DETERMINATION OF SOME HEAVY METALS IN DUMPSITE SOIL AND *Abelmochus esculentus* FRUIT GROWN NEAR DUMPSITES IN KAFANCHAN METROPOLIS, KADUNA STATE, NIGERIA

BY

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P13SCCH8036

A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES,

AHMADU BELLO UNIVERSITY, ZARIA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD

OF

MASTER OF SCIENCE (ANALYTICAL CHEMISTRY)

DEPARTMENT OF CHEMISTRY

FACULTY OF SCIENCE

AHMADU BELLO UNIVERSITY,

ZARIA, NIGERIA

OCTOBER, 2016

DECLARATION

I declare that the work in this dissertation entitled **"DETERMINATION OF SOME HEAVY METALS IN DUMPSITE SOIL AND FRUIT OF *Abelmoschusesculentus* FRUIT GROWN NEAR DUMPSITES IN KAFANCHAN METROPOLIS, KADUNA STATE, NIGERIA"** has been carried out by me in the Department of Chemistry, under the supervision of Prof. (Mrs.) E.B. Agbaji and Dr. K.I. Omoniyi. The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at any university.

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Name of Student	Signature	Date

CERTIFICATION

This dissertation entitled **"DETERMINATION OF SOME HEAVY METALS IN DUMPSITE SOIL AND FRUIT OF *Abelmoschusesculentus* FRUIT GROWN NEAR DUMPSITES IN KAFANCHAN METROPOLIS, KADUNA STATE, NIGERIA"** bySHEMANG YOHANNA CHINDO meets the regulation governing the award of Master of Science degree in Analytical Chemistry of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

Prof. (Mrs) E.B. Agbaji ____________________ ________________
Chairman Supervisory Committee Signature Date

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Member Supervisory Committee Signature Date

Prof. V.O Ajibola ____________________ ________________
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Dean, School of Postgraduate Studies Signature Date

DEDICATION

I dedicate this work to God Almighty, my parents Hon. and Mrs. Yohanna Chindo and my late brother Ayock Y. Chindo

ACKNOWLEDGEMENT

Glory, honour and majesty be accorded to God Almighty whose divine providence kept me throughout the period of this academic pursuit through his unseen hands that always uphold and bring me closer to my purpose of creation. I am also grateful to my parents, Hon. and Mrs. Yohanna B. Chindo for their care, prayers, financial support and encouragement that inspire me to pursue academic excellence.

For the development and ultimate success of this research work, I am highly indebted to my supervisors, Prof. E.B. Agbaji and Dr. K.I. Omoniyi for their understanding, immense contributions and relentless efforts by day and night. They motivated me to put in my best effort and to work hard. They patiently pursued me to keep to schedule and meet the deadlines. I will ever remain grateful.

My profound gratitude goes to the Head of Chemistry Department, Ahmadu Bello University Zaria, in person of Prof. V.O. Ajibola, whose leadership skills facilitated the timely completion of the research. Thank you so much sir.

I want to also thank Dr. Emeka Thompson, Mr Bawa Emmanuel, Mr. William and staff members of National Fertilizer Development Centre, Goningora, Kaduna.

To colleagues and loved ones, Clifford, Umar, Ayodele, Thaddeus, Philip, Wale, Martins, Sheba, Babakura, Kenedy, Dogara, Enoch, Joshua, Usman, Rukayya, Bunmi and all those whose names do not appear, I say thank you for your brotherly advice and kindness.

Finally, my brothers, Arch Bawa Chindo and Jacob Chindo, my niece Jadyn and nephew Joel thank you for your cooperation. You made it easier for me to fulfill God’s will for my life.

ABSTRACT

In this study, the seasonal variations in concentrations of Cd, Cr, Cu, Ni and Pb in soil and *Abelmochus esculentus* fruit grown near five (5) dumpsites in Kafanchan metropolis, Nigeria were investigated during the rainy and dry seasons of 2015 using Atomic Absorption Spectrophotometry. The dumpsite soils and control sites were sandy loam in nature and alkaline in the wet season. The cation exchange capacity, soil particle size distribution, pH, nitrogen, phosphorus and organic matter had higher values in the dry season compared to the wet. The mean levels of Cd in the dumpsite soils in the wet season was 21.86 - 58.27 mg/kg, Cu 41.33 - 81.21 mg/kg, Cr 25.86 - 44.69 mg/kg, Ni 31.44 - 77.44 mg/kg, Pb 23.62 - 56.63 mg/kg, while in the dry season, the ranges were Cd 11.38 - 30.67 mg/kg, Cu 106.52 - 158.42 mg/kg, Ni 52.09 - 119.69 mg/kg, Pb 94.19 - 308.35 mg/kg and Zn 98.43 - 332.83 mg/kg. The concentrations of the studied metals increased from wet to dry season at most dumpsites. The speciation of the soil indicated higher concentrations of heavy metals in the residual fractions (wet season 3.18 – 24.03 mg/kg; dry season 4.08 – 132.37 mg/kg); while the water soluble fractions had the least concentration (wet season 0.55 – 17.35 mg/kg; dry season 0.00 – 25.50 mg/kg). The non-residual fractions (wet season 37 – 95%; dry season, 26 – 82%) had higher percentage than the residual (wet season 5 – 63%; dry season, 18 - 74%). The concentrations of the heavy metals in the dumpsite soils were at levels above the Federal Environmental Protection Agency FEPA (1991) and European Commission (1986) maximum tolerable limits for these heavy metals in soils with few exceptions. The soil pollution load index in the wet season was 1.95 and 1.73 in the dry; contamination factor was 0.90 – 4.55 in the wet season and 0.59 – 5.78 in the dry season, while the geo accumulation index (wet season -0.51 – 1.11; dry season -0.92 – 1.35) showed that the soils of the dumpsites were polluted with the heavy metals studied. The mean cadmium, chromium, copper, nickel and lead contents in *Abelmoschus esculentus* fruits ranged from 8.51 to 14.36; 7.98 to 14.29; 7.35 to 18.80; 1.33 to 16.75; and 4.08 to 12.63 respectively. *A. esculentus* fruits had relatively low transfer factor for the metals. This study showed that the soils within the vicinity of the dumpsites were polluted by heavy metals. This calls for proper waste management practices and policy implementation.

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LIST OF ABBREVIATIONS AND ACRONYMS

AAS: Atomic Absorption Spectrophotometry

ABJ: Abuja Street Dumpsite

ABR: Albarka Street Dumpsite

ANOVA: Analysis of Variance

ATSDR: Agency for Toxic Substances and Disease Registry

BA: Bioavalable

CEC: Cation Exchange Capacity

CF: Contamination Factor

CTR: Control Site

DNA: Deoxyribonucleic Acid

EC: Electrical Conductivity

EU: European Union

FEPA: Federal Environmental Protection Agency

FAO: Food and Agricultural Organization

GRJ: Garaje Dumpsite

ICP-AES: Inductively Coupled Plasma Atomic Emission Spectroscopy)

I-geo: Geo-accumulation Factor

NRF: Non-Residual Fraction

OM: Organic Matter

PLI: Pollution load Index

RLQ: Railway Quartres Dumpsite

RF: Residual Fraction

TF: Transfer Factor

UNDP: United Nations Developmental Program

UNEP: United Nations Environmental Program

UNICEF: United Nation Children’s Fund

USEPA: United States Environmental Protection Agency

WHO: World Health Organization

CHAPTER ONE

1.0 INTRODUCTION

1.1 Heavy Metal Pollution

Pollution is the cause of many diseases, which affect not only the old but also the young, the energetic likewise animals and plants (Kanmony, 2009). Pollution is a worldwide problem and its potential in influencing the health of human population is great (Khan and Ghouri, 2011). The impact of pollution on overcrowded cities as a result of industrial effluents and automobile discharge has reached a disturbing magnitude and is arousing public awareness (Begum *et al*., 2009). Excessive levels of pollution has caused a lot of damage to human and animal health, also to plants including the tropical rain forests as well as the wider environment (Khan and Ghouri, 2011). Pollution and subsequent contamination of the environment by toxic heavy metals are of great concern due to their sources, widespread distribution and multiple effect in the ecosystem.

Heavy metals are elements of high molecular masses, most of which belong to the transition elements (Silberberg, 2000). Studies have shown that soils of refuse dumpsite contain different kinds and concentrations of heavy metals (Odukoya *etal*., 2000). In recent times, it has been reported that these elements accumulate and persist in soils at an environmentally hazardous levels (Alloway, 1996)

Heavy metal concentration in soil is associated with biological and geochemical cycles and are related to actions such as agricultural practices, industrial activities and waste disposal methods (Eja *etal*., 2003). The knowledge of heavy metal accumulation in soils, the origin of these metals and their possible interactions with soil properties are a priority in many environmental monitoring (Qishlaqi and Moore, 2007).The most common environmental pollutants in the world are heavy metals (Papatilippaki *etal*., 2008). The accumulation of heavy metals in agricultural soils is of increasing concern due to food safety issues and potential health risks, as well as its detrimental effects on soil ecosystems (Qishlaqi and Moore, 2007). The presence of heavy metals at trace level and essential elements at elevated concentration do cause toxic effects if exposed to human population (Fong *et al*., 2008).

Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air (Begum *et al*., 2009). Heavy metals can accumulate in soils to toxic levels as a result of long term application of untreated wastewater and fertilizers. Soil being irrigated by wastewater do accumulate heavy metals in the surface, and when the capacity to retain heavy metals is reduced due to repeated application of wastewater, heavy metals will leach into ground water or soil solution will be available for plant uptake (Papafilippaki *et al*., 2008). Research findings indicate that application of heavy doses of fertilizer, pollute ground water by nitrates and heavy metals through leaching (Mico *et al*., 2006). Metal poisoning arises from heavy metals that have toxic properties being released, leading to adverse effects on human and the ecosystem (Voet *et al*., 2008). Although acute poisoning from heavy metal poisoning is rare through ingestion or dermal contact, chronic exposure to even small doses can be disastrous (Sherameti and Varma, 2010). Chronic exposure to heavy metals leads to accumulation in the food chain which leads to an increased stock in the biota, therefore magnifying human dose accumulated (Voet *et al*., 2008). The chronic problems associated with long term heavy metal exposure include: serious haematological and brain damage, anaemia and kidney malfunctioning (Sonayei *et al*., 2009).

Heavy metals such as Pb and Cd are lethal even in very small doses. Lead has a negative influence on the somatic development, decreases the visual acuity and auditive thresholds (Simeonov *et al*., 2010). Acute exposure to lead causes brain damage, neurogical symptoms, brain damage and could lead to death (Simeonov *et al*., 2010). Cd exposure on the other hand, causes renal dysfunction, calcium metabolism disorders and also increase incidence of some forms of cancer (Kumar, 2009).

Manganese toxicity affects the central nervous system, visual reaction time, hand steadiness and eye-hand coordination (Calkins, 2009). A syndrome named manganism is characterised by feelings of weakness and lethargy, tremors, a masklike face and psychological disturbance. Respiratory effects have also been noted in workers who were chronically exposed to inhaled Mn dust. Impotence and loss of libido have also been noted in male workers afflicted with manganism (Calkins, 2009). Zinc toxicity is rare, but at concentrations in water up to 40 mg/L, it may induce toxicity characterised by symptoms of irritability, muscular stiffness and pain (Al-Weher, 2008).

1.2 Heavy Metals in Dumpsites

Modern civilization is completely dependent on a large range of metals for all aspects of daily life. There is a long historic association between metals and human development. Heavy metal pollution not only affects the production and quality of crops, but are environmentally problematic due to their high persistence and toxic effects (Esakku *et al*., 2003).

Nigeria is becoming a dumping ground for technological waste, especially used electronics and automobiles from the developed countries. It is a known fact that some of these products contain hazardous metals such as lead, mercury, nickel, cadmium, copper, zinc, arsenic etc. The indiscriminate dumping of damaged parts of these imported and other similar locally produced materials in different forms can perturb the distribution and concentration of these metals in the environment. The Nigerian government at all levels through their agencies have invested much in waste management and enforcement of sanitation laws but little has been achieved so far (Ojeshiria, 1999).

1.3 Solid Waste

According to Oxford Advanced Learners Dictionary of current English (2000), waste are ‘‘materials that are no longer needed and are thrown away’’. Waste is any substance that could be solid, liquid or gas or mixture for which no direct use is envisaged but which is transported for processing, dumping, elimination or other methods of disposal (Yakowitz, 1988). Waste is directly linked to human development, both technologically and socially (Adriano, 2005). Solid waste could be any non-liquid and non-gaseous product of human activities, regarded as being useless, it could take the forms of refuse, garbage and sludge (Leton and Omotosho, 2004). Sources of solid waste in Nigeria among others are commercial, industrial, household, agricultural and educational establishments. The solid waste types include pesticide containers, paint cans, batteries, nylon, various cleaning agents, dead animals, disposable diapers, grease and oils, bottles, woods, bones, electronic gadgets wastes and rubber among others. Out of the total solid waste generated in Ibadan, 66.1 % are domestic, 20.3 % commercial and 11.4 % industrial (Adewumi *et al*., 2005).

Solid waste management has remained an intractable environmental sanitation problem in Nigeria. This problem has manifested in the form of piles of indiscriminately disposed heaps of uncovered waste and illegal dumpsites along major roads and at street corners in cities and urban areas, this problem is compounded by rapid urbanization and population growth which have led to generation of enormous quantities of solid waste which are often discarded by open dumping (Uwakwe, 2012). Nigeria's major urban centres are today striving to clear mounting heaps of solid waste from their environments. Many strategic centres of beauty, peace and security are being overtaken by the messy nature of heaps of unattended solid wastes emanating from household sources, markets and business centres (Oyedele *et al*., 2008). City officials appear unable to combat unlawful and haphazard dumping of hazardous commercial and industrial wastes, which are a clear violation of the Clean Air and Health Edicts in our environmental sanitation laws. Refuse generation and its likely effects on the health, quality of environment and the urban landscape have become a burning national issue in Nigeria today (Uzairu *et al.,* 2013).

A United Nations Report in August 2004 noted that while developing countries are improving access to clean drinking water, they are falling behind on sanitation goals. At a summit in 2004, a joint report made by World Health Organization (WHO) and United Nations Children's Fund (UNICEF) that "about 2.4 billion people will likely face the risk of needless disease and death by the target of 2015 because of bad sanitation". The report also noted that bad sanitation, decaying sewage system and toilets fuel the spread of diseases like cholera and basic illness like diarrhoea, which kill a child every twenty one seconds (Uwaegbulam, 2004).

1.4 Health Implications of Dumpsites

Poor waste management poses a great challenge to the well-being of city residents, particularly those living around the vicinity of the dumpsites due to the potential of the waste to pollute water, food sources, land, air and vegetation. The poor disposal and handling of waste thus leads to environmental degradation, destruction of the ecosystem and may cause great risks to public health. The resultant accumulation of waste poses a health hazard to urban inhabitants, and also threatens the surrounding environment (UNEP, 2005).

According to Marshal (1995), open dumpsites are a major problem to the environment, especially on the air that the people inhale. Dumpsites emit obnoxious odours and smoke that cause illness to people living in, around or closer to them. In a number of community health surveys, a wide range of health problems, including respiratory symptoms, irritation of the skin, nose and eyes, gastrointestinal problems, psychological disorders and allergies, have been discovered. A number of researches have been carried out in response to concerns of the public, often triggered by nuisances caused by emissions of volatile organic compounds. According to Dolk (1997), dumpsites closer to residential areas are always feeding places for dogs and cats. These pets, together with rodents, carry diseases with them to nearby homesteads. UNEP (2005) states that wastes that are not properly managed, especially excreta and other liquid and solid wastes from households and the community, constitute a serious health hazard and could lead to the spreading of diseases.

Normally, wet waste decomposes and releases bad odour. The bad odour affects the people that are settled next to the dumpsite, which clearly shows that the dumpsites have serious effects on people settled around them (Ekwumemgbo *et al*., 2013). Wastes from agriculture and industries can also cause serious health risks. Other than this, co-disposal of industrial hazardous wastes with municipal wastes can expose people to chemical and radioactive hazards. Uncollected solid waste can also obstruct stream water runoff, resulting in the formation of stagnant water bodies that become breeding grounds for disease causing organisms. Wastes dumped near a water source also cause contamination of the water body or the ground water source. The direct dumping of untreated wastes in rivers, seas and lakes result in the accumulation of toxic metals and organic pollutants in man through the food chain (Medina, 2002). This clearly shows how waste disposal seriously affects the health of residents located closer to dumpsites.

