ASSESSMENT OF HEAVY METALS IN SOME SELECTED VEGETABLE FIELDS IRRIGATED WITH WASTE WATER ALONG KUBANNI WATER COURSE IN ZARIA METROPOLIS

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A DISSERTATIONSUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF A MASTER DEGREE IN WATER RESOURCES AND ENVIRONMENTAL ENGINEERING

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AHMADU BELLO UNIVERSITY,
ZARIA, NIGERIA.

MARCH, 2016

DECLARATION

I hereby declare that this dissertation workentitled "**Assessment of Heavy Metals in Some Selected Vegetable Fields Irrigated with Wastewater along Kubanni Watercourse in Zaria Metropolis"**is a record of a research work that was undertaken and written by me. It has not been presented before for any degree or diploma or certificate at any university or institution. Information derived from personal communications, published and unpublished works were duly referenced in the text.

AHMODU, Emmanuel Ocholi _____ _____
P13EGWR8012 **Signature** **Date**

CERTIFICATION

This is to certify that the dissertation entitled "**Assessment of Heavy Metals in Some Selected Vegetable Fields Irrigated with Wastewater along Kubanni Watercourse in Zaria Metropolis"** by AHMODU, Emmanuel Ocholi meets the regulations governing the award ofMaster Degree in the Department of Water Resources and Environmental Engineering, Faculty of Engineering, Ahmadu Bello University, Zaria, and it is approved for its contribution to scientific knowledge and literary presentation.

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DEDICATION

This research work is dedicated to God Almighty and my lovely family which includes my parents Mr. and Mrs. John Abdullahi Ahmodu, my elder brother Mr. Nathaniel Ahmodu, and my beautiful sisters, Mrs. Dorcas Mark, Blessing Ahmodu, Joy Ahmodu and Victoria Ahmodu.

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It is my earnest prayer that God will bless you ALL.

ABSTRACT

The need to assess the heavy metals uptake by vegetables cultivated and irrigated with wastewater along the watercourse of a stream, have led to a controlled field experiments in Zaria Metropolis. Five heavy metals; Cadmium (Cd), Chromium (Cr), Lead (Pb), Manganese (Mn) and Zinc (Zn) were determined using the Atomic Absorption Spectrophotometer (AAS).The pollution load index (PLI), plant transfer factor (TF), daily intake of metals (DIM) and health risk index (HRI) were used to study the pollution status and the health risks the consumers may be exposed to by the consumption of the heavy metal contaminated vegetables in the metropolis. In this study, the quality of the stream (Kubanni River) contaminated with municipal wastewater and used for irrigation of carrot, spinach and cabbage was investigated at three sampling points (A, B, and C) for its heavy metal buildup. The contaminated water used for irrigation at each irrigation date, and the irrigated vegetables harvested after maturity were collected and analyzed for their metal concentrations. The results show that the stream water used for irrigation was contaminated with Cr, 0.4214mg/l, 0.291mg/l and 0.3774mg/l, and Mn, 0.245mg/l, 0.2127mg/l and 0.1618mg/l at point A, B and C respectively, which is above Food and Agriculture Organisation (FAO) threshold value. Pb and Zn were below the threshold and Cd was not detected in the wastewater samples collected during the study. The maximum Health Risk Index (HRI) was found in *Daucus carota* and *Brassica oleracea* which coincidently share the same value 0.2225. HRI of Cd, Cr, Pb, Mn, and Zn ranged between 0.17-0.19, 0.0033-0.0041, 0.1850-0.2225, 0.0236-0.0385 and 0.0168-0.0300 respectively. It was therefore concluded that irrigated crops harvested from these areas

should be carefully washed and decanted after boiling before eating in order to prevent accumulation of these metals in man's body metabolism.

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ABBREVIATIONS

ATSDR - Agency of Toxic Substances & Disease Registry

CCREM - Canadian Council of Resource and Environment Ministers

Cd - Cadmium

CDCP - Centres for Disease Control & Prevention

CEC – Cation Exchange Capacity

CHNRI – Child Health and Nutrition Research Initiative

Cr - Chromium

CSC – Canadian Society for Chemistry

CWA – Clean Water Acts

DIM – Daily Intake of Metals

DNA - Deoxyribonucleic Acid

EC – Electrical Conductivity

EC_e - Electrical Conductivity of Soil

EC_{iw} - Electrical Conductivity of Water

EDTA – Ethylenediaminetetraacetic Acid

EPA – Environmental Protection Agency

FAO – Food and Agricultural Organisation

FEPA – Federal Environmental Protection Agency

HCL – Hydrochloric Acid

HRI – Health Risk Index

IARC - International Agency for Research on Cancer

$K_2Cr_2O_7$ – Potassium Dichromate (VI)

LULCC - Land-Use/Land-Cover Changes

Mn - Manganese

MSS - Municipal Sewage Sludge

N,P K – Nitrogen, Phosphorus and Potassium

Pb - Lead

PCF – Plant Crop Factor

PLI – Pollution Load Index

POD - Peroxidase

PVC - PolyVinyl Chloride

RfD – Reference Oral Dosage

RML= Recommended Maximum Limit

RNA - Ribonucleic Acid

SAR – Sodium Absorption Ratio

SOD - Superoxide Dismutase

TF – Transfer Factor

UNEP – United Nation Environmental Programme

USDL - United States Department of Labour

U.S. EPA – United State Environmental Protection Agency

WHO – World Health Organisation

Zn - Zinc

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND TO THE STUDY

Water is a fundamental and an irreplaceable resource to all forms of life on earth. The growing dearth of water has threatened the profitable development, quality of the environment, sustainable human livelihood, and a multitude of other public goals in many developing Asian and African regions (Nawaz *et al.,* 2012). In order to solve the problem of water shortage, Nigeria especially northern areas has begun to use wastewater for irrigation. It contains plant nutrients and organic matter, so this approach may increase soil fertility. However, wastewater composition is variable and contains high levels of toxic metals; therefore heavy metal contamination of agricultural soils has also become increasingly serious in sewage irrigation area (Mustafa, 2003; Jintao, 2011). Studies have shown that heavy metals are potentially toxic to crops, animals and humans when contaminated soils were used for crop production, because heavy metals are easily accumulated in vital organs to threaten crop growing and human health (Sharma *et al.,* 2007; Jintao, 2011).

Globally, around 20 million hectare of land is irrigated with municipal wastewater (raw, diluted or treated) (Qaisar*et al.,* 2012). This figure is most likely to increase noticeably over the next few decades in responses to the growing levels of water stress in inhibited catchments. In Nigeria, wastewater is increasingly being used for agricultural irrigation in urban and peri-urban areas especially during dry season farming. It drives significant economic activity, supports countless livelihoods particularly those

of poor farmers, and substantially changes the water quality of natural water bodies (Marshall *et al.,* 2007). There are serious drawbacks of using wastewater without ample safeguards for human health and the environment (Scott *et al.,* 2004; Nawaz *et al.,* 2012).

Heavy metal contamination of environment is a worldwide phenomenon that has attracted a great deal of attention (Qingjie, 2008; Ogunkunle and Fatoba, 2012). This is because, heavy metals are ubiquitous in the environment, as a result of both natural and anthropogenic activities and humans are exposed to them through various ways (Wilson and Pyatt, 2007; Khan *et al.,* 2008). Wastewater irrigation, solid waste disposal, sludge applications, vehicular exhaust, and industrial activities are the major sources of soil contamination with heavy metals and an increased uptake by food crop grown on such contaminated soils is often observed (Khan*et al.,* 2008). Compared with other pathways such as inhalation and dermal contact, dietary intake is the main route of exposure to heavy metals for most people (Tripathi*et al.,* 1997; Qian*et al.,*2010; Yeganeh *et al.,* 2012; Chen *et al.,* 2013).

Runoff from heavy downpour may lead to horizontal leaching from dump sites causing metal uptake by roots of plants; the rest may find their way into open water bodies and the entire aquatic ecosystem. Extreme accumulation of heavy metals in agricultural soils through wastewater irrigation may not only result in soil contamination but also lead to elevated heavy metal up-take by crops, threatening food quality and safety (Muchuweti*et al.,* 2006). The entry into the food chain of these metals lead to increased susceptibility and exposure to metal poisoning of local population (Orish*et al.,* 2012).

Heavy metals can be very harmful to the human body even in low concentrations as there is no effective excretion mechanism (Ghosh*et al.,* 2012; Chen *et al.,* 2013). A number of drastic health challenges can arise as a result of excessive up-take of dietary heavy metals. Furthermore, the consumption of heavy metal contaminated food can seriously deplete some essential nutrients in causing a decrease in immunological defenses, intrauterine growth retardation, impaired psycho- social behaviors, disabilities associated with malnutrition and a high prevalence of upper gastrointestinal cancer (Arora *et al.,* 2008; Orisakwe *et al.,* 2012).

Although, some heavy metals have nutritional functions and are essential to maintain the metabolism of the human body. Metals like copper (Cu), manganese (Mn) and zinc (Zn) are essential for physiological processes; certain enzymes need metal ions for their catalytic activity. On the other hand, Cadmium (Cd) and lead (Pb) are toxic metals. All of them may be harmful if excessive amounts are consumed (Donadini*et al.,* 2008; Pizzol*et al.,* 2011; Tadele and Ariaya, 2014).

The present study aims to determine human health risks associated with food chain contamination of heavy metals routing from irrigation using urban and peri-urban wastewater. Irrigating water, soil and vegetables were analyzed for Cr^{2+}, Pb^{2+}, Cd^{2+}, Mn^{2+} and Zn^{2+}; Transfer Factor (TF), Daily Intake of Metals (DIM) and Health Risk Index (HRI) were also calculated.

1.2 STATEMENT OF RESEARCH PROBLEM

It is essential to study the relationship between human health risks and food chain (vegetables) contamination by heavy metals. The establishment of a clear

relationship between human health risks-food chain contaminations of heavy metal is difficult due to the large number of variables which are associated with the process. It is more challenging to quantify the impact of heavy metals, as heavy metals are potentially toxic to crops, animals and human when contaminated soils are used for crop production, because heavy metals are easily accumulated in vital organs of crops grown on these contaminated soils. Humans and animals that consume such crops are also prone to this potential toxicity (Liang *et al.*, 2011; Ogunkunle and Fatoba 2012). This gave impetus to the study on environmental problems of soil pollution by heavy metals in the last few decades (Zhang *et al.*, 2007; Ogunkunle and Fatoba, 2012) with the development of an ecological geochemistry survey to aid in determining levels of heavy metal pollution and its potential risk. Furthermore, the Kubanni River passes through settlement areas and places of commercial activities towards its mouth, which are sources of pollutants. This is the source of water for irrigation of crops.

1.3 AIM AND OBJECTIVES

1.3.1 Aim

The aim of the study is to investigate the uptake of heavy metals by vegetables irrigated with wastewater contaminated with heavy metals and the perceived health risk to the metropolitan.

1.3.2 Objectives of the Study

1. To determine some physiochemical parameters (such as pH, EC, SAR, % organic matter of soil and soil texture) of the wastewater and soil of the plots used.

2. To determine the concentration of some selected heavy metals (Cr^{2+}, Pb^{2+}, Cd^{2+}, Mn^{2+} and Zn^{2+}) in the irrigation water along Kubanni watercourse in Zaria, Metropolis.
3. To determine the concentration of some selected heavy metals (Cr^{2+}, Pb^{2+}, Cd^{2+}, Mn^{2+} and Zn^{2+}) in the soil of the irrigated farms.
4. To determine the concentration of the selected heavy metals in the selected vegetables cultivated on the soil and irrigated with the water from Kubanni watercourse in Zaria, Metropolis.
5. To determine the Daily Intake of Metals (DIM) and the Health Risk Index (HRI) for the locals through the consumption of contaminated vegetables.

1.4 JUSTIFICATION OF THE STUDY

World Health Organization (WHO) estimates that about a quarter of the diseases facing mankind today occur due to prolonged exposure to environmental pollution (Pruss-Ustun and Corvalan, 2006; Kimani, 2007; Njagi. 2013). The usual belief that wastes are sometimes hazardous to health cannot be overemphasized. The improper discharge of untreated wastes (both solids and liquids) into drainage channels which empties itself into watercourse, and planting of dumpsites along watercourse by small scale industries, domestic and agricultural activities are a common site in Zaria and other urban and peri-urban areas in Africa. These discharges are not only eyesores, but a health hazard. This results into a substantial buildup of heavy metals in wastewaters. Excessive accumulation of heavy metals in agricultural soils through wastewater irrigation, may not only result in soil contamination, but also lead to elevated heavy metal uptake by crops, and thus affect food quality and safety (Muchuweti*et al.,* 2006). Heavy metal

accumulation in soils and plants is of increasing concern because of the potential human health risks. Till date, there is relatively scanty information on environmental dynamics and health implications of heavy metals in plants irrigated with contaminated wastewater. This study aims to fill in this knowledge gap by assessing the occurrence of heavy metals in vegetable plants growing along Kubanni watercourse area, in Zaria metropolis.

1.5 SCOPE AND LIMITATION OF THE STUDY

This research work covered the determination of human risks associated with food chain contamination of heavy metals routing from irrigation water of Kubanni watercourse in Zaria metropolis. The study area is a flood plain as such wet season farming of vegetables in that farm site is difficult because the entire area is flooded during the wet season, hence, wet season vegetables farming is not obtainable.

CHAPTER TWO

LITERATURE REVIEW

2.1 WATER POLLUTION

Pollution is defined as the presence of undesirable substances in quantities which are harmful to man, vegetation or properties (Agbaire and Akporhonor, 2014). It is the introduction into the environment of substances that has harmful effects on the environment. Pollution caused by heavy metals isincreasing with the increase usage of chemicals in industry and agriculture.

Water pollution is the contamination of streams, lakes, underground water, bays, or ocean by substances harmful to living things. Water pollution is a major global problem which requires ongoing evaluation and revision of water resource policy at all levels (international down to individual aquifers and wells). It has been suggested that water pollution is the leading worldwide cause of deaths and diseases (Pink and Daniel, 2006; Larry and West, 2006), and that it accounts for the deaths of more than 14,000 people daily (Larry and West, 2006). An estimated 580 people in India die of water pollution related illness every day (CHNRI, 2010). About 90% of the water in the cities of China is polluted, and as of 2007, half a billion Chinese had no access to safe drinking water. In addition to the acute problems of water pollution in developing countries, developed countries also continue to struggle with pollution problems. For example, in the most recent national report on water quality in the United States, 45 percent of assessed stream miles, 47% of assessed lake acres, and 32% of assessed bays and estuarine square miles were classified as polluted (U.S. EPA, 2007). The head of China's

national development agency said in 2007 that one quarter of the length of China's seven main rivers were so poisoned that the water harmed the skin (Richard *et al*, 2007).

2.1.1 Point Source Pollution

Pollutants that originate from an established source are considered point source pollution. Point source pollution, as defined by the U.S. EPA, is "any discernible, confined and discrete conveyance, such as a pipe, ditch, channel, tunnel, conduit, discrete fissure, or container …from which pollutants are or may be discharged" (U.S. EPA, 2004b; Aull, 2005). Wastewater facilities and industrial factories discharging waste directly into surface waters are a form of point source pollution.

Point source water pollution refers to contaminants that enter a waterway from a single, identifiable source, such as a pipe or ditch. Examples of sources in this category include discharges from a sewage treatment plant, a factory, or a city storm drain. The U.S. Clean Water Act (CWA) defines point source for regulatory enforcement purposes. The CWA definition of point source was amended in 1987 to include municipal storm sewer systems, as well as industrial storm water, such as from construction sites.

2.1.2 Non-Point Source Pollution

A second form of pollution to surface waters is through nonpoint source discharges. Nonpoint source pollution comes from many diffuse sources, where contaminants on land surfaces are transported by stormwater or snowmelt runoff into water bodies. Examples of nonpoint source pollution include agricultural runoff and runoff from highly urbanized areas where a majority of the surfaces are paved. These

sources of pollution are not regulated and are considered the leading remaining cause of water quality problems reported by state officials (U.S. EPA, 2004d; Aull, 2005).

Effects from nonpoint source pollutants include excess sediment accumulating in water bodies, high levels of nutrients (for example, heavy metals), and bacterial contamination. Sediment transport into water bodies is greatly affected by construction sites with little or no erosion control measures. High levels of nutrients are produced by runoff transporting pesticides, manure, and other nutrient containing wastes into water bodies. Nutrients affect water quality by providing excess nitrogen or phosphorous, leading to extreme plant and algal growth. Bacterial contamination can result from wildlife, domestic, or livestock feces contaminating water, or from overburdened or deteriorating septic systems.

2.2 HEAVY METALS

Heavy metals are usually described as metals with atomic weight greater than iron and/or have density greater than 5 g mL-1(Velaiappan*et al*., 2002; Abdullahi *et al*., 2013). The human body requirestrace amounts of some heavy metals, including zinc, copper, iron, cobalt and others, butthese can be dangerous at high levels. Other heavy metals such as mercury, lead, arsenicand cadmium have no known benefits and their accumulation over time can cause seriousillness and even premature death (Singo, 2013).

Heavy metals are ubiquitous in the environment, as a result of both natural and anthropogenic activities, and humans are exposed to them through various pathways (Wilson and Pyatt, 2007). Because they cannot be degraded or destroyed, heavy metals are persistent in all parts ofthe environment. Contamination of soil is a constant danger.

Effects of soil pollution byheavy metals can make it infertile and unsuitable for plants. This affects the organism in thefood-web (Alloyways& Ayres, 1993; Singo, 2013).

