

**ASSESSMENT OF HEAVY METALS CONCENTRATIONS IN SUGARCANE
(LEAVES AND JUICE) AND SOILS AND THEIR EFFECT ON SUCROSE
CONTENT IN SAVANNAH SUGAR COMPANY LIMITED, NUMAN,
ADAMAWA STATE, NIGERIA**

BY

Humphrey APAGU

**A RESEARCH WORK SUBMITTED TO THE DEPARTMENT OF BOTANY,
FACULTY OF LIFE SCIENCES,
AHMADU BELLO UNIVERSITY,
ZARIA, NIGERIA**

APRIL, 2019

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NUMAN, ADAMAWA STATE, NIGERIA**

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**A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE
STUDIES, AHMADU BELLO UNIVERSITY, ZARIA IN PARTIAL
FULFILLMENT FOR THE AWARD OF MASTER OF SCIENCE**

**DEPARTMENT OF BOTANY,
FACULTY OF LIFE SCIENCES,
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ZARIA, NIGERIA**

APRIL, 2019

DECLARATION

I declare that the work in this dissertation entitled **ASSESSMENT OF HEAVY METALS CONCENTRATIONS IN SUGARCANE (LEAVES AND JUICE) AND SOILS AND THEIR EFFECT ON SUCROSE CONTENT IN SAVANNAH SUGAR COMPANY LIMITED, NUMAN, ADAMAWA STATE, NIGERIA** has been performed by me in the Department of Botany. The information derived from the literature has been duly acknowledged in the text and the list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

Humphrey APAGU

Signature

.....

Date

CERTIFICATION

This dissertation entitled **‘ASSESSMENT OF HEAVY METALS CONCENTRATIONS IN SUGARCANE (LEAVES AND JUICE) AND SOILS AND THEIR EFFECT ON SUCROSE CONTENT IN SAVANNAH SUGAR COMPANY LIMITED, NUMAN, ADAMAWA STATE, NIGERIA** By Humphrey APAGU, meets the regulations governing the award of the degree of Master of Science (M.Sc.) in Botany of the Ahmadu Bello University, Zaria, and is approved for its’ contribution to scientific knowledge and literary presentation.

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DEDICATION

This dissertation is dedicated to the following; Almighty God who saw me throughout my studies. My parents, Pharm. (RT) Justin Apagu Awi, and also to Mr Donald Apagu and Waja Philip Paul whose collective support and love encouraged me to pursue the Master of Science Degree.

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ABSTRACT

The accumulation of heavy metals in the environment is increasing becoming a concern due to continuous accumulation of these metals through industrial activities. Sugarcane juice are common beverages in the usual diet and are also use for sugar production which may contribute significantly to the nutritional intake of heavy metals in the manufactured sugar from Sugar companies. In present study, the levels of heavy metals Zn, Cd, Pb and Cr in sugarcane juice, leaves, soil, fumes and water sampled from four sample plots at Savannah sugar company limited, Numan. Were determined using Micro-wave Atomic Emission Spectrophotometer. Sucrose content levels of the sugarcane juice were determined using refractometer (%). The general results of heavy metals in sugarcane juice samples varied from 0.30-4.20kg/mg (Zn), 0.03-0-03mg/kg (Cd), 3.20-7-90mg/kg (Pb) and 1.30-35.50mgkg (Cr) while sugarcane leaves varied from 1.10-4.30kg/mg, 0.33-0.40kg/mg, 3.70-16.0kg/mg and 3.4-53.33kg/mg for Zn, Cd, Pb and Cr respectively. The amount of Zn, Cd, Pb and Cr in the soil varied from 0.2-4.40 kg/mg, 0.1-1.0 kg/mg, 6.2-37.37 kg/mg and 7.20-121.00 kg/mg respectively. The heavy metals concentrations between fumes and water were observed to be; 0.10 and 536.36 mg/kg for Zn, 0.20 and 3.30mg/kg for Cd, 393.00 mg/kg and 22.57 mg/kg for Pb and 45.35 mg/kg and 332.95 mg/kg for Cr. The sucrose content levels of the sugarcane juice ranged from 9.00-23.00% which indicated no or little effect of heavy metals in the sucrose levels of sugarcane juice. The transfer factor of heavy metals from soil to sugarcane (juice) indicated a trend in the order: Cd<Pb<Cr<Zn. Significant differences in the heavy metal concentrations in samples from Gyewana block 2, kem block 1, Kem block 2 and Gyewana block 2-08 were observed. The concentration of Zn, Cd, Pb and Cr in the sugarcane juice exceeded the Worth health Organization maximum permissible limits (Zn 0.60 mg/kg, Cd 0.20mg/kg, Pb 2.00 mg/kg and 1.30 mg/kg). The

levels of Zn, Cd, Pd and Cr in soil were observed below the permissible limits set by WHO. Sugarcane juice, leaves and soil are contaminated by heavy metals (Zn, Cd, Pb and Cr) originated from fumes emitted by chimneys and irrigated water from Dam which endangers lives of humans through consumption of raw sugarcane. It was recommended among other recommendations that, there should be regular monitoring of heavy metal concentrations in both soil and sugarcane stems because of the possibility of being transferred to man through consumption.

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CHAPTER ONE

1.0 INTRODUCTION

Heavy metals pollution has been a global concern with worries expressed in many different countries. This is due to the toxicity, extensive sources, non-biodegradable properties and accumulative behaviors of heavy metals (Hui-na *et al.*, 2012; Dou *et al.*, 2013). The term heavy metal refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004). Heavy metals can also be defined as a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm³, or 5 times or more, greater than water (Hawkes, 1997). Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe), and the platinum group elements (Zalups, 2005)

Toxicity studies have established that trace metals can directly damage the human body via impairment of mental and neurological function and alteration of numerous metabolic body processes (Greenwood and Earnshaw, 1986). For example, lead (Pb) diminishes calcium (Ca) in the bones, impairs the synthesis of haemoglobin and affects the kidney and central nervous system (Bridges and Zalups, 2005). In fact, this metal has no known importance in human biochemistry and physiology, and consumption even at very low concentration can have serious health implications (Nolan, 2003). Copper is non-toxic, but its soluble forms are poisonous when present in large amounts (Scheinberg, 1991). Zinc is an essential micronutrient that can be found in all tissues of the body and is essential for cell growth, differentiation, healthy immune system and DNA synthesis (WHO, 1996). Zinc toxicity and gastric distress can occur from

moderately high intakes of Zn greater than 150 mg day⁻¹ over long period of time (Samman, 2007).

Heavy metals are common components of natural systems, some are essential for living organism, but man's activities have increased the quantities and distribution of these metals in the site our water, rivers, lakes, streams and seas and in the atmosphere. Heavy metals are highly toxic when present in these systems in high concentration and when they accumulate above maximum levels in any physiological system; they tend to be highly injurious to health (Ukpong *et al*, 2013).

Heavy metals can be introduced into the environment by both natural and anthropogenic causes. The major causes of emission are the anthropogenic sources specifically industrial activities (Nriagu, 1988; Kelepertis, 2014). In some cases, even long after industrial activities have ceased, the emitted metals continue to persist in the environment over the last decades there has been an increased interest in soil contamination and its effects on humans and environment (Naveedullah *et al*. 2013; Kelepertzis, 2014). Among soil contaminants, heavy metals raise great concern due to their persistence in soils and high potential risks to human health and ecosystems (Thompson *et al*. 1988). Naturally the concentration of heavy metals in soils is generally low and dependent on the geological parent material; hence, for most metals, anthropogenic sources are known to dominate over lithogenic contributions (Niu *et al*. 2013). Anthropogenic inputs such as sewage irrigation, pesticides, excessive use of fertilizers and emission from the pipelines are responsible for the increase of heavy metals concentrations in agricultural soils (Mico *et al*. 2006; Peris *et al*. 2007; Wei and Yang, 2010). In these soils, the presence of heavy metals deserves careful monitoring since they can accumulate in less soluble forms or be transferred into soil solution and

consequently deteriorate groundwater and crop quality (Sun *et al.* 2013; Yang *et al.* 2014).

Heavy metal contamination of soil due to various anthropogenic activities has become a major cause of concern throughout the world. The increase in levels of heavy metals such as Cr, Cu, Co, Cd and Pb in arable soils due to application of agrochemicals and contaminated irrigation water led to the deterioration of soil health (Rayment *et al.*, 2002; Kaur *et al.*, 2014). From soil, the heavy metals are taken up by food and fodder plants. Although metals such as Cr, Cu and Co etc. are essential for plant metabolism, but at levels exceeding food and fodder safety levels, they pose severe health risk (Wang *et al.*, 2012; Katnoria *et al.*, 2011). Heavy metal contents in soils and crops are dependent on the soil physico-chemical properties, cropping practices, availability and species of metal in soil, solubility of metals in soil and type of plant (Sinha *et al.*, 2006; Dheri *et al.*, 2007). Soil has long been recognized as a repository for pollutants due to the adsorption processes which binds inorganic and organic pollutants to it (Popoola *et al.*, 2012).

When agricultural soils are polluted, these metals are taken up by plants and consequently accumulate in their tissues (Trueby, 2003). Animals that graze on such contaminated plants and drink from polluted waters, as well as marine lives that breed in heavy metal polluted waters also accumulate such metals in their tissues and milk (Habashi, 1992; Garbarino *et al.*, 1995; Horsfall and Spiff, 1999; Peplow, 1999; Yang *et al.* 2014). Humans are in turn exposed to heavy metals by consuming contaminated plants, and this has been known to result in various biochemical disorders. In summary, all living organisms within a given ecosystem are variously contaminated along their cycles of food chain. Crops absorb whatever is present in the soil medium and therefore these hazardous metals are also absorbed and become bio-accumulated in the roots,

stems, fruits, grains and leaves of the crops which may finally be transferred to man in the food chain (Fatoki, 2000).

Unlike developed countries, it is difficult to estimate the level of health hazard from heavy metals in the urban environment in developing countries because urban farming is usually unregulated and soils are rarely tested (Nabulo, 2006). The level of heavy metals in urban areas of less industrialized countries is generally far lower than those in industrial countries. There exists a global need to identify vulnerable areas and regulate farming in these locations to ensure food safety.

Brazil is the biggest sugarcane producer World-wide; nevertheless, studies on heavy metal accumulation in soils are still scarce (Conceicao and Orr, 2012). Sugarcane, are several species of tall perennial true grasses of the genus *Saccharum*, native to the warm temperate to tropical regions of South Asia and Melanesia, and used for sugar production. It has stout, jointed, fibrous stalks that are rich in sugar (sucrose), which accumulates in the stalk internodes. The plant is two to six meters (six to twenty feet) tall. All sugarcane species interbreed and the major commercial cultivars are complex hybrids. Sugarcane belongs to the grass family (Poaceae) Peter, 2000

Sugarcane (*Saccharum officinarum* L.) is a tropical, perennial grass that forms lateral shoots at the base to produce multiple stems, typically three to four meters high and about five cm in diameter. The stems grow into cane stalk, which when mature constitutes approximately 75% of the entire plant. A mature stalk is typically composed of 11–16% fibre, 12–16% soluble sugars, 2–3% non-sugars, and 63–73% water. A sugarcane crop is sensitive to the climate, soil type, irrigation, fertilizers, insects, disease control, varieties, and the harvest period (Solomon, 2012). The average worldwide yield of sugarcane crops in 2013 was 70.77 tons per hectare. The most

productive farms in the world were in Peru with a nationwide average sugarcane crop yield of 133.71 tons per hectare (<http://en.wikipedia.org/w/index.php?oldid=522854888>) Savannah Sugar Company Limited (SSCL) is an existing cane sugar production operation located on 32,000 hectares of land in Numan, Adamawa State, Nigeria, with a milling capacity of 50,000 tons of sugar per annum. At present, SSCL produces refined sugar from just 6,750 hectares of sugar cane cultivated on its sugarcane fields. As part of our growth strategy, SSCL is undergoing rehabilitation and expansion so that more of its land can be planted and harvested effectively. This expansion project will increase sugar milling capacity to some 260,000 tons of sugar per annum, from sugarcane produced on approximately 25,000 hectares of cultivated land. The project will include the development of out-growers scheme and the refurbishment of infrastructure within the estate, as well as a significant upgrade to its existing factory from 3000 TCD to 6000 TCD; and installation of a 12000 TCD diffuser factory, to process the increased sugarcane supply.

(<http://dangotesugar.com.ng/operations-overview/sugarproduction/savannah-sugar-company-limited/>, 2017).

1.1 Statement of Research Problem

Pollution caused by the first industrial revolution led to serious environmental degradation in many parts of the World. Many industries discharged foul, sometime toxic, solid, liquid, and gaseous wastes. These emissions blackened air and water and affect the ecosystems (Christian, 2011). The concentrations of heavy metals in the ecosystem have been increasing overtime because of anthropogenic activities which can lead to the pollution of environment (Adediran, *et al.*, 1990). Humans are exposed to heavy metals by consuming contaminated plants and this has been known to result in various biochemical disorders (Zhuang *et al.*, 2009). The company, during production of sugar release fumes from tall pipes into the atmosphere which may settle on the soil,

plants and water over a period of time in the study area and similar case has been reported in literatures that industrial activities is of concern in developing on heavy metals accumulation. Although appreciable numbers of studies have been published on heavy metal accumulation in plant, to the best of our knowledge, only few studies are available on heavy metal in sugarcane especially in Nigeria. Furthermore, literatures are scarce on the effect of heavy metal accumulation on the sucrose content of sugarcane. Moreso, we do not know of any study that has attempted to compare heavy metals accumulation in Sugarcane exposed to different sources.

1.2 Justification

The assessment of heavy metals in sugarcane and soils is not only of interest for environmental monitoring but also for purposes of health impacts as high concentrations of essential elements like Lead and Zinc can be very toxic (Udosen, 2000). It is important therefore to monitor the level of heavy metals in sugarcane and soil. This study will provide information on the levels of heavy metals and the uptake rate of these metals by sugarcane grown in the study area. It is important to reveal the heavy metals concentrations of sugarcane cultivated in industrial areas since information relating to heavy metals accumulation in sugarcane juice and leaves, soil, water and fumes in the study area is inadequate. Sugarcane is among the most important plant grown in the world and therefore a concern that very few studies have paid attention on heavy metals in sugarcane (Collin and Doelsch, 2010). Furthermore, consumption of sugarcane grown in potentially polluted soil could lead to adverse health effects to human beings. However, in general there is little or no literatures in the elemental composition in the water, fumes, sugarcane plants and soil in the study area and this study intend to

reveal the level of heavy metals in the water, fumes, sugarcane plants and soils in the study area.

1.3 Aim of the Study

The aim of this study is to assess the heavy metals concentrations in sugarcane (juice and leaves) and soils and their effect on the sucrose content in the study area.

1.4 Objectives of the Study

The aim of the study will be achieved through the following objectives

- i. To determine the concentrations of heavy metals in the soil at different locations in the study area.
- ii. To determine the concentrations of heavy metals in the sugarcane juice and leaves at different locations in the study area.
- iii. To determine the concentration of heavy metals in the water and the fumes emitted in the study area.
- iv. determine the effect of heavy metals concentration on the sucrose content of sugarcane juice from different locations in the study area.

1.5 Hypotheses

- i. There is no significant difference in the concentrations of heavy metals in the soil at different location in the study area.
- ii. There is no significant difference in the concentrations of heavy metals in the juice and leaves of sugarcane at different locations in the study area.
- iii. There is no significant difference in the concentration of heavy metals in the water and the fumes emitted in the study area.

- iv. There is no significant effect of heavy metals in the sucrose content of sugarcane collected from different locations.

CHAPTER TWO

2.0 LITERATURE REVIEW

There are certain classes of metal elements whose interactions with living system are considered either essential or toxic. These elements have specific density of more than 5g/cm^3 and are referred to as heavy metals. Common examples include Pb, Cu, Zn, Cd, Fe and Cr. However at certain concentrations the essential elements become harmful to the organism. In addition some elements are harmful even in trace amounts. For an element to be considered essential or toxic depends on the metal itself and its quantity in an organism. For example zinc is micronutrient for growth of animals when present in trace amounts while lead is poisonous even in trace quantities. The impact on human health from heavy metals has been from occupational exposure, environmental contamination and accumulation in foods. They are known to have poisonous effects that lead to chronic degenerative changes nerves system, organs, and are also known to be carcinogens and teratogens (Karalliedde and Brooke, 2012). Plants form an important part of diet for both human beings and animals. As plants extract essential nutrients from soil, they also uptake non-essential and toxic elements to their tissues. These elements build up amounts over a period and they could reach toxic levels at the edible parts (Wang *et al.*, 2012). Heavy metals accumulation and bio-magnification across the food chain pose a health risk to both plants and animals including humans. Therefore, it's important to determine heavy metals accumulation in foods. On the other hand, the characteristic tendency of some plants to accumulate relatively large concentrations of heavy metals has resulted to an interest in using these plants for environmental treatment of soil contaminated by heavy metals. Plant uptake of heavy metals and resultant accumulation is determined by several factors. Heavy metals are both essential and toxic to plants. Moderate concentrations of some of these elements in

the soil are a requirement for plant growth. However, soils with relatively large heavy metals levels hinder plant growth. Other factors that influence heavy metal uptake by plants are organic content, soil pH, cation exchange capacity, metal content and solubility sequence, and plant species (Abdus-salam *et al.*, 2008; Chandra *et al.*, 2008). Though heavy metals are natural components of the earth's crust, anthropogenic activities progressively contribute to the elevated concentrations in the soil. Therefore continuous addition of heavy metals into the environment has resulted to accumulation of these elements. For example heavy metal pollution of agricultural land has been due to activities such as industrial emissions, agronomics and irrigation with water from industrial waste. Due to the increasing economic development and human activities, this problem is expected to intensify (Zhao *et al.*, 2012).

