring and winter wheat trials. This suggests that N volatilization losses from urea application are not significant in high pH calcareous soils [Jackson *et al.*, 1986].

P fertilizers typically don't have long-term impacts on soil pH, but short-term microsite effects are evident between varying P fertilizers such as TSP and DAP. TSP is an acidic fertilizers that has pH values of approximately 1.0 whereas DAP is alkaline fertilizer with a pH near 8.0. Microsite pH may temporarily shift in response to a given P application thus possibly having impact on the availability of P and other nutrients near the fertilizer granule. A research conducted in the southern U.S. analysed the interaction effects between P fertilizer pH changes and NH volatilization when urea was applied with DAP and TSP. Results obtained shown that when urea was applied on the surface at 440 lb/ac with TSP, NH_3 volatilization dropped as compared to urea alone and increased when applied with DAP [Fan *et al.*, 1993]. This suggests that microsite pH changes attributed to P fertilizer sources can affect N loss through volatilization and hence the yields. However, the soil pH change is also influenced by other factors including soil texture, pH and buffering capacity, which may decrease microsite effects. K fertilizers may have a slightly alkaline (higher pH) effect on soil because of the addition of K^+ cations to the soil solution fertilizers but the effect on pH is negligible [Fan *et al.*, 1993].

The acidity of a fertilizer material is measured as calcium carbonate equivalent (CCE) and this value is often given on the fertilizer label. CCE is the number of pounds of calcium carbonate required to neutralize 100 pounds of a given fertilizer. As equivalent acidity increases, fertilizer's acidifying effect on the soil increases, due to acid produced as ammonium undergoes nitrification process. From several studies the fertilizers such as anhydrous ammonia and ammonium sulfate have the highest potential to acidify soil per pound of fertilizer. Therefore, fertilizers can cause soil pH to change, but these effects are only expected to be substantial on poorly buffered sandy soils [Rachhpal and Nye, 1984].

2.8 Solubility of Inorganic Fertilizers in Soil Water

Fertilizer solubility is termed as a measure of how much fertilizer material will dissolve in water. This property strongly influences the availability of nutrients to a crop and type of application method to use. Readily soluble fertilizers will dissolve easily in water and the soil solution, making nutrients available for plant absorption. Readily soluble fertilizers are required for their effective application with irrigation water systems. On contrary, low solubility fertilizers will not readily dissolve in water and nutrients may be insoluble therefore precipitate becoming less available for plants. Almost all N and K fertilizers are completely soluble in water meaning the entire available nutrient is soluble. On the other hand, the solubility of phosphate fertilizers varies between carriers and is dependent on the composition and the processes of manufacturing. It is suggested that in order to achieve high crop yields, triple superphosphates (TSP) contain high amounts of water-soluble P (more than 90%) and ammonium phosphate materials provide between 50 and 70% water-soluble P content [Bartos *et al.*, 1992].

Because P availability is important for early plant growth therefore recommended for banded starter fertilizers to contain high soluble forms of P more than 60%. Most commercial P fertilizers supply enough total P solubility to meet these recommendations. Highly-soluble P fertilizers may be used in fertigation systems, although if the irrigation water contains high amounts of calcium (Ca) or magnesium (Mg) and Ca/Mg-P compounds can form and precipitate. In addition to ineffective P fertilizing, this can result to scaling and plugging problems in farming equipments [Westfall *et al.*, 2001].

The solubility of micronutrient fertilizers in water varies and this is related to the process used in manufacturing and the primary product used as a source of micronutrient. Since many micronutrient fertilizers are manufactured from industrial by-products and are not water soluble, most require acid-treatment to increase their solubility. Chelation also increases metal solubility in water. Research has shown that, under similar application rates a highly soluble micronutrient fertilizer is able to supply more nutrients to a plant than a similar fertilizer with lower water solubility. Thus, to effectively supply micronutrients to crops it is recommended to obtain fertilizers with at least 50% micronutrient water solubility [Amrani *et al*., 1999].

2.9 Effect of Soil Texture on Nutrient Availability in the Soil

Soil texture is the amount of sand, silt and organic matter in the soil and it affects the soil's ability to retain water and nutrient. It is an important characteristic that influences infiltration rates of storm water. The textural class of soil is determined by the percentage of sand, silt and clay and the four classes of soil texture include:

(i) Clay soils; is a fine-textured soil

(ii) Sand soil; is a coarse-textured soil.

(iii) Silt

(iv) Loam

Soil texture influences numerous soil properties which include: water holding capacity, drainage, aeration, organic matter content, susceptibility to erosion and cation exchange capacity. Well drained soils have good soil aeration thus contain air which is conducive to healthy root growth hence healthy crops. Soil texture impacts organic matter content in a way it breaks down organic matter faster in sandy soils than un fine-textured soils in a similar environmental conditions, tillage and fertility management. This is due to higher oxygen availability for decomposition in the light-textured sandy soils. The cation exchange capacity of the soil increases with clay percentage and organic matter content and the pH buffering capacity of a soil (its ability to resist pH change on addition of lime) is based on clay and organic matter content (www.ristormwatersolutions.org). Soils with large amounts of clay or organic matter tend to hold water and nutrients more effectively than sand soils. Sand does not hold nutrients and water tightly so as water drains through the sand soil it carries nutrients along with it and nutrients become unavailable to plants. Clay has the ability to attract and hold nutrients in the soil hence fewer nutrients are lost through leaching. However, too much clay in the soil can cause water logging during wet weather hard rock when they dry-out. Presence of too much sand or clay in the soil can be remedied by adding organic matter in the soil which mimics the positive effects of clay without the disadvantage [Brent, 2013].

2.10 Phosphorus Retention Capacity by the Soil

Phosphorus is an essential nutrient for all plant and animal life and it is often in short supply. Agricultural fertilizers and other soil amendments such as mineral phosphorus (P) fertilizers and animal manure that is available to plants. The long term availability of phosphorus to plants is influenced by geochemical transformations while short-term availability is strongly influenced by biochemical processes that affect organic matter. The nature of phosphorus species in the subsurface depends with the soil type, location and system of management. A phosphorus movement in the soil is described as both dissolved reactive phosphorus and particulate unreactive phosphorus. Both organic phosphorus (po) and inorganic phosphorus (pi) species interact with soil components hence they are subject to various chemical transformations that influence the retention of phosphorus element. The main challenges in subsurface P management are depletion and oversupply. Oversupply occurs when amendments are applied in excess of crop requirements which may happen when manure is applied to satisfy the nitrogen requirements of crops. Depletion occurs when there is practice of low input agriculture involving land clearing and continuous cultivation that reduce both inorganic phosphorus (pi) and organic phosphorus (po). Surplus P can be transported in runoff after rains, snowmelt or irrigation that may contribute to eutrophication in water bodies. Eutrophication stimulates plant algal growth which subsequently dies and decomposes hence reducing dissolved oxygen concentrations in water columns which detrimental to aquatic life [Jeffrey, 1998]. The major mechanisms of phosphorus retention are surface adsorption and precipitation therefore depressing its availability after fertilizer application. Carbonates and oxide clays play a role in phosphorus retention in calcareous soils. Phosphorus available to plants is negatively correlated to the amount of lime in soil, but not to Fe, clay content, or CCE [Afif *et al*., 1995]. Phosphorus retention increases with the ratio of Fe oxides to $CaCO_3$ and that noncarbonated clays provide most of the phosphorus adsorbing surfaces in many calcareous soils, especially at low phosphorus concentrations [Torrent *et al*., 1995]. Tunesi *et al.* [1999] concluded that in soils with a high reservoir of exchangeable cations, precipitation is the predominant mechanism in the reduction of available phosphorus and that poorly crystalline Fe oxides have a distinct tendency to occlude phosphorus. Added manure or litter and native organic matter have significant effects on subsurface phosphorus retention. Manure not only affects sorption and precipitation of phosphorus, but it contains significant amounts of the element, which is deliberately or incidentally added to the land [Kelling *et al*., 2004].

The effects of manure on phosphorus availability in various soils has been that it is a source of; interacts with soil components in a manner that increases phosphorus recovery by crops and enhances the effectiveness of inorganic fertilizer. Phosphorus added from manure and other sources, however, tends to become less available to plants with the passing of time [Soper *et al*., 1980]. Manure application guidelines are frequently based on the nitrogen requirements of crops, and phosphorus is therefore often oversupplied and liable to either accumulate or be removed by surface or subsurface transport. Manure and mineral (KH_2PO_4) fertilizer appear to contribute to different phosphorus because it is efficient at increasing $CaCl_2$ extractable P and Mehlich-3 P, while manure (especially chicken manure) has a greater effect on modified Morgan P, as well as other types of P [Griffin *et al.,* 2003]. Alkaline soils subjected to long-term manure amendments accumulate substantial quantities of phosphorus, with 50–66% in plant available forms. The affinity constants and sorption capacities of soils for P are reduced by organic amendments, especially manure due to competition for phosphorus fixation sites by organic acids, and/or the complexing of exchangeable Al and Fe by components of manure [Hue *et al.*, 1986].

The ability of soils and sediments to retain phosphorus depends on processes of phosphorus sorption and precipitation with different forms of Fe, Al and Ca [Reddy *et al.,* 1980]. Sorption refers to both adsorption on solid surfaces and absorption into solid phases of Al and Fe oxides and other mineral surfaces [Bache, 1964]. Phosphorus adsorbs to mineral surfaces and once all surface sites are filled, P begins to diffuse into the particle via absorption [Reddy *et al.*, 1999]. Sorption processes are temporally dependent on pH.

CHARPTER THREE

MATERIALS AND METHODS

3.1 Study Sites

This study was aimed at determining heavy metal concentrations, alteration of primary macronutrients and soil pH in soil and the impact of fertilizers on soil with respect to heavy metal concentration levels, primary nutrients and soil pH in Kerita maize farms in Trans- Nzoia County, in Kenya. In this area inorganic fertilizers are used extensively for maize production. The control site was at Kiptuimet Primary School football pitch which is adjacent to Kerita farm and also has the same type of soil but it has not been cultivated and no fertilizers have been applied to this pitch for a long period of time.

Trans Nzoia is one of the counties in Kenya known for large scale commercial production of maize by application of large quantity of chemical fertilizers. It is located in north of the Great Rift Valley approximately between latitudes 00 52' and 10 18′ North of the equator and longitudes 340. 38' and 350 23′ East of the great meridian with an altitude of 1300m above sea level. The county borders Bungoma to the west, Uasin Gishu and Kakamega to the south, Elgeyo Marakwet to the east, West Pokot to the north and the republic of Uganda to North West. Trans Nzoia covers an area of 2495.5 square kilometres. The county is largely Agricultural with both large scale and small scale wheat, maize and dairy farming. The county is fondly referred to as the basket of Kenya for its role in food production in the country. The Kerita maize farm, occupy a total surface area of 750 Ha (hectares) all has been under maize production for more than 20 consecutive years. Intensive maize farming is done with fertilizers including Di-ammonium Phosphates (DAP) applied during planting season, Urea being applied when maize crop is at knee high and Calcium of Ammonium Nitrate (CAN) which is applied when the plant is about to fruit. Calcium ammonium nitrate(CAN) is applied at the rate of 185 kg/Ha, DAP at a rate of 250 kg bags/Ha Urea and 308kg bags/Ha CAN per year.

Most of the rainfall is received during the long rain season, which is from March to May while the short rains season is from September to November with average annual rainfall of 11200 mm. The average annual temperature ranges from 10^{o}C mean annual minimum to a mean annual maximum of 37^{o}C.

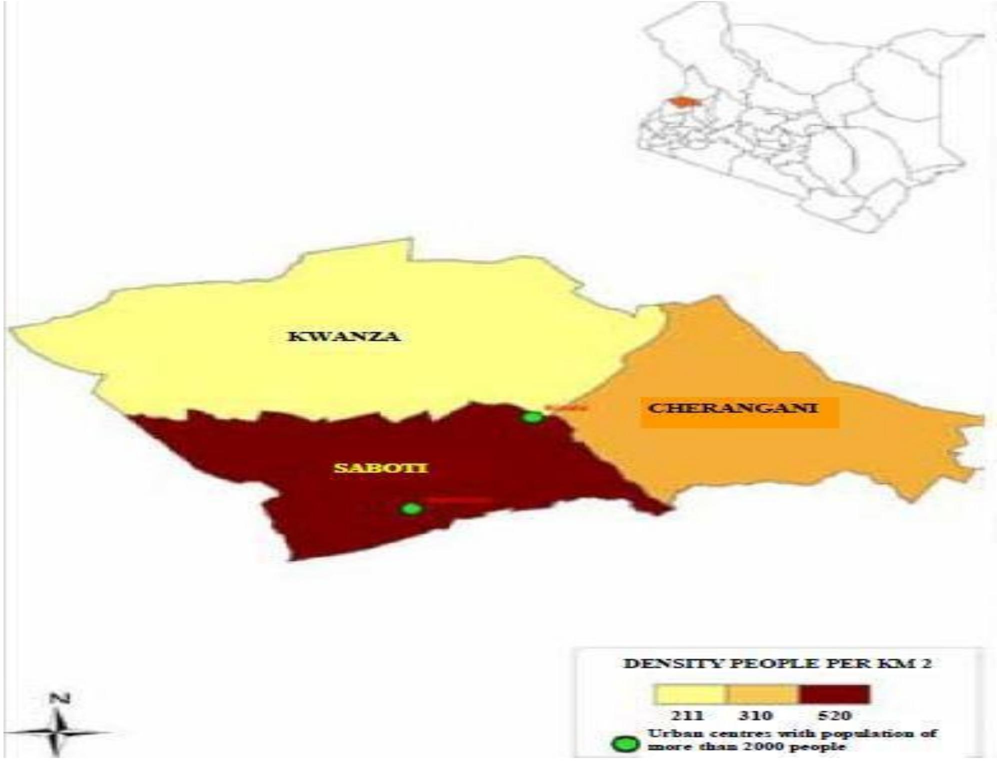

Figure 3.1: Map of Kenya Where Trans Nzoia is Located.

3.2 Sample Collection

Soils from Kerita, a 750 Hectares maize farm in Trans Nzoia County, Kenya were randomly sampled according to Omwoma *et al*. [2010] at a depth of 0 – 20 cm using a PVC pipe of approximately 1.5 cm diameter. The PVC pipe was inserted up to 20 cm into the soil at 12 different spots then the contents were emptied into plastic cylindrical containers of 250 g and transported to the laboratories for analysis. Sampling from these maize growing farms was done with the aim of obtaining representative samples for the region. Two main types of soil samples were taken; soil from farmlands which have seen at least 20 years of fertilizer application and land with no fertilizer application (Kiptuimet Primary School football pitch) which was used as the control site. Soil samples (2 spots) from Kiptuimet Primary School football pitch were termed as control soil (CS) while soil samples obtained from farm lands with 20 years of fertilizer application were termed as fertilizer amended soils (FAS). Samples from each spot of collection were divided into 3 groups. Fertilizer samples from frequently used brands namely; Di-ammonium phosphate (DAP), Urea and Calcium of Ammonium nitrate (CAN) were purchased from the nearby Kolongolo market for heavy metal content analysis. All the samples were air dried and crushed with a pestle and mortar, sieved through a mesh and kept in clean plastic containers before digestion.