The smelly and unsightly conditions of dumpsites are worse in summer, because of extreme temperatures, which speed up the rate of bacterial action on biodegradable organic material. Disposal of solid wastes on land without careful planning and management can present a danger to the environment and the human health (USEPA, 2006).

1.5 Research Problem

Like many cities in Northern Nigeria, Kafanchan in Kaduna State faces problems of environmental sanitation such as improper disposal of refuse near residential areas; poor refuse collection and handling, it is common to find huge refuse dumpsite within residential areas and farmers use them as fertilizers. This however, leads to accumulation of heavy metals in plants grown on dumpsite soils or fertilised withdumpsite manure, which on subsequent transfer through food chain end up in man, posing potential health risk.

The rise in population and civilization in Kafanchan metropolis has increased the number of dumpsite due to poor waste management schemes. It is a common practice to burn dumpsite wastes, this burning gets rid of organic matter and become ashes which are richer in metal contents. These ashes are either dissolved in rain water and leached into the soil contaminating the underground water, or washed away by runoff into streams and rivers, thereby contaminating the environment, it is based on these facts that this study is aimed at determining the total concentration of cadmium, copper, nickel, lead and chromium in dumpsite soils and *Abelmochus esculentus* fruit planted on dumpsite soil in Kafanchan metropolis, Kaduna State, Nigeria.

1.6 Justification

Heavy metals can be hazardous in their ability to cause cancer or neurological damage, the determination of such heavy metals in vegetables and soil samples collected from dumpsites within Kafanchan metropolis of Kaduna State, Nigeria would assist in ascertaining the contamination pattern of some metals in planted vegetables from dumpsite soils and so would help to ascertain the quality of life of consumers of such vegetables. On the other hand, resources like land have remained constant leading to over-crowding of population around towns and main cities. The biggest challenge resulting from this overcrowding is waste disposal.

Kafanchan a growing town which is in the southern part of Kaduna State, is one of the large towns in Kaduna State. Kafanchan faces problems of environmental sanitation such as improper disposal of refuse, poor refuse collection in residential areas within the metropolis, these wastes are found on large open dumpsites serving as breeding grounds for pathogens and as reservoir of heavy metals leaching into the surrounding soil and fresh water, These activities have necessitated the study of their effects on the surrounding.

1.7 Aim and Objectives

The aim of this work is to determine the levels of some selected heavy metals in dumpsite soil and *Abelmochus esculentus*fruit samples in the vicinity of solid waste dumpsites in Kafanchan metropolis, Nigeria. The aim will be achieved through the following objectives:

(i) Determination of the physico-chemical parameters (cation exchange capacity, pH, soil particle size distribution, soil texture, nitrogen, chlorine, phosphorus and organic matter) of soil samples collected from five dumpsites in Kafanchan, Nigeria;

(ii) Determination of the concentrations of cadmium, copper, nickel, lead and chromium in the dumpsite soils and *Abelmochus esculentus* fruit grown near the dumpsites;

(iii) Determination of the concentration of cadmium, copper, nickel, lead and chromium in soil and *A. esculentus*fruit samples from the selected control area without refuse dump in Kafanchan;

(iv) Fractionationof the soil collected from the dumpsites in order to determine the bioavailability of the selected heavy metals;

(v) Determination of the geo-accumulation index (I-geo), transfer factor, contamination factor (CF) and pollution load index (PLI) of the selected heavy metals in the dumpsite soil samples and

(vi) Comparison of the levels of the selected metals in the soils and fruit samples near the dumpsites using statistical analysis.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Municipal Solid Waste Management

Municipal solid waste management is a major responsibility of state and local government agencies. In order to curtail the problems associated with solid waste generation and other related problems, the Federal Government of Nigeria has promulgated various laws and regulations to safeguard the environment. The Federal Environmental Protection Agency Act of 1988, pursuant to the FEPA Act, each state and local Government in the country set up its own environmental protection body within its jurisdiction. The agencies are charged with the responsibility of handling, employing and disposing of solid waste generated. The state and local government agencies generate fund from subvention from internally generated revenue through sanitary levy and stringent regulations with heavy penalties for offenders of illegal dumping and littering of refuse along streets (Ogwueleka, 2003). Waste handling facilities are lacking in many highly populated areas in most developing and underdeveloped countries due to cost and lack of enforcement of relevant enactment. Poor regional and urban planning, lack of enforcement of relevant laws and edicts on waste disposal, lack of organized landfill sites contribute to the presence of dumpsites within living areas in developing nations. This results in the discharge of household sewage and refuse into the environment untreated. The surface run-off and leachates from dumpsites are sources of fresh water contamination (Abdus-Salam *et al*., 2011).

The recent population and industrial growth has led to increasing production of domestic, municipal and industrial wastes, which are indiscriminately dumped in landfill and water bodies without treatment (Ogunyemi *et al*., 2003). Municipal solid waste management constitutes one of the most crucial health and environmental problems facing governments of African cities. This is because even though these cities are using 20-50 percent of their budget on solid waste management, only 20-80 percent of the waste is collected. The uncollected or illegally dumped wastes constitute a disaster for human health and result to environmental degradation (Achankeng, 2003). Thousands of old landfills and dumpsites exist throughout developing countries that may pose threat to human health in the next decades, unless appropriate measures are taken. Most developing countries follow the practice of open dumping of solid wastes causing environmental and health risks(Kurian *et al*., 2003). Industrialization, population growth and unplanned urbanization have partially or totally turned our environment to dumping sites for waste materials (Ikem *et al*., 2002).

2.2 Effects of Municipal Solid Waste on the Environment

Poor waste management poses a great challenge to the well-being of city residents, particularly those living adjacent to dumpsites due to the potential of the waste to pollute water, food, land, air and vegetation. The poor disposal and handling of waste thus leads to environmental degradation, destruction of the ecosystem and may cause great risks to public health. The resultant accumulation of waste poses a health hazard to urban inhabitants, and also threatens the surrounding environment (UNDP, 2006).

The environmental problems posed by solid waste ranges from health hazards, soil and water pollution, repulsive sight and offensive odour. The resultant effect of these is the degradation of environmental quality (Abdus-Salam *et al*., 2011). Dumpsites are usually located within the vicinity of living communities and wetlands. These dumpsites are often not lined nor basement prepared for selective adsorption of toxic substances. Therefore, it is prone to release pollutants to nearby water and to the air through leachates and dumpsite gases respectively (Alimba *et al*., 2006). Many water resources have been rendered wholesome and hazardous to man and other living systems, as a result of indiscriminate dumping of refuse (Bakare *et al*., 2005).

Most uncontrolled dumps are many years old, having grown over time from small dumps to large, unmanaged waste sites. Uncontrolled dumps have significant environmental impacts. Solid waste poses the greatest threat to life since, it has the potential of polluting the terrestrial, aquatic and aerial environments (Odukoya *et al*., 2000). Soil samples represent an excellent media to monitor heavy metal pollution resulting from anthropogenic activities. Heavy metal contaminated soil affects the ecosystem due to leaching into ground water or when they are taken up by plants and animals, which results in great risks due to bioaccumulation (Bhagure and Mirgane, 2010).

Heavy metals and persistent organic pollution are of concern due to their potential harmful effects to humans and the environment. Wong *et al*. (2003) showed that heavy metals are potentially toxic to crops, animals and humans when contaminated soils are used for crop production. Pollution of the biosphere with heavy metals, induced by industrial, agricultural and domestic activities pose serious problems for safe use of agricultural lands (Fytianos *etal*., 2001).

In some dumpsites, wastes are burnt in the open and the ashes abandoned at the sites, with no regard to environmental implications. This poses a direct safety threat because of the danger of explosion. The burning of wastes gets rid of the organic materials and oxidizes the metals, leaving the ash richer in metal contents. After the processes of oxidation and corrosion, these metals get dissolved in rain water and are then leached into soil from where they are picked up by growing plants thereby entering the food chain (Benson and Ebong, 2005).

Heavy metal concentrations in soil are associated with biological and geochemical cycles and are influenced by anthropogenic activities such as agricultural practices, industrial activities and waste disposal methods (Zukowska and Biziuk, 2008).

Waste dumpsites can transfer significant levels of toxic and persistent metals into the soil environment (Udosen *et al*., 2006). These metals are taken up by plants and transferred into the food chain (Benson and Ebong, 2005). Cultivated plants take up these metals either as mobile ions in the soil solution through their roots (Udosen *et al*., 2006) or through their leaves thereby making them unfit for human consumption (Yusuf *et al*., 2003).

Consequently, higher levels of heavy metal in soil can result to higher uptake level by plants (John *et al*., 1972). The rate of metal uptake by a plant could be influenced by factors such as metal species, plant species, plant age and plant part (Singh *et al*., 2010).

2.3 Soil Pollution

Soil is a very important natural resource to man as it is a source of life on planet, earth. Without soil, the earth would be as barren as the moon, hence lifeless (Misra and Mani, 2009). Despite its importance, soil is often contaminated by human activities and this is reflected in the high horizontal and vertical variability brought about by the anthropogenic influence on soil formation and development (Fong *et al.,* 2008). A variety of human activities including municipal waste disposal, industrial emissions, military testing and agricultural practices have left their impacts on soils in the form of elevated and high level of toxicants (Van and Krivolutsky, 1996).

Materials that find their entry into the soil system persist and accumulate in toxic levels, hence becoming sources of pollution in the soil (Misra and Mani, 2009). The concentration of heavy metals in soil and their impact on ecosystems can be influenced by many factors such as the parent rock, climate and anthropogenic activities (Jia *et al*., 2010).

2.4 Effects of Some Heavy Metals on the Environment

2.4.1 Lead

Lead (Pb) is a well-known neurotoxin. Impairment of neurodevelopment in children is the most critical effect of lead poisoning. Exposure in the uterus, during breastfeeding and in early childhood may all be responsible for the effect. Lead accumulates in the skeleton and its transfer from bones during pregnancy and lactation causes exposure to foetuses and breastfed infants (ATSDR, 2007). Chronic exposure to Pb can affect physical growth and cause anaemia, kidney damage, headache, hearing problems, speaking problems, fatigue or irritable mood (Simeonov *et al*., 2010). The toxicity by Pb has multiple biochemical effects. It has the ability to inactivate enzymes, compete with calcium for incorporation into bones and interfere with nerve transmission and brain development (Ediin *et al.,* 2000). It has been suggested that lead on a cellular and molecular level may permit or enhance carcinogenic events involved in DNA damage, DNA repair and regulation of tumour suppressor and promoter genes (Silbergeld, 2003).

The common sources of lead are car batteries, tyre materials, coals, plastics and insecticides. The high level of Pb in soil, could be attributed to Pb from car exhaust fumes, derived from leaded petrol (Alloway, 1996). The main sources of Pb in the environment include, dust from leaded paints of older houses, leaded gasoline and tap water from soldered pipes (Ediin *et al*., 2000). The maximum allowable limits of leadin the soil in UK and USA are 100 mg/kg and 200mg/kg respectively (Mamtaz and Chowdhury, 2006), while it is 0.05 mg/kg in Nigeria (FEPA, 1991)

2.4.2 Cadmium

Cadmium (Cd) is a heavy metal characterised by high mobility in biological systems. It is emitted to the atmosphere in combustion processes, mainly in the form of oxides (Wieczorek *et al*., 2004). Cd uptake by plants is partly limited by presence of calcium, phosphorus and chelating compounds in the soil (Wieczorek *et al*., 2004). Cadmium has atomic number of 48, atomic mass 112.4, density 8.7gcm^{-3}, meltingpoint 321^{o}C and boiling point 767^{o}C. The metal is a lustrous, silver-white, ductile, very malleable metal. It is soluble in acids, but not in alkalis. It is usually found as a mineral combined with other elements such as oxygen as cadmium oxide, chlorine as cadmium chloride, or sulphur as cadmium sulphate and cadmium sulfide (Schult-Schreeppimg and Piscator, 2000). Thesources of Cd in the environment include: mining and smelting of metal ores, fossil fuel combustion and also phosphate fertilizers (Challa and Kumar, 2009). Cd is used in the production of nickel-Cd rechargeable batteries when this is deposited in sewage sludge, it raises the levels of Cd in the environment (Challa and Kumar, 2009). Farming practices such as tobacco growing also increases the level of Cd in the environment, as tobacco is known to accumulate Cd in its tissues (Selinus and Alloway, 2005). The sources of Cd in the urban areas are much less well defined than those of Pb, but metal plating and tire rubber are considered the likely sources of Cd (Jaradat and

Momani, 1999). Cd is also found in lubricating oils as part of many additives and car tyres as a result of the vulcanization process. The industrial activities; the metal is widely used in electroplating, pigments, plastics, stabilizers and battery industries (Mehbrahtu and Zebrabruk, 2011). Cd is highly toxic and responsible for several cases of poisoning through food. Small quantities of Cd cause adverse changes in the arteries of human kidney. It replaces zinc biochemically and causes high blood pressures and kidney damage (Mehbrahtu and Zebrabruk, 2011). The recommended concentration of cadmium in soil is 3kg/mg (EU, 1986).

2.4.3 Chromium

The most common forms of chromium are chromium (VI) and chromium (III) (Hilgenkamp, 2006). Although chromium toxicity in the environment is rare. It still presents some risks to human health since chromium can be accumulated on skin, lungs, muscle, fat, in liver, dorsal spin, hair, nails and placenta where it is traceable to various health conditions (Adeleken and Abegunde, 2011).

The health effects brought about by the exposure to chromium (VI) include lung cancer, malignant neoplasia, chromium dermatitis and skin ulcers (Sarkar, 2005). Perforations and ulcerations of the nasal septum and bronchial asthma have also been reported. In one of the studies, a four-fold increase in childhood leukemia was attributed to possible consumption of water with chromium (VI) levels above standard recommended value of 300 mg/kg (Sarkar, 2005). The sources of chromium in the environment include, cement, leather, plastics, dyes, textiles, paints, printing ink, cutting oils, photographic materials, detergents, wood preservatives among others (Hilgenkamp, 2006). Other sources of chromium are power plants, liquid fuels, brown and hard coal and industrial and municipal wastes. Non biodegradability of chromium is responsible for its persistence in the environment and once mixed with soil, it undergoes transformation into various mobile forms before ending into environmental sink (Adeleken and Abegunde, 2011). The maximum allowable limit of chromium in the soil set by United Kingdom is 300 mg/kg (EU, 1986) while the limit set by FEPA (1991) is 0.03 mg/kg in Nigeria.

2.4.4 Nickel

Nickel is an essential trace element in animals, although the functional importance of nickel has not been clearly demonstrated. However, there is evidence of uptake and accumulation in certain plants. Nickel deficiency is manifested primarily in the liver. Its effects include abnormal cellular morphology, oxidative metabolism and increase and decrease in lipid levels. The essentiality of nickel in humans has not been established and nickel dietary recommendations have not been established for humans (ATSDR, 2003).

Nickel compounds are known carcinogens in both human and animal models (Feder *et al*., 1996). There is evidence that the geno-toxic effects of nickel compounds may be indirect through the inhibition of DNA repair systems. As a result of this inhibition it has been suggested that accumulation of nickel in breast tissue may be closely related to malignant growth process (ATSDR, 2005).

2.4.5 Copper

Copper is an essential nutrient that is incorporated into a number of metalloenzymes involved in hemoglobin formation, drug/xenobiotic metabolism, carbohydrate metabolism, catecholamine biosynthesis, the crosslinking of collagen, elastin and hair keratin, and the antioxidant defense mechanism. Copper-dependent enzymes, such as cytochrome C oxidase, superoxide dismutase, ferroxidases, monoamine oxidase and dopamine β-monooxygenase, function to reduce activated oxygen species or molecular oxygen. Symptoms associated with copper deficiency in humans include normocytic, hypochromic anaemia, leukopenia, and osteoporosis (ATSDR, 2004).