2.2 Heavy Metal in Soils

The origin of heavy metals in the soil are geogenic and pedogenic, both are natural (Khan *et al.*, 2013; Zhao *et al.*, 2012). They are constituents of the earth's crust and therefore it is expected that soil will have a substantial amount of these elements. However human activities have also resulted to additional amounts of the elements in the environment. The fact that the metals in the environments could be attributed to these two sources has been illustrated by findings on the high level of Zn and Fe in Lakes Nakuru and Bogoria sediment (Minkina *et al.*, 2012.). They concluded that an elevated Fe level was because of the volcanic activities in the area. Fe is the most plentiful metal in the earth crust and so that observation was expected. On the other hand the unanticipated high amount of Zn in Lake Nakuru sediment could only be attributed to the anthropogenic activities in Nakuru City. Heavy metals from geogenic sources are usually present in forms that have low availability to plants. The processes of sorption and desorption determine the availability of specific chemical species and

their content in the soil (Minkina *et al.*, 2012). This is determined by the interaction between metals and soil's solid phase, water content and constituent air which is comprised of four physico-chemical processes: cation exchange, co-precipitation, specific adsorption and organic ligand complexation (Omwoma *et al.*, 2010). These processes are dependent on covalent bonding with the matrix of the soil, metal-anion exchange at the surface of the soil and creation of water insoluble precipitates. Plant uptake is highly influenced by the elements' solubility and mobility. It has been found that heavy metals in soils resulting from natural sources have relatively low mobility and hence low phyto-availability. Collin and Doelsch, (2010) found out that despite the high levels of heavy metals in soil from natural sources, the elements had low mobility and a phyto-availability that was below the threshold. They found, for instance, that the mobile fraction of Cr, Cu and Zn was very small. The measured mobile Zn concentration was 0.81% of the total amount of the metal in the soil. It is anthropogenic activities that are the main cause of increase metal levels in soils and accumulation in plants (Park *et al.*, 2011). Accumulation of heavy metals in plant is influenced largely by bioavailability of the elements in soil. The dynamic process of heavy metal bioavailability in soil is dependent on combination of biological, chemical and environmental parameters (Hajar *et al.*, 2014). Metals resulting from anthropogenic sources have speciation that influences positively their bioavailability in soil. Hu *et al.*, (2014) compared the total heavy metal concentrations and the bioavailable (Diethylene-triamine-pentaacetic acid - extracted) in paddy fields and deduced a strong positive correlation ($r_{Zn} = 0.435$, $r_{Cd} = 0.855$, $r_{Mn} = 0.735$, $r_{Cu} = 0.798$, $r_{Ni}=0.812$, $r_{Co} = 0.580$; $p<0.01$). They concluded that the heavy metal bio-availability in plant was strongly influenced by the total levels of the metals in the soil which was as a result of pollution of paddy fields. Soil plays an important role in our society as it is the basis on

which food crops are grown. However it is also the sink for most heavy metals. Heavy metals are not subject to chemical or biological degradation and therefore heavy metal pollution of soil poses long-term environmental problem with serious health implications on human beings and animals. Moreover, contaminated soil is the primary reservoir of heavy metals (Mahmood and Malik, 2014; Wei and Yang, 2010). In fact it has been suggested that soil ingestion is the main source of Pb in children's blood (Florido *et al.*, 2011). In addition, Oyoo-Okoth *et al.*, (2013) linked the heavy metal concentration in children's hair to those detected in the soil. For example the geometric mean of Cr levels in children hair varied from 0.4 to 1.6 $\mu\text{g/g}$ at exposed locations as compared at the reference site which had four times less (0.1–0.4 $\mu\text{g/g}$). The Cr amounts in soil from the reference site were 6.7 $\mu\text{g/g}$ while the levels in the exposed areas were 11.8 $\mu\text{g/g}$. The exposure was attributed to dust inhalation, water, soil ingestion or through food crops. Although heavy metals do not degrade, the chemical conditions in the soil determine the fate and transport of the metals from the source (Omwoma *et al.*, 2010). There are several factors that influence the chemical form of an element in soil: parent materials, soil organic matter, crop residues, soil pH, solubility, presence of other metals, fertilizers and the type and amount of clay (Barzegar *et al.*, 2005; Nayak *et al.*, 2014). These factors create chemical characteristics of the soil that determines the solubility and mobility of the metals. For instance, pH of soil and organic constituent influences significantly mobility of metals in soils (Yang *et al.*, 2010). Kamau *et al.*, (2014) reported a positive correlation value ($r = 0.67$) from a comparison between sediment pH and dissolved Zn concentration is known to be the increase in pH the higher the concentration of Zn in solution. This was attributed to chemisorption of oxides and aluminosilicates at higher pH values. They also reported positive correlation ($r = 0.50$) between dissolved Zn and organic matter, which was due to the release of

organic bound Zn. Harguinteguy *et al.*, (2014) also reported significant correlations ($r_{Cu}=0.58p<0.001$, $r_{Pb}=0.32p<0.05$, $r_{Zn}=0.46p<0.001$) between heavy metal concentration and the organic content in sediment from Suquía River in Argentina. Activities such as industrialization, urbanization, agriculture and mining are among the main causes of elevated amounts of heavy metals. Mining and application of waste water or sludge have been singled out as the leading sources of heavy metal pollution of soil (Jung, 2008; Li *et al.*, 2006). It is projected that approximately 240, 0.5, 310 and 250 million tonnes of Pb, Cd, Cu and Zn respectively, have ended up in soil as a result of mining activities (Yun-Guo *et al.*, 2006). Muohi *et al.*, (2003) used the Turkey honest test to reveal that there was a substantial difference ($p = 0.00012$) for the average amounts of Cd, Pb, Zn and Cu between Makupa Creek and Port Reitz Creek. The notably elevated values were attributed to the increasing anthropogenic activities. Kelepertzis, (2014) also used the Turkey honest test to detect significant statistical differences between the levels. Therefore, it was an indication that agriculture was contributing to the increase of heavy metals levels in soils. A study by Ngure *et al.*, (2014) reported that concentration of As, Pb, Hg and Cd in the Lake Victoria region had exceeded the maximum allowable concentration standards by both World Health Organization (WHO) and Food and Agriculture Organization (FAO). For example they reported that the concentration ranges of Cd and Pb in soil were 4.5-570 and 5.5-619 mg/kg in comparison to WHO/FAO limits 0.1-10 and 10-70 mg/kg respectively (Ngure *et al.*, 2014). Several works have shown that the use of sludge for agricultural activities has resulted to the significant increase of heavy metals levels in the environment and their availability (Jamali *et al.*, 2009). Latare *et al.*, (2014) detailed that application of sludge could lead to an increase of extractable Zn and Fe content in post-harvest rice soils by 68% and 49% and in post-harvest wheat soil by 87% and 36% respectively.

Another study by Florido *et al.*, (2011) reported statistical correlation between the total concentration of Zn ($r = 0.97$), Cu ($r = 0.72$) and Pb ($r = 0.6$) in soil and the available amounts of the metals after the soil had been amended with biosolid from waste water treatment. Similarly, there was an increase of Mn, Cu, Cd and Zn by 40% and 20% for Pb, Ni and Cr concentrations in sludge amended soil in comparison to the unamended (Singh and Agrawal, 2007). Moreover, Nogueira *et al.*, (2013) reported that sludge application in soil led an increase of extractable Cd ($p < 0.01$) and total recoverable Cd ($p < 0.01$). The authors also reported significant correlation between extractable Cd and total recoverable Cd ($r^2 = 0.91$) in soil which was a confirmation that sludge was the source of the element. The heavy metals sources in soil can be indicated by the use of correlation studies. The ratios of specific metal element to other metals in a soil can indicate the parent material from which the soil originated from. The elements concentrations in the soil are usually closely correlated. However, an external source can alter the proportions of the metals in the soil. Therefore the initial association between the amounts of metal in the soil could be eliminated and new ones formed depending on the external source. For example a study by Nabulo *et al.*, (2010) reported a close correlation ($r^2 = 0.90$) between the concentrations of Zn and Cd in soil. It was an indication that the two elements had shared industrial and geochemical source. The deficiency of covariance for the other metal concentration showed that they originated from different sources rather than a common one.

2.3 Heavy Metals in Plants

The tendency for plants to accumulate heavy metals in substantial amounts has ramifications on human and animal health. The existence of plants is heavily reliant on the water and nutrients in soils. Plants absorb trace metal elements from the soil and retain them in their tissues. Most edible crops do not discriminate in the extraction of

nutrients from the soil and therefore uptake unwanted heavy metals as well as required vital nutrients (Oyedele *et al.*, 2008). Heavy metal uptake by plant and resultant bio-magnification across the food chain and bioaccumulation in human and animal tissues is important to both the environment and human health (Singh and Kalamdhad, 2013). Nakayama *et al.*, (2012) compared the amount of heavy metals in plants and that in hippopotamus *amphibius* liver and reported a bio-accumulation factor value 5.0 for Hg an indication of bioaccumulation of the metal from plant to the animal. Several factors influence the heavy metals concentration within and on the plants. They include atmospheric deposition, climate, type of soil where a plant is growing and plant's maturity at the time it is harvested. Plants uptake of trace elements is distinctive for each element and varies with species or varieties. The interaction of individual elements with plants is relative to factors specific to that element. For example, uptake of Cu is depended on total amount of Cu in the soil and plants ability to transfer the metal across the soil–root interface (Hajar *et al.*, 2014). Rahman *et al.*, (2014) reported that rice samples from Bangladesh, Vietnam, India and Pakistan had substantial differences in the heavy metal concentrations in comparison with Australian grown rice. For example the amount of Cu, Mn, Pb and Zn in Bangladesh rice was 1.6 $\mu\text{g kg}^{-1}$, 14.7 $\mu\text{g kg}^{-1}$, 19.0 $\mu\text{g kg}^{-1}$ and 13.4 $\mu\text{g kg}^{-1}$ as compared to those in Australian rice which were 2.9 $\mu\text{g kg}^{-1}$, 24.4 $\mu\text{g kg}^{-1}$, 375 $\mu\text{g kg}^{-1}$ and 17.1 $\mu\text{g kg}^{-1}$ respectively. It was also observed that the levels of heavy metals in different Australian grown rice varieties differed significantly. It reported that the concentrations of Cu, Mn, Ni and Zn in brown rice varieties were higher than those in white rice varieties, demonstrating that Australian brown rice could be a potential contribute to dietary heavy metals. Another study by Li *et al.*, (2007) reported great differences in metal concentrations in plants species with Mn ranging from 16-3280 mgkg^{-1} , Cd 0.06-2.27 mgkg^{-1} , Cu 2.9-27.2

mgkg⁻¹ , Fe 88-9311 mgkg⁻¹ and Pb 0.2-10.6 mgkg⁻¹ . The connection between plants and soil, in relation to heavy metals, is classified into three types namely excluders, indicators and accumulators. Excluders are plants that limit metal transport to the shoot and retain low amounts of the metals in the shoot in comparison to the level of the metals in the soil. Indicators are plants that show a response to metal levels in the soil. Accumulators are plants that tend to translocate and retain relatively large amounts of heavy metals in sections of the plant that are above ground. A group of the accumulators called hyperaccumulators have the ability of retaining more than 1000 µg/g. For instance, Ghaderian and Ravandi, (2012) found out plants such as *Polypogon fugax* and *Epilobium hirsutum* Cu concentrations were 4000 and 1500 µg/g respectively and therefore could be considered as Cu hyper-accumulators. For plant species that can accumulate a certain heavy metal species, it must be able to resist the harmful effects of that element. Since heavy metals can be toxic, plants are required to have a certain level of tolerance to the elements in order to accumulate these elements in their tissues. The heavy metal tolerance level of a certain plant is associated to the balance between the rate of metal uptake and their detoxification effectiveness within that specific plant (Hajar *et al.*, 2014). Some plant species have developed strategies to resist accumulation of high amounts of heavy metals. Li *et al.*, (2007) reported that *Melastoma dodecandrum* had surprisingly normal levels of Fe, Mn, Pb and Cu which was an indication of the plant's ability to avoid metal accumulation. Plant tolerance to heavy metals is evaluated using different methods. Bio-concentration factor describes the accumulation level of chemical elements in plants and is derived by the ratio of the amount of metal in the plant and the total amount in the soil. Another index is the translocation factor which is the ratio between the metal concentration in the plant and the amount of the metal in the soil that is mobile (Minkina *et al.*, 2012). Transfer factor

is an important parameter that describes the bioavailability of an element at a specific part of a plant species. It is the ratio of the metal concentration in the edible part and the total metal levels in the soil (Gebrekidan *et al.*, 2013). The effectiveness of diverse plants species in absorbing the heavy metals can be assessed by either soil to plant transfer factors or plant uptake of the heavy metals (Wang *et al.*, 2012). Several studies have also shown that crops accumulate trace elements varying within the different plant parts. Hajar *et al.*, (2014) investigated the amounts of metal in the leaves, flowers and stems of *Stevia rebaudiana* and reported that the metals were concentrated differently in the different parts of plants. For instance the amount of As and Cd was in the order leaves < flowers < stems, while the amount Cu were in the order flowers < leaves < stems. Amount of Fe was in the order stems < flowers < leaves. Another study by Li *et al.*, (2006) reported that a general trend where the roots accumulated slightly larger Cd, Pb and Cu than the leaves. Minkina, *et al.*, (2012) also reported different amounts of Zn, Pb and Cu in the various parts of barley. They found out that Zn amounts were higher roots, Cu in the grains while Pb in the straw. Waste water irrigation is a practice that has resulted to an increase in levels of heavy metals in soils and plants. The practice of dam water irrigation has therefore resulted to an increase of amounts heavy metals in soil and plants (Muchuweti *et al.*, 2006; Zhao *et al.*, 2012). Furthermore, the amounts of Fe, Cd, Cr and Pb in soils from the vegetable farms varied from 16225-11803, 9.43-21.4, 1806-2020 and 57.7-693 mgkg⁻¹ respectively. These amounts were above the permitted levels for agriculture of 425, 0.1, 100 and 0.3-1mgkg for Fe, Cd, Cr and Pb respectively. Another activity that contributes to increased amount of the metal in plants is the use of dam water for agriculture purpose. The amount of Cd, Ni and Zn surpassed the Indian allowable limits for edible parts of *Beta vulgaris*. The metal uptake increased with the increased irrigated water with the

exception of Pb and Mn. This was indicative that uptake of metals by *Beta vulgaris* was influenced by increasing availability of heavy metals in the soil. However, the discrepancies in the trend for Pb and Mn were because the plants did not absorb all metals in equal amount and metal uptake is not concentration dependent for all elements. Another study by Chandra *et al.*, (2008) reported that wheat and mustard plants accumulated heavy metals when irrigated with effluents. The plants retained metals to amounts that were beyond permissible limit and therefore the plants were not suitable for consumption by both human and cattle. Latore *et al.*, (2014) showed that application of sludge could lead to rise in the amounts Zn, Mn, Cu, and Fe in wheat and rice grains. The amounts of Cu, Zn, Fe and Mn increased by 29%, 43%, 23% and 54% in rice and 64%, 40%, 40%, and 38% in wheat respectively. Soil pH is singled out as among the important influences that determine heavy metals content in food crops. Soil pH influences the solubility and mobility of heavy metals by altering their forms in soil. For example, a change in pH would lead to chemical changes in the soil which could convert naturally occurring metals and those introduced by anthropogenic means bioavailable by changing their speciation and influencing chemisorption (Omwoma *et al.*, 2010; Zhao *et al.*, 2011). Zeng *et al.*, (2011) reported significant negative correlation coefficients between the soil pH with concentrations of Zn ($r = -0.652$, $P < 0.001$), Mn ($r = -0.680$, $P < 0.001$), Cu ($r = -0.593$, $P < 0.001$) and Fe ($r = -0.501$, $P < 0.001$) in the straw, suggesting that amounts of Zn, Cu, Mn and Fe were lower with relatively higher pH and vice versa. Another factor that influences the heavy metal levels in plant is the total levels of heavy metals in soil. Soil is an important resource from which plants absorb essential and non-essential nutrients. Even though plants absorb heavy metal from deposits on parts that are exposed to air and soils, the latter is the main origin of these elements in plants. Minkina *et al.*, (2012) reported that an increase of Zn, Cu and

Pb amounts in soil would result to more accumulation of the metals in the plant. They showed that the addition of Zn concentrations of 100mg/kg or more led to higher concentration of Zn in grain which exceeds the maximum allowable concentration of Zn (50 mg/kg). Khan *et al.*, (2013) reported significant correlation between levels of heavy metals in soil with those in plants. For example Cr and Ni levels in *Zea mays* were significantly and positively correlated ($r = 0.886$ and $r = 0.975$) with amounts of these metals in the soil. There was also a positive correlation ($r = 0.879$) between the levels of Mn in *Benincasa hispida* and in the soil. However, Zn soil concentration revealed a negative significant correlation ($r = -0.909$) with the amount of the element in *Allium cepa*. This denoted that not all heavy metals in the soil were present in extractable forms for plant uptake. Quite a number of studies reported that the higher concentrations heavy metals in soil the higher the amounts of the metals in plants. This is an indication of the effect of the pollution of soil relative to bioaccumulation of heavy metals in plants. Nayak *et al.*, (2014) found out that amounts of Fe, Cu, Mn, Zn, Cd, Cr and Pb in rice grain and straw increased with increasing metal concentrations in soil. The metal amounts in straw were greater than those in grain for all metal elements studied with the exception of Cu, which was higher in the grain. This was attributed to the different cellular bioaccumulation mechanisms that influence the translocation of metals in plant systems. Similarly, Hu *et al.*, (2014) found that rice grown in polluted soils in paddy fields accumulated heavy metals with Cd being singled out because 90% of the samples exceeding the Chinese maximum allowable amounts ($0.2 \mu\text{g g}^{-1}$) and 50% had amounts that made the rice toxic ($1.0\mu\text{g g}^{-1}$). Grytsyuk *et al.*, (2006) three years work reported a high positive correlation between the metal concentration and accumulation of the elements in clover and perennial cereal grasses (in some cases $R^2 > 0.70$). It showed increase in concentration of metals in the soil corresponded to an increase in the

amounts of the metals in the plant. Harguinteguy *et al.*, (2014) compared levels of Cu, Fe, Pb and Zn in *Stuckenia filiformis* for a period of three years and reported a relative increase in the amounts of the metals. They reported a positive significant correlation between amounts of the metals in sediments and the amount in leaves of *Stuckenia filiformis* ($r_{Cu} = 0.55$, $r_{Mn} = 0.53$, $r_{Pb} = 0.62$ and $r_{Zn} = 0.76$, $p < 0.001$). Plants have been used to remediate contaminated soils in a cost effective and environmental friendly method referred to as phytoremediation (Chen *et al.*, 2014). Phytoremediation involves a process of extraction of metals from soils using plants by uptake and accumulation of the elements into biomass (Abreu *et al.*, 2012). The process of removal and retention in the plant's biomass is referred to as phytoextraction. Abreu *et al.*, (2012) reported that the castor oil plant could be used as a viable alternative to decontamination of soil. Another study by Li *et al.*, (2007) suggested that a variety of plants could be used to remedy a restored Mn mine land. They suggested the use of indigenous species *Phytolacca acinosa*, *Castanea henri* and *Pinus massoniana* to remedy the mine. Yun-Guo *et al.*, (2006) work on several plants showed that *Poa pratensis*, *Gnaphalium affine*, *Phytolacca acinosa*, *Coynza canadensis* and *Phragmites communis* were hyper-tolerant to Mn and had a high tolerance for Pb and Cd. Therefore these plants could be considered for phytoremediation since they had a relatively high ability to accumulate these metals though not as hyper-accumulators. For instance the reported concentrations of Pb, Cd and Mn in *Phragmites communis* were 549.50, 39.65 and 146500.00 $\mu\text{g g}^{-1}$, respectively.