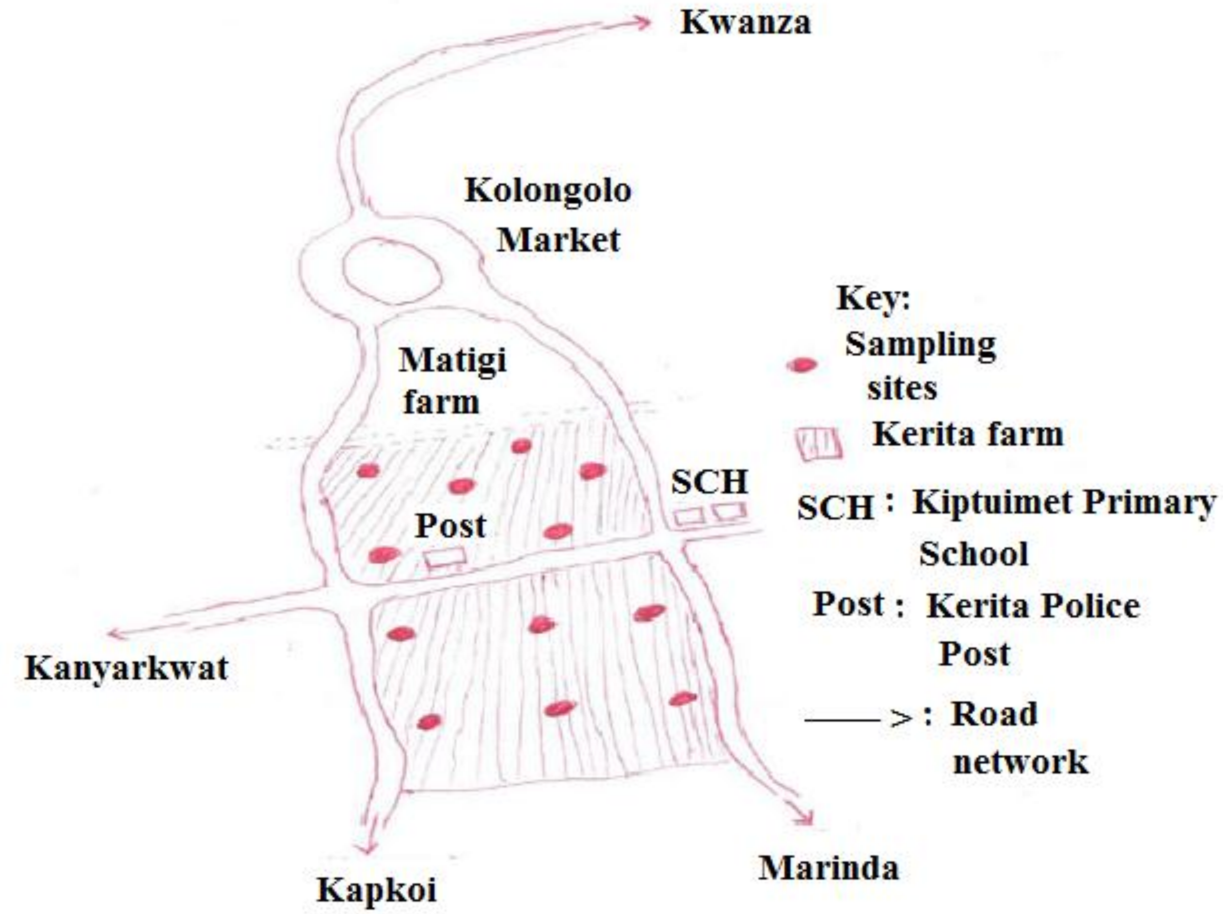

Figure 3.2: Sketch Showing the Map of the Sampling Area and Sampling Points.

3.3 Soil Characterisation

3.3.1 Determination of Soil pH

Samples of the soil were weighed and mixed with distilled water in the water to soil ratio of 1: 1 in the laboratory [Geotechnical Engineering Bureau, 2007]. The mixture was stirred to obtain slurry and then covered with watch glass. The sample was allowed to stand for a minimum of one hour, stirring every 10 to 15 minutes. This was to allow the pH of the slurry to stabilize. Soil pH was then measured using pH meter and the mean values of pH were calculated.

3.3.2 Determination of Soil Texture

Soil texture was determined using the Hydrometer Method for Particle Size Analysis [Milford, 1997]. Air-dry sample of soil was placed in a shaker bottle, weighed, its weight recorded and then transferred into the bottle. 50 grams of soil sample was used. 2.0 grams of sodium metaphosphate was added in order to break up any aggregates in the soil sample to ensure that smaller silt and clay particles do not bind to each other, allowing them to settle as if they were sand particles. Distilled water was added until the bottle was two-thirds full then the bottle capped and the sample shaken by hand for every few hours over a 2-day period. Soil moisture correction was done by weighing10 grams of soil then oven drying it for 24 hours at a temperature of 105 degrees C. Soil samples were re-weighed when it had slightly cooled and the following relationship was used for correcting the weight of soil added to the system:

$$MCF = 1 - [(AD - OD) \div AD] \quad \text{......} \quad (3.0)$$

Where: MCF = Moisture Correction Factor

AD = air-dry weight

OD = oven-dry weight

Soil samples were transferred from the bottle into a settling cylinder by rinsing remaining soil from bottle and capping into cylinder using distilled water from a wash bottle to remove all particles from the bottle with no loss. The cylinder was filled to the 1000 ml mark with distilled water, stopped, turned end-over-end several times and returned to upright position.

Time was recorded then the cylinder gently placed where it was stand for at least 2 hours undisturbed to avoid great temperature fluctuation of the sample. After 20 minutes hygrometer was inserted into the suspension gently and if foam persisted on the surface of the suspension, one or two drops of iso-amyl alcohol were added to break the surface tension. Hydrometer reading was taken exactly 40 seconds after the cylinder had been returned to an upright position as well as the temperature of the suspension using thermometer. This was repeated until a consistent hydrometer reading was obtained and the value was recorded on the table. The cylinder was allowed to sit undisturbed for 2 hours then hydrometer and temperature reading was taken after a settling for period of 2 hours which was recorded in the data table. Weight of Dry Soil shall be determined by the equation:

Weight of Dry Soil = Air-dry Soil x moisture correction factor (MCF)................................. (3.1)

Correcting Hydrometer Reading was done using the expression:

For temperatures above 20 degrees Celsius:

Hydrometer reading =Measured reading g/l + [(measured temperature – 20) x 0.36 g/l]…… (3.2)

For temperatures below 20 degrees Celsius:

Hydrometer reading =Measured reading g/l – [20 – (measured temperature) x 0.36 g/l]…… (3.3)

Finally, Sand, Silt and Clay Percent were determined as follows;

$$\%\ \text{clay} = \frac{\text{Corrected 2}-\text{hour hydrometer reading} \times 100}{\text{oven}-\text{dry weight of samples}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.4)}$$

$$\% \text{ sand} = \frac{\text{Corrected } 40-\text{second hydrometer reading } \times 100}{\text{oven}-\text{dry weight of soil}} \quad \ldots\ldots \quad (3.5)$$

$$\% \text{ silt} = 100 - \% \text{ sand plus clay} \quad \ldots\ldots \quad (3.6)$$

3.3.3 Determination of Total Organic Carbon by Wet Chemistry Technique

Potassium dichromate ($K_2Cr_2O_7$) and concentrated H_2SO_4 was added to 0.5 g of soil sample and the solution was gently boiled at 150 degrees Celsius for 30 minutes. Then the solution was swirled and allowed to cool as a result of the exothermic reaction when the potassium dichromate and sulphuric acids were mixed prior to addition of water to halt the reaction. Gentle boiling at a controlled temperature allowed complete oxidation of organic Carbon. After the solution had cooled, H_3PO_4 was added to the digestive mix so as to help eliminate interferences from the ferric (Fe^{3+}) iron that was present in the sample [Tiessen and Moir, 1993]. The chemistry behind this extraction procedure is as follows:

$$2Cr_2O_7^{2-}+3C+16H^+ = 4Cr^{3+} + 3CO_2 + 8H_2O. \quad \ldots\ldots \quad (3.7)$$

Manual titration was performed to determine the quantity of organic carbon present in the soil where Ortho-phenanthroline ferrous complex (commercially available as “Ferroin”) indicator solution was added to the digest [Nelson and Sommers, 1996]. Then the excess $Cr_2O_7^{2-}$ was titrated with ferrous ammonium sulphate [$Fe(NH_4)_2(SO_4)_2.6H_2O$] until colour in the sample changed from green to reddish brown.

3.4 Determination of selected Heavy Metals in the Samples

The fertilizer and soil samples were digested using the method of the Association of Official Analytical Chemists [AOAC, 1984]. A triplicate sample from each spot of 2.50 g was dissolved in 5-ml distilled water and 20ml of aquaragia (mixture of HNO_3 and HCl) in the ratio of 1.3. The mixture was digested in the hot plate for about 30 minutes and was filtered into a 50 ml volumetric flask using Whitman filter paper, grade 541. The residues were thoroughly washed with warm water and the volume adjusted with the distilled water to 50 ml. The digest obtained was analyzed for Cd, Cr, Pb, and Zn using an atomic absorption spectrophotometer.

3.5 Method Validation (Spiking Method)

The method of digestion and AAS analysis were validated by preparation of a multi- standard solution which was prepared from commercial available standards. A sample from a given sampling site was first digested, run through an AAS and metal contents in the unspiked sample were determined from the calibration curve. An aliquot of the multi-element standard solution was obtained using graduated pipette and used to spike a sample from the same sampling site. This was followed by the digestion of the spiked sample, aspiration and finally determination of metal contents from the calibration curve. The amount of spiked metal content recovered after the digestion of the spiked samples was used to calculate the percentage recovery. The readings of heavy metal concentrations were obtained from AAS in terms of absorbance which was later used to get their concentrations in ppm from the standard curve.

3.6 Preparation of the Standard Stock Solutions

3.6.1 Cr: 1000 mg ml^{-1}

1.000g of chromium wire (purity: 99.99%) was weighed and transferred into a beaker. The metal was dissolved in a minimum volume of 1:1(v/v) nitric acid. The solution was transferred into a1000 ml volumetric flask and diluted to the mark with distilled water. The solution was put in a polyethylene bottle and stored in a fridge.

Working conditions were set as follow:

Lamp current used was 7 mA together with Nitrous Oxide as the support gas. Acetylene was used as the fuel and the wave length was set as 357 nM. The detection limit of the chromium metal was set at 0.005 ppm

3.6.2 Cu: 1000 mg ml^{-1}

1.000g of copper metal (purity: 99.99%) was weighed and transferred into a 1000 ml volumetric flask containing minimum volume of 1.1 nitric acid to dissolve it. Then the flask was diluted to the mark with distilled water, transferred to the polyethene bottle and stored in a fridge.

Working conditions for copper analysis were set as follows:

The Support/oxidant gas used was air while the Lamp current was set at 3.0mA. Fuel used was acetylene while wavelength and detection limit were set at 324.7 nm and 0.003 ppm respectively.

3.6.3 Pb: 1000 mg ml^{-1}

1.000 g of lead metal (purity: 99.9%) was weighed and transferred into a 1000 ml volumetric flask containing minimum volume of 1.1 nitric acid to dissolve it. Then the flask was diluted to 1 litre with distilled water, transferred to the polyethene bottle and stored in a fridge.

Working conditions:

The Lamp current used was 8.0mA while the Support/oxidant was air. Acetylene was used as fuel,wavelength was set at 217.0 nm and the detection limit was 0.02 ppm.

3.6.4 Zn: 1000 mg ml^{-1}

1.000 g of zinc metal granules (purity: 99.99%) was weighed and dissolved in 40 ml 1.1 hydrochloric acid in a beaker. The solution was transferred in a 1000ml volumetric flask and diluted to 1 litre with distilled water, put in a polyethene bottle and stored in a fridge.

Working conditions for copper analysis were set as follows:

Lamp current used was set as 5.0mA, while the Support/oxidant used was air. The fuel used for zinc analysis was acetylene, wavelength and detection limit were set at 213.9 nm and 0.002ppm respectively.

3.7 Determination of Potassium (K_2O) in the Samples using the Flame Photometer

0.1 gram of the sample was weighed into a digestion tube. 20 ml of conc. HNO_3 to oxidize all the oxidizable matter in the sample and 30 ml of perchloric acid added to the sample. The sample was then covered and heated in the oven for up to 2 hours at a high temperature. The solution was cooled after digestion and transferred into a 250 ml volumetric flask and made up to volume with distilled water. A potassium standard and blank solution was prepared in the same way. The solutions were taken to the flame photometer for reading which were used to calculate the percent K_2O in the sample through the equation:

$$\%\,\mathrm{K} = \frac{\text{Reading} \times \text{volume of extract} \times 100}{\text{Weight of sample} \times 10^6} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.8)$$

The above calculation gives the concentration of potassium in its elemental K form. In order to calculate potassium in the oxide K_2O form, a conversion factor of 1.2 according to Ann McCauley *et al.* [2009] was used. Thus giving:

% K_2O = $\left(\frac{\text{Reading} \times \text{volume of extract} \times 100}{\text{Weight of sample} \times 10^{6}}\right) \times 1.2$ ……………………………………...(3.9)

3.8 Determination of Phosphorus (P_2O_5) using the UV-Visible Spectrophotometer

The technique is based on the principle of the Beer-Lambert law. Stock solution was prepared by diluting 140 ml of conc. H_2SO_4 with distilled warm (50°c) water to 1 litre; 12 grams of ammonium molybdate were dissolved in distilled water to 250ml in a 250 ml volumetric flask; 0.2908 gram of Antimony potassium nitrate was dissolved in 100 ml of distilled water; the three solutions were then mixed together and made to a volume of 2 litres solution with distilled water. The mixture was transferred to a reagent bottle and stored in a dark, cool place. 1.056 grams of Ascorbic acid were then dissolved in the 2 litre solution and mixed thoroughly. It was prepared on the same day of the analysis. Digestion of the samples and blanks were done in the digestion tubes with H_2SO_4 - salicylic acid - H_2O_2 and selenium. Sulphuric acid and selenium powder mixture was prepared by dissolving 3.5 g of selenium powder in 1 litre of Sulphuric acid (concentrated) followed by heating to about 300°c until the colour turns from black via green, blue to clear yellow. 3.2 g of Salicyclic acid was dissolved in 100ml of sulphuric acid-selenium mixture to make the digestive mixture which should not be stored for more than 48 hours.

The sample (0.1 g) was weighed into a digestion tube, 3ml of digestion mixture added to the tube and the reagent blanks and then digested at 110°C for 1 hour. The contents of the digestive tube were cooled and three-successive portions of hydrogen peroxide were added followed by continued heating at the temperature of 330°C. 25 ml of distilled water was added to the mixture then mixed well, cooled and made up to 250 ml with water. An aliquot of 2 ml was taken from the 250 ml solution into a 50 ml volumetric flask and 10 ml of distilled water added. A drop of paranitrophenol solution was added and drops of NH_3 solution added until the solution turn yellow; at this point a neutralization point had been reached. 8 ml of stock solution was then added for colour development which was read with a calorimeter at 400 nm wavelength setting. Amount of phosphorus present in the samples were read off from a calibration curve.

A blank and a standard were prepared in the same way as the sample just that the blank did not contain the analyte of interest. Phosphorus standard solution (1000 ppm P) was prepared by weighing 1.0982 g of oven-dried $K_2H_2PO_4$ which was dissolved in distilled water and made up to 250 ml. 10 ppm P working solution was prepared by diluting 10 ml of 1000 ppm P solution to 1 litre with distilled water. Calibration curve was obtained from the standard solutions by pipetting 0, 5,10,15,20, 25,30,35,40 and 45 ml of standard 10 ppm P into 50 ml volumetric flasks. They were treated in the same as the samples and the following readings were obtained: 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9 ppm P. The reading from the blank was used to eliminate background readings (Okalebo,Gathua, and Woomer,2002).

The calculation for determining phosphorus (P) is:

$$\% \text{ P} = \left(\frac{\text{Reading} \times \text{volume of extract} \times 100}{\text{Weight of sample} \times \text{aliquot} \times 10^6}\right) \ldots\ldots (3.10)$$

The above calculation gives the concentration of the phosphorus in its elemental form. In order to determine the value of phosphorus in the P_2O_5 form, a conversion factor of 2.3 according to the method by McCauley et al. [2009]:

$$\% \; P_2O_5 = \left(\frac{\text{Reading} \times \text{volume of extract} \times 100}{\text{Weight of sample} \times \text{aliquot} \times 10^6}\right) \times 2.3 \;\ldots\ldots \quad (3.11)$$

Where Volume of extract = 250 ml; Aliquot= 2 ml; Weight of sample = 0.1gram; Reading = reading from the UV/Visible spectrophotometer.