Although copper homeostasis plays an important role in the prevention of copper toxicity, exposure to excessive levels of copper can result in a number of adverse health effects including liver and kidney damage, anaemia, immunotoxicity and developmental toxicity. Many of these effects are consistent with oxidative damage to membranes or macromolecules. Copper can bind to the sulfhydryl groups of several enzymes, such as glucose-6-phosphatase and glutathione reductase, thus interfering with their protection of cells from free radical damage (ATSDR, 2004). A few examples of human activities that contribute to copper release are mining, metal production, wood production and phosphate fertilizer production. Because copper is released both naturally and through human activity, it is very widespread in the environment. The metal is often found near mines, industrial settings, landfills and waste disposals (Schult and Kelling, 1999).

2.5 Methods of Heavy Metal Analysis

Several techniques for the determination of heavy metal elements are currently in use. These include flame atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Sonayei *et al*., 2009). Atomic Absorption Spectroscopy is used in many studies because of its simplicity, reliability and sensitivity (Sarkar, 2005). A lot of studies on heavy metals in water, soil plants and animals have used atomic absorption spectroscopy as the method of analysis for heavy metals. Similarly, Fong *et al*. (2008) in the analysis of copper, cadmium, manganese, lead and zinc in urban roadside soils used atomic absorption spectroscopy for the analysis. Other researchers who have employed atomic absorption spectroscopy in the analysis of heavy metals include: Mamtaz and Chowdhury (2006) in the study of iron, copper, manganese and zinc levels in urban solid waste; Awokunmi *et al*. (2010) in the study of cadmium, cobalt, chromium, copper, lead, manganese, nickel and zinc levels in soils from a dumpsite in Nigeria; Mico *et al*. (2006) employed atomic absorption spectroscopy method in analysis of cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead and zinc in the agricultural soils of Segura River Valley in Spain. Furthermore, Al-Weher (2008), analysed levels of Cadmium, copper and zinc in three species of fish using atomic absorption spectroscopy.

2.6 Heavy Metal and Contamination Pattern

Heavy metal are metallic element of high molecular masses, most of which belong to the transition element (Silberberg, 2000).There are different types of pollution, but pollution caused by toxic level of heavy metal pollutants is called heavy metal (Bose and Hemantaranjan, 2005). Heavy metal pollution has received the attention of researchers all over the world, mainly due to their harmful effects on living beings (Misra and Mani, 2009).

Contamination pattern is an environmental pathway indicating the implications of contamination at and around the site of waste deposition. An assessment of such pattern consists of determining the nature and extent of contamination (South Macomb Disposal Authority, Michigan, 2009). Alma *et al.* (2010) in the study conducted on two plant species grown at three different stations, indicated that heavy metals enter the biological cycle through the roots and leaves of plants and are enriched in various plant organs. Heavy metals can directly affect the growth of plants; an excess dietary intake of contaminated plants could also be dangerous to the health of humans and animals, the chemical composition of plants reflects almost the elemental composition of the soil.

Elaigwe, (2007) carried out the biomonitoring of vegetables and reported that farming in dumpsites have a negative impact on human health due to high concentration of trace metals in plants from the environment which subsequently enters the food chain.Kikelomo *et al*. (2008) reported the damaging effects of heavy metals especially Cdon sperm quality and formation. The kidney is reported to be the most sensitive tissue to long – term Cd exposure in Michigan, U.S.A (ATSDR, 2009)

Adeleken and Abegunde (2011) noted that heavy metals have low environmental mobility as a result of this, a single contamination could set a stage for a long term exposure of heavy metals to human, microbial, fauna, flora and other edaphic communities. The problem of atmospheric heavy metal pollution is not going to disappear overnight. On the contrary it will remain a legacy of mass industrial activity for many generations and is likely to escalate further in the future. In this regard, the compilation of past and present catalogues of atmospheric heavy metal concentration is an activity of great importance (Shrivastav, 2001).

A study carried out on the chemical fractionation, mobility and bioavailability of Cd, Cu, Mn, Pb and Zn in refuse waste soils of some dumpsites in Zaria metropolis, indicated that the mean of the total extractable metals in the samples analysed for Cd, Cu, Mn, Pb and Zn ranged from 25.86 – 95.71, 1.70 – 446.43, 141.92 – 423.22, 39.9 – 739.10 and 122.45 – 511.57 $mgkg^{-1}$ dry weight, respectively. Cd and Pb were mostly found to be in the mobile phase of the samples indicating that the metals are potentially more bioavailable to the environment than the other metals studied. On the overall, the order of mobility and bioavailability of the metals is Cd > Pb > Zn > Mn > Cu (Uba *et al*., 2008). The mobility, bioavailability and liability of some heavy metals (Fe, Co, Ni and Mn) in soils around automobile waste dumpsites in Northern part of Niger Delta were assessed by Osakwe and Otuya (2008) using Tessier *et al*. (1979) five step sequential chemical extraction procedure. The results showed that majority of the iron and manganese were associated with the residual fraction with average levels of 29.2% and 24.43% respectively. The exchangeable fraction was the most important fraction for cobalt, with the average level of 39.53%, while the organic fraction contained the predominant species of nickel with an average level of 22.97%. For the total concentrations of the metals, iron with range 768.30 - 2897.00 ($mgkg^{-1}$) was the highest, followed by manganese with range from 1.78 - 19.92 ($mgkg^{-1}$) and then cobalt and nickel which ranged from 0.28 - 2.42 and 0.084 - 0.512 mg/kg respectively. The mobility factors for the metals in all the sites ranged from 20.37 - 90.90 for cobalt, 15.83 - 62.07 for nickel, 25.50 - 60.43 for manganese and 16.49 - 32.13 for iron, following the order: Co > Ni > Mn > Fe. The relatively high mobility factors observed for cobalt in some sites coupled with its comparatively high concentration in the exchangeable fraction, indicates high mobility, liability and bioavailability for cobalt in the soils studied. The other metals (Fe, Ni and Mn) which are strongly bound to the soil matrix are not readily available for introduction into the food chain. The results suggest that there is no serious contamination hazard with the metals studied.

Also, the seasonal variation in the physicochemical properties and concentration of heavy metals in road side soil in Yauri, was determined during the two major seasons of Nigeria in 2007/2008. The ranges of the levels of heavy metals obtained using atomic absorption spectrophotometer were 1.15 - 3.14, 0.14 - 7.0,1.64 - 22.36, 4.86 - 29.30, 2001 - 8091, 351.6 - 843.3, 35.9 - 306.7, and 79.6 - 202.4 μg/g for As, Cd, Cr, Cu, Fe, Ni, Pb and Zn in the dry season and ND – 13.04 μg/g, ND - 7.02, ND - 13.79, 0.99 - 23.72, 748 - 6000, 201.13 - 507.10, 24.00 - 316.14 and 33.84 - 131.06 μg/g for the wet season respectively. The study revealed that there was strong correlation between the dry and wet season values for all the metals with exception of Ni. Generally, higher mean levels of heavy metal were recorded in the soil during the dry season compare to in the wet season. However, both the wet and dry seasons levels of most of the heavy metals were above the natural heavy metals concentrations for surface soil and so calls for concern (Yahaya *et al*., 2009).

Study of heavy metals in the abandoned Isolo dumpsite soil and *Amaranthus cruentus* planted on the dumpsite soil indicated that the concentration of heavy metals in *Amaranthus* at the dumpsite and the control were: Pb (35.00 and 23.68 mg/kg); Zn (8.70 and 4.00 mg/kg); Cu (7.68 and 4.34 mg/kg); Cr (0.08 and 0.05 mg/kg) and Fe (98.00 and 24.50 mg/kg) respectively. Also, the concentrations of heavy metals in the tomato planted at the dumpsite were: Pb (46.75 mg/kg); Zn (85.64 mg/kg); Cu (13.35 mg/kg); Cr (0.25 mg/kg) and Fe (86.94 mg/kg). The levels of heavy metals in the dumpsite soil and the soil after harvesting the tomato plant were: Pb (127.50 and 56.75 mg/kg); Zn (157.60 and 65.80 mg/kg); Cu (27.60 and 12.25 mg/kg); Cr (3.60 and 1.50 mg/kg) and Fe (785.50 and653.75 mg/kg) respectively. The *Amaranthus* species on the dumpsite soil were found to accumulate more heavy metals than that of the control. The level of heavy metal in the dumpsite soil decreased drastically after harvesting the tomato plant (Oyelola *et al*., 2009).

Various physico-chemical techniques were used to investigate the characteristics and heavy metal concentration of soils in some selected waste dumpsites in Port Harcourt. The results showed that the soils are moderately acidic with a mean pH value of 5.5 for the 1 m subsoil and 5.8 for 30 cm soil depth in the various dumpsites, in addition, the total organic carbon (TOC) levels of the soil was low with 3.41% and 2.90% for depths 30 cm and 1 m respectively. The cation exchange capacity (CEC) of the soils had the range 21.36 – 28.79 meq/100g for a depth of 30 cm and 20.94 – 26.44 meq/100g for the depth 1m soil across the dumpsites. The textural class of the soils was observed to be a mixture of sand, clay and loam in all the sites. Low sand fractions (> 40%) was observed for almost all the sites except for Elekahia and Eleme roads that had 64.7% and 56.4%, respectively. The results of the heavy metal concentration in all the locations of the dumpsites were above the permissible limits set by World Health Organization (1998). In this study, the soil did not meet up with the moisture requirement for a waste land filling and could therefore be prone to porosity, surface flooding and underground water pollution. The use of impermeable geo-membrane is suggested to minimize seepage of leachates from causing pollution of both surface and groundwater resources (David*et al*., 2009)

Leaching of Cd, Cr, Cu, Pb, Ni and Zn from fresh and partially decomposed municipal solid wastes using Acid digestion (AD), Multiple Extraction Procedure (MEP), Toxicity Characteristic Leaching Procedure (TCLP) and Equilibrium Leach Test (ELT) was carried out. Sequential Extraction (SE) studies were conducted to evaluate the mobility of heavy metal ions by fractionation into exchangeable, acid extractable, oxidisable, reducible and residual fractions. The extraction efficiency of the tests decreased in the following order: AD > MEP > TCLP > ELT. Less than 45 % of the metal contents were bioavailable (exchangeable and acid extractable) form, except Ni. Total and TCLP extractable metal contents were within the limits prescribed by United State Environmental Protection Agency (1986) compost and TCLP regulating limits, respectively (Essaku*et al.*, 2010).

Assessment of the levels of copper, zinc and lead in soils and vegetation around solid waste dumpsites in Port Harcourt and environs were carried out in 2005 using atomic absorption spectrophotometry. Physical parameters such as pH and particle size were also determined. The results show that the mean concentrations of copper in transect and profile soils and vegetation were 1.20 ± 0.83 mg/kg, 2.57 ± 1.87 mg/kg, 1.48 ± 1.61 mg/kg respectively at the East – West road dumpsite and 2.42 ± 1.87 mg/kg, 1.40 ± 0.61 mg/kg, 1.39 ± 0.67 mg/kg respectively at the Kaduna/Afam street dumpsite. The mean concentrations of zinc in soil and vegetation along the transect were 12.83 ± 4.65 mg/kg, 2.68 ± 1.82 mg/kg, 1.33 ± 0.64 mg/kg, 0.80 ± 0.60 mg/kg respectively at the Kaduna/Afam street dumpsite. The mean concentrations of lead in the soil and vegetation were 0.26 ± 0.21 mg/kg, 0.28 ± 0.24 mg/kg, 1.48 ± 0.12 mg/kg respectively at the East – West road dumpsite and 0.45 ± 0.37 mg/kg, 0.20 ± 0.08 mg/kg, 0.39 ± 0.17 mg/kg respectively at the Kaduna/Afam street dumpsite. The order of occurrence of the heavy metals in the top soils of the study areas was Zn > Cu > Pb. The levels of copper and zinc in soils from the waste dumpsite were significantly different ($P < 0.05$) from soil sample elsewhere. The differences in the levels of copper, zinc and lead in soils and vegetations as well as dumpsite and outside dumpsite were not significant ($P < 0.05$). The results indicate that solid wastes contributed to the levels of heavy metals in soils and vegetation. Also the concentrations of the metals in soils do not depend on the age of the dumpsite rather it depends on the source, composition and the topography of the dumpsite (Ideriah *et al*., 2005).

A study of speciation of Cu, Cd, Pb, Ni, Zn, Mn, Fe, Cr and Hg was carried out by Olanipekun and Fagbote (2010) on soils of Agbabu, Nigeria, using sequential extraction procedure with atomic absorption spectroscopy. From the results obtained in the two seasons, most of the metals had high abundance in the residual fractions indicating lithogenic origin and low bioavailability of the metals considered. The average potential mobility for the metals studied in the two seasons gave the order: Zn > Cr > Cu > Mn > Cd > Fe > Ni > Pb > Hg (Olanipekun and Fagbote, 2010).

Study on the effect of leaching of heavy metals at dumpsites was conducted by analyzing samples of soil collected from different dumpsites located within Ikere and Ado Ekiti metropolis, South Western Nigeria. The samples were analyzed for concentrations of Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni, Sn and Zn. The results of the analyses showed a significant difference in the concentration of these metals from the centre of each dumpsite at interval of 10 – 70 m down the slope ($p < 0.05$). The dumpsites were found to contain significant amount of toxic heavy metals (Awokunmi *et al*., 2010).

Geochemical implication of heavy metals was evaluated on groundwater surrounding a municipal solid waste dumpsite at Olusosun waste disposal site in Lagos. Twenty groundwater samples and a leachate were investigated around the dumpsite and analysed. The results revealed dominance of Pb, Fe and, Mn when compared with to WHO and SON standard, while all the metals were found to be high in the leachates. Contamination assessment revealed that Fe and Pb extremely contaminated the groundwater, while geoaccumulation factor showed that farther away from the dumpsite the contamination reduced significantly. Pb, Mn, Fe found to be from anthropogenic source and their levels correlated significantly Pb - Cd (0.84), Mn - Pb (0.90), Fe - Cd (0.76). Thus, if the levels of Pb, Fe and Mn is not checked it could lead to major health problems like tooth decolouration, low mental development and kidney problems in the populace (Laniyan *et al*., 2011).

Study was carried out by Odukoya *et al.* (2015) to assessthe trace element concentrations in soils of active and abandoned dumpsites in Lagos, Nigeria. Thirty six trace and rare earth elements were analysed in the soil samples using Inductively Coupled Plasma Mass Spectrometry. From the results, only Pb, Cd, Zn, Cr, Cu, As, Mo and Mn were at significant amounts for both sites while V, Sc, Sr and La were only significant for the active and abandoned dumpsites respectively.The results of contamination indices such as enrichment factor and contamination factor showed that the soil samples of the two dumpsites fell within depletion to minimal enrichment with Mo, Cr, Ni, Sc, V, Sr, La and low to very high degree of contamination with As, Cd, Pb, Zn and Cu. Geoaccumulation index showed that soil samples were within background to moderate contamination with As, Cr, Mn, La, Mo, Sr and V while Cd, Pb, Zn and Cu were in the class of moderate to strong to extremely strong contamination for all the samples.

The distribution and speciation pattern of the toxic heavy metals in dumpsites soil samples collected randomly from three sites Ojota, Oke Afa, and Isolo in Lagos, Nigeria for a period of five weeks between the months of October and November, 2006 was carried out using the five step extraction procedure previously proposed by Stone and Marsalek, (1996) with modification. The extracts were analyzed for heavy metals using atomic absorption spectrophotometry. Tovide *et al.,* (2011) reported that the concentrations of solubilised fraction profile for Cd and Pb in the refuse waste soil from Lagos Nigeriawere 1.20 and 1.60 (Ojota), 3.00 and 7.20 (Isolo), 1.47 and 2.10 Oke-Afa (μg/kg). Conversely, the unsolubilised fractions of Cd and Pb in the soil samples showed the profile (8.40) (Pb) and 2.70 μg/kg (Cd) for Ojota, 2.40 (Pb) and 1.90 μg/kg (Cd) for Isolo while 13.60 μg/kg was obtained for Pb and Cd was not detected in Oke-Afa soil sample. The pH values ranged from 7.14 -7.68 with Ojota soil sample recording the highest value of 7.68, while the moisture content value of the soil samples ranged from 17.35 - 47.36% respectively (Tovide *et al*., 2011).