2.2.1 Cadmium

Cadmium occurs naturally in the environment. Some of its presence in the environment is as a result of natural processes such as forest fires, volcanic emissions, and weathering ofsoil and bedrock. Its presence is mostly the result of human activities, particularly metalproduction, fuel burning, transportation, solid waste disposal, and sewage sludge treatment(Environment Canada & Health Canada, 1994).

It is mostly used to make nickel-cadmium batteries, but is also used in pigments, includingthose for ceramic glazes, polyvinyl chloride (PVC) plastics, industrial coatings, hair and bodyproducts (Environment Canada & Health Canada, 1994). Cadmium from body and haircreams can be absorbed into the human body through contact via the skin (Ayenimo*et al.*,2010).Cadmium is absorbed into the body, accumulating in the kidney and the liver, although it canbe found in almost all adult tissues (Elinder, 1985). The total amount absorbed by humans has been estimated to be between 0.2 and 0.5 μg/day (Health Canada, 2010), withabsorption via skin estimated to be 0.5 per cent (Health Canada, 2009). Little absorbedcadmium is eliminated with humans getting rid of 50 per cent of cadmium from the body only10-12 years after exposure (Hamer, 2003).

Cadmium and cadmium compounds are considered to be “carcinogenic to humans” by theInternational Agency for Research on Cancer (IARC, 2010) and are considered “toxic” inCanada because of their carcinogenicity and environmental effects (Environment Canada &Health Canada, 1994). It and its compounds are also classified as

known humancarcinogens by the United States Department of Health and Human Services (ATSDR, 2008). Cadmium (Cd) is persistentand accumulates mainly in the kidney and liver of vertebrates,producing severe diseases in these organs (UNEP,2006).

2.2.2 Chromium

Chromium occurs naturally in the environment as a result of volcanic emissions and weathering ofsoil and bedrock. Its presence is mostly the result of human activities, tanneries and electroplating (EPA, 1990).

Chromium occurs in a number of oxidation states, but Cr(III) (trivalent chromium) andCr(IV) (hexavalent chromium) are of main biological relevance. There is a great differencebetween Cr(III) and Cr (VI) with respect to toxicological and environmental properties, andthey must always be considered separately. Chromium is similar to lead typically foundbound to particles. Chromium is in general not bioaccumulated and there is no increase inconcentration of the metal in food chains. Cr (III) is an essential nutrient for man in amounts of 50 - 200 μg/day. Chromium is necessary for the metabolism of insulin. It is also essential for animals, whereas it is not knownwhether it is an essential nutrient for plants, but all plants contain the element. In general,Cr(III) is considerably less toxic than Cr(VI).

Cr(VI) has been demonstrated to have a numberof adverse effects ranging from causing irritation to cancer. Hexavalent chromium is ingeneral more toxic to organisms in the environment than the trivalent chromium. Almost allthe hexavalent chromium in the environment is as a result of human activities. Chromium canmake fish more susceptible to infection; high concentrations can damage and/or accumulatein various fish tissues and

in invertebrates such as snails and worms. Reproduction of thewater flea Daphnia was affected by exposure to 0.01 mg hexavalent chromium/litre. Hexavalentchromium is accumulated by aquatic species by passive diffusion. In general, invertebratespecies, such as polychaete worms, insects, and crustaceans are more sensitive to thetoxic effects of chromium than vertebrates such as some fish. The lethal chromium level forseveral aquatic and terrestrial invertebrates has been reported to be 0.05 mg/litre. It inhibits seed germination and seedling growth, seed germination, inhibits diastase, (Ghafoor *et al*., 1995). Decreases dry matter production and yield (Agarwal, 2002). It also causes cancer of the digestive tract and stomach (EPA, 1990) in human, mucodermal ulceration, cancer of respiratory tract and allergic contact dermatitis of skin.

2.2.3 Lead

Lead is a dense, bluish-gray naturally occurring metallic element on the earth crust. It is widely distributed all over the world in form of its sulfide and ore galena. While a little may enter through natural processes (for example, erosion and runoff), human industrial activities such as metal smelters or refineries are responsible for the bulk of its presence in the environment (Environment Canada, 2010).

Lead has been used extensively, particularly in the making of lead-acid batteries (Environment Canada, 2010). It is also used to make lead shot and fishing weights, sheet lead, solder, some brass and bronze products, pipes, professional paints (other than paints for use by children), some ceramic glazes, dyes in paints and pigments, medical equipment (radiation shields), scientific equipment, and military equipment (ATSDR, 2007).

Lipstick can become contaminated with lead through the use of contaminated raw materials or the use of pigments that contain lead (USDL, 2004). Lead exposure in Canada hasdecreased since the 1970's, although everyone is exposed to trace amounts through air, soil, household dust, food, drinking water and various consumer products (Environment Canada, 2010). If lead is ingested, adults will absorb about 10 per cent into their blood, while children will absorb about 40 to 50 per cent (Ziegler *et al.,* 1978; ATSDR, 2007; Health Canada, 2009) and of the 30 to 50 per cent of available particulate matter that is inhaled, adults will absorb 80 per cent (Health Canada, 2009).

Skin contact with lead occurs every day, and the routine handling of inexpensive jewellery containing high levels can transfer lead to the skin (ATSDR, 2007). Some lead has been found to be absorbed through the skin (Health Canada, 2009). Dermal absorbed lead has been shown to be distributed throughout the body (Rastogi& Clausen, 1976; Lilley *et al.,* 1998). Pregnant women and young children are particularly vulnerable because lead can cross the placenta with ease and enter the foetal brain (USDL, 2004). Lead can also be transferred to infants via breastfeeding (ATSDR, 2007). Lead stored in bone serves as a source of foetal lead exposure (Rothenberg *et al.,* 2000).

After immediate exposure, humans are able to get rid of 50 per cent of the lead within two to six weeks (Health Canada, 1992), but it takes 25 to 30 years to get rid of 50 per cent of lead that has accumulated in the body over time (ATSDR, 2007; Health Canada, 2007). No safe blood level of lead is known, with even the lowest levels having been shown to affect a fetus and the central nervous systems in children (CDCP, 2010).

Small amounts are recognized as being hazardous to human health (Environment Canada, 2010). Infants, toddlers, children, fetuses, and pregnant women are most susceptible to its chronic low-dose effects (Health Canada, 2009; Health Canada, 2010). Chronic low-level exposure may affect the kidneys, cardiovascular system, blood, immune system, and especially the central and peripheral nervous systems (ATSDR, 2007). IQ deficits have been associated with high blood lead levels (ATSDR, 2007), and also those of low levels (Solomon *et al.*, 1995). Lead exposure has also been linked to miscarriages, hormonal changes, reduced fertility in men and women, menstrual irregularities, delays in puberty onset in girls (CSC, 2007), memory loss, mood swings, nerve, joint and muscle disorders, cardiovascular, skeletal, kidney and renal problems (Aremu, 2008). Lead and inorganic lead compounds have been classified as possible and probable carcinogenic to humans, respectively (IARC, 2010).

It was also one of the first substances to be considered "toxic" in Canada (Environment Canada, 2010). High-level acute exposures can cause vomiting, diarrhea, convulsion, coma, and death (Health Canada, 2007). In Canada, lead is restricted in gasoline and controlled when released from secondary lead smelters and steel mills (Health Canada, 2010, Singo, 2013).

2.2.4 Manganese

According to Microsoft Encarta premium, (2009), manganese is a slivery white, brittle metallic element principally used in the production of alloys. It does not occur in Free State, except in meteors but is widely distributed over the world in the form of ores, such as pyrolusites, rhodochrosites, franklinite, psilomelane, and manganite. It is hard to

melt, but easily oxidized. Manganese is reactive when pure, and as a powder it will burn in oxygen, it reacts with water (it rusts like iron) and dissolves in dilute acids (Bailey *et al.*, 1984).

Manganese is used to decolorize glass and make violet coloured glass. PotassiumPermanganate is a potent oxidizer and used as a disinfectant. Manganese dioxide is used in the production of fertilizers and ceramics, and also used as the cathode (electron acceptor) material in zinc-carbon and alkaline batteries. Manganese is essential for normal development and body function across thelife span of all mammals (Keen *et al.*, 2000; Njagi, 2013). Manganese binds to and/orregulates many enzymes throughout the body. It is a required co-factor forarginase, which is responsible for urea production in the liver, superoxidedismutase, which is critical to prevent against cellular oxidative stress, andpyruvate carboxylase, an essential enzyme in gluconeogenesis. The brain is themajor target organ for manganese toxicity as it retains manganese much longerthan other tissues. Following chronic overexposure, manganese can produce aprogressive, permanent neurodegenerative disorder, with few options fortreatment and no cure (Carl and Gallagher, 1994; Keen *et al*., 2000; Crossgroveand Zheng, 2004; Njagi, 2013).

2.2.5 Zinc

Zinc is a metallic chemical element found in reasonable abundance around the world. It is classified among the transition metals, along with nickel and mercury, among others. The metal is used in a variety of alloys and compounds which have a range of uses, from sunscreen to fine art.Living organisms also rely on it as a valuable nutritional

trace element; many foods are excellent sources, including seeds and whole grains (Newchurch*et al.*,1984, Singo, 2013).

Zinc is an essential nutrient in humans and animals and is necessary for thefunction of a large number of metalloenzymes. These enzymes include alcoholdehydrogenase, alkaline phosphatase, carbonic anhydrase, leucineaminopeptidase, superoxide dismutase, and deoxyribonucleic acid (DNA) andribonucleic acid (RNA) polymerase. An acute oral dose of zinc may causesymptoms such as tachycardia, vascular shock, dyspeptic nausea, vomiting,diarrhoea, pancreatitis and damage of hepatic parenchyma (Salgueiro*et al*., 2000; ATSDR, 2005).

When high levels of zinc are ingested inhibition of copper absorption throughinteraction with metallothionein at the brush border of the intestinal lumenoccurs. Both copper and zinc appear to bind to the same metallothioneinprotein; however, copper has a higher affinity for metallothionein than zinc anddisplaces zinc from metallothionein protein. Copper complexed withmetallothionein is retained in the mucosal cell, relatively unavailable fortransfer to plasma, and is excreted in the feces when the mucosal cells aresloughed off. Thus, an excess of zinc can result in a decreased availability ofdietary copper, and the development of copper deficiency (Gyorffy and Chan, 1992; Barone*et al*., 1998).

On the other hand zinc deficiency has been associated with dermatitis,anorexia, growth retardation, poor wound healing, hypogonadism withimpaired reproductive capacity, impaired immune function, and depressedmental function; increased incidence

of congenital malformations in infants hasalso been associated with zinc deficiency in the mothers (Sandstead, 1981; Elinder, 1986; Cotran*et al*., 1989).

2.3 SOURCES OF HEAVY METALS

Heavy metals exist naturally in the soil from the soil forming processes of disintegration of parent resources at rare levels (<1000 mg kg−1) and infrequently poisonous (Kabata-Pendias and Pendias, 2001; Pierzynski*et al*., 2000; Kamran *et al.*, 2013). Heavy metals comes from man-made sources trying to be more moveable in the soil, hereafter biologically available than soil forming phenomena (Kuo*et al*., 1983; Kaasalainen and Yli-Halla, 2003). Metal-containing solids at polluted places can originate from an extensive variation of man-made sources in terms of metal mine stakeouts, leaded gasoline and paints that are lead based, application of fertilizer, discarding high metal wastes in inappropriately protected landfills, animal manures, bio solids (sewage sludge), coal combustion remainders, compost, petrochemicals, pesticides and deposition in atmosphere (Basta *et al*., 2005; Khan *et al*., 2008; Zhang et al., 2010) are discussed here.

2.3.1 Fertilizer

Huge amounts of fertilizers are frequently applied to soils in concentrated farming systems to deliver suitable N, K and P for crop growth. The complexes used to offer these elements comprise rare quantity of heavy metals (for example Cadmium and Lead) as contaminations, that, after continual fertilizer application may meaningfully proliferate their quantity in the soil (Jones and Jarvis, 1981). Metals like Cadmium and Lead have no recognizedphysiological actions. Certain phosphatic fertilizer applications

unintentionally add Cd and other possibly dangerous elements for the soil, including F, Pb and Hg (Raven *et al*., 1998).

The use of organic manure and waste from dumpsite and the siting of dumpsite near farmland have contributed significantly to soil heavy metal pollution. Cadmium is a contaminant inchemical fertilizer, manure and sewage sludge (Ademoroti, 1996a; Ademoroti, 1996b; Ladigbolu and Balogun, 2011; Galadima and Garba, 2012). Waste dumpsites can transfer significant levels of toxic and persistent metalsinto the soil environment (Alloway, 1996; Olajire and Ayodele, 1996; Cobb *etal*., 2000; Udosen*et al*., 2006). These metals are taken up by plants andtransferred into the food chain (Benson and Ebong, 2005). Cultivated plantstake up these metals either as mobile ions in the soil solution through theirroots (Udosen*et al*., 2006) or through their leaves thereby making them unfitfor human consumption (Onianwa and Egunyomi, 1983; Chapel, 1986;Zupancic, 1997; Yusuf *et al*., 2003).Consequently, higher soil heavy metal concentration can result in higher levelsof uptake by plants (John *et al*., 1972). The rate of metal uptake by a plantcould be influenced by factors such as metal species, plants species, plant ageand plant part (Juste and Mench, 1992; Moreno *et al*., 2005; Amusan*et al*.,2005; Singh et al., 2010).

A common context of run-off deals with agriculture. When farmland is tilled and bare soil is revealed, rainwater carries billions of tons of topsoil into waterways each year, causing loss of valuable topsoil and adding sediment to produce turbidity in surface waters (FAO, 2007). The other context of agricultural issues involves the transport of agricultural chemicals (nitrates, phosphates, pesticides, herbicides, heavy metals etc) via surface runoff. This result occurs when chemical use is excessive or poorly timed with

respect to high precipitation. The resulting contaminated runoff represents not only a waste of agricultural chemicals, but also an environmental threat to downstream ecosystems (Ahmodu, 2012).

2.3.2 Pesticides

Numerous known insecticides used widely in agriculture in the past contained considerable amounts of metals. As in the recent past, near 10% of the chemicals have permitted for use as pesticides and in UK fungicides were based on complexes which comprise Cu, Hg, Pb, Mn or Zn. For Example, such pesticides that are fungicidal spray that contained copper like copper oxychloride and Bordeaux mixture that consists of copper sulphate (Jones and Jarvis, 1981). Lead arsenate was applied in fruit orchards for several years to regulate some parasitic pests. Compounds that consist of arsenic were applied widely to control livestock ticks and for the control of insects in banana in New Zealand and Australia, wood has been well-preserved with preparations of Copper, Chromium and Arsenic (CCA), and there are currently many neglected sites where soil amounts of these elements largely surpass background focuses. Such pollution has the capacity to result in problems, especially if sites are improved for other agricultural or non-agricultural purposes. Linked with fertilizers, the application of these ingredients has been more restricted, being localized to special sites or crops (McLaughlin et al., 2000).

2.3.3 Bio-Solid and Manures

The supply of various bio solids for example., composts, cattle's manure and municipal sewage sludge (MSS) to land unconsciously points towards the build-up of heavy metals like Arsenic, Cadmium, Chromium, Copper, Lead as well as Hg, Se, Ni,

Mo, Zn, Sb, in the soil (Basta*et al*., 2005). Some animal wastes like livestock, poultry and pig manures created in agriculture are usually supplied to crops and meadows either in the form of solids or semi solids (Sumner, 2000). Though most compost can be seen as valued fertilizers, in the poultry and pig industry, the Copper and Zinc are included in foods as growth enhancers and Arsenic presence in poultry fitness products may have the ability to cause metal pollution of the soil (Sumner, 2000; Chaney and Oliver, 1996; Kamran *et al.,* 2013). The manures that are created from animals as a result of these diets possess greater amounts of Cu, As and Zn and, if continually supplied to prohibited areas of land, can result in reasonable accumulation of these metals in the longer period of time in these soils.

Bio solids (including sewage sludge) are basically solid products organic in nature, formed by treatment processes of wastewater that can be usefully recycled (USEPA, 1994). Heavy metals most usually established in bio solids include Ni, Pb, Cd, Cu, Cr and Zn, and the metal amounts are ruled by nature and the strength of the industrial processes, as well as the sort of activity worked during the treatment of bio solids (Mattigod and Page, 1983). Under specific situations, metals supplied to soils by applying bio solids can be percolated downwards by the soil horizons and may have the ability to pollute groundwater (McLaren et al., 2005). Latest researches on some soils of New Zealand applied with bio solids have resulted in increased amounts of Ni, Cd and Zn in drainage percolates (Keller et al., 2002; McLaren et al., 2004).

2.3.4 Industrial Waste and Metals Mining Processing

Withdrawal and milling of metal minerals joined with industries have bequeathed various countries, the bequest of extensive circulation of metal pollutants in soil. Through withdrawal, tailings (larger particles settled at the end of the flotation cell while mining) are straight discharged in naturally occurring depressions, as well as onsite wetlands resulting in high amounts (Devolder, 2003). Widely, Lead (Pb) and zinc (Zn) mineral withdrawal and smelting have resulted in pollution of soil that causes danger to human and environmental health. Many retrieval methods that are used for these places are prolonged and costly and may not result in restoration of soil efficiency. Soil heavy metal's ecological threats to humans are connected to bioavailability. Assimilation routes encompass the incorporation of plant material that is grown in contaminated soils (food chain), or the ingestion of contaminated soils directly (Basta and Gradwohl, 1998; Kamran *et al.*, 2013).