3.9 Total Nitrogen Analysis by Kjeldahl Method

0.1 gram of the samples was weighed into a Kjeldahl digestion flask and 3 grams of Devarda's alloy (consisting of 50% Cu, 45% Al and 5% Zn) were added to the samples to reduce the NO_3^- into NH_3 in an alkaline condition. One tablet of a Kjeldahl catalyst (containing $CuSO_4$ to accelerate digestion and K_2SO_4 to raise the boiling point of the acid so that loss of acid by volatilization is prevented) was added. 10 ml of H_2SO_4 was then added to the sample in the flask and heated in the digestion unit for two hours at a temperature of 350 °C till sample was totally digested to convert any organic nitrogen into $(NH_4)_2SO_4$. The digestion temperature and time was very important since at lower temperatures below 300 °C, the digestion may not had completed, while at higher temperatures above 410 °C, loss of NH_3 may had occurred. Distilled water was then added to the digested sample solution and transferred into a 50ml volumetric flask and made to volume. A 5 ml aliquot was pipetted from the 50 ml solution into a distillation flask and 10mls of 40% sodium hydroxide (NaOH) added to the solution in the flask. The $(NH_4)_2SO_4$ in the solution was converted to NH_4OH. 5ml of the resulting solution was distilled off into a receiving flask containing 5 ml of 2% boric acid (H_3BO_3) using methylene blue - methyl red indicator until the purple colour of the boric acid changed to blue. At this stage, it was evidence that NH_3 had been trapped.

The blue boric acid- ammonia solution was then titrated against 0.01M HCl solution until the colour of the boric acid solution changed back to purple. The volume was recorded and the process repeated one more time.

A blank determination was run by treating the reagents as the sample while the distillation recovery was done by taking an aliquot of 5.0 ml of standard ammonium sulphate solution in place of the sample.

The mean titre was calculated and used to determine the Total Kjeldahl Nitrogen (TKN) as follows:

$$\% \text{ N} = \left(\frac{\text{N} \times \text{titre} \times 0.014 \times \text{volume of extract} \times 100}{\text{Weight of sample} \times \text{aliquot taken}} \right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.12)}$$

Where N= molarity of HCl = 0.01; Volume of extract = 50 ml; Weight of sample = 0.1 grams; Aliquot taken = 5 ml; 1 ml of 0.01M HCl = 0.014 grams.

3.10 Determination of Phosphorus Retention Capacity by the Soil

Phosphorus adsorption study was carried out according to standard procedure Nair *et al.*, [1984]. 2.5 gram of air dried soil that was passed through a 2mm sieve into a 50ml centrifuge was weighed into series of 50 ml plastic bottles into which twenty five millilitres of solution containing 0, 5, 10, 20, 30, 40, 50 and 100 ppm P was added. Three to four drops of toluene were added to the solutions to inhibit microbial activity. Each soil series was replicated three times. Volumetric flasks from 500 ppm P stock solutions of oven dried KH_2PO_4 and the volume was made up with distilled water and the bottles capped tightly. The soil and phosphorus solution in bottles was equilibrated by shaking for 24 hours then centrifuging at 500 rpm for 15 minutes and finally the soil suspension was filtered through 0.045µm filter paper. 10 ml aliquot of clear filtrate was analysed for P by using the method of Murphy and Riley, [1962]. Absorbance was determined at a wavelength of 880 nm using spectrophotometer. The concentration of original P solution was determined from the standard P curve. The difference between the quantity of phosphate in solution after shaking with soil and the quantity initially present was calculated as the quantity of P adsorbed by the soil in µg g^{-1}. Corrections for reagent blank values from blank analysis were made and the data obtained from the phosphate adsorption experiment were inserted to the Langmuir adsorption model:

$$\frac{c}{x/m} = \frac{1}{kb} + \frac{c}{b} \quad \text{.......} \quad (3.13)$$

where x/m is the amount of P sorbed per unit soil mass in (mg kg^{-1})

c is the equilibrium solution concentration of P,

b *is* adsorption maximum,

k is a constant related to the binding energy.

A plot of $\frac{c}{x/m}$ against the equilibrium P concentration (c) gave a slope whose reciprocal is the adsorption maxima equation;

The Langmuir model has advantages in comparison to Freundlich's, as it provides more information on P sorption parameters Nair *et al.*, [2000]. It assumes that adsorption occurs at specific sites and that once these sites are occupied no further adsorption occurs.

3.11 Data Analysis

Data entry management and preliminary summaries were done on MS Excel spread sheet. The means, ranges and standard deviations of the data collected was determined using Microsoft Excel. Experimental treatment significant differences ($\alpha < 0.05$) were determined using Levene's test for equality of variance and student t tests for equality of means. Linear correlations were determined using the Pearson product-moment correlation. All statistical analyses were performed using SPSS v16 version software programme.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Characterization of Soil from Kerita Maize Farm and Kiptuimet Primary School Football Pitch

4.1.1 Determination of Soil pH

Soil pH in soil samples from Kerita maize farm field and control site at different sampling points were determined as shown in Table 4.1. Maize farm soil recorded a pH that ranged from 4.74.8±0.37 to 5.54.8±0.42, while the pH for control site ranged from 6.2±0.66 to 6.5±0.48 (Table 4.1). Maize farm soil recorded the lowest pH at FAS6 with a pH of 4.74.8±0.37 while the control site recorded its low at CS1 with a pH of 6.2±0.66. In Kerita maize farm field the highest pH was recorded at FAS5 with a pH of 5.54.8±0.42 while in the control site the highest pH recorded at CS1 with a pH of 6.5±0.48.

The total mean soil pH for maize farm soil from the 12 (twelve) sampling points and the two sites from the control field was recorded and observed that Kerita maize farm soil was more acidic with an average pH of 5.035± 0.25 as compared to the control site which recorded a total average pH of 6.35±0.21. A *t* test reveal a statistically reliable significant difference between the mean concentration of pH that the maize farm soils had (M = 5.034, s = 0.25) and that the control site soil had (M = 6.35, s = 0.21), $t(12) = 6.99$ at $p = 0.001$ and $\alpha = 0.05$ as shown in Table 4.2. However, both the two sites had generally a low pH of less than 7.0. The low pH for both fields was attributed to the composition of the parent rock from which the soils were formed and inherent factors affecting soil pH such as climate, mineral content and soil texture which cannot be changed.

The decrease in soil pH in maize farm soils as compared to the adjacent control site was attributed to fertilizer application, which was in agreement with Nartey et al., [2012] who observed that fertilizer applied soils have generally lower pH than natural soils and concluded that fertilizer tends to lower soil pH due to the nitrates and phosphates content and therefore may influence heavy metal levels in fertilizer applied soils. Quansah, [2010] also noted a significant decrease in soil pH when measured after soil treatment with fertilizers. In his study, Quansah, 2010 observed that the soil pH before the application of fertilizers ranged from 5.34 to 6.95 and the soil pH range after fertilizer application and plant harvest was between 4.64 to 5.95, indicating an increase in soil acidity. In this study, since the soil samples were collected and pH measurement done after maize harvest, the low pH observed could be in agreement with what was observed by Quansah in 2010. Omwoma et al.[2010] and Manoharan, [1997] further reported that different fertilization treatments leads to reduce soil pH to different extents, dependent on type of the fertilizer as well as type of soil.

Soil pH has an effect on the availability of fertilizer nutrients to plants. Soil pH levels that are too high or too low lead to deficiency of many nutrients, decline in microbial activity, decrease in crop yield, and deterioration of soil health [McCauley *et al*., 2009]. Cornell University, extension education Center, New York, 2008 reported that if the pH is 4.5, about 75% of applied fertilizer nutrients may be unavailable to plants, if the pH is 5, about 54% of applied fertilizer nutrients may be unavailable to plants, if the pH is 5.5, about 33% of applied fertilizer may be unavailable to plants, if the pH is 6.0, about 20% of applied fertilizer may be unavailable to plants and if the pH is 7.0, about 0% of applied fertilizer should be unavailable to plants. Therefore, from the results obtained with the total average soil pH of 5.035± 0.25 for the Kerita farm soil, about 54% of applied fertilizer applied to the soil may be unavailable to plants at Kerita maize farm field.

Table 4.1: pH (mean ± SD mg kg-1 of dry weight) of Soil from Sample Points in Kerita Farm and Control Site.

Site	**pH**
FAS1	4.88±0.33
FAS2	5.0±0.37
FAS3	4.94±0.42
FAS4	5.38±0.29
FAS5	5.54±0.42
FAS6	4.74±0.37
FAS7	4.94±0.50
FAS8	4.74±0.62
FAS9	5.14±0.57
FAS10	5.24±0.65
FAS11	4.84±0.14
FAS12	5.04±0.73
CS1	6.2±0.66
CS2	6.5±0.48
Mean (FAS)	**5.034±0.25**
Mean (CS)	**6.35±0.21**

Sample Size (n) = 14.

Table 4.2: Levene's Test for Equality of Variances and t-test for Equality of Means for pH between Maize Farm Soils and the Control Site.

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
pH	Equal variances assumed	.174	.684	-6.993	12	.000	-1.31500	.18805	-1.72474	-.90526
	Equal variances not assumed			-7.905	1.505	.033	-1.31500	.16634	-2.31103	-.31897

Where: F= F- test value

Sig= significance of F- test

t = t-test value

df= degree of freedom associated with t-test

As the soil pH decreases below 5.5, the availability of aluminum and manganese increase and may reach a point of toxicity to the plant. Excess aluminum in the soil solution interferes with root growth. The decrease in soil pH due to fertilizer application is attributed to the process of nitrification which occurs in steps. In the first step of nitrification, ammonia-oxidizing bacteria oxidize ammonia to nitrite according to the following equation:

$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$.. (4.1)

Nitrosomonas is the most frequently identified genus associated with this step.

In the second step of the process, nitrite-oxidizing bacteria oxidize nitrite to nitrate according to the following equation:

$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$.. (4.2)

Nitrobacteria are the most frequently identified genus associated with this second step.

Hydrogen (H^+) is released in the process of nitrification, and free hydrogen ions increase the acidity. The higher the percentage of ammonium (or urea) in the fertilizer, the greater the acidification potential.

Another reason that NH_4^+ increases acidity has to do with plant uptake. As plant roots absorb NH_4^+ they secrete H^+ ions into the soil solution to maintain a chemical charge balance.

Therefore, Urea (46% N) and Ammonium nitrate (34% N) products frequently used in Kerita farm soils are acidifying because they contain ammonium, or produce ammonium when applied to the soil. But they are less acidifying than Di-Ammonium Phosphate (DAP).

When anhydrous ammonia (NH_3) is applied to the soil, it reacts with water to form ammonium-N and the hydroxide ion, which is basic.

$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$.. (4.3)

This reaction initially raises the pH of the soil. It is only after the $NH4^+$ undergoes nitrification that it begins to acidify the soil (through the release of H^+). These two reactions (the basic effect of ammonia reacting with water vs. the acidifying effect of nitrification) don't entirely balance each other out. The end result is an acidifying effect.

Urea is less acidifying than DAP because in soil solution, urea first reacts with water and free H+ ions to form ammonium and bicarbonate.

$CO(NH_2)_2 + 2H_2O + H^+ \rightarrow 2NH_4^+ + HCO_3^-$ ....(4.4)

This reaction is immediately followed by another reaction that takes H^+ ions out of soil solution:

$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$.. (4.5)

Both these reactions "soak up" free H^+ ions in soil solution, which reduces acidity. This reduction in acidity is more than balanced out by the acidifying reaction of the nitrification of ammonium. As with anhydrous ammonia, the overall net effect is acidifying. Therefore farmers are recommended to avoid these acidifying inorganic fertilizers and start using the less acidifying inorganic ones or the organic fertilizers such as compost manure or farmyard manure.

4.1.2 Determination of Soil Texture

From the fourteen collected soil samples, four different textural soil classes (Sandy Clay Loam, Sandy Clay, Silty Clay loam and Clay) were identified and allocated based on percentage of particle size (Table 4.3). All the four different textural soil classes were detected in Kerita maize farm soils while the control site had only Sandy Clay soil type. Comparing Tables 4.1 and 4.3 there was no relation observed between soil texture and soil pH. Also in the four textural soil classes, there was no pattern that clearly related soil texture and the heavy metal concentrations.

Table 4.3: Soil Texture Classes Observed In Kerita and Control Sites.

Site	**Soil Texture**			
	% Sand	**% Clay**	**% Silt**	**Textural Class**
FAS1	64	26	10	Sandy Clay Loam
FAS2	59	32	9	Sandy Clay Loam
FAS3	50	46	4	Sandy Clay
FAS4	48	44	8	Sandy Clay
FAS5	33	47	20	Clay
FAS6	30	51	19	Clay
FAS7	12	36	52	Silty Clay Loam
FAS8	29	42	29	Clay
FAS9	36	45	19	Clay
FAS10	39	53	8	Sandy Clay
FAS11	62	24	14	Sandy Clay Loam
FAS12	54	21	25	Sandy Clay Loam
CS1	50	46	4	Sandy Clay
CS2	39	55	6	Sandy Clay

Sample Size (n) = 14

4.1.3 Soil Total Organic Carbon

Total organic carbon was analysed and recorded in Table 4.4. Total organic carbon in Kerita farm soils ranged from 0.97% to 1.2%. A low total organic Carbon of 0.97% at site FAS2 and a high total organic carbon of 1.2% at FAS1 were observed. On the other hand, TOC for the control site ranged from 0.91% to 0.92% with the lowest total organic carbon of 0.91% at CS2 and its high of 0.92% at CS1. Overall, there was a low total organic carbon in both the maize farm and the control site soils. The results showed that FAS soils had a mean TOC of 1.11±0.87% while CS soil had a mean of 0.915±0.01%. A *t* test revealed a statistically significant difference between the mean concentration of Total Organic Carbon that the maize farm soils had (M = 1.11, s =

0.87) and that the control site soil had (M = 0.915, s = 0.01), *t*(11.7) = 7.696 at *p* = 0.001 and α = 0.05 as shown in Table 4.5. This was in agreement with Hoyle and Paterson [2011] who reported that some sites in south Western Australia showed a significant increase in the level of soil organic carbon when converted to agricultural land. Anke and co-workers [2013] also noted that long-term fertilization significantly influenced total organic carbon concentrations and storage in southwest China and that long-term chemical fertilizer alone can increase soil total organic carbon sequestration. Similar results to this study were also observed by Johnson *et al*. [1998] in Oklahoma where soil total organic Carbon increased with increasing Nitrogen fertilization applied at three of the four sites which was consistent with work by Blevins *et al*. [1983] and McAndrew and Malhi [1992] who demonstrated increases in soil total organic Carbon with increasing Nitrogen applied.

Clay textural soil had higher total organic carbon compared to sandy clay loam, silty clay loam soils and sandy clay. Milne (2012) observed that soil texture affects TOC because of the stabilizing properties that soil with more clay has on organic matter. Organic matter is trapped in the very small spaces between clay particles making them inaccessible to micro-organisms and therefore slowing decomposition. In addition, clay offers chemical protection to organic matter through adsorption onto clay surfaces, which again prevents organic matter from being decomposed by bacteria. Soils with high clay content therefore tend to have higher soil organic carbon (SOC) than soils with low clay content under similar land use and climate conditions. As clay acts to physically protect soil organic carbon from decomposition, soils with high clay contents are capable of holding more soil organic carbon than those with low clay contents like sands [Hoyle and Paterson, 2011].

Table 4.4: % TOC of Dry Weight in Soil from Kerita Farm and Control Site.