2.4 Accumulation of Heavy Metals in Sugarcane

The importance of sugarcane (*Saccharum officinarum*) cannot be underestimated. It is the highest ranking crop worldwide with a yearly production in excess of 1.59 billion tonnes (Collin and Doelsch, 2010). It is main raw material for production of sucrose,

molasses and bio-ethanol. Despite its obvious usefulness, it is therefore a concern that very few studies have concentrated on the amount of heavy metals in sugarcane. The plant and its products are consumed by billions of people and hence the lack of enough information on the heavy metal accumulation by the plant could adversely affect human health. A number of studies have found out that sugarcane has the ability to uptake and retain heavy metals in significant amounts. For instance, a study by Abdus-salam *et al.*, (2008) reported sugarcane had the ability to bioaccumulate heavy metals and therefore posed a health risk to humans by biomagnification of the elements through the food chain. The study found out that even though the concentrations of Pb and Cd were not detected (below the detection limit of AAS) in the irrigation water, the elements were detected in sugarcane juice extracted from plants farmed in the same area (0.16 - 0.42 mg/l for Pb and 0.01 - 0.02 mg/l). These amounts were beyond the permitted levels of World Health Organization standards for drinking water (0.05 mg/l for Pb and 0.01 mg/l for Cd). They also found a significant correlation (95% confidence limit) for the two elements which suggested a common source of the pollutants. Muchuweti, *et al.*, (2006) work in Zimbabwe also reported that amounts of Zn and Cu in sugarcane stalks were beyond the permitted levels by European Union (50 mg/kg for Zn) and United Kingdom (20 mg/kg for Cu) guidelines. It has been reported that amounts of heavy metals in soil influence the amounts of these elements in sugarcane. A study by Kapungwe, (2013) reported that the concentration of Cu (29.45 ± 2.03 mg/kg), Pb (12.09 ± 1.27 mg/kg), Cr (4.21 ± 1.20 mg/kg) and Ni (6.19 ± 1.42 mg/kg) in sugarcane stems were above the permitted limits by Food and Agriculture Organisation/World Health Organisation. They singled out Cu contamination and attributed it to the large amounts of Cu in the soils (219 ± 25.34 mg/kg) from copper mines. Li *et al.*, (2006) found out that sugarcane cultivated in a reclaimed Mn mine had Pb (1.3 mg/kg) and Cd (0.19 mg/kg) levels in their edible parts

that were beyond the safety limits and thus not safe for human consumption. This was attributed to large amounts of the two elements in the soil. Nogueira *et al.*, (2013) showed increase of the concentrations of Cu ($p < 0.05$), Ni ($p < 0.05$) and Zn ($p < 0.01$) in soil with the amount in the sugarcane juice. They however could not find correlations for Se and Cr which was an indication that heavy metal amounts in the soil was not the only factor determining levels in the plant. The other factors include type of soil, plant species, and other elements in the soil. For example Barzegar *et al.*, (2005) reported high Cd amounts in sugarcane (15.8mg/kg). This was due to presence of Cd in the soil which is known to increase the bioavailability of Cd. Another work by Adekola and Akinpelu, (2002) indicated that the irrigation water quality also influenced the levels of trace elements in the cane juice. There was a strong correlation between the metal levels in irrigation water and the concentrations of heavy metals in two varieties of sugarcane juice ($r = 0.9848$ and 0.7570). There was also a strong association of the metal concentrations in juice with those in top soil ($r = 0.5677$). The study concluded that indiscriminate farming of sugarcane along riverbeds on which untreated industrial effluents was a serious risk on health. Some sugarcane varieties have been observed to have relatively lower abilities to uptake and retain heavy metal in their biomass. Wang *et al.*, (2012) worked on heavy metals accumulation indifferent sugarcane varieties and he reported that a sugarcane variety (Guiyin9) had comparatively lower heavy metals accumulation in contrast to six other varieties in the study. They also found that there was no significant correlation between concentration of heavy metal in sugar cane juice and soil's heavy metal concentration. They suggested that the level of heavy metals in the sugarcane juice is influenced by the relative ability of the cane to enrich the metals. This finding was conflict with Collin and Doelsch, (2010) who reported that there was correlation between total heavy metal concentration in soil and subsequent heavy metal

levels in juice. In fact, the highest correlation coefficient (r^2) observed was for Cu (0.19). However, Sirengo (2001) reported that Zn levels sugarcane roots and leaves positively correlated ($r = 0.75$) with the Zn levels in the soil. On the other hand, sugarcane has been thought as an alternative plant for phytoremediation, a plant based method to remove heavy metals from polluted soils. A suitable plant species suited for phytoremediation should be an efficient accumulator of the metal, produce high biomass and is tolerant to heavy metal concentration in soil. Sugarcane is an outstanding biomass producer and is known to be tolerant to heavy metals. In an investigation by Zhang *et al.*, (2014), soil was induced with Cu (60–125 mg/kg), Zn (150–300 mg/kg) and Pb (500–1000 mg/kg). Despite very high extractable metal concentrations and heavy metal contents greater than the concentration threshold, sugarcane root biomass increased ($p < 0.01$). Sereno *et al.*, (2007) also showed that sugarcane is an outstanding Cd accumulator and also tolerant to high amounts of Cd. They demonstrated that the sugarcane could tolerate 500 μM Cd whereas most convection plants are affected by amounts below 20 μM . The plant also showed Cd accumulation in its shoot tissues to 451 mg/kg. They also reported that sugarcane could accumulate significant amount of Cu (45 mg/kg) even though it is not highly tolerant to the metal. Studies have shown uneven distributions of various metal elements between the various parts of the sugarcane. Zhang *et al.*, (2014) found out that the distribution of heavy metal in the sugarcane stem was irregular. The top part of the cane had higher Zn concentration ($p < 0.001$) in the juice while higher amounts Pb, Sn and Cu were found to be in the juice from the bottom parts. The retention of most metals in the lower parts could be as result of heavy metals bindings to negatively charged walls and extracellular precipitation. Furthermore, SeguraMun-oz *et al.*, (2006) used transfer factors to show that most heavy metal were retained mainly in the roots. The soils to root transfer factors for Cu, Mn, Pb

and Zn were 0.25, 1.28, 0.93 and 0.67 respectively as compared to soil to stem transfer factors which were 0.23, 1.03, 0.79 and 0.64 respectively. They further noted that amounts of these elements in comestible parts of sugar cane were about 80% to 90% of the amounts detected in the root. This was in agreement with Sirengo (2001) who reported that Zinc levels in sugarcane roots were larger than in leaves and stems. Plants constantly uptake heavy metals and their concentrations within the organisms could build-up to levels larger than those in the environment (Gebrekidan *et al.*, 2013; Nogueira *et al.*, 2013). Since the toxicity of any material to a living system is dependent on the amount of that substance in cells of the organism, these metals are not always considered as toxic (Du *et al.*, 2013). In fact some heavy metals, at trace levels, are essential. However the metals are non-biodegradable and tend to have an extended biological half-lives and hence prolonged consumption of food crops with risky levels of heavy metals can result to a chronic accumulation of these elements in the kidney and liver of human beings, thereby triggering disruptions of many biochemical processes (Inoti *et al.*, 2012; Mahmood and Malik, 2014; Tsafe *et al.*, 2012). Therefore numerous studies have been done on the heavy metals and their accumulation in food crops. Some heavy metals species have been singled out because of their toxicity even in trace amounts. Among the most common heavy metals are Pb, Cr, Ni and Cd. Pb and Cd have ability to accumulate in critical organs of humans and their half-life could reach 30 years (Hussein, *et al.*, 2008). Excessive exposure to Pb is associated with the damage of the skeletal, enzymatic, circulatory, endocrine and nervous and immune systems. Cd has been linked with lung cancer, hypertension, kidney dysfunction and bone fractures among other complications (Li *et al.*, 2014). Pb and Cd are also known to cause teratogenesis and mutagenesis (Alissa and Ferns, 2011; Gebrekidan *et al.*, 2013). Furthermore, hexavalent chromium is regarded to be carcinogenic to human beings by

the International Agency for Research on Cancer and the United States Environment Protection Agency while Ni is associated with emphysema, asthma, chronic bronchitis and cancer of the lungs (Li *et al.*, 2014).

2.5 Source of Contamination

There are different sources of heavy metals in the environment such as

- i. Natural sources
- ii. Agricultural sources
- iii. Industrial sources
- iv. Domestic effluent

Heavy metal pollution can originate from both natural and anthropogenic sources. Activities such as mining and smelting operations and agriculture have contaminated extensive areas of world such as Japan, Indonesia and China mostly by heavy metals such as Cd, Cu and Zn (Herawati *et al.* 2000), Cu, Cd and Pb in North Greece (Zanthopolous *et al.* 1999), in Albania (Shallari *et al.* 1998) and Cr, Pb, Cu, Ni, Zn and Cd in Australia (Smith 1996). Heavy metals originate within the Earth's crust; hence their natural occurrence in soil is simply a product of weathering process

Natural sources of heavy metals

The most important natural source of heavy metals is geologic parent material or rock outcroppings. The composition and concentration of heavy metals depend on the rock type and environmental conditions, activating the weathering process. The geologic plant materials generally have high concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Hg and Pb. However, class-wise the heavy metal concentrations vary with in the rocks. Soil formation takes place mostly from sedimentary rock, but is only a small source of heavy metals, since it is not generally or easily weathered. However, many igneous

rocks such as olivine, augite and hornblende contribute considerable amounts of Mn, Co, Ni, Cu and Zn to the soils. Within the class of sedimentary rocks, shale has highest concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Hg and Pb followed by limestone and sand stone. Volcanoes have been reported to emit high levels of Al, Zn, Mn, Pb, Ni, Cu and Hg along with toxic and harmful gases (Seaward and Richardson 1990). World wide data on emission of heavy metals from natural sources are particularly scanty, but a summary of literature survey has (Pacyna 1986). Wind-blown dusts and volcanic eruptions are of particulate relevance to ecosystem inventories and budgets of heavy metals. Wind dust, which arises from desert region such as Sahara, has high levels of Fe and lesser amounts of Mn, Zn, Cr, Ni and Pb (Ross 1994). Marine aerosols and forest fires also exert a major influence in the transport of some heavy metals in many environments. While the long range transport of dusts, particularly from the Sahara, has received considerable recent attention, (SCOPE 1974), the transport of dusts originating in Asia and elsewhere to the Pacific, Arctic and Antarctic has also been investigated (Davidson *et al.* 1985). Some major eruptions had more far-reaching effects e.g., emissions from Mount Etna, Sicily include 10^9 to 10^6 kg per year⁻¹ of Cd, as well as Cr, Cu, Mn and Zn (Climino and Ziino 1983). The activity of this volcano also significantly enhanced the Hg content of plants and soil in the surrounding area (Barghiani *et al.* 1987).

Agricultural sources of heavy metals

The inorganic and organic fertilizers (Fertilizer is a substance added to soil to improve plants growth and yield.) are the most important sources of heavy metals to agricultural soil include liming, sewage sludge, irrigation waters and pesticides, sources of heavy metals in the agricultural soils. Others, particularly fungicides, inorganic fertilizers and phosphate fertilizers have variable levels of Cd, Cr, Ni, Pb and Zn depending on their

sources. Cadmium is of particular concern in plants since it accumulates in leaves at very high levels, which may be consumed by animals or human being. Cadmium enrichment also occurs due to the application of sewage sludge, manure and limes (Nriagu 1988; Yanqun *et al.*, 2005). Although the levels of heavy metals in agricultural soil are very small, but repeated use of phosphate fertilizer and the long persistence, time for metals, there may be dangerously high accumulation of some metals (Verkleji 1993). Animal manure enriches the soil by the addition of Mn, Zn, Cu and Co and sewage sludge by Zn, Cr, Pb, Ni, Cd and Cu (Verkleji 1993). The increase in heavy metal contamination of agricultural soil depends on the rate of application of the contributors with its elemental concentration and soil characteristics to which it is applied. Heavy metal accumulation in soil is also due to application of soil amendments such as compost refusing and nitrate fertilizers (Ross, 1994). Liming increases the heavy metal levels in the soil more than the nitrate fertilizers and compost refuse. Sewage sludge is one of the most important sources of heavy metal contamination to the soil (Ross 1994). Several heavy metal-based pesticides (Pesticides kill unwanted pests) are used to control the diseases of grain and fruit crops and vegetables and are sources of heavy metal pollution to the soil (Verkleji 1993; Ross 1994). The orchards where these compounds have been used frequently resulted into contamination of orchard soil with high levels of heavy metals such as Cu, As, Pb, Zn, Fe, Mn and Hg (Ross 1994). Pesticides such as lead arsenate were used in Canadian orchards for more than six decades and were found to be enriched with Pb, As and Zn having greater consequences for food contamination. Continued irrigation of agricultural soil can lead to accumulation of heavy metals such as Pb and Cd. The contamination of soil by heavy metals may also be from irrigation water sources such as deep wells, rivers, lakes or irrigation canals (Ross 1994).

Industrial sources of heavy metals

Industrial sources of heavy metals include mining, refinement (spoil heaps and tailings, transport of ores, smelting and metal finishing and recycling of metals). Mining operation emits different heavy metals depending on the type of mining. For example, coalmines are sources of As, Cd, Fe, etc., which enrich the soil around the coalfield directly or indirectly. The utilization of Hg in gold mining and the mobilization of significantly high amounts of Hg from old mines have become a significant source of this pollutant to the environment (Lacerda 1997). This traditional practice had been nearly forgotten since 1960. Presently, it is rapidly spreading throughout the tropics, particularly in Latin America and Asia involving over 10 million people (Lacerda 1997). High temperature processing of metals such as smelting and castings emit metals in particulate and vapor forms. Vapor form of heavy metals such as As, Cd, Cu, Pb, Sn and Zn combine with water in the atmosphere to form aerosols. These may be either dispersed by wind (dry deposition) or precipitated in rainfall (wet deposition) causing contamination of soil or water bodies. Contamination of soil and water bodies can also occur through runoff from erosion of mine wastes, dusts produced during the transport of crude ores, corrosion of metals and leaching of heavy metals to soil and ground water. Soil contamination of heavy metals occurs due to different types of processing in refineries. Energysupplying power stations such as coal burning power plants, petroleum combustion, nuclear power stations and high tension lines contribute many heavy metals such as Se, B, Cd, Cu, Zn, Cs and Ni to the environment (Verkleji 1993). Other industrial sources include processing of plastics, textiles, microelectronics, wood preservation and paper processing. Contamination of plants growing beneath the power line with high concentration of Cu is reported to be toxic to the grazing animals (Kraal and Ernst 1976).

Domestic effluents

These waste waters probably constitute the largest single source of elevated metal values in rivers and lakes. Domestic effluents may consist of (1) untreated or solely mechanically treated waste waters (2) substances which have passed through the filters of biological treatment plants (3) waste substances passed over sewage outfalls and discharged to receiving water bodies often end up into the sea from coastal residential areas. The use of detergents creates a possible pollution hazard, since common household detergent products can affect the water quality. Angino *et al.*, (1970) found that most enzyme detergents contained trace amounts of the elements Fe, Mn, Cr, Co, Zn, Sr and B. With regard to pollution resulting from urbanized areas, there is an increasing awareness that urban runoff presents a serious problem of heavy metal contamination. A statistical summary by Bradford (1997) revealed that urban storm water runoff has long been recognized as a major source of pollutants to surface waters. Studies by Bolter *et al.*, (1974) indicate that lead is leached by humic and other acids, thus increasing its availability for runoff rather than seepage into the upper soil layer. Atmospheric sources. Natural and man-made processes have been shown to result in metal containing airborne particulates. Depending on prevailing climatic conditions, these particulates may become wind-blown over great distances; nonetheless, they are subjected to the fate that they are ultimately returned to the lithosphere as precipitations by rain or snowfall. Additional sources of atmospheric metal enrichment, such as the high temperature anthropogenic sources, are of special importance on a global scale. Geothermal sources, such as volcanic eruptions, have caused significant atmospheric pollution (Eshleman *et al.*, 1971).