Extra materials are produced by a variation of industries such as tanning, textile, petrochemicals from unintentional oil spills or consumption of petroleum-based products, insecticides and pharmaceutical industries and are extremely variable in configuration. Although certain products are disposed of on soil, some have assistances for agriculture and forestry. In addition, various are possibly dangerous due to their constituents of heavy metals like Cr, Pb and Zn or poisonous organic mixtures and are sometimes, if ever, supplied to land. Some others are actually little in plant nutrients or have no soil conditioning effects (Sumner, 2000).

2.3.5 Air Borne Sources

Aerial resource of metals that include chimney or duct releases of air, vapor streams or gas and brief discharge like dust from storage places and waste piles. Metals that are from airborne sources are usually discharged as particulates consist on the gas stream. Some metals like Cd, As and Pb can similarly volatilize by high temperature activities. These metals will change to oxides and shrink as smaller particulates until a reducing air is upheld (Smith et al., 1995; Kamran *et al.,* 2013). Emissions from chimney may be circulated over an extensive area by natural air flow still dry and/ or wet precipitation actions eliminate them from the gas tributary. Another chief source of soil pollution is the floating release of Pb from the burning of petrol having tetraethyl lead; this enhances considerably the part of Pb in soils of urban areas and in those next to main roads. Zinc and Cadmium can also be applied to soils next to roads; the sources include tyres and lubricant oils (USEPA, 1996).

2.3.6 Wastewater

Wastewater, which is also written as waste water, is any water that has been adversely affected in quality by anthropogenic influence. Wastewater can originate from a combination of domestic, industrial, commercial or agricultural activities, surface runoff or storm water, and from sewer inflow or infiltration (Tilley *et al.,* 2015). "Wastewater," also known as "sewage." Originates from household wastes, human and animal wastes, industrial wastewaters, storm runoff, and groundwater infiltration. Wastewater, basically, is the flow of used water from a community. It is 99.94% water by weight (Water Pollution Control Federation, 1980; Lin, 2007), and it is characterized by

volume or rate of flow, physical condition, chemical and toxic constituents, and its bacteriologic status (which organisms it contains and in what quantities). The remaining 0.06% is material dissolved or suspended in the water. It is largely the water supply of a community after it has been fouled by various uses (Lin, 2007).

The supply of wastewater coming from industrial land, municipal sources and associated wastes to soil dates back 400 years and is a usual practice now in different parts of the globe (Reed et al., 1995). Internationally, it is projected that 20 million (20m) hectares (ha) of arable land are watered with some sort of waste water. In various African and Asian cities, studies propose that agriculture relied on watering with wastewater contributes for 50 % of the vegetable source to urban areas (Bjuhr, 2007). Farmers usually are not worried about environmental welfares or dangers and are principally concerned with maximizing their productions and profits. Though the metal amounts in wastewater discharges are comparatively low, long-term watering of land with such wastewater can finally cause heavy metal build-up in the soil.

The use of urban wastewater in agriculture is an old practice which is receiving renewed attention due to the increasing scarcity of freshwater resources (Scott *et al.*, 2005). It is noted by Kirkham (1999) that the rising demands for water by agricultural, industrial and domestic sector has resulted in increased competition for limited freshwater resources available for use, which is estimated to be about 1% of the total water on our planet. Water needs and withdrawals were projected to grow in the future so new interventions would be required to bridge the shortfall. Rowe and Abdel-Magid (1995) states that the shortfall in supply of freshwater is sometimes covered by re-using

wastewater for toilet flushing, cooling in industries, artificial recharge of aquifers, landscaping and fire protection (Monyamane, 2011).

2.3.6.1 The Origin of Wastewater

The production of waste from human activities is unavoidable. Human waste (feces, used toilet paper or wipes, urine, or other bodily fluids), also known as blackwater, usually from lavatories, cesspit leakage, septic tank discharge, sewage treatment plant discharge, washing water (personal, clothes, floors, dishes, etc.), also known as greywater or sullage. Rainfall collected on roofs, yards, hard-standings, etc. Groundwater infiltrated into sewage; Surplus manufactured liquids from domestic sources (drinks, cooking oil, pesticides, lubricating oil, paint, cleaning liquids, etc.); Urban rainfall runoff from roads, car parks, roofs, sidewalks/pavements (contains oils, animal feces, litter, gasoline/petrol, diesel or rubber residues, soap scum, metals from vehicle exhausts, etc.).

A significant part of this waste will end up as wastewater (Mogens *et al.*, 2008). The quantity and quality of wastewater is determined by many factors. Not all humans or industries produce the same amount of waste. The amount and type of waste produced in households is influenced by the behaviour, lifestyle and standard of living of the inhabitants as well as the technical and juridical framework by which people are surrounded (Henze *et al.*, 2008). In households most waste will end up as solid and liquid waste, and there are significant possibilities for changing the amounts and composition of the two waste streams generated (Mogens *et al*., 2008). For institution, commercial and industry, similar considerations apply.

Wastewater use for agricultural irrigation can have multiple benefits for almost all countries, but it is particularly beneficial and cost-effective in low-income arid and semi-arid countries. In such areas additional low-cost water resources can have a high payoff in human welfare and health, with increased possibilities for food production and increased employment opportunities for poor population groups living in the peripheries of towns and cities, which are the source of copious wastewater streams.

The design of the sewer system affects the wastewater composition significantly. In most developing countries separate sewer systems are used. In these the storm water is transported in trenches, canals or pipes.

2.3.6.2 Wastewater Compositions

The constituents in wastewater can be divided into main categories according to Table 2.1. The contribution of constituents can vary strongly.

Table 2.1: Constituents present in domestic wastewater

Wastewater constituents		
Microorganisms	Pathogenic bacteria, virus and worms eggs	Risk when bathing and eating shellfish
Biodegradable organic materials	Oxygen depletion in rivers, lakes and fjords	Fish death, odours
Other organic materials	Detergents, pesticides, fat, oil and grease, colouring, solvents, phenols, cyanide	Toxic effect, aesthetic inconveniences, bio-accumulation in the food chain
Nutrients	Nitrogen, phosphorus, ammonium	Eutrophication, oxygen depletion, toxic effect
Metals	Hg, Pb, Cd, Cr, Cu, Ni	Toxic effect, bioaccumulation
Other inorganic materials	Acids, for example hydrogen sulphide, bases	Corrosion, toxic effect
Thermal effects	Hot water	Changing living conditions for flora and fauna
Odour (and taste)	Hydrogen sulphide	Aesthetic inconveniences, toxic effect.
Radioactivity		Toxic effect, accumulation

Source:Henze*et al.,* 2002

2.4 THE EFFECTS OF LAND USE ON WASTEWATER QUALITY

Land use is the management of land to meet human needs. This includes rural land use and also urban and industrial use (FAO, 1993). Pollutants from non-point

sources can vary widely due to the types of land uses within a watershed especially during the rainy season. A number of studies have been carried out to determine the relationship between land uses and various parameters of water quality. Some of the studies are discussed below;

2.4.1 Urban Land Use

Urban land uses are defined within this thesis as areas of increased impervious surfaces. However, urban land uses are not limited only to problems incurred by impervious surfaces. Other land uses classified under urban uses may include residential, industrial, and commercial areas, as well as roads and highways. The land's natural tendency to filter water is reduced when natural land is converted into impervious surfaces, such as roads, driveways, parking lots, and rooftops (Mallin*et al*., 2001).

Sowana*et al*, (2011),studied extensively on how expansion of land use in coastal areas resulted in natural resources being degraded, particularly by soil and water pollution. The researchers studied heavy metals contaminations through land-use types. In the study, of land-use types influence of heavy metals contamination of soils in Pattani Bay, Thailand, high-resolution SPOT satellite images were used and analyzed using ArcView GIS 3.2a and ENVI 3.5 software. Collections from 16 soil-sampling sites with topsoil and subsoil layers (0–20 and 21–50 cm in depth) from nine land-use types were carried out during March and April 2006. The heavy metals mercury, lead (Pb), cadmium, arsenic (As), and zinc were analyzed using a Perkin Elmer Optima 2100 DV. Results found that land uses in 2006 were mainly dominated by agricultural, residential, and mangrove-forest areas (Sowana et al., 2011).

Bannerman *et al*. (1993) studied critical urban source areas, which were defined as areas that produced large contaminant loading. Loading was evaluated by sampling from stormwateroutfalls that were representative of runoff from urban land uses. The samples were analyzed for 16 constituents including total and dissolved phosphorous, total and suspended solids, total and recoverable cadmium, chromium, copper, lead, and zinc, hardness, and fecal coliform bacteria. The geometric mean was analyzed in order to compare the data to loads outside of the sample area. The locations observed consisted of a residential area with 66.7% pervious surfaces, a commercial area with no pervious surfaces, and an industrial area with 38.4% pervious surfaces. Runoff from the streets had the largest mean concentrations in 10 out of the 16 contaminants studied in this test. Total recoverable zinc concentrations were highest in runoff collected from industrial roofs, and phosphorus was found in highest concentrations from lawns. Lawns contributed significant amounts of phosphorous loading, 2 – 18 times greater than other residential runoff sources (Bannerman *et al*., 1993; Aull, 2005).

Rooftops from urban areas were found to be a significant source of contamination by Van Metre and Mahler (2003). The researchers studied contaminant loadings from galvanized metal and asphalt shingles. These two types of rooftops are typically found within urban land uses. Twenty-two pollutants were measured, including, zinc, lead, pyrene, and chrysene. Rooftops were found to significantly contribute to loading of zinc and lead. 20% and 18 % of the total watershed load of zinc and lead, respectively, came from rooftops. The concentrations of zinc were in the range of 141 - 6200 mg/kg and lead ranged from 36 - 390 mg/kg for the 22 sampling dates (Van Metre and Mahler, 2003).

Basnyat*et al*. (1999) studied areas with different urban uses that contributed nonpoint source pollution to Weeks Bay, which eventually connects with the Gulf of Mexico. The water quality within the watershed was affected due to urban land use activities. Residential land uses observed in this study produced the greatest amount of nitrate in runoff (Basnyat*et al.*, 1999; Aull, 2005).

2.4.2 Agricultural Land Use

Agricultural and industrial pollution release large amounts of heavy metals into the atmosphere, surface water, soil, and plants (Cruz-Guzma´n et al., 2006). These toxic metals are washed off the atmosphere and soil surfaces as runoff into surface water bodies such as streams, lakes, rivers, etc. Agricultural land has been found to have significant, long lasting effects on water quality. Agricultural land uses include land used for the growth of crops, orchards, pastures, and sod, as well as livestock management.

Buck *et al*. (2003) studied areas in New Zealand, which were primarily used as agricultural lands for farming sheep and deer. Total nitrogen and nitrate were found to have a 99% statistical significance for the two study areas, as well as with turbidity and total phosphorous. High levels of bacterial indicators were observed during the high flood seasons in July reaching concentrations of 88,000 cfu/100 mL, 2000 times higher than the May sampling (Buck *et al*., 2003).

Large amounts of fertilizer and manure are put on agricultural lands in order to increasenutrients for crop growth. Elevated levels of nitrogen were observed in the Sumas River located in Washington state and British Columbia, resulting in surplus values averaging 120 kg/ha·yr. Levels 20 to 70 percent greater than the tolerance level

(100 kg N/ha) were observed by Berka*et al*. (2000). Agricultural land also has the capability to contribute sediments through runoff, which is the second highest contribution of nitrate in water (Basnyat*et al*., 1999; Aull, 2005).

Sowana*et al,* (2011),studied extensively on how expansion of land use in coastal areas resulted in natural resources being degraded, particularly by soil and water pollution. The researchers studied heavy metals contaminations through land-use types. In the study, of land-use types influence of heavy metals contamination of soils in Pattani Bay, Thailand, high-resolution SPOT satellite images were used and analyzed using ArcView GIS 3.2a and ENVI 3.5 software. Collections from 16 soil-sampling sites with topsoil and subsoil layers (0–20 and 21–50 cm in depth) from nine land-use types were carried out during March and April 2006. The heavy metals mercury, lead (Pb), cadmium, arsenic (As), and zinc were analyzed using a Perkin Elmer Optima 2100 DV. Results found that land uses in 2006 were mainly dominated by agricultural, residential, and mangrove-forest areas (Sowana *et al*., 2011).

In a later study performed by Mallin*et al,* (2001), stream fecal coliform counts weresignificantly higher in rural areas where animal production was located when compared to swampy areas with animal production. Mallin*et al*. (2001) concluded that waterbornemicrobial pathogens could be reduced through the reduction of impervious surfaces. Thiswas confirmed by Tufford and Marshall (2002), who showed that fecal coli formabundance was correlated to large areas of impervious surfaces (Aull, 2005).

2.4.3 Other Land Use Factors

Buck *et al*. (2003) showed that the influence of land use on water quality was scale dependant.The conclusions from this study showed that local land use was a significantfactor for smaller streams where upstream land use was a significant factor for largerstreams. Not only can land use affect the quality of water, but also the distance of theland use from the water source can affect quality. This was shown from 95% statisticallysignificant correlations of land use and sediment phosphorous levels 4000 meters awayfrom the source (Houlahan and Findlay, 2004).

In addition to land use, seasonal differences also impact receiving water quality (Berka*etal*., 2000). In this study, increased activity (26% increase of agricultural land use) wascorrelated to an increase in water pollution. In conjunction, a high amount of nitrates wasfound in the tributary during the winter (57% - 75% higher than summer seasons).Ammonia, phosphate, and coliforms were elevated during wet winters (Berka*et al*.,2000).

2.5 WASTEWATER USE IN URBAN AGRICULTURE

Increasing demand for irrigation water and organic fertilizers in urban centres to meet the demand of their rapidly growing population has led to the intensive use of organic waste products and wastewater in urban agriculture (Nafiu, 2010). Wastewater reuse as a substitute for clean water irrigation has equally spread to downstream of urban centres (Scott et al, 2004). Globally, around 20 million hectare of land is irrigated with municipal wastewater (raw, diluted or treated) (Qaisar et al., 2012). This figure is most likely to increase noticeably over the next few decades in responses to the growing levels

of water stress in inhibited catchments. Homsi (2000) reported that less than twenty percentage (< 20%) of these black waters (wastewaters) receive treatment in developing countries.

Wastewater irrigation plays a vital role in the fight against food insecurity through dry season farming produce of food crops to meet the ever increasing food demand of the growing population. It contains plant nutrients and organic matter, so this approach may increase soil fertility. However, wastewater composition is variable and contains high levels of toxic metals,therefore heavy metal contamination of agricultural soils has also become increasingly serious in sewage irrigation area (Mustafa, 2003; Jintao, 2011).

Wastewater use for agricultural irrigation can have multiple benefits for almost all countries, but it is particularly beneficial and cost-effective in low-income arid and semi-arid countries. In such areas additional low-cost water resources can have a high payoff in human welfare and health, with increased possibilities for food production and increased employment opportunities for poor population groups living in the peripheries of towns and cities, which are the source of copious wastewater streams (Hillel, 2010). However, in humid areas of low- and middle-income countries, wastewater flows from large urban areas are untreated and laden with the full spectrum of excreted bacterial, viral, protozoan, and helminthic pathogens endemic in the community, thus presenting a serious health risk when entering water sources used for irrigation (Shuval, 2010).

The use of urban wastewater in agriculture is an old practice which is receiving renewed attention due to the increasing scarcity of freshwater resources (Scott *et al.*, 2005). Agriculture has become water intensive according to the types of cash crops

grown for a growing global population which is estimated at over 6 billion (Battilani*et al.*, 2010; Monyamane, 2011). According to Gleick (1998), agriculture being the largest single user of water at 70% of total available freshwater is largely inefficient with only 40% of water supplied being ultimately used to grow crops. Mutengu*et al.* (2007)suggested that the use of urban wastewater for crop production is receiving increased attention in most parts of the world due to the increasing scarcity and high cost of fresh water resources and food especially in semi-arid and arid regions (Monyamane, 2011).

2.6 STANDARD OF IRRIGATION WASTEWATER IN AGRICULTURE

According to WHO (2005), municipal wastewater contains a number of potentially toxic elements such as Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Zinc, etc. which has invariably made heavy metal contamination of agricultural soils become increasingly serious in sewage irrigation area. Studies have shown that heavy metals are potentially toxic to crops, animals and humans when contaminated soils were used for crop production, because heavy metals are easily accumulated in vital organs to threaten crop growing and human health (Sharma et al., 2007; Jintao, 2011).

The control of water pollution has reached its point of primary importance both in developed and a number of developing countries.The prevention of pollution at source, the precautionary principleand the prior licensing of wastewater discharges by competent authorities have becomekey elements of successful policies for preventing, controlling and reducing inputs ofhazardous substances, nutrients and other water pollutants from point sources intoaquatic ecosystems.

In Nigeria, the Federal Environmental Protection Agency (FEPA) issued, in 1988, a specificdecree to protect, to restore and to preserve the ecosystem of the Nigerian environment. Thedecree also empowered the agency to set water quality standards to protect public health and toenhance the quality of waters. The standard of irrigation wastewater according to FEPA, FAO and Canadian regulator are tabulated in Table 2.2

Water quality criteria for irrigation water generally take into account, amongst otherfactors, such characteristics as crop tolerance to salinity, sodium concentration andphytotoxic trace elements. The effect of salinity on the osmotic pressure in theunsaturated soil zone is one of the most important water quality considerations becausethis has an influence on the availability of water for plant consumption. Sodium inirrigation waters can adversely affect soil structure and reduce the rate at which watermoves into and through soils. Sodium is also a specific source of damage to fruits.Phytotoxic trace elements such as boron, heavy metals and pesticides may stunt thegrowth of plants or render the crop unfit for human consumption or other intended uses.