Site	**%** TOC
FAS1	1.2
FAS2	0.97
FAS3	1.01
FAS4	1.08
FAS5	0.99
FAS6	1.06
FAS7	1.22
FAS8	1.14
FAS9	1.17
FAS10	1.19
FAS11	1.17
FAS12	1.15
CS1	0.92
CS2	0.91
Mean (FAS)	**1.11±0.87**
Mean (CS)	**0.915±0.01**

Sample Size (n) = 14

A *t* test reveal a statistically reliable difference between the mean percentage of total organic carbon from the maize farm soils which has (M =1.11, s =0.87) and that of the control site soil which has (M =0.91, s = 0.01), *t* (11.685) =7.96, *p* = 0.000, α = .05 as shown in Table 4.5. The higher levels of total organic carbon in farm soils as compared to control site could be attributed to the cultivation of maize crop as well as application of fertilizers which increases carbon sequestration.

Table 4.5: Levene's Test for Equality of Variances and t-test for Equality of Means for TOC between Maize Farm Soils and the Control Site

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	T	Df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
TOC	Equal variances assumed	6.635	.024	3.097	12	.009	.19750	.06378	.05854	.33646
	Equal variances not assumed			7.696	11.685	.000	.19750	.02566	.14142	.25358

Where: F= F- test value

Sig= significance of F- test

t = t-test value

df= degree of freedom associated with t-test

The results of analysis of correlation between soil pH and Total Organic Carbon are shown in Table 4.6. A correlation coefficient of -0.685 was established, which suggest a small negative correlation between soil Total Organic Carbon and the soil pH which was in agreement with Duinker et al. (1982), who indicated that apart from fertilizers playing a great role in pH reduction, the soil total organic carbon content in soil could also contribute to lowering of the soil pH.

Table 4.6: Coefficient of Correlation between TOC and pH in Soil Samples.

		TOC	pH
TOC	Pearson Correlation	1	-0.685**
	Sig. (2-tailed)		0.007
	N	14	14
pH	Pearson Correlation	-0.685**	1
	Sig. (2-tailed)	0.007	
	N	14	14

** Correlation is significant at the 0.01 level (2-tailed).

Pearson product-moment correlation is useful when finding the relationship between two or more normally distributed interval variables.

Where: Sig(2-tailed) is the significance of the pearson correlation

N = sample size

4.2 Nitrogen, Phosphorus and Potassium Concentration in Major Fertilizers Used In Kerita Farm

Primary macronutrients in major fertilizers used in Kerita farm were analysed. The fertilizers included Di-ammonium Phosphate (DAP), Urea and Calcium of Ammonium Nitrate (CAN). The results were tabulated in Table 4.8.

Table 4.7: Phosphorus (P) Standards.

Standards	Concentration(ppm)	Absorbance
A	0	0
B	5	1
C	10	2
D	15	3
E	20	4
F	25	5
G	30	6
H	35	7
I	40	8
J	45	9

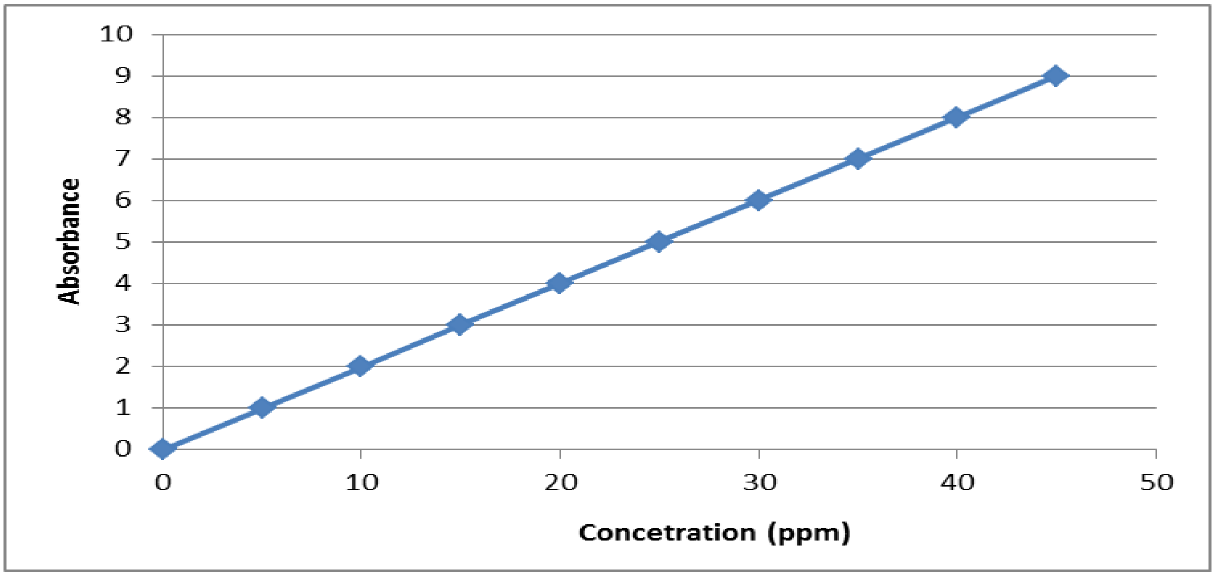

Figure 4.1: Phosphorus (P) Calibration Curve.

Table 4.8: N P K Concentrations (Mean ± SD mg/ Kg of Dry Weight) In Major Fertilizers Used For Growing Maize at Kerita Farm.

Site	**% P_2O_5**		**%K**		**%N**	
	Observed	**Expected**	**Observed**	**Expected**	**Observed**	**Expected**
UREA	0	-	0	0	43.8	46
CAN	0	-	0	0	16.5	26
DAP	66.7	46 – 54	0	0	20.3	18 – 21

Concentrations of primary macronutrients in this study were not in agreement with labelled contents reported by producers despite fertilizer laws requiring product registration and/or licensing to assure that statements made on the label are correct.

Regardless of the name, fertilizers are labelled according to the relative amounts of each of these three primary macronutrients by weight (i.e., mass fraction). Thus the DAP fertilizer selected had a label of 18−46−0 fertilizer grade which was supposed to contain, by weight, 18% nitrogen (N), 46% phosphorus (P), and 0% potassium (K). However Phosphorus content in DAP fertilizer sample was 66.7% a value that was higher than the standard requirement for DAP fertilizers composition of 46% - 54%. Nitrogen content in DAP fertilizer sample of 20.3% was within the standard requirement for fertilizers composition of 18% - 21% and Potassium content in DAP fertilizer met the recommended requirement composition of 0%.

Urea fertilizer selected had been labelled 46%N, but the measured Nitrogen content in Urea fertilizer sample was 43.8%N a value that was slightly below the minimum standard requirement for fertilizers composition of 46%N but the Potassium and phosphorus contents in Urea fertilizer met the recommended requirement composition of 0%. Nitrogen content in CAN fertilizer sample was observed to be 16.5%, a value below the minimum standard requirement for fertilizers composition of 26%N. These findings of concentrations of major elements in this study are in agreement with Otero *et al*. [2005] who observed discrepancies in NPK fertilizers that in his study; the P contents in NPK was lower than those labelled contents reported by producers, but they were in contrast with Sheriff *et al*. [2012] who investigated validity of specifications indicated by manufacturers on their fertilizer products in Ghana and found out that there was generally good agreements (98% and above) between the measured values and the certified values for the primary macronutrients nitrogen, phosphorus and potassium (N, P and K). Absence of potassium in all the major fertilizers analyzed was attributed to an old belief that soils in Kenya have sufficient amounts of potassium and would not benefit from Potassium fertilizers [Hinga and Foum, 1997; Muchena, 1974].

Sheriff et al. [2012] noted that Replenishing soil fertility with fertilizers does not just solve the problem of soil infertility and it is therefore important that, the right amount of nutrients are added to the soil since under application of nutrients may slow plant growth and excess fertilizer application may lead to situations such as fertilizer burns in crops resulting in a drying out of the roots and damage or even death of the plant, and further cause problems to the environment.

The problem of fertilizer quality in Kenya was traced back in 1974 [Takashi and Ayumi, 2010]. From 1974 to 1984, a state parastatal, the Kenya Farmers Association (later Kenya Grain Growers Cooperative Union), had significant control over fertilizer procurement and domestic distribution. As a result, the Kenyan government had extensive controls over imports, pricing, and marketing of fertilizer using policy instruments such as price subsidies, price control, licensing of importers and distributors, and import quotas (Freeman and Kaguongo, 2003). Since the mid1980s, however, the government encouraged private firms to enter the market, even though it maintained tight controls over the market in the beginning [Jayne *et al*., 2002]. Because of uncertainty about possible government interventions, private firms were reluctant to enter the fertilizer market. In 1993, the government finally withdrew from the fertilizer market and therefore today most of the fertilizers are imported and the major importers of inorganic fertilizers into Kenya are private companies from different countries.

Despite the government withdrawing from fertilizer import control, mechanisms were put in place for quality control which ensures that once a trader imports fertilizer destined for local market, the product is inspected at the point of loading and as well at the point of unloading. Once declared appropriate, the importer is issued with Certificate of Conformity. At the point of entry, for example, Mombasa port the imported fertilizer is subjected to local standards as prescribed under World Trade Organization to minimise the risk of unsafe and substandard goods entering Kenya market, thus ensuring health, safety and environmental protection for Kenyans but dubious dealers and shopkeepers are selling fertilizer that is unsuitable for crop application by misusing the commodity through re-packaging of the fertilizer and poor storage. Stockist and shopkeepers in some cases meddle with the product by either mixing the original content with other commodities such as salt and chalk. This is due to unsound monitoring mechanism up-to the farmer level and lack of sound regulatory framework and weak legislation. Fertilizers and animal Feeds Act Cap 345 lacks tough penalties to anyone found selling substandard commodity to farmers among other misconducts [Ministry of Agriculture, 2013].

4.3 Nitrogen, Phosphorus and Potassium Concentration in Soil Samples from Kerita Farm and the Control Site

Primary macronutrients Nitrogen, Phosphorus and Potassium were analysed and the results recorded in Table 4.9. Concentration of phosphorous level in the maize farm soil ranged from 35 ppm to 44 ppm with the highest concentration of 44 ppm at FAS4 and the lowest concentration of 35 ppm at FAS5 while Concentration of phosphorus level in the control site was at 15 ppm. Amounts of Phosphorus required vary from plant to plant [Quansah, 2012]. The 35 ppm-44 ppm range was regarded as adequate phosphorus levels in for maize growth [KARI, 2013].

Table 4.9: N, P and K concentrations (mean ± SD mg kg^{-1} of dry weight) in soil samples from Kerita farm and the control site.

Site	P ppm	%K	%N
FAS1	40	0.6	0.12
FAS2	36	0.42	0.1
FAS3	41	0.55	0.1
FAS4	44	0.64	0.11
FAS5	35	0.48	0.1
FAS6	38	0.59	0.12
FAS7	42	0.44	0.1
FAS8	35	0.65	0.12
FAS9	39	0.51	0.11
FAS10	40	0.64	0.11
FAS11	39	0.52	0.11
FAS12	43	0.48	0.11
CS1	15	1.16	0.12
CS2	15	1.14	0.12
Mean (FAS)	**39.33±2.96**	**0.54±0.08**	**0.109±0.01**
Mean (CS)	**15.00±0.00**	**1.15±0.01**	**0.12±0.00**

Sample Size (n) = 14

A *t* test reveal a statistically reliable difference between the mean concentration of phosphorus that the maize farm soils had (M = 39.33, s = 2.96) and that the control site soil had (M = 15, s = 0.0), *t*(12) = 11.23 at significance of *t test (p)* = 0.001 and confidence level of the study(α) = 0.05 as shown in table 4.10. The significant difference of phosphate in the two study areas was attributed to phosphate fertilizers that have been applied to maize farm soil for more than 20 years. Abo *et al*. [1995] associated the increase in available Phosphorus in the soil to application of phosphate fertilizers. However the effect of the fertilizers on soil phosphorus varied from one soil to another. Once phosphorus is built to a good level after fertilizer application, that level would remain for many years without any additional phosphorus input. The reason is that phosphorus is less soluble in water and leaching is minimal [Hue and Silvia, 2000]. It is estimated that as much as 90 % of added fertilizer phosphorus is fixed in soils (Potash and Phosphate Institute, 2003) and made unavailable to plants. Quansah, [2012] noted a significant increase in soil phosphorus when measured after crop harvest and before, that is the soil phosphorus range before the application of treatments was lower than the soil phosphorus range after harvest, indicating an increase in soil available phosphorus after harvest. Addition of Phosphorus to the soil year after year, builds up P in soil. This could be the reason why the concentration of phosphorus was higher than nitrogen and potassium at Kerita farm soils.

Table 4.10: Levene's Test for Equality of Variances and t-test for Equality of Means for NPK between Maize Farm Soils and the Control Site

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
Pppm	Equal variances assumed	3.574	.083	11.225	12	.000	24.33333	2.16773	19.61024	29.05642
	Equal variances not assumed			28.435	11.000	.000	24.33333	.85576	22.44982	26.21685
K	Equal variances assumed	4.656	.052	-10.307	12	.000	-.60667	.05886	-.73491	-.47842
	Equal variances not assumed			-24.011	11.211	.000	-.60667	.02527	-.66215	-.55118
N	Equal variances assumed	3.155	.101	-1.868	12	.086	-.01083	.00580	-.02347	.00180
	Equal variances not assumed			-4.733	11.000	.001	-.01083	.00229	-.01587	-.00580

Where: F= F- test value

Sig= significance of F- test

t = t-test value

df= degree of freedom associated with t-test

Phosphorus is a structural component of DNA and RNA, the two genetic entities that are essential for the growth and reproduction of living organisms. Living organisms whether plants or humans, also derive their internal energy from Phosphorus containing compounds mainly adenosine diphosphate (ADP) and adenosine triphosphate (ATP). This means that inadequate phosphorus supply will result in a decreased synthesis of RNA, the protein maker, leading to depressed growth (Hue and Silvia, 2000). Phosphorus-deficient plants, therefore, are stunted with a limited root system and thin stems. In many plants, seedlings look stunted and older leaves may turn purple because of the accumulation of anthocyanins or purple pigments. The plants may produce only one small ear containing fewer, smaller kernels than usual. Grain yield is often severely reduced (Jones et al., 2003). Plants concentrate phosphorus in the seed, which is usually harvested. The stem leaves and roots of a mature crop tend to be lower in phosphorus and contribute only a small part of the next crop's phosphorus requirements.

Total Nitrogen in farm soil ranged from 0.11% to 0.12% while in the control site the total nitrogen was 0.12% with an overall mean of 0.109±0.01 and 0.12±0.00 between the farmlands and the control site indicating lower total nitrogen in farm soil as compared to the control site. A *t* test did not reveal a statistically reliable significant difference between the mean concentration of total nitrogen that the maize farm soils had (M = 0.109, s = 0.01) and that the control site soil had (M = 0.12, s = 0.0), $t(12) = 1.87$ at $p = 0.086$ and $\alpha = 0.05$ as shown in table 4.10 contrary to this works expectation of an increase in total nitrogen after inorganic fertilizer application. Total nitrogen percentage concentration in the Kerita farm soil was regarded as low since it fell within the range of 0.05%-0.11%, which is normally regarded as low for maize production [Okalebo et al., 2002]. Values from the control soil samples were regarded as normal since it fell in the normal range of 0.12%-0.25%. Chen et al., 2006 and Fu et al., 2000 obtained similar results where Total Nitrogen contents in the uncultivated farmlands were higher compared to those in the farmland and concluded that Total nitrogen contents could be expected to increase significantly after the farmland had been abandoned for ten years and that application of inorganic fertilizer alone is not sufficient to maintain level of nutrients under conditions of conventional management in which no aboveground crop residues are returned to the soil.

