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Comparative Evaluation of the Components of Biogas Digestate Slurries and Effects on Agricultural Soils

By:

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DECLARATION

I declare that the thesis presented herein is my original work, which has not been submitted for examination at any other University.

Signature…………………………………………………..Date…………………………..

Spencer Kirawa Lusi (S56/5745/2017)

Supervisors' Approval

This thesis has been submitted with our knowledge and approval as the University supervisors.

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DEDICATION

This thesis is dedicated to my family and friends. I derived the mental strength to pull through from their support.

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ABSTRACT

Biogas production is a good source of clean energy and organic fertilizer in the form of digestate slurry. This study sought to characterize by composition, the biogas digester slurries (digestate) and assess the potential impact of their usage as organic fertilizer on crop productivity and environment. The study was informed by the need to allow crop scientists, as well as environmentalists, determine how individual biogas feeds affect the composition of the final digestate released as a by-product of biogas production and hence the impact the digestates could have on the crops or environment through their agricultural application as Biofertilizers. Different digestates from human waste, animal waste, and abattoir waste feedstock were sampled for the study. They were sun-dried to maintain the integrity of their composition then ground into a fine powder for size reduction and to homogenize the samples. Three pellets were prepared from each sample using a hydraulic press, with a 400 mg portion of the samples going through the pressing to form the triplicates of the analyzable samples. The pellets were then analyzed using EDXRF spectroscopy for elemental components. After the requisite statistical analysis, the human waste digestate had the highest concentration values for most elements, as compared to the animal or abattoir waste. In human waste, essential elements were determined at 40600 ± 2000, 19000 ± 1140, 1300 ± 400, 200 ± 30, 900 ± 260 ppm for Ca, Fe, Mn, Zn and Cu respectively, as compared to Ca (26400 ± 1400), Fe (9500 ± 440), Mn (820 ± 190), Zn (180 ± 40), Cu (360 ± 70), in animal waste. In abattoir waste, the mean content was 49500 ± 4100 for Ca, 15220 ± 1350 for Fe, 1090 ± 90 for Mn, 200 ± 50 for Zn and 140 ± 50 for Cu. Variations were observed between different digestates and within the same digestate type. Potentially toxic elements Hg and Cd were determined below detection limits, while Pb concentrations were highest in human waste at 20.81 ppm. The high amounts are associated with the micro industrial activities in Kibera, including paintings and motor vehicle batteries disposed off casually. The findings imply that while human wastes might be the best in supplementing the essential soil nutrients for agricultural crop performance purposes, it remains the most probable threat to environmental integrity if the Pb that makes up the composition of the digestate accumulates beyond the threshold. Indeed, in addition to the possibility of Pb remaining the leading environmental threat, an unchecked accumulation of the other elements might be counterproductive for both the environment and agricultural applications. Also, for agricultural professionals, there is the opportunity to match crops with the digestates from which the specific crops would benefit the most, given unique crop requirements. In conclusion, the high nutrient content observed in this study could be beneficial in enhancing crop productivity due to the essential role played by different trace elements, in addition to modifying soil texture due to high organic matter content. That notwithstanding, the environmental monitoring of the continued application of the digestates discussed herein is critical. Otherwise, there is a potential risk of bioaccumulation of these elements to toxic levels.

The application of the slurries as Biofertilizers should, therefore, be regulated and closely monitored to avoid heavy metal pollution. This is especially important for slurries emanating from digesting human wastes, especially if the digesters are in urban setups where Lead concentrations were found to be highest. Most of the other elements were found to be within an acceptable range; hence, the only necessary precaution should be to avoid bioaccumulation that would then reverse the intended soil fertility improvement.

KEYWORDS: Digestate Slurry, Biofertilizers, Feedstock, Pellets, Homogenize, EDXRF Spectroscopy, Trace elements, Soil Texture, Bioaccumulation, Biogas

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List of Abbreviations and Acronyms

4IR	Fourth Industrial Revolution
AD	Anaerobic Digestion
AXIL	Analysis of X-ray spectra by Iterative Least Squares
BDS	Biogas Digester Slurry
C/N Ratio	Carbon/Nitrogen Ratio
EDXRF	Energy Dispersive X-Ray Fluoroscopy
FAO	Food and Agriculture Organization
GOK	Government of Kenya
IAEA	International Atomic Energy Agency
INST	Institute of Nuclear Science and Technology
ISP	International Science Program
KCIC	Kenya Climate Innovation Center
MoE	Ministry of Energy
NEMA	National Environment Management Authority
NH_4^+–N	Ammonium-Nitrogen
NPK	Nitrogen, Phosphorus, and Potassium
PO_4^{3-}–P	Orthophosphate-Phosphorus
PPM	Parts per Million
TXRF	Total Reflection X-Ray Fluorescence Analysis
UK	United Kingdom Government
WDXRF	Wavelength Dispersive X-Ray Fluoroscopy
XRF	X-Ray fluoroscopy

CHAPTER ONE

INTRODUCTION

1.1 Background

Plants, as well as animals, both need micro and macronutrients in varying amounts depending on the class in which the nutrients fall. For micronutrients, they are required in limited quantities, while the macronutrients are needed in relatively higher amounts. The amount of the nutrients required in each case does not make either category more critical, as plant and animal bodies need both to function correctly. For plants, especially those considered as crops, these nutrients are often supplemented to maximize functionality and hence increased productivity. One of the sources of these essential nutrients is inorganic fertilizers. Alternatively and preferably, the use of organic fertilizers is recommended (Elamin and Elagib, 2001). This is because they are environmentally friendly in comparison to inorganic fertilizers. One of the sources of organic fertilizers is biogas digestate, a byproduct during biogas production.

Apart from the isolated cases where the developers of digesters dispose of the slurry as a waste, the common use of digestate slurry from a biogas digester is in agriculture, as an organic fertilizer (Koszela and Lorencowicz, 2015). The use of these slurries in agriculture is more pronounced in smallholder farms where they would be sufficient, given the non-extensive land sizes and hence small-scale needs for nutrients supplements. Coincidentally, such smallholder farms are common in urban settings where the culture of developing biogas as an alternative source of energy is becoming common. A study carried out in Nyeri, Kenya, for example, indicates that more Locals are adopting Biogas production, and as such, the use of biogas slurries as farm manure is becoming common as well (Ikonya, 2018).

In Kenya, irrespective of the raw materials used as feed for the digesters, the semi-solid or liquid slurry finds use as fertilizers with little knowledge of the elemental components of the slurries. The flexibility of the Anaerobic Digestion (AD) means a lot of different organic materials can be used as raw materials in biogas digesters, ending up with the varied quality of the slurry. The other factors that would influence the micronutrient and macronutrient composition of the slurry include climatic conditions under which the digestion is carried out and the age, type, sex of animal whose wastes are fed into the digester (Lukehurst *et al*., 2010). Additionally, the digester types; fixed dome, floating drum, balloon, earth pit, etc. are critical in determining the components of the slurry (Kajsa *et al*., 2017). While the above are, by extension, the factors that affect the quality of the biogas slurries, they are more prominent in determining as well the quality and quantity of the biogas. At the design stage, a decision is needed on whether or not the prototype is to produce both biogas and other products like the slurry. That decision would, therefore, influence the final digester type and conditions inside the digester, like the ability to regulate the temperature.

While studies exist that focus on the slurries produced alongside the biogas production endeavours across the world, there is minimal research geared towards providing valuable information to the agronomists and environmentalists on the suitability of the varied slurry types owing to the difference in the raw materials fed into digesters. According to the Food and Agriculture Organization of the United Nations, FAO (2006), it is necessary for the agronomists to get information that can help them in deciding the slurry type that best fits a specific class of crops and their needs. That would be an improvement from the generalization of information that slurries are useful in the provision of nutrients to the crops as organic fertilizer. Similarly, an environmentalist would need information on differences in biogas slurry composition relative to the feedstock. As such, decisions concerning the suitability of disposal method or crop match is made from a position of specific knowledge, rather than the generalized assumptions currently prevalent in the field.

The increasing preference for biogas in both rural and urban setups in Kenya as a source of renewable energy means more biogas slurry would be produced. It is, therefore, necessary to analyze the different chemical composition of the various slurries, predict their effects on the soils to which they are released, and match them with the crops for which their effects would help optimize the yield. Moreover, if there are chemicals in the slurries whose long or short term effects would negate the intended increase in yield or endanger the life of humans and other animals, it is necessary that the probable consequences are determined and documented.

1.2 Problem Statement

An increase in the efforts to find alternative sources of energy has made biogas production a popular research and investment focal area. The production of the gas comes with similarly increasing amounts of biogas digestate slurries, which are often used in crop production as organic fertilizer or disposed into the environment. The availability and affordability of Biogas slurries to farmers as an alternative to commercial fertilizers have made it popular. However, the Kenyan farmers have little information on the suitability of the different slurry types to the varied crops on which they apply the slurries. It is crucial, therefore, to analyze and document the elemental composition of the different slurry types and determine their probable effect on the soils and environment onto which they are released.

While the current status may appear normal, there is an opportunity to improve on the current practices, which would be solved by studying closely the relationship between these classifications and better performances of crops. Given the relatively better performance of crops in the current condition where all slurries are considered applicable to all classes of crops, it is arguably an opportunity that lies unexploited if the same could be customized to specific crop types. In addition to the customized information with the aim of improving yield, the environmental impacts of the slurries on both the agricultural soils and the general environment differ with the classes of slurries, as discussed earlier. Some slurries could be richer in certain essential nutrients, for example, zinc as compared to others, while another could be introducing heavy metals to the environment, thus contributing to environmental pollution.

1.3 Objectives

1.3.1 Overall Objective

To comparatively evaluate the elemental components of varied Biogas Digestate Slurries hence their probable impacts upon application as Biofertilizers.

1.3.2 Specific Objectives

The specific objectives were to;

a) Analyze cow dung, human waste and abattoir waste biogas digestate slurries for comparative characterization.

b) Establish the chemical composition of the different Biogas Digester Slurries.

c) Assess the probable effects of the application of the digestate slurries when applied as Biofertilizers.

1.4 Justification

Kenya has up to 20,000 biogas systems, spread across 36 Counties (MoE, GOK, 2017). The Country's potential is much higher. With the huge number of digesters coming up, the management of the digestate needs to be given fair attention. The general and popular use of the digestate as an organic fertilizer is devoid of the detailed information that is required in order to make it effective. Worse still, the popular use could have adverse effects on the soils and environment. This would negate the very reason for which the world encourages the use of Biogas; environmental conservation and clean energy use.

According to the Kenya Climate Innovation Center (2017), over two and a half million people in Kenya eat less food of low nutritional value resulting in malnutrition. Partly, these statistics are down to the inability to have the required agricultural inputs to improve crop productivity and nutritional value. As such, the interest in growing crops under the application of digestate is of interest to both policymakers and agronomists. It can be a cost-effective way to enhance crop productivity and by extension, tackle food insecurity problems. However, different crops and growth stages have varying nutrient requirements. Therefore, it is important to determine the potential and suitability of different digestate, based on the feedstock. Such information will also be crucial in assessing potential environmental impact, for example, heavy metal toxicity.

It is, therefore, essential to know the composition of digestate, as well as the best method for accurate application to growing crops. This will minimize any unintended negative impact on the environment and also maximize farmers' profits. To the agronomist, this information is useful in matching the crop nutrient requirement to the right digestate application. On the other hand, it enables environmentalists to determine the extent to which the release of the digestate affects Flora and Fauna. To the design Engineer and Scientists, the design of the biogas digesters should take into consideration the expected wastes and formulate solutions that solve the exact components problem or need.

1.5 Scope of the Study

In this study, three biogas digestate slurries were considered; slurries from cow dung feedstock, abattoir waste digestate and human waste digestates. The concentration of essential nutrients; Ca, Mn, Fe, Cu, and Zn were determined. The nutrients were chosen out of their modal appearance among the rest of the elements out of the eighteen elements that were of focus during the x-ray fluoroscopy. Further, the scope of this study was on elements as opposed to elemental compounds. Also, toxic metals like Pb, Hg, and Cd were evaluated. The energy dispersive XRF was used in determining the elemental composition of the samples. The fluoroscopy instrument had detection limits in parts per million (ppm).

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Currently, the world is facing serious issues which include global warming, emission of greenhouse gases, deteriorating air quality and nitrate and phosphate enrichment of coastal and inland waters (Klaus, 2018). These challenges mainly emanate from over-reliance on fossil fuels, hence the calls for more efficient sources of power, heat, food production and transport. In the agricultural sector, for instance, manufacture and usage of inorganic fertilizers are a key source of air pollution due to fossil fuel usage and emission of nitrous oxides. Anaerobic digestion of organic materials has been recognized as a viable alternative to fossil fuel, as it is both a source of renewable energy (biogas), as well as organic fertilizer, i.e. digestate (Lukehurst, 2010).

In anaerobic digestion (AD), breakdown of organic matter by micro-organisms in limited oxygen environments (airtight) takes place. Biogas, which is an important renewable energy source and digestate, and a highly valuable organic fertilizer are produced. This process can use a wide range of organic material (feedstock) such as agricultural crops, animal manures, food and agri-food processing residues, organic household and industrial waste, municipal solid waste, sewage sludge, among others (Lukehurst, 2010). The feedstock can either be a single substrate or a combination of two or more substrates. The AD process can also be categorized based on the dry matter content of the feedstock into wet digestion (dry matter < 15%) or dry digestion (dry matter > 15 %). Therefore, the associated benefits of AD include reduced usage of fossil fuels and mineral fertilizers, reduced greenhouse gas emissions, open manure storage, and offers an efficient way for resource recycling (Crolla *et al*., 2013; Lukehurst, 2010). Figure 2.1 gives a summary of the anaerobic digestion process.

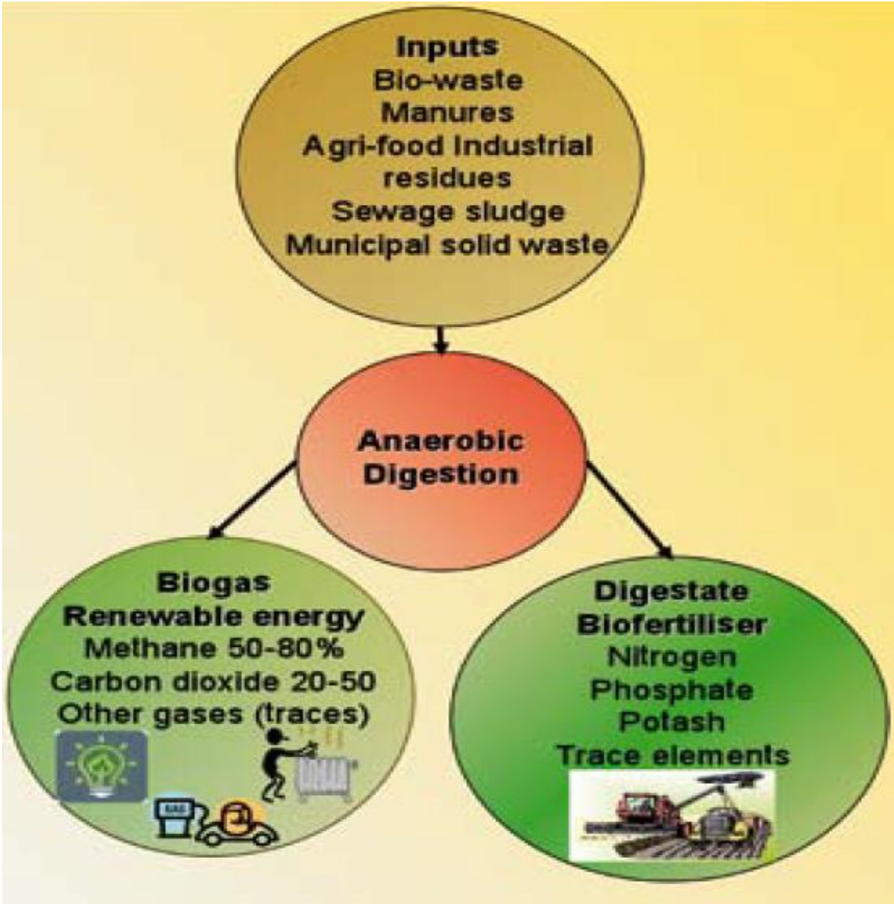

Figure 2.1: Anaerobic digestion process as presented by Van Haandel and Van der Lubbe, (2007).

In principle, biogas production involves anaerobic digestion (breakdown) of biodegradable organic matter such as crop residue, human and animal waste, and household waste. During the digestion process, nutrients are transformed, for example, P into PO_4^{3-}–P and N into NH_4^{+}–N (Burke, 2001), pathogens die-off, and volatile fatty acids are consumed (Monreal *et al*., 2012; Crolla and Kinsley, 2008). Consequently, the land application of the digestate, a by-product in the biogas production process, could have enormous agronomic and environmental benefits. For instance, nutrients transformation into readily available inorganic forms has been associated with increased crop productivity (Crolla and Kinsley, 2008).

Anaerobic digestion involves four stages that may occur simultaneously (Van Haandel and Van der Lubbe, 2007). In the first stage, the polymer chains in the feedstock are broken down, and the smaller molecules are dissolved, a process called hydrolysis. The composite organic substances are further broken down into fatty acids, basic sugars, and amino acids. The second phase involves advanced digestion by acidogenic bacteria of the remaining components, i.e., acidogenesis. In this phase, CO_2, NH_4, H_2S alongside other by-products are formed. The third phase is called acetogenesis, whereby the basic sugars and molecules produced in the earlier stages are further broken down into CO_2, acetic acid, and hydrogen by acetogens (Shakib & Rashid, 2019). Finally, all the intermediate products formed during the digestion process are transformed into methane, CO_2, and water, in a process called Methanogenesis.