2.6 Effect of Heavy Metals

Pollution of the biosphere by toxic metals has increased dramatically since the beginning of the industrial revolution. The main sources of this pollution include the burning of fossil fuels, mining and smelting of metal ores, municipal wastes, fertilizers, pesticides and sewage. Emissions of heavy metals to the environment occur via a wide range of processes and pathways, including to the air, to surface waters, to the soil and into groundwater. In terms of human health, atmospheric emissions tend to be of most concern due to the amounts involved and the extensive dispersal and potential for exposure that frequently ensues (Jacobson, 2002). Heavy metals are among the most harmful pollutants in the environment and can cause various diseases including cancer, acute poisoning, and damage to the nervous system, muscles and bones (Baawain *et al.*, 2011). Heavy metals can contribute to degradation of marine ecosystems by reducing species diversity and abundance and through accumulation of metals in living organisms and food chain (Naser, 2013). Exposure to potentially harmful chemicals by humans can be through physical and 28 biological agents in air and food and water consumption. There is a completed pathway of exposure when there is contact at a boundary between a human and the environment which has a particular concentration of contaminant at a specified time (Griffin, 2009). Particular heavy metals cause acute toxic effects and cancer in animals, and this is due to DNA damage (Taylor and Little, 2014). Because heavy metals incline to bioaccumulate within tissues of organisms they are dangerous. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. It is argued that compounds are accumulated in living things whenever they are taken up and stored quicker than they are broken down (metabolized) or excreted (Griffin, 2009). Breathing heavy metal particles, even at levels well below

those considered toxic, can have serious health effects (Griffin, 2009). The immune system function related to all aspects of animal and human is compromised by the inhalation of heavy metal particulates. Moreover, it has been found that toxic metals are able to increase allergic reactions, cause genetic mutation, compete with "good" trace metals for biochemical bond sites, and act as antibiotics, killing both harmful and beneficial bacteria within human systems (Jacobson, 2002). A large amount of the damage caused by toxic metals stems from the increase of oxidative free radicals they cause (Jacobson, 2002). A free radical is an actively unstable particle, consisting of an unpaired electron which "steals" an electron from another particle to return it to its equilibrium. Naturally, free radicals result once cell particles respond with oxygen (oxidation). However, with a heavy toxic load or occurring antioxidant deficiencies, uncontrolled free-radical production happens. Unimpeded, free radicals can lead to damaging tissue all over the body; free-radical damage causes all degenerative diseases. Some heavy metals such as Cu, Zn and Fe are necessary in low concentrations for all living organisms, but most of them present toxicity hazard at high concentrations (Abdul Rida and Bouché, 1997). Additionally, toxic metals set up circumstances which cause irritation in arteries and tissues, which lead to drawing more calcium to the area as a buffer. The calcium covers the irritated areas in the blood vessels such as a bandage, patching up a problem but generating another, that is the solidifying of the artery walls and progressive impasse of the arteries. Moreover, without replacement of calcium, the stable removal of this significant mineral from the bones will create osteoporosis (loss of bone thickness causing brittle bones) (Davydova, 2005). All heavy metals are considered dangerous at higher levels (Freije, 2014). Lead, Cadmium, Copper, Chromium, Selenium and Mercury are mostly considered to be more toxic worldwide than the rest of the metals (de Mora, 2004). Long term exposure to lead can cause acute

or chronic damage to the nervous system in humans (Haddad, 2012). Cadmium exposure is associated with renal dysfunction. The primary indication of the renal lesion is frequently a tubular dysfunction, attested by an increased emission of low molecular weight proteins [such as β 2-microglobulin and α 1-microglobulin (protein HC)] or enzymes [such as N-Acetyl- β -D-glucosaminidase (NAG)]. It has been proposed that the tubular damage is reversible, but there is good evidence indicating that the cadmium damage to tubes is irreversible (Edwards *et al.*, 2001). Fumes or particles of the inhalation of cadmium can be life intimidating, and while severe pulmonary impacts and deaths are unusual, irregular instances still occur (de Mora, 2004). Animal experiments have suggested that cadmium may be a risk factor for cardiovascular disease, but studies of humans have not been able to confirm this (Edwards *et al.*, 2001). However, a Japanese study showed 30 cardiovascular failures in cadmium-exposed persons they were with signs of tubular kidney damage compared to individuals without kidney damage (Ueshima *et al.*, 2003). Increased exposure can cause disruptive lung disease and has been associated with lung cancer, and damage to the respiratory systems of human (Abdul Rida and Bouché, 1997). Children are mainly at risk of exposure as a result of increased gastrointestinal uptake and the porous blood–brain wall (Brito *et al.*, 2005). Both Copper and Mercury are known to cause damage to the human brain and central nervous system (Edwards *et al.*, 2001). Mercury is a toxic material and in human biochemistry has no known function. The route of exposure to mercury is food, fish being a major source of methyl mercury exposure. The public does not encounter an important health risk from methyl mercury, though specific groups with increased fish consumption could achieve blood levels linked to a low risk of neurological damage to adults. Because there is a risk to the foetus particularly, it is therefore important that pregnant women must stay away from a high intake of specific fish taken from

contaminated fresh waters (Edwards *et al.*, 2001). Copper is considered as a fundamental material to human life, however in increased doses it can cause anaemia, damage to the liver and kidney, and irritation to the stomach and intestines. Chromium is employed in metal alloys and colors for paints, paper, cement, rubber and other materials. Low-level exposure can cause irritation to the skin and ulceration. Long-term exposure can cause damage to the kidney and liver, as well as damaging circulatory and nerve tissue. Chromium frequently builds up in marine life, counting to the danger of consuming fish which might have been exposed to increased levels of chromium (Edwards *et al.*, 2001). It has been estimated that the lowest observable Cr effect limit in sea fish is 0.03 mg kg⁻¹ dry weight, while the limit in water concentrations for sea fish is 170- 400 mg l⁻¹ (Ayres and Hellier, 1998)

2.7 Accumulation of Metals in Plants and Plant Uptake Factor

In various literature plant uptake factor is also called enrichment ratio, enrichment coefficient, translocation coefficient, transfer factor, soil-plant transfer coefficient, accumulation factor, phyto-accumulation factor, biological adsorption coefficient, plant uptake factor, bio-concentration factor and uptake coefficient (Zgorelec, 2009; Kisic *et al.*, 2011). Currently, there are nine plant uptake factors (PUF). However, majority of the plant uptake literature focuses on the uptake of chemicals from sludge or bio-solids and only little literature has focused on the uptake from atmospheric deposition. The relationship between contaminant concentrations in soil and edible plant material is highly specific to the plant species. The relationship between contaminant concentration in edible produce and the concentration in soil is described using the plant uptake factor (PUF), which is defined as follows;

$$\text{PUF} = \frac{\text{Concentrations in edible portion of plant (mg/kg)}}{\text{Concentration in soil (mg/kg)}}$$

High accumulator plants EC between 1-10

Moderately accumulator plants EC between 0.1-1.0

Low accumulator plants EC between 0.01 – 0.1

Non accumulator plants EC < 0.01

Plants differ widely in their ability to accumulate heavy metals (Nouri *et al.*, 2009). Heavy metal contents of the soils and six desert plants distributed in the six Kuwait Governorate areas representing the residential, industrial and recreational sites were assessed and showed higher levels in the sequence of leaves>soil> shoot>root irrespective of the species and areas (BuOlayan and Thomas, 2009). Translocation Factor (TF) and Plant uptake Factor (PUF) in all the plants were >1, thus labeling the plants, especially *Chrozophora tinctoria*, as the main heavy metals accumulator and pollution indicator than all the other species. In another study of the pollution of soils with Pb, Cd, and Hg, and the transfer of these elements into the above-ground organs of four dominant herb species by Kuklova *et al.*, 2010, the concentrations of Pb (1.54-8.05 kg/mg d.m) and Cd (0.15-1.92 kg/mg-1 d.m), found in *Vaccinium myrtillus*, *Dryopteris dilatata*, *Luzula luzuloides*, and *Rubus idaeus* species were within the toxicity range. The transfer coefficients of Cd was substantially higher than 1 in the case of *D. dilatata*, *R. idaeus* and *L. luzuloides* species. Nazir *et al.*, 2011 reported higher levels of all the metals studied (Cu, Pb, Zn) in the shoots than in the roots in more than 50% (24 plant species) of the 43 plant species investigated. These plant species which include *Amaranthus viridis L.*, *Alternanthera pungens Kunth.*, *Achyranthes aspera L.*, *Brachiariareptans (L.) Gardner and Hubb.*, *Cenchrus pennisetiformis Hochst.* and *Steud.ex Steud.*, *Cannabis sativa L.*, *Cynodon dactylon (L.) Pers.*, *Chenopodium 48 album L.*, *Cyperus rotundus L.*, *Dactyloctenium aegypticum L.*, *Eclipta alba (L.) Hassk.*,

Eleusine indica (L.) Gaertn., *Erigeron conyzanthus* L., *Ipomoea hederacea* Jacq., *Malvastrum coromandelianum*(L.) Garcke, *Parthenium hysterophorus* L., *Portulaca oleracea* L., *Persicaria barbata* (L.) Hara, *Rumex nepalensis* Spreng., *Ricinus communis* L., *Sorghum halepense* (L.) Pers., *Solanum nigrum* L. and *Xanthium strumarium* L. may be useful for phyto-stabilization since they could tolerate and accumulate heavy metals.

The trend in the bioaccumulation for metals in *E. indica* was in the following sequence: Zn>Cu>Pb>Mn>Cd>Cr (Abdallah *et al.*, 2012). However, the results indicated low bioaccumulation of metals by *E. indica*. Abdallah *et al.*, 2012, therefore, remarks that further dumping of toxic waste could lead to toxicity to man through the food chain.

2.8 Principal Pathways of Chemical Uptake and Accumulation in Plants

There are three principal uptake pathways of chemicals in plants. These pathways include passive and active uptake through the root system, gaseous and particulate deposition to aboveground shoots, and direct contact between soil and plant tissues.

2.9 Soil-root interactions

In general, plant roots are the most important site for uptake of chemicals from soil (Bell, 1992). Root systems take up organic chemicals from both water and air, which involve passive and diffusive transport, with chemicals carried into the plant during the natural transpiration cycle. Although chemical properties are important predictors of uptake potential, the 50 physiologies and composition of the plant root itself is also a significant influence (Collins *et al.*, 2006). Chemical transfers from the soil into the root are primarily mediated by the uptake of soil pore-water during plant transpiration. Therefore, the factors that influence the chemical concentration in porewater also exert control over the passive uptake process. In principle, as the organic matter content of a

soil increases (typically measured using the weight fraction of organic carbon present), so the proportion of the chemical in the porewater decreases. As the weight fraction of soil organic carbon increases, so the total amount of chemical taken up by the root decreases. Several models use the fraction of organic carbon as a key variable in the prediction of the uptake of contaminants by plants.

2.10 Particulate deposition on plant surfaces

Organic chemicals bound to soil particles may be deposited on above-ground leaves and shoots as a result of wind resuspension or rain splash, and is a well-recognised phenomenon for metals and radionuclides (Smith and Jones, 2000; Thorne *et al.*, 2004). Dry deposition of suspended particles with subsequent permeation into the cuticle represents the major pathway of contamination. Wet deposition is the process of gravitational coagulation of solid particles with water droplets. Relatively little information is available on the wet deposition of particle bound and gaseous phase organic chemicals to plant surfaces, and this pathway is seldom considered when looking at the contamination of vegetation (Smith and Jones, 2000). Dry deposition of particles to plant surfaces involves diffusion, interception, impaction and sedimentation processes (Chamberlain, 1991). Once particles have been deposited on plant foliage they are subject to removal and degradation. Above-ground plant parts may become contaminated with organic chemicals via pathways involving direct contact between soil particles and plant surfaces, and chemicals retained on plant surfaces may subsequently be taken up into or through the plant cuticle (Riederer, 1995). Small particle-bound compounds may be taken up via the stomata, but the stomatal entry route will generally only be significant for chemicals present in air in the gaseous phase (Smith and Jones, 2000). The most likely transfer pathway is through physical contact between the particle and the waxy leaf surface, where chemical transfer occurs via diffusion. Organic

chemicals entering the plant cuticle become adsorbed to lipophilic tissues or permeate into the leaf interior (Riederer, 1995). There is currently insufficient understanding of this process and in particular, of how the physicochemical properties of organic compounds influence transfer from particles into the leaf.

2.11 Influence of Plant Species on Uptake of Chemicals

Plant uptake varies considerably between types of plant and individual species (Bell, 1992) and are influenced by certain factors like root growth and depth, transpiration rate, active uptake mechanisms, growth period, location of fruits and tubers, and the size and shape of leafy foliage (Buckley, 1982). Several researchers have also found that the exposed surface area of the plant foliage influence the foliar uptake rate for a variety of species (McCrary and Maggard, 1993; Schreiber and Schönherr, 1992). Plant characteristics that affect the rate of particle deposition and retention include the exposed surface area of the foliage and the presence or absence of leaf hairs. Little and Wiffen (1977) observed that rough or hairy leaf surfaces were more efficient at collecting aerosols than smooth surfaces, explained by the increased surface area and projection of roughness elements through the leaf-air boundary layer. Leaf loss and senescence can lead to the transfer of chemicals from plant foliage to the surrounding soil, thus reducing the chemical concentration in foliage. However, edible plant parts are likely to be harvested before leaf loss and senescence become significant chemical transport pathways. For deposition during the growth stage of agricultural plants, the parameters associated with contamination by foliar absorption are relatively influential in long-term contamination as well as short-term contamination (Reeds, 2003). However, in most cases with active deposition occurring, the foliar interception pathway is usually dominant over the root uptake pathway (Reeds, 2003). 54 2.12.2 Growth dilution Plant growth have been recognized as an important variable in the plant uptake

of radionuclides by root uptake and aerial deposition (Thorne *et al.*, 2004). Over the growing season the biomass of plant increases, diluting the chemical concentration within plant tissues relative to the flux of chemical uptake, and increasing the aboveground canopy for interception of aerial deposition. The importance of growth dilution has been recognised in several dynamic plant uptake models (Samsøe-Petersen *et al.*, 2003; Trapp and Matthies, 1995; Hung and Mackay, 1997). Collins and Finnegan (in preparation) noted the importance of growth dilution in predicting foliar uptake of organic chemicals. Using growth dilution, the Trapp and Matthies (1995) model predicted a plateau region in uptake above octanol-air partition coefficients of greater than seven, in the region predicted by McLachlan (1999) to be kinetically limited.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 Area of Study

This study was carried out at Savannah Sugar Company Limited, Numan, Adamawa State (North-Eastern part of Nigeria) located at latitude 9°35'N and longitude 11°54'E. Situated at elevation 158 meters above sea level, as at 2006 Census, it had a population of 91,549 making it 4th largest city in Adamawa State (NPC, 2006). The major activity of the people within the area is farming. The climate of Numan is classified as tropical with much rainfall in the summer than in the winter, this constitute the average annual rainfall of 921 mm. The average annual temperature is 27.8 °C. (<https://en.climate-data.org/africa/nigeria/adamawa/numan-373406/>)

3.1.2 Consumables materials

Sugarcane (juice and leaves), soils, water and fumes

3.1.3 Non-consumables materials

Masking tape, a marker, polythene bags, a plastic spoon, a ruler, GPS device, a tape, a plier, filter papers, sample bottles and conical flasks.

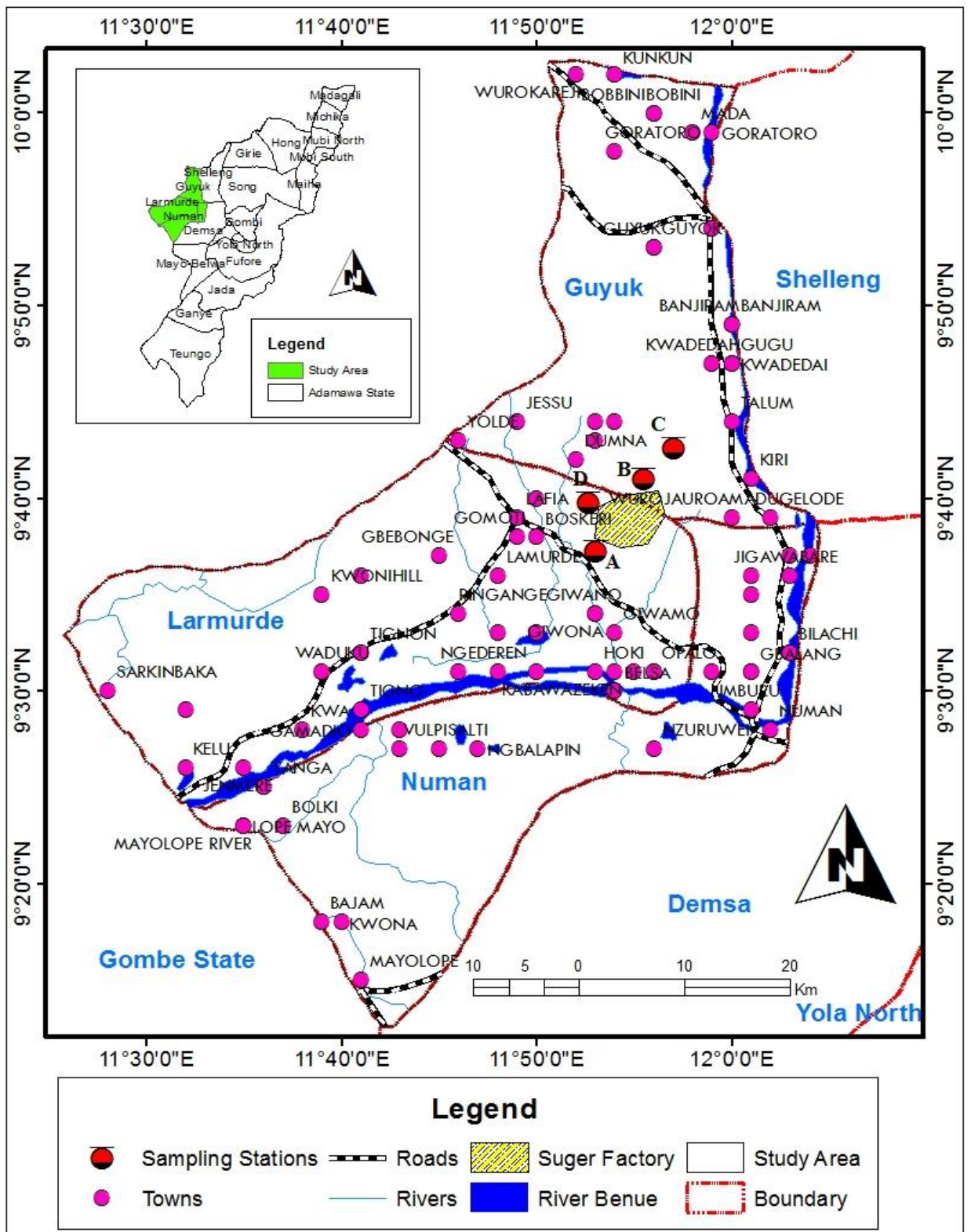


Figure:1 Map of Adamawa state showing sampling locations at Savannah sugar company limited.