Potassium in farm soil ranged from 0.42% to 0.65%, while in the control site the potassium concentration was between 1.14% and 1.16%. A *t* test reveal a statistically reliable difference between the mean concentration of Phosphorous that the maize farm soils had (M = 0.54, s = 0.08) and that the control site soil had (M = 1.15, s = 0.14), *t* (12) = 10.31 at *p* = 0.001 and α = 0.05 as shown in table 4.10. Maize farm had lower mean concentration of 0.5433±08% as compared to the control site that had a mean concentration of 1.15±0.14%. The difference was in agreement with studies by Nandwa, [1988], ICRAF, [1995], and Kanyanjua and Buresh, [1999] which showed that intensively cropped soils have developed potassium deficiency, in contrast to an old belief that soils in Kenya have sufficient amounts of potassium and would not benefit from potassium fertilisers [Hinga and Foum, 1997; Muchena, 1974].

Potassium is needed in large quantities by many crops as indicated by Hue and Silvia, (2000). It is required for maintaining the osmotic potential of cells and turgidity of plants. Since Potassium regulates the osmotic potential of cells, and the closure or opening conditions of stomata, it plays an important role in water relations in the plant. Potassium is involved in water uptake from the soil, water retention in the plant tissue, and long distance transport of water in the xylem and of photosynthates in the phloem (Marschner, 1995).

Potassium affects cell extension. With adequate potassium, cell walls are thicker, thereby improving plant resistance to lodging, pests and diseases (Bergmann, 1992). Fruits and vegetables grown with adequate Potassium seem to have a longer shelf life. Consequently, Potassium deficient plants show low resistance to diseases and their seeds and fruits are small and shriveled (Prevel, 1989; Perrenoud, 1993). In maize, the maturity is delayed and ears are smaller when potassium is deficient. The stalks are weak and lodging is common. The most visual potassium deficiency symptom is the scorching or firing along leaf tips and margins (Bergmann, 1992; Perrenoud, 1993; Singh and Trehan, 1998).

4.4 Quality Assurance

Spiking, digestion and analysis of the heavy metals were done in triplicate Results of the recoveries of spiked soil samples are given in Table 4.11. Percentage recoveries obtained for the metals under investigation (Cr, Pb, Zn, Cu and Cd) varied between 91.25 ± 3.26 % and 99.5± 0.14 %. Acceptable recoveries were obtained in all cases, which shows that the digestion method used for soil samples and AAS analysis were reliable.

Table 4.11: Percentage recoveries of heavy metal from spiked soil (mean ± SD).

Trace metal	Spike level	Expected concentration in spiked samples	Observed concentration in spiked samples	% recovery ±SD
Cr	30 mL of (1.8mgL^{-1} of Pb and Cd, 5 mgL^{-1} of Zn and Cr) and 3mg L^{-} of Cu standard solutions	5	4.985	99.5± 0.14 %
Pb		1.8	1.74	96.2 ±2.82%
Zn		5	4.68	93.68± 2.37%
Cu		3	2.78	92.69±1.93%
Cd		1.8	1.64	91.25±3.26%

Table 4.12: Copper (Cu) Standards.

Standards	Concentration(ppm)	Absorbance
A	0	0
B	0.5	0.061
C	1	0.123
D	1.5	0.184
E	2	0.242

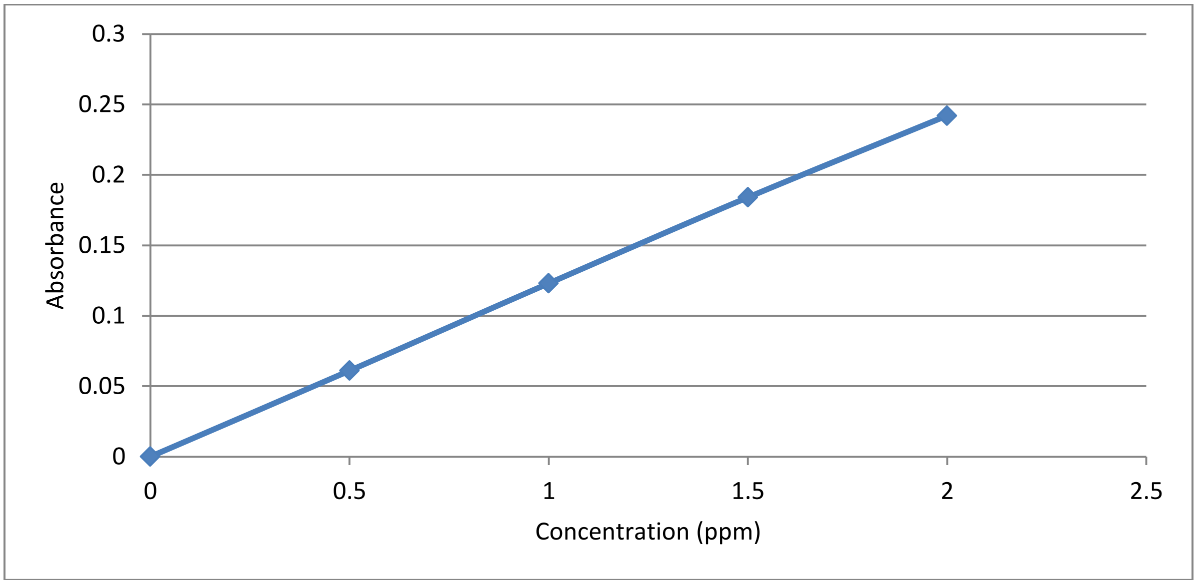

Figure 4.2: Copper (Cu) Calibration Curve.

Table 4.13: Cadmium (Cd) Standards.

Standards	Concentration(ppm)	Absorbance
A	0	0
B	0.5	0.106
C	1	0.214
D	1.5	0.322
E	2	0.42

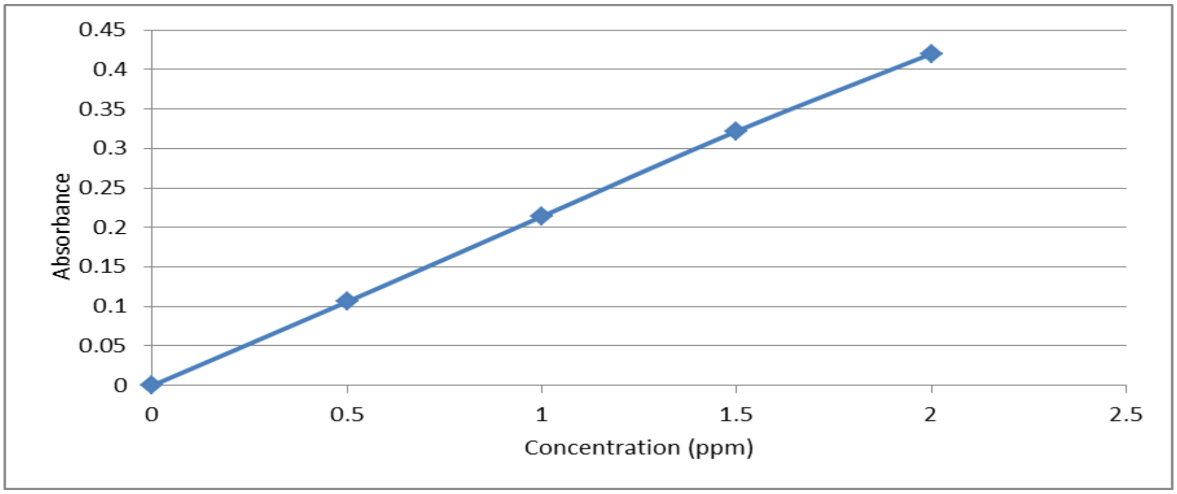

Figure 4.3: Cadmium (Cd) Calibration Curve.

Table 4.14: Lead (Pb) Standards.

Standards	Concentration(ppm)	Absorbance
A	0	0
B	1	0.04
C	1.5	0.06
D	2.5	0.098
E	5	0.184

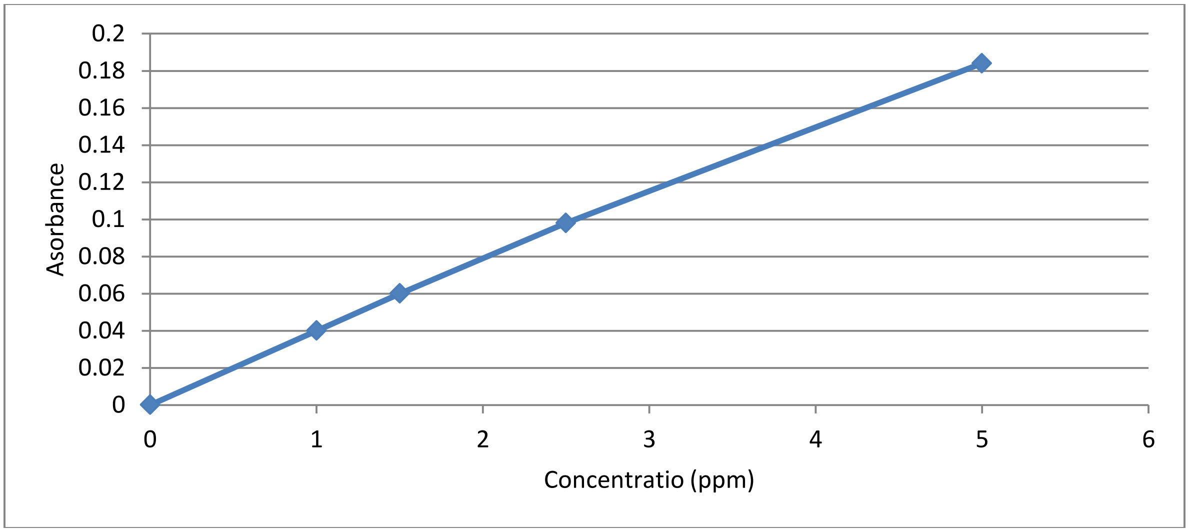

Figure 4.4: Lead (Pb) Calibration Curve.

Table 4.15: Chromium (Cr) Standards.

Standards	Concentration(ppm)	Absorbance
A	0	0
B	0.5	0.025
C	1	0.053
D	2	0.105
E	5	0.264

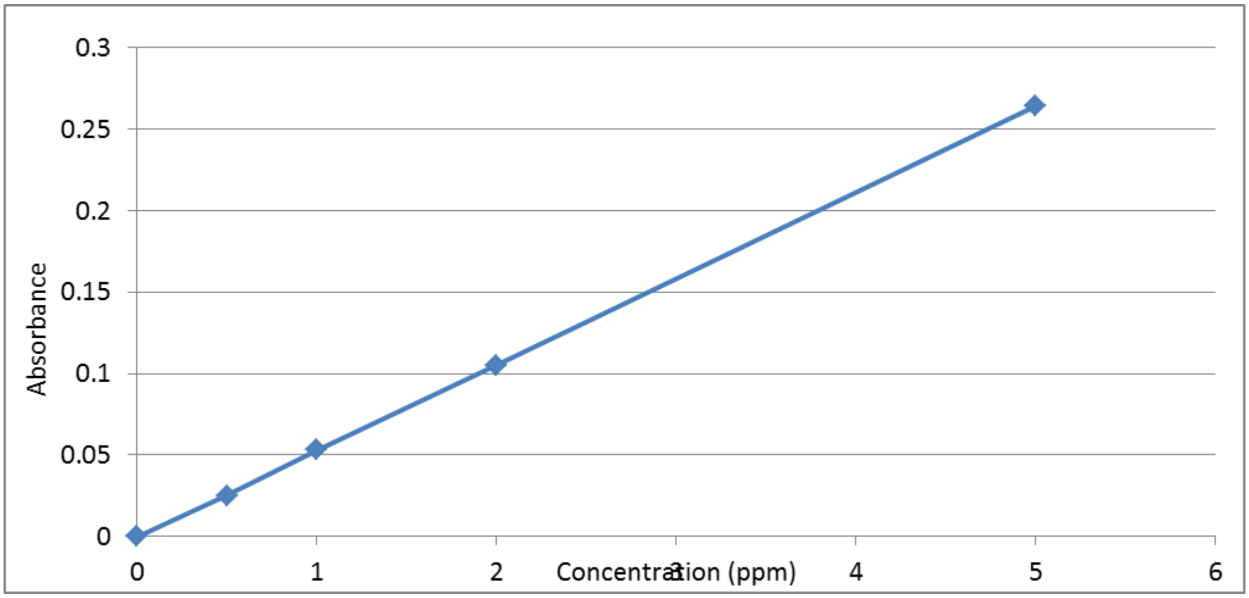

Figure 4.5: Chromium (Cr) Calibration Curve.

Table 4.16: Zinc (Zn) Standards.

Standards	Concentration(ppm)	Absorbance
A	0	0
B	0.5	0.092
C	1.5	0.274
D	2.5	0.459
E	5	0.982

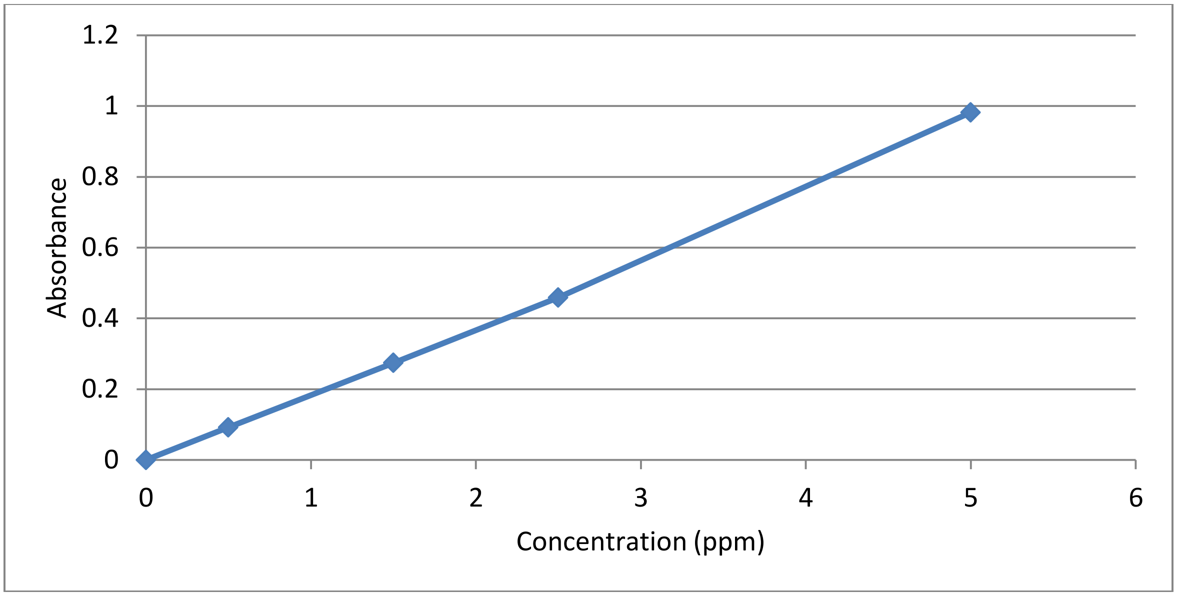

Figure 4.6: Zinc (Zn) Calibration Curve.

4.5 Heavy Metal Levels in Major Fertilizers Used For Growing Maize at Kerita Farm

Heavy metal levels in three major fertilizers (DAP, Urea and CAN) used for growing maize in Kerita farm were determined and recorded in Table 4.17. These metals included copper, cadmium, lead, chromium and zinc. The data indicated that concentration of heavy metals varied considerably with metal and the type of fertilizers. DAP fertilizer recorded the highest levels of all the five metals followed by CAN then Urea which recorded the lowest concentration in the study. High levels of zinc were recorded in DAP fertilizer at 342.60±0.57 mg/kg, followed by chromium at 301.53±0.59 mg/kg then copper at 22.21±0.09 mg/kg, then lead with 16.38±0.06 mg/kg and finally cadmium with mean value of 1.67±0.00 mg/kg. In CAN fertilizer, the concentration of lead was the highest at mean value of 13.83±0.11 mg/kg followed by copper at 0.78± 0.07 mg/kg then cadmium with mean value of 0.73± 0.00 mg/kg, while chromium level was below the detectable limit of the instrument of 0.005 ppm. In Urea only copper (Cu) was detected at mean value of 0.03±0.02 mg/kg while the rest were below the detectable limit of the instrument.