Table 2.2: Selected Water Quality Criteria for Irrigational Waters (mgl^{-1})

Elements	FAO	Canada	Nigeria
Cadmium	0.01	0.01	0.01
Chromium	0.1	0.1	0.1
Lead	0.2	$(0.2 - 0.4)^1$	$(0.2 - 0.4)^1$
Manganese	0.2	0.2	0.2
Zinc	2.0	$(1.0 - 5.0)^2$	$(0.0 - 5.0)^2$

Where; (^{1}) represents the range for neutral and alkaline fine-textured soils and (^{2}) represents the range with soil pH > 6.5.
Sources: FAO, 1985; CCREM, 1987; FEPA, 1991

2.7 EFFECTS OF HEAVY METALS ON PLANTS

Soil is a valuable and non-renewable resource essential for germination of seeds, survival and growth of plants thus supporting every live form on earth. However in the modern world, numerous soil pollutants restrict the growth of plants. Abiotic stress factors including salinity, drought, extreme temperatures, chemical toxicity and oxidative stress from the environment are the major causes of worldwide crop loss that pose serious threats to agricultural produce. With the ongoing technological advancements in industrialization and urbanization process, release of toxic contaminants like heavy metals in the natural resources has become a serious problem worldwide. Metal toxicity affects crop yields, soil biomass and fertility.

Presence of heavy metals, like cadmium, lead, chromium, manganese and zinc in air, soil and water can cause bioaccumulation affecting the entire ecosystem and pose harmful health consequences in all life forms. Greater quantity of Heavy Metals in soils has been testified to prevent plant's progress in growth, uptake ofnutrients, physiological as well as metabolic processes. This also affects chlorosis, harm to root tips, minimizedwater and uptake of nutrients and impairment to enzymes (Baisberg-Påhlsson, 1989; Sanità di ToppiandGabbrielli, 1999; Kamran *et al.*, 2013).

Lead (Pb) has been reported to strongly affect the seed morphology and physiology. It inhibits germination, root elongation, seedling development, plant growth, transpiration, chlorophyll production, and water and protein content, causing alterations in chloroplast, obstructing electron transport chain, inhibition of Calvin cycle enzymes, impaired uptake of essential elements, Mg and Fe, and induced deficiency of CO_2 due to

stomatal closure (Pourrut*et al.*, 2011). Pb toxicity has been reported to retard the radical emergence via enhanced protein and carbohydrate contents, affecting the activity of peroxidases and polyphenol oxidases, oxidizing ability of roots and overall lowering of carbohydrate-metabolizing enzymes–α-amylases, β-amylases, acid invertases and acid phosphatases, (Singh *et al.*, 2011), and altering genomic DNA profile (Mohamed, 2001).Pb-polluted soils have been shown to inhibit seedling growth via increased lipid peroxidation, and activation of superoxide dismutase (SOD), guaiacol peroxidase (POD) and ascorbate peroxidase (APX) enzymes and the glutathione (GSH)-ascorbate cycle thus playing dominant role in removing H_2O_2. It also caused up-regulation of HSP70. Together with lipid peroxidation, HSP70 are reported to be markers for Pb-induced stress in soils (Wang *et al.*, 2010).

The major effects of heavy metals on seeds are manifested by overall abnormalities and decrease in germination, reduced root and shoot elongation, dry weight, total soluble protein level (Wang *et al.*, 2003), oxidative damage, membrane alteration, altered sugar and protein metabolisms, nutrient loss (Ahmad and Ashraf, 2011), all contributing to seed toxicity and productivity loss.

2.8 EFFECTS OF HEAVY METALS ON HUMAN

All heavy metals affect human and environment in different ways. For example, lead in the environment is mainly particulate bound with relatively low mobility and bioavailability. Lead does, in general, not bioaccumulate and there is no increase in concentration of the metal in food chains. Lead is not essential for plant or animal life. Of particular concern for the general population is the effect of lead on the central nervous

system. Lead has been shown to have effects on haemoglobin synthesis and anaemia has been observed in children at lead blood levels above 40 μg/dl. Lead is known to cause kidney damage (Baysal et al, 2013).

Metals can contaminate the general environment through many routes. Becauseof their stability, they may penetrate environmental compartments, in somecases, many years after the initial deposition pollution of the soil and watersystems may also arise from the weathering of disposed product (Nordberg *etal*., 2005). Heavy metal accumulations in plant and soil from natural andartificial sources and subsequent consequences represent importantenvironmental pollution problems. Food safety issues and potential adversehealth risks make this one of the most serious environmental concerns (Cui *etal*., 2004; Singh *et al*., 2011).

Some heavy metals such as copper, zinc, manganese, cobalt and molybdenumact as micronutrients for the growth of animals and human beings whenpresent in trace quantities, whereas others such as cadmium, arsenic andchromium acts as carcinogens (Freig*et al*., 1994; Trichopoulos*et al*., 1997).Mercury and lead are associated with the development of abnormalities inchildren (Gibb and Chen, 1989; Pitot and Dragan, 1996; Saplakoglu and Iscan,1997; Hartwig, 1998) have reported that long term intake of cadmium causesrenal, prostate and ovarian cancers.

Generally, at the biochemical levels, the toxic effects caused by excessconcentrations of heavy metals include competition for sites with essentialmetabolites, replacement of essential ions, reactions with –SH groups, damageto

cell membranes and reactions with the phosphates groups (AllowayandAyres, 1997; Nikolic and Sokolovic, 2004 ; Okoronkwo*et al*., 2005).

2.9 SOIL CHARACTERISTICS

2.9.1 Mineral Particles

Mineral particles are the largest ingredient and make up approximate 45% of soils. They are the original rock that got broken down by weathering and erosion to form the basis of soil. The type of rock that was broken down to form it is called the parent rock. The type of parent rock that got broken down to form the soil determines the degree of contamination of heavy metals of the formed soil.

2.9.2 Organic Matter

Organic matter is decayed vegetation that is broken down by micro organisms in the soil to form humus. Humus is a dark jelly like substance that binds the soil together and improves its texture. It increases the soils ability to retain moisture. Brown earths develop in area of deciduous woodland where there is an abundance of plant litter available to decay. When heavy metals contaminated plants are being used as sources of manure and for mulching, consequently, the soil becomes polluted with heavy metals.

2.9.3 Air and Water

Air is vital for the survival of micro-organisms and without these there would be a shortage of humus. Brown earths have a granular structure which allow for good aeration. Plants cannot survive without water present in the soil.Mineral particles are

soluble in water and the roots of plants can only absorb the nutrients of them after they have been dissolved.

2.9.4 Soil Colour

Lighter coloured soils deflect sunlight while dark soils absorb more light. This allows the soil to heat up much more quickly and encourages seed germination and crop growth. Heat is also important in the humification process. Brown earths have a high humus content which makes it a darker soil and thus supports good crop growth.

2.9.5 pH value

pH scale measures the degree of acidity and alkalinity of a substance. The ideal pH value for agriculture is 6.5 which is slightly acidic. A soil which is too acidic lacks calcium and potassium which are essential for growth and has low levels of organisms which are vital for humification. Soils which are quite acidic are peaty soils which have a pH value of less than 4and are found mainly in the mountainous areas of the west. They have suffered from leaching and tend to be waterlogged also. Brown earths have a pH value of between 5 and 7, ideal values that are known to be very fertile supporting a wide variety of plant life

2.9.6 Soil Texture

Soil texture refers to the relative amounts of differently sized soil particles, or the fineness/coarseness of the mineral particles in the soil. Soil texture depends on the relative amounts of sand, silt, and clay. In each texture class, there is a range in the amount of sand, silt, and clay that class contains.Texture is how a soil feels when you

touch it. The proportions of sand silt and clay determines the soils texture. The texture determines how well moisture and roots can penetrate the soil and how well excess moisture can drain away.

2.10 TYPES OF SOILS

2.10.1 Loamy Soil

Loam is the soil material that is medium-textured. It feels as though it contains a relatively even mixture of sand, silt and clay because clay particles with their small size, high surface areas and high physical and chemical activities, exert a greater influence on soil properties than those of sand and silt. Loam soils are rather soft and friable. It has a slightly gritty feel, yet it is fairly smooth and slightly sticky and plastic when moist. Casts formed from this type of soils can be handled freely without breaking (Oyebode, 2010; Ahmodu, 2012).

2.10.2 Clay Loam Soil

This consists of soil material having the most even distribution of sand, silt and clay of any of the soil textural grade. When felt, it feels as if it posses more clay than sand or silt. Sticky and plastic when wet, it forms casts that are firm when moist and hard when dry. The moist soil forms a thin ribbon that will barely sustain its own weight when squeezed carefully between the thumb and fingers (Oyebode, 2010; Ahmodu, 2012).

2.10.3 Sandy Loam Soil

Sandy loams consist of soil materials containing somewhat less sand and more silt and clay than loamy sands. As such, they possess characteristics, which fall between the finer-textured sandy clay loam and the coarser-textured loamy sands. Many of the individual sand grains can still be seen and felt, but there is sufficient silt and/or clay to give coherence to the soil so that casts can be formed that will bear careful handling without breaking (Oyebode, 2010; Ahmodu, 2012).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

3.1.1 Equipment

Atomic Absorption Spectrophotometer, Serial number; AA500, made in Germany

Flame photometer, Model PFP 7, JENWAY

pH meter, Model pHS-25, made in China

Electrical conductivity meter, Model HI9835, USA

Water Pumping Machine and Hose

Pipette Hand pump, WREE Department, A.B.U, Zaria

Hand gloves, Latex Agary Pharmaceutical Limited Malaysia.

Geographical Positioning Systems (GPS), Geography Department, A.B.U, Zaria

Mechanical Stirrer, Soil Science Department, A.B.U, Zaria

Weighing balance,G & G, J.J 3000 Gallenkamp Ltd

Soil auger, Soil Science Department, A.B.U, Zaria

2mm Sieve

Filter paper-Whatman No. 39

Mortar and pestle, Soil Science Department, A.B.U, Zaria

Oven (Thelco)

Thermometer

Hydrometer

Retort stand with clamp

Hoe and Cutlass, Samaru Market, Zaria

Polyethylene bags, Samaru Market, Zaria

Plate 1: AAS, (Mode; AA500) **Plate 2:**The pH meter (model pHS-25)

Plate 3: Flame photometer (model PFP 7, JENWAY), **Plate 4:** EC meter (HI9835)

3.1.2 Reagents

Sodium pyrophosphate solution

Potassium dichromate solution ($K_2Cr_2O_7$), BDH Chemical Limited Pool England

Ammonium ferrous sulphate solution,SG 0.88 Griffin/George Middlesex England

O-phenanthroline-ferrous sulphate indicator, BDH Chemicals Limited Poole England

Tetraoxosulphate (VI) acid (H_2SO_4),BDH Pool Limited England

Hydrochloric acid (HCL), BDH Pool Limited England

Perchloric Acid, BDH Pool Limited England

Ethylenediaminetetraacetic acid (EDTA), solution (950g/c) Analytical grade BDHUK

Ammonium hydroxide (buffer solution) BY BOH UK

Nitric acid (HNO_3),Josephine Bergers International

Distilled water

Ammonium chloride

Ferrochrome black T

3.1.3 Glass wares

Burette, PYREX 250 mlENGLAND

Pipette, JAYTEC BS 700 TYPE 1 10 ml ENGLAND

Erlenmeyer flask, PYREX 250 mlENGLAND

Sterile tight bottles

Beaker,PYREX 50ml ENGLAND

Beakers,PYREX 250 ml ENGLAND

Conical flasks,PYREX 50 ml ENGLAND

Volumetric flask, 100ml Technico BS 1792 B in 20^oC

Sterile sample plastics (swam water plastics)

Funnel

3.2 DESCRIPTION OF PROJECT AREA

3.2.1 Study Area

Zaria metropolis comprises Zaria and SabonGari Local Governments of Kaduna State, Nigeria. It is situated on the High Plains of Northern Nigeria and it is approximately 670m above sea level. It is located on latitude 11^0 42^1 N and longitude 07º 04' E according to Arowolo(2000); Inobeme *et al., (*2011); Obadaki(2007). Zaria Metropolis is presently one of the most importantcities in Northern Nigeria (Uba *et al.*, 2007). It has a land mass of 300km^2 and it is the seat of a number of well recognized and prominent tertiary institutions such as; the great Ahmadu Bello University, Federal Institute of Chemical and Leather Research, Nigeria College of Aviation Technology and Federal College of Education.

Zaria metropolis has a stream whose watercourse runs through it, and the stream has a number of tributaries. The stream is well known as Kubanni River, and it has its source from the Kampagi hill in Shika near Zaria. It flows in aSoutheast direction through the premises of Ahmadu Bello University. The Samaru streamwhich is one of the tributaries of Kubanni River has a stream length of 1.05km within an area of 2.28km^{2}and has drainage density of 0.4605 km/km^2 (Yusuf and Shuaib, 2012). The study site is a low-lying plain underlined with shallow aquifers known as "Fadama" in Hausa. It is usually water-logged and flooded during the rainy season. The vicinity is the seat of a number of economic activities ranging from automobile wash and repair services to agricultural activities involving the cultivation of the land using the wastewater generated in absence of rain. Figure 3.1 shows the map of the study area.

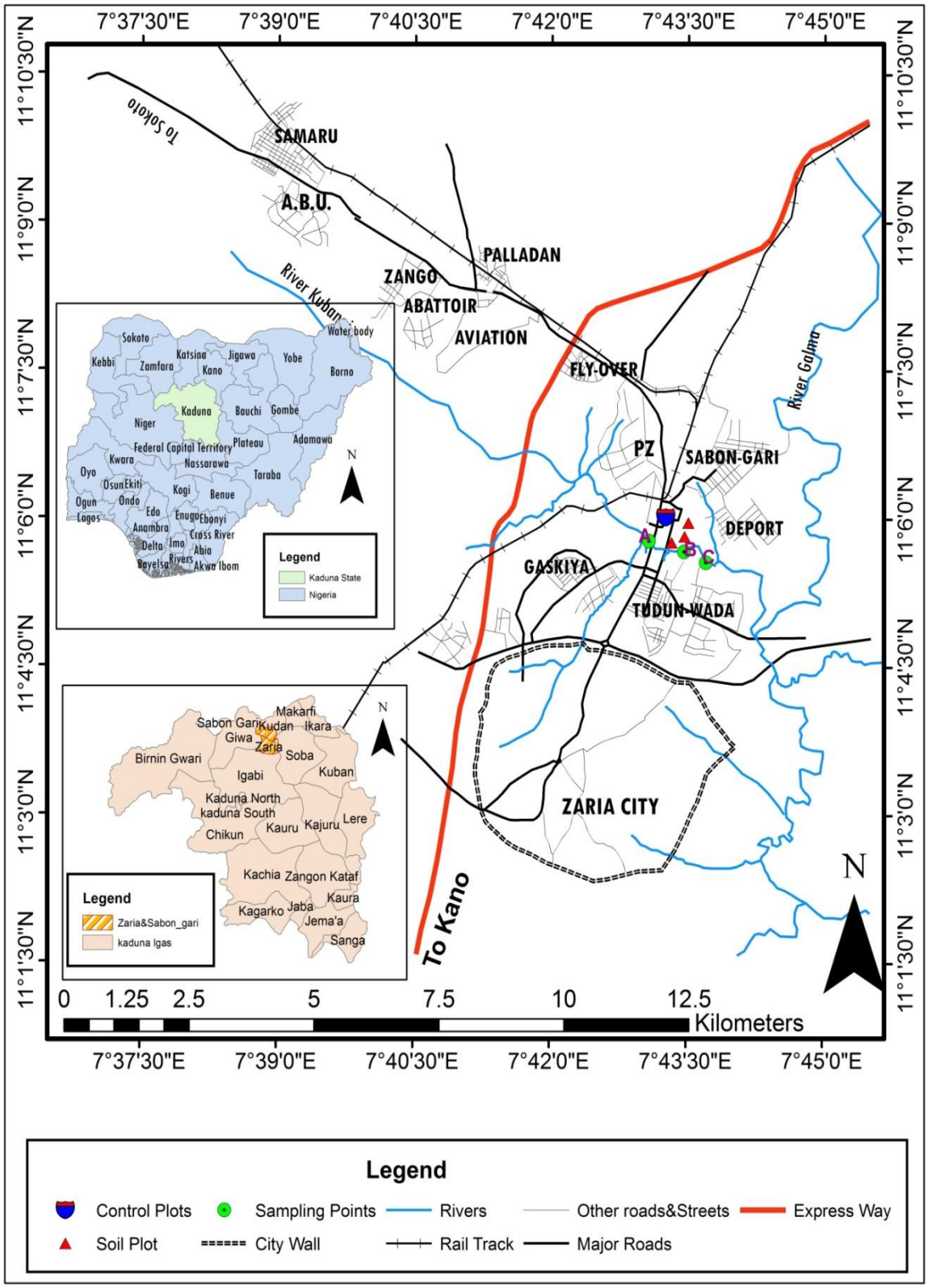

Figure 3.1: Map of Zaria Metropolis Showing Sampling Sites**.**
Source: Zaria Quirk Bird (2014).