Source: Modified From Administrative Map of Adamawa State.

3.2 Methodology

3.2.1 Experimental design

At harvest period, soils and plant materials (stems and leaves) were collected in a transect manner from 4 sample locations in a distance of 0, 20, 40, 60, 80 and 100 meters respectively from the edge of each of the selected block within the Company namely location A (Gyewana Block 2), location B (Kem block 1), location C (Kem Block 2-09) and Location D (Gyewana Block 2-08). Coordinates were taken for each sample location using a GPS device. Water and fumes samples were also collected from the water source (Dam) and fumes released from the factory pipes.

Table 3.1: Location and coordinates of the sample locations

| Location | Coordinate |
|---------------------|--------------------------------------|
| A (Gyewana block 2) | Latitude 09°34' and Longitude 11°54' |
| B (Kem 1) | Latitude 09°36' and Longitude 11°56' |
| C (Kem 2) | Latitude 09°36' and Longitude 11°55' |
| D (Gyewana 2-08) | Latitude 09°34' and Longitude 11°55' |

3.2.2 Samples collection

Soil and sugarcane samples were collected at the same point from the four sample locations.

3.2.3 Soil collection

A total of 24 samples were collected from 4 sample locations; 6 samples from each of the locations in a depth of 0-10 cm from a distance of 0, 20, 40, 60, 80 and 100 m respectively using a clean plastic spoon and was immediately transferred into a labeled polythene bags and was brought to Department of Botany (Postgraduate Laboratory), ABU Zaria for sample preparations.

3.2.4 Sugarcane collection

A total of 48 plant samples (stems and leaves) were collected from 4 sample locations; 6 samples of stems and leaves from each of the locations in a distance of 0, 20, 40, 60, 80 and 100 m respectively. The stems of sugarcane were cut from the base with the aid of an axe and was further cut into pieces, put into a polythene bags and was brought to Department of Botany (Postgraduate Laboratory), ABU Zaria for sample preparations.

3.2.5 Water and fumes collection

A sample of water was collected into a sample bottle from the reservoir and fumes were trapped with aid of Safety Department, Savannah Sugar Company, Numan, from the factory pipes by placing polythene bags where the fumes are being emitted and was equally taken to laboratory for preparation.

3.3 Samples Preparation

3.3.1 Soil samples preparation

Soil samples from each sampling location were spread in plastic trays and air dried to constant weight and passed through a 2mm sieve to remove coarse particles. The sieved soils were placed in polythene bags prior to analysis Nuonomet *al.*, (2000). Physical and chemical properties (soil pH, soil conductivity, total dissolved solid and textural class) and heavy metals (zinc, cadmium, chromium and lead) were analysed in the soil samples using Micro-wave Plasma Atomic Emission Spectrophotometer (MP-AES).

3.3.2 Plant samples preparation

Plant samples were properly washed with deionized water and were rinsed with distilled water to remove any attached soil particles. Small portions of leaves were used for easy grinding to powder form. The leaves were placed in a labeled envelope and were oven dried at 70⁰C for 48 hours. The dried leaves samples were grounded into fine particles using mortar and pestle (Nuonomet *al.*, 2000). The sugarcane juice from the stem was extracted by crushing the stalk in hydraulic press as described by Solomon, (2012).

3.3.3 Water and fumes preparation

Water sample was measured into a 250 ml conical flask in a volume of 50ml while fumes were weighed into a beaker in 2 g for digestion.

3.4 Determination of Physical and Chemical Parameters

3.4.1 Concentration of hydrogen ion (soil pH):

This was determined using the method of Black *et al.* (1965). Dried soil (20.00 g) was weighed into a 100.00ml beaker, distilled water (40.00 ml) was added into the beaker, the mixture was then stirred with a glass rod and allowed to stand for 30 minutes. A pre

calibrated, HANNA pH meter (model H1991000) was inserted into the beaker and the pH value was recorded.

3.4.2 Electrical Conductivity and Total Dissolved Solid (Soil):

These were determined with the digital HANNA instrument (model H1991000) using the same soil sample that was used in determination pH value.

3.4.3 Analysis of Soil Particle-Size Distribution

The dry samples were dispersed in water and 10% calgon solution in a volume dispersing cup and filled up to mark with distilled water. The suspension was vigorously stirred, quantitatively transferred to the sedimentation cylinder and filled up to mark with distilled water. Three drops of amyl alcohol was added to the suspension to remove froth, a hydrometer was gently placed into the column and hydrometer readings were taken at 40 seconds to measure silt and clay, and after 2 hours for clay in the suspension (Bouyoucos, 1962).

3.5 Digestion of Samples

3.5.1 Digestion and analysis of soil samples

Soil samples collected were digested for heavy metal analysis using the method described by Ogunfowokan *et al.* (2009). Each sample (1g) was digested in volumetric flask with 30 ml aqua-regia (HNO_3 ; HCl, 3:1) on hot-plate at 150°C for 40 minutes. The volumetric flask with its content was removed from the hot-plate to cool off. Hydrofluoric acid (5 ml) was added and heated further for 15 min. The volumetric flask with its content was allowed to cool down to room temperature and then filtered. The filtrate was quantitatively transferred into 50ml volumetric flask and made up to mark with distilled-deionized water. Zinc, cadmium, lead and chromium concentrations were determined using Microwave Plasma-Atomic Emission Spectrophotometer in the multi-user laboratory, Department of Chemistry, Ahmadu Bello University, Zaria.

3.5.2 Digestion and analysis of sugarcane samples

Leaves samples were digested according to method described by Erwin and Ivo (1992). Dried powdered plant samples (0.5g) was weighed into 100ml beaker, a mixture of 5ml concentrated HNO_3 (Nitric acid) and 2ml HClO_4 (Perchloric acid) was added and digested at low heat using hot plate until the content was reduced to about 2ml. The digest was allowed to cool and then filtered into 50ml standard flask. The beaker was rinsed with small portions of distilled-deionized water and then filtered into the flask.

The nitric acid digestion procedure for water (American Public Health Association 1992) was used for the wet-acid digestion of the sugarcane juice. The sugarcane stems were cut at two nodal intervals, washed, rinsed with distilled deionized water, peeled and cut into small pieces with a stainless steel knife. The specimens were subsequently crushed with a stainless steel plier. The juice was filtered by pressing it through a filter paper; 20ml of the sugarcane juice extract were introduced into a 250mL pyrexconical flask and 20ml of concentrated nitric acid added. The mixture was allowed to slowly evaporate on a hot plate until precipitation occurred. 5ml of Nitric acid were then added slowly until the solution turned clear and digestion complete. Thereafter 1ml of 30% hydrogen peroxide was added to the flask, swirled and reheated for 10 min. When the solution remained clear upon cooling, 25ml of deionized distilled water were added, and the solution boiled again. After further cooling, the contents were quantitatively transferred to a 25ml volumetric flask and made to volume of 50ml. After settling for another 5 hours, the contents were transferred to labeled plastic bottles. The concentrations of Zinc, Cadmium, Lead and Chromium were determined using MP-AES.

3.5.3 Digestion and analysis of water and fumes samples

Water sample was digested by measuring 50ml of water into a conical flask with 20ml of nitric acid added and heated for 15 minutes. On cooling 5 ml of 30% hydrogen peroxide was added and further heated for 5 minutes and was transferred into 50ml sample bottles after filtration for metals analysis.

Fumes sample (2g) was digested in volumetric flask with 30 ml aqua-regia (HNO₃ : HCl, 3:1) on hot-plate at 150 °C for 40 minutes, afterward it was allowed to cool, then, 5 ml HF (Hydrofluoric acid) was added and heated further for 10 min. The volumetric flask with content was allowed to cool down to room temperature and filtered. The filtrate was quantitatively transferred into 50ml sample bottles and made up to mark with distilled-deionized water. Zinc, cadmium, lead and chromium concentrations were determined using Microwave Plasma-Atomic Emission Spectrophotometer.

3.6 Estimation of Transfer Factor

Transfer factor is the parameter that describes the bioavailability of metals at a specific part of a plant (Tsafe *et al.*, 2012). It is the ratio of the concentration of the metal in the edible part and the total metal concentration in the soil (Gebrekidan *et al.*, 2013). It is the relative tendency of a particular species of plant to accumulate heavy metal. Thus soil-to-plant transfer factors were used to evaluate the efficiency of the plant in absorbing heavy metal from the soil. Transfer factors were obtained by dividing the amount of an element in the plant with the corresponding amount in the soil.

(TF) was calculated as follows:

$$TF = C_{\text{sugarcane juice}} / C_{\text{Soil}}$$

Where $C_{sugarcane\ juice}$ and C_{soil} represents metal concentration in extracts of sugarcane juice and soils, respectively.

This was computed to surmise the extent of transfer of soil metals into the plant edible part.

3.7 Determination of Sucrose Content of Sugarcane Juice

The grand total of sucrose content of sugarcane juice was determined using refractometer. The sugarcane juice was gotten after crushing the sugarcane stem in a hydraulic press, two drops of juice were placed on the prism of the refractometer with kirkhouse house (pipette) and the sucrose levels were determined in percentages as described by Sonal *et al.*, (2017).

3.7 Data Analyses

The data obtained were subjected to;

- One-way Analysis of variance (ANOVA) was used to check the significant difference between heavy metals in soil and plant with respect to distance and location.
- Duncan Multiple Range Test ($p \leq 0.05$) was used to separate the means where there was significant difference.
- Pearson correlation was used to determine the relationship between the heavy metals in sugarcane juice and the sucrose content of the juice.
- T-test was used to compare the concentration of heavy metal in water and fumes.
- Using SPSS version 20 software package.

CHAPTER FOUR

4.0 RESULTS

4.1 Heavy Metals Concentrations in the Soils

Concentrations of Zn, Cd, Pb and Cr in the four sample locations are given in Tables 4.2, 4.3, 4.4 and 4.5.

There was highly significant difference ($p \leq 0.05$) between each element in respect to distance while in respect to concentration, Zn recorded the lowest (1.10 mg/kg) at 40 and 60 m while at 0 m it was recorded highest (1.90 mg/kg), Cd was found to be lowest with 0.03 mg/kg at 20 and 40 m while the highest concentration of 0.70 mg/kg was found at 100 m, Pb concentration was recorded lowest (9.40 mg/kg) and highest (15.20 mg/kg) at 100 m and 0 m respectively, and at 80 m the concentration of Cr was recorded the least (7.20 mg/kg) while at 20 m the highest (28.00 mg/kg) was recorded in (Table 4.2).

Table 3 indicates highly significant difference ($p \leq 0.05$) in respect to distance in all the elements except Pb where there was no significant difference ($p \geq 0.05$) in elements' interval according to distance in the location. In this location, the highest concentration of Zn (3.20 mg/kg) was recorded in 40 m while the least concentration (1.50 mg/kg) was found at 60 m, Cd recorded the least concentration of 0.00 mg/kg at 60, 80 and 100 m while 0.40 mg/kg was recorded as the highest at 0 m, Pb was highest (37.10 mg/kg) but not significant at 0 m while 6.20 mg/kg was recorded the lowest at 20 m, and Cr concentration was recorded highest (66.70 mg/kg) at 100 m while the least (12.00 mg/kg) at 60 m.

The Zn concentration (4.40 mg/kg) was significantly highest at 0 m compared to the other distances while Cd (0.40 mg/kg), Pb (19.20 mg/kg) and Cr (121.00 mg/kg) were all significantly highest at 20 m. Cd (0.30 mg/kg) was significantly lowest at 20, 60 and

80 m, while Pb (12.80 mg/kg) and Cr (28 mg/kg) were significantly lowest at 0 m (Table 4.4).

There was highly significant difference in respect to distance in all the elements except Pb where there was no significant difference in elements' interval referring to distance. The concentrations of Zn (3.90 mg/kg) was highest at 100 m while it was lowest (0.10 mg/kg) at 80 m, Cd recorded 1 mg/kg as the highest concentration at 40 m while at 20 m the concentration of 0.10 mg/kg was observed the lowest, 26.10 mg/kg of Pb was found to be highest at 80 m while 15.23 mg/kg at 40 m was found to be lowest, and Cr concentrations was found to be highest (64.4 mg/kg) at 40 m while at 60 m the concentration was observed lowest with 12 mg/kg (Table 4.5).

Table 4.2: Heavy metals concentrations of G2 Soil

| Heavy metals concentration (mg/kg) | | | | |
|------------------------------------|------------------------------------|------------------------|-------------------------|-------------------------|
| Distance (m) | Zn | Cd | Pb | Cr |
| 0 | 1.90±0.02 ^a | 0.40±0.03 ^b | 15.20±0.04 ^a | 27.00±0.05 ^b |
| 20 | 1.80±0.04 ^{a^b} | 0.03±0.01 ^d | 10.00±0.06 ^d | 28.00±0.06 ^a |
| 40 | 1.10±0.05 ^d | 0.03±0.02 ^d | 9.90±0.03 ^d | 8.10±0.06 ^d |
| 60 | 1.10±0.06 ^d | 0.30±0.04 ^c | 12.90±0.05 ^b | 8.10±0.05 ^d |
| 80 | 1.70±0.06 ^b | 0.20±0.05 ^c | 11.50±0.08 ^c | 7.20±0.04 ^e |
| 100 | 1.40±0.05 ^c | 0.70±0.06 ^a | 9.40±0.06 ^e | 25.00±0.06 ^c |
| P-value | 0.000 | 0.000 | 0.000 | 0.000 |

Means with the same superscript per column did not differ significantly ($P>0.05$), using DMRT. ND=Not detected. NA=not analysed. *=significant at $P\leq 0.005$. **=highly significant at $P\leq 0.001$

Table 4.3: Heavy metals concentrations of K1 Soil

| Heavy metals concentration (mg/kg) | | | | |
|------------------------------------|------------------------|------------------------|--------------------------|-------------------------|
| Distance (m) | Zn | Cd | Pb | Cr |
| 0 | 3.10±0.05 ^a | 0.40±0.04 ^a | 37.10±27.95 ^a | 35.00±0.06 ^a |
| 20 | 2.70±0.06 ^b | 0.20±0.01 ^b | 6.20±0.05 ^a | 21.50±0.04 ^f |
| 40 | 3.20±0.04 ^a | 0.03±0.01 ^c | 8.30±0.08 ^a | 30.80±0.06 ^c |
| 60 | 1.50±0.02 ^d | 0.00±0.00 ^c | 9.30±0.06 ^a | 42.50±0.09 ^c |
| 80 | 1.90±0.03 ^c | 0.00±0.00 ^c | 7.70±0.04 ^a | 52.70±0.13 ^b |
| 100 | 1.80±0.05 ^c | 0.00±0.00 ^c | 8.90±0.03 ^a | 66.70±0.09 ^a |
| P-value | 0.000** | 0.000** | 0.416 | 0.000** |

Means with the same superscript per column did not differ significantly (P>0.05), using DMRT. ND=Not detected. NA=not analysed. *=significant at P≤0.005. **=highly significant at P≤0.001

Table 4.4: Heavy metal concentrations of K2 Soil

| Heavy metals concentration(mg/kg) | | | | |
|-----------------------------------|------------------------|------------------------------------|-------------------------|--------------------------|
| Distance (m) | Zn | Cd | Pb | Cr |
| 0 | 4.40±0.03 ^a | 0.30±0.4 ^{ab} | 12.80±0.05 ^c | 28.90±0.05 ^e |
| 20 | 0.30±0.01 ^c | 0.40±0.01 ^a | 19.20±0.06 ^a | 121.00±0.06 ^a |
| 40 | 1.10±0.06 ^b | 0.20±0.05 ^b | 14.40±0.08 ^d | 37.60±0.06 ^b |
| 60 | 0.30±0.02 ^c | 0.30±0.06 ^{a^b} | 15.30±0.09 ^c | 36.30±0.07 ^c |
| 80 | 0.30±0.01 ^c | 0.30±0.01 ^{a^b} | 15.30±0.06 ^c | 33.03±0.08 ^d |
| 100 | 1.10±0.05 ^b | 0.20±0.06 ^b | 16.17±0.28 ^b | 36.40±0.04 ^c |
| P-value | 0.000** | 0.209 | 0.000** | 0.000** |

Means with the same superscript per column did not differ significantly ($P>0.05$), using DMRT. ND=Not detected. NA=not analysed. *=significant at $P\leq 0.005$. **=highly significant at $P\leq 0.001$

Table 4.5: Heavy metal concentrations of G2-08 Soil

| Heavy metals concentration(mg/kg) | | | | |
|-----------------------------------|------------------------|------------------------------------|--------------------------|-------------------------|
| Distance (m) | Zn | Cd | Pb | Cr |
| 0 | 0.80±0.04 ^c | 0.30±0.06 ^b | 17.60±0.06 ^a | 28.00±0.10 ^b |
| 20 | 0.20±0.06 ^e | 0.10±0.00 ^{c^d} | 23.20±1.01 ^a | 64.40±0.06 ^a |
| 40 | 2.20±0.03 ^b | 1.00±0.08 ^a | 15.23±10.61 ^a | 24.70±0.09 ^d |
| 60 | 0.60±0.05 ^d | 0.20±0.03 ^{bc} | 24.20±0.04 ^a | 12.00±0.04 ^e |
| 80 | 0.10±0.00 ^e | 0.00±0.00 ^d | 26.10±0.08 ^a | 25.20±0.28 ^c |
| 100 | 3.90±0.06 ^a | 0.30±0.05 ^b | 23.30±0.03 ^a | 24.70±0.07 ^d |
| P-value | 0.000** | 0.000** | 0.486 | 0.000** |

Means with the same superscript per column did not differ significantly ($P>0.05$), using DMRT. ND=Not detected. NA=not analysed. *=significant at $P\leq 0.005$. **=highly significant at $P\leq 0.001$

4.2 Heavy Metals concentrations in Sugarcane Juice and Leaves in all locations

The concentrations of heavy metals in sugarcane (juice and leaves) are given in tables below.