2.7 Physico – chemical Parameters of Soils and Environmental Implications

Obasi *et al.* (2012) carried out a study to determine the pH, electrical conductivity, % moisture, cation exchange capacity, TOC, TOM, total nitrogen, %PO_4^{3-}, SO_4^{2-}) and the chemical fractionation, mobility and bioavailability of heavy metals (Cd, Cu, Mn, Pb, Zn, Fe, Ni and Cr) in refuse waste soils of some dumpsites along Enugu-Port Harcourt expressways, South-East, Nigeria were investigated and compared with control soils from the same terrain using standard analytical methods. The results showed significantly ($p < 0.05$) higher levels of the physico-chemical properties examined relative to those in the control site. This implies that the waste soil is fertile. Also, mean of total extractable metals Cd, Cu, Mn, Pb, Zn, Fe, Ni and Cr ranged from 23.41-107.18, 10.58-238.50, 141.21 -442.03, 35.11 - 635.31, 186.38 - 505.57, 76.46 - 371.73, 13.00 - 221.97 and 13.55- 26.77 $mgkg^{-1}$ dry weight, respectively. Cd followed by Fe and then Pb were the metals in very high amounts in the mobile phase of the soil samples indicating that the metals were potentially more bio-available to the environment than the other metals studied. In the overall, the order of mobility and bioavailability of the metals is Cd > Fe > Pb > Mn > Zn > Cr > Ni > Cu (Obasi *et al*., 2012).

Tripathi and Misra (2012) assessed the qualities of contaminated soils of three municipal waste dumpsites in Allahabad, Uttar Pradesh. The pH of the dumpsite soils ranged from 6.42 ± 0.46 to 7.16 ± 0.81. Water holding capacity and moisture content at dumpsites were in moderate amounts (30.43 ± 1.33 to 48.58 ± 1.19 and 35.53 ± 1.79 to 50.77 ± 1.32 % respectively). Organic matter was higher (1.60 ± 0.39 to 2.55 ± 0.48%) in the dumpsites compared to their adjoining areas. Clay texture class played a significant role in differentiating normal soils of adjoining area than dumpsite soils. Total metal concentrations of Cr, Cu, Fe, Ni, Pb and Zn were elevated in the dumpsite soils (32.46 ± 1.07 to 108.85 ± 3.99 mg/kg) compared to the control. Metal contamination dumpsite was in the order of Pb > Zn > Fe > Ni > Cu > Cr > Cd, with the highest contamination of the Daraganj dumpsite while Phaphamau dumpsite was least contaminated. Cr and Cd were not detectable in all the adjoining areas while Pb, Zn, Fe, Ni and Cu were present in the least amounts (7.32 ± 0.30 to 37.94 ± 4.22 mg/kg). Physico-chemical properties and heavy metal concentrations of each dumpsite correlated with the others. Zinc level was highly correlated with the concentrations of Cu, Ni and Pb ($r = -0.66$ to 0.86, $p < 0.05$). Concentrations of Cr were also significantly correlated with Ni and Pb ($r = -0.62, -0.69$,
$P < 0.05$). The study evidently indicates that the level of heavy metal contamination is higher at dumpsites which may be a cause of concern for their surrounding environment and organisms.

2.8 Soil Quality

Soil is a crucial component of rural and urban environments and in both places land management is the key to soil quality (Chukwulobe and Saheed, 2014).

The quality of soil depends on both its physical properties which include colour, texture, moisture content, pH and chemical properties which include cation exchange capacity, phosphate-phosphorous, sulphate-sulphur, nitrate and nitrite-nitrogen. The physical properties and chemical properties largely determine the suitability of a soil for its planned use and the management requirements to keep it most productive.

The behaviour and fate of metals are governed by a range of different physico-chemical processes, which dictate their availability and mobility in the soil or sediment system. In the water phase, the chemical form of a metal determines the biological availability and chemical reactivity (sorption/desorption, precipitation/dissolution) towards other components of the system (Osazee *et al*., 2013). The binding form in the solid phase is related to the kinetics and equilibria of metal release to the liquid phase and hence the likelihood of remobilization and bioavailability (Tack *et al.*, 1996).

Heavy metals and metalloids can be involved in a series of complex chemical and biological interactions. The most important factors which affect their mobility are pH, sorbent nature, presence and concentration of organic and inorganic ligands, including humic and fulvic acids, root exudates and nutrients. Furthermore, redox reactions, both biotic and abiotic, are of great importance in controlling the oxidation state and thus, the mobility and the toxicity of many elements, such as chromium, selenium, cobalt, lead, arsenic, nickel and copper (Tack *et al.*, 1996).

2.8.1 pH

pH is considered as an important ecological factor, with increasing pH, the solubility of most metals decreases due to their increased adsorption (Takac *et al*., 2009). Most drinking water have pH from 4 to 9 and the majority are slightly alkaline due to carbonates and bicarbonates calcium and magnesium dissolved in such water (Hutton*et al.*, 2006). pH is generally acknowledged to be the principal factor governing concentration of soluble and plant available metals (Brallier *et al*., 2001). Metal solubility tends to increase at lower pH and decrease at higher pH values (Garcia *et al.*, 2009).

2.8.2 Cation exchange capacity

Cation exchange capacity of soil is the capacity of the soil to hold cations. Soil particles are composed of silicate and alumina silicate clay. Cation exchange capacity therefore increases as the clay content increases and also as the organic matter increases in the soil. Cation exchange capacity also depends on the density of the negative charges on the surfaces of soil colloids and the relative charges on the metal species in solution and on the soil surface (Evans, 1877).

2.8.3 Nitrogen

Nitrate is an end product of the decay of nitrogenous materials such as nitrate fertilizers or animals and human excreta (Hutton*et al.*, 2006). The nitrogen content of cultivated soil is generally enriched and renewed artificially by fertilizers containing nitrates and ammonium salts. The excretion and decay of animals and plants return nitrogen compounds to the soil and air and some bacteria in soil decompose nitrogen compounds and return the element to the air (Raschid *et al*., 2009).

Nitrogen itself, being inert, is innocuous except when breathed under pressure, in which case it dissolves in the blood and other body fluids above the normal concentration. These can cause muscle and joint pain, fainting, partial paralysis and even death. These symptoms are referred to as "the bends" or decompression sickness (Matsuno, 2011).

2.8.4 Phosphorus

In the tropics, phosphorus is often the most limiting plant nutrient. This is primarily due to the challenges in the management of phosphorus. In plants, the concentration of phosphorus ranges from 0.1-0.5%. The orthophosphates, $H_2PO_4^-$ and HPO_4^{2-}, are the primary forms of phosphorus taken up by plants. When the soil pH is less than 7.0, $H_2PO_4^-$ is the predominant form in the soil. Although less common, certain organic phosphorus forms can also be directly taken up by plants. Plant roots absorb phosphorus from the soil solution. In comparison to other macronutrients, the phosphorus concentration in the soil solution is much lower and ranges from 0.001 mg/L to 1 mg/L (Brady and Weil, 2002). Abundant bioavailable amounts of essential nutrients, including phosphorous and calcium, can decrease plant uptake of non-essential but chemically similar elements, including arsenic and cadmium, respectively. Phosphate ions reduce the uptake of Cd and Zn in plants and diminish the toxic effects of As, as observed on soils treated with arsenic pesticides (Smilde *et al*., 1992).

2.8.5 Soil texture

Soil texture is a property of soil that refers to relative proportions of sand, silt and clay particles in a sample of soil. Clay size particles are smallest being less than 0.003 mm in size. Silt is medium size between 0.002 – 0.05 mm while sand particles are greater than 0.05 mm (Vaskorg *et al.,* 2010). Soil colour when examined, indicates the condition of the soil. The colour of the surface soil varies from almost white through shades of brown and grey, to black. Light colour indicates low organic matter content while dark colour indicates high organic matter content (Jais *et al*., 2011).

2.9 Heavy Metals in Vegetables

Vegetables constitute an important part of human diet because they are a source of nutrients. Vegetables contain protein, vitamins, iron, calcium and other nutrients which have marked health effects (Arai, 2002).

Contamination of foods by heavy metals has become a challenge for producers and consumers. The main sources of heavy metals in vegetable crops are their growth media (soil, air, nutrient solutions) from which these heavy metals are taken up by the roots or foliage (Lokeshwari and Chandrappa, 2006). The toxic and detrimental impacts of heavy metals become apparent only when long-term consumption of contaminated vegetables occur. Therefore, regular monitoring of heavy metals in vegetables and other food items should be carried out in order to prevent excessive buildup of these heavy metals in the human food chain (Khanna and Khanna, 2011).

Vegetables can take up and accumulate heavy metals in quantities high enough to cause clinical problems to humans (Alam *et al*., 2003). Daily metal intake estimate does not take into account the possible metabolic ejection of the metals but can easily tell the possible ingestion rate of a particular metal. Dietary intake of food results in long-term low level body accumulation of heavy metals and the detrimental impact becomes apparent only after several years of exposure (Orisakwe *et al*., 2012).

Okoronkwo *et al.* (2006) carried out the risk and health implications of metals in polluted soils used for crop production. The results of the analysis showed heavy metal contaminations of the dumpsite soils. The study concluded that there is higher risk of exposure of the consumer to heavy metals due to plant uptake of these toxic elements from polluted soils, abandoned waste dumpsite soil and any other form of polluted soil for agricultural purposes. Of all the five heavy metals studied by Okoronkwo *et al.* (2006), the highest mean concentration ($mgkg^{-1}$) was 133.74 ± 10.60 recorded for Pb followed by 22.27 ± 3.03 for Cr, 8.14 ± 0.33 for Ni and 5.97 ± 0.32 for As in the soils; while the least mean concentration of 1.64 ± 0.11 was recorded for Cd. Sand, organic matter and cation exchange capacity (CEC) correlated significantly and positively with Cr and Pb, indicating that these factors largely control the concentration of these elements in the soils.

2.10 Levels of Some Heavy Metals in the Selected Plant Specie Studied

2.10.1 *Abelmoschus esculentus* (okra)

Okra is a widely cultivated vegetable in tropical and subtropical regions. It is grown for its leaves,fruits, seeds, flora parts and stems. These are edible at young and succulent stage of the plant. The freshunripe and tender pods (fruits) are sliced, grated then boiled, steamed or fried to be used in soup. Thissoup facilitates the swallowing of relatively rough or coarse textured starchy foods (Schippers, 2000).The mature stems of some varieties contain crude fibre which is beneficial in increasing intestinal peristalsis (Oyolu, 1980).Heavy metalcomposition of food is of interest because uptake oftoxic heavy metals from contaminated soils by foodand forage plants comprises a prominent path forsuch elements to enter the food chain, as they are eventually ingested by humans. Ingestion and eventualaccumulation of toxic heavy metals in man could pose a threat tohuman health (WHO, 1973).

An assessment of the uptake of heavy metals by *Hibiscus esculentus* grown on abandoned dumpsites in Effurun, Nigeria showed that the soil samples exhibited high levels of the heavy metals Zn(59-214), Pb (0.9-4.2), Cu (301-714), Fe (712-2186), Ni (7.1-14.9) and Hg (0.61-1.14) expressed in mg/kg dry weight basis, while parts of the plant (Okro) showed low concentrations, with leaves having the highest levels of Zn, Cu, Fe, and Ni, stem contain the highest levels of Pb and Hg and the fruit had a low safe limits. The study provided nutritional data on heavy metal composition Okro (*Hibiscusesculentus*) grown on abandoned dump sites and serves as a pathway for investigating how such elements enter the food chain and will finally be ingested by humans (Akpofure, 2012).

2.11 Pollution Indices Used for Soil Analysis

In order to have an idea about the levels of contamination of the dumpsites soil, data obtained were compared with the background values. The background value of an element is the maximum level of the element in an environment beyond which the environment is said to be polluted with the element (Puyate *et al*., 2007).

2.11.1 Transfer factors (TF)

Transfer factor (TF) is the ratio of the concentration of heavy metal in a plant to the concentration of heavy metal in soil. It signifies the amount of heavy metals in the soil that ended up in the vegetable crop site (Chamberlain, 1983; Harrison and Chirgawi, 1989; Smith, 1996). Transfer factor (TF) is calculated to understand the extent of risk and associated hazard due to ingestion consequent upon heavy metal accumulation in edible portion of vegetables. Different heavy metals from soil to vegetation are one of the key components of human exposure to metals through the food chain.A study was conducted on vegetable gardens in and around Jos on the Jos Plateau, North central Nigeria; the study seek to assess the degree of contamination of the soils and the compost, the transfer factor (TF) from the agricultural soil to vegetables and its health risk index (HRI) were calculated and the results showed that the agricultural soils were severely contaminated by As, Cd, Zn and Pb (CF= 10-25). Other elements such as Cr, Cu and Ni moderately contaminated the soil. All the vegetables seemed to have been severely contaminated by Se and As (Se>As>Zn) and therefore are good accumulators of these toxic metals. The leafy and the root vegetables appear to be the major accumulator of Se and As respectively. The TF of As in all the different varieties of vegetables was >1, indicating that this element is readily absorbed by these plants. The health risk index value for As, Pb and Zn is >1 for all the vegetables (Lar *et al*.,2014).

2.11.2 Geo-accumulation index (I-geo)

The geo-accumulation index introduced by Muller (1969) is used to assess the metal pollution load, I-geo is classified into seven descriptive classes as follows: < 0 = practically uncontaminated; 0-1 uncontaminated to slightly contaminated, 2-3 = moderately to highly contaminated, 4-5 = highly to very strongly contaminated, > 5 = very strongly contaminated.

A study on evaluation of heavy metal in soils from Enyimba dumpsite in was carried out in Aba, southeastern Nigeria using contamination factor and geo-accumulation index, in the study, contamination factor, geo-accumulation index, correlation and principal component analysis were used for determining the environmental quality of soils from dumpsite in terms of heavy metal accumulation and other soil properties. The result revealed the following trend in the order of geo-accumulation in the soil: Cd > Co > Cu >Zn > As > Pb > Mn > Ni > Cr. There was a very strong correlation between organic matter content on cadmium and copper metal accumulation, suggesting that the soil around the dumpsite are moderately and slightly contaminated with cadmium and copper respectively. Contamination factor and geo-accumulation index further confirmed that the soil from the dumpsite was moderately contaminated with Cd, slightly contaminated with Cu and presently uncontaminated with Co, Zn, As, Pb, Mn, Ni and Cr (Amadi and Nwankwoala, 2013).

2.11.3 Contamination factor (CF)

The assessment of soil contamination is also carried out using the contamination factor. CF is a quantification of the degree of contamination relative to either average crustal composition of respective metal or to the measured background values from geologically similar and uncontaminated area (Tijani *et al.*, 2004).

CF is defined according to four categories as follows:

$CF < 1$ - Low contamination factor

$1 < CF < 3$ - Moderate contamination factor

$3 < CF < 6$ - Considerable contamination factor

$6 < CF$ - Very high contamination factor.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

All the reagents used for the study were of analytical grade. The list of reagents and glasswares are in Appendix I.

3.2 Preparation of Standard Stock Solutions.

All glass wares, plastic containers, crucibles, mortar and pestle were washed thoroughly. Glasses were washed with liquid soap, rinsed with distilled water and then soaked in 10 % HNO_3 solution for 24 hours (Todorovi *et al*., 2001). They were then washed with distilled water and dried in drying oven DHG – 9053A at 80^{o}C for 5 hour, in order to prepare solutions or use them to collect samples.

3.2.1 Standard solution of copper

PowderedCu$(NO_3)_2.3H_2O$ (3.803 g) was weighed and dissolved in 5 cm^3 concentrated HNO_3 in a volumetric flask. It was then made up to 1 dm^3 with distilled water in a volumetric flask giving 1000 mg/ dm^3 standard solution of copper.

3.2.2 Standard solution of lead

Lead stock solution (1000 mg/dm^3) was prepared by dissolving 1.59 g of lead (II) nitrate in 500 cm^3 of distilled water and then made up to 1 dm^3 solution using distilled water in a volumetric flask.