3.2.2 Vegetation and Land Use

Zaria falls within the grass or shrub land vegetation belt known as northern guinea savannah. It is mostly dominated by perennial grasses with clumps of trees.Due to intensive fallow type of agricultural practice and grazing of the land, the area is dominated by stunted shrubs; interspersed with moderate height tree and perennial foliage. Similarly, due to human activities and land use abuse which is characteristic of most expanding urban centre in Nigeria, the site is fast losing its remaining tree species to development. The issue of land-use/land-coverchanges (LULCC) in urban areas has always been amajor concern (Saleh, 2009) especially agricultural land.Therefore, land-use change continues to put agriculturalland at risk of conversion (Saleh *et al.*, 2014). Although, some parts of the area is still being used as farm and grazing land by the residents of Zaria and her environs as it drives significant economic activity, supports countless livelihoods particularly those of farmers and effective in reducing hunger and malnutrition.

3.2.3 Climate

3.2.3.1 Rainfall

The climate of the study area is a tropical savannah climate, with distinct dry and wet seasons (Aw climate Koppens classification). It possesses a tropical climate with a pronounced dry season, lasting up to seven months (October - May). During the dry season, a cold period is usually experienced between November and February.' This emanates from the influence of the North-Easterly winds (the Harmattan) which control the tropical continental air mass coming from the Sahara. The wet season also known as

rainy season, lasts from May to September/October with long-term annual rainfall of 1040mm in about 90 rainy days.

3.2.4 Soils of the Area

The major soil found in this area is the sandy loam type with a sparse distinction of the sandy–clay soil and sandy soils. This has so far encouraged the residents of Zaria metropolis and neighboring villagers to use the land for agricultural activities such as farming and grazing by the nomadic cattle farmers.

3.2.5 Sampling Points and Plots Description

From April, 2015 to June, 2015, three sampling points (A, B and C) were randomly selected along Kubanni watercourse for physiochemical analysis of some water quality parameters in order to understand the relationship between human health risks and food (vegetables) chain contamination of heavy metals as a result of wastewater irrigation. A total of thirty (30) wastewater samples were collected for analysis during dry season irrigation. Figure 3.1, shows the sampling points and their coordinates are; $11^0\ 05^1\ 43.74^{11}$N and $7^0\ 43^1\ 06.93^{11}$Efor A, $11^0\ 05^1\ 39.22^{11}$N and $7^0\ 43^1\ 17.06^{11}$Efor B and $11^0\ 05^1\ 40.52^{11}$N and $7^0\ 43^1\ 23.76^{11}$ E for C. The sampling points were taken at random. The mid sample point was the water sources point (water pump suction point) for wastewater irrigation, while the two other sample points were far away at both sides along the watercourse. All sample points were approximately 200m apart.

The exact size of each plot was the estimated size of the catchment planned for the study. Three project plots of dimensions 3m X 4m were used for this study. Each plot

was properly tilted and all necessary land preparations required for planting the vegetables were properly carried out. Each plot was essentially cultivated as a monoculture; only a vegetable crop from a class of vegetables was planted on a plot. The vegetables planted and their classes are; *Daucuscarota*, common name: Carrot, Hausa name: Karas, class: Root crop (Plot A), *Spinaciaoleracea,* common: name Spinach, Hausa name: Alayyafo, class: Leaf crop (Plot B), *Brassica oleracea,* common name: Cabbage, Hausa name: kabeji, class: Head crop (Plot C). They were considered as representative of vegetable species commonly consumed in the area under study.Ridges were made for both cabbage and carrot plots after disturbing the soil unlike for spinach plot where it was raised and levelled bed. Plate 1 and 2, shows the farm site and a sampling point.

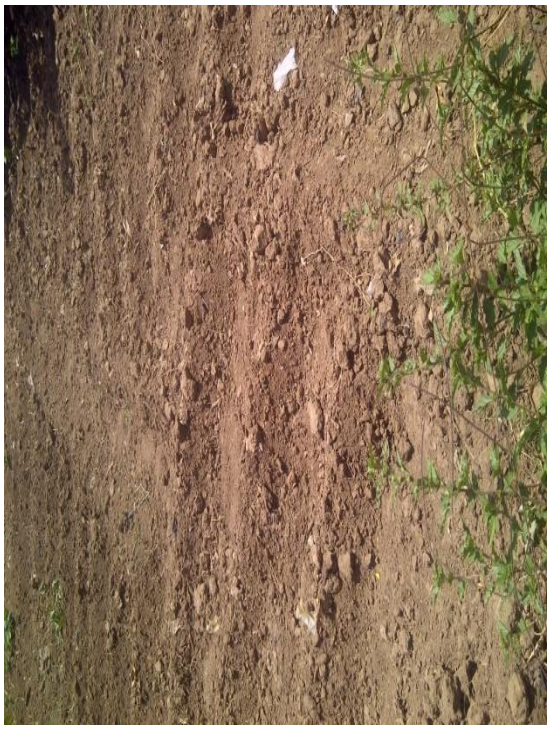

Plate 5: Site preparation

Plate 6: The irrigation source point in front of a dumpsite and a man making the connections.

3.3 Methods of Measurement

3.3.1 Soil Analysis

Soil samples were collected from each plot using a hand auger. The auger was position vertically upright on the soil surface. The handle was turned clockwise until the cylinder was full. It was lifted from the hole and the content emptied into a container. The samples were taken at a depth of 20cm. A composite sample was composed of five subsamples at each sampling site. The sample was labelled before taking the next sample point. The soil samples were individually sealed into polyethylene bags to avoid cross-contamination and transferred to the laboratory on the same day of sampling. The labelled soil samples were air-dried in the laboratory to constant weight, after which the samples were crushed and passed through a 2mm sieve to get fine fractions and stored for further analysis. A total of nine (9) soil samples were collected and analyzed.

3.3.1.1 Particle Size Analysis

The analysis was carried out according to Bouyoucos (1962). A sample (50 grams) of air dry soil was weigh into a 250ml beaker. 100ml of dispersing agent (sodium pyrophosphate solution) is added to the soil sample, mixed and allowed to soak for at least 30 minutes. The suspension is mixed for about 3 minute with a mechanical stirrer before transferring the content into a sedimentation cylinder and filled to mark with distilled water. A hand stirrer was inserted into the sedimentation cylinder to mix the content thoroughly and the time of completion of stirring was noted. A hydrometer was carefully lowered into the suspension and reading was taken after 40 seconds (R_{40}). The sands settled in about 40 seconds (silt and clay remains in suspension) and a hydrometer

reading taken 40seconds determined the grams of silt and clay remaining in suspension. The hydrometer was removed and the temperature of the suspension was taken using a thermometer. The suspension was disturbed. Two hour after the final mixing of the suspension sand and silt would have settled (only clay remains in suspension). Another hydrometer and temperature reading was taken (R_{2hrs}). A blank sample containing 100ml of dispersing agent and 1 liters of distilled water was measured into a cylinder. The hydrometer was lowered into the solution carefully and readings were taken after 40 seconds (R_a) and readings after two hours (R_b). After the hydrometer readings have been obtained, the soil water mixture is poured over a screen to remove the entire sand fraction. The separated soil Percentage is calculated from eqn 3.1 and 3.2 respectively.

$$\% \text{ Sand} + \text{loamy} = \frac{(\text{Reading after forty seconds} - R_a) + R_c}{\text{Weight of soil}} \text{ X } 100 \quad (3.1)$$

$$\% \text{ loamy} = \frac{(R_{2hrs} - R_b) + R_d}{\text{weight of soil}} \times 100 \quad (3.2)$$

Where;

R_a= 40 sec, blank hydrometer reading

R_b= 2 hr, blank hydrometer reading

R_c= 40sec (Temperature × 0.360)

R_d = 2 hr correction factor (temperature × 0.36)

W = weight of soil sample used.

3.3.1.2 Soil Textural Class

The textural class was determined from the particle size analysis. After determining the distribution of sand, silt and clay from the particle size analysis, the soil was assigned a textural class based on the USDA soil textural triangle. Within the textural triangle are various soil textures which depend on the relative proportion of sand, silt and clay particles.

3.3.2 Organic Carbon

The analysis was performed according to Walkley-Black (1979). To 1g of soil sample in a 250ml erlenmeyer flask, 5ml of $K_2Cr_2O_7$ was added and swirled to disperse the soil. Thereafter, 10ml of concentrated H_2SO_4 was added and swirled for 1 minute. The Erlenmeyer flask was then kept on an asbestos sheet for the next 30 minutes (because end point is easily reached if suspension is cold). 5 drops of indicator (O-phenanthroline-ferrous sulphate) was added and the solution was titrated with ammonium ferrous sulphate solution with a white background. A blank sample was also made without the soil samples in similar manner. The organic carbon percentages of the soils were then estimated using the eqn 3.3.

$$OrgC\% = \frac{(blanktitre - actualtitre) \times 0.3 \times m \times f}{Weight\ of\ air\ dry\ soil\ taken} \quad (3.3)$$

Where;

m = Concentration of ammonium ferrous sulphate (mg/l).

f = Correction factor (1.33)

3.3.2.1 Organic Matter

The organic matter of the soil samples were estimated using the eqn 3.4 below and the determined organic carbons.

$$\% OM = \%OC \times 1.724 \quad (3.4)$$

Where;

$\% OM$= Percentage organic matter

$\%OC$= Percentage organic carbon

3.3.3 Soil pH

To 10g of 2mm sieved air-dried soil sample in a 50ml beaker, 25ml of distilled water was added and stirred for 30 minutes. Then, the soil suspension was allowed to stand for about 30 minutes more undisturbed. A pH meter calibrated with buffer solution, 4.0, 7.0, and 9.0 was then used to determine the pH of the soil. The pH probe was suspended in the liquid until the pH meter indicated a stable reading was achieved. Thereafter, the above procedure was used with 0.01M $CaCl_2$ solutions and the reading was noted.

3.3.4 Cation Exchange Capacity (CEC)

The Cation Exchange Capacity of the soils from the experimental plots was estimated with the eqn 3.5 (Foth, 1943).

$$\mathrm{CEC} = (2.5 \times \%\mathrm{O.M}) + (0.57 \times \%\mathrm{Clay}) \quad (3.5)$$

3.3.5 Extractable Heavy Metals

To 1g of 2mm sieved air-dried soil sample in a 100ml plastic bottle, 50ml of 0.1M HCL was added, which is the extracting agent. The mixture was thoroughly shaken for 30 minutes. The mixture was then passed through a filter paper whatman paper. The filtrates were then stored in plastic bottles and were analyzed for lead, cadmium, chromium, zinc, and manganese by atomic absorption spectrophotometer model AA500 in Soil Science Department, Ahmadu Bello University, Zaria.

3.4 WASTEWATER ANALYSIS

3.4.1 Wastewater pH

The measurement of pH was by electrometric method according to standard methods (Apha*et al.,* 1998) an analysis of hydrogen ions activity in a water sample. A pH meter model pHS-25 was used to determine the pH value or hydrogen ions activity in the water samples. The pH and temperature probes were suspended in the liquid until the pH meter indicated a stable reading.

3.4.2 Electrical Conductivity (EC)

The measurement of electrical conductivity was by electrometric method according to standard methods (Apha *et al.,* 1998). An electrical conductivity meter of model HI9835 was used to determine the EC of the samples. The probe was suspended in the wastewater until the EC meter indicated a stable reading.

3.4.3 Soluble Calcium and Magnesium

The measurement of soluble calcium and magnesium was done accordance with the standard methods by titrating 10 ml of water sample with 0.01 normal EDTA in the presence of ammonium chloride + ammonium hydroxide buffer solution using ferrochrome black T as indicator (Apha *et al.,* 1998).

3.4.4 Sodium and Potassium

The same water samples were analyzed according to standard methods with flame photometer, model PFP 7, JENWAY.

3.4.5 Sodium Absorption Ratio (SAR)

Sodium adsorption ratio of water samples was calculated with the eqn 3.6.

$$S.A.R = \frac{Na^{+}}{\sqrt{\frac{1}{2}(Ca^{2+}+Mg^{2+})}} \quad (3.6)$$

Where;

S.A.R = Sodium adsorption ratio

Na^{+} = Concentration of sodium ions (meq/l)

Ca^{2+} = Concentration of calcium ions (meq/l)

Mg^{2+} = Concentration of magnesium ions (meq/l)

3.4.6 Heavy Metals

The water samples were digested with 0.1M of HCL, poured into plastic bottles and was taken for analysis of lead, cadmium, chromium, zinc, and manganese by using atomic absorption spectrophotometer model AA500 in Soil Science Department, Ahmadu Bello University, Zaria.

3.5 PLANTS ANALYSIS

A total of one hundred and twenty (120) vegetables samples were collected in the polythene bags and the vegetable crops were taken to the laboratory within one hour of harvesting and washed as would be done during normal food preparation to remove any surface deposits. They were separated into edible and non-edible parts and five composite samples formed for each species. Only the edible part of each vegetable sample was used for analysis.The samples were air dried in the laboratory for two days after washing and then oven dried at 104^0C for 3hours.

One gram of oven dried plant sample was taken in 50ml conical flask and was kept for overnight after adding 5ml concentrated nitric acid and 5ml perchloric acid. Next day 5ml concentrated nitric acid was added again and then digested on the hot plate till material became clear. The digested material was cooled down and its volume was made up to 20ml with double distilled water by using volumetric flask and then stored in clean air tight bottles for the analysis of lead, cadmium, chromium, zinc and manganese by atomic absorption spectrophotometer (Rashid, 1986), model AA500 in Soil Science Department, Ahmadu Bello University, Zaria.

3.6 DATA ANALYSIS

All statistical analysis were done with Microsoft excel 2007.

3.6.1 Transfer Factor

Heavy metal concentrations in the extracts of soils and plants were calculated onthe basis of dry weight. The plant concentration factor (PCF) was calculated using the eqn 3.7 (Cui *et al*., 2005).

$$PCF = \frac{C_{Plant}}{C_{Soil}} \quad (3.7)$$

Where;

PCF = Plant concentration Factor

C_{Plant}= Heavy metal concentration in plant (mg/l)

C_{Soil} = Heavy metal concentration in soil (mg/l)

3.6.2 Pollution Load Index

The degree of soil pollution for each metal was measured using the pollutionload index (PLI) technique depending on soil metal concentrations. The following modified eqn 3.8 was used to assess the PLI level in soils (Liu *et al*., 2005).

$$PLI = \frac{C_{Soil}}{C_{Ref}} \quad (3.8)$$

Where;

C_{Soil} = Heavy metal concentration in sampled soils of the cultivated plots (mg/l).

C_{Ref} = Heavy metal concentration of referenced soil (mg/l)

PLI = Pollution load index of the soil

3.6.3 Daily Intake of Metals (DIM)

The daily intake of metals (DIM) was determined by the following eqn 3.9 (Rattan *et al.*, 2005).

$$DIM = \frac{C_{Metal} \times C_{factor} \times D_{food\ intake}}{B_{Weight\ average}} \quad (3.9)$$

Where;

DIM= Daily intake of metals (mg/day)

C_{Metal} = Heavy metal concentration in plant (mg/kg)

C_{factor} = Conversion factor (0.085)

$D_{food\ intake}$ = Daily intake of vegetables (g/day)

$B_{Weight\ average}$ = Average body weight (kg)

3.6.4 Health Risk Index

The health risk index (HRI) for the locals through the consumption of contaminated vegetables was assessed based on the food chain and the reference oral dose (RfD) for each metal using the eqn 3.10 (US – EPA, 2002).

$$HRI = \frac{DIM}{RfD} \quad (3.10)$$

Where;

DIM= Daily intake of metals (mg/day)

RfD = Reference oral dose (mg/kg bw/day)

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 SOIL

The soil characteristics of the three plots considered for this dissertation were analyzed in Soil Science Department of Ahmadu Bello University, Zaria, and its results are discussed below.

4.1.1 Soil Texture

The results of the textural class of the soil in the experimental plots as determined from the department of soil science laboratory using USDA soil texture triangle, are shown in Table 4.1, 4.2 and 4.3, which shows the different percentages of the various soil components which makes up the loamy soil. Loam, for many reasons, is a rich, nutritious and healthy mixture that helps a diverse group of plants and vegetables thrive.

Table 4.1: Textural properties of representative soil unit of Carrot experimental plot

Sampling Dates	% Sand	% Silt	% Clay	Soil Type
16th April, 2015	49	42	9	Loam
14th May, 2015	47	43	10	
17th June, 2015	48	44	8	
Minimum	47	42	8	
Maximum	49	44	10	
Average	48	43	9	
Standard Dev.	1	1	1	

Table 4.2: Textural Properties of the Spinach plot

Sampling Dates	% Sand	% Silt	% Clay	Soil Type
16th April, 2015	48	44	8	Loam
14th May, 2015	46	45	9	
17th June, 2015	47	43	10	
Minimum	46	43	8	
Maximum	48	45	10	
Average	47	44	9	
Standard Dev.	1	1	1	

Table 4.3: Textural Properties of the Cabbage Plot

Sampling Dates	% Sand	% Silt	% Clay	Soil Type
16th April, 2015	43	47	10	Loam
14th May, 2015	39	49	12	
17th June, 2015	44	45	11	
Minimum	46	45	10	
Maximum	44	49	12	
Average	42	47	11	
Standard Dev.	1	1	1	

Soils generally have specific ranges of particle sizes. The smallest particles are clay particles and are classified by the USDA and FAO as having diameters of less than 0.002 mm. while the largest particles are sand particles with their diameters larger than 0.05 mm in diameter. Furthermore, large sand particles can be described as coarse,

intermediate as medium, and the smaller as fine (Ahmodu, 2012).Details of which are presented in Table 4.4 below. More so, soil texture plays an important role in mobility of metals in soil, as it reflects the particle size distribution of the soil and thus the content of fine particles like oxides and clay. These compounds are important adsorption media for heavy metals in soils (Shreene, 2010).