Table 4.6 indicates high concentrations of heavy metals in leaves compared to juice. Leaves recorded high concentrations of Zn and Pb at 0 m while Cr at 20 m, Cd was below the detectable limit in juice while it was detected at 80 and 100 m in leaves.

In location B, the concentration of Zn was higher at 0 m in juice than in the leaves but at the subsequent distance the concentrations were higher in the leaves, Cd was below the detectable limit in both the juice and leaves while leaves recorded the highest concentrations of Pb and Cr at 80 m which were higher compared to those concentrations in the juice (Table 4.7).

Table 4.8 shows the concentration of heavy metals between juice and leaves of sugarcane. The concentrations of Zn and Cr were higher in leaves compared to the juice concentrations across all distance, Cd was not detected or it was below detectable limit while Pd was observed to be higher in leaves than in juice across all distance except at 60 and 100 m where it higher.

The highest concentration of Zn and Cr were observed at 0 m in leaves which were also higher than the concentrations that was recorded in juice while at 20 and 100 m the concentrations of Zn were higher in juice compared to leaves. Cd was only detected at 60, 80 and 100 m though distance were not significantly different ($p > 0.005$) and Pb was observed higher in leaves compared to juice across all distances (Table 4.9).

Table 4.6: Heavy metals concentrations in sugarcane juice and leaves in location A

| Heavy metals concentrations (mg/kg) | | | | | | | | |
|-------------------------------------|---------------------|---------------------|-------|-------------------|---------------------|---------------------|---------------------|---------------------|
| Distance (m) | Zn | | Cd | | Pb | | Cr | |
| | Juice | Leaves | Juice | Leaves | Juice | Leaves | Juice | Leaves |
| 0 | 0.90 ^{cd} | 2.80 ^a | ND | ND | 6.80 ^{ab} | 11.10 ^a | 5.50 ^c | 10.60 ^c |
| 20 | 1.73 ^a | 2.10 ^b | ND | ND | 6.90 ^a | 7.90 ^d | 14.60 ^a | 27.40 ^a |
| 40 | 1.20 ^b | 1.67 ^c | ND | ND | 6.00 ^c | 6.80 ^e | 4.90 ^d | 8.10 ^d |
| 60 | 0.70 ^{cd} | 1.10 ^e | ND | ND | 4.70 ^e | 9.50 ^b | 6.90 ^b | 8.10 ^d |
| 80 | 0.50 ^d | 1.40 ^d | ND | 0.33 ^a | 6.60 ^b | 9.60 ^b | 4.20 ^e | 7.20 ^e |
| 100 | 1.10 ^{bc} | 1.50 ^c | ND | 0.40 ^a | 5.40 ^d | 8.40 ^c | 2.47 ^f | 25.00 ^b |
| P-value | 0.001 ^{**} | 0.000 ^{**} | NA | 0.168 | 0.000 ^{**} | 0.000 ^{**} | 0.000 ^{**} | 0.000 ^{**} |

Means with the same superscript per column did not differ significantly ($P>0.05$), using DMRT. ND=Not detected. NA=not analysed. *=significant at $P\leq 0.005$. **=highly significant at $P\leq 0.001$

Table 4.7: Heavy metals concentrations in sugarcane juice and leaves in location B

| Heavy metals concentrations (mg/kg) | | | | | | | | |
|-------------------------------------|-------------------|-------------------|-------|--------|-------------------|--------------------|-------------------|--------------------|
| Distance(m) | Zn | | Cd | | Pb | | Cr | |
| | Juice | Leaves | Juice | Leaves | Juice | Leaves | Juice | Leaves |
| 0 | 2.10 ^a | 1.90 ^b | ND | ND | 3.50 ^b | 4.00± ^e | 0.60 ^f | 15.30 ^b |
| 20 | 1.70 ^b | 1.70 ^b | ND | ND | 3.70 ^b | 5.90 ^b | 3.50 ^e | 3.40 ^e |
| 40 | 0.60 ^c | 1.80 ^b | ND | ND | 3.20 ^c | 3.70 ^f | 5.90 ^d | 3.40 ^e |
| 60 | 0.00 ^d | 2.50 ^a | ND | ND | 4.30 ^a | 5.60 ^c | 7.90 ^a | 3.80 ^d |
| 80 | 0.00 ^d | 1.40 ^c | ND | ND | 4.30 ^a | 6.20 ^a | 6.10 ^c | 23.50 ^a |
| 100 | 1.70 ^b | 1.20 ^c | ND | ND | 4.50 ^a | 4.90 ^d | 7.20 ^b | 13.10 ^c |
| P-value | 0.000** | 0.000** | NA | NA | 0.000** | 0.000** | 0.000** | 0.000** |

Means with the same superscript per column did not differ significantly ($P>0.05$), using DMRT. ND=Not detected. NA=not analysed. *=significant at $P\leq 0.005$. **=highly significant at $P\leq 0.001$

Table 4.8: Heavy metal concentrations in sugarcane juice and leaves at location C

| Heavy metals concentrations (mg/kg) | | | | | | | | |
|-------------------------------------|-------------------|-------------------|-------|--------|--------------------|-------------------|--------------------|--------------------|
| Distance (m) | Zn | | Cd | | Pb | | Cr | |
| | Juice | Leaves | Juice | Leaves | Juice | Leaves | Juice | Leaves |
| 0 | 0.50 ^a | 3.20 ^c | ND | ND | 4.95 ^d | 9.60 ^a | 6.55 ^d | 12.80 ^e |
| 20 | 0.00 ^c | 4.20 ^a | ND | ND | 5.70 ^c | 9.50 ^a | 12.65 ^b | 76.70 ^c |
| 40 | 0.00 ^c | 2.70 ^d | ND | ND | 5.65 ^c | 7.70 ^b | 33.00 ^a | 12.90 ^e |
| 60 | 0.30 ^b | 3.80 ^b | ND | ND | 6.30 ^b | 4.40 ^d | 11.0 ^c | 87.20 ^b |
| 80 | 0.55 ^a | 2.30 ^e | ND | ND | 6.40 ^b | 7.60 ^b | 0.50 ^f | 95.00 ^b |
| 100 | 0.00 ^c | 2.10 ^f | ND | ND | 16.40 ^a | 6.80 ^c | 1.30 ^e | 19.60 ^d |
| P-value | 0.000** | 0.000** | NA | NA | 0.000** | 0.000** | 0.000** | 0.000** |

Means with the same superscript per column did not differ significantly ($P>0.05$), using DMRT. ND=Not detected. NA=not analysed. *=significant at $P\leq 0.005$. **=highly significant at $P\leq 0.001$

Table 4.9: Heavy metals concentrations of sugarcane juice and leaves in location D

| Heavy metals concentration (mg/kg) | | | | | | | | |
|------------------------------------|-------------------|-------------------|-------------------|-----------|-------------------|--------------------|--------------------|--------------------|
| Distance (m) | Zn | | Cd | | Pb | | Cr | |
| | Juice | Leaves | Juice | Leaves | Juice | Leaves | Juice | Leaves |
| 0 | 1.20 ^e | 4.30 ^a | ND | ND | 7.90 ^a | 16.00 ^a | 25.70 ^c | 53.33 ^b |
| 20 | 3.60 ^b | 2.70 ^b | ND | ND | 6.80 ^b | 14.30 ^d | 35.50 ^a | 27.98 ^d |
| 40 | 1.35 ^d | 4.20 ^a | ND | ND | 5.85 ^d | 13.50 ^f | 7.90 ^d | 44.90 ^c |
| 60 | 1.05 ^f | 2.30 ^c | 0.03 ^a | ND | 6.50 ^c | 14.60 ^c | 32.00 ^b | 29.00 ^d |
| 80 | 2.30 ^c | 2.40 ^c | 0.00 ^a | ND | 5.57 ^e | 15.20 ^b | 7.30 ^e | 27.50 ^a |
| 100 | 5.80 ^a | 1.80 ^d | 0.03 ^a | ND | 5.10 ^f | 13.90 ^e | 4.70 ^f | 43.83 ^c |
| P-value | 0.000 | 0.000 | 0.571 | NA | 0.000 | 0.000 | 0.000 | 0.000 |

Means with the same superscript per column did not differ significantly ($P>0.05$), using DMRT. ND=Not detected. NA=not analysed. *=significant at $P\leq 0.005$. **=highly significant at $P\leq 0.001$

4.3 Average Heavy Metal Concentrations of Different Location for Juice, Leaves and Soil

Figure 2 shows the average concentration of Zn, Cd, Pb and Cr in Gyewana 2 (location A). However, the concentrations of Cd, Pb and Cr was observed higher in soil compared to juice and leaves while the concentration Zn was observed higher in leaves than in the juice and soil, and there was no co concentration of Cd shown in the juice.

In this location (Kem 1), soil recorded the highest average concentrations among all the metals while juice shown high concentration of Pb compared to leaves (Figure 3)

Figure 4 shows the average concentrations of Zn, Cd, Pb and Cr in Kem 2 (location C). The concentrations of Zn and Cr was observed higher in leaves compared to juice and soil while Cd and Pb were recorded higher in soil than were recorded in juice and leaves. However, it was also observed that Cd was not recorded in juice and leaves in this location.

Zn and Cr were found to have high concentrations in leaves than in juice and soil while Cd and Pb were observed high in soil than in juice and leaves, though, Cd was only shown in soil (figure 4).

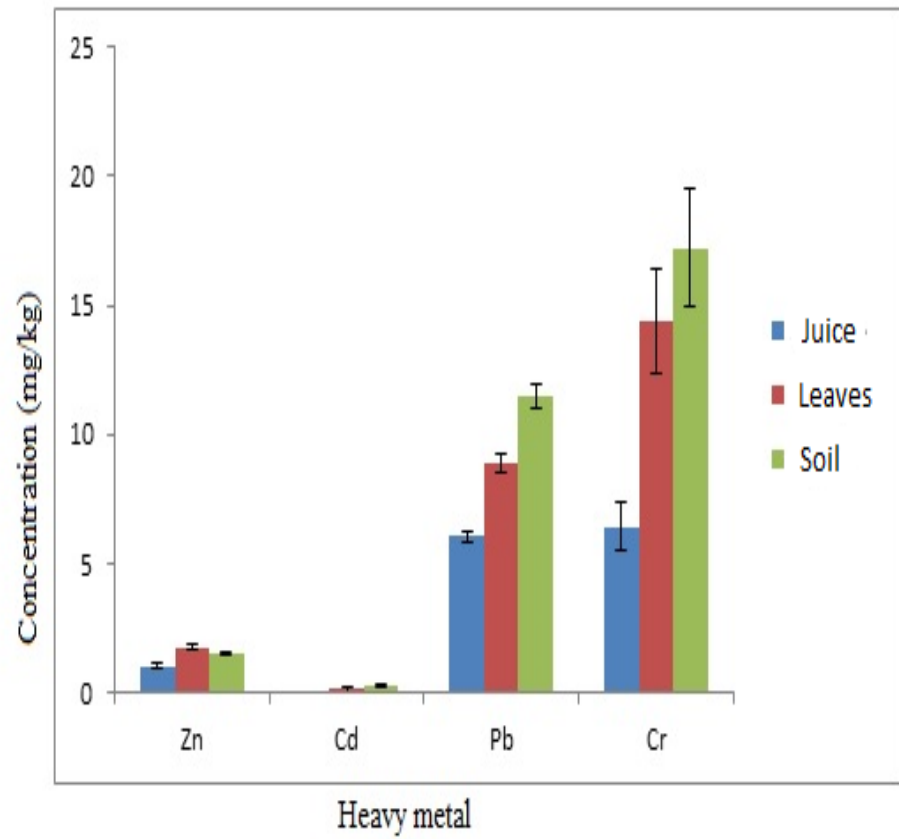


Figure 2: Average concentrations of heavy metal in location A for juice, leaves and soil

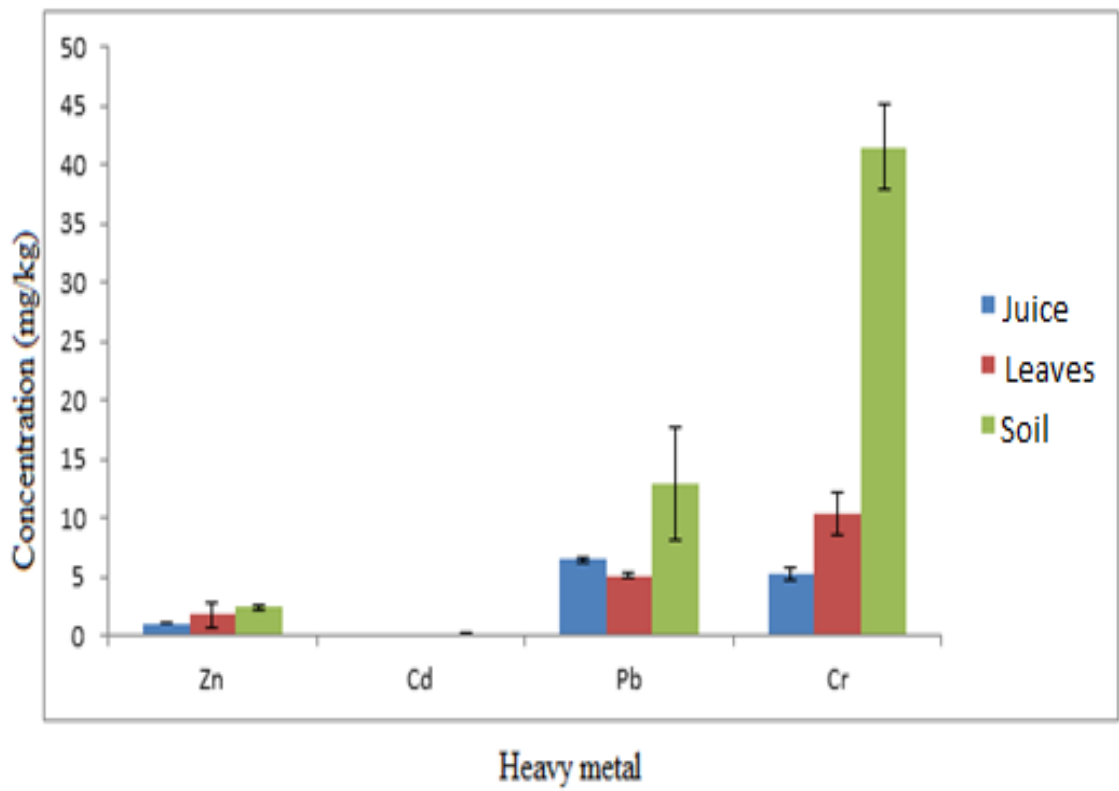


Figure 3: Average concentrations of heavy metal in location B for juice, leaves and soil

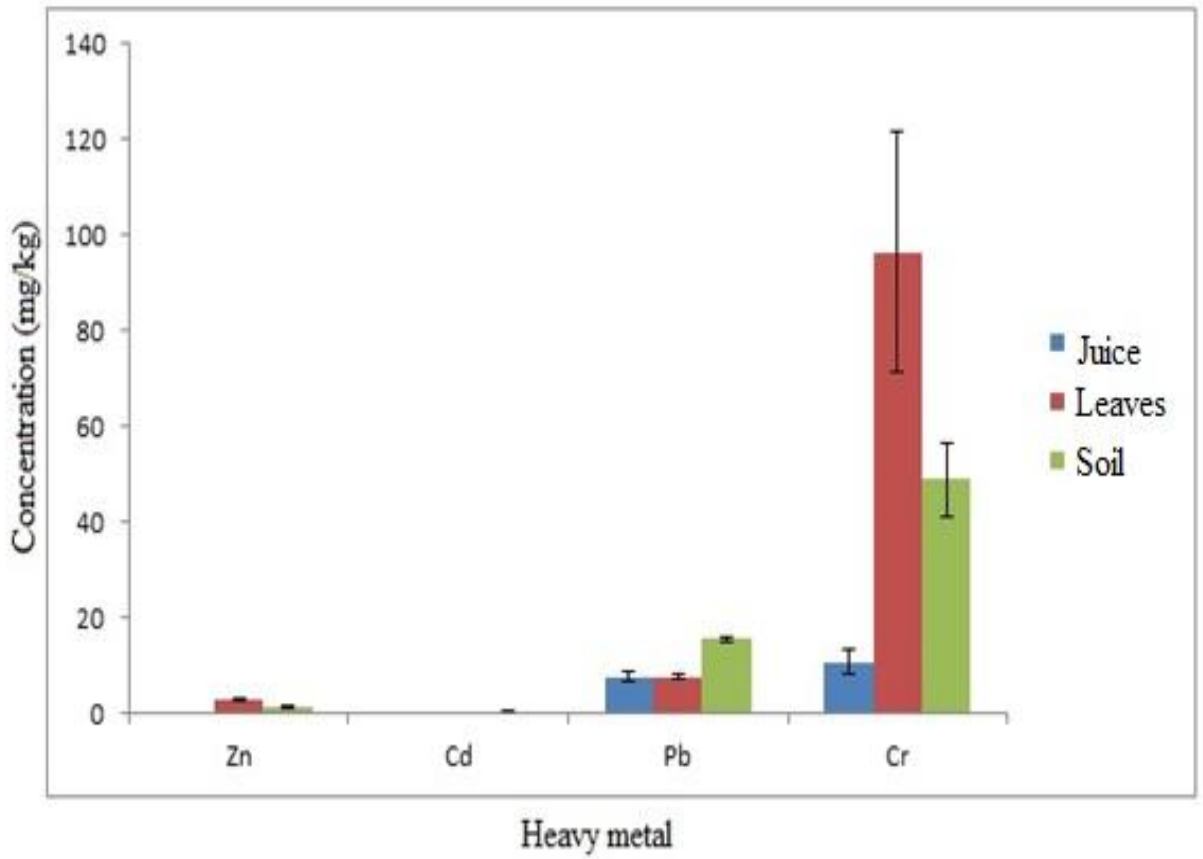


Figure 4: Average concentrations of heavy metal in location C for juice, leaves and soil