Table 4.17: Heavy metal loads (mean ± SD mg kg^{-1} of dry weight) in Major fertilizers used for Growing maize at Kerita farm.

	Cu	Cd	Pb	Cr	Zn
UREA	0.03± 0.02	< 0.006	< 0.02	< 0.005	< 0.002
CAN	0.78±0.07	0.73± 0.00	13.83±0.11	< 0.005	1.13±0.02
DAP	22.21±0.09	1.67±0.00	16.38±0.06	301.53±0.59	342.60±0.57

Sample Size (n) = 3.

Analysis of fertilizers used in the farms revealed that they are contaminated with the studied heavy metals though not above international standards (Tables 4.18 and Figure 4.7). Although Zn was relatively high in DAP with 342.60±0.57 mg/kg, it is much lower than the tolerance limit for phosphate fertilizers (2750 mg/kg in Kenya and 2800 mg/kg for USEPA). Being an essential plant and animal micronutrient, a high level may not necessarily be toxic. The data indicated that effect of heavy metals from chemical fertilizers on soil could be minimal. Nonetheless, other possible inputs of heavy metals to agricultural soils, such as organic fertilization as sewage sludge, aerial deposition and overdose of inorganic fertilizers, must not be ignored.

Table 4.18: Heavy metal concentration in fertilizers used in Kerita farms in comparison with international standards (as ppm per unit (1%) of P_2O_5 .macronutrients (N, P).

	Cd	**Pb**	**Zn**	**Cr**	**Cu**
USEPA (1999)	-	300	2800	-	1500
Kenya (2012)	20	400	2750	1750	750
UREA*	< 0.006	< 0.02	< 0.002	< 0.005	0.03
CAN*	0.73	13.83	1.13	< 0.005	0.78
DAP*	1.67	16.38	342.6	301.53	22.21

*This study

USEPA (1999): United States Environmental Protection Agency. Estimating risk from contaminants contained in agricultural fertilizers, EPA 68-W-98-0085

Kenya (2012): Government Notice: Department of Agriculture, Forestry and Fisheries 10 September 2012.

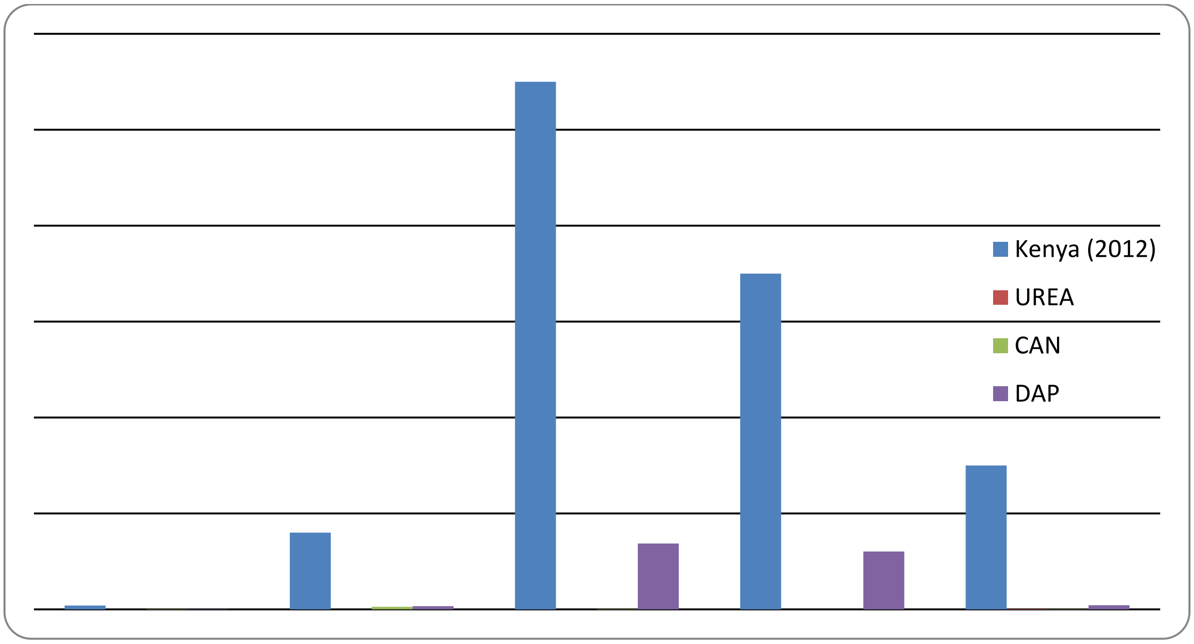

Figure 4.7: Comparison of Various Heavy Metals in Fertilisers with Kenyan Recommended Standards.

Availability of the selected heavy metal in the analysed chemical fertilizers is not unique. According to Mortvedt, [1987], fertilizers may contain concentrations of trace elements and heavy metals due to the mineralogy and manufacturing processes of the material or the addition of waste derived material. Metals of concern in fertilizers and amendments include arsenic (As), cadmium (Cd), lead (Pb), and to a lesser extent copper (Cu) and zinc (Zn). The first three are considered non-nutritive metals as they provide no nutritional value for a plant. The latter metals, however, are essential plant and animal micronutrients and high levels may not necessarily be toxic. Fertilizer products containing P inherently contain metals are constituent of Rock phosphate (RP). Manufacturing processes only remove a small percentage of heavy metals from Rock Phosphate (RP), while the majority remains in the final product. RP-derived material from the western U.S. Generally contains higher Cd and other metal levels than eastern U.S. sources [Mortvedt, 1987].

4.6 Heavy Metal Levels in Soil Samples

Table 4.19 shows the heavy metal levels recorded in the soils from the two sites (the maize farm and the control site). In farm soils, the levels of Chromium were relatively high with FAS mean of 42.11±3.25 mg/kg followed by Lead that had FAS mean of 37.72±3.44 mg/kg then Zinc at FAS mean of 29.36±2.74 mg/kg followed by copper at FAS mean of 8.52±1.56 mg/kg**.** Cadmium was the least since its concentrations were below detection limit of the instrument. This trend was replicated within the control site with chromium recording the highest mean of 19.15±1.56 mg/kg, followed by Lead that had CS mean of 18.98±0.88 mg/kg then Zinc at mean of 14.71±0.63 mg/kg followed by copper at mean of 5.12±0.71 mg/kg then cadmium was also the least since its concentrations were below detection limit of the instrument.

Table 4.19: Heavy Metal Concentrations (Mean ± SD mg/Kg of Dry Weight) In Soil Samples from Kerita Farm.

Site	Cu	Cd	Pb	Cr	Zn
FAS1	11.56±0.69	< 0.006	48.73±0.67	45.48± 0.07	38.93±0.64
FAS2	10.64± 0.07	< 0.006	41.83±1.13	47.87±2.08	32.18±1.62
FAS3	7.81± 0.05	< 0.006	32.67±0.20	37.60±1.31	27.13±0.99
FAS4	9.95±0.02	< 0.006	35.81±0.70	43.13±2.22	27.09±1.00
FAS5	6.55± 0.03	< 0.006	23.63±0.04	31.00±0.07	26.01±0.06
FAS6	5.82± 0.03	< 0.006	28.35±0.43	43.41±0.61	19.30±0.92
FAS7	6.19± 1.66	< 0.006	22.99±0.25	35.19±0.76	16.59±2.80
FAS8	6.98± 0.17	< 0.006	33.95±0.38	38.18±1.87	30.57±0.02
FAS9	6.40± 0.07	< 0.006	38.84±0.10	26.00±0.75	29.42±0.27
FAS10	6.95± 0.10	< 0.006	30.33±0.40	38.60±0.15	25.55±0.80
FAS11	12.83± 0.02	< 0.006	59.29±0.51	52.55±1.44	41.16±0.85
FAS12	10.23± 0.09	< 0.006	56.18±0.65	66.35±3.40	38.39±0.71
CS1	5.47± 0. 28	< 0.006	18.43±0.53	18.79±0.71	15.11±0.50
CS2	4.96±0.65	< 0.006	20.52±0.32	19.50±0.26	14.31±0.19
Mean (FAS)	**8.52±1.56**	**-**	**37.72±3.44**	**42.11±3.25**	**29.36±2.74**
Mean (CS)	**5.12±0.71**	**-**	**18.98±0.88**	**19.15±1.56**	**14.71±0.63**

Sample Size (n) = 14.

In general levels of heavy metals between the maize farm and the control site were statistically different in all metals, $\alpha < 0.05$ according to Table 4.20 with maize farm having higher means as compared to the control site for all the metals.

Table 4.20: Levene's Test for Equality of Variances and t-test for Equality of Means for Heavy Metal Concentrations between Maize Farm Soils and the Control Site.

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
Cu	Equal variances assumed	6.690	.024	1.903	12	.081	3.40000	1.78686	-.49324	7.29324
	Equal variances not assumed			4.312	10.113	.001	3.40000	.78848	1.64581	5.15419
Pb	Equal variances assumed	3.274	.095	2.161	12	.042	18.74167	8.67263	-.15437	37.63771
	Equal variances not assumed			5.407	11.484	.000	18.74167	3.46616	11.15171	26.33162
Cr	Equal variances assumed	2.150	.168	2.979	12	.012	22.96833	7.71061	6.16836	39.76831
	Equal variances not assumed			7.496	11.278	.000	22.96833	3.06425	16.24423	29.69244
Zn	Equal variances assumed	2.611	.132	2.664	12	.021	14.65000	5.49983	2.66690	26.63310
	Equal variances not assumed			6.637	11.612	.000	14.65000	2.20716	9.82315	19.47685

Where: F= F- test value

Sig= significance of F- test

t = t-test value

df= degree of freedom associated with t-test

The highest concentration of Chromium was recorded at FAS12 with mean value of 66.35±3.40 mg/kg while the lowest was recorded at FAS9 with mean value of 26.00±0.75 mg/kg. But the concentration in these samples was much below the toxic limit (Table 4.21 and Figure 4.8). The concentration of chromium in the control site ranged from 18.79±0.71 mg/kg to 19.50±0.26 mg/kg. A *t* test reveal a statistically reliable difference between the mean concentration of chromium that the maize farm soils has (M = 42.11, s = 10.54) and that the control site soil has (M = 19.15, s = 0.50), *t*(12) = 2.98, *p* = 0.012, α = .05 as shown in Table 4.20. The higher levels of chromium in farm soils as compared to control site could be attributed to application of phosphate fertilizers which was found contaminated with chromium elements at 301.53±0.59 mg/kg.

Table 4.21: Comparison of Various Heavy Metals in Maize Soils with Acceptable Toxic Element Content of Soils.

Site	Cu	Cd	Pb	Cr	Zn
Mean (FAS)	8.52±1.56	< 0.006	37.72±3.44	42.11±3.25	29.36±2.74
Mean (CS)	5.12±0.71	< 0.006	18.98±0.88	19.15±1.56	14.71±0.63
Hungary, 2001	75	1	100	75	200
USEPS,2002	NG	70	400	230	23600
FAO/WHO	100	3	50	NG	300

Figures 4.8 shows the comparison of the heavy metals under investigation in maize farm soils with Hungarian recommended standards. It reveals that zinc had the greatest variation followed by copper, then lead and finally chromium. Cadmium could not be compared since it was not given under Hungarian recommended standards.

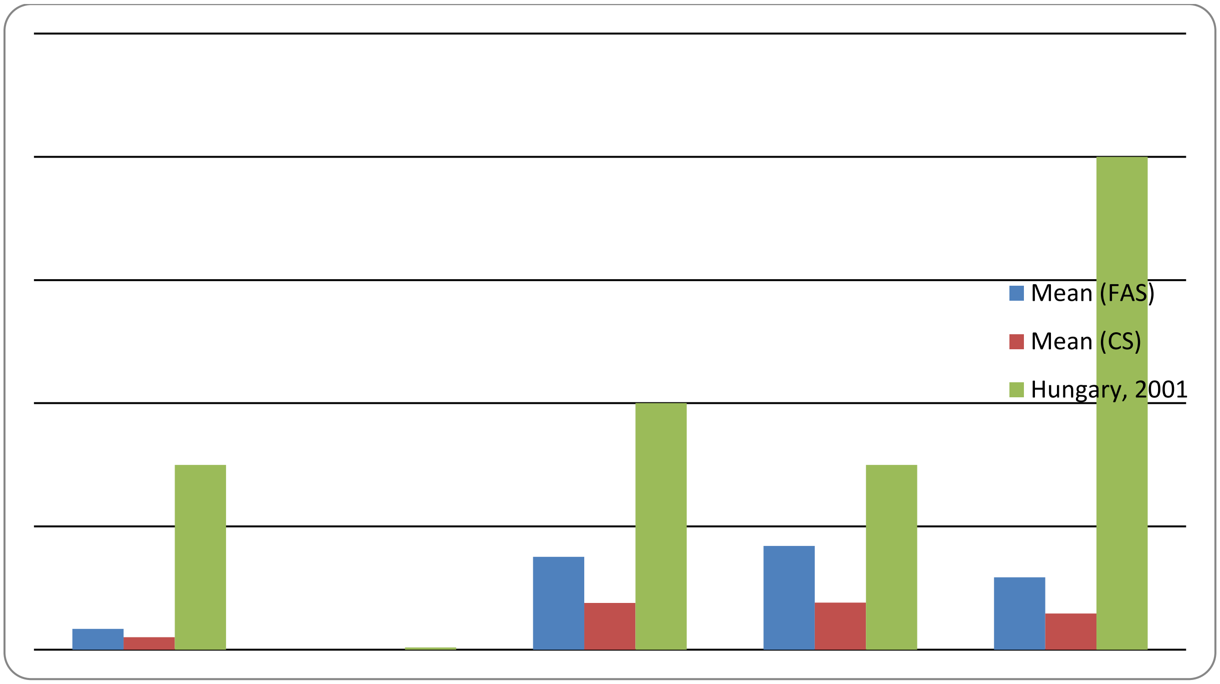

Figure 4.8 Comparison of Various Heavy Metals in Maize soils with Hungarian Recommended Standards.

Chromium usually appears most commonly in the environment as a trivalent salt (Cr-III or Cr^{3+}), found in air, water, soil and some foods. It is an essential trace element, aiding in the metabolism of carbohydrates. Hexavalent Chromium (Cr^{6+}) is the by-product of industrial applications, including steel making, tanning, plating, and textiles. Considered by the USEPA to be a carcinogen, (Cr-VI or Cr^{6+}) is readily absorbed by the body, and can lead to ulceration of the liver, nasal septum and action of stomach digestion tends to change Cr-VI to Cr-III, but Cr-VI is a strong oxidizer and can damage cell walls easily. Sources of Cr-VI in the fertilizer stream include steel manufacturing, tannery wastes, leather by-product, and sewage sludge. Chromium attaches tightly to soil particles, and the usual exposure pathways are due to exposure to dusts, sediments. It can be stated that in the more than 20-year long-term fertilization application at

Kerita farm, the effect of treatments in case of Cr content of soil could be detected in a great extent.

Zinc concentrations in the soil samples under study showed a wide variation. The highest concentration of Zinc was recorded at FAS11 with concentration level of 41.16±0.85 mg/kg, while the lowest concentration of zinc in maize farm soil was observed at FAS7 with concentration level of 16.59±2.80 mg/kg. But the concentration in these samples was much below the toxic limit (Table 4.21 and Figure 4.8). For the control site; the highest concentration was detected at CS1 with concentration level of 15.11±0.50 mg/kg, while the lowest concentration was observed at CS2 with 14.31±0.19mg/kg as shown in table 4.16. A *t* test reveal a statistically reliable difference between the mean concentration of zinc that the maize farm soils has (M = 29.36, s = 7.52) and that the control site soil has (M = 14.71, s = 0.57), *t* (12) = 2.66, *p* = .0.021, α =0 .05 as shown in Table 4.20.