Biogas is made up of CH_4 and CO_2 with smaller amounts of water vapour, H_2S, and possibly NH_3 (Rajendran *et al.*, 2012). Table 2.1 outlines the composition. It can be used in power generation and for domestic purposes like heat generation. For optimal production, AD is dependent on a number of different factors. These may include feedstock type, temperature, carbon-nitrogen ratio, pH, and mixing efficiency (Rajendran *et al.*, 2012). The C/N ratio is particularly important since the bacteria responsible for the digestion process require both nitrogen and carbon. However, the bacteria consumption of carbon is higher than that of nitrogen by a factor of thirty. According to Rajendran *et al.*, (2012), if all the other parameters are ideal, then a C/ N ratio of 30:1 is perfect for the feedstock.

Table 2.1: Chemical composition of biogas

Component	**Concentration range**	**Mean value**
Methane (CH_4)	45 – 75 %	60 %
Carbon dioxide (CO2)	25 – 55 %	35 %
Water vapor	3 – 10 %	6 %
Nitrogen	0.01 – 5 %	1 %
Oxygen	0.01 – 2.5 %	0.3 %
Hydrogen	0 – 1 %	< 1 %
Ammonia	0.01 – 2.5	0.7 %
Hydrogen sulphide	10 – 10000 mg m^{-3}	< 500 mg m^{-3}

The digestate from AD is a valuable byproduct, bio-fertilizer. During AD, the organic matter in the feedstock decreases, but the more degradation resistant component remains, that is, digestate. It not only contains the residual organic matter after the digestion process but also the entire nutrients originally contained in the feedstock. Land application of raw digestate (unprocessed) contributes significantly to crop nutrient supply and soil organic matter and is common with small scale digesters. Further processing of the digestate separates the inorganic nitrogen-containing wet fraction from mostly phosphate and organic material containing a dry fraction of the digestate (Corre and Conijn, 2016; Kowalczyk-Juśko *et al*. 2015). Processing the digestate helps to reduce transportation costs and for nutritional value addition (Biernat *et al*. 2012).

2.2 Production of Biogas Digestate Slurries

Since the general global trend is on the substitution for hydrocarbon fuels with those that are considered renewable and clean, biogas digestion is gaining momentum both as a way of handling wastes and as a means to producing energy for heating, among other uses like generation of electricity (Oludhe and Okoola, 2010). The increasing popularity of biogas production in Nairobi and neighbouring regions imply as well that the production comes with the wastes with which the production is associated. As such, there is a need to develop ingenious ways of disposing of these wastes. For those at the centre of urban setup, the natural decision is to dispose of them as council wastes. However, in agricultural zones of the Country or within the outskirts of the urban, these 'wastes' find use in food production as organic fertilizers. Primarily, therefore, the digestate discussed herein emanates from the process of production of biogas, and hence, as a secondary product of the process, it occasionally takes the intervention of third parties to get the digestate into agricultural use.

Since the production of biogas does not entail the use of a single raw material for digestion, the digestates are as varied as the raw materials used in the production of the biogas. If a digester is fed human wastes as the raw material, both the amount of gas and the nature of the final digestate vary from a case where the raw material is say, cow dung. These differences are in both quantitative ratios and in qualitative components of the digestates that end up available to the agronomists for application in the farms (Rehl and Müller, 2011). The interest in getting the differences among the digestates emanates from the possibility of matching the crops with digestates that suit their elemental requirements the most.

Most of the existing literature gives a generalized composition-mainly by percentages- of BDS. For instance, Lukehurst (2010) is primarily focused on the use of the digestate but overlooks the fact that different biogas raw materials would result in varied digestates hence the need to close in on the variations. Further, apart from the soil macronutrients in Nitrogen, Phosphorus, and Potassium (NPK), most research works disregard the elemental composition of other elements. The definition given by UK Government (2017), as an example, states that BDS is composed of Nitrogen, Phosphorus, and Potassium (NPK) elementally and that these are between 4-11 Kg per tonne of BDS. Notice here that the literature is conspicuously silent on the over 99 percent of the composition of the BDS.

Granted, a majority of the digestate composes the major nutrients in NPK, but the differences in the microelements make some BDS classes more appropriate for corresponding crops that are in need of the micronutrients more than others. While on the one hand, a majority of researchers clamp the slurries together, there is the group of research documentation on the other hand whose focus is on comparing the BDS to other manure and/or fertilizer types. Research done by Risberg *et al*. (2017) falls into this group. They focused on comparing how the two categories of soil nutrients boosters affected the physical and chemical behaviours of soil, for example, their effects on soil respiration. They, however, stopped short of stating the elemental compositions of each category of fertilizers, and more prominently of BDS.

From the preceding, it is necessary to analyze the elements in different types of BDS. This would assist those applying the same as organic manure to tell which crops would need what category of Biogas slurries. Better still, for environmentalists, there is a need for certainty on what elements (both primary and trace) are introduced on both agricultural lands and on the general environment when these slurries are disposed of as wastes.

2.3 Digestate as a Bio-fertilizer

Intensive usage of mineral fertilizers has been associated with high production cost, loss of soil carbon, and nitrate pollution. One of the viable alternatives is soil fertilization using organic matter (Corbeels, Cardinael, Powlson, Chikowo, & Gerard, 2019). Extensive research has been carried out on traditional organic amendments like sewage sludge, compost, and manure. This is, however, not the case for biogas digestate, whose impact on soil and environment is largely unexplored. Consequently, the potential and effectiveness of digestate as a bio-fertilizer and in soil amendment is still debatable (Nkoa, 2014). According to Al Seadi and Lukehurst, (2012), the low confidence in digestates' quality and safety has resulted in its slow adoption as a suitable alternative to mineral fertilizer in many countries, hence the need for quality assurance measures.

The most documented biogas slurry handling method is as organic manure. Most studies are concerned with the effects of the said slurry on soil fertility and/ or how it alters the composition of the soil nutrients. For instance, Stefanie *et al*. (2015), focused on comparing the behaviour of soil with and without the application of Biogas slurry on it as an organic fertilizer, while Abdullah *et al*. (2017), focuses on the difference in biogas contents, its byproducts, and its effects when some of the raw materials are mixed and introduced into the biogas digester. The available literature does not focus on the slurry; neither do they focus on the elemental differences of the slurries as relates to the different raw material fed into the digesters.

Johansen *et al*. (2013) conducted a comparative study between digestate and farmyard manure for land application. Digestate was found to have high nitrogen content and low carbon content. The N: C ratio was determined at ten times that of farmyard manure, thus of better quality. Crolla *et al*. (2013), observed that the AD process results in the transformation of nutrients into forms that are readily adsorbed by plants. For example, the organic N in the feedstock is converted to inorganic NH_4^+–N, while organic phosphate is converted to inorganic PO_4^{3-}—P. The enhanced concentration of readily available inorganic nutrients leads to increased crop productivity (Gerardi, 2003). A review by Nkoa (2014), noted the need for proper management and handling of digestate as an organic fertilizer/ amendment. Compared to undigested manure, the digestate was found to have a higher potential to impact human's health and environment negatively. For example, the digestate was linked with higher ammonia emissions, while higher Zn, Mn and Cu concentration could result in bioaccumulation in agricultural soils.

Alburquerque *et al*. (2012) assessed the suitability of different digestates from agroindustry and farm residual feedstock as bio-fertilizer. The digestates were found to be of high potential fertilizer value attributable to high N, P, K, and micronutrients contents. For instance, a large proportion of nitrogen content, > 70 %, in the digestate samples were contained the inorganic NH_4-N form. Digestates with high inorganic NH_4-N content was considered to be of high fertilizing potential, because it is easily nitrified under favourable conditions hence improved bioavailability to crops. Trace element content was determined within the recommended nutritional and safety limits. However, high Zn (200 - 4700 mg kg^{-1}) and Cu (80 – 700 mg kg^{-1}) levels were reported in some digestates. The authors identified Zn and Cu content, biodegradability odour emission, hygiene, and phytotoxicity as some of the limiting factors to full exploitation of digestate benefits. Therefore, it is important to ensure the digestate quality is up to acceptable levels. This can be achieved by monitoring the quality of feedstock as well as of the digestate.

According to Fuchs *et al*. (2007), digestate application can positively or negatively influence soil quality and plant health. Based on an assessment of different digestate samples, the quality of the feedstock was noted to be the key determinant to digestate quality. The nutritional and organic matter content greatly varied between different digestates. Similar findings were made by Lukehurst *et al*. (2010), in addition to digester characteristics, and mode and time of application. Therefore, it is important to understand the fertilizer composition of the digestate, as well as the best method for accurate application to growing crops.

In conclusion, there is a knowledge gap in agronomic characteristics of digestate as well as their effects on agricultural soils and the environment in general. Most studies focus on major elements N, P, and K content, in addition to physiochemical parameters like salinity and organic matter content. Little attention is accorded to trace elements that play a crucial role in plant health and also a potential source of environmental toxicity due to their tendency to bio-accumulate

2.4 Role of trace elements in plant nutrition

The role of trace elements/ micronutrients in plant nutrition has been attracting greater attention lately, due to increased awareness of the adverse effects of deficiency and toxicity of these elements. For optimal crop health and yields, a certain concentration threshold that is particular for each trace element and crop variety is required. Examples of some of the essential trace elements include Fe, Mn, B, Mo, Zn, Cu and chlorine, and are required for different processes and enzymatic actions. Therefore, the essential nutrients need to be present in the soil at sufficient plant-available levels for optimum productivity. Other elements like Ni, Cr, F, and Se do not have any recognizable function in plant nutrition.

Initially, the soil's trace element content largely depends on the parent material from which it originates. However, enrichment through nutrient cycling using fertilizers and organic manures, as well as depletion through erosion and leaching, can take place in particular soil profiles (Kamau *et al*., 2014; Nayak *et al*., 2014). In dust prone areas, deposited dust can also lead to trace elements enrichment. Human activities like mining and industrial waste can significantly influence the concentration levels. In soil, these elements exist in different forms that depend on physicochemical parameters like pH. Also, the elements are usually complexed with organic and inorganic ligands (Hajar *et al*., 2014).

Trace elements uptake by plants is distinctive for every element and may differ with varieties or species. The element- plant interactions is relative to factors specific to that particular element. For example, Cu uptake is dependent on the total concentration of Cu in the soil as well as plants' ability to transfer it across the soil-root interface (Hajar *et al*., 2014). One of the critical factors that influence the bioavailability of trace elements to plant is pH. Once in the plant, these elements play a critical role in plants' health and productivity.

In soil, Cu occurs mainly in the divalent form, Cu^{2+}, and primarily present in the mineral crystal lattice. It is particularly adsorbed to soil organic matter carbonates and Fe, Al, and Mn hydrous oxides. In a plant, Cu plays a role in the activation of enzymes in various growth processes. Besides, it helps in the production of vitamin A and protein synthesis. Therefore, Cu is an essential plant nutrient. Some of the symptoms associated with Cu deficiency include poor pigmentation, stunted growth, and eventually death of leaf tips.

Iron is an essential micronutrient in the plant. It is adsorbed as a ferrous ion, Fe^{2+}. Some of the roles of Fe in the plant include the formation of chlorophyll and activation of biochemical processes like photosynthesis, symbiotic nitrogen, and respiration. Although Fe deficiency is rare, it may occur in alkaline soils. Turf, ornamentals, and individual trees are especially susceptible to iron deficiency. Symptoms associated with Fe deficiency include twig dieback, interveinal chlorosis, especially in young plants, and if extreme cases, it may result in plant death.

Plant adsorb Mn nutrient from the soil in the form of Mn^{2+}. Manganese serves as an activator for enzymes in various growth processes, and it assists iron in chlorophyll formation. The deficiency of Mn in the soil is rare but may occur of alkaline sandy soils (pH > 8). Crops most responsive to Mn are beans, potato, onions, strawberries, apples tomato, spinach, peas, raspberries, and grapes. The Mn deficiency symptoms are similar to those of Fe, e.g. interveinal chlorosis of young leaves and leaf discolouration.

Zinc is an essential component of various enzymes in plants. It is adsorbed as the Zn^{2+} by plants. It plays a role in chlorophyll and protein production and regulates the synthesis of indoleacetic acid, which is an essential plant growth regulator. Zinc deficiencies have been associated with sandy soils with low organic matter content. Additionally, the solubility of Zn decreases in very alkaline soils making it less bioavailable. In the soil, Zn and P exhibit antagonistic effects, whereby, Zn becomes readily available in soils with high P content. Symptoms of Zn deficiency include decreased stem length and fruit bud formation, resetting of terminal leaves, interveinal chlorosis, and dieback of twigs.

Calcium offers a building block for membranes and cell walls and is necessary for cell formation. It is a constituent of crucial plant carbohydrates, like cellulose and starch. Calcium promotes proper root and stems growth, plant rigidity, and vigour. Plants adsorb calcium in the form of the Ca^{2+}. Calcium deficiency can be remediated by liming. Deficiency symptoms include growing point dieback, death of terminal buds and root tips, weakened stem, stunted root growth, and premature shedding of buds and blossoms

Table 2.2: Properties of Select Elements

Element	Form of availability	Role in Plants	Symptoms of Deficiency
Cu	Cu^{2+}	Activation of Enzymes, Protein Synthesis	Poor Pigmentation Stunted Growth Death of leaf tips
Fe	Fe^{2+}	Formation of chlorophyll	Twig dieback Chlorosis
Mn	Mn^{2+}	Chlorophyll formation	Chlorosis
Zn	Zn^{2+}	Chlorophyll formation	Decreased stem length, fruit bud formation
Ca	Ca^{2+}	Cell formation	Death of terminal buds, stunted growth

2.5 X-Ray Fluoroscopy (XRF)

XRF is an analytical method of determining the chemical composition of all kinds of materials. This is the definition given by Brouwer, (2013). Other than the chemical composition, the method, he says, can be useful in determining depths of coatings and paintings. ThermoFisher Scientific (2015), on the other hand, asserts that XRF is a non-destructive analytical technique that is useful in determining the elemental composition of substances. Both sources agree that the method is useful irrespective of the physical state of the substance to be analyzed; solid, liquid, air or a mixture of the states.

The mechanism of the technique, according to Brouwer, (2013), begins from an X-Ray source. When the X-Rays irradiate a sample, the elements in the sample emit fluorescent X-Ray radiations of characteristic energies. Stosnach, (2007), however, says that when atoms are irradiated with X-rays, they emit secondary X-Rays called fluorescence radiation. This makes XRF analysis possible because the wavelengths and energies are specific to elements while the fluorescence intensity is useful in determining the concentration of individual elements. The analysis of the fluorescent radiations is called XRF spectroscopy. From spectroscopy, a spectrum is obtained, showing the intensity of the fluorescent X-Rays in counts per second as a function of Energy, as in Figure 2.2.

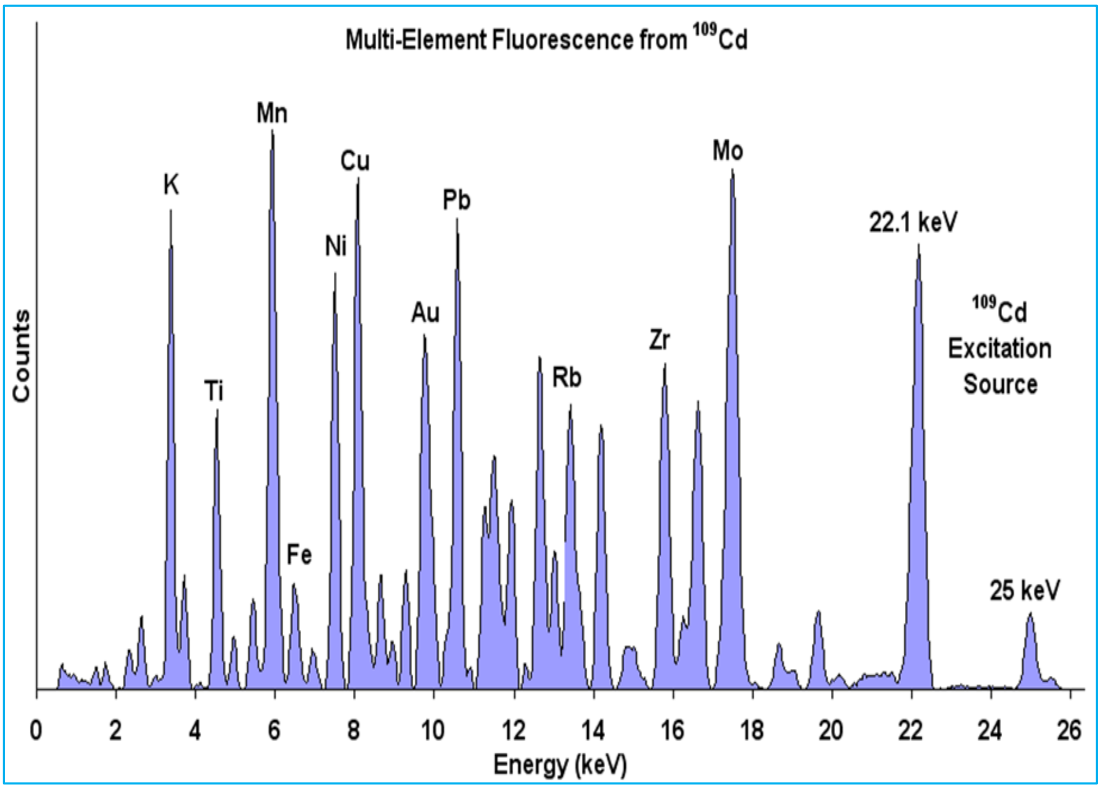

Figure 2.2: An XRF spectra (Brouwer, 2013)

The XRF spectroscopy has two approaches; Energy Dispersive X-Ray Fluoroscopy (EDXRF) spectroscopy and Wavelength Dispersive X-Ray Fluoroscopy (WDXRF) spectroscopy. The primary difference in the two methods is the detection of the fluorescent X-Rays and the analysis method involved. In EDXRF, the detection system focusses on the measurement of the energies of the emitted X-Rays. The working principle is on the generation of electron-hole pairs in a semiconductor material. The generated X-rays are directed to a detector, which converts the X-Ray energies into voltage signals through the formation of electron-hole pairs. A pulse processor then measures the energies of these signals then passes them on to an amplifier. They then are converted into digital signals for analysis. Energy is characteristic for each element in the material.