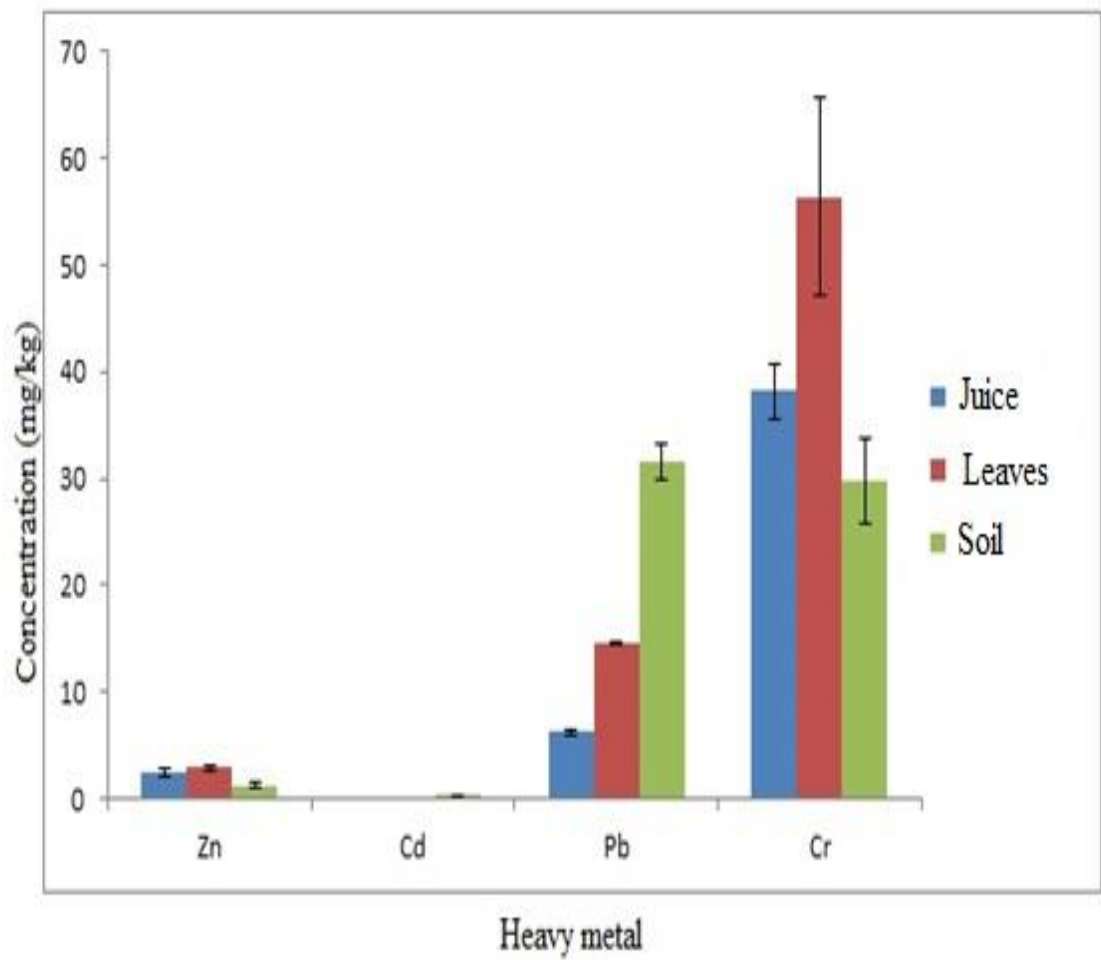


Figure 5: Average concentrations of heavy metals in location D for juice, leaves and soil

4.4: Correlation between Heavy Metals in Juice, Leaves and Soil in Location A, B, C and D

4.4.1.: Correlation between heavy metals in juice, leaves and soil in location A

There was a strong relationship between Zn-J and Cr-S and weak relationship between Zn-J and Zn-S (Appendix Ia). Cd-J shows no relationship with Zn-S, Cd-S, Pb-S and Cr-S, there was a strong link between Pb-J and Cd-S but a negative relationship was recorded between Pb-J and Cr-S. Cr-J has a positive connection between all heavy metals (Zn, Cd, Pb, and Cr) in which the relationship was stronger with Cd-S. Zn-L shows also a strong bond with Zn-S and Cr-S than with moderately Pb-S and also the relationship between Zn-L and Cd-L was negative (-0.019). Cd-L has a weak or negative relationship amongst Zn-S, Cd-S, Pb-S and Cr-S. Pd-L shows a positive relationship with all the metal-S, strongly with Zn-S and Pb-S, moderately and weak with Cd-S and Cr-S. There was also a strong correlation between Cr-L and Cr-S and a weak link between Zn-S (0.294) and Cd-S (0.230).

4.4.2: Correlation between Heavy Metal In Juice, Leaves and Soil in Location B

In Kem1 (location B) there was a moderate link among Zn-J and Zn-S (0.481*), Zn-J and Pb-S, a strong bond between Zn-J and Cd-S and a negative weak expression between Zn-J and Cr-S (Appendix Ib). Cd-J and Cd-L shows no or negative link with the metal in the soil of this location, there was also a strong negative link between Pb-J and Zn, a weak relationship between Pb-J and Pb-S and strong bond between Pb-S and a strong bond between Pd-J and Cr-S. The presence of Zn, Cd and Pb has a negative link with Cr in the juice however, Cr-J and Cr-S has a strong bond of 0.544*. Zn-L has a positive link with Zn-S, Cd-S and Cr-S but a moderately negative link was observed between Zn-L and Cr-S. Pb-L and Cr-L indicated a positive relationship with all the

metal in the soil of location B with Pb-L and Zn-S has a strong relationship along Cr-L and Cr-S.

4.4.3: Correlation between Heavy Metal in Juice, Leaves and Soil In Location C

In this location, Zn-J has a weak relationship with Zn-s and Cr-S along Pb-S which recorded a strong negative link with Zn-J (Appendix Ic). Cd in the juice was observed to have no relationship with the metals (Zn, Cd, Pd and Cr) in soil, Pb also has a weak negative bond with Pb-S and Cr-S while there was a weak positive observation between Pb-J and Zn-S. A strong positive was recorded between Pb-J and Zn-S and a moderate link wererecorded among Cr- and Cr-S. There was also a moderate bond between Zn-L and Zn-S and very weak link of 0.079 between Zn-L, and Cr-S, Pb-L and Cr-L recorded a strong connection with Zn-S while the link was weak with Pb-S and Cr-S (0.177 and 0.177) respectively.

4.4.4: Correlation between Heavy Metal In Juice, Leaves and Soil in Location D

(Zn-J and Zn-S) and (Zn-J and Pb-S) indicated strong positive of, a moderate connection with Cd-S while Zn-J and Cr-S recorded a weak negative link of, there was no relation between Cd in the juice and the soils heavy metal (Zn, Cd, Pb and Cr) of this location, there was a strong connection between Pb-J and Pb-S and a moderate bond between Pd-J and Cr-S and also there was a moderate and a weak connections between Pd-L with Zn-S, Cd-S, Pb-S and Cr-S \while Cr-L was moderately linked with Zn-S (appendix Id).

4.5: Average Mean of Heavy Metal across all locations

Figure 6 shows the average concentrations of Zn, Cd, Pb and Cr among all the locations. The concentrations of Zn and Pb were observed higher in G2 and G2-08 compared to K1 and K2, while Cr was recorded higher in K2 among all other locations. Thus, there was little or no concentration of Cd as shown in the figure.

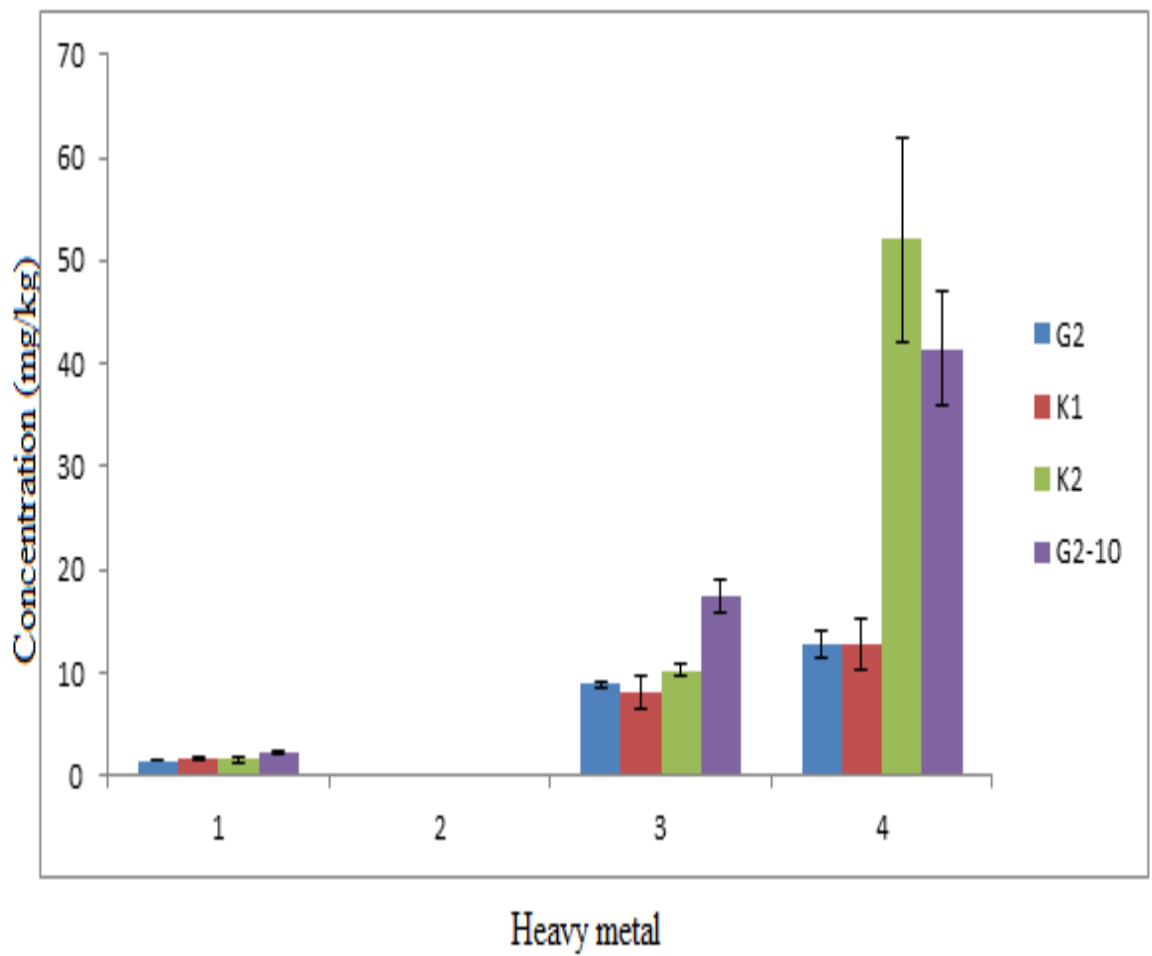


Figure 6: Average mean of heavy metal in all locations

Key

G2=Gyewana block 2

K1=Kem block 1

K2=Kem block 2

G2-08=Gyewana block 2-08

4.6: Comparison of Heavy Metal Concentration between Water and Fumes

Table 4.9: Indicates in the concentrations of Zn, Cd, Pb and Cr between Water and Fumes. The concentrations of Zn, Cd, and Cr were higher in fumes than it was observed in water while Pb was recorded high in water than it was seen in fumes. However, there was highly significant difference between each element in water and fumes ($P \leq 0.01$).

Table 4.10: Comparison of heavy metals concentrations between water and fumes

| Heavy metals | Water | Fumes | P-value |
|--------------|-------------|-------------|--------------|
| (mg/kg) | | | |
| Zn | 0.10±0.00 | 536.50±0.06 | 0.000 |
| Cd | 0.20±0.05 | 3.30±0.04 | 0.001 |
| Pb | 393.00±0.06 | 22.57±9.28 | 0.001 |
| Cr | 45.35±0.04 | 332.95±0.08 | 0.000 |

4.7: Sucrose Contents of Sugarcane Juice across all locations

Table 4.10: Shows the sucrose contents of sugarcane juice in various locations. There was no significant difference ($p > 0.05$) in sucrose contents amongst distances 0 to 100m in location Gyewana2. In location Kem1, the sucrose content at 100m (23.00%) was significantly highest ($p < 0.05$), followed by 20.00% each at distance 0 and 80m, 19.00%, 17.00% and 17.10% at distance 60, 40 and 20m respectively. At distance 80m (14.40%) sucrose level was significantly highest ($p < 0.05$) in location Kem 2; at 60m, 40m and 60m, the corresponding sucrose contents were 13.00%, 11.00% and 12.00%; while at distance 0m (9.00%), the sucrose content was lowest. In location Gyewana 2-08, at 100m (21.00%) of sucrose level was significantly highest, at 60, 80 and (40 and 20) the correspond sucrose contents were 20.00%, 19.00% and 14.00% respectively; while the sucrose level was lowest at distance 0m (19.00%).

Table 4.11: Sucrose contents of sugarcane juice for across all locations

| Distance (m) | G2-Sc (%) | K1-Sc(%) | K2-Sc(%) | G2-10 Sc(%) |
|----------------|--------------------------|-------------------------|-------------------------|-------------------------|
| 0 | 20.00±0.06 ^a | 20.00±0.05 ^b | 9.00±0.06 ^e | 10.00±0.05 ^f |
| 20 | 18.00±0.06 ^a | 17.10±0.06 ^e | 12.00±0.05 ^c | 14.00±0.06 ^e |
| 40 | 13.00±07.05 ^a | 17.80±0.05 ^d | 11.00±0.04 ^d | 14.60±0.03 ^d |
| 60 | 19.80±0.05 ^a | 19.00±0.08 ^c | 13.00±0.05 ^b | 20.00±0.06 ^b |
| 80 | 21.00±0.07 ^a | 20.00±0.06 ^b | 14.40±0.06 ^a | 19.00±0.02 ^c |
| 100 | 20.00±0.08 ^a | 23.00±0.03 ^a | 13.00±0.4 ^b | 21.00±0.05 ^a |
| P-value | 0.639 | 0.000** | 0.000** | 0.000** |

Means with the same superscript per column did not differ significantly ($P>0.05$), using DMRT. *=significant at $P\leq 0.005$. **=highly significant at $P\leq 0.001$

4.8 Correlation between Heavy Metal Concentrations and Sucrose Content of Sugarcane Juice

The correlation between heavy metals concentrations and sucrose contents of sugarcane juice in various locations, in location Gyewana 2, Zn and Pb indicated a weak positive relationship (0.058 and 0.039), there was no link between Cd and sucrose contents of sugarcane juice and the presence of Cr in the location indicated non-significant relationship with sucrose level. In location kem1 the sucrose content had a positive significant correlation with Zn and Cr (0.205 and 0.237) respectively and a strong barrier was observed with Pb (-0.643**). In location kem2, sucrose contents had a very weak relationship with Zn (0.012) and Cr (0.086) while non-significant relationship was observed between the sucrose content and Pd. Similarly, Zn, Cd and Cr were linked with sucrose level in correspondence of 0.234, 0.168 and 0.192 and also Pb has a negative barrier with sucrose content of sugarcane juice (Appendix IIa).

4.9 Heavy Metals Transfer Factor for across all locations

Zn transfer factor was observed to be significantly highest with 1.97 in location D while it was recorded lowest in location C; there was no transfer of Cd from soil to plant relationship, Pb was below 1mg/kg in across all locations while Cr was observed above 1mg/kg in location D only.

Table 4.12 Transfer factor of heavy metals in all locations

| Heavy metal | Location A | Location B | Location C | Location D |
|-------------|------------|------------|------------|------------|
| Zn | 0.68 | 0.38 | 0.18 | 1.97 |
| Cd | 0.00 | 0.00 | 0.00 | 0.03 |
| Pd | 0.53 | 0.49 | 0.48 | 0.20 |
| Cr | 0.37 | 0.13 | 0.22 | 1.27 |

CHAPTER FIVE

5.0. DISCUSSION

5.1. Heavy Metals Concentrations in Soil

The result obtained based on distance across all locations revealed that, virtually all the metals were significantly different but not from 0 to 100 m. The observed insignificant difference in the increase of distance from 0 to 100 m is an indication of multiple heavy metals pollutant source and this is in line with the report of Li *et al* (2001) who stated that the presence of heavy metals in soils may be due to the various anthropogenic activities such as industrial waste, fuel combustion and polluted water. The concentrations of Zn, Cd, Pb and Cr across all locations ranged from 0.2-4.40 mg/kg, 0.00-1.00mg/kg, 6.20-37.10 mg/kg and 7.20-121.00 mg/kg respectively (Table 4.1-4.4) in a trend of Cr>Pb>Zn>Cd. The highest concentration of Cr (121.00 mg/kg) and Pb (37.10 mg/kg) were observed in Table 4.3 and 4.2 respectively. The high concentrations of element recorded in soil could be as a result of long term deposition of fumes from chimneys which indicates presence of these elements (Baawain *et al.*, 2011) the elements are released by industrial emissions in the form of gaseous particulate matter into the atmosphere which eventually settles on the earth surface. In this study, the soil contamination of these metals has not exceeded the permissible limit (WHO 1996).