3.2.3 Standard solution of cadmium

Cd $(NO_3)_2.4H_2O$ (2.744 g) was weighed and dissolved in 5 cm^3 concentrated HNO_3. The solution was then made up to 1 dm^3 with distilled water in a volumetric flask giving 1000 mg/dm^3 cadmium standard solution.

3.2.4 Standard solution of chromium

Chromium stock solution (100 mg/dm^3) was prepared by dissolving 0.289 g of chromium (III) nitrate salt in 300 cm^3 of distilled water and then made up to 1 dm^3 of solution using distilled water. A working Cr standard solution (20 mg/dm^3) was made by diluting 20 cm^3 of the stock solution to 100 cm^3 of solution. The calibration graph was made using solutions with the following concentrations; 0.5, 1, 1.5, 2, and 2.5 mg/dm^3 of chromium.

3.2.5 Standard solution of nickel

Nickel solution was prepared by dissolving 4.9542 g of $Ni(NO_3)_2.6H_2O$ in distilled water and made up to mark in a 1 $dm^3$with distilled water volumetric flask giving 1000 mg/dm^3 nickel solution. Through serial dilutions, standard working solutions of 1, 2, 3, 4 and 5 mg/dm^3 of the respective metal ions were made and used to obtain the calibration curves.

3.3 Study Area

The study was carried out in five solid waste dumpsites (Gurara Street (GRR), Abuja Street (ABJ), Albarka Street (ABR), Railway Quartres (RLQ) and Garaje (GRJ)) and one Control (CTR) within Kafanchan metropolis, Kaduna State, Nigeria. Garara Street dumpsite (GRR) is located behind the general hospital and it is about 30 years old with an area of 34231 m^2. Abuja Street dumpsite (ABJ) is located at Abuja Street which is 100 m from Borno Street junction with an area of 58371 m^2. Albarka Street dumpsite (ABR) is located along the road leading to back gate of Kaduna State University, Kafanchan campus with an area of 200644 m^2. Railway quartersdumpsite (RLQ) is located behind the old market with an area of 420416 m^2. Garaje dumpsite (GRJ) is located along Kafanchan – Kagoro road with an area of 14231 m^2. Control site is located at Goska 2km from railway quarters dumpsite.

Kafanchan is a town in the southern part of Kaduna State North – West Nigeria and is located at latitude, 9° 34' 36'' N and longitude, 8° 16' 19'' E. The climate of Kafanchan is tropical with two distinct seasons, dry and rainy seasons and approximately mean high temperature of 28^{o}C. The dry season last for six months (October – April). Kafanchan, with estimated population of about 83,092 is densely populated, primarily by Nikyop and Fantswam people. It generates large volume of waste which are deposited at designated dumpsites (Google map gazette 2015). Vegetable plants are also grown by local farmers at close proximity to such dumpsites. Figure 3.1 shows the study area (Appendix XXI – XXVI).

3.4 Methods

3.4.1 Sample collection

a. Soil

Five (5) dumpsites and one control site (2.0 km from Railway quarters dumpsite) were divided into four quadrants in a diagonal basis following the methods of Nuonom *et al.,* (2000). The dumpsite soils were collected from each site with the aid of clean stainless steel spoon at 20 cm below the top soil,the soil samples were placed in a well labelled polythene bags and taken to the laboratory for treatment and analysis. The soil sample collection was done from 15th June, 2015 (wet season) to 15th November, 2015 (dry season).

b. *Abelmoschus esculentus* fruit

Three fruit samples each of the*Abelmoschus esculentus* were collected from each farm near to each dumpsite (5 m from the dumpsite) in diagonal lines and also from the control siteson the 15th November, 2015. The fruit were carefully harvested and then bagged in a labelled polythene bag and then taken to the laboratory.

3.4.2 Sample Pre-Treatment

a. *Abelmoschus esculentus* fruit

The okro fruits samples collected were properly rinsed with tap water and then with distilled water to remove any attached soil particles. They were then cut into smaller portions and placed in large clean crucibles and air driedat room temperature in enclosed chamber for about two weeks and then pulverized to fine powder using a stainless grinder. Powdered fruit samples were then collected in labelled polythene bags and were placed in a desiccator awaiting laboratory analysis(Nuonom *et al*., 2000).

b. Soil

The soil samples collected from each dumpsite were homogenized and then air dried in a circulating air in the oven at 30^{o}C overnight and then passed through a 2 mm sieve. The sieved soils were then placed in polythene bags prior to laboratory analysis (Awofolu, 2005).

3.5 Determination of Physico-chemical Parameters of the Dumpsite Soil

3.5.1 pH Measurements

The pH of the samples was determined with a handheldHanna pH meter (model H12211) using the methods described in Kumar *et al*., 2008. Where a 20 g of the dried soil was weighed into a 50 cm^3 beaker, 20 cm^3 of distilled water was then added. The mixture was stirred with a glass rod and allowed to stand for 30 minutes. A pre calibrated HANNA pH meter was inserted into the slurry and the pH was recorded.

3.5.2 Electrical conductivity

The Electrical conductivity (EC) was determined using the modified method of Kumar *et al*., 2008, and Kalra and Maynard (1991); where 25 g of an air-dried soil sample placed in a 250 cm^3 beaker, distilled water was added slowly drop by drop over the entire soil surface in a uniform pattern, until the soil appeared wet. A stainless steel spatula was used to form a homogeneous soil paste. The beaker was then covered with a Petri - dish, 50 cm^3 of distilled water was added and shaken for 1 hour. 40 cm^3 of the diluted extract was transferred into 100 cm^3 beaker and the electrode of the conductivity meter inserted to record the electrical conductivity of the soil recorded in µS/cm.

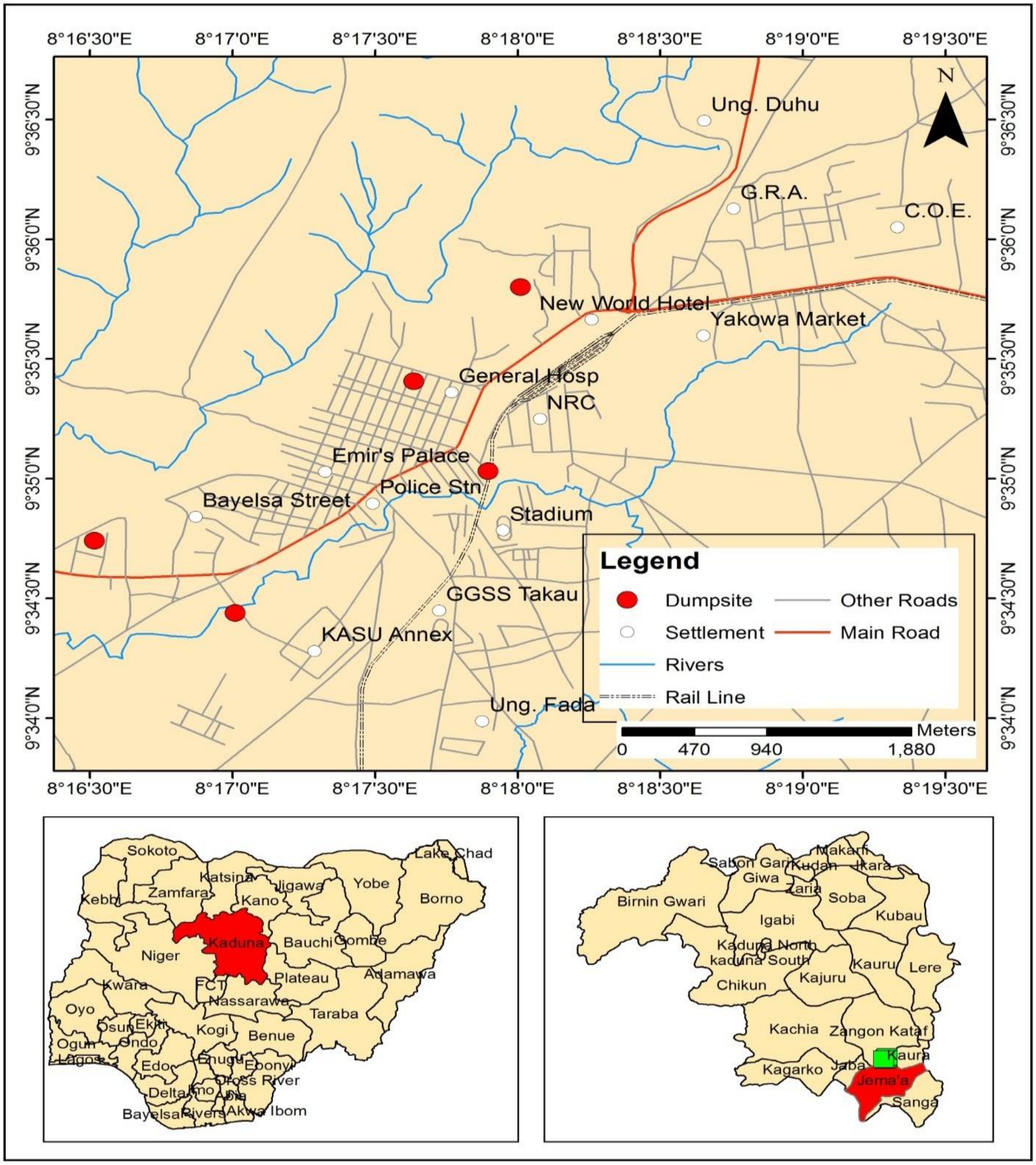

Figure 3.1: Map of Study area

3.5.3 Particle size distribution

Fifty grams (50g) of 2 mm sieved soil was weighed into a 250 cm^3 plastic beaker after which 100 cm^3 of 50% calgon was added and then stirred with a glass rod. Distilled water (100 cm^3) was then added and stirred with a glass rod. The beaker was then left to stand for about 30 minutes with occasional stirring and then transferred into a 250 cm^3 plastic container and shaken on an end to end shaker for ten minutes. The shaken sample was then transferred into a 1000 cm^3 measuring cylinder and made up to the mark with distilled water. The suspension in the cylinder was mixed vigorously using a long handle plunger making sure that the sediment at the bottom was thoroughly disturbed before the hydrometer reading was taken. Readings at 40 secs and 2 hrs were taken.

A blank solution was prepared by making 100 cm^3 of the 50% calgon solution up to the 1000cm^3 marks with distilled water. The blank hydrometer reading was taken at respective time interval. The temperature of the suspension and blank were also taken.

The corrected hydrometer readings C (g/dm^3) were obtained by subtracting the blank reading R_L (g/dm^3) from the hydrometer readings in the soil suspensions R (g/dm^3) and adding 0.36 g/dm^3 for every degree above 20^oC (Gee and Or, 2002).

Calculation

$$C = R - R_L + 0.36T \qquad 3.1$$

Where T = Room temperature at 20^oC

$$\%\ \text{Silt} = \frac{\text{Corrected 40 secs reading - blank}}{\text{weight of soil taken}} \times 100 \qquad 3.2$$

$$\%\ \text{Clay} = \frac{\text{Corrected 2 hrs reading - blank}}{\text{weight of soil taken}} \times 100 \qquad 3.3$$

$$\%\ \text{Sand} = 100 - (\%\ \text{clay} + \%\ \text{silt}) \qquad 3.4$$

3.5.4 Texture

The soil texture was determined from the texture triangle (Appendix XX).

3.5.5 Determination of chloride ion (Cl^-)

Preparation of reagents

Silver Nitrate (0.01M): $AgNO_3$(1.7 g) was dissolved in distilled water and made up to 1 $dm^3$with distilled water in a standard volumetric flask.

Potassium Chromate (0.1M): K_2CrO_4(24.6 g) was dissolved in distilled water and made up to 1 $dm^3$with distilled waterin a standard volumetric flask.

Procedure

Five grammes of the soil sample was weighed into a 100 cm^3 flask and 50 cm^3 of distilled water added and was shaken for 1 hour. The suspension was filtered into a 250 cm^3 beaker and the residue was washed with distilled water and added to the filtrate. A burette was filled with a 50 $cm^3$of 0.01 mol/$dm^3$$AgNO_3$ solution. By using a pipette, 10 cm^3 of the filtrate obtained was transferred into a 250 cm^3 conical flask and made up to 50 $cm^3$with distilled water, then 2cm^3 of 0.1 mol/dm^3 K_2CrO_4 solution was added as indicator, these were mixed thoroughly and titrated with the 0.01 mol/dm^3 $AgNO_3$ solution until muddy yellow colour was observed.(Henson, 1973)

$$Cl^- \text{ (mg/kg)} = \frac{\text{Titre value x 35.5 x 1000 x conc. of } AgNO_3}{\text{Weight of sample x volume } (cm^3)} \qquad 3.5$$

3.5.6 Determination of nitrate – nitrogen ($NO_3^{-}N$)

Preparation of reagents

Potassium Chloride (2M):KCl (149 g) was dissolved in distilled water and made up to 1dm^{3}with distilled waterin a standard volumetric flask.

Sulphamic Acid (0.021M): Sulphamic acid (2.039 g) was dissolved in distilled water and made up to 1 dm^{3}with distilled waterin a standard volumetric flask.

Sulphuric Acid (0.01M): H_2SO_4(0.6 cm^3) was dissolved in distilled water and made up to 1 dm^3 in a standard volumetric flask.

Procedure

Ten grammes of each dumpsite soil was weighed into 250 cm^3 extracting bottle and 100 cm^3 of 2M KCl solution was added, followed by 1cm^3 of 0.021Msulphamic acid in order to destroy NO_2-N. The bottle was shaken on a mechanical shaker for 1 hr, after which the suspension was then filtered through a filter paper (Whatman No. 42) and then stored in a refrigerator.A 10 cm^3 portion of the filtrate was pipetted into a Kjeldahl distillation flask and 0.2 g of Devarda alloy was added through a long-stem funnel (to reduce NO_3- N to NH_4-N). The flask was attached to the distillation apparatus and the distillate was collected in a 50 cm^3 Erlenmeyer flask containing 5 cm^3 aliquot of boric acid-indicator solution. When 30 cm^3 of the distillate had been collected, the distillation was stopped and the distillate titrated with 0.01M H_2SO_4 solution. The end-point was reached when a colour change occurred from green to a permanent faint pink (Allen, 1974).

Calculation

1 cm^3 of 0.01M $H_2SO_4 \equiv$ 70mg of NH_4-N 3.6

$$NO_3^- \ (mg/kg) = \frac{\text{Titre value x 14 x 1000 x M}}{\text{Weight of sample x volume } (cm^3)} \qquad 3.7$$

Where: M = concentration of H_2SO_4

3.5.7 Determination of Phosphate – phosphorous (PO_4^{3-} - P)

Preparation of reagents

Ammonium Fluoride (1M): NH_4F (37.04 g) was dissolved in distilled water and made up to 1 $dm^3$with distilled waterin a standard volumetric flask.

Potassium chloride (0.5M): HCl (18.25 g) was dissolved in distilled water and made up to 1 $dm^3$with distilled waterin a standard volumetric flask.

Procedure

Fifteen cm^3 of a 1 mol/dm^3 NH_4F and 25 cm^3 of 0.50 mol/dm^3 HCl were mixed with 450 cm^3 of distilled water and the mixture was stored in a glass bottle to give the extraction solution. KH_2PO_4 (0.2197 g) was oven dried at 150^oC for 1 hour. This was dissolved in distilled water and diluted to 1 dm^3 in a volumetric flask giving the standard phosphate stock solution (100 mg/dm^{-3}). Working standards of 0, 5, 10, 15 and 20 mg/dm^3 were prepared. Absorbances were read and a calibration curve of absorbance versus concentration was plotted. A volume of 35 cm^3 of extraction solution was pipetted into a volumetric flask, containing 5 g of the weighed dry soil sample which was then shaken for 1 minute and filtered, after which 0.40 cm^3 of ammonium molybdate reagent (Denige's reagent) and 2 drops of stannous chloride reagent were added to 10 cm^3 of the filtrate.

Absorbance was measured using Jenway 6305 UV - VIS spectrophotometer after 11 minutes for all the samples and the concentration was read from the curve (Agbenin, 1995).