This difference in zinc levels in the maize farm soils and the control site under study may be attributed to differences in soil pH between the two sites. According to Hafeez et al. [2013], Zinc availability is highly dependent on pH and that when the pH is above 6; the availability of Zn is usually very low which is in agreement with this study which recorded a pH of 6.35 and 5.04 in the control site and maize farm soils respectively. The availability of Zn in alkaline soils is reduced due to lower solubility of the soil Zn. Thus it is more probable that Zn deficiency will occur in alkaline rather than acidic soils.

Fertilizer application to the soil could also have had an impact on concentration of zinc in maize farm soil as noted by Adriano, 1989 who noted that Zinc is a metal that is consistently added to soils in increasing quantities in the form of fertilizers, pesticides, livestock manures, sewage sludges and industrial emissions. Even though the Zinc concentration in the maize farm soil was higher than the control site, it was not as high as compared to what was observed in phosphate fertilizer. This was attributed to lower soil pH which could have increased plant metal uptake because Zn becomes easily available for plants.

Zinc is a heavy metal of much interest since it is a plant micronutrient as well as a potential contaminant in soils. In soil solution, the speciation of Zn, and thus the free Zn activity determines the availability of Zn for plants as a micronutrient and its characteristics as a heavy metal contaminant. The Zn plays very important role in plant metabolism by influencing the activities of hydrogenase and carbonic anhydrase, stabilization of ribosomal fractions and synthesis of cytochrome [Tisdale and Weil, 1984]. Plant enzymes activated by Zn are involved in carbohydrate metabolism, maintenance of the integrity of cellular membranes, protein synthesis, and regulation of auxin synthesis and pollen formation [Marschner, 1995]. The regulation and maintenance of the gene expression required for the tolerance of environmental stresses in plants are Zn dependent [Cakmak, 2000]. Its deficiency results in the development of abnormalities in plants which become visible as deficiency symptoms such as stunted growth, chlorosis and smaller leaves, spikelet sterility. Micronutrient Zn deficiency can also adversely affect the quality of harvested products; plants susceptibility to injury by high light or temperature intensity and to infection by fungal diseases can also increase [Marschner 1995, Cakmak 2000]. Zinc affects the capacity for water uptake and transport in plants and also reduces the adverse effects of short periods of heat and salt stress [Kasim, 2007]. As Zn is required for the synthesis of tryptophan which is a precursor of IAA (indoleacetic acid), it also has an active role in the production of an essential growth hormone auxin [Brennan, 2005]. The Zn is required for integrity of cellular membranes to preserve the structural orientation of macromolecules and ion transport systems.

Its interaction with phospholipids and sulphydryl groups of membrane proteins contributes for the maintenance of membranes [Disante *et al*., 2010]. The threshold of Zn toxicity varies among plant species, time of exposure to Zn stress and composition of the nutrient growth medium. Photosynthesis is strongly affected in plants exposed to heavy metals excess. High Zn concentrations in plants can cause phytotoxicity. The yield may be reduced when plant leaf Zn concentrations reaches about 300 - 1000 mg/kg.

The concentration of Copper in soil samples analysed ranged from 5.82± 0.03 mg/kg to 12.83±0.02 mg/kg in maize farm soils with the lowest being recorded at FAS6 and the highest being recorded at FAS11. In the control site, the concentration of copper ranged from 4.96±0.65 mg/kg to 5.47± 0. 28 mg/kg with the lowest observed at CS2 and the highest at CS1 an overall mean of 5.12±0.71 mg/kg. A *t* test reveal a statistically reliable difference between the mean concentration of Copper that the maize farm soils has (mean = 8.52, s = 2.44) and that the control site soil has (M = 5.12, s = 0.50), *t* (10.11) = 1.90, *p* = 0.01, α = .05 as shown in Table 4.20. Low concentration in both the control soil and the maize farm soils was attributed to low pH, according to Schulte and Kelling *et al*. (2004), increasing the soil pH by liming increases the amount of copper held by soil and organic matter. Fertilizer application to the soil could also have had an impact on concentration of copper in maize farm soil as compared to the control soil. Copper levels were expected to be higher in maize farm soil due to the use of fungicides and pesticides on the farms. These agrochemicals are known to contain high levels of copper.

Copper is an essential metal for plants. It plays key roles in photosynthetic and respiratory electron transport chains, in ethylene sensing, cell wall metabolism, oxidative stress protection and biogenesis of molybdenum cofactor. A deficiency in the copper supply alters essential functions in plant metabolism. Excess copper can be potentially toxic to plants, causing phytotoxicity by the formation of reactive oxygen radicals that damage cells, or by the interaction with proteins impairing key cellular processes, inactivating enzymes and disturbing protein structure.

The concentration of lead in maize farm soil samples ranged from 22.99±0.25 mg/kg to 59.29±0.51 mg/kg with the lowest being recorded at FAS7 and the highest being recorded at FAS11. In the control site, the concentration of lead ranged from 18.43±0.53 mg/kg to 20.52±0.32 mg/kg with the lowest observed at CS1 and the highest at CS2. A *t* test reveal a statistically significant difference between the mean concentration of Lead that the maize farm soils has (M = 37.72, s = 11.86) and that the control site soil has (M = 18.98, s = 0.77), t (12) = 2.16 at $p = 0.42$, $\alpha = .05$ as shown in table 4.20. The results were in agreement with Onder, *et al*. [2006], who established that the addition of artificial fertilizer and pesticides causes an increase of lead levels in agricultural soil. In addition, lead comes from pollution resulting from tractor exhaust output during ploughing.

Cadmium content in both the control site and the maize farm soil samples was below the detectable level and therefore the t Test could not be computed because the standard deviations of both groups are 0. This indicated that fertilizer application had had no impact on the accumulation of cadmium in the cultivated soils. The results obtained were in agreement with Lehoczky *et al*. [2004] who established that increasing amounts of Phosphate fertilizers applied for 28 years had not influenced significantly the available Cd content of soils.

Numerous field studies were conducted worldwide in relation to Cadmium accumulation in soils following long-term Phosphate fertilization, yet results were conflicting and appear to be dependent upon source of fertilizer material, application rates, location, and soil properties (e.g., texture, pH, organic matter). An extensive study conducted by Holmgren *et al.* [1993] across the U.S. found soils of the western U.S., including Montana and Wyoming, to have moderately high Cd levels (average of 0.30 ppm) compared to other regions of the country. Hypothesized causes for these data included soil parent material high in Cd or a greater use of western Rock Phosphate-derived Phosphate fertilizer in the western U.S. Additionally, the study found general correlations to occur between metal accumulations and weathering processes (highly weathered soils were lowest in metal concentrations) and soil texture (most metals generally increased with increasing clay concentrations).

Another study looking at both soil and plant tissue concentrations of heavy metals following Phosphate fertilization resulted in mixed findings according to Mortvedt, [1987] where some fertilized soils had greater Cd levels than non-fertilized soils, while other sites showed no significant change in Cd levels between fertilized and non-fertilized soils. Plant tissue Cd concentrations did not differ between any of the fertilized and non-fertilized sites. A study conducted in Montana to assess metal concentrations following twenty years of DAP and/or TSP fertilization found that, in general, fertilized soils did not have significantly higher metal concentrations than non-fertilized soils or non-irrigated soils. In most cases, non-fertilized soils had significantly higher concentrations of both available and total metals [Jones *et al.*, 2002]. These findings indicated that long-term fertilization was not increasing metal concentrations in Montana soils. The mixed results of these studies and others suggest that while metal accumulation in soils and crops following P fertilizer application is a potential problem, there are numerous factors that can affect the magnitude of their accumulation.

4.7 Soil Phosphorus Retention Capacity

Soil phosphorous retention capacity was analysed and results recorded in table 4.22. Analysis of P sorption potentials indicated differences in P sorption capacity among sites, and highest P retention efficiency was 765.09 g/kg at FAS6 while the lowest P retention efficiency was 121.00 g/kg being recorded at FAS2. The four soils varied in their adsorption behaviour and were influenced by the texture of soils. Clay soils had the highest adsorption maxima which ranged from 365.53 g/kg to 765.09 g/kg. This was followed by sandy clay soil with adsorption maxima that ranged from 215.56 g/kg to 380.9 g/kg followed by silt clay loam that had adsorption maxima of 243.44 while sandy clay loam had the least adsorption maxima which ranged from 121.00 g/kg to 196.53 g/kg.

Table 4.22: Soil Phosphorus Retention Capacity and Texture.

	Soil Texture				**Phosphorus Adsorption Capacity "b"**
	% Sand	**% Clay**	**% Silt**	**Textural Class**	
FAS1	64	26	10	Sandy Clay Loam	196.53
FAS2	59	32	9	Sandy Clay Loam	121.00
FAS3	50	46	4	Sandy Clay	302.92
FAS4	48	44	8	Sandy Clay	286.19
FAS5	33	47	20	Clay	597.03
FAS6	30	51	19	Clay	765.09
FAS7	12	36	52	Silty Clay Loam	243.44
FAS8	29	42	29	Clay	544.53
FAS9	36	45	19	Clay	365.53
FAS10	39	53	8	Sandy Clay	380.9
FAS11	62	24	14	Sandy Clay Loam	192.17
FAS12	54	21	25	Sandy Clay Loam	187.56
CS1	50	46	4	Sandy Clay	230.97
CS2	39	55	6	Sandy Clay	215.56

Sample Size (n) = 14.

The data in Table 4.22 shows that P sorption capacity was highly correlated with soil texture: r = 0.783, N=14 and sig (2-tailed) as shown in table 4.23.

Table 4.23: Correlations between Phosphorus Retention Capacity and Soil Texture.

		Phosphorus adsorption maxima (b)	Soil Texture
B	Pearson Correlation	1	0.783**
	Sig. (2-tailed)		0.001
	N	14	14
Texture	Pearson Correlation	0.783**	1
	Sig. (2-tailed)	0.001	
	N	14	14

**. Correlation is significant at the 0.01 level (2-tailed).

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

5.1.1 Characterisation of the soils.

The pH of the soils under study, were found to be generally slightly acidic since it had pH less than 7.0. This could be due to the composition of the parent rock from which the soils were formed and inherent factors affecting soil pH such as climate, mineral content and soil texture which cannot be changed as well as continued fertilizer application. The total organic content in the soil under study was generally low. This could be due to the soil texture as it was observed that clay textural soil had higher total organic carbon (TOC) compared to sandy clay loam, silty clay loam soils and sandy clay. Soil texture affects TOC because of the stabilizing properties that soil with more clay has on organic matter.

5.1.2 Nitrogen, phosphorus and Potassium in major fertilizers

Concentrations of nitrogen, phosphorus and Potassium in major fertilizers in this study were not in agreement with labelled contents reported by producers. The biggest variation was observed in phosphorus in Di-ammonium Phosphate (DAP) fertilizer which had very high concentration above the indicated content. The probable reason could be that Stockist and shopkeepers may have meddled with the product by either mixing the original content with other commodities.

5.1.3 Nitrogen, phosphorus and Potassium in Maize Farm Soils

Phosphorus levels in maize farm soil where regarded as adequate for maize growth since they fell within the range of 35ppm-44ppm [Okalebo,et al., 2002]. Nitrogen levels in farm soil was regarded as low since it fell within the range of 0.05%-0.11 % below 0.12 % which is regarded normal for maize production [Okalebo, et al., 2002]. Potassium in the soil was found deficient for maize production whose range was 0.42%-0.65% below 0.75% which is regarded as minimum level for maize production.

5.1.4 Selected heavy metal content in major fertilizers and in soil

The results obtained in this study in regard to heavy metals showed that both the fertilizers and farm soil had significant levels of chromium, cadmium, lead copper and zinc. DAP fertilizer recorded the highest levels of all the five metals with zinc levels being the highest. However, the experimental results of toxic elements show that the long term use of chemical fertilizers did not result in higher values than the accepted concentration level such as the USEPA and, even they did not approach it.

5.1.5 Phosphorus retention capacity of soil.

Soils from the study sites indicated an average soil phosphorus retention ability that was highly correlated with soil texture.

5.2 Recommendations

i. The soil (pH) is acidic for plants' growth. It is recommended that actions be put in place to raise the soil pH in the studied area by avoiding acidifying fertilizers like DAP and urea.

ii. During land preparation apply well decomposed manure or compost manure which has a positive influence on the build-up of soil organic matter and thus improves the "intrinsic" fertility of the soil, as well as the soil structure.

iii. At planting, it is recommended that 100 kg/acre of compound fertilizer N: P: K 23:23:0 should be applied which should be followed by top dressing with 50 kg/acre of calcium ammonium nitrate (CAN) to improve the deficiency of Nitrogen and Phosphorous in the soil. Introduction potash fertilizers to balance the reducing trend of potassium content in Agricultural soils are also recommended.

iv. Continue testing fertilizers especially phosphate fertilizers of potential concern for heavy metal levels.

v. There is need for continuous environmental monitoring in similar agricultural systems where intensive fertilizer application is practiced for mitigation purposes.

vi. There is need to provide updated information to the public about potential risks of heavy metals from chemical fertilizers.

vii. Further investigations need to be carried out on all fertilizers periodically to ensure strict compliance of label specifications and recommended limits of required nutrients in all the fertilizer samples. Investigations should be undertaken into fertilizers at retail points since most Kenyan farmers obtain fertilizers at low quantities from the retailers. These shops could be an easy source of fertilizer adulteration by greedy business men.

viii. The findings of this report be shared with other county government of Trans Nzoia and state agencies, including the Kenya Bureau of Standards, Ministry of Agriculture and National Environment Management authority.

REFERENCES

Afif, E., Matar, A., and Torrent, J. (1993). *Availability of phosphate applied to calcareous soils of West Asia and North Africa*. Soil Science Society of America Journal, **57**:756-760.

Alloway, B. J. (1995). *Heavy Metals in Soils*. Blackie Academic and Professional, Glasgow, Scotland, Second Edition.

Amrani, M.,Westfall, D. G., and Peterson, G. A. (1999). *Influence of Water Solubility of Granular Zinc Fertilizers on Plant Uptake and Growth.* Plant Nutritional Journal, **22**:1815-1827.

Ashraf, E. M. K., and Al-sewaidan, (2008). *Uranium and Heavy Metals in Phosphate Fertilizers*. International Conference on Radioecology & Environmental Radioactivity, Bergen- Norway.

Ashraf, E. M. (2006). *Determination of Lead in Environmental Samples using different Radio-Analytical Technique*. Journal of Radio-Analytical and Nuclear Chemistry, **3 (269):** 609-619.

Bache, B. W., and Williams, E. G. (1971). *A Phosphate Sorption Index for Soils*. Journal of Soil Science, **22**: 289–301.

Bartos, J. M., Mullins, G. L.,Williams, J. C., Sikora, F. J., and Copeland, J. P. (1992). *Water-Insoluble Impurity Effects on Phosphorus Availabilityi in Monoammonium Phosphate Fertilizers*. Soil Science American Journal, **3**: 972-976.

Bergmann, W. (1992**)**. *Nutritional Disorders of Plants*. Gustav Fischer, New York.

Brady, N. C., and Weil, R. R. (1999). *The Nature and Properties of Soil*. Prentice Hall, Upper Saddle River, NJ, U.S.A.

Blevins, R. C.,Thomas, G.W., Smith, M. S., Frye, W. W., and Cornellius, P. L. (1983). *Changes in Soil Properties after Ten Years of Continued Non- Tilling*. Soil Tillage Response, **3**:135-136.

Brennan, R. F. (2005). *Zinc Application and its Availability to Plant*. Ph.D. Dissertation, School of Environmental Science, Murdoch University.

Brigden, K., Stringer, R., and Santillo, D. (2002). *Heavy Metal and Radionuclide Contamination of Fertilizer Products and Phosphogypsum Waste Produced by The Lebanese Chemical Company, Lebano*. Greenpeace Research Laboratories, University Of Exeter,UK.