At the initial stage of the sample analysis, the EDXRF display shows peaks, as in figure 2.3 below. The visual presentation is then analyzed both quantitatively and qualitatively to characterize the sample.

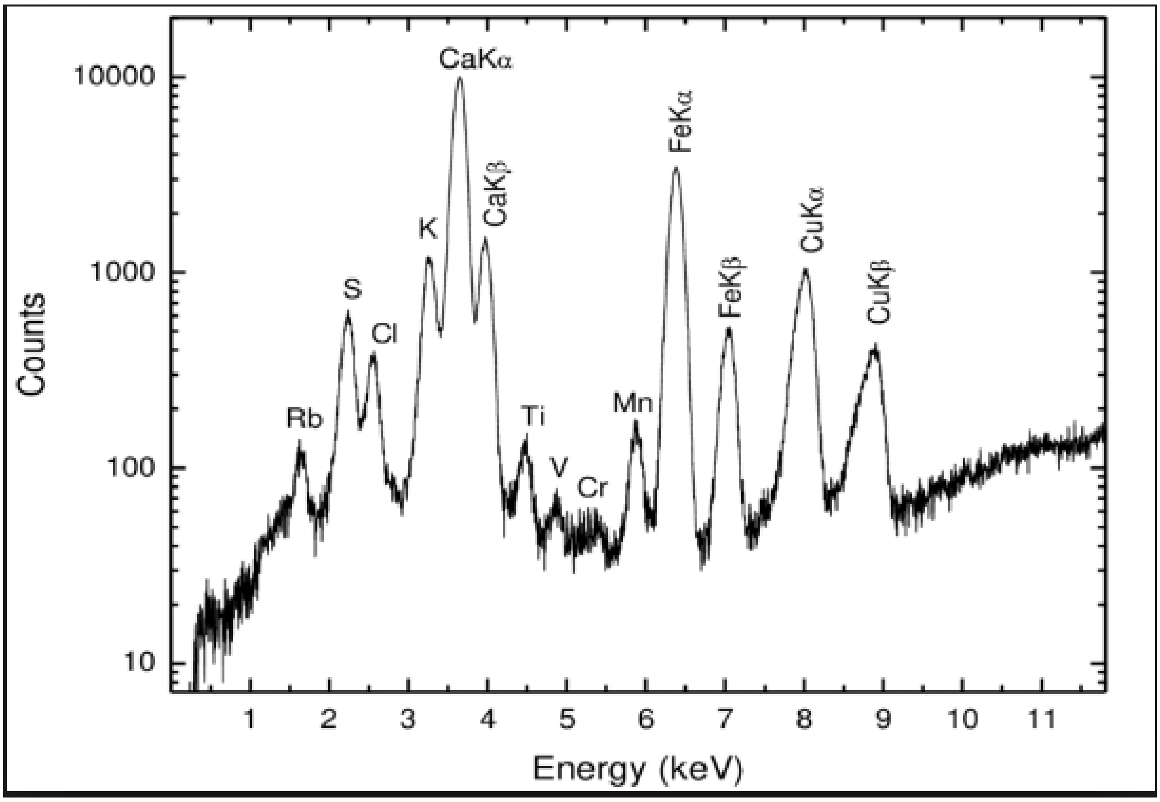

Figure 2.3: AXIL software display during sample analysis

For the WDXRF, the incoming X-rays from a sample are directed onto a crystal, which then diffracts them according to their wavelengths in different directions like a prism. The detector is placed at different angles to measure the intensities of different X-Rays (Brouwer, 2013). To measure the intensities of different X-Rays, the detector is rotated to cover different angles. Similar to the EDXRF method, a different wavelength is characteristic of different elements.

Total reflective x-ray fluorescence (TXRF) is a special kind of EDXRF with the difference being in the excitation geometry (Kawai, 2018). In it, the beam is nearly parallel to the surface of the reflector on which the sample rests. This extreme grazing angle allows placing the detector very close to the sample resulting in a large solid angle for the detection of the fluorescence hence high detection efficiency. The excitation of the sample is by both the primary and reflected beam; thus, the signal of the fluorescence is twice as intense as in standard EDXRF.

Table 2.3: Comparison between EDXRF and WDXRF (Brouwer, 2013)

Property Compared	**EDXRF**	**WDXRF**
Sensitivity	Not Recommended for light elements Good for heavy elements	Reasonable for light elements Good for heavy elements
Resolution	Less optimal for light elements Recommended for heavy elements	Less optimal for heavy elements Better resolution for light elements
Power consumption	Low (5-1000 W)	High (2000-4000 W)
Measurement	Simultaneous	Sequential/ Simultaneous
Critical Moving Parts	No	Crystal
Detection Limits	Less optimal for light, recommended for heavy elements	Suitable for Be and all heavier elements
Costs	Relatively affordable	Relatively Expensive

X-ray Fluorescence (XRF) spectrometry has become one of the most used techniques for the analysis of trace elements. X-ray spectrometry is efficient, reproducible, and accurate for the determination of elements with Z >13 (Jbrgensen *et al*., 2005). It is considered to have low detectability limit (ppm-ppb) and quality selectivity (Szyczewski *et al*., 2009). This technique is non-consumptive and is applied for multi-element determination and quantification of samples with a wide range of matrix forms (Towett *et al*., 2013).

X-ray spectrometry has been used widely to study substances that would be difficult to analyze with other conventional methods because of sample matrixes. X-ray spectroscopy can be used in the non-destructive analysis, which means that the sample matrix is preserved. Therefore, it has been utilized for the determination of trace elements in various types of samples with the advantage of avoiding digestion with corrosive acids.

2. 6 Summary of Literature Review

Most current research focuses on solving the global climatic complications that are associated with the Fourth Industrial Revolution (4IR). These revolve around climate change and the menace of greenhouse gas emissions. One of the leading problems with these emissions is that of the use of inappropriate fossil fuels, which are leading pollutants. Biogas is one of the solutions to the extremes of the continued use of fossil fuels. Similarly, in Agricultural practices, the use of inorganic fertilizers is a continued concern for environmentalists. As such, there are efforts to replace fertilizers with organic options. One of the leading organic options is the use of biogas digestate slurries, which are majorly considered as a byproduct of the production of Biogas for fuel.

Biogas production, therefore, solves the twin problems by lowering the production of gases with greenhouse effects as well as the availability of organic fertilizers. The research herein focuses on the second bit of producing organic fertilizers from the Anaerobic Digestion (AD) process of biogas production. While the AD process remains relatively similar while digesting the varied organic raw materials fed to biogas digesters across the globe, the end product used as agricultural fertilizer varies in composition from one feedstock to the next. The differences of this composition informed the need for this research with focus and interest narrowing to the possibility of certain crops getting suited more to specific Biogas Digestate Slurries (BDS) as compared to others. As well, some BDSs could be more harmful to the environment compared to others.

Most existing research and literature reviewed in this field overlooks the variations that this research set out to ascertain. Indeed, nearly all the literature in the field focuses on NPK components of the BDS since agriculturally, these are considered primary elements without which most crops would fail. On the positive though, a specific crop, like kale, would benefit more from say a BDS extracted from digesting human wastes as compared to the BDS got from cow dung-based disasters given the possible variation in the elemental composition of the different slurries. Given the rising interest in trace elements like; Fe, Mn, B, Mo, Zn, Cu, and Cl, it is needful to get the individualized composition of the different digestates as contained in the subsequent sections of this work. These micronutrients determine the quality of crops in addition to the quantity of the same. In different crops, they help with the development of specific parts of interest like leaves, tubers, flowering, among other critical sections.

The above classifications are possible through Energy Dispersive X-ray Fluoroscopy (EDXRF), which is a non-destructive analytical technique that is useful in determining the elemental composition of substances. The basic working principle behind the science of the EDXRF spectroscopy is that when the X-Rays irradiate a sample, the elements in the sample emit fluorescent X-Ray radiations of characteristic energies. The energies are then reverted to tell which element is present in the irradiated sample. The technology has the capability of determining the amount of the element in addition to showing what element it is. In this study, the second part of the use of EDXRF is as vital as the first since, alongside telling which elements are present in the samples irradiated, the research interests itself in knowing the quantities. The same would tell what crop is most fit for a specific crop if an agronomist had to choose between using one digestate instead of the other for a particular crop.

This literature review, therefore, focused on determining the knowledge gap and the need to justify the proposed research on the elemental composition of the different Biogas Digestate Slurries (BDS) available through the production of Biogas across the Republic of Kenya and using the samples from Nairobi and the metropolitan regions. It then narrowed into the process of production of the said BDS, and the uses of the same, given that their agricultural application is steadily on the rise with the need to replace the inorganic fertilizers. The review then delved into the micronutrients and their needs in crops before finalizing with the technology through which the results are analyzed.

CHAPTER THREE

MATERIALS AND METHODS

3.0 Overview

The used methodology involved the following main stages;

a) Sample collection and preparation;
b) Sample analyses using EDXRF Spectroscopy;
c) Quality control and method validation and
d) Data processing and analyses.

3.1 Sample collection and Preparation

3.1.1 Sampling

Stratified sampling was preferred as a sampling method given the unique variation in the composition of the digestates available from the digestion process of the different Feedstocks used in biogas production across the locations, as documented by Ahmed (2009). The different categories of digestate slurry based on the feedstock were collected and analyzed for trace element content. This would help in determining their suitability as bio-fertilizers and if they pose any significant environmental risk. These categories included digestates resulting from the human waste feedstock, abattoir feedstock and cow dung. Three sites were selected; Kibra estate in Nairobi for human waste digestate, Kiserian area in Kajiado for abattoir digestate, and Alliance high school in Kiambu where animal waste (cow dung) was being used. Figure 3.1 is a Google map extract of the three locations, which are all within or around the County of Nairobi.

Of the three regions in and around the County of Nairobi, there were identified five points in each of the three and a sample collected from each of the five points. That implied a collection of fifteen samples from the different digesters in each visit. The fifteen samples were collected three times. A total of forty-five total samples therefore were collected.

Figure 3.1 shows the regions from where the samples were collected relative to the position of Nairobi City County.

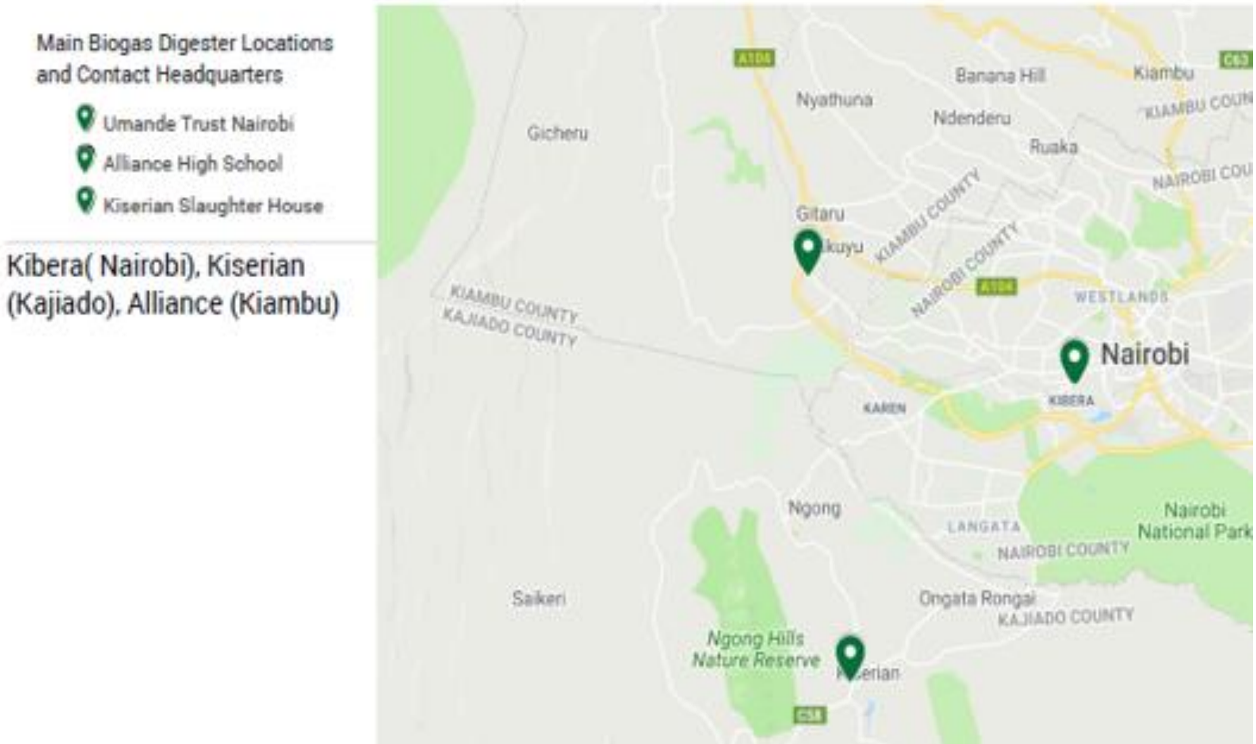

Figure 3.1: The Nairobi Metropolitan areas from which the samples were collected.

Kibra is an informal settlement located in Nairobi. It is characterized by high population density and extremely low income, with the majority of the residents earning under a dollar per day. The unemployment rate is high. The residents don't have access to clean water and sewerage systems. This has resulted in a sanitation crisis, characterized by overflowing latrines and open defecation, commonly referred to as 'flying toilet.' To overcome this challenge, treatment of human waste into biogas and bio-fertilizer is being implemented by different organizations as a sustainable way to manage waste. Human waste from the installed toilets is collected and fed into holding tank and bio-digesters. In this study, five different digester installations in Kibra were selected for sampling, and three samples collected from each. That resulted in fifteen samples from Kibra alone (Human waste digestates).

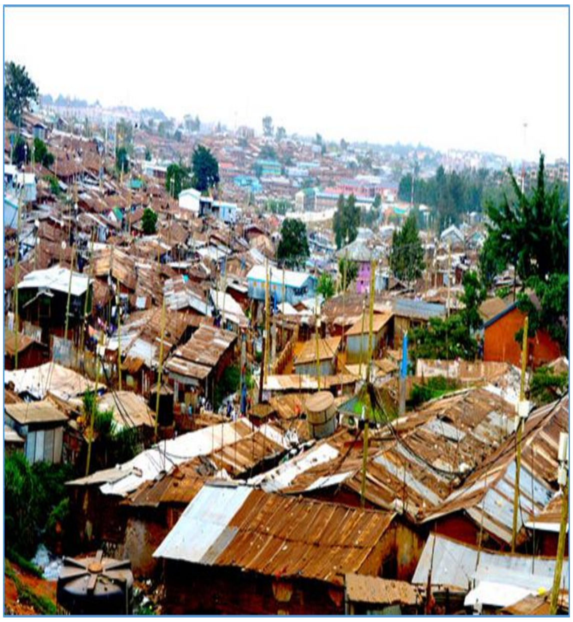

Figure 3.2: Sample Collection in Tosha II and Aerial image of Kibra settlement

Kiserian town is located in Kajiado County and lies at the foot of the Ngong hills. Livestock farming is a crucial economic driver in the region. Most of the animals for slaughter, i.e. cattle, sheep and goats are transported to Keekonyokie abattoir located in the town centre. The abattoir is a community-based enterprise that served livestock farmers in Kajiado and Narok Counties and was initiated to help the farmers get competitive prices. Beef from the slaughterhouse is supplied to Nairobi and neighbouring areas. One of the key challenges to the enterprise was huge volumes of waste from the facility in excess of 30 metric tonnes, putting it at imminent closure by the environment regulatory body NEMA. To be able to manage the waste from the abattoir, bio-digesters have been installed. All the abattoir waste is directed to the digesters for treatment and biogas production. The biogas is piped to a storage facility, where it is used to generate electricity to run equipment and power the cold room, plus packaging it for sale. In addition to cost-saving measures and additional income, the project also supports the fight against deforestation and climate change. Fifteen (15) digestate samples therefore were collected in three sampling periods from Kiserian.