Table 4.4: Soil Classification

Name of soil separate	Diameter limits (mm) (USDA and FAO classification)
Clay	less than 0.002
Silt	0.002–0.05
Very fine sand	0.05–0.10
Fine sand	0.10–0.25
Medium sand	0.25–0.50
Coarse sand	0.50–1.00
Very coarse sand	1.00–2.00

Source: Oyebode, (2010)

4.1.2 Soil Organic Matter

The results of the organic matter of the soils in the experimental plots are shown in table 4.5, which shows the different percentages (%) of this vital component of the soil in each plot used for the cultivation of *Daucuscarota*, *Spinaciaoleracea*and *Brassica oleracea*. *Daucuscarota* plot has percentage organic matter range, average and standard deviation of 2.51-2.56, 2.53 and 0.02516, while *Spinaciaoleracea*and *Brassica oleracea*plots have ranges, averages and standard deviations of 1.79-1.98, 1.86 and 0.102144 and 1.79-1.98, 2.03 and 0.078102 respectively. The results showed that, the organic matter rating for each plot was moderate according to the organic matter rating of

Soil Science Department of Ahmadu Bello University, Zaria. Although, it value decreased as the rainy season approached due to seasonal variation in weather conditions as well as soil physical conditions.

The positive impacts of soil organic matter result from a number of complex, interactive edaphic factors; a non-exhaustive list of soil organic matter's effects on soil functioning includes improvements related to soil structure, aggregation, water retention, soil biodiversity, absorption and retention of pollutants, buffering capacity, and the recycling of storage of plant nutrients. It increases soil fertility by providing cation exchange sites and acting as reserve of plant nutrients, especially nitrogen (N), phosphorus (P), and sulphur (S), along with micronutrients, which is slowing released upon soil organic matter mineralization. As such, there is a significant correlation between soil organic matter and soil fertility.

Table 4.5: The Soil percentage organic matter of the experimental plots

Sampling Dates	% Organic Matter		
	Carrot Plot	Spinach Plot	Cabbage Plot
16th April, 2015	2.56	1.98	2.12
14th May, 2015	2.53	1.82	1.99
11th June, 2015	2.51	1.79	1.98
Minimum	2.51	1.79	1.79
Maximum	2.56	1.98	1.98
Average	2.53	1.86	2.03
Standard Dev.	0.02516	0.102144	0.078102

4.1.3 Soil pH

The results of the pH of the soils as determined using water in the experimental plots are shown in Table4.6. In the *Daucuscarota* (Carrot) plot results showed that the soil pH value ranged from between 6.30-7.10, with an average and standard deviation of 6.77 and 0.416333, while *Spinaciaoleracea*(Spinach), and *Brassica oleracea*(Cabbage) had their range, average and standard deviation as, 6.90-7.40, 7.20, 0.264575 and 7.20-7.60, 7.40 and 0.20 respectively. The changes in the pH of the soil within the growing period of the vegetables could be traced to the irrigation water applied to the soil which had slightly higher pH value compared to the soil pH value as shown in Table 4.13. The pH of the vegetable farms ranged between slightly acidic to slightly alkaline medium. These soil pH values are within the range for cultivation of such vegetables. A pH range of 6.6-7.3 is neutral, pH values lower than 6.6 are acid, pH values higher than 7.3 are alkaline.

Table 4.6: The Soil pH of the experimental plots

Sampling Dates	Soil pH		
	Carrot Plot	Spinach Plot	Cabbage Plot
16th April, 2015	6.30	6.90	7.20
14th May, 2015	7.10	7.40	7.40
11th June, 2015	6.90	7.30	7.60
Minimum	6.30	6.90	7.20
Maximum	7.10	7.40	7.60
Average	6.77	7.20	7.40
Standard Dev.	0.416333	0.264575	0.2

4.1.4 Electrical Conductivity of Soil (EC_e)

Table 4.7 shows the electrical conductivity of the experimental plots during the dry season wastewater irrigation land cultivation. The electrical conductivity (EC_e) of the entire experimental plots during the dry season irrigation farming with wastewater, had an EC_e range, average and standard deviation of values; 0.250-0.275ds/m, 0.265ds/m and 0.000175, 0.085-0.087ds/m, 0.086ds/m and 0.000001, and 0.070-0.075ds/m, 0.072ds/m and 0.0000063, for carrot, spinach and cabbage plots respectively. According to A and L laboratories (2005), the electrical conductivity of soils increases with increasing soluble salts, and the soil maybe considered as saline when the conductivity reading reaches 0.2 to 0.3 ds/m. Hence, the EC_e of the experimental plots were below salinity limit, except the Carrot plot which had an EC_e between 0.2-0.3ds/m and therefore saline. Hence, experimental plot A was saline and its salinity increased with the applied irrigation wastewater.

Table 4.7: The Electrical Conductivity (EC_e) of the experimental plots

Sampling Dates	Electrical Conductivity of Soil (EC_e) in ds/m		
	Carrot Plot	Spinach Plot	Cabbage Plot
16th April, 2015	0.250	0.085	0.075
14th May, 2015	0.275	0.087	0.070
11th June, 2015	0.270	0.086	0.072
Minimum	0.250	0.085	0.070
Maximum	0.275	0.087	0.075
Average	0.265	0.086	0.072
Standard Dev.	0.000175	0.000001	0.0000063

4.1.5 Cation Exchange Capacity (CEC)

Table 4.8 shows the estimated cation exchange capacity of the experimental plots during the dry season land cultivation. Cation exchange capacity measures the soil's ability to hold nutrients such as calcium, magnesium, and potassium, as well as other positively charged ions such as sodium and hydrogen. According to A and L laboratories (2005), the CEC of a soil is dependent upon the amounts and types of clay minerals and organic matter present. Hence, the CEC of three plots fall between sandy soil with low CEC value of less than 3 Cmol/kg and that of heavier clay soil or organic matter with much CEC value of greater than 20 Cmol/kg. According to UGA, (2014), CEC of loam soil ranges between 5 Cmol/kg and 15 Cmol/kg.

Table 4.8: The Cation Exchange Capacity (CEC) of the experimental plots

Sampling Dates	Cation Exchange Capacity (CEC) in Cmol/kg		
	Carrot Plot	Spinach Plot	Cabbage Plot
16th April, 2015	11.53	9.51	11.00
14th May, 2015	12.025	9.68	11.815
11th June, 2015	10.835	10.175	11.22
Minimum	10.835	9.51	11.00
Maximum	12.025	10.175	11.815
Average	11.46	9.79	11.35
Standard Dev.	0.597795	0.345483	0.421634

4.1.6 Soil Heavy Hetals

The results of the metals concentration of the soilsare shown in Table 4.9, 4.10, 4.11 and 4.12. The levels of the metals; Cd, Cr, Mn, Pb, and Zn present in the

experimental plots were relatively tangible, but far below the permissible limits. This is as a result of the past and present irrigation and fertilizer application pattern practice, of using untreated wastewater and organic manure (Taki Hausa) on the farmland.

The concentrations of the heavy metals on the soils varied between 0.19mg/kg Cd and 133.56mg/kg Zn for *Daucuscarota*plot, 0.13mg/kg Cd and 115.56mg/kg Zn for *Spinaciaoleracea*plot, and 0.12mg/kg Cd and 111.92mg/kg Zn for *Brassica oleracea*plot, while the controlled plot varied between 0.11mg/kg of Cd to115.78mg/kg of Zn. The trend of the heavy metals investigated in the soils revealed that in the *Daucuscarota*plot, Zn>Mn>Cr>Pb>Cd, while in the trend of *Spinaciaoleracea*plot, Zn>Mn>Pb>Cr>Cd, *Brassica oleracea*plot, has the trend, Zn>Mn>Cr>Pb>Cd, and the referenced plot had Zn>Mn>Cr>Pb>Cd.

*Daucuscarota*soil had the highest in the EC, CEC and % organic matter but least in pH value which according to Horckman et al., (2007), a decrease in soil pH increases the mobility of positively charged heavy metals as a result proton competition with these metals and decrease in negative binding. Under alkaline conditions, functional groups present in soil organic matter dissociate, thereby increasing the bio-availability of heavy metals that are bound to organic matter (Fineet al., 2005; Abdu, 2010). These plants bio-accumulates heavy metals from the soiland when they are eaten by human beings and animals, the heavy metalaccumulate in the body with serious health hazards (USEPA, 2002; UNDP,2006; Rotich*et al*., 2006).

Table 4.9: The concentration of the heavy metals in the carrot plot.

Sampling Dates	Heavy Metal Concentration in mg/kg				
	Cd	Cr	Mn	Pb	Zn
16Th April	0.19	17.40	74.96	12.02	131.82
14Th May	0.20	17.84	76.72	12.84	133.56
11Th June	0.19	18.16	77.96	13.72	136.12
Minimum	0.19	17.40	74.96	12.02	131.82
Maximum	0.20	18.16	77.96	13.72	136.12
Average	0.193	17.79	76.51	12.86	133.89
S.D	0.006	0.38	1.50	0.85	2.16
FAO/WHO RML	3	50	2000	100	300
EU RML	3	100	2000	100	300

RML= Recommended Maximum Limit
Sources of the RML: FAO/WHO (2001); Lante *et al.*, (2014) and European Union Standards European Union (2006).

Table 4.10: The concentration of the heavy metals in the spinach experimental plot.

Sampling Dates	Heavy Metal Concentration in mg/kg				
	Cd	Cr	Mn	Pb	Zn
16Th April	0.13	8.70	66.58	13.42	113.26
14Th May	0.12	8.88	67.76	13.76	115.32
11Th June	0.13	9.72	67.96	14.02	118.08
Minimum	0.12	8.70	66.58	13.42	113.26
Maximum	0.13	9.72	67.96	14.02	118.08
Average	0.13	9.14	67.37	13.73	115.60
S.D	0.006	0.53	0.72	0.30	2.42
FAO/WHO RML	3	50	2000	100	300
EU RML	3	100	2000	100	300

Table 4.11: The concentration of the heavy metals in the Cabbage experimental plot.

Sampling Dates	Heavy Metal Concentration in mg/kg				
	Cd	Cr	Mn	Pb	Zn
16Th April	0.12	26.08	66.84	13.42	110.08
14Th May	0.13	26.48	67.34	13.76	111.98
11Th June	0.12	27.28	67.70	14.02	113.72
Minimum	0.12	26.08	66.84	13.42	110.08
Maximum	0.13	27.28	67.70	14.02	113.72
Average	0.123	26.61	67.29	13.73	111.93
S.D	0.006	0.61	0.43	0.30	1.82
FAO/WHO RML	3	50	2000	100	300
EU RML	3	100	2000	100	300

Sources of the RML: FAO/WHO (2001); Lante *et al.*, (2014) and European Union Standards European Union (2006).

Table 4.12: The concentration of the soil heavy metals in the reference plot.

Sampling Dates	Heavy Metal Concentration in mg/kg				
	Cd	Cr	Mn	Pb	Zn
16Th April	0.12	29.92	65.96	13.76	114.92
14Th May	0.13	30.28	65.72	14.08	115.96
11Th June	0.11	30.66	66.00	14.40	116.46
Minimum	0.11	29.92	65.72	13.76	114.92
Maximum	0.13	30.66	66.00	14.40	116.46
Average	0.12	30.29	65.89	14.08	115.78
S.D	0.01	0.37	0.15	0.32	0.79
FAO/WHO RML	3	50	2000	100	300
EU RML	3	100	2000	100	300

The concentrations of the heavy metals in the experimental plots were far below the FAO/WHO (2001), and EU (2006) standard. Although, Zinc had higher concentration values in all the three plots which is in accordance with the works of Tewari and Pande, (2013) in India. This can also be related to the research work of Uba*et al.,* (2013), where leachates from dumpsites in Zaria metropolis were observed to have higher concentration of zinc, and this could be seen as a source of zinc and other metals to the farms because some of these dumpsites are situated by the watercourse or by its tributary. As such, the bioavailability of zinc in Zaria metropolis is high and one of the major routes through which it is contaminating the agricultural soils and eventually gaining entrance into the food chain, is majorly by wastewater contamination with leachate from the dumpsites in Zaria metropolis. Which either percolates (directly or indirectly through tributaries) into the watercourse or is being washed into the watercourse by runoff and these contaminated wastewater is being used for irrigation.

4.2 WASTEWATER

4.2.1 pH

The results of the pH of the wastewater from Kubanni watercourse as determined from the department of water resources and environmental engineering laboratory are shown in Table 4.13. The mean pH and standard deviation values of the collected wastewater from the randomly selected sampling points along the Kubanni watercourse are; 7.879 ± 0.454, 7.742 ± 0.291 and 7.57 ± 0.269 for sampling point A, B and C respectively. The pH values all fell within the slightly alkaline class. The pH values of the irrigation wastewater were within the permissible limit for wastewater irrigation (FAO, 1994).

Table 4.13:pH of wastewater samples along the Kubanni watercourse in Zaria Metropolis during the dry season

Sampling Dates	Wastewater pH		
	Point A	Point B	Point C
23rd April, 2015	8.23	7.93	7.79
26th April, 2015	8.12	7.94	7.69
30th April, 2015	7.96	7.71	7.59
3rd May, 2015	8.30	7.96	7.78
7th May, 2015	7.94	7.80	7.78
14th May, 2015	7.86	7.68	7.51
21st May, 2015	8.11	8.01	7.70
28th May, 2015	7.98	7.86	7.56
4th June, 2015	7.56	7.48	7.40
11th June, 2015	6.73	7.05	6.40
Mean	7.879	7.742	7.57
Standard Dev	0.4540	0.2913	0.269

4.2.2 Electrical Conductivity (EC_{iw})

The results of the EC_{iw} of the sampled water used for irrigation of the vegetables as determined from the department of water resources and environmental engineering laboratory are shown below in Table 4.14. The EC_{iw} values ranged from 0.3539mmhos/cm to 0.3704mmhos/cm across the sampled points, and each sampled point; A, B and C had a mean and standard deviation of 0.3539±0.0288, 0.3704±0.0331, and 0.3553±0.0279 respectively. The EC of the sampled water at all the three sampled points fell below the permissive level (FAO, 1985).

Table 4.14: The Electrical Conductivity (EC_{iw}) of thewastewater samples along the Kubanni watercourse in Zaria Metropolis during the dry season

Sampling Dates	Electrical Conductivity (EC_{iw}) in µs/cm		
	Point A	Point B	Point C
23rd April, 2015	335	418	418
26th April, 2015	383	338	338
30th April, 2015	342	385	385
3rd May, 2015	372	372	372
7th May, 2015	375	345	345
14th May, 2015	325	320	320
21st May, 2015	380	366	366
28th May, 2015	365	340	340
4th June, 2015	356	335	335
11th June, 2015	344	338	338
Mean	357.70	355.70	355.70
Standard Dev	20.32	29.44	29.44

4.2.3 Sodium Adsorption Ratio

Sodium adsorption ratio (SAR) is the ratio of exchangeable sodium to calcium and magnesium ions in wastewater to be used for irrigation which tends to have an impaired influence on soil physical structure. The SAR values determined for the sampled points are represented in table 4.15. SAR values were calculated using the formula in equation 3.6. The SAR ranged from 0.35 to 0.95 with a mean and standard deviation, 0.685 ± 0.185 for sampled point A, while sampled point B and C had 0.52-1.11, 0.903±0.174, and 0.37-0.86, 0.698±0.150 respectively. All the SAR was below the recommended maximum limit (James *et al*., 1982). However, point B suggested the re-introduction of sodium ions sources such as detergents from the municipal activities through the drainages. A continued use of water having a high SAR leads to a breakdown

in the physical structure of the soil. Sodium is adsorbed and becomes attached to the soil particles. The soil then becomes hard and compact when dry and increasingly impervious to water penetration. Fine textured soils, especially those high in clay, are most subjected to this action. The concentrations of constituent ions are in the appendices.

TABLE 4.15: The Sodium Absorption Ratio (SAR) of thewastewater samples along the Kubanni watercourse in Zaria Metropolis during the dry season

Sampling Dates	Sodium absorption ratio (SAR)		
	Point A	Point B	Point C
23rd April, 2015	0.35	0.52	0.37
26th April, 2015	0.52	0.80	0.54
30th April, 2015	0.58	0.85	0.78
3rd May, 2015	0.62	1.08	0.76
7th May, 2015	0.64	0.84	0.66
14th May, 2015	0.68	0.85	0.64
21st May, 2015	0.80	0.99	0.77
28th May, 2015	0.79	0.94	0.76
4th June, 2015	0.95	1.11	0.86
11th June, 2015	0.92	1.05	0.84
Mean	0.685	0.903	0.698
Standard Dev	0.185	0.174	0.150

4.2.4 HEAVY METALS IN WASTEWATER

4.2.4.1 Cadmium

The concentration of cadmium in the wastewater samples taken at different sample points A, B and C were below the detection limits of the atomic absorption spectrophotometer AA500. This suggested that cadmium was not a constituent of the Kubanni stream during the sampling periods.

4.2.4.2 Chromium

Chromium concentration in wastewater samples collected at different points is tabulated in table 16. The measured range for all the sampled points; A, B and C was 0 – 1.739mg/l. The average and standard deviation of the sampled points A, B and C were 0.4214±0.6178, 0.291±0.6234 and 0.3774±0.6390 respectively, which suggested recontamination of chromium at point B by the drainage which empties itself in the stream. This drainage carries community wastewater and liquid and solid waste of the economic activities such welding, mechanic, battery charging, car wash etc around the vicinity it passes. The average concentration of chromium was discovered to be above the threshold limit for FAO, Canada and Nigeria FEPA recommended limits.