5.2. Heavy Metal in Sugarcane (Juice and Leaves)

This study revealed that, the concentrations of all the heavy metals in leaves were higher than it was observed in juice and this is in line with the report of Epub, (2016) who stated that, in generally, heavy metals concentrations in juice were lesser compared to that of leaves. This could be as a result of atmospheric deposition of these pollutants on leaves of sugarcane which is in agreement with the report of Nakayama, (2012) who relate high concentrations of heavy metals on plants leaves with atmospheric

deposition. The amounts of Zn and Cd in sugarcane juice in the study area were different to those reported by Collins and Doelsch (2010) who stated that, Zn concentrations ranging from 4.2-32.8mg/kg in the sugarcane juice which is higher than the concentration that was observed in present study. The difference could have been as a result of variation in metals content availability and varieties of sugarcane in which the varieties that were studied are; SP71-6189 and B47-419. Cd in the sugarcane juice was not detected or it was below detectable limit and there was a strong indication that the heavy metals level that was observed in leaves and soil were atmospheric pollution since it was only present in leaves and soil.

5.3. Heavy Metals in Water and Fumes

The concentrations of Zn (536.50 mg/kg), Cd (3.30 mg/kg), and Cr (332.95 mg/kg) were higher in fumes than it was observed in water (0.10, 0.20 and 332.95 mg/kg respectively) while Pb was recorded highest (393.00 mg/kg) in water than it was seen in fumes (22.57 mg/kg). The high concentrations of Zn, Cd and Cr in fumes agrees with literature in the sense that, emissions of fumes from industries are of concern on heavy metals and this comply with the report of Kaur *et al.*, (2014) who stated that the emissions of fumes from industries are the major pollutants of these metals into the environment (soils, water and plants). The low concentrations of Zn, Cd and Cr in the water is in conflict with the report of Ojo, (2017) reported that heavy metals from industrial source are directly deposited into water bodies and are also leached into or are washed away by runoffs into water bodies, resulting in water pollution but agrees with high concentration of Pb in water. The high concentrations of Pb in water it could be also be as a result of long term deposition of such metals in the water body or the metal has high persistence in the water than the other metals. By implication the

concentrations of Zn, Cd, Pb and Cr in water and fumes are not safe for the immediate environment (WHO, 1996)

5.4. Effect of Heavy Metals on Sucrose Content of Sugarcane Juice

There was a weak positive correlation between the concentrations of Zn and Pb in juice at location Gyewana 2 and this could be as a result of low concentration of metal in the soil. According to the report of Collin and Doelsch, (2010) the amounts of Pb and Zn in sugarcane would be more dependent to soil environment rather than on the differing varieties of plants. Negative relationship was observed between Pb and sucrose contents as the concentration of the metal increase (Kem1, Kem2 and gyewana2-08). This negative relationship could affect the level of sucrose in the sugarcane. It was also observed that high and low concentration of Cr shows no effect on level of sucrose content.

5.5. Transfer Factors (TF) of Heavy Metals in Sugarcane

Since it was observed that there were differences in amounts of heavy metal in the sugarcane juice and soil, it was important to show the availability of each metal in specific part of the sugarcane. Generally, the leaves revealed higher metal levels than the roots and stems in this research. This could be attributed to the larger exposure area of the leaves than the other parts to wind action, the surface adsorption of particulate matter. This high rate of assimilation of heavy metals from the environment agreed with the findings of Keane *et al.*, (2001) and Al-Kateeb and Leilah (2005). This result also agrees with other reports that metal concentrations in leaves are usually much higher than those in sugarcane juice (Reuben *et al.*, 2008 ; Jung, 2008) Zn and Cr was above 1mg/kg in location Gyewana2-08 and this could be as a result of transfer of metal from

leaves into stem of sugarcane and thus not safe for human consumption (Nogueira *et al.*, 2013).

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATION

6.1 Conclusions

In this study, the concentrations of all the soil heavy metals were assessed across the study locations and KEM2 had the highest concentrations of Zn (4.40 mg/kg), Cd (0.70 mg/kg) in the soil. KEM 1 recorded the highest concentration of Pb (37.10 mg/kg) while the highest level of Cr (121.00 mg/kg) was recorded at KEM 2. However, in respect to distance per location, the concentrations of all metals were observed significant yet metals were not more concentrated at 0 m. All elements were below permissible limit set by World Health Organisation (WHO) Zn (50 mg/kg), Cd (0.8 mg/kg), Pb (85 mg/kg) and Cr 100 (mg/kg) except for Cr.

The heavy metals concentrations in the sugarcane juice and leaves were highly significant with respect to distance in all locations, yet the concentrations of metals were not more concentrated at 0 m. However, this study revealed high concentrations of metals in leaves compared to juice with average concentrations of Zn (2.88 to 1.21 mg/kg), Pb (9.03 and 6.59 mg/kg) and Cr (39.89 and 19.72 mg/kg) of leaves and juice respectively. Thus, the average concentrations of Zn, Pb and Cr of sugarcane juice were above the permit limit of WHO 1996 except for Cd which was below detectable limit.

From the results, the sugarcane juice (stem) and leaves as well as soils were identified as the major sink of heavy metals from fumes and water, Zn (536.50 mg/kg), Cd (3.30 mg/kg) Cr (332.95 mg/kg) and Pb (393.00 mg/kg) respectively, which were highly polluted with heavy metals.

The presence of heavy metal in low concentrations in sugarcane stem has no or little positive effect on the sucrose level of sugarcane juice, while the increase in the

concentration of the metals (Pb) has a negative effect on the sucrose content of sugarcane juice.

6.2 Recommendations

- i. In view of these findings, Savannah land use planning should go beyond soil fertility assessment, to integrate eco-toxicity study of the environment to achieve integrated sustainable agricultural practices and sugarcane production, since it has been observed that atmospheric and water pollutants like Zn, Cd, Pb and Cr from factory pipes emission and irrigated water from the Dam may result in high concentration of pollution than the desired levels in the soils of Savannah community and neighboring.
- ii. Further assessments should be carried out on the refined sugar from Savannah Sugar Company Ltd, Numan, to assess the level of heavy metals concentrations.
- iii. Similar studies should be conducted at early stages of planting, middle and at maturity in order to reveal the concentrations of heavy metals in sugarcane in respect to time and also assess sugarcane roots and stems (top and bottom) to reveal the uptake of such pollutants from soil to plant.

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APPENDIX I

Appendix Ia: Correlation Between Heavy Metal In Juice, Leave And Soil In

Location A

| Variables | Zn-S | Cd-S | Pb-S | Cr-S |
|-----------|---------|--------|---------|---------|
| Zn-J | 0.234 | -0.249 | -0.441 | 0.540* |
| Cd-J | 0.000 | 0.000 | 0.000 | 0.000 |
| Pb-J | -0.234 | 0.570* | 0.382 | -0.458 |
| Cr-J | 0.322 | 0.573* | 0.090 | 0.362 |
| Zn-L | 0.716** | -0.019 | 0.459 | 0.701** |
| Cd-L | 0.064 | 0.395 | -0.257 | -0.016 |
| Pb-L | 0.509* | 0.394 | 0.886** | 0.172 |
| Cr-L | 0.294 | 0.230 | -0.530* | 0.776** |

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

* . Correlation is significant at the 0.05 level (2-tailed)

Appendix Ib: Correlation Between Heavy Metal in Juice, Leave and Soil In

Location B

| Variables | Heavy metal (Mean±SE) | | | |
|-----------|-----------------------|----------|--------|---------|
| | Zn-S | Cd-S | Pb-S | Cr-S |
| Zn-J | 0.481* | 0.703** | 0.327 | -0.150 |
| Cd-J | 0.000 | 0.000 | 0.000 | 0.000 |
| Pb-J | -0.919** | -0.506* | 0.243 | 0.786** |
| Cr-J | -0.734** | -0.914** | -0.425 | 0.544* |
| Zn-L | 0.035 | 0.162 | 0.159 | -0.405 |
| Cd-L | 0.000 | 0.000 | 0.000 | 0.000 |
| Pb-L | 0.669** | 0.330 | 0.268 | 0.166 |
| Cr-L | 0.215 | 0.044 | 0.164 | 0.581* |

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

* . Correlation is significant at the 0.05 level (2-tailed)

Appendix Ic: Correlation Between Heavy Metal In Juice, Leave and Soil in Location C

| Variables | Heavy metal (Mean±SE) | | | |
|-----------|-----------------------|-------|---------|--------|
| | Zn-S | Cd-S | Pb-S | Cr-S |
| Zn-J | 0.089 | 0.000 | -0.564* | 0.212 |
| Cd-J | 0.000 | 0.000 | 0.000 | 0.000 |
| Pb-J | 0.021 | 0.000 | -0.286 | -0.035 |
| Cr-J | 0.581* | 0.000 | -0.232 | 0.423 |
| Zn-L | 0.363 | 0.000 | -0.149 | 0.079 |
| Cd-L | 0.227 | 0.000 | -0.339 | -0.154 |
| Pb-L | 0.552* | 0.000 | 0.185 | 0.082 |
| Cr-L | 0.477* | 0.000 | 0.177 | 0.117 |

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

* . Correlation is significant at the 0.05 level (2-tailed)

Appendix Id: Correlation between heavy metal in juice, leaves and soil in location D

| Variables | Heavy metal (Mean±SE) | | | |
|-----------|-----------------------|--------|----------|--------|
| | Zn-S | Cd-S | Pb-S | Cr-S |
| Zn-J | 0.634* | 0.331 | 0.591* | -0.114 |
| Cd-J | 0.000 | 0.000 | 0.000 | 0.000 |
| Pb-J | -0.394 | -0.142 | 0.646** | 0.397 |
| Cr-J | 0.153 | -0.136 | 0.392 | 0.408 |
| Zn-L | 0.597** | 0.248 | -0.557** | -0.294 |
| Cd-L | -0.247 | 0.071 | -0.114 | -0.325 |
| Pb-L | 0.205 | 0.105 | 0.192 | 0.195 |
| Cr-L | 0.339 | -0.252 | 0.252 | 0.206 |

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

* . Correlation is significant at the 0.05 level (2-tailed)

**Appendix Ie: Correlation between heavy metal and sucrose contents of sugarcane
juice for all the sampling locations**

| Variables | SC-G2 | SC-K1 | SC-K2 | SC-G2-08 |
|-----------|---------|----------|----------|----------|
| Zn-G2 | 0.058 | -0.374 | -0.374 | -0.295 |
| Cd-G2 | 0.000 | 0.000 | 0.000 | 0.000 |
| Pb-G2 | 0.059 | -0.542** | -0.659** | 0.414 |
| Cr-G2 | -0.119 | -0.736** | -0.113 | -0.366 |
| Zn-K1 | -0.148 | 0.205 | -0.637** | -0.552* |
| Cd-K1 | 0.000 | 0.000 | 0.000 | 0.000 |
| Pb-K1 | -0.350 | -0.643** | -0.763** | -0.838** |
| Cr-K1 | 0.059 | 0.237 | 0.781** | 0.927** |
| Zn-K2 | -0.175 | 0.144 | 0.012 | -0.130 |
| Cd-K2 | 0.000 | 0.000 | 0.000 | 0.000 |
| Pb-K2 | -0.097 | 0.824** | -0.353 | -0.621** |
| Cr-K2 | 0.421 | -0.667** | 0.086 | -0.341 |
| Zn-G2-08 | -0.154 | 0.560* | 0.366 | 0.234 |
| Cd-G2-08 | -0.073 | 0.282 | 0.192 | 0.169 |
| Pb-G2-08 | -0.0109 | -0.411 | -0.748** | -0.806** |
| Cr-G2-08 | 0.040 | 0.223 | 0.458 | 0.192 |

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

* . Correlation is significant at the 0.05 level (2-tailed)

APENDIX II

Appendix IIa: Combined G2 Juice, G2 leave G2 soil

| Locations | Heavy metals (mg/kg) | | | |
|-----------|----------------------|------------|-------------|-------------|
| | Zn | Cd | Pb | Cr |
| G2 Juice | 1.02±0.10b | 0.00±0.00b | 6.07±0.20c | 6.43±0.94b |
| G2 Leaves | 1.76±0.13a | 0.12±0.06b | 8.88±0.33b | 14.40±2.05a |
| G2 Soil | 1.50±0.08a | 0.28±0.05a | 11.48±0.49a | 17.23±2.30a |
| P-value | 0.000 | 0.001 | 0.000 | 0.000 |

Appendix IIb: Combined K1 for Juice, Leave and Soil

| Distance (m) | Heavy metals (mg) | | | |
|--------------|-------------------|------------|-------------|-------------|
| | Zn | Cd | Pb | Cr |
| K1 Juice | 1.02±0.02c | ND | 6.42±0.12a | 5.20±0.60b |
| K1 Leaves | 1.75±1.03b | ND | 5.05±0.23a | 10.42±1.84b |
| K1 Soil | 2.37±0.16a | 0.11±0.04a | 12.92±4.72a | 41.53±3.60a |
| P-value | 0.000 | 0.001 | 0.103 | 0.000 |

Appendix IIc: Combined K2 for Juice, Leave and Soil

| Distance (m) | Heavy metals (mg) | | | |
|--------------|-------------------|------------|-------------|--------------|
| | Zn | Cd | Pb | Cr |
| K2 Juice | 0.23±0.06c | ND | 7.57±0.97b | 10.84±2.64b |
| K2 Leaves | 3.05±0.19a | ND | 7.60±0.43b | 96.53±25.32a |
| K2 Soil | 1.25±0.35b | 0.28±0.03a | 15.53±0.47a | 48.87±7.85b |
| P-value | 0.000 | 0.000 | 0.000 | 0.001 |

Appendix IId: Combined G2 10Sc for Juice, Leave and Soil

| Distance (m) | Heavy metals (mg) | | | |
|--------------|-------------------|-------------|-------------|--------------|
| | Zn | Cd | Pb | Cr |
| G2 Juice | 2.55±0.41a | 0.01±0.001b | 6.29±0.22c | 56.41±9.17a |
| G2 Leaves | 2.95±0.23a | 0.00±0.00b | 14.58±0.20b | 38.18±12.53a |
| G2 Soil | 1.30±0.33b | 0.32±0.08a | 31.61±1.76a | 29.83±3.95a |
| P-value | 0.003 | 0.000 | 0.000 | 0.126 |

Appendix IIe: Average mean of heavy metals in all locations

| Heavy metal (Mean±SE) | | | | |
|-----------------------|------------|-------------|-------------|-------------|
| Location | Zn | Cd | Pb | Cr |
| G2 | 1.43±0.08b | 0.13±0.03a | 8.81±0.37b | 12.69±1.23b |
| K1 | 1.71±0.12b | 0.04±0.02b | 8.13±1.62b | 19.05±2.58b |
| K2 | 1.51±0.21b | 0.09±0.02ab | 10.23±0.64b | 52.08±9.96a |
| G2-10 | 2.27±0.21a | 0.11±0.03ab | 17.49±1.56a | 41.48±5.46a |
| P-value | 0.002 | 0.058 | 0.000 | 0.000 |

APPENDIX III

Appendix IIIa: Soil particles size for all locations

| Location | Clay (%) | Silt (%) | Sand(%) | Textural class |
|-----------------|----------|----------|---------|----------------|
| Gyewana2 | 34.8 | 24 | 41.2 | Clay loam |
| Kem 1 | 42.8 | 28 | 29.2 | Clay loam |
| Kem 2 | 32.8 | 30 | 37.2 | Clay loam |
| Gyewana 2-08 | 47.9 | 21 | 31.1 | Clay loam |

Appendix IIIb: physico-chemical parameters of location A (Gyewana2)

| Distance (meter) | Concentration of Hydrogen ion (pH) | Electrical conductivity (K) | Total dissolved solid (TDS) mg/l |
|------------------|------------------------------------|-----------------------------|----------------------------------|
| 0 | 08.80 | 950 | 392 |
| 20 | 08.23 | 820 | 480 |
| 40 | 08.06 | 940 | 578 |
| 60 | 08.25 | 948 | 482 |
| 80 | 07.95 | 984 | 448 |
| 100 | 08.02 | 784 | 490 |

Appendix IIIc: physico-chemical parameters of location B (Kem 1)

| Distance (meter) | Concentration of Hydrogen ion (pH) | Electrical conductivity (K) | Total dissolved solid (TDS) mg/l |
|------------------|------------------------------------|-----------------------------|----------------------------------|
| 0 | 08.72 | 633 | 384 |
| 20 | 09.54 | 941 | 423 |
| 40 | 09.37 | 952 | 552 |
| 60 | 08.10 | 1080 | 592 |
| 80 | 08.17 | 920 | 465 |
| 100 | 08.35 | 512 | 197 |

Appendix IIId: physicochemical parameters of location C (Kem2)

| Distance (meter) | Concentration of Hydrogen ion (pH) | Electrical conductivity (K) | Total dissolved solid (TDS)mg/l |
|------------------|------------------------------------|-----------------------------|---------------------------------|
| 0 | 08.56 | 1085 | 550 |
| 20 | 09.06 | 850 | 428 |
| 40 | 09.10 | 845 | 424 |
| 60 | 09.00 | 866 | 438 |
| 80 | 08.95 | 838 | 423 |
| 100 | 08.87 | 854 | 431 |

Appendix IIIe: physicochemical parameters of location Gyewana 2-08 soil

| Distance (meter) | Concentration of Hydrogen ion (pH) | Electrical conductivity (K) | Total dissolved solid (TDS) mg/l |
|------------------|------------------------------------|-----------------------------|----------------------------------|
| 0 | 08.10 | 1002 | 641 |
| 20 | 08.24 | 1040 | 672 |
| 40 | 08.80 | 1012 | 680 |
| 60 | 08.91 | 1101 | 691 |
| 80 | 09.01 | 1141 | 731 |
| 100 | 08.02 | 854 | 581 |

APPENDIX IV

Appendix IVa: Physico-chemical parameters of water and fumes

| pH | | Electrical Conductivity | | Total dissolved solid (mg/l) | |
|-------|-------|-------------------------|-------|---------------------------------|-------|
| Water | Fumes | Water | Fumes | Water | Fumes |
| 9.58 | 9.82 | 139 | 1703 | 69 | 860 |

APPENDIX V

Appendix IVa: World Health Organization for heavy metals permissible limits for soil and plant (1996)

| Heavy metals | Soil target value | Permissible values of edible plants |
|--------------|-------------------|-------------------------------------|
| Zn | 50 | 0.60 |
| Cd | 0.8 | 0.20 |
| Pb | 85 | 2.00 |
| Cr | 100 | 1.30 |