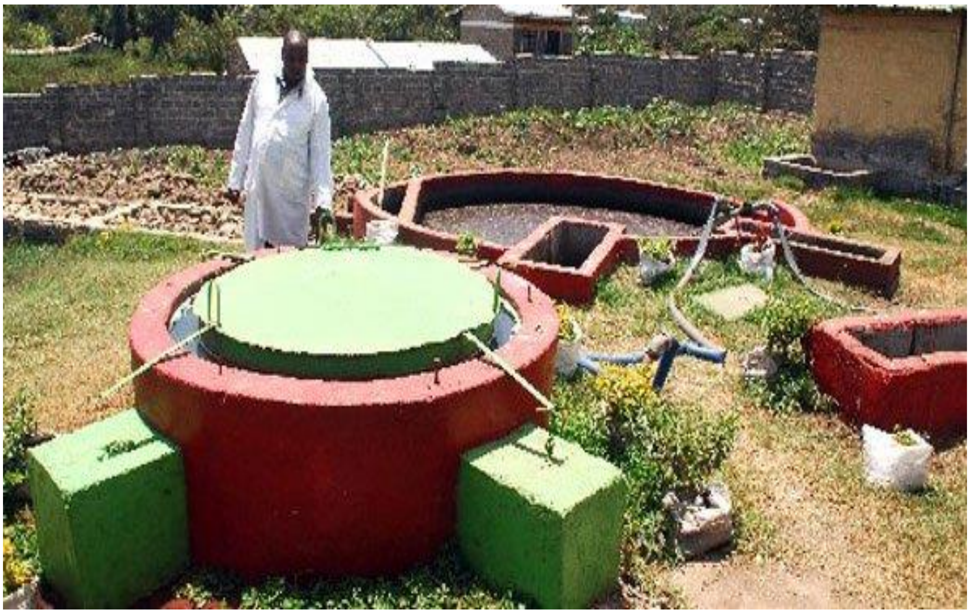

Fig 3.3 Biogas digester installation at Keekonyokie abattoir

Located in Kiambu County and Kikuyu sub-County on the outskirts of the Capital city of Nairobi, Alliance boys' high school is one of the top-rated schools in Kenya. It has a student population of over two thousand. The National Secondary school has numerous projects that serve both the academic purposes of training the large students' population as well as help the institution manage the limited finances it receives in government revenue, alongside the collections it receives from the students' sponsors, among other fundraising methods. To cater for the milk demand in the school and cut the cost of purchase, the school ventured into dairy farming. Also, biogas plants were established to provide an environmentally friendly and sustainable power source, which will contribute to reducing deforestation and pollution. The manure from the animals is fed into the digester. The resultant byproduct, the digestate slurry, is applied to the fodder fields. Fifteen (15) samples were collected from the school and the neighbouring farms that were using cow dung as the digester feedstock.

3.1.2 Preparation of specimen

The process of preparing the samples involved four stages. The first of the four is the drying of the samples in the form they are when sampled from the digester locations. Once dried, the samples were separately crushed and pulverized using the electronic pulverizing equipment at the INST. Once crushed, the samples were used to create three pellets out of each sample using the press equipment. The triplicate formation of pellets aided in achieving the repeatability of the output from the analysis. The three pellets were then placed in Petri dishes, separated by pieces of papers. The separation thus prevented contamination and cross-contamination

The drying was done naturally through the sun. The natural drying help preserves the integrity of the elements in the BDS; hence, when the EDXRF is used to analyze the samples, all the elements in the original sample collected would thus be present (Takahashi, 2015). Once dry, the samples were ground into a fine powder (< 75 µm) for size reduction and to homogenize the samples. The homogenization aids in forming the pellets. From each sample, the pellets were prepared using a hydraulic press, where a 400 mg portion of the samples was pressed into pellets. The samples were then analyzed using EDXRF spectroscopy.

Figure 3.4: (A) Sample drying and (B) Sample Crushing

3.2 Sample analyses using EDXRF spectroscopy

The prepared digestate sample pellets were analyzed using the EDXRF spectrometer (AMPTEK Experimenters XRF kit), available at the Institute of Nuclear Science and Technology, University of Nairobi. The technical specifications of the spectrometer are presented in table 3.1, while a schematic representation is given in Figure 3.5 (a). The calibration and stability was ensured through checks and daily comparison with the standards. The sample pellets were placed on the sample holder and irradiated with an x-ray beam for 200 seconds. An x-ray tube with a silver target was used as the radiation source. Accuracy and calibration adherence was checked before each analysis. Quantitative and qualitative analyses of the obtained spectra data were then carried out using AXIL (Analysis of X-rays by Iterative Least Squares) software from IAEA.

Results from data analysis point to how each digestate could impact the agricultural soils.

Table 3.1: Technical specifications of the used EDXRF spectrometer.

Spectrometer Component	Specifications
X-ray generator	X-ray tube with a silver target
Detector	Silicon drift detector
Processor	DP5 digital signal processor
Operating Current and Voltage	30 Kv and 80 µA
Element range	Na – U

The prepared samples in sample holders are then set up, as shown in Figure 3.5(a).

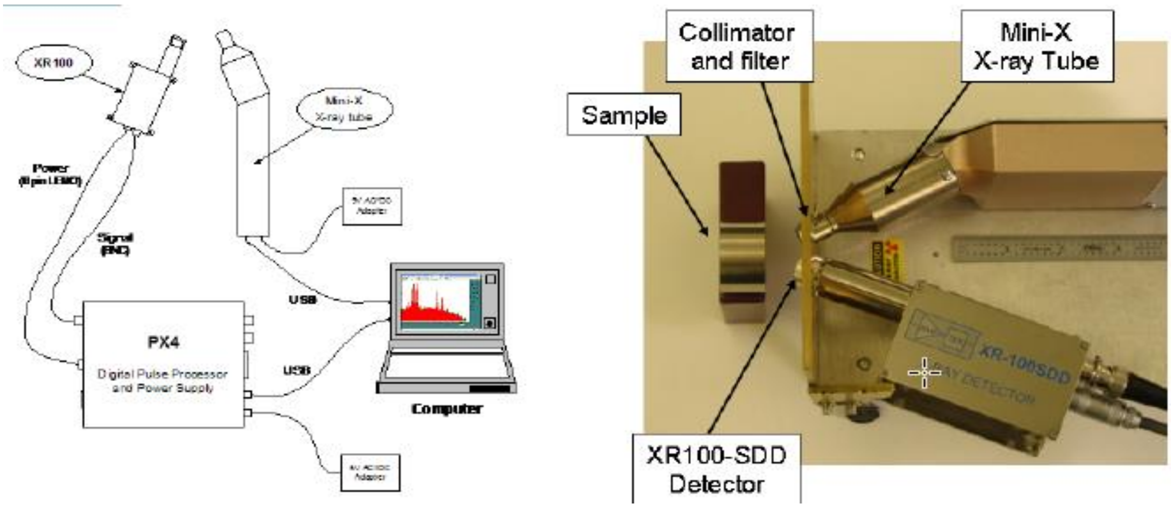

Figure 3.5 (a): EDXRF Set Up Outline

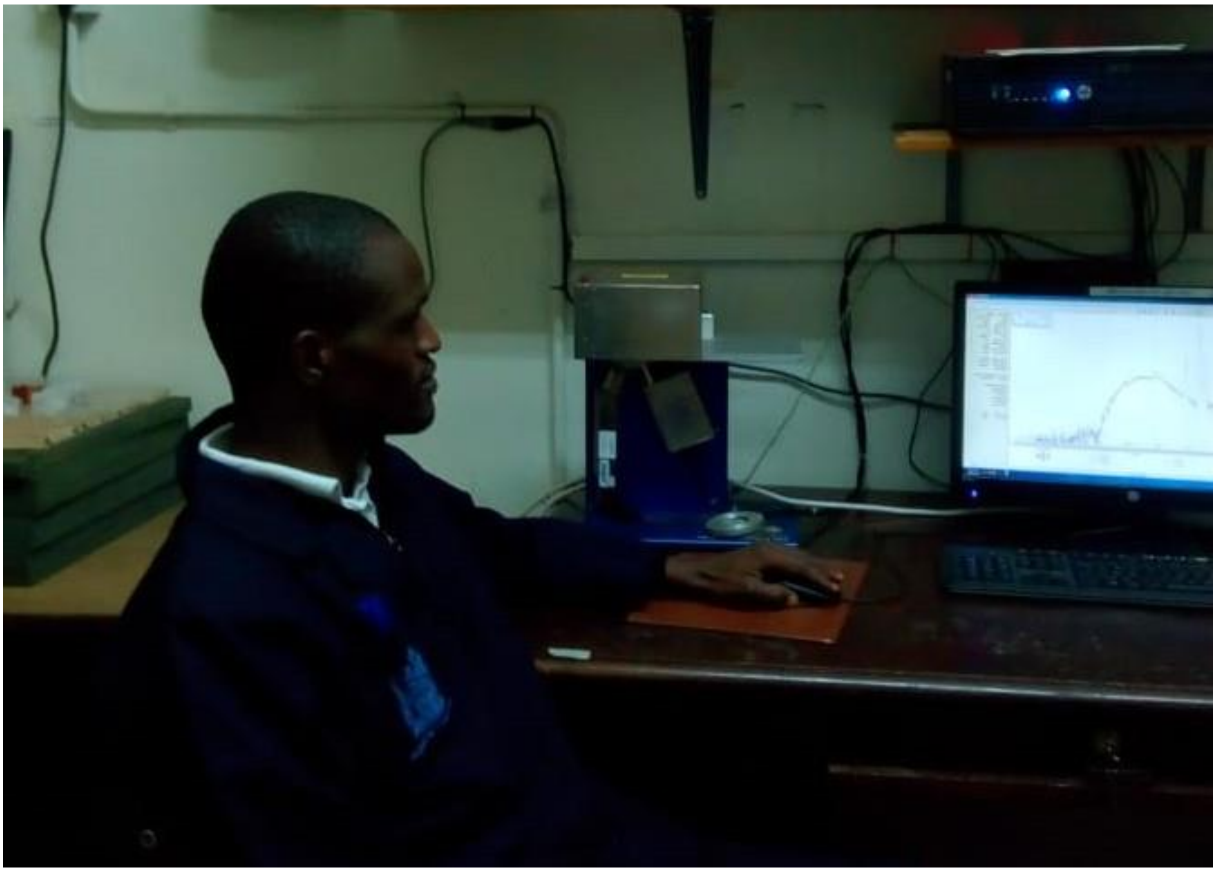

Figure 3.5 (b): EDXRF equipment Application

3.3 Quality assurance

To verify the performance of the used analytical method and the sample preparation procedure, certified reference materials were used. In this case, organic materials were used. The obtained experimental values in this study were compared with the provided certified values. A T-test was used to verify if there was a significant difference between the two values. To check the precision of the analyses, both samples and reference materials were prepared and analyzed in three replicates.

According to Borgese *et al*. (2011), the lowest limits of detection can be defined as the minimum quantity of an element in a sample that can be detected by an instrument based on statistical inspection of the peak area and the subjacent spectral background. In addition, the element is detectable if the peak area is three times the background count and can be calculated using equation 3.1

$$\mathrm{LLD} = \frac{3\mathrm{C}\sqrt{\mathrm{Nb}}}{\mathrm{Np}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ Equation 3.1}$$

Where;

LLD is the lowest detection limit.

C is the concentration of element i,

N_p is the area of the fluorescence peak in counts,

N_b is the background area subjacent the fluorescence peak,

3.4 Statistical analyses

AXIL software from IAEA was used for peak deconvolution and quantification. Using the energy of the peaks and the peak area, the contained elements and their respective concentration were determined. The obtained data were presented as mean and standard deviation. For further data processing and visualization, the R statistical package version 3.5.3 was used.

The AXIL (Analysis of X-ray spectra by Iterative Least Squares) software, among other features, has a modelling algorithm in the background whose purpose is to evaluate the energy dispersive x-ray spectra using mutually orthogonal polynomials. Off this function is the visible images that appear on the display of the software as peaks and troughs to represent the energies of the varied elements captured through the analysis of the sample.

The qualitative approach of the software in distinguishing the energies dispersed relies on the equation;

$$E_x = RhC(Z-\sigma)^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ Equation 3.2}$$

Where;

E_x is the characteristic x-ray energy
R is the Rydberg constant = 1.09737×10^{7} m^{-1}
h is the Plancks constant = 6.6262×10^{-34} J·s
C is the speed of photons
Z is the Atomic number
σ is the shielding constant
n_1 and n_2 are the energy series, e.g. K-shell, L-shell

The quantitative approach (count rate) of the software then takes the path given by the equation;

$$I_K = \frac{KI_0}{\mu_0 + \mu_K} \times W_K \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ Equation 3.3}$$

Where;

I_K is the K layer characteristics of the X-Ray of the measured element

I_0 is the count rate of the incident X-rays

μ_0 is the absorption coefficient of the tested substance to the incident x-rays

μ_K is the absorption coefficient of the tested substance to the tested element's layer K

W_K is the measure of the content elements

K is the calibration constant

The R statistical software, like a majority of similar software, has a variety of uses in statistical analysis. In the instance of this analysis, however, the software was used in the analysis of the visual representation of the overall mean and correlation of the main elements considered in this study. It thus brought out the visual representation of the variations of each as they appear in the different sample collection points and in relation to the type of the digester raw material. From it, therefore, correlation matrices were achieved, the correlation scatter plots as well as the box plots. The results are presented under Chapter four of the Results and Discussions.

Considering the Ca, Mn, Fe, Cu and Zn elements, the Analysis of the Data for Correlational Matrices based on the Pearson Method using the "cor" function in the "Corr" Package in R was used in checking how the elements (micronutrients) vary/correlate with each other in the 3 sites. The criteria for correlational matrix is: -1 (strong negative correlation), 0 (weak correlation) and 1 (strong positive correlation). A correlation coefficient "R" varies between ---1, 0, and 1, with 1 being perfect correlation while a zero implies no correlation at all. -1 implies a strong negative correlation. Anything above 0.7 is a strong correlation.

The use of a box plot is based on the Tukey's fence formula that gives a summary statistic of a given data set. The information contained in a box plot includes information about the median (in the middle of the box), the 25th Quartile (first quartile), the lower part of the box, and the

75th Quartile (which is the upper part of the box. In addition, there is also the maximum and the minimum (the lowest and highest part of the boxes). The dots show a measure of outliers. The size of the box plot can tell you whether the data is normally distributed or not. Evenly distributed box plots show normal distribution. The reverse is true. For this case, box plots are used to indicate the distribution of micronutrients (each element), specifically in the three sites, as presented in chapter four.

Correlation Scatter Plots using gg scatter function in the “ggbur” package in R studio is presented in chapter four. The scatter plot with their corresponding R and p-values help in showing the correlation between a variable like Calcium in one site and Calcium in another site. The R-value shows whether the correlation is strong or weak. The p-value in a correlation scatter plot shows whether the correlation is statistically significant. If p-value<0.05 there is statistically significant.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Overview

This chapter presents the results of the study, where the microelement content in digestate slurry from different feedstock was analyzed. Elements considered in this study were Iron (Fe), Manganese (Mn), Copper (Cu), Carbon (C), and Zinc (Zn). Potentially toxic elements; Lead (Pb), Mercury (Hg), and Cadmium (Cd), were also evaluated. Results for the analyses of the certified reference material as a quality assurance measure are also be presented.

4.2 Quality Assurance

Table 4.1 shows the results of the analyses of the reference material prepared and analyzed in a similar manner as the samples. The experimental values of all elements of interest were determined within the certified range. The certified and experimental values were further compared using the paired t-test. There was no significant difference between the experimental and the certified values.

Table 4.1: Results for the analyses of certified reference material

Element	Experiment Value	Certified Value
Ca	40600 ± 2000	41060 ± 2220
Fe	120 ± 10	119 ± 14
Zn	35 ± 10	32.30±2.80
Mn	17 ± 3	14 ± 2
Cu	5 ± 1	4.8 ± 0.6
Pb	15 ± 5	2.49 ± 0.6

4.3 Microelement content

Soil is the primary source of micronutrients in the food chain. Application of digestate can help in replenishing the soils' nutritional content, which is vital for the proper growth of plants and enhancing productivity. However, there is a potential risk of environmental contamination in case these elements of accumulation beyond a specific limit. In addition to the results of the content of essential micronutrients and potentially toxic ones in digestate slurry, the content in different digestates are also compared and discussed

The general trend is that the human wastes digesters have the highest concentration of most elements. The next high concentration is that of abattoir wastes digesters. Animal waste digesters have the lowest concentration of most elements. One likely explanation of the trend is that both human and abattoir waste digesters have complex composition. The ones for human wastes would for example be attributed to the varied dietary preference of human beings. Further, the digestive system of humans is more efficient in comparison to those of cows (Chesson et al., 1999). In addition to the feedstock factors above, several factors determine the composition of both biogas and digestate slurries. Some of the factors include the temperature at which digestion occurs, the design of the digesters, and the length of time allowed for digestion.

The obtained calcium concentration for the different digestates considered in this study is represented in Figure 4.1. The highest Ca concentrations were realized in abattoir waste samples at a mean value of 50 ± 10g kg^{-1}. However, the obtained values were not normally distributed, with wide variation in concentrations being exhibited. The least Ca mean values were observed in animal waste digestate (30 ± 10 g kg^{-1}), while in human waste digestate, it was determined at 40 ± 10 g kg^{-1}. A significant difference was observed in Ca concentrations between animal waste digestate and the other two digestate types (t-test, $p < 0.05$). The significant difference would be a result of the nature of feedstocks. While cow dung is presumably a result of a diet consisting primarily of unprocessed greens, human wastes and abattoir wastes are a mixture of several constituents, including meats and greens, which are mostly processed or converted.