TABLE 4.16: Chromium concentration at sample A, B and C

Sampling Dates	Heavy Metals concentrations in mg/l		
	Point A	Point B	Point C
23rd April, 2015	1.739	ND	0.870
26th April, 2015	0.000	1.304	1.739
30th April, 2015	1.148	1.148	1.148
3rd May, 2015	0.002	0.002	0.002
7th May, 2015	0.659	0.659	0.002
14th May, 2015	0.659	0.002	0.002
21st May, 2015	0.002	0.002	0.006
28th May, 2015	0.003	0.008	0.003
4th June, 2015	0.001	0.084	0.001
11th June, 2015	0.001	0.04	0.001
Minimum	0.000	0.000	0.000
Maximum	1.739	1.739	1.739
Mean ± S.D	0.4214±0.6178	0.291±0.6234	0.3774±0.6390
FAO (mg/l)	0.1	0.1	0.1
Canada(mg/l)	0.1	0.1	0.1
Nigeria(mg/l)	0.1	0.1	0.1

4.2.4.3 Lead

Lead concentration in wastewater samples collected at different points is tabulated in table 17. The measured range for all the sampled points; A, B and C was 0.003 – 0.389mg/l. The average and standard deviation of the sampled points A, B and C were 0.1396±0.1646, 0.138±0.1651 and 0.1331±0.1517 respectively, which shows a gradual decrease in the concentrations of the metal lead, from sample point A (upstream) through point B (mid stream) and point C (downstream). The average concentration of lead was discovered to be below the threshold limit for FAO, Canada and Nigeria FEPA recommended limits. The sources of lead in Zaria Metropolis includes batteriesparticularly used in the making of lead-acid batteries (Environment Canada, 2010), sheet lead, solder, some brass and bronze products, pipes, professional paints (other than paints for use by children), some ceramic glazes, dyes in paints and pigments, medical equipment (radiation shields), scientific equipment, and military equipment (ATSDR, 2007). Plate 1, shows the dumpsite along the watercourse where waste are dumped.

PLATE 8: The irrigation source point beside where waste generated from the economic activities in the area is dumped and a man without safety wears making the connections

TABLE 4.17: Lead concentrations at sample A, B and C

Sampling Dates	Heavy Metals concentrations in mg/l		
	Point A	Point B	Point C
23rd April, 2015	ND	ND	ND
26th April, 2015	ND	ND	ND
30th April, 2015	ND	ND	ND
3rd May, 2015	0.389	0.389	0.389
7th May, 2015	0.389	0.389	0.297
14th May, 2015	0.297	0.297	0.297
21st May, 2015	0.189	0.186	0.205
28th May, 2015	0.108	0.100	0.118
4th June, 2015	0.021	0.016	0.022
11th June, 2015	0.003	0.003	0.003
Minimum	0.003	0.003	0.003
Maximum	0.389	0.389	0.389
Mean ± S.D	0.1396±0.1646	0.138±0.1651	0.1331±0.1517
FAO (mg/l)	0.2	0.2	0.2
Canada(mg/l)	$(0.2 – 0.4)^1$	$(0.2 – 0.4)^1$	$(0.2 – 0.4)^1$
Nigeria(mg/l)	$(0.2 – 0.4)^1$	$(0.2 – 0.4)^1$	$(0.2 – 0.4)^1$

4.2.4.4 Manganese

Manganese concentration in wastewater samples collected at different points is tabulated in table 18. The measured range for all the sampled points; A, B and C was

0.014 – 0.395mg/l. The average and standard deviation of the sampled points A, B and C were 0.245±0.1841, 0.2127±0.2231 and 0.1618±0.1379 respectively, which shows a gradual decrease in the concentrations of the metal manganese, from sample point A (upstream) through point B (mid stream) and point C (downstream). The average concentration of manganese was observed to be above the threshold limit for FAO, Canada and Nigeria FEPA recommended limits at point A and B but below the threshold at point C.

TABLE 4.18: Manganese concentrations at sample A, B and C

Sampling Dates	Heavy Metals concentrations in mg/l		
	Point A	Point B	Point C
23rd April, 2015	0.063	ND	ND
26th April, 2015	0.070	0.083	0.096
30th April, 2015	0.653	0.734	0.413
3rd May, 2015	0.395	0.443	0.363
7th May, 2015	0.379	0.205	0.078
14th May, 2015	0.205	0.014	0.014
21st May, 2015	0.156	0.150	0.150
28th May, 2015	0.245	0.240	0.220
4th June, 2015	0.188	0.168	0.186
11th June, 2015	0.098	0.090	0.098
Minimum	0.063	0.014	0.014
Maximum	0.395	0.395	0.363
Mean ± S.D	0.245±0.1841	0.2127±0.2231	0.1618±0.1379
FAO (mg/l)	0.2	0.2	0.2

Canada(mg/l)	0.2	0.2	0.2
Nigeria(mg/l)	0.2	0.2	0.2

4.2.4.5 Zinc

Zinc concentration in wastewater samples collected at different points is tabulated in table 19. The measured range for all the sampled points; A, B and C was 0.003 – 0.522mg/l. The average and standard deviation of the sampled points A, B and C were 0.1356±0.0885, 0.1818±0.1876 and 0.1895±0.1759 respectively, which shows a gradual increase in the concentrations of the metal zinc, from sample point A (upstream) through point B (mid stream) and point C (down stream). This can also be related to the research work of Uba*et al.,* (2013), where leachates from dumpsites in Zaria metropolis were observed to have higher concentration of zinc, and this could be seen as a source of zinc as dumpsites are mounted along the Kubanni watercourse. Plate 4.5 shows one of the dumpsites along the watercourse.

Plate 9: Dumpsite and some of the human activities along the watercourse

TABLE 4.19: Zinc concentrations at sample A, B and C

Sampling Dates	Heavy Metals concentrations in mg/l		
	Point A	Point B	Point C
23rd April, 2015	0.068	0.091	0.136
26th April, 2015	0.102	0.147	0.159
30th April, 2015	0.144	0.522	0.129
3rd May, 2015	0.280	0.272	0.239
7th May, 2015	0.291	0.259	0.262
14th May, 2015	0.173	0.169	0.169
21st May, 2015	0.102	0.102	0.098
28th May, 2015	0.064	0.064	0.060

4th June, 2015	0.100	0.100	0.64
11th June, 2015	0.032	0.092	0.003
Minimum	0.032	0.049	0.003
Maximum	0.292	0.522	0.262
Mean ± S.D	0.1356±0.0885	0.1818±0.1876	0.1895±0.1759
FAO (mg/l)	2.0	2.0	2.0
Canada(mg/l)	$(1.0 – 5.0)^2$	$(1.0 – 5.0)^2$	$(1.0 – 5.0)^2$
Nigeria(mg/l)	$(0.0 – 5.0)^2$	$(0.0 – 5.0)^2$	$(0.0 – 5.0)^2$

In general, the variation in the concentrations of the heavy metals considered in this research work was seen to vary in the decreasing order, gradually from sampled point A (a point few meters away from the Zaria city tributary which crosses through Gaskiya and empties in the Kubanni stream) through sampled point B and sampled point C except Zn which was rather increasing from point A through point B to C as a result of leachate contamination. In addition, the concentrations of the metals were observed to fluctuate slightly higher than that of sampled point A at point B and C, this can be accounted for by the car wash, mechanic, welding and painting activities within the vicinity. The average concentration of the heavy metals followed the trend Cr>Pb>Mn>Zn>Cd.

4.3 HEAVY METAL UPTAKE BY VEGETABLES

The results of the heavy metals concentration of the vegetables cultivated with wastewater in the experimental plot are shown in Table 4.20, 4.21, and 4.22. The concentration of heavy metals; Cd, Cr, Pb, Mn, and Zn, in the cultivated *Daucuscarota* in the experimental plots had ranged between and mean ± s.d; 0.98-1.82 and 1.37±0.32,

18.82-56.48 and 44.23±14.80, 6.14-7.46 and 6.40±0.59, 5.50-9.78 and 8.46±1.73, and 62.20-69.70 and 64.79±2.86 respectively. For Spinacia*oleracea,* it ranged between 32.94-38.82 and 35.29±3.22, 0.92-7.46 and 5.36±2.55, 8.56-8.86 and 8.71±0.15, and 62.52-62.96 and 62.70±0.24 for Cr, Pb, Mn, and Zn respectively. Cd was not detected in the *Spinaciaoleracea.* While *Brassica oleracea,* had range, mean±satandard deviation for the metals; Cd, Cr, Pb, Mn and Zn as 0.14-1.82, 1.20±0.80; 32.94-50.58, 42.35±6.70; 6.14-7.46, 6.40±0.59; 4.74-5.96, 5.62±0.50 and 33.00-38.40, 36.22±2.34, respectively.

The levels of the metals; Cd, Cr, Mn, Pb, and Zn present in the vegetables were significantly high. Cd which had not been detected in the water sample was detected in two of the vegetables cultivated. It was detected in carrot and cabbage samples, but further investigations showed that it was up taken from the organic and inorganic manure (decomposing waste on dumpsite) applied, known as taki hausa in Hausa. Cadmium is also a contaminant inchemical fertilizer, manure and sewage sludge (Ademoroti, 1996a; Ademoroti, 1996b; Ladigbolu and Balogun, 2011; Galadima and Garba, 2012). The metal concentrations of the vegetables were higher when compared to the heavy metals concentrations for soils and water which is similar to the research work of Orisakwe *et al.,* (2012) in Owerri, south east Nigeria.

TABLE 4.20: The concentrations of the heavy metals in*Daucuscarota*(mg/kg)

Sample	Concentration of heavy metals in mg/kg				
Number	Cd	Cr	Pb	Mn	Zn
1	1.54	50.58	6.14	8.70	64.26
2	1.82	44.70	6.14	9.78	63.70
3	1.26	50.58	7.46	5.50	69.70
4	1.26	56.48	6.14	8.70	64.08

5	0.98	18.82	6.14	9.62	62.20
Minimum	0.98	18.82	6.14	5.50	62.20
Maximum	1.82	56.48	7.46	9.78	69.70
Mean±S.D	1.37±0.32	44.23±14.80	6.40±0.59	8.46±1.73	64.79±2.86
FAO/WHO	0.3	-	5		60

TABLE 4.21: The concentrations of the heavy metals in *Spinaciaoleracea*

Sample	Concentration of heavy metals in mg/kg				
Number	Cd	Cr	Pb	Mn	Zn
1	ND	38.82	6.14	8.86	62.96
2	ND	32.94	0.92	8.56	62.96
3	ND	38.82	6.14	8.70	62.52
4	ND	32.94	7.46	8.86	62.52
5	ND	32.94	6.14	8.56	62.52
Minimum		32.94	0.92	8.56	62.52
Maximum		38.82	7.46	8.86	62.96
Mean±S.D		35.29±3.22	5.36±2.55	8.71±0.15	62.70±0.24

FAO/WHO	0.3	-	5		60

TABLE 4.22: The concentrations of the heavy metals in *Brassica oleracea*

Sample Number	Concentration of heavy metals in mg/kg				
	Cd	Cr	Pb	Mn	Zn
1	0.70	44.70	6.14	5.96	34.50
2	2.10	32.94	7.46	5.80	38.40
3	1.82	44.70	6.14	5.80	33.00
4	1.26	38.82	6.14	4.74	37.68
5	0.14	50.58	6.14	5.80	37.50
Minimum	0.14	32.94	6.14	4.74	33.00
Maximum	1.82	50.58	7.46	5.96	38.40
Mean±S.D	1.20±0.80	42.35±6.70	6.40±0.59	5.62±0.50	36.22±2.34
FAO/WHO	0.3	-	5		60

4.4 DATA ANALYSIS

4.4.1 Pollution Load Index (PLI)

The PLI values were estimated using equation 3.7 (Liu *et al*., 2005) and the estimated values of the wastewater-irrigated soils were not significantly different. Table 4.23 shows the PLI estimated values. The PLI values for each of the heavy metals considered; Cd, Cr, Pb, Mn and Zn, ranged between 1.03-1.60, and a mean value of 1.24 for Cd, 0.3-0.88, and a mean value of 0.59 for Cr, 0.91-0.98 and 0.96 for Pb, 1.02-1.16 and 1.07 for Mn and 0.97-1.16 and 1.04 for Zn. The PLI had the trend Cd>Mn>Zn>Pb>Cr.

Table 4.23: The pollution load index of the experimental plots

Plots	Cd	Cr	Pb	Mn	Zn
Daucuscarota	1.60	0.59	0.91	1.16	1.16
Spinaciaoleracea	1.08	0.30	0.98	1.02	1.00
Brassica oleracea	1.03	0.88	0.98	1.02	0.97
Mean	1.24	0.59	0.96	1.07	1.04

4.4.2 Transfer Factor (TF)

Table 4.24 summarises the metal transfer factor in vegetables from the experimental plots. The transfer of heavy metals from soils to vegetables was dependent on the vegetable species. TF for the vegetables grown in the plots ranged between 7.10-9.76, 1.59-3.86, 0.39-0.50, 0.08-0.13, and 0.32-0.54 for Cd, Cr,Pb, Mn, and Zn respectively. Cd and Cr showed higher TF than other metals in the vegetables, suggesting that Cd and Cr were the most bio-available. The trend of TF in the vegetables are Cd>Cr>Pb>Zn>Mn for *Daucuscarota*, Cr>Zn>Pb>Mn>Cd, for *Spinaciaoleracea*, while Cd>Cr>Pb>Zn>Mn for *Brassica oleracea*.

Table 4.24: The transfer factors of the irrigated vegetables with wastewater

Vegetables	Cd	Cr	Pb	Mn	Zn
Daucuscarota	7.10	2.49	0.50	0.11	0.48
Spinaciaoleracea	-	3.86	0.39	0.13	0.54
Brassica oleracea	9.76	1.59	0.50	0.08	0.32

4.4.3 Daily Intake of Metals (DIM)

Values of DIM was calculated with equation 3.8 (Ratten *et al.,* 2005) with average body weight of 60kg and converting factor of 0.085 and daily intake of vegetable

as 98g/person/day as used by Shuaibu *et al.,* (2013) in Kastina, because both places have the same socio-cultural and behavioural practice. In addition, Kastina state was formally in Kaduna state. DIM values ranged between 0.00017-0.00019, 0.00490-0.00614, 0.00074-0.00089, 0.00078-0.00127 and 0.00503-0.00900 for Cd, Cr, Pb, Mn, and Zn respectively. The trend in the DIM by the locals is Zn>Cr>Mn>Pb>Cd for *Daucuscarota,*Zn>Cr>Mn>Pb>Cd for *Spinaciaoleracea,* and Cr>Zn>Pb>Mn>Cd for *Brassica oleracea*.

TABLE 4.25: The daily intake of metals by the locals

Vegetables	Cd	Cr	Pb	Mn	Zn
Daucuscarota	0.00019	0.00614	0.00089	0.00127	0.00900
Spinaciaoleracea	-	0.00490	0.00074	0.00121	0.00870
Brassica oleracea	0.00017	0.00588	0.00089	0.00078	0.00503

4.4.4 Health Risk Index (HRI)

The HRI for heavy metals by consumption of the vegetables cultivated at the experimental plots were calculated with equation 3.9 (U.S-EPA, 2002), using RfD value for Cd, Cr, Pb, Mn and Zn which are 0.001, 1.5, 0.004, 0.033, and 0.30 respectively (US-EPA, IRIS, 2006), and the values are given in Table 4.26. The maximum HRI was found in *Daucuscarota* and *Brassica oleracea* which coincidently share the same concentration value of 0.2225. HRI of Cd, Cr, Pb, Mn, and Zn ranged between 0.17-0.19, 0.0033-0.0041, 0.1850-0.2225, 0.0236-0.0385 and 0.0168-0.0300 respectively. The HRI <1 means the exposed population isassumed to be safe. As such, the Zaria Metropolis is safe with the consumption of these vegetables. Although, the HRI will be high if the Zaria

Metropolis adopts the recent WHO daily intake of vegetables which is 400g/person/day against the current daily intake of vegetables of 98g/person/day.

TABLE 4:26: The health risk index of consuming the vegetables on the study area

Vegetables	Cd	Cr	Pb	Mn	Zn
Daucuscarota	0.1900	0.0041	0.2225	0.0385	0.0300
Spinaciaoleracea	-	0.0033	0.1850	0.0367	0.0290
Brassica oleracea	0.1700	0.0039	0.2225	0.0236	0.0168

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

i. River Kubanni is contaminated with chromium and manganese, and there is a buildup of other toxic heavy metals in the river majorly as a result of the economic activities and dumpsites along the watercourse.

ii. The long term wastewater irrigation and application of decomposing waste on dumpsite (Taki Hausa) to the agricultural lands have led to an ample buildup of toxic heavy metals in the wastewater irrigated soils although, not above the recommended threshold.

iii. The concentration of heavy metals in the vegetable samples was higher than the recommended threshold by FAO/WHO, which suggested that the vegetables' specie cultivated had strong adsorptive nature.

iv. The ingestion of metals by the populace through the consumption of the vegetables is nearly free to risk but for Pb and Cd which showed significant risks in the consumption of carrot (*Daucus carota)* and cabbage (*Brassica oleracea*).