Calculation

$$PO_4\text{-P}\ (\text{mg/kg}) = \frac{\text{conc. (from curve) x extractant volume}}{\text{Sample weight}} \qquad 3.8$$

3.5.8 Cation exchange capacity

Preparation of reagents

Barium Chloride dihydrate (0.1M): $BaCl_2.2H_2O$(24.4 g) was dissolved in distilled water and made up to 1 $dm^3$with distilled waterin a standard volumetric flask.

Magnesium Sulphate (5mM): 0.60g of $MgSO_4$ was dissolved in distilled water and made up to 1 $dm^3$with distilled water in a standard volumetric flask.

Magnesium Sulphate (1.5mM): $MgSO_4$(1.8 g) was dissolved in distilled water and made up to 1 $dm^3$with distilled waterin a standard volumetric flask.

Sulphuric Acid (0.05M): H_2SO_4(2.7 cm^3) was dissolved in distilled water and made up to 1 $dm^3$with distilled waterin a standard volumetric flask.

Procedure

The CEC of the soil samples were determined by the $BaCl_2$ Compulsive Exchange Method as described in Ross and Ketterings (1996). This method determines CEC as the pH and ionic strength of the soil. In the procedure, about 2 g of the soil was transferred to a funnel containing low grade filter paper and slowly leached with 20 cm^3 of 0.1 M $BaCl_2.2H_2O$ allowing each addition to soak into the soil before adding more. The soil samples were further leached with 60 cm^3 of 2 mM $BaCl_2.2H_2O$ in six 10 cm^3 portions. The pH of the last 10 cm^3 of leachate was determined and recorded. After leaching, the filter paper plus samples were transferred to a pre-weighed 125 cm^3 flask and 10 cm^3 of 5 mM $MgSO_4$ added and stirred occasionally for 1hour. The conductivity of the 1.5 mM $MgSO_4$ solution and the samples were determined. Distilled water was then added with mixing, until the sample solution's conductivity was that of the 1.5 mM $MgSO_4$. The pH of the sample solutions was determined and if it was not within 0.1 units of the previous measure, 0.05 M H_2SO_4 was added drop-wise until pH was in the appropriate range. The pH and conductivity were adjusted alternately until the endpoints were reached. The CEC of the soils were calculated thus:

Total solution (cm^3) = final tube weight (g) - tube tare weight (g) - 2 g [a] 3.9

mg in solution, not on CEC (meq) = total solution (cm^3) x 0.003 (meq/cm^3) [b] 3.10

Total mg added (meq) = 0.1 meq + meq added in 0.1 M $MgSO_4$ [c] 3.11

CEC (meq/100g) = ([c] – [b]) x 50 (3.7). 3.12

3.5.9 Determination of Organic Matter

Preparation of reagents

Potassium dichromate solution (0.2 M)**:** $K_2Cr_2O_7$(58.84 g) was dissolved in distilled water and made up to 1 $dm^3$with distilled waterin a standard volumetric flask

Ferrous ammonium sulphate solution (0.4 M)**:** Ferrous ammonium sulphate salt (39.2 g) was dissolved in distilled water and made up to 250 cm^3.

Procedure

One gram of the dumpsite soil sample was weighed into 250 cm^3 conical flask and 10 cm^3 of 0.2M K_2CrO_7 solution was added, the flask was swirled gently to disperse the soil in the solution, after which 20 cm^3 of concentrated H_2SO_4 was added quickly and then mixed thoroughly. The mixture was allowed to cool for 30 minute after which 200 cm^3 of water was added, followed by 10 cm^3 of concentrated phosphoric acid and 2-3 drops of Ferroin indicator. The solution was titrated against 0.4M ferrous ammonium sulphate solution. A colour change from bluish green to brilliant green being observed indicated the end point (Walkey-Black, 1937).

Blank titration was carried out using deionized water without the soil sample.

Calculation

$$\% \text{ OM} = \frac{10(B-S)}{WB} \times \frac{12}{4000} \times \frac{1.72}{0.77} \times 100 \quad 3.13$$

Where B = titre value for blank, S = titre value for sample, W= weight of soil sample used 1.72 = Factor for organic matter from carbon, 0.77 = Walkey's recovery factor, $\frac{12}{4000}$ = meq weight of carbon, 10 = conversion factor for units.

Therefore,

$$\% \text{ OM} = \frac{(B-S)\times 6.7}{WB} \quad 3.14$$

3.6 Digestion of Samples

3.6.1 Digestion of soil samples

The dumpsite soil samples were digested according to Ogunfowokan *et al.* (2009). For each sample, 1 g of the sample was digested in Teflon cup with 30 cm^3 aqua - regia

(HCl: $HNO_{3,}$ 3:1) on a thermostat hot plate at 150^{o}C. After, about 2 hours of digestion, the Teflon cup with its content was removed from the hot-plate to simmer. Then, 5 cm^{3}of concentrated HF added and heated further for 30 min. The Teflon cup with the content was allowed to cool down to room temperature and filtered. After which the filtrate was quantitatively transferred into 50cm^3 volumetric flask and made up to mark with distilled water. A blank determination was carried out using the procedure described above without the sample. Then Cd, Cr, Cu, Ni and Pb concentrations in the digest were determined using Atomic Absorption Spectrometer (Model – PG 990) in triplicate at National Fertilizer Development Centre, Goningora,Kaduna. Nigeria July 2015 and December 2015.

3.6.2 Digestion of the fruit of *Abelmoschus esculentus* samples

The *Abelmoschus esculentus* fruitsamples were digested according to method described by Awofolu (2005). A 0.5 g amount of the dried *Abelmoschus esculentus* fruit was weighed into a 100 cm^3 beaker, then a mixture of 5 cm^3 concentrated HNO_3 and 2 cm^3 $HClO_4$ were added and digested at low heat using hot plate until the content was about 2 cm^3 with distilled water being occasionally added to avoid drying. The digest was allowed to cool and then filtered into 50 cm^3 standard flask. The beaker was then rinsed with small portions of distilled water and then filtered into the flask and made up to the mark. Each digestion was carried out together with the blank in triplicate then concentrations of Cd, Cu, Pb, Cr and Ni were determined using Atomic Absorption Spectrometer (Model – PG 990) in triplicate at National Fertilizer Development Centre, Goningora, Kaduna. Nigeria in December 2015.

3.7 Quality Assurance of the AAS Machine

Validation of the atomic absorption technique was conducted on the digested *Abelmoschus esculentus* fruit and soil samples. This was done by spiking the pre-digested samples with multi-element standard solution (5 mg/dm^3 of Cd, Cu, Ni, Pb and 0.5 mg/dm^3 Cr) as reported by Awofolu (2005).

3.7.1 Preparation of multi-element standard solution (MESS)

$Cd(NO_3)_2$(0.006g), $Ni(NO_3)_2.6H_2O$ (0.0124g), $Pb(NO_3)_2$ (0.0040g), $Cu(NO_3)$ (0.0025g) and $K_2Cr_2O_7$(0.0014g) each weighed in 100 cm^3 Erlenmeyer flask, dissolved in a minimum amount of distilled water and transferred into a 500 cm^3 standard flask. The mixture was then mixed thoroughly and diluted to mark with distilled water. The 500 cm^3 solution in the standard flask gave a 5 mg/dm^3 of Cd, Cu, Ni, Pb and 0.5 mg/dm^3 Cr.

3.7.2 Spiking experiment

(i) Fruit samples

A 50cm^3 of the Multielement standard solution (MESS) was drawn with a graduated pipette and used to spike 0.5g of the pre-digested plant samples weighed in a 100cm^3 beaker. The spiked and the 0.5g unspiked samples were digested as in section 3.6.2. The digest was run on atomic absorption spectrometry equipment. Concentrations of metals in the spiked and unspiked samples were used to calculate the percentage recovery in order to validate the method.

(ii) Soil samples

A 50cm^3 of the Multielement standard solution (MESS) was drawn with a graduated pipette and used to spike 5g of the pre-digested soil samples weighed in a

100cm^3 beaker. The spiked and 0.5g of the unspiked samples were digested as in section 3.6.1. The digest was run on atomic absorption spectrometry equipment. Concentrations of metals in the spiked and unspiked samples were then used to calculate the percentage recovery in order to validate the method.

Calculation

Amount of metal used to spike a sample

$$= \frac{\text{Vol.of MESS used} \times \text{conc.of metal in MESS (mg/L)}}{1000} = \text{X mg} \qquad 3.15$$

Amount of metal in a spiked sample

$$= \frac{\text{Vol.of digest of spiked sample x conc.of metal in spiked (mg/L)}}{1000} = \text{Y mg}$$

3.16

Amount of metal in an unspiked sample

$$= \frac{\text{Vol.of digest of unspiked x conc of metal in unspiked.(mg/L)}}{1000} = \text{Z mg} \qquad 3.17$$

Recovered amount of metal used in a spiked sample = Y – Z 3.18

$$\text{\% Recovery} = \frac{\text{Y}-\text{Z}}{\text{X}} \text{ X } 100 \qquad 3.19$$

3.8 Sequential Fractionation of Heavy Metals in Dumpsite Soil

Chemical fractionation of the heavy metals (Cd, Cu, Pb, Cr and Ni) were carried out on the soils collected from each of the dumpsites and control using the method described by Finzgar *et al.* (2007). This method modified the conventional method developed by Tessier *et al.* (1979).The modified method determines fractionation of heavy metals into six (6) geochemical fractions as follows:

Preparation of reagents

Magnesium nitrate (1M): $Mg(NO_3)_2.6H_2O$ (64.10 g) was dissolved and made up to 250 cm^3 with distilled water

Ammonium acetate (1M): CH_3COONH_4(77.08 g) was dissolved and made up to 1 dm^3 with distilled water

Hydroxylammonium Chloride (0.1M): $HONH_3Cl$ (69.49 g) was dissolved and made up to 1 dm^3 with distilled water

Nitric acid (0.02M): HNO_3 (1.26 cm^3) was measured into 1 dm^3volumetric flask containing small amount of distilled water, shaken and made up to the mark to 1 dm^3 with distilled water.

Procedure

Fractions I, F1 (fraction soluble in soil solution):

Air – dried soil sample (1 g) from each dumpsite was mixed with 10 cm^3 of deionized water with continuous agitation using a mechanical shaker for 1 hour, then centrifuged. The supernant was then decanted and made up to 50 cm^3 with deionized water. The analysis of the metals (Cd, Cu, Pb, Cr and Ni) were then carried out.

Fractions II, FII (Exchangeable Fraction):

The residue from F I was leached at room temperature with 10 cm^3 of 1 M $MgNO_3$ at pH 7.0 with continuous agitation for 1 hour and then centrifuged, The supernatant was decanted and made up to 50 cm^3 with deionized water prior to analysis. $MgNO_3$ displace ions electrostatically bound in the soil matrix.

Fractions III, FII (Acid extractable – carbonate bound Fraction):

Residue from F II was leached at room temperature with 10 cm^3 of 1M NaOAc (pH 5 adjusted with HOAc) with continuous agitation for 5 hour, then centrifuged. The supernatant was decanted and made up to 50 cm^3 with deionized water prior to analysis. NaOAc solubilises carbonates (calcite, dolomite) and releases entrapped metal.

Fractions IV, FIV (Reducible – Fe – Mn Oxides and Hydroxide Fraction):

Residue from F III was leached with 20 cm^3 of 0.1 M $NH_2OH.HCl$ (pH adjusted with 25%v/v HOAc) at 96 ^oC for 6 hour with occasional agitation and then centrifuged. The supernatant was decanted and made up to 50 cm^3 with deionized water prior to analysis. $NH_2OH.HCl$ reduces Fe and Mn oxides to soluble forms.

Fraction V, FV (Oxidizable – Organic Matter Bound Fraction):

To the residue from F IV, 3 cm^3 of 0.02M HNO_3 and 30 %v/v H_2O_2 was added. The mixture was then heated to 85^oC in a water bath for 3 hr. After cooling, 5 cm^3 of 1 M NaOAc was then used for the extraction with occasional agitation for 3 hour at 85^oC. The mixture was centrifuged and the supernatant obtained was decanted and made up to 50 cm^3 in a volumetric flask with deionized water prior to analysis. HNO_3 and H_2O_2 oxidize organic matter and solubilise sulphides. Oxidized organic matter release complexes, adsorbed and chelated metals.

Fractions VI, FVI (Residual and Inert Fraction):

The residue from F V was digested with a mixture of 8 ml of 5:1 mixture of conc. HF and $HClO_4$ in acid digestion Teflon cup. Then the mixture was dry ashed for 2 hrs and evaporated to dryness. The residue was then diluted to 50 cm^3 in a volumetric flask with deionized water prior to analysis.

Appropriate reagents blanks was prepared and analysed for each extraction type. All extracts were analysed for the heavy metals (Cd, Cr, Cu, Ni and Pb) by Atomic Absorption Spectrometer (Model – PG 990) in triplicate at National Fertilizer Development Centre, Goningora, Kaduna. Nigeria July 2015 and December 2015.

3.9 Determination of Pollution Indices of the Dumpsite Soils

3.9.1 Contamination factor

Contamination factor is a quantification of the degree of contamination relative to either average crustal composition of respective metal or to the measured background values from geologically similar and uncontaminated area (Tijani *et al.*, 2004). It is expressed as:

$$CF = Cm/Bm \qquad 3.20$$

Where Cm is the mean concentration, while Bm is the background concentration of metal directly determined from a geologically similar area (control sample) (Lar and Shehu, 2014).

3.9.2 Geo-accumulation index

Geo-accumulation index (I-geo) have been widely used to evaluate the degree of heavy metal contamination in terrestrial and aquatic environments as expressed:

$$\mathrm{I-geo} = \ln\left(\mathrm{Cm}/1.5 \times \mathrm{Bm}\right) \qquad 3.21$$

Where Cm is the mean concentration, while Bm is the background concentration of metal and 1.5 is a factor for possible variation in the background concentration due to lithologic differences (Lokeshwari and Chandrappa, 2006).

3.9.3 Transfer Factor

The transfer factor (TF) of the metals (Cd, Cr, Cu, Ni and Pb) from the dumpsite soil to *Abelmoschus esculentus*fruit is calculated using the formular:

$$TF = C_{plant}/C_{soil} \qquad 3.22$$

Where C_{plant} and C_{soil} represent the concentrations of the toxic metal in the plants and soils respectively (Lokeshwari and Chandrappa, 2006).

3.8.4 Pollution Load Index

The study evaluated the pollution load index (PLI) of the dumpsite soil obtained from Kafanchan as defined by Tomlison *et al*. (1980) will be evaluated with the expression:

$$PLI = [\pi^{n} i(C_f)]^{1/n} \qquad 3.23$$

Where, C_f is the contamination factor of each metal obtained by the ratio of concentration of each metal in soil or plant to that of the metal in background soil or plant; π is the geometrical mean operator; n is the number of metals investigated and i is each metal. When PLI value is below or close to one, it indicates heavy metal loads at the baseline, while values above one indicate heavy metal accumulation or pollution in plant or soil from the test site (Agunbiade and Fawale, 2009).

3.10 Statistical analysis

All treatments in the experiments were triplicated. The mean and standard deviations (SD) were calculated by the Microsoft Office Excel 2013. Two way analysis of variance (ANOVA) was carried out with SPSS 20.0.

3.10.1 Analysis of variance (ANOVA)

A two-factor ANOVA with replication was carried out at α level of 0.05 for the dumpsite soil samples using Microsoft Excel® 2013 to test the following hypothesis:

${}^{1}H_o$: There is no seasonal effect on the level of Cd, Cr, Cu, Ni, and Pb in the dumpsite soil and *Abelmoschus esculentus* samples obtained from the various dumpsites.

${}^{2}H_o$: There is no significant difference in the levels of the heavy metals within the soil samples.

${}^{3}H_o$: There is no interaction between metals and the seasons.

A single-factor ANOVA was also carried out on the results obtained for *Abelmoschus esculentus* samples using Microsoft Excel® 2013 to test the hypothesis:

Ho: There is no difference in the levels of the heavy metals in *Abelmoschus esculentus* samples of the various sampling sites.