The observed Ca concentrations were higher than those reported in related studies. Studies like those by Aladjadjiyan *et al*. (2016), nutritional content in compost manure was assessed. A mean Ca concentration was determined at 21 ± 13 g kg^{-1}, which is half the value reported in this study. In a related study, Alburquerque *et al*. (2012) published a mean Ca concentration in digestate at 2.8 ± 1.7 g kg^{-1} for pig slurry and 1.9 ± 1.3 g kg^{-1} in cattle slurry. The considerable difference between these values and what was observed in the current study could be associated with differences in the digestate component analyzed, whereby, the study looked into the semi-liquid phase of the digestate.

Calcium is an essential nutrient in plants. It plays a role in cell wall formation and as a building block for membranes, in addition to promoting proper root and stem growth, plant rigidity, and vigour (White and Broadly, 2013). From this study, it can be noted that the best source of Ca would be human waste and abattoir digestate.

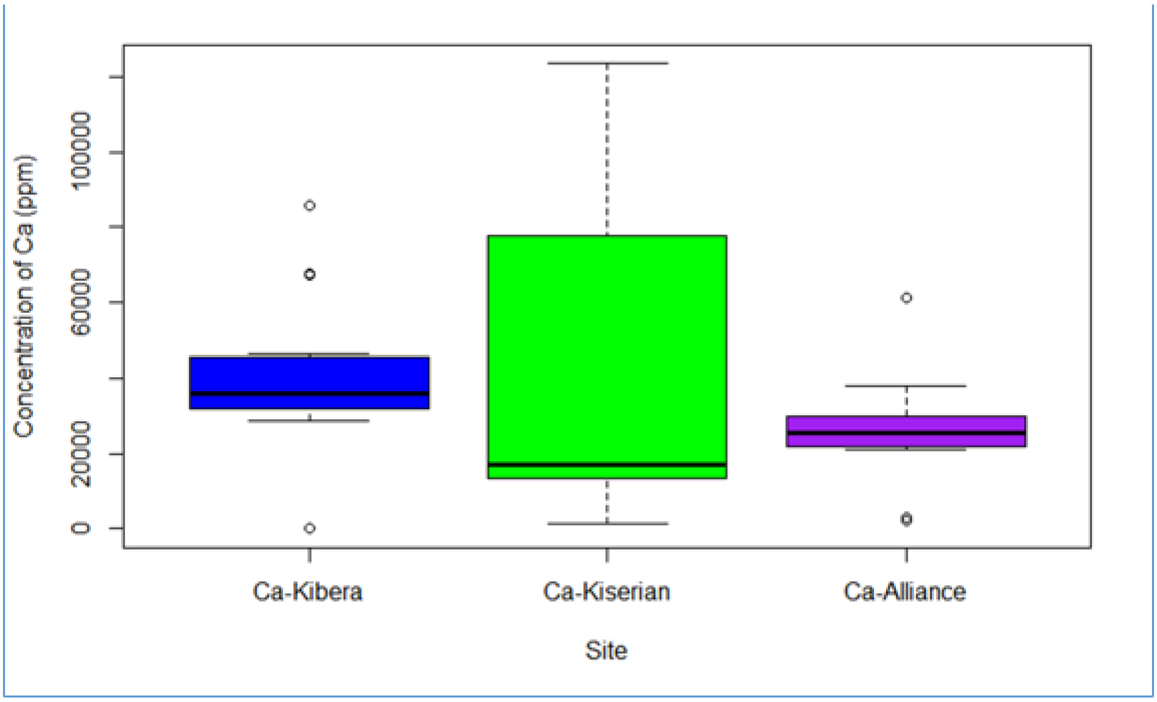

Figure 4.1: Distribution of Ca for the three digestate types; human waste (Kibera), Abattoir waste (Kiserian), and animal waste (Alliance).

The box plot represents the median (in the middle of the box), the 25th Quartile (first quartile), the lower part of the box, and the 75th Quartile values (upper part of the box). In addition, there is also the maximum and the minimum (the lowest and highest part of the boxes). The dots show a measure of outliers. The mean concentrations of Calcium in the three sites (Kibera, Alliance, and Kiserian) were 40600 ± 2000, 26400 ± 1400, and 49500 ± 4200 ppm, respectively.

From the box plot, Kibera had the highest median concentration of Calcium compared to Kiserian, which had the lowest concentration. In addition, the distribution of Calcium in Alliance and Kibera site is almost normally distributed compared to the one in Kiserian site. More outliers were noted in the Kibera site compared to the Alliance site.

Manganese as well is an essential nutrient in plants that serves as an activator for enzymes in various growth processes, and it assists iron in chlorophyll formation. The mean concentration of Mn in Kiserian was 1100 ± 90 mg kg^{-1}, while the mean concentrations in Kibera and Alliance were 1300 ± 400 mg kg^{-1} and 820 ± 200 mg $kg^{-1,}$ respectively. From the box plot in Figure 4.2, Kibera and Alliance sites had an almost normal distribution of Mn while that of Kiserian was not normally distributed. In addition, Kiserian site had the lowest median concentration of Mn while Kibera had the highest concentration. Outliers were observed in Kiserian and Alliance sites.

The Mn content in the digestates observed in this study is higher than those reported in different studies. For instance, Aladjadjiyan *et al*. (2016) determined the chemical composition of organic manure. The mean Mn concentration was determined at 500 ± 20 ppm compared to a mean of 820 ± 200 mg kg^{-1} for animal waste digestate and 1300 ± 400 mg kg^{-1} for human waste digestate. Comparable values were obtained by Koszel and Lorencowicz (2015). A study by Galgalo (2015) found a strong positive correlation between extractable Mn concentration and the soils' total Mn content. This would, therefore, mean there is a high likelihood that the Mn in the digestate to be bioavailable to plants upon application.
Using the R statistical software, the mean concentration of Manganese in Kiserian was 1100 ± 90 ppm, while the mean concentrations in Kibera and Alliance were 1300 ± 400 and 800 ± 190 ppm respectively. From the box plot, Kibera and alliance sites had an almost normal distribution of Mn while that of Kiserian was not normally distributed. In addition, the Kiserian site had the lowest median concentration of Mn, while Kibera had the highest concentration. Apart from the difference in the feedstock and digester properties, this study could not establish the variations in concentrations. Outliers were observed in Kiserian and Alliance sites.

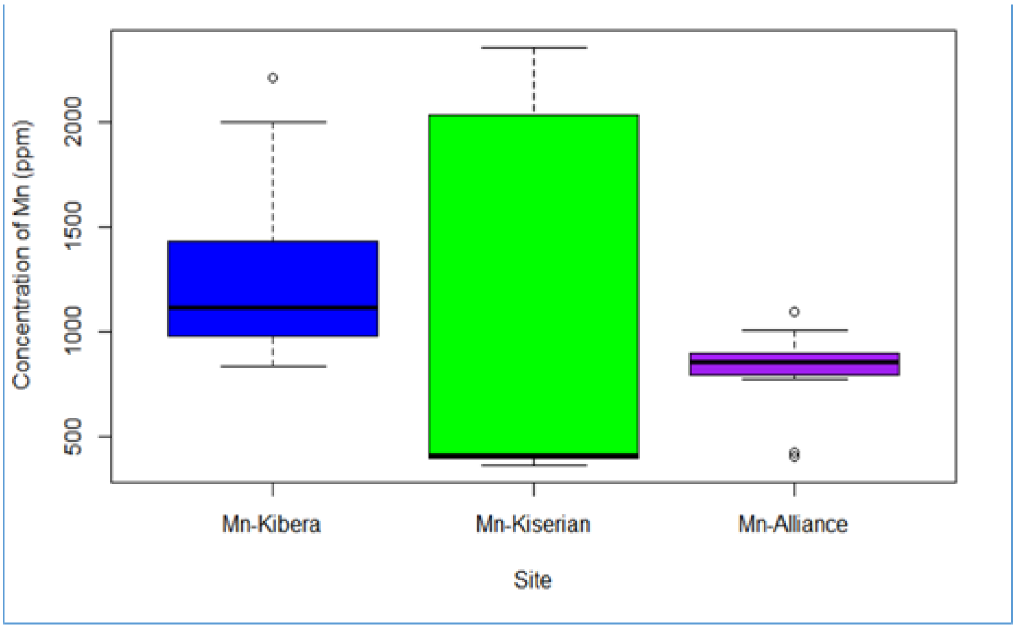

Figure 4.2: Distribution of Mn for the three digestate types; human waste (Kibera), Abattoir waste (Kiserian), and animal waste (Alliance).

Figure 4.3 gives the distribution of Fe concentration for the three digestates. The highest Fe content was reported in human waste samples at a mean of 18 ± 5 g kg^{-1}, compared to animal waste and abattoir digestate at 15 ± 4 g kg^{-1} and 9.4 ± 3 g $kg^{-1,}$ respectively. The Fe content in abattoir waste was significantly lower than the other two. According to Lukehurst *et al*. (2012), different digestates exhibit variation in nutrients since digestate characteristics are specific not only for different feedstock but also for each batch. This could explain the wide difference between and within digestate types.

Iron deficiency is rare, especially in Kenyan soils. However, with increased cultivation, it is important to replenish the nutrients. This study shows digestate application can be an important source of Fe, among other benefits.

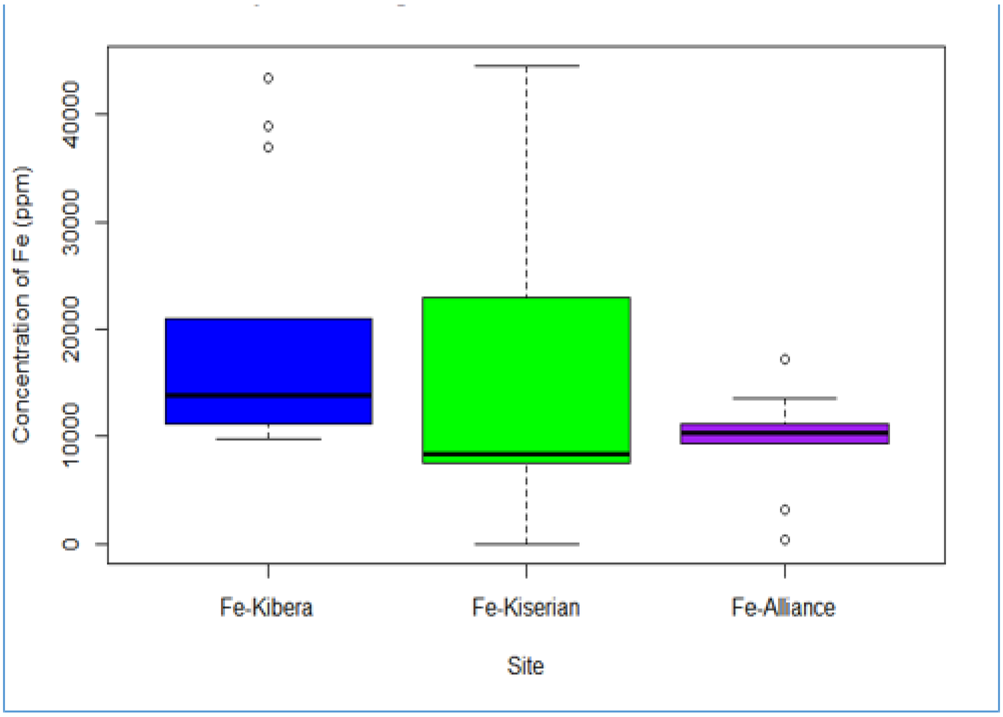

Figure 4.3: Distribution of Fe for the three digestate types; human waste (Kibera), Abattoir waste (Kiserian), and animal waste (Alliance).

The mean concentration of Copper in the three sites was 180 ± 45 mg kg^{-1}, 200 ± 30 mg kg^{-1}, and 200 ± 50 mg kg^{-1}in Alliance, Kibera, and Kiserian samples, respectively, as presented in Figure 4.4. These values are higher than those reported by Lukehurst *et al*. (2012) at 51 ± 20 mg kg^{-1} and 65 ± 30 mg kg^{-1} for dairy and poultry waste digestate, but lower than Cu content in pig slurry. R statistical software returns the mean concentration of Copper in the three sites was 9500 ± 450, 19000 ± 1100, and 15200 ± 1350ppm in Alliance, Kibera, and Kiserian, respectively.

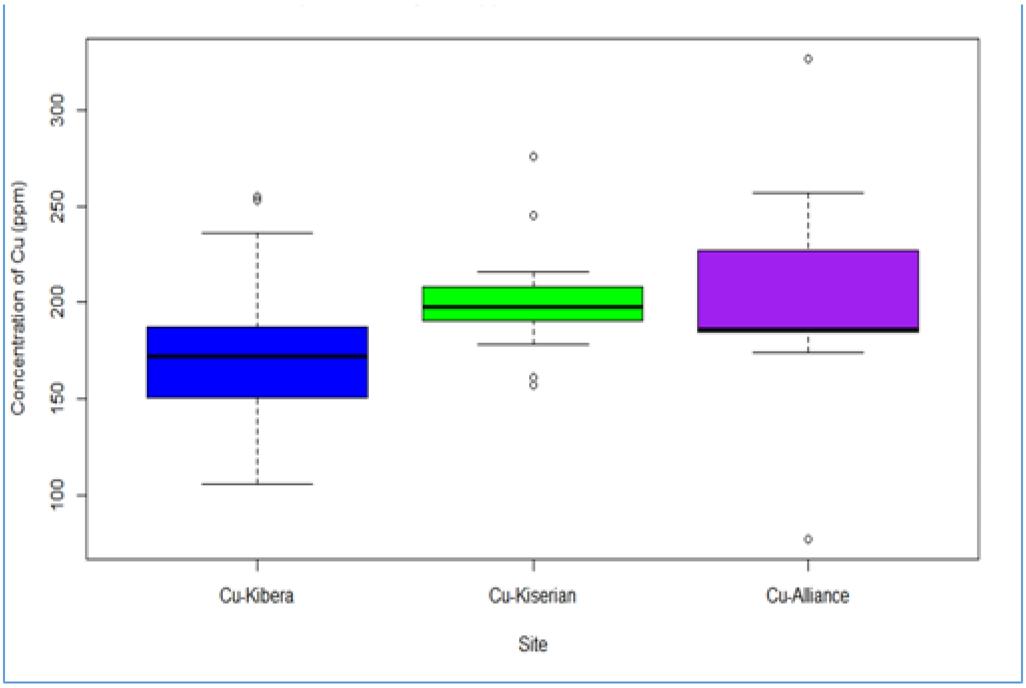

Figure 4.4: Distribution of Cu for the three digestate types; human waste (Kibera), Abattoir waste (Kiserian), and animal waste (Alliance).

Zinc is an important component of various enzymes in plants. It plays a role in chlorophyll and protein production and regulates the synthesis of indoleacetic acid, which is an essential plant growth regulator. In this study, high Zn values were observed in human waste slurry (900 ± 260 mg kg^{-1}), which is higher than animal waste (350 ± 80 mg kg^{-1}) and abattoir (140 ± 50 mg kg^{-1}) slurry by a factor of two and four respectively (Figure 4.5). Comparable high values were reported by Alburquerque *et al*. (2012) in animal waste digestate at a range of 76 – 682 mg kg^{-1}. Al Seadi and Lukehurst, (2012), determined the Zn content in compost manure at 174 ± 46 mg kg^{-1}, while Lukehurst *et al*. (2012) in an investigation on heavy metal composition in dairy, pig and poultry slurry determined the mean Zn content at 176 ± 22 mg kg^{-1}, 403 ± 63 mg kg^{-1} and 423 ± 95 mg kg^{-1}, respectively.

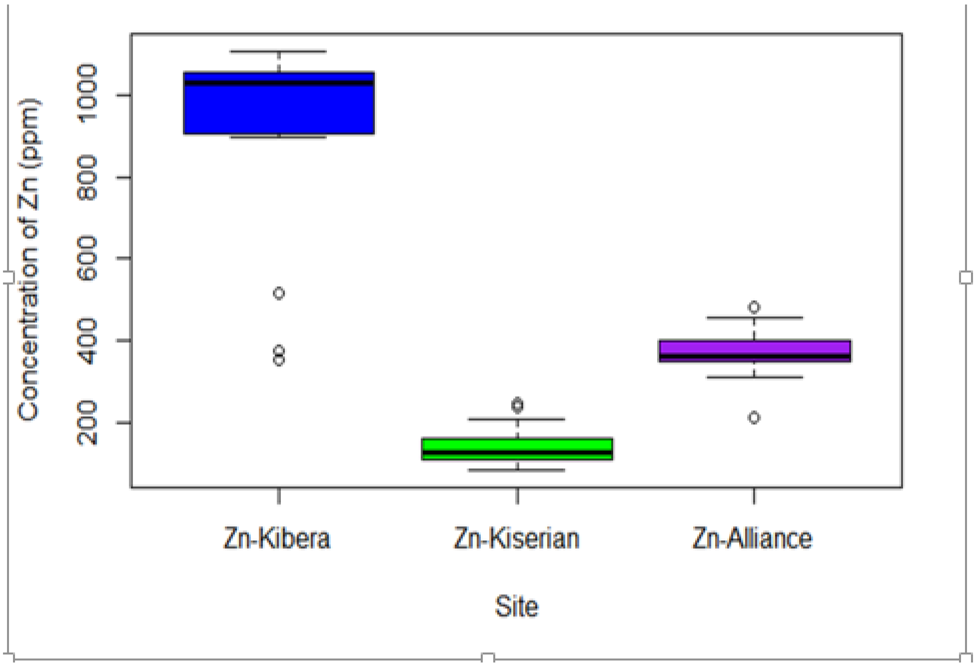

Figure 4.5: Distribution of Zn for the three digestate types; human waste (Kibera), Abattoir waste (Kiserian), and animal waste (Alliance).