Cakmark, I. (2000). *Role of Zinc in Protecting Plant Cells from Reactive Oxygen Speciation*. Plant Phsiology Journal, **6**: 185-205.

Chen, X., Wright, J. and Peurrung, L. (1997). *Effect of pH on Heavy Metal Sorption on Metal Apatite*. Environmental Science and Technology, **3**: 624-631.

Chen, Y. P., Rekha, P. D., Arushe, A. B., Lai, W. A., and Young, C. C. (2006). *Phosphate Solubilizing Bacteria from Subtropical Soil and their Tricalcium Phosphate Solubility Ability*. Applied Soil Ecology, **34**: 33-41.

Cunningham, J. D., Keeney, D. R., and Ryan J. A. (1963). *Phytotoxicity and Uptake of Metals added to Soils as Inorganic Salts or in Sewage Sludge*: Journal on Environmental Quality, **4:**460–462.

Davies, B. E., White, H. M., Singh, S., and Kumar, M. (1995). *Heavy Metal Load of Soil, Water and Vegetables in Periurban Delhi*: Environmental Monitoring and Assessment, **120**: 79–91.

Disante, K. B., Fuentes, D., and Cortina, D. (2010). *Response of Drought of Zinc Stressed Quercusberl Seedlings*. Environmental Experimental Botany,**70**: 96-103.

Duinker, J. C., Nolting, R. F.,and Michel, D. (1982). *Effects of Salinity, Ph and Redox Conditions on Behaviour of Cd, Zn, Ni, and Mn in the Scheldtestuary and Thalassia Jugosl*: **18**:191‑201.

Fan, M. X., and Mackenzie, A. F. (1993). *Urea and Phosphate Interactions in Fertilizer Microsites, Ammoniag Volatilization and pH Changes*. Soil Science American Journal, **57**: 839-845.

Fenn, L. B., and Miyamoto, S. (1981). *Ammonia Loss and Associated Reactions of Urea in Calcareous* Soil.Soil Science American Journal, **45**:537-540.

Freeman, H. A., and Kaguongo, W. (2003). *Fertilizer Market Liberalization and Private Retail Trade in Kenya*: Food Policy, **28:** 505-518.

Government of Kenya Notice. (2012). Department of Agriculture, Forestry and Fisheries.

Goyer, R.A., and Clarkson, T. W. (2001). *Toxic Effects of Metals in Casarett and Doullis Toxicology*. The Basic Science of Poisons, Sixth Edition Mc-Graw-Hill, New York, p811-867.

Havlin, J. L., Beaton, J. D., Tisdale, S. L., and Nelson, W. L. (1999). *Soil Fertility and Fertilizers*. 6th Edition, Upper Saddle River, N.J: Prentice-Hall, p 499**.**

Hinga, G. A., and Foum, M. A. (1997). *The Effects of Potassium, Phosphorus and Magnesium on Dry Matter Yield and Nutrient Uptake by Tomatoes in the Green House*. Annual Report by Agricultural Laboratories in Kenya, Soil and Agriculture Chemistry Section, p 34-40.

Holmgren, G., Meyer, M., Chaney, R. and Daniels. (1993). *Cadmium, Lead, Zinc, Copper, and Nickel in Agricultural Soils of the United States of America*. Environmental Quality Journal, **22**: 335-0348.

Hoyle, F. C., and Paterson, J. (2011). *Soil Organic Carbon Role in Rainfed Farming System in Australian Soil.* Western ausralian Agriculture Authority,Soil Science Society of America Journal, **63**:1350-1358.

Hue, K. N., and Silvia, A. (2000). *Organic Sources of Nitrogen, Phosporus and Potassium*. American Journal of Soil Science, **64**: 1689-1698.

Ige, D. V., Akinremi, O. O., Flaten, D. M., Ajiboye, B., and Kashem, M. A. (2005). *Phosphorus sorption Capacity of Alkaline Manitoba Soils and its Relationship to Soil Properties*. Soil Science journal, **85**: 417–426.

Jackson, M. L. (1986). *Soil Chemical Analysis*. Prentice-Hall, Englewood Cliffs, USA, **p** 498.

Jayne, T. S., Govereh, J., Wanzala, M., and Demeke, M. (2003). *Fertilizer Market Development*, A Comparative Analyses of Ethiopia,Kenya and Tanzania. Food policy, **28**: 293-316.

Jeffrey, A. T., (1998). *Trends in Eutrophication Research and Control*. Hydrological Process Journal, **2:** 295-313.

Jones, C. A., Jacobsen J., and Lorbeer, S. (2002). *Metal Concentration in Three Montana Soils Following 20 Years of Fertilization and Cropping*. Communication in Soil Science and Plant Analysis, **33**: 9 -10.

KARI, (1995). *Fertilizer Use and Recommendations for Various Disricts*. National research laboratories Kenya, **1**:16-24.

KARI, (2013). Agricultural Research. Canadian Centre of Science and Education, **2**: 2.

Kasim, W. A. (2007). *Physiological Consequences of Structural and Ultra-Structural Changes Induced by Zinc Stress in Phaseoulus Vulgaris in Growth and Photosythetic Apparatus*. Botany International Journal **1**: 15-22.

Kelling, K. A., Meyers,M., and Peters, J. B. (2004). *What Ignoring Lime Can Do to Corn and Soya Beans*. Proceedings of Wincousin Ferilizer,Agricultural Lime and Pest Management. Conference p411-414.

Kpomblekou, A. K.,and Tabatabai, M. A. (1994). *Metal Contents of Phosphate Rocks Communications in Soil*. Science and Plant Analysis, **25**: 2871 –2882.

Lal, N., Sharma, P. K., Sharma, Y.P., and Nagpaul, K. K. (1985). *Determination of Uranium in Fertilizers using Fission Track Method*. Fertilizer Residue, **6**: 85–89.

Lal, R. (2004). *Soil Carbon Sequestration to Mitigate Climate Change*: Geoderma, **123**: 1.

Lehoczky, E., Debreczeni, K., and Szalai, T. (2004). *Effect of Long-Term Fertilization on the Available Toxic Element Content of Different Soils*: Journal of Central European Agriculture **4**: 309-314.

Lepp, N. W. (2001). *Effect of Heavy Metals on Plants Toxic and Essential Metal Interaction*. Applied Science Journal, **17**:37–50.

Li, Y. C., Alva, A. K., and Calvert, D. V. (1972). *Transport of Phosphorus and Fractionation of Residual Phosphorus in Various Horizons of a Spodsol*. Water, Air, and Soil Pollution, **109**: 303–306.

Lieu, E. F., Shen, J., Yang, L.Y., Zhang, E. L., Meng, X. H., and Wang, J. J. (2010). *Assessment of Heavy Metal Contamination in the Sediments of Nansihu Lake Catchment, China:* Environmental Monitoring and Assessment, **161**: 217-227.

Manoharan V. (1997). *Changes in Solution Component and Aluminium Speciation under Legume Based Pastures in Response to Long -Term Phosphate Fertilizer Application*. Australian Journal on Social Response, **34**: 985-998.

Marschner, H. (1995). Mineral Nutrition of Higher Plants. Academic Press, New York pp 299-312.

Marschner, P., Kandeler, E., Marschner, B. (2003). *Structure and Function of the Soil Microbial Community in a Long-Term Fertilizer Experiment*. Soil Biology and Biochemistry Journal, **35**: 453‑461.

McCauley, A., Jones, A. and Jacobsen, J. (2009). *Soil pH and Organic Matter, Nutrient Management.* Montana State University Extension, Module No.8.

Milne, E. (2012). *Soil Organic Carbon*. Land Use and Land Cover Change Natural Resources Management Authority and Policy, **6**: 087.

Ministry of Agriculture, (2013). Agriculture,Fisheries and Food Act no: 13, **2**: 11-26.

Modaihsh, A. S., Al-Swailem, M. S. and Mahjoub, M. O. (2004). *Heavy Metals Content of Commercial Inorganic Fertilizers Used in the Kingdom of Saudi Arabia*. Agricultural and Marine Sciences, **1**: 21-25.

Mortvedt, J. J., Mays, D. A., and Osborn, G. (1981). *Uptake by Wheat of Cadmium and Other Metal Contaminants in Phosphate Fertilizers*. Environmental Quality Journal, **10**: 193-197.

Mortvedt, J. J. (1987). *Cadmium Levels in Soils and Plants from some Long-Term Fertility Experiments in the United States of America*. Environmental Quality Journal, **16**: 137-142.

Muchena, F. (1974). *The Availability of Potassium in the Kenyan Soils.* Kenya Soil Survey, National Agricultural Laboratories.

Nair, P. S., Logan, T. J., Sharpley, A. N., Sommers, L. E., Tabatabai, M. A., and Yuan, T. L. (2000). *Inter-Laboratory Comparison of a Standardized Phosphorus Adsorption Procedure*. Journal of Environmental Quality, **13**: 591-595.

Nair,V. D., Greatz, D. A., and Portier, K. M. (1984). *Forms of Phosphorus in Soil Profile from Diaries of South Florida*. Soil science American Journal, **59**: 1244-1249.

Nartey, V. K., Haizel, M., Doamekpor, L. K., and Dankyi, E. (2012). *Studies on the Contribution of Fertilizers to Heavy Metal Levels in Soils and Cocoa from some Cocoa Farms in the Western Region of Ghana*. Journal of Natural Sciences Research, **8**: 111.

Nelson, D. W., and Sommers L. E. (1982). *Total Carbon, Organic Carbon, and Organic Matter*: Methods of Soil Analysis, 2nd edition, **p** 539–580.

Geotechnical Engineering Bureau. (2007). *Test Method for the Determination of pH Value of Water or Soil by pH Meter*. New York State Department of Transportation.

Okalebo, J. R., Gathua, K. W., and Woomer, P. L. (2002). *Laboratory Methods of Soil and Plant Analysis*. A Working Manual, TSBF-CIAT and SACRED Africa, Nairobi.

Omwoma, S., Lalah, J. O., Ongeri, M. K. D., and Wanyonyi, B. M. (2010). *Impact of Fertilizers on Heavy Metal Loads in Surface Soils in Nzoia Nucleus Estate Sugarcane Farms in Western Kenya*. Bulletin of Environmental Contamination and Toxicology, 00128-010-0133-7.

Onder, S., Dursun, S., Gezgin, S., and Demirbas, A. (2007). *Determination of Heavy Metal Pollution in Grass and Soil of City Centre Green Areas*, Journal of environmental, **1**: 145 – 154.

Otero, N.,Victoria, L., Soler, A., and Canals, A. (2005). *Fertiliser Characterisation: Major, Trace and Rare Earth Elements*. Applied Geochemistry, **20**: 1473–1488.

Parnes, R., (1986). *Organic and Inorganic Fertilizers*: Woods End Agricultural Institute, Mt Vernon, ME.

Potash and Phosphate Institute. (2003). *Agronomical Threshholds for Soil Phosphorus*. Alberta.

Quansah G. W (2012). *Organic and Inorganic Fertilizer Application on the Growth and Yield of Artemisia Annua L. in the Humid Tropics of Ghana*. African Journal of Agricultural Research, **2**: 177-182.

Rachhpal, S, and Nye, P. H. (1984). *The Effect of Soil pHand High Urea Concentration on Urease Activity*. Soil science Journal, **35**: 519-527.

Reddy, K. R., Overcash, M. R., Khaleel, R., and Westerman, P. W. (1980). *Phosphorus Adsorption-Desorption Characteristics of two Soils utilized for Disposal of Animal Wastes*: Journal of Environmental Quality, **9**: 86–92.

Rothbaum, H. P., McGaveston, D. A., Wall, T., Johnston, A. E., Mattingly, G. E. G. (1979). *Uranium Accumulation in Soils from Long-continued Applications of Superphosphate:* Journal of Soil Science, **1**: 147-153.

Sanchez, P. A. (1976). *Properties and Management of Soils in Tropics*. Newyork.

Sanchez, P. A., Shepherd, K. D., Soule, M. J., Place, F. M., Mokwunye, A. U., Buresh, R. J., and Woomer, P. L. (1997). *Soil Fertility Replenishment in Africa*. Soil Science Society of America and American Society of Agronomy Madison, Wisconsin, U.S.A, 1−46.

Savits, J., Hettenbach, T., and Wiles, R. (1995). *Toxic Waste and Fertilizer in Oregon:* Environmental Working Group, Washington DC.

Schreder, E. (2001). *Holding the Bag: How Toxic Waste in Fertilizer Fails Farmers and Gardeners:* A Washington Toxics Coalition Report.

Schroeder, H. A., and Balassa, J. J. (1963). *Cadmium Uptake by Vegetables from Superphosphate and Soil*. American Journal of Chemistry, **4**: 228-233.

Semu, E., and Singh, B. R. (1995). *Accumulation of Heavy metals in Soils and Plants after Long-Term use of Fertilizers and Fungicides in Tanzania*. Fertilizer Research, **3**: 241-248.

Sheriff, E. B., Yeboah, O. P., Akoto, B. S., Kwablah, A. A., Abole, H., Lebene, K., Hanson, J. E. K., Ahiamadjie, H. and Gyamfi, T. E. (2012). *Quality Control Analysis of Imported Fertilizers Used in Ghana*. Proceedings of the International Academy of Ecology and Environmental Sciences, **1**: 27-40.

Singh, B. R. (1994). *Trace Element Availability to Plants in Agricultural Soils, with Special Emphasis on Fertilizer Inputs*. Environmental Review Journal, **2**:133-146.

Singh, B. R. (1991). *Unwanted Components of Commercial Fertilizers and their Agricultural Effects*. The Fertilizer Society, London, UK. **p**28.

Singh, S., and Kumar, M. (2006). *Heavy Metal Load of Soil, Water and Vegetables in Periurban Delhi*. Environmental Monitoring and Assessment, **120**: 79–91.

Stevenson, F. J. (1986). *Cycles of Soil- Carbon, Nitrogen, Phosphorus,Sulfur,Micronutrients*. National Library of Australia, xviii, **p** 380.

Strawn, D. G., and Sparks, D. L. (2000). *Effects of Soil Organic Matter on the Kinetics and Mechanisms of Pb (II) Sorption and Desorption in Soil*. Soil Science, American Journal, **64**: 144-156.

Takashi, Y. and Ayumi, A. (2010). *Fertilizer Policies, Prices and Application in East Africa*. Grips Discussion Paper, **p**10-24.

Tisdale, S. L, Nelson, W. L. (1993). *Soil Fertility and Fertilizers*. Mc Graw- Hill Inc.New York.

Ukpabi ,F. L., Akubugwo E., Agbafor K., Lebe N., Nwaulari N., and Nneka N. (2012). *Appraisal of Heavy Metal Contents in Commercial Inorganic Fertilizers Blended and Marketed in Nigeria*. American Journal of Chemistry, **4**: 228-233.

United States Environmental Protection Agency, (1999). *Estimating risk from contaminants contained in agricultural fertilizers,* EPA 68-W-98-0085.

Westfall, D. G., Gangloff, W. J., Peterson, G. A., and Mortvedt, J. J. (2001). *Organic and Inorganic Zn Fertilizers and their Relative Availability*. Western Nutrient Management Conference Proceedings, **4**: 123-1299.

Williams, S. (1984). *Official Methods of Analysis of the Association of Official Analytical Chemists (AOAC)*. Arlington,VA.

Wong, J., and Lai, K. (2001). *Availability of Heavy Metals for Brassica Chinensis Grown in an Acidic Loamy Soil Amended with a Domestic and an industrial sewage Sludge*. Water, Air and Soil Pollution Journal, **128**: 339-353.

APPENDICES: PHOTOS

Appendix 1: Kerita Farm.

Appendix 2: Soil Samples Collection.

Author: Sample Collection in Kerita Farm

Appendix 3: Laboratory Analysis

Atomic Absorption Spectrophotometer (AAS)