CHAPTER FOUR

4.0 RESULTS

4.1 Quality Assurance

The results of the validity of the precision and accuracy of the atomic absorption spectrophotometer using spiking experiments gave the mean percentage recoveries of Cd, Cr, Cu, Ni and Pb in the digested dumpsite soil and *Abelmoschus esculentus*fruit samples (Table 4.1). The mean percentage recoveries of the heavy metals in the dumpsite soil samples varied from 87.66 ± 3.00% - 94.32 ± 1.00%, while the fruit samples had, the percentage recoveries ranging from 83.85 ± 1.20% - 91.47 ± 3.00%. The highest mean recovery of 94.32 ± 1.00% and 91.47 ± 3.00% respectively were recorded for Ni in the soil and fruit samples, while the lowest percentage recovery were 87.66 ± 3.00% for Pb in the soil and 83.85 ± 1.20% for Cr in the fruit. The pattern of the recovery efficiency for the soil and plant samples followed the orders: Ni > Cu > Cd > Cr > Pb and Ni > Cu > Cd > Pb > Cr respectively.

4.2 Physicochemical Parameters of the Dumpsite Soil

The particle size distribution of the dumpsite soil and the control site collected in the wet and dry season of 2015 is presented in Table 4.2. The result shows that all the study areas were sandy with the textural class being predominantly loamy sand with the control site being loamy sand. The percentage of sand across the sites ranged from 78.00% in Gurara Street dumpsite (GRR) and in Abuja Street dumpsite (ABJ) to 84.00% in Garaje dumpsite (GRJ) with the control recording 72.00% sand. The percentage of silt ranged from 12.00% in GRJ to 18.00% in GRR and ABJ; on the other hand the percentage of clay was with an average of 4.00% with the control recording mean percentage of 18.00% and 72.00% of silt and sand across all sites.

Table 4.3 and 4.4 show the physico-chemical properties of the dumpsite soil and control site in the wet and dry seasons of 2015. The dumpsite soil samples had the lowest pH value of 7.10 (GRR) in wet season and pH of 6.67 in the dry season in GRR, the highest pH of 8.90 (wet season) and 7.98 (dry season) were recorded in Railway quarters dumpsite (RLQ) with the control site having pH 7.40 and 7.30 in the wet and dry seasons respectively. The electrical conductivities (EC) of the dumpsite soils ranged from 0.50 μScm^{-1} (GRR) to 2.05 μScm^{-1} (RLQ) and 0.40 μScm^{-1} (ABJ) to 1.75 μScm^{-1} (RLQ) in the wet and dry seasons of 2015 respectively; with the control site recording 0.11 and 0.17 μScm^{-1} in the wet and dry season.

NO_3^- -N contents in the soil during wet season ranged from 0.03 $mgkg^{-1}$ at both ABR and ABJ to 0.07 $mgkg^{-1}$ at GRR while in the dry season it was 0.03 $mgkg^{-1}$ at ABJ to 0.08 $mgkg^{-1}$ at GRR with the control sites recording 0.02 mg/kg for both the wet and dry seasons.

The cation exchange capacity (CEC) of the dumpsite soils ranged from 8.00 $Cmol^+/kg$ (ABR) to 9.50 $Cmol^+/kg$ (GRJ and ABJ) in the wet season and 8.03 $Cmol^+/kg$ (ABR) to 10.30 $CMol^+/kg$ (ABJ) in the dry season. The control site had values of 6.00 $Cmol^+/kg$ and 6.11 $Cmol^+/kg$ in the wet and dry season respectively.

The highest and the lowest organic matter (OM) content of the dumpsite soil was highest and lowest respectively in the samples from ABJ and ABR respectively in the two seasons with ABJ having 6.80% (wet season) and 6.21% (dry season), and ABR had 3.85% and 4.15% in the wet and dry seasons respectively.

Table 4.1 Mean Percentage Recovery of Heavy Metals in the Dumpsite Soil and *Abelmoschus esculentus*Fruit

Metals	Soil samples (%)	Fruit samples (%)
Cd	91.48±1.00	86.54±2.50
Cu	93.25±2.00	90.80±1.20
Ni	94.32±1.00	91.47±3.00
Cr	89.21±1.40	83.85±1.20
Pb	87.66±3.00	84.98±2.00

Table 4.2: Characterization of Particle Size of the Dumpsite Soil from Kafanchan

Location	**Sand (%)**	**Silt (%)**	**Clay (%)**	**Texture Class**
ABR	80	16	4	Loamy Sand
GRR	78	18	4	Loamy Sand
GRJ	84	12	4	Loamy Sand
ABJ	78	18	4	Loamy Sand
RLQ	82	14	4	Loamy Sand
CTR	72	18	10	Sandy Loam

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

Table 4.3: Physicochemical Parameters of the Dumpsite Soil in the Wet Season of 2015

Location	pH (H_2O)	EC (µS/cm)	NO_3^--N (mg/kg)	PO_4^-(mg/kg)	Cl^- (mg/kg)	CEC (Cmol/kg)	OM (%)
ABR	8.32±0.01	0.87±0.04	0.03±0.02	75.17±0.02	6.32±0.01	8.00±0.01	3.85±0.02
GRR	7.10±0.01	0.50±0.01	0.07±0.01	52.80±0.03	7.08±0.03	8.70±0.04	4.67±0.14
GRJ	7.22±0.02	1.38±0.12	0.04±0.03	42.53±0.01	2.75±0.01	9.50±0.01	5.88±0.03
ABJ	8.00±0.02	0.53±0.05	0.03±0.01	105.60±0.03	12.54±0.02	9.50±0.02	6.80±0.02
RLQ	8.90±0.01	2.05±0.03	0.04±0.02	61.14v0.02	6.98±0.01	8.50±0.03	5.40±0.02
CTR	7.40±0.02	0.11±0.01	0.02±0.03	18.03±0.01	1.73±0.01	6.00±0.01	2.83±0.04

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site;EC: Electrical conductivity; CEC: Cation exchange capacity; OM: Organic Matter;

Table 4.4: Physicochemical Parameters of the Dumpsite Soil in the Dry Season of 2015

Location	pH (H_2O)	EC (µS/cm)	NO_3^--N (mg/kg)	PO_4^-(mg/kg)	Cl^- (mg/kg)	CEC (Cmol/kg)	O M (%)
ABR	7.56±0.02	0.90±0.01	0.04±0.01	57.11±0.50	5.72±0.01	8.03±0.04	4.15±0.04
GRR	6.67±0.01	0.42±0.01	0.08±0.03	56.05±0.03	8.18±0.03	9.51±0.02	5.02±0.02
GRJ	7.20±0.02	1.20±0.02	0.05±0.01	48.68±0.21	4.63±0.01	9.85±0.02	6.20±0.01
ABJ	7.01±0.01	0.40±0.02	0.03±0.01	102.45±0.03	8.24±0.02	10.30±0.06	6.21±0.12
RLQ	7.98±0.02	1.75±0.03	0.05±0.02	63.00±0.02	2.54±0.01	9.81±0.02	6.01±0.02
CTR	7.30±0.02	0.17±0.03	0.02±0.01	19.23±0.01	2.12±0.01	6.11±0.03	2.81±0.02

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site; EC: Electrical conductivity; CEC: Cation exchange capacity; OM: Organic Matter

The control soil samples contained OM of amount 2.83% and 2.81% in the wet and dry season of 2015 respectively.

PO_4^{3-} -P amount in the soil ranged from 42.53 mg/kg(GRJ) to 105.60 mg/kgat (ABJ) in the wet season and from 48.68 mg/kg (GRJ) to 102.45 mg/kg (ABJ) in the dry season. The Cl^- content soil ranged from 2.75 mg/kg (GRJ) to 12.54 mg/kg (ABJ) in the wet season and 2.54 mg/kg (RLQ) to 8.24 mg/kg (ABJ) in the dry season (Table 4.3 and 4.4).

4.3 Concentrations of Heavy Metals in the Dumpsite Soil from Kafanchan

The mean concentrations of Cd, Cr, Cu, Ni and Pb in the dumpsite soil and the control site is presented in Figure 4.1 and 4.2. From the result, the mean concentration of Cd ranged from 21.86 (GRR) to 58.27 mg/kg (ABJ), and 13.00 (GRR) to 24.60 mg/kg (ABR) in the wet and dry season respectively. The concentration for chromium recorded in the study area in the wet and dry season ranged from 25.86 (RLQ) to 44.69 mg/kg (ABR) and 20.34 (RLQ) to 52.89 mg/kg (ABJ) respectively (Appendix II and III). The copper contents for the wet and dry season ranged from 41.33 (RLQ) to 81.21 mg/kg (GRJ), and 61.45 (RLQ) to 161.30 mg/kg (GRR) respectively.

On the other hand, the mean concentrations of lead in the wet and dry seasons in the dumpsite soil ranged from 23.62 (RLQ) to 56.63 mg/kg (GRR), and 42.70 (RLQ) to 72.13 mg/kg (GRR) respectively. Similarly, the mean concentration of nickel in the wet and dry seasons ranged from 31.44 (RLQ) to 77.44 mg/kg (GRJ), and 22.88 (RLQ) to 79.85 mg/kg (GRR) respectively. The mean concentrations of the metals in the control site were 24.18, 22.90, 23.23, 43.23 and 12.45 mg/kg in the wet season for Cd, Cr, Cu, Ni and Pb and 21.93, 19.13, 18.03, 27.90 and 32.28 mg/kg in the dry season respectively.

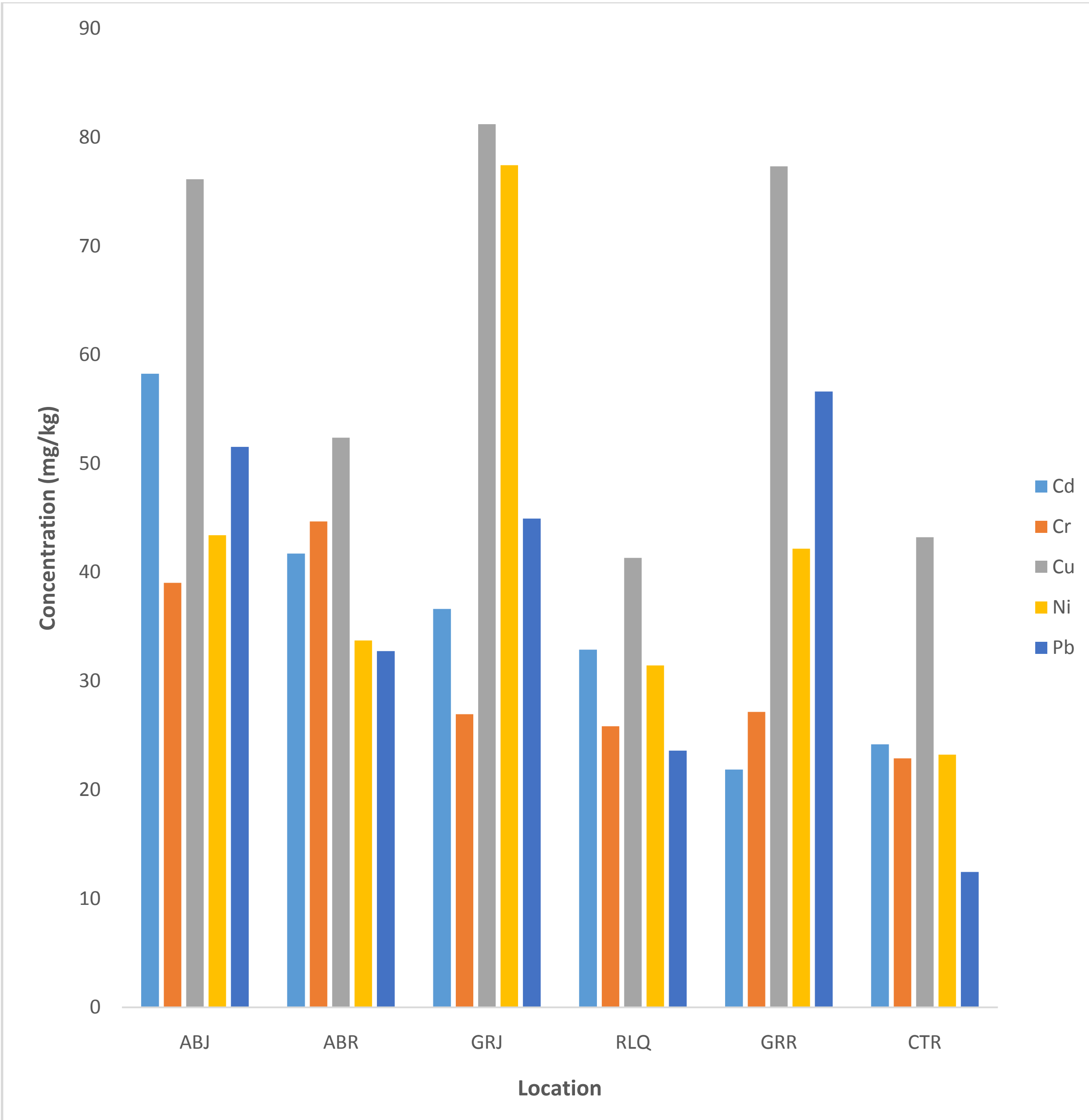

Figure 4.1: Mean Concentration of metals in the dumpsite soils and the control site in Kafanchan in the wet season

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

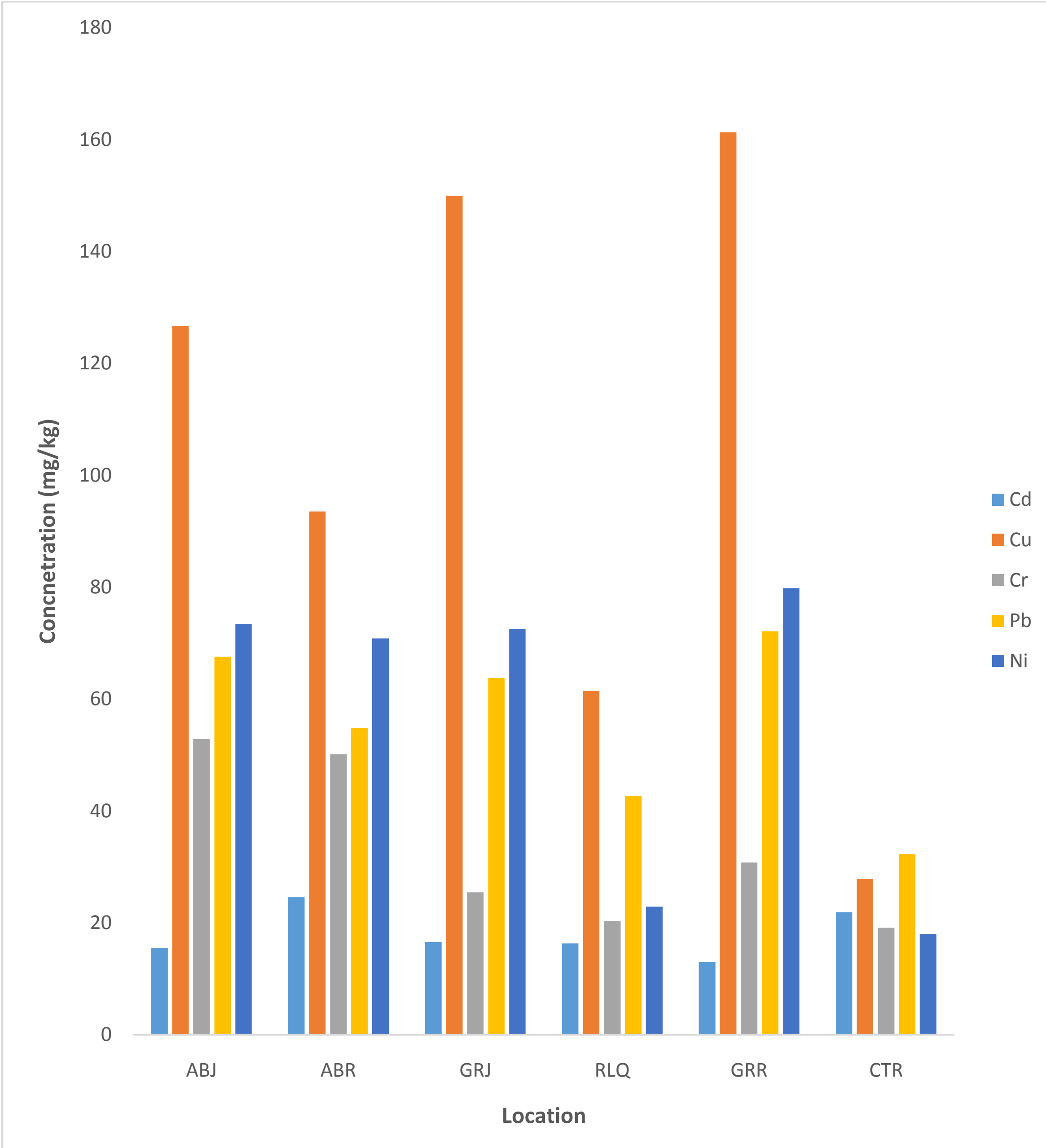

Figure 4.2: Mean Concentration of metals in the dumpsite soils and the control site in Kafanchan in the dry season

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

4.4 Metal Content in *Abelmoschus esculentus* Fruit Obtained from Kafanchan Dumpsite

Figure 4.3 shows that the mean metal content in *Abelmoschus esculentus*fruit ranged from 8.51 (ABR) to 14.36 (GRJ), 7.98 (GRR) to 14.29 (GRJ), 7.35 (RLQ) to 18.80 (GRJ), 1.33 (RLQ) to 16.75 (ABJ), and 4.08 (GRR) to 12.63 (ABJ) for cadmium, chromium, copper, nickel and lead respectively. The control area had the mean metal levels being 31.97 mg/kg, 7.00 mg/kg, 12.95; 2.95 mg/kg and 2.75 mg/kg for Cd, Cr, Cu, Ni and Pb respectively (Appendix IV).