Tables 4.2 – 4.4 give correlation matrices between elements for different digestate types. For human waste digestate, a strong positive correlation was observed between Mn and all the other elements except Ca and Zn and between Ca and Fe. A similar trend was also observed for the other digestates. The positive correlation implies that irrespective of the digester feedstock, concentrations of elements increase uniformly except for zinc. Zn in the abattoir digestate was found to correlate with other elements negatively. A positive correlation could also imply a good balance to nutrient content in the feedstock.

Table 4.2. Correlation matrix for micronutrient elements in human waste digestate

	Ca	**Mn**	**Fe**	**Cu**	**Zn**
Ca	1.000	0.448	0.744	0.570	-0.150
Mn	0.448	1.000	0.692	0.616	0.690
Fe	0.744	0.692	1.000	0.496	0.355
Cu	0.570	0.616	0.496	1.000	0.109
Zn	-0.150	0.690	0.355	0.109	1.00

Table 4.3. Correlation matrix for micronutrient elements in abattoir waste digestate

	Ca	**Mn**	**Fe**	**Cu**	**Zn**
Ca	1.000	0.817	0.825	0.384	-0.775
Mn	0.817	1.000	0.859	0.354	-0.907
Fe	0.825	0.859	1.000	0.443	-0.855
Cu	0.384	0.354	0.443	1.000	-0.239
Zn	-0.775	-0.907	0.855	-0.239	1.00

Table 4.4. Correlation matrix for micronutrient elements in animal waste

	Ca	Mn	Fe	Cu	Zn
Ca	1.000	0.635	0.289	0.510	0.572
Mn	0.635	1.000	0.748	0.708	0.829
Fe	0.289	0.748	1.000	0.581	0.709
Cu	0.510	0.708	0.581	1.000	0.815
Zn	0.572	0.829	0.709	0.815	1.00

Correlation Scatter Plots using gg scatter function in the "ggbur" package in R studio

The scatter plot in Figure 4.6 with their corresponding R and p-values helps in showing the correlation between the variable (Calcium) in one site and Calcium in another location.

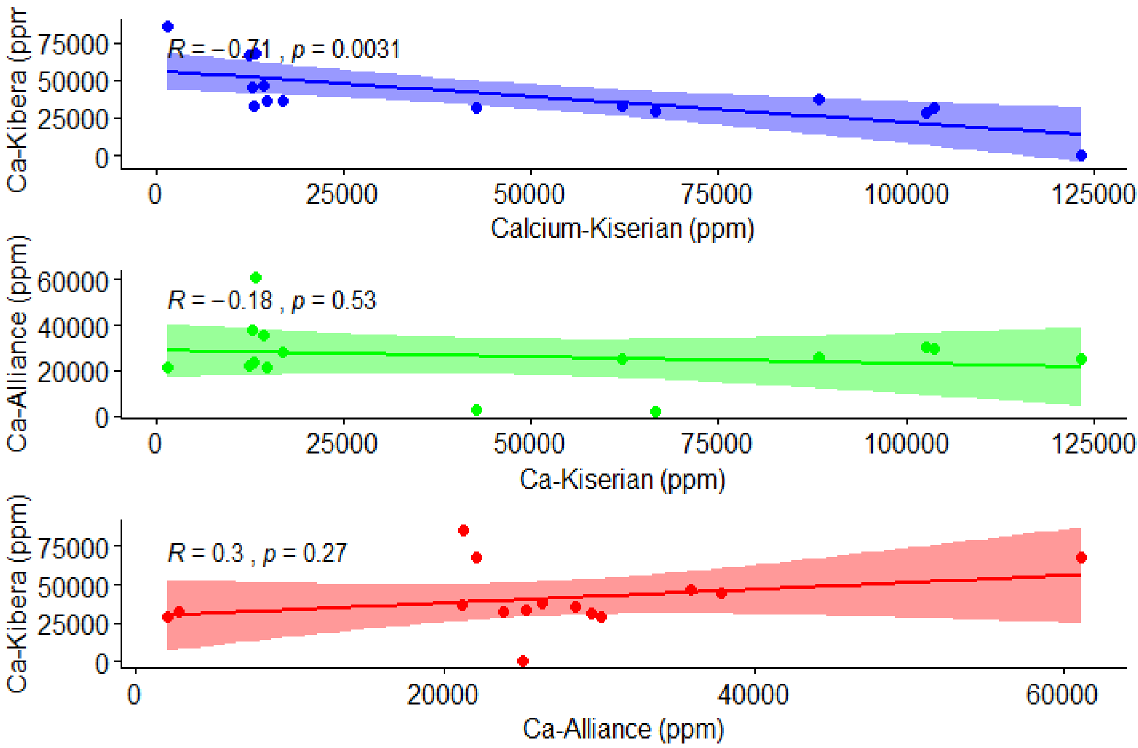

Figure 4.6: The correlations scatter plot of Calcium in the three sites.

A strong but negative correlation exists between the amount of Calcium in the Kibra site compared to that of Calcium in the site in Kiserian, as seen in the value of R=-0.71. The value of p=0.0031 is less than that of alpha (0.05) hence an indication that the correlation is statistically significant at a 95% confidence interval. There was almost no correlation between Calcium in alliance and that in Kiserian was observed as depicted by R=-0.018 and p>0.05 hence indicating no significant correlation between the two. Given that the two sample groups do not share feedstock, the correlation could be traced to the digester factors. In addition, at a 95% confidence interval, there was a weak correlation between Calcium in Kibra and that in Alliance.

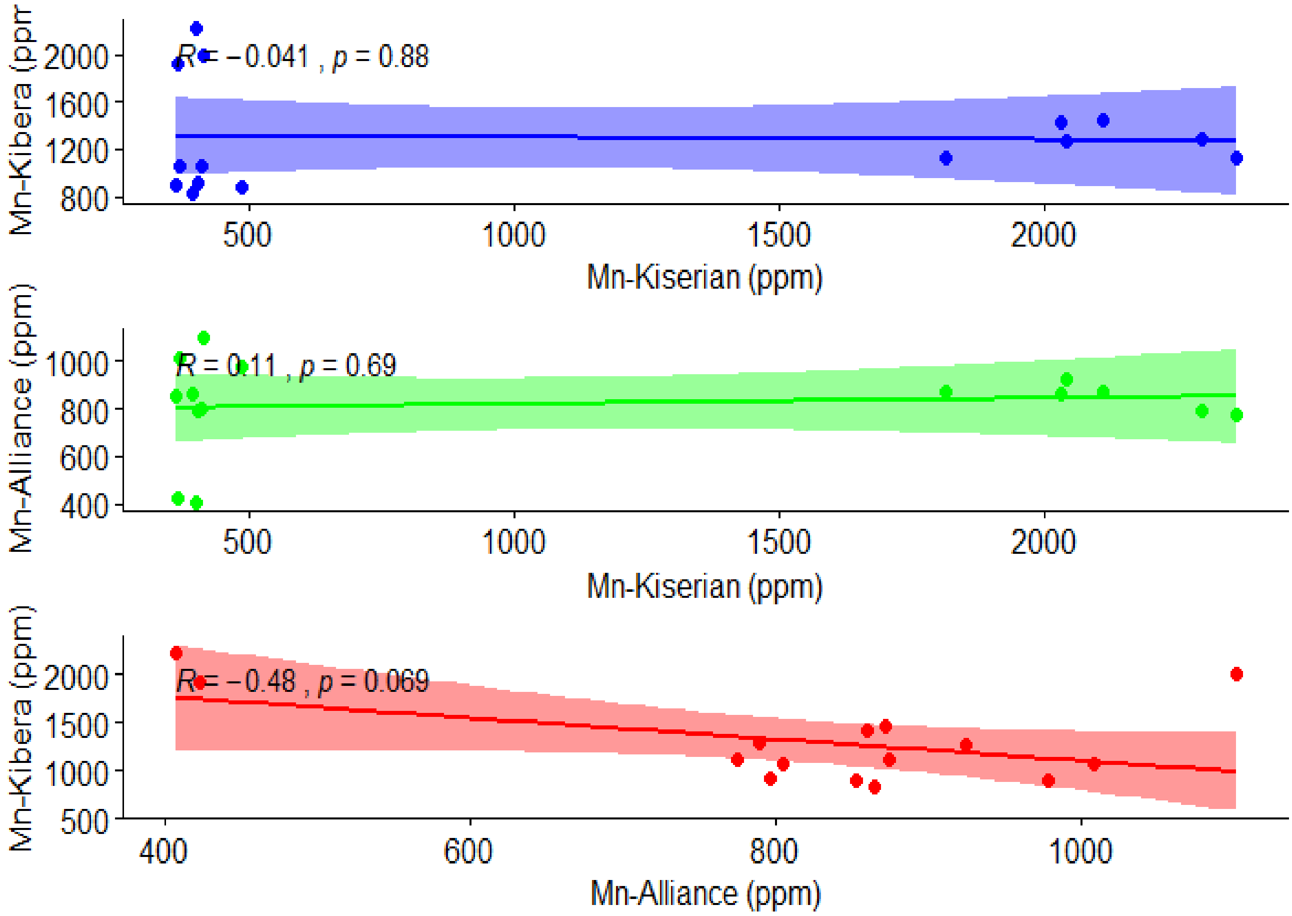

Figure 4.7: The scatter correlation of Manganese in the three sites

There does exist statistically insignificant values of p for all the three correlation scatter plots as they are all above the value of 0.05. There are weak negative correlations for manganese in Kibra in relation to that in Kiserian as well as those in Kibra in relation to those in Alliance. There, however, is a weak positive correlation between those in Alliance and Kiserian.

Similarly, these correlations could be traced back to the digester factors as they are independent of the feedstock.

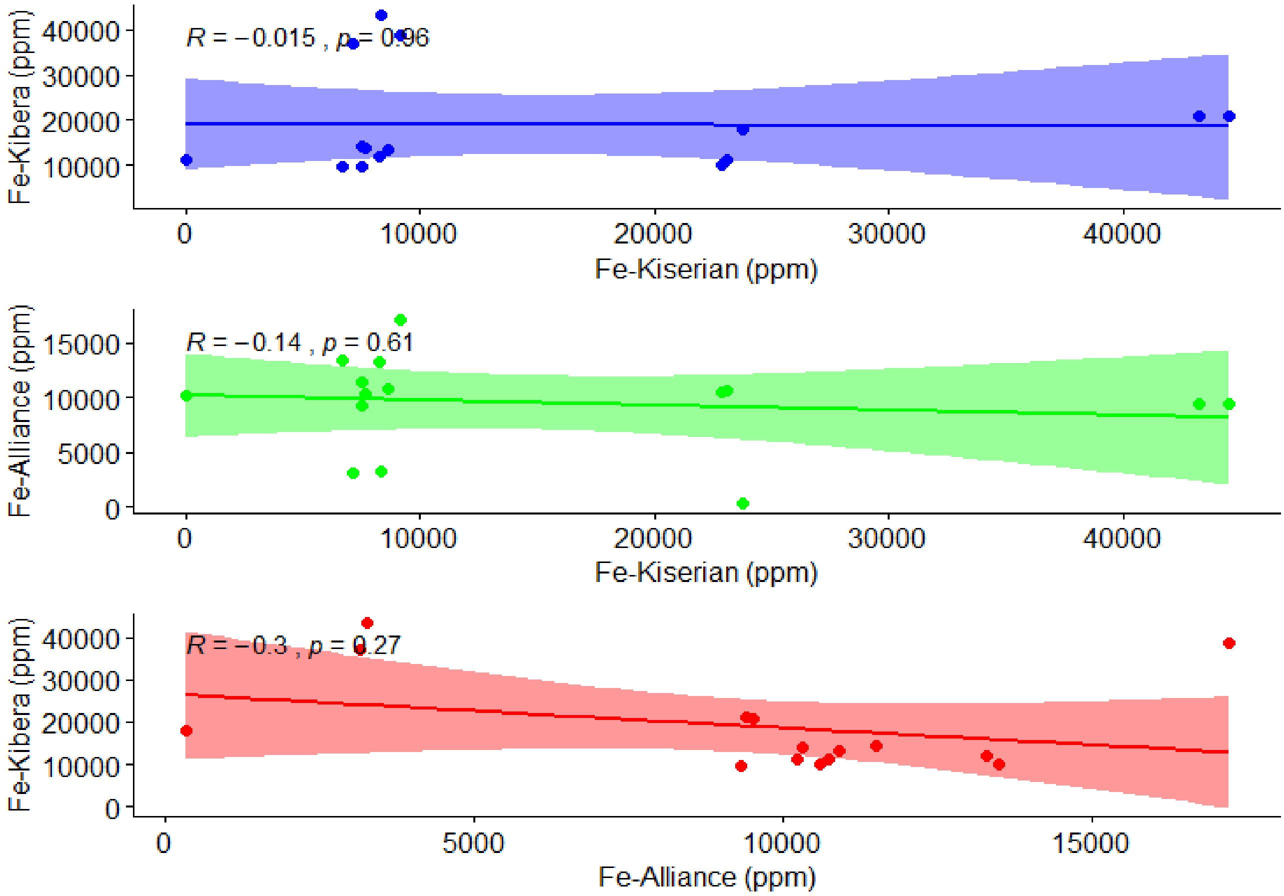

Figure 4.8: The correlation scatter plot for Iron in the three sites

A weak negative correlation exists between the amount of Iron in Kibera site compared to that of Iron in the site in Kiserian, as seen in the value of R=-0.015. The value of p=0.96 is greater than that of alpha (0.05) hence an indication that the correlation is statistically insignificant at a 95% confidence interval. There was a weak negative correlation between Fe in Alliance and that in Kiserian was observed as depicted by R=-0.14 and p<0.05 hence indicating a significant correlation between the two. In addition, at a 95% confidence interval, there was a weak correlation between Fe in Kibera and that in Alliance. Alliance and Kiserian share some similarities in feedstock hence the correlation.