5.2 Recommendation

The following recommendations can be given to improve the safety of vegetable production in Zaria Metropolis;

i. Farmers should be admonished against the use of decomposing waste from dumpsite for the cultivation of their farmlands rather should adopt mulching with organic manure such as plant remains, grass, animal excreta etc.

ii. Since dumpsites have shown to directly contribute to the pollution of the streams, soils and vegetables in Zaria Metropolis, thus, waste should be classified by local municipal authority into safe biodegradable and non-biodegradable with the first sited at location accessible to farmers for mulching and latter should be recycled.

iii. There should be legislation on discharge of untreated wastewater and sludge from most waste generating entities especially institutions and commercial center (e.g tertiary institutions, abattoir and tannerings). The local municipal authority should design a threshold toxic level of contaminants allowable to be discharged into the metropolitan streams.

iv. Bioremediation is one among the effective and cheap methods of treating heavy metal polluted soils that is accepted around the globe, as such, it should be

adopted for the cleaning up of the farm area by cultivating strong heavy metals absorptive plants specie, harvest them when matured and burn it at a safe site, in order to avoid further buildup and uptake by food crops.

v. Further studies should be encouraged in the researches of heavy metals uptake by other food crops and also the perceived health risk index should be estimated.

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APPENDICES

PLATE 10: The AAS Operator, Mr. Ilu, analyzing my samples

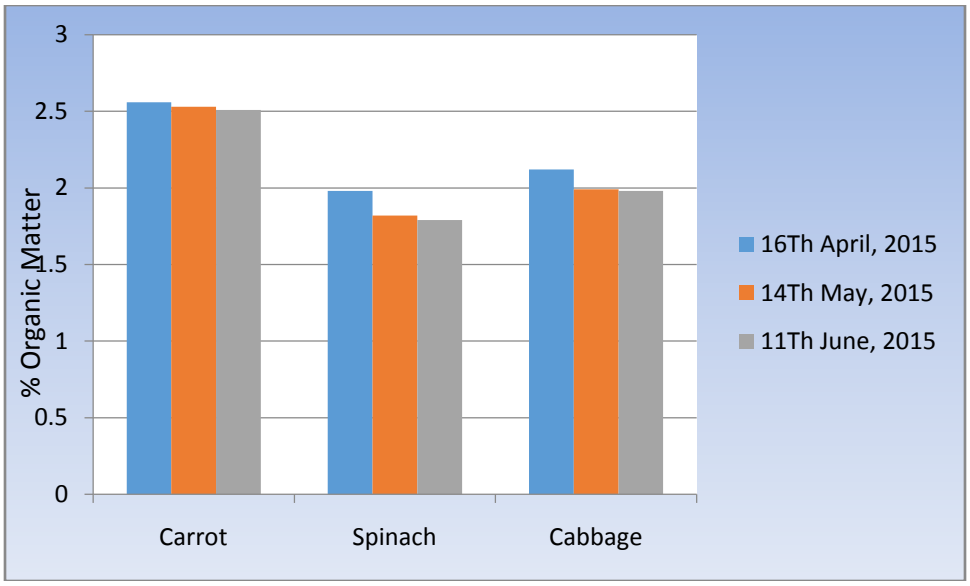

Figure 4.1: Percentage organic matter in the experimental plots during the dry season farming

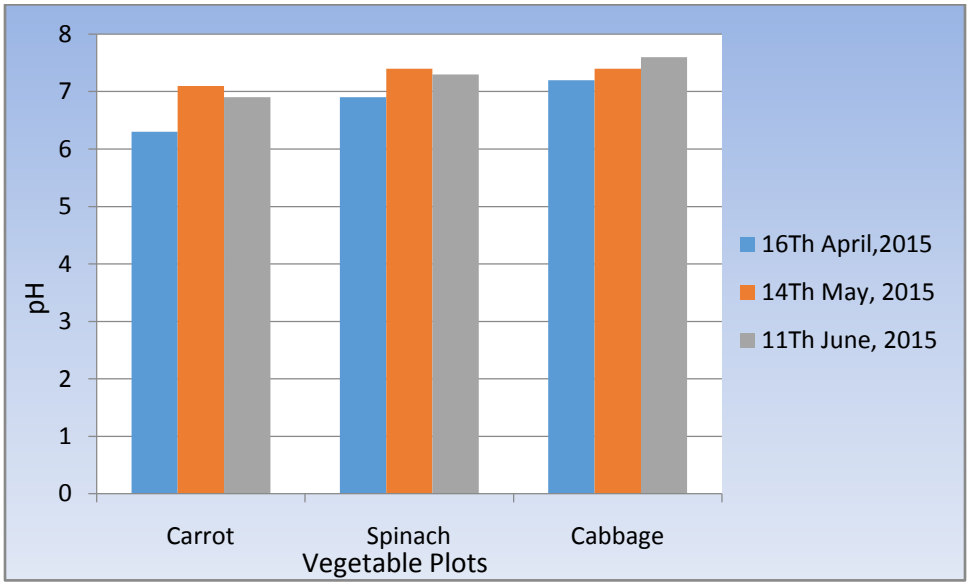

Figure 4.2: Soil pH in the experimental plots during the dry season irrigation

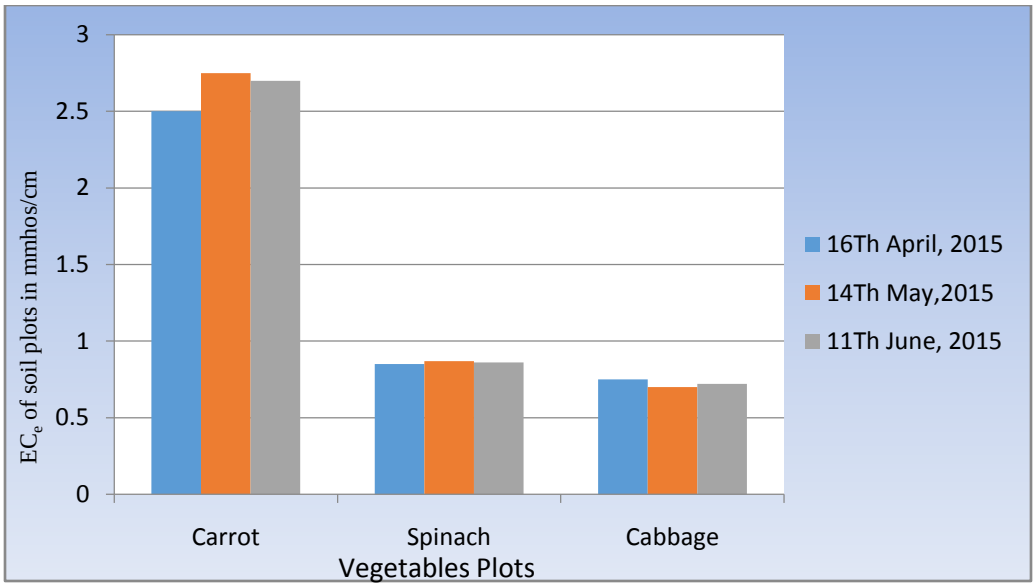

Figure 4.3: Shows the soil electrical conductivity (EC_e) 0f the experimental plots during the dry season farming

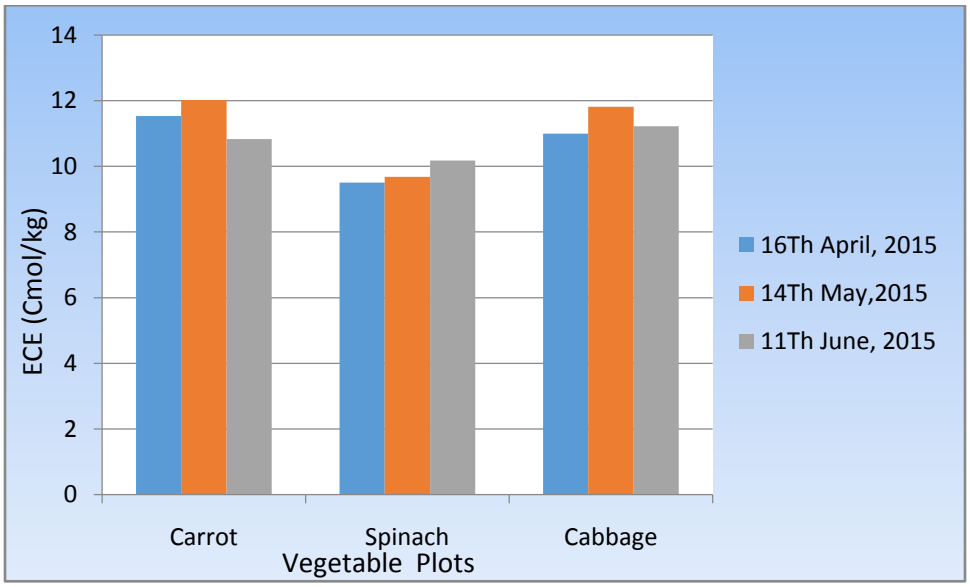

Figure 4.4: Shows the level of ECE in the vegetable plots during the dry season.

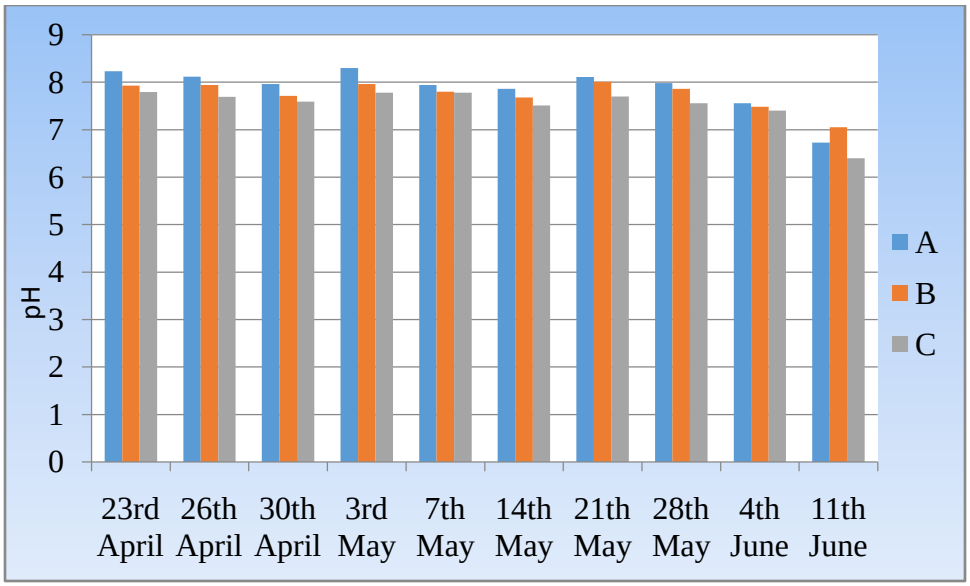

Figure 4.5: Shows the pH of wastewater samples along the Kubanni watercourse in Zaria Metropolis during the dry season.

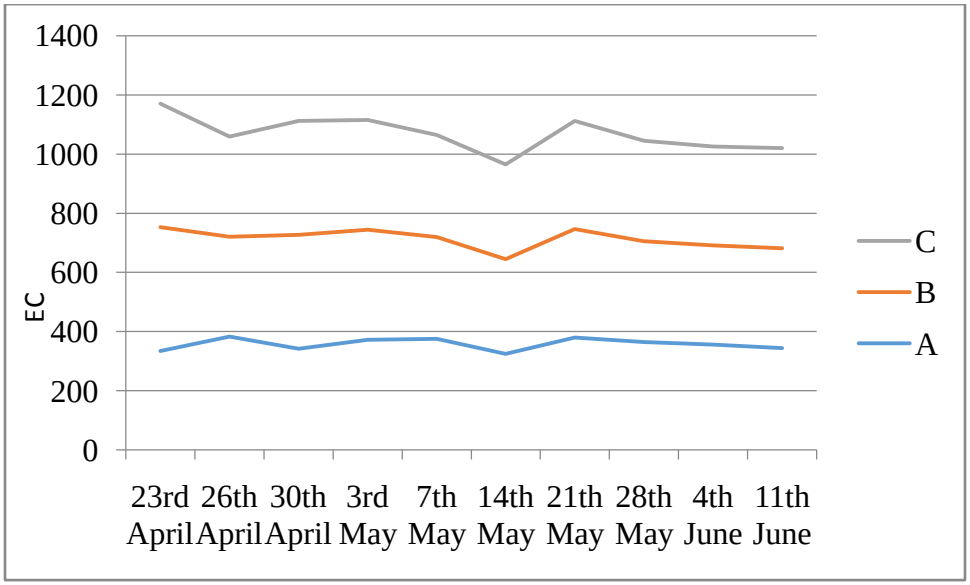

Figure 4.6: Shows the EC_{iw} of wastewater samples along the Kubanni watercourse in Zaria Metropolis

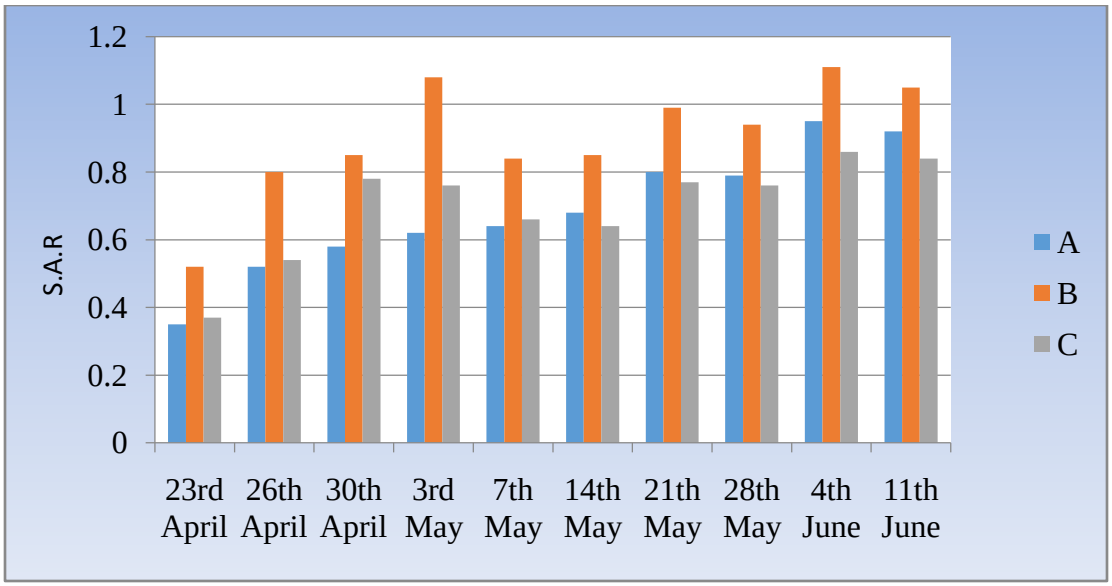

Figure 4.7:SAR of wastewater samples along the Kubanni watercourse in Zaria Metropolis.

Table 4.27: The Sodium Absorption Ratio (SAR) of the wastewater samples at point A along the Kubanni watercourse in Zaria Metropolis during the dry season

Sampling Dates	Ca^{2+} (meq/l)	Mg^{2+} (meq/l)	Na^{+} (meq/l)	SAR
23rd April, 2015	76.91	316.99	22.00	0.35
26th April, 2015	76.92	165.50	25.00	0.52
30th April, 2015	58.7	163.52	27.00	0.58
3rd May, 2015	48.58	183.74	30.00	0.62
7th May, 2015	64.77	187.75	32.00	0.64
14th May, 2015	61.45	203.97	35.00	0.68
21st May, 2015	53.56	164.88	37.00	0.80
28th May, 2015	50.44	195.44	39.00	0.79
4th June, 2015	63.86	140.76	42.00	0.95
11th June, 2015	47.62	191.03	45.00	0.92

Table 4.28: The Sodium Absorption Ratio (SAR) of the wastewater samples at point B along the Kubanni watercourse in Zaria Metropolis during the dry season 111

Sampling Dates	Ca^{2+} (meq/l)	Mg^{2+} (meq/l)	Na^{+} (meq/l)	SAR
23rd April, 2015	74.99	276.60	31.00	0.52
26th April, 2015	68.82	140.30	32.00	0.80
30th April, 2015	42.51	129.20	35.00	0.85
3rd May, 2015	44.53	86.78	38.00	1.08
7th May, 2015	61.34	183.98	41.00	0.84
14th May, 2015	59.38	200.45	43.00	0.85
21st May, 2015	48.21	151.69	44.00	0.99
28th May, 2015	47.34	189.76	46.00	0.94
4th June, 2015	60.92	139.70	49.00	1.11
11th June, 2015	44.26	188.40	51.00	1.05

Table 4.29: The Sodium Absorption Ratio (SAR) of the wastewater samples at point C along the Kubanni watercourse in Zaria Metropolis during the dry season 111

Sampling Dates	Ca^{2+} (meq/l)	Mg^{2+} (meq/l)	Na^{+} (meq/l)	SAR
23rd April, 2015	91.08	270.52	22.00	0.37
26th April, 2015	52.63	149.39	24.00	0.54
30th April, 2015	44.53	66.58	25.00	0.78
3rd May, 2015	46.56	95.86	28.00	0.76
7th May, 2015	72.87	159.45	31.00	0.66
14th May, 2015	60.22	195.04	32.00	0.64
21st May, 2015	46.58	150.44	34.00	0.77
28th May, 2015	45.84	176.66	36.00	0.76
4th June, 2015	62.11	133.50	37.00	0.86
11th June, 2015	42.76	180.10	40.00	0.84