4.5 Speciation of Metals in the Dumpsite Soils and the Control Site

The concentrations of Cd, Cr, Cu, Ni and Pb in the different fractions based on sequential extraction method are presented in Figures 4.4 - 4.13 and Appendix VII – XVII.

Chemical association of cadmium was dominated in the non-residual fraction in both wet and dry season. Cd in the residual fraction ranged from 25 (ABR) to 50% (GRR) in the wet season while in dry season the range was from 24 (ABJ) to 46% (GRR). Cd in the non-residual fractions ranged from 50 (GRR) to 75% (ABR) in the wet season while in the dry season it was 54 (GRR) to 76% in ABJ. The range of the bioavailable Cd in the soil was 33 (ABJ) to 50% in ABR and RLQ in the wet season while it was 40% (GRR) to 51% (ABR) in the dry season. The percentages of Cd in the non-residual, residual and bioavailable fractions for the control site was 45, 55 and 37% respectively in the wet season while in the dry season percentages of the non-residual, residual and bioavailable fractions for the control site was 64, 36 and 32 respectively.

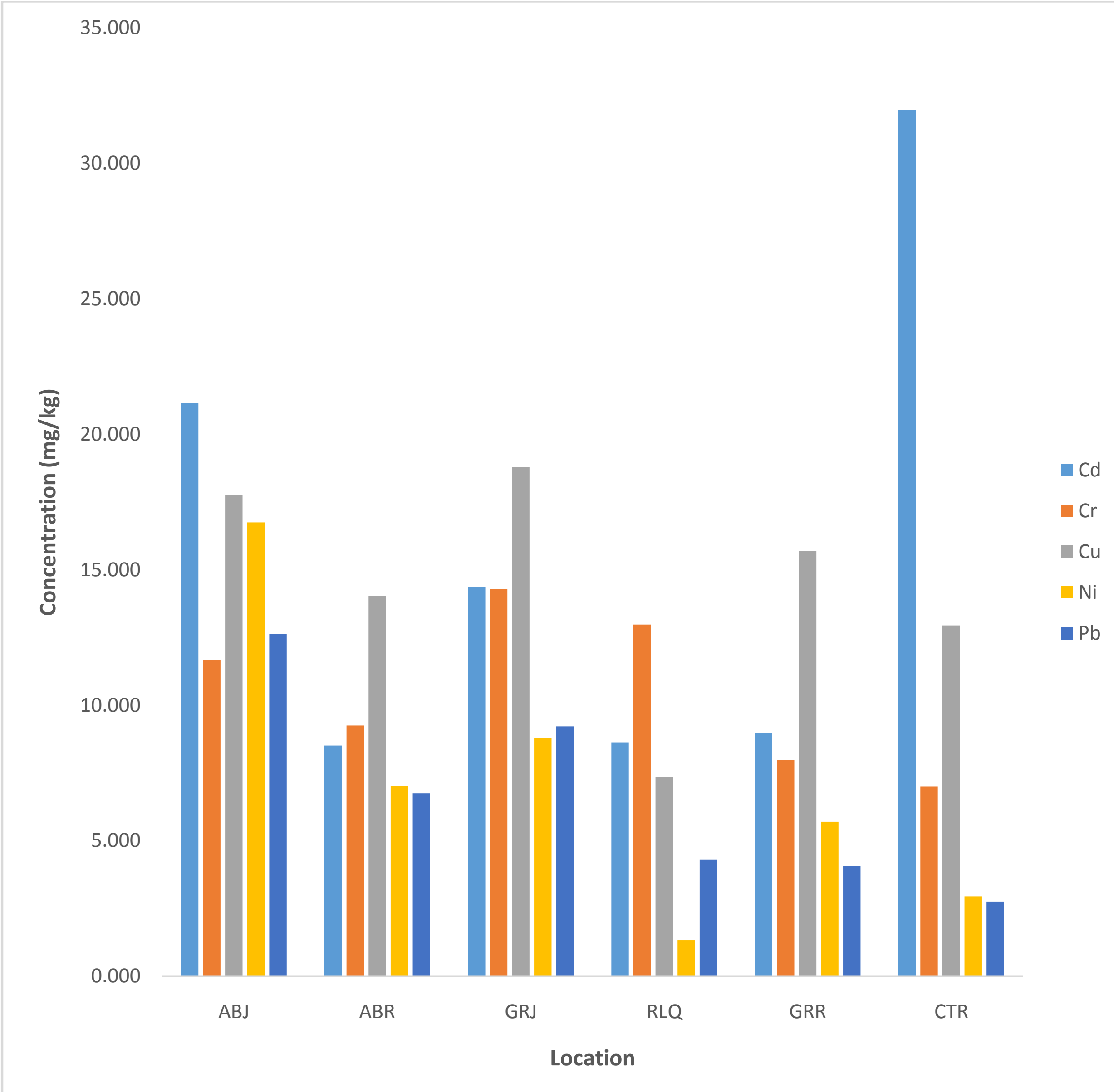

Figure 4.3: Concentration of heavy metals in *Abelmoschus esculentus*fruit planted on the dumpsite soil and the control site

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

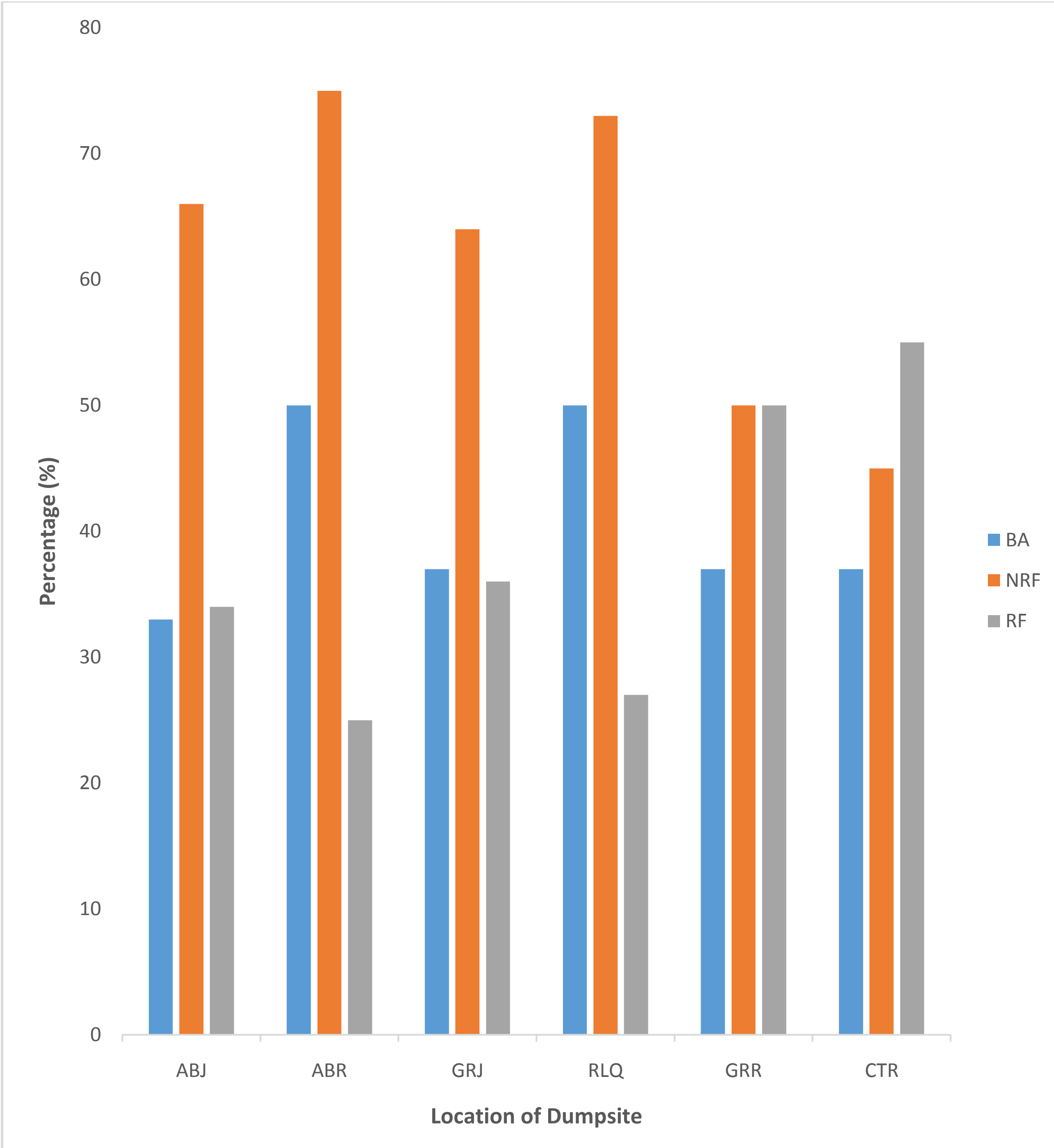

Figure 4.4: Percentage of the Bioavailable (BA), Residual (RF) and Non-residual (NRF) Cadmium in the Wet Season Dumpsite Soils from Kafanchan

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

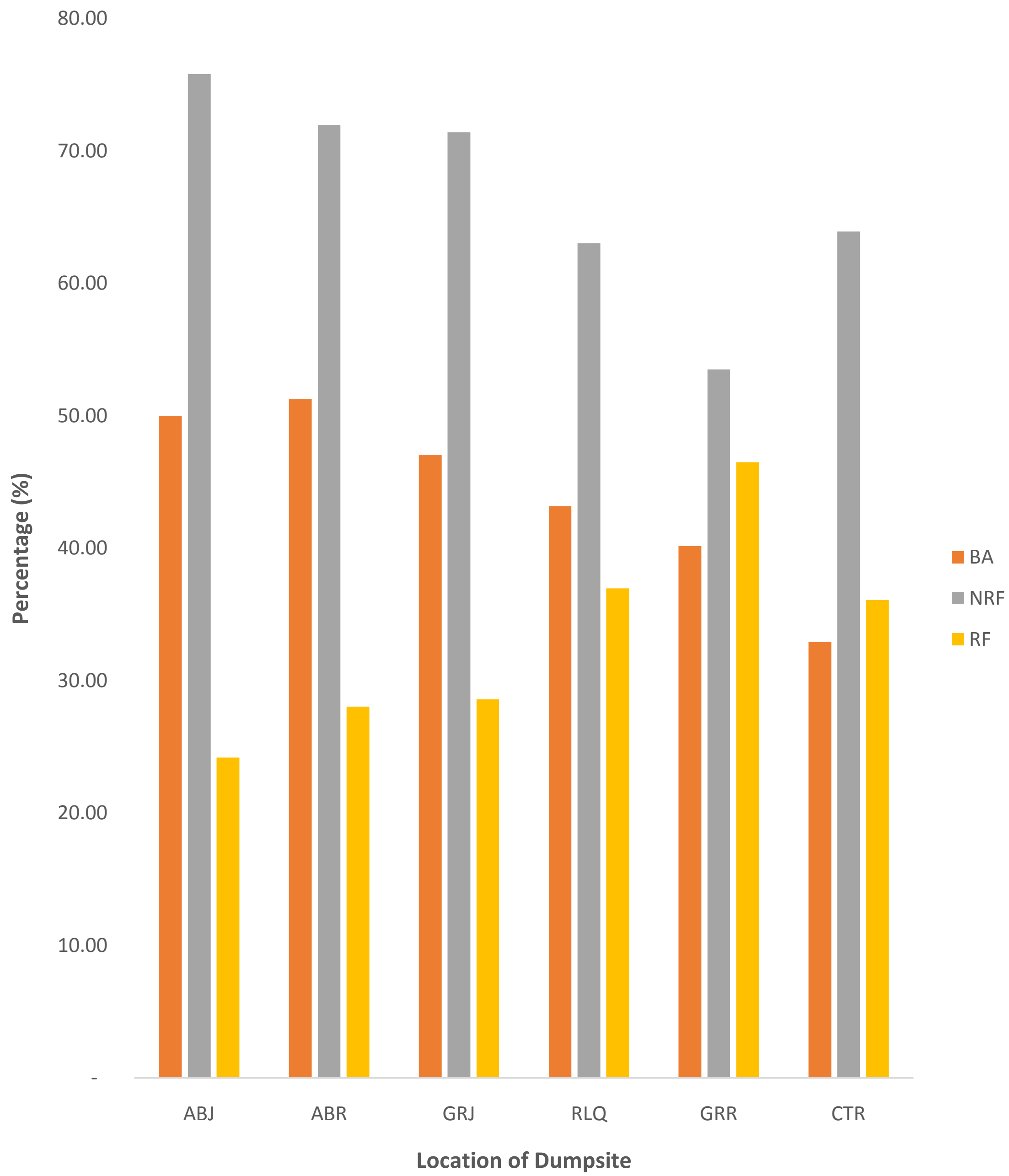

Figure 4.5: Percentage of the Bioavailable (BA), Residual (RF) and Non-residual (NRF) Cadmium in the Dry Season Dumpsite Soils from Kafanchan

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

Copper in the bioavailable, non-residual and residual fractions of the soil in the wet season ranged from 44 (ABJ) to 53% (GRJ), 59 (RLQ) to 72% (GRJ), and 28 (GRJ) to 41% (RLQ) respectively. However, during the dry season the ranges were 11 (GRR) to 47% (ABR), 26 (GRR) to 70% (ABR), 30 (ABR) to 74% (GRR) for the bioavailable, non-residual and residual fractions, respectively. The control site had 31, 58 and 42% of Cu in the non-residual, residual and bioavailable fraction respectively in the wet season, while it was 28, 64 and 36% for the non-residual, residual and bioavailable fraction respectively in the dry season samples.

The results of chemical fractionation of chromium in the dumpsite soil is presented in Figure 4.8 and 4.9 for the wet and dry season. The values of Cr ranged from 37 (GRR) to 78% (ABR) for the non-residual fractions, 22 (ABR) to 63% (GRR) for the residual fractions and bioavailable fraction had values ranging from 13 (GRR) to 59% (ABR) in the wet season of 2015, for the dry season however, Cr level ranged from 43 (RLQ) to 82% (GRJ) for the non-residual fractions, and 18 (GRJ) to 57% (RLQ) for the residual fraction, the bioavailable amount of Cr ranged from 30 (RLQ) to 70% (GRJ). The control site had Cr being 66, 34, and 65% for the non-residual, residual and bioavailable fraction respectively, in the wet season samples while the values were 56, 44, and 37% for non-residual, residual and bioavailable fraction respectively during the dry season.