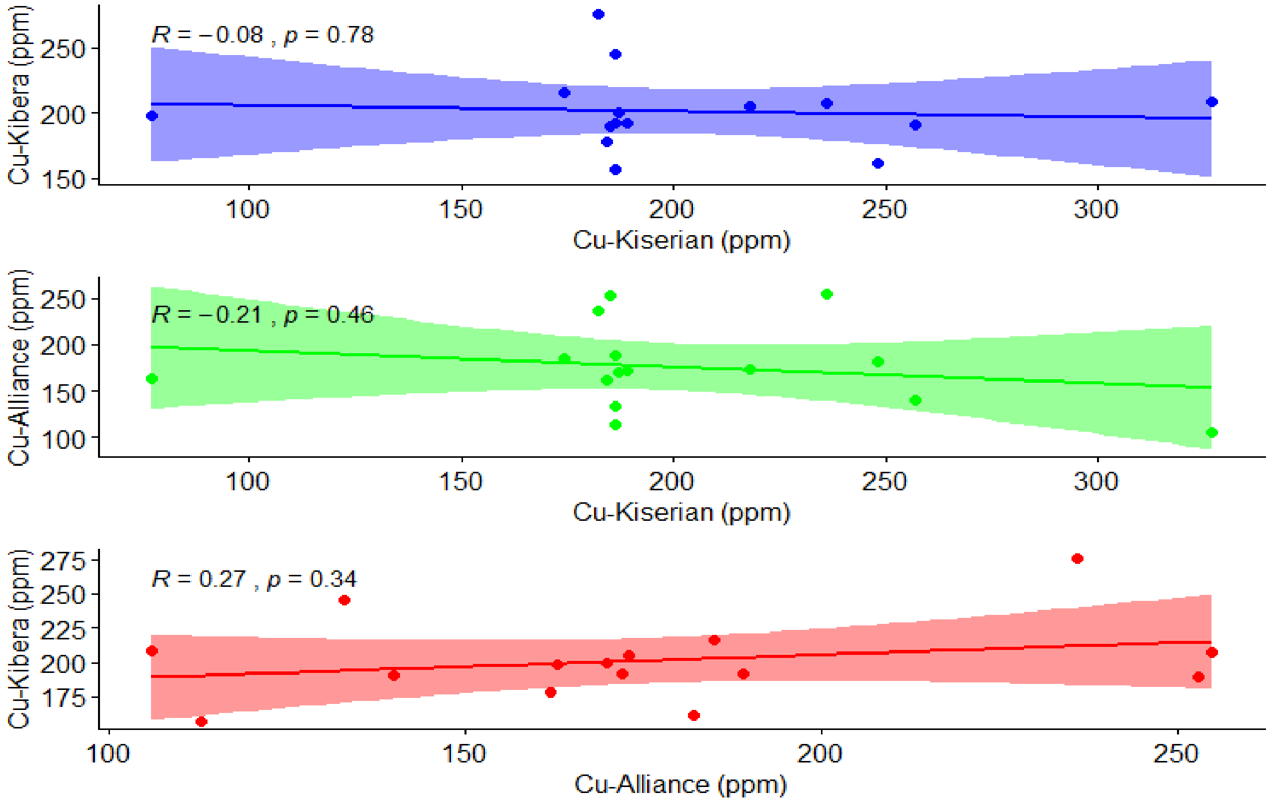

Figure 4.9: The correlation scatter plot for Copper in the three sites

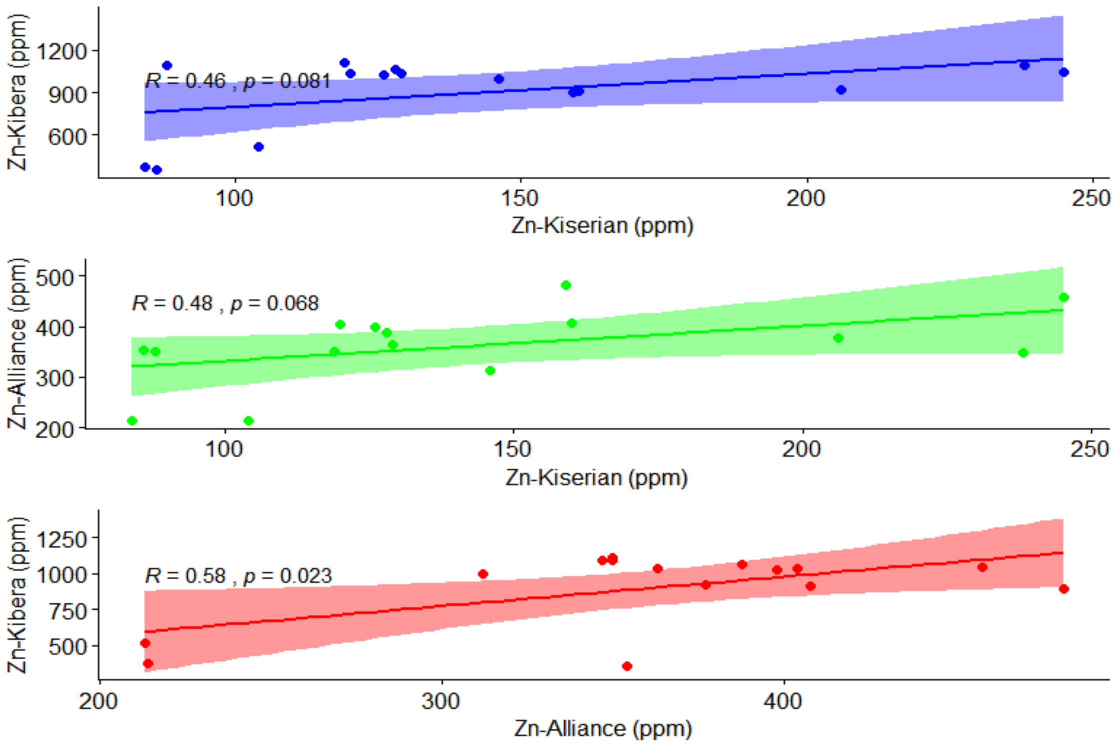

Figure 4.10: The correlation scatter plot for Zinc in the three sites

4.4 Concentration of potentially toxic elements

Some elements such as Pb, Hg, and Cd do not have a known physiological role and hence considered potentially toxic even in low concentrations. Additionally, the elements have the potential to bio-accumulate in nature, thus the need for close monitoring. In this study, the Pb concentration was determined at a mean of 15 ± 10 mg kg^{-1}, 20 ± 10 mg kg^{-1}, and 14 ± 8 mg kg^{-1} in animal waste, Human waste, and abattoir waste digestate respectively. The Pb concentration in human waste slurries was higher than the acceptable amounts of 20 mg kg^{-1}. In the other two digestate types, however, the concentration of Pb was not dangerous to the environment. As for Hg and Cd, their content was determined below the detection limit (< 1 mg kg^{-1}), as presented in Table 4.5.

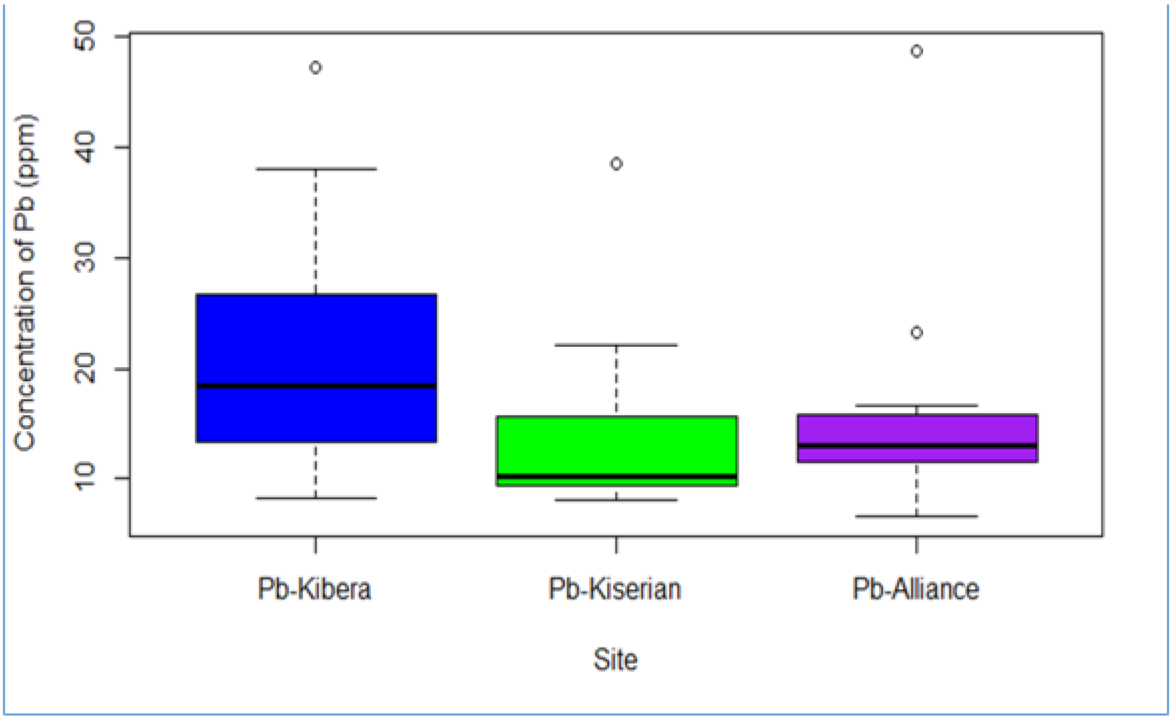

Figure 4.11: Distribution of Pb for the three digestate types; human waste (Kibera), Abattoir waste (Kiserian), and animal waste (Alliance).

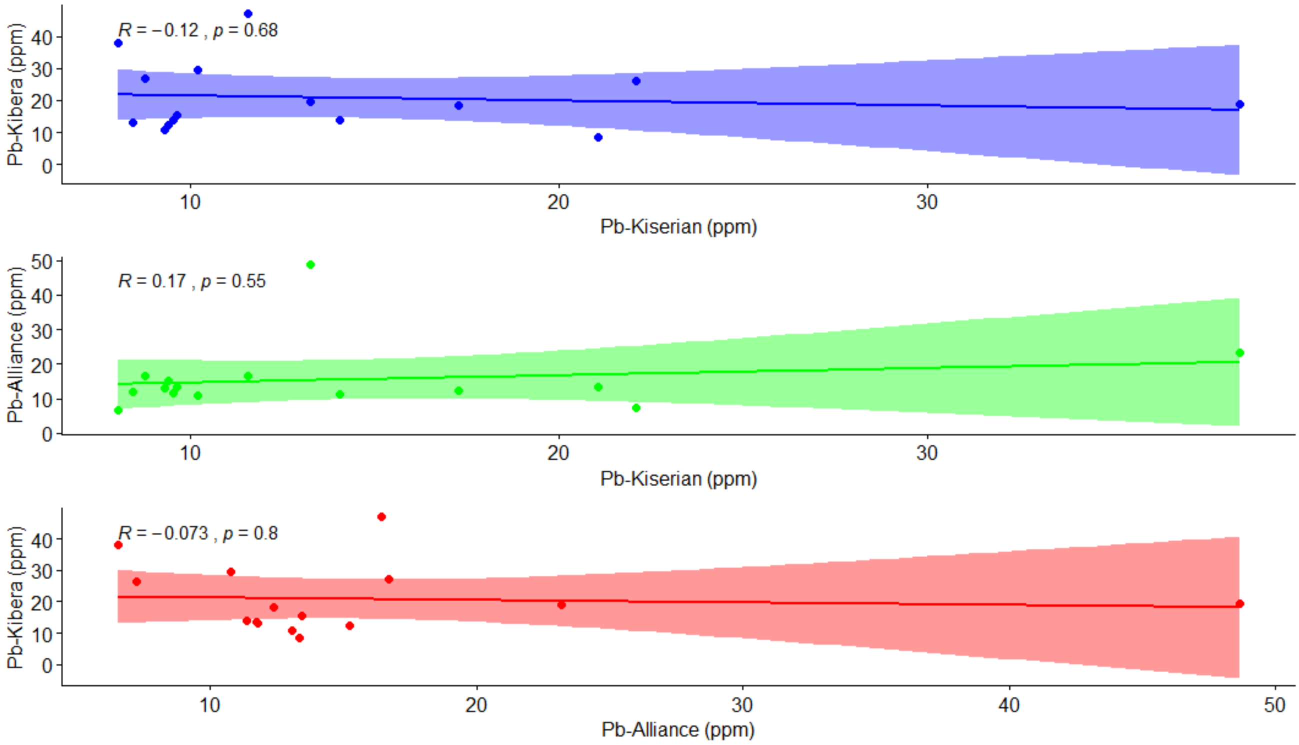

Figure 4.12: The correlations scatter plot of Lead as a heavy metal in the three sites

Table 4.5: Hg and Cd in all digestate types

Element	**Concentration**
Mercury	< 1 mg kg^{-1}
Cadmium	< 5 mg kg^{-1}

4.5 Potential Impact of digestate application

Digestate has been used as an alternative to mineral fertilizers. Its fertilizer value is mainly dependant on the nutritional content of the feedstock. However, the digestate is a product of a living process, and thus, it is also characteristic of the digester tank. The resultant digestate characteristics may vary between batches of the same digester and even within the same batch of digestate, following storage. Table 4.6 gives a summary of the nutritional content in the digestates. The human waste digestate had the highest concentration values for most elements. The high concentrations could be attributed to a wide range of products that may find a way into the sewerage system, as compared to animal or abattoir waste. Unlike human waste, trace elements in animal and abattoir wastes are introduced mainly through diet. Unfortunately, limited research has been carried out in digestate waste with regards to macro and microelement content. Regulatory limits are also lacking, especially for the essential trace elements. However, compared to other studies (Alburquerque *et al*., 2012; Lukehurst *et al*., 2012; Koszel and Lorencowicz, 2015), higher content was observed in this study.

Table 4.6: Elemental Components of the digestates

Elements	**Human waste (PPM)**	**Animal waste (PPM)**	**Abattoir waste (PPM)**
Ca	40600 ± 2030	26400 ± 1400	49500 ± 4160
Fe	19000 ± 1100	9500 ± 4500	15000 ± 1350
Mn	1300 ± 400	800 ± 190	1100 ± 900
Zn	200 ± 30	180 ± 45	200 ± 50
Cu	900 ± 260	350 ± 80	140 ± 50
Pb	20 ± 5	15 ± 5	14.1 ± 8
Cd	< 5	< 5	< 5
Hg	< 1	< 1	<1

The high content of essential plant elements Ca, Mn, Zn, Fe, and Cu were found in the digestates. Therefore, the use of digestate as bio-fertilizer could have a positive impact through the full utilization of the contained nutrients, which are essential for plant and microbial growth. For instance, Ca It plays a role in cell wall and membranes formation, promoting proper root and stem growth, plant rigidity, and vigour, while Mn serves as an activator for enzymes in various growth processes, and it assists Fe in chlorophyll formation. This is in addition to substantial amounts of macronutrients (N, P, and K) contained in the digestate.

Digestate is a good source of macronutrients. A study by Johansen *et al*. (2013) found digestate to contain high nitrogen and low carbon content, thus of better quality as bio-fertilizer. Crolla *et al*. (2013), observed that the AD process results in the transformation of nutrients into forms that are readily adsorbed by plants. For example, the organic N in the feedstock is converted to inorganic NH_4^+–N, while organic phosphate is converted to inorganic PO_4^{3-}—P. The enhanced concentration of readily available inorganic nutrients leads to increased crop productivity (Gerardi, 2003). Therefore, with proper management and handling, digestate can be used in soil amendment.

Trace elements play an essential role in crop production. However, these elements are non-biodegradable, thus can bio-accumulate, leading to contamination of the environment. For example, Pb in human wastes was determined above the limits accepted for introduction in soil (20 mg kg^{-1}). Most of the other elements were of acceptable concentrations. However, their excessive application poses the danger of bioaccumulation. For Pb, the application needs to be regulated to avoid the possibility of lead contamination. It is important to ensure the digestate quality is up to acceptable levels.

4.6 Summary of the Findings

For the non-heavy elements, and using the T-test, all the experimental values for the elements were determined to fall within acceptable ranges of the certified values, as shown in Table 4.1. These were 40600 ± 2000, 120 ± 10, 35 ± 10, 17 ± 3, and 5 ± 1 ppm against the certified values of 41060 ± 2220, 119 ± 14, 32.30±2.80, 14 ± 2, and 4.8 ± 0.6 ppm for Ca, Fe, Zn, Mn, and Cu respectively.

The analysis further showed that the slurry from Human wastes had the highest concentration of most chemicals. The possible reason for the trend is the nature of the raw substances fed into these digesters. The concentration of calcium from the study was high, relative to other studies. The same was observed with Manganese. Copper Iron and Zinc were within similar ranges as in other studies.

Of the three probed heavy elements, high Lead concentration was found to be present in all the three slurries. In slurries from human waste digesters, however, the amount detected rose up to 20±5 against the certified values of 2.49 ± 0.6 ppm, which indicates possible environmental hazards if used as Biofertilizers. Mercury and Cadmium were both found to be below detection limits, as shown in Table 4.5.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study successfully characterized three classes of biogas digestate slurries using their elemental components. Using the Energy Dispersive X-ray Fluoroscopy (EDXRF), the levels of concentration of each of the essential elements and the heavy metals analyzed showed the differences which could, therefore, indicate what crops would best fit specific slurry types. The nutritional contents and potentially toxic elements (Pb, Hg, and Cd) were determined in three digestate types (human, animal, and abattoir waste). Human waste digestate had high concentration values for most elements, which could be associated with the wide range of products that may find a way into the sewerage system, as compared to in the animal or abattoir waste. In human waste, essential elements were determined at 40600 ± 2000, 19000 ± 1100, 1300 ± 400, 200 ± 30, 900 ± 260 for Ca, Fe, Mn, Zn and Cu respectively, as compared to Ca (26400 ± 1400), Fe (9500 ± 450), Mn (800 ± 200), Zn (180 ± 50), Cu (350 ± 80), in animal waste. In abattoir waste, the mean content were 49500 ± 4100for Ca, 15200 ± 1300 for Fe, 1100 ± 90 for Mn, 200 ± 50 for Zn and 140 ± 50 for Cu. Variations were observed between different digestates and within the same digestate type.

Potentially toxic elements, Pb, Hg, and Cd, were also analyzed. Hg and Cd were determined below detection limits. For Pb, the highest concentrations were found in human waste. Considering the location of the human waste Biogas Digesters, the possible justification for the high Pb concentrations are the economic activities that are common within urban centres. Some of the economic activities synonymous with urban set up include painting and handling of electronic materials and equipment, which are common sources of Lead. Some of these materials would find their way into the sewerage system if poorly disposed of.

The high nutrient content observed in this study could be beneficial in enhancing crop productivity due to the essential role played by different trace elements. Other benefits of digestate application include modifying soil texture due to high organic matter content, supplying macronutrients N, P, and K, in a readily available form and altering soil pH. However, there is a potential risk of bioaccumulation of these elements to toxic levels. Toxic levels of the elements pose a danger to the environment and for Agricultural practices specifically.

5.2 Recommendations

5.2.1 Applications of the Findings

a) For optimal outcomes, crops need to be matched with the biogas digestate slurries (from cow dung, human wastes and abattoir waste digesters) that have the highest amounts of elements that are required for the development of the part of the plant, which is of nutritional value to humans.

b) There is a need for regulatory standards of the amount of each type of Biogas Digestate Slurry that can be applied to a standard measure of agricultural land.

c) The use of Human wastes slurries, especially those emanating from urban setups, ought to be strictly monitored owing to the relatively high amounts of Lead that they contain.

5.2.2 Need for Further Research

a) There needs to be a study specifically aimed at explaining the differences in elemental components of the various slurries as a result of both the feedstock and location of the digesters.

b) A study is necessary to ascertain the degree of preference of various crops to the varied types of digestate slurries.

c) More studies need to be conducted in different digestate types in order to build a database on which regulatory policies can rely.

d) In addition to elemental content, it is important to investigate the potential of the digestates as bio-fertilizer with respect to macronutrient content and other physiochemical parameters like pH and organic matter.

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APPENDICES

A1. Sample Weights

a). Kibera Samples Weight per Pellet

ANALYZED KIBERA SAMPLES		
No.	***Sample Code***	***Sample Weight ×(1/10000)g***
1	Kb1(I)a	4053
2	Kb1(I)b	4071
3	Kb1(I)c	4484
4	Kb1(II)a	4251
5	Kb1(II)b	4684
6	Kb1(II)c	4074
7	Kb1(III)a	4851
8	Kb1(III)b	4831
9	Kb1(III)c	4904
10	Kb2(I)a	4119
11	Kb2(I)b	5335
12	Kb2(II)a	4101
13	Kb2(II)b	4683
14	Kb2(III)a	5898
15	Kb2(III)b	6214
16	Kb2(III)c	5643
17	Kb3(I)a	4414
18	Kb3(I)b	4602
19	Kb4(III)c	3806
20	Kb3(I)c	
21	Kb3(II)a	4373
22	Kb3(II)b	4174
23	Kb3(II)c	4366
24	Kb3(III)a	4548
25	Kb3(III)b	4477
26	Kb3(III)c	4130
27	Kb4(I)a	4232
28	Kb4(I)b	4120
29	Kb4(I)c	4784
30	Kb4(II)a	4866
31	Kb4(II)b	4700

32	Kb4(II)c	4456
33	Kb4(III)a	4267
34	Kb4(III)b	4178
35	Kb5(I)a	4350
36	Kb5(I)b	4234
37	Kb5(I)c	4135
38	Kb5(II)a	4233
39	Kb5(II)b	4372
40	Kb5(II)c	4624
41	Kb5(III)a	4191
42	Kb5(III)b	4814
43	Kb5(III)c	4952

b). Kiserian Samples Weight per Pellet

ANALYZED KISERIAN SAMPLES		
No	***Sample Code***	***Sample Weight ×(1/10000)g***
1	Ks1(III)a	2327
2	Ks1(III)b	3501
3	Ks1(I)b	3652
4	Ks5(III)c	3794
5	Ks3(II)a	3992
6	Ks3(III)c	4007
7	Ks2(II)c	4031
8	Ks1(I)a	4118
9	Ks1(III)c	4134
10	Ks2(I)a	4144
11	Ks3(I)c	4150
12	Ks3(I)b	4190
13	Ks1(II)a	4193
14	Ks2(I)b	4194
15	Ks5(I)b	4234
16	Ks3(II)c	4243
17	Ks2(III)c	4254
18	Ks2(II)a	4279
19	Ks2(III)b	4284
20	Ks3(II)b	4286
21	Ks2(II)b	4294
22	Ks1(I)c	4309
23	Ks1(II)b	4317

24	Ks4(II)c	4329
25	Ks5(I)a	4350
26	Ks4(I)c	4365
27	Ks4(III)c	4373
28	Ks4(I)b	4439
29	Ks3(II)a	4459
30	Ks3(III)a	4459
31	Ks4(I)a	4474
32	Ks4(II)b	4547
33	Ks2(I)c	4625
34	Ks4(III)b	4640
35	Ks4(III)a	4656
36	Ks2(III)a	4676
37	Ks3(III)b	4699
38	Ks1(II)c	4700
39	Ks3(I)a	4754
40	Ks4(II)a	4776
41	Ks5(II)c	5673
42	Ks5(III)b	5703
43	Ks5(II)a	6594
44	Ks5(II)b	7131

c). Alliance Samples Weight per Pellet

ANALYZED ALLIANCE SAMPLES		
No.	***Sample Codes***	***Sample Weights ×(1/10000)g***
1	Al1(I)a	4200
2	Al1(I)b	4228
3	Al1(I)c	4216
4	Al1(II)a	4132
5	Al1(II)b	5311
6	Al1(II)c	4474
7	Al1(III)a	4713
8	Al1(III)b	5999
9	Al1(III)c	4916
10	Al2(I)a	4173
11	Al2(I)b	4150
12	Al2(I)c	4233
13	Al2(II)a	4270
14	Al2(II)b	4181
15	Al2(II)c	3825

16	Al2(III)a	4542
17	Al2(III)b	4290
18	Al2(III)c	4491
19	Al3(I)a	4699
20	Al3(I)b	4218
21	Al3(I)c	4040
22	Al3(II)a	4128
23	Al3(II)b	4223
24	Al3(II)c	4170
25	Al3(III)a	4542
26	Al3(III)b	6106
27	Al3(III)c	4827
28	Al4(I)a	4386
29	Al4(I)b	4702
30	Al4(I)c	4316
31	Al4(II)a	4576
32	Al4(II)b	4772
33	Al4(II)c	5452
34	Al4(III)a	4612
35	Al4(III)b	3984
36	Al4(III)c	4127
37	Al5(I)a	4130
38	Al5(I)b	4293
39	Al5(I)c	4223
40	Al5(II)a	4357
41	Al5(II)b	4348
42	Al5(II)c	4221
43	Al5(III)a	4524
44	Al5(III)b	4293
45	Al5(III)c	4232

A2. Sample Analytic Report from the EDXRF Spectrometer

ANALYSIS-REPORT	Date:	#######					
===============							
Sample:	NO_ID	Date					
Method:	Emission-Tra	Mass					
Element	Energy	counts	Concentr	Error	F		
K	3.31	280	9612.4	ppm	+-	950.2	24.1152
Ca	3.69	1634	3	w%	+-	0.14	18.4904
Ti	4.51	131	881.9	ppm	+-	112	11.3178
Mn	5.89	417	763.7	ppm	+-	56.2	5.8822
Fe	6.4	10698	1.25	w%	+-	0.04	4.8365
Ni	7.47	467	265.8	ppm	+-	17.3	3.408
Cu	8.04	609	269.4	ppm	+-	19.5	2.9287
Zn	8.63	951	312.5	ppm	+-	14.6	2.5586
Ga	9.24	77	20.8	ppm	+-	3.8	2.2709
Br	11.91	193	26	ppm	+-	2.5	1.6125
Rb	13.38	398	44.2	ppm	+-	3.5	1.4443
Sr	14.14	1198	125.1	ppm	+-	5.6	1.382
Y	14.93	121	11.6	ppm	+-	2.3	1.3301
Zr	15.75	2024	192.2	ppm	+-	7.7	1.2866
Nb	16.58	406	38.1	ppm	+-	3.8	1.2501
Pb	10.54	48	13.2	ppm	+-	3.4	1.8655
Th	12.95	35	4.6	ppm	+-	1.9	1.4851
U	13.6	12	1.4	ppm	+-	1.7	1.4249
ANALYSIS-REPORT	06/02/2019						
===============							

A3. Results from Select Samples

i. Sample Al3II

Sample AL3II Mean Results			
Element	***Concentration(ppm)***	***Error***	***Units***
K	1.02	0.09	w%
Ca	3.59	0.18	w%
Ti	945.46	120.5	ppm
Mn	804.56	58.43	ppm
Fe	1.33	0.05	w%
Cu	189.9	19.56	ppm
Zn	312.4	16.5	ppm
Br	24.1	2.86	ppm
Rb	45.96	3.3	ppm
Sr	139.73	6.1	ppm
Y	12.53	2.46	ppm
Zr	219.7	8.63	ppm
Nb	42.8	4.23	ppm
Pb	16.7	3.53	ppm
Th	5	2.9	ppm
U	4.3	2	ppm

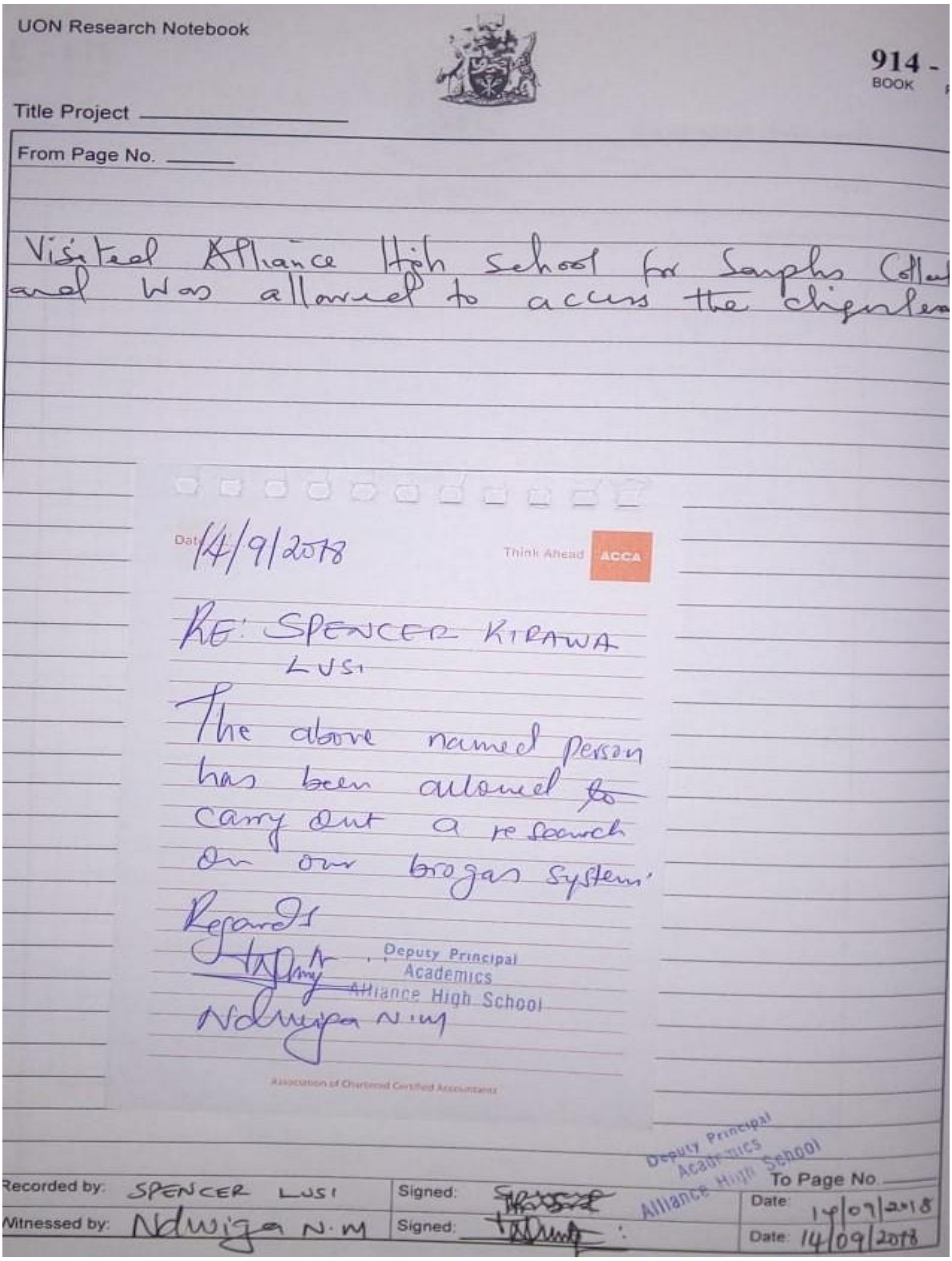
ii. Sample Kb3II

Sample Kb3II Mean Results			
Element	Concentration	Error	Units
K	3567.10	623.40	ppm
Ca	4.48	0.21	w%
Ti	664.36	113.86	ppm
Mn	1062.10	67.60	ppm
Fe	0.98	0.04	w%
Cu	190.93	17.10	ppm
Zn	1107.36	44.50	ppm
Br	7.20	1.83	ppm
Rb	22.93	2.50	ppm
Sr	271.70	10.86	ppm
Y	6.16	2.10	ppm
Zr	136.13	7.06	ppm
Nb	19.20	3.33	ppm
Pb	10.90	3.33	ppm
Th	2.60	1.4	ppm
U	2.75	1.66	ppm

iii. Sample Ks3II

Sample Ks3II Mean Results			
Element	***Concentration***	***Error***	***Units***
K	2549.80	520.40	ppm
Ca	1.29	0.07	w%
Ti	642.53	86.40	ppm
Mn	369.20	30.96	ppm
Fe	6712.43	300.66	ppm
Cu	185.56	11.53	ppm
Zn	119.63	8.20	ppm
Br	59.03	3.33	ppm
Rb	13.43	2.50	ppm
Sr	187.73	7.66	ppm
Y	2.95	2.56	ppm
Zr	65.00	4.63	ppm
Nb	15.25	3.23	ppm
Pb	9.30	2.50	ppm
Th	2.15	1.53	ppm
U	2.30	1.53	ppm

A4. Alliance Biogas Digester Visit Authorization



UON Research Notebook

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BOOK

Title Project ____________

From Page No. ______

Visited Alliance High school for Samples Collect
and was allowed to access the digester

Date 14/9/2018

Think Ahead ACCA

RE: SPENCER KIRAWA
LUSI

The above named person
has been allowed to
carry out a research
on our biogas system.

Regards

Deputy Principal
Academics
Alliance High School

Ndwiga N.M

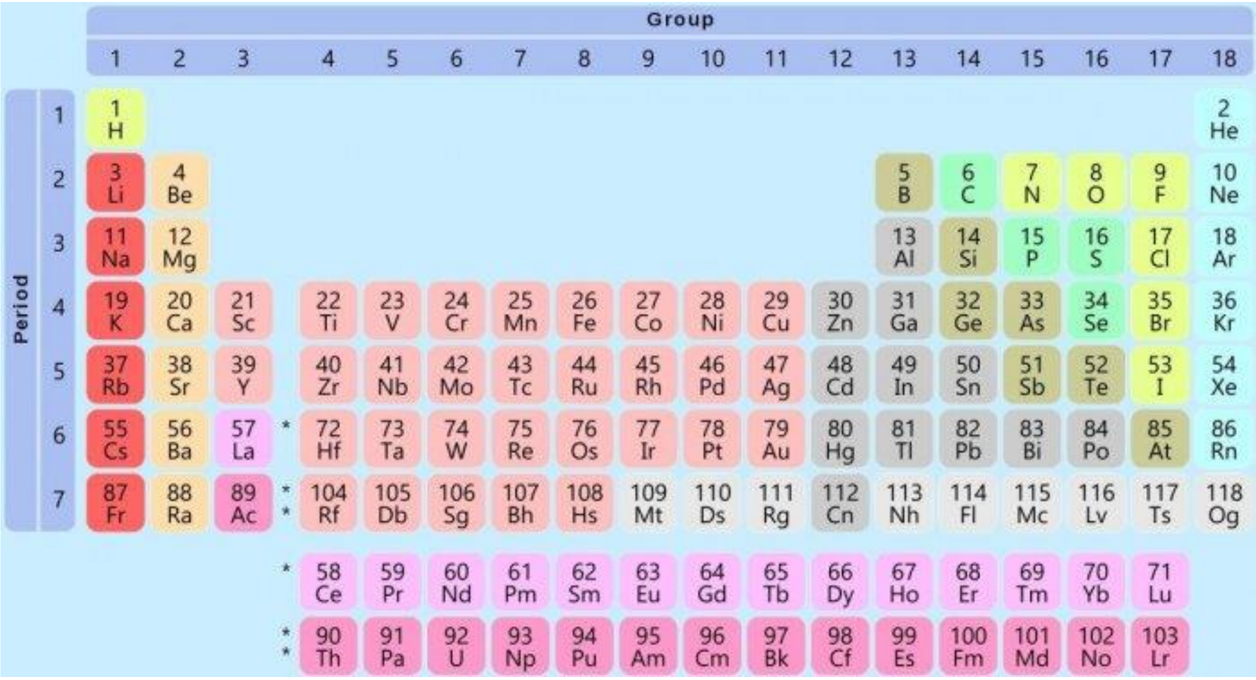
Association of Chartered Certified Accountants

Deputy Principal
Academics
Alliance High School

Recorded by: SPENCER LUSI | Signed: | To Page No. | Date: 14/09/2018

Witnessed by: Ndwiga N.M | Signed: | Date: 14/09/2018

A5. The Periodic Table



A6. Definition of terminologies

a) The **Fourth Industrial Revolution** (4IR) is the fusion of technology into industrial advancement, which is a continuation of the 18th-century industrial revolution. It cuts across all sectors of economies and is intended to simplify most of the industrial processes by lowering the need for human input into the same.

b) The **R statistical software** is a freely available software which analyses most statistical inputs to result in graphical and computed outputs. It is compatible with most of the Operating systems of computers available across the globe.

c) The **P-value** is used to test hypotheses in statistics and is usually accepted at 0.05. A value smaller than 0.05 is strong evidence against the null hypothesis hence indicates statistical significance.

d) **Anaerobic Digestion** is the process through which microorganisms digest the organic materials devoid of oxygen to produce both the BDS and Biogas.

e) **Biogas Digester Slurry** is a byproduct of the anaerobic digestion process which intends to produce biogas primarily. It can be solid, semi-solid, or liquid.

f) **Energy Dispersive X-Ray Fluoroscopy** is a non-destructive analytical technique that is useful in determining the elemental composition of substances. The basic working principle behind the science of the EDXRF spectroscopy is that when the X-Rays irradiate a sample, the elements in the sample emit fluorescent X-Ray radiations of characteristic energies.

g) **Global Warming** is the gradual increment in the temperature of the earth's surface. It is primarily attributed to the release of greenhouse gases into the atmosphere.

h) **Greenhouse Gases** are those gases that contribute to the greenhouse effect by absorbing the infrared radiation. The most common examples of the gases include chlorofluorocarbons and carbon dioxide.

i) **Fossil Fuels** are those having been formed as a result of organic remains and having gone through the geological alterations to become consumable fuels. Examples include petroleum and coal.

j) **Biofertilizers** contain microbes and, when applied to soils, increase fertility by improving the availability of the needed nutrients to the crops grown therein.

k) A **feedstock** is what is fed into the Biogas Digester to produce Biogas and the Biogas Digestate Slurry (BDS). It mostly refers to the agricultural organic substances fed into the digester. In this context, the term refers to human wastes, Cow dung, and abattoir wastes.

l) **Carbon/Nitrogen Ratio** is the ratio of the mass carbon to that of Nitrogen in a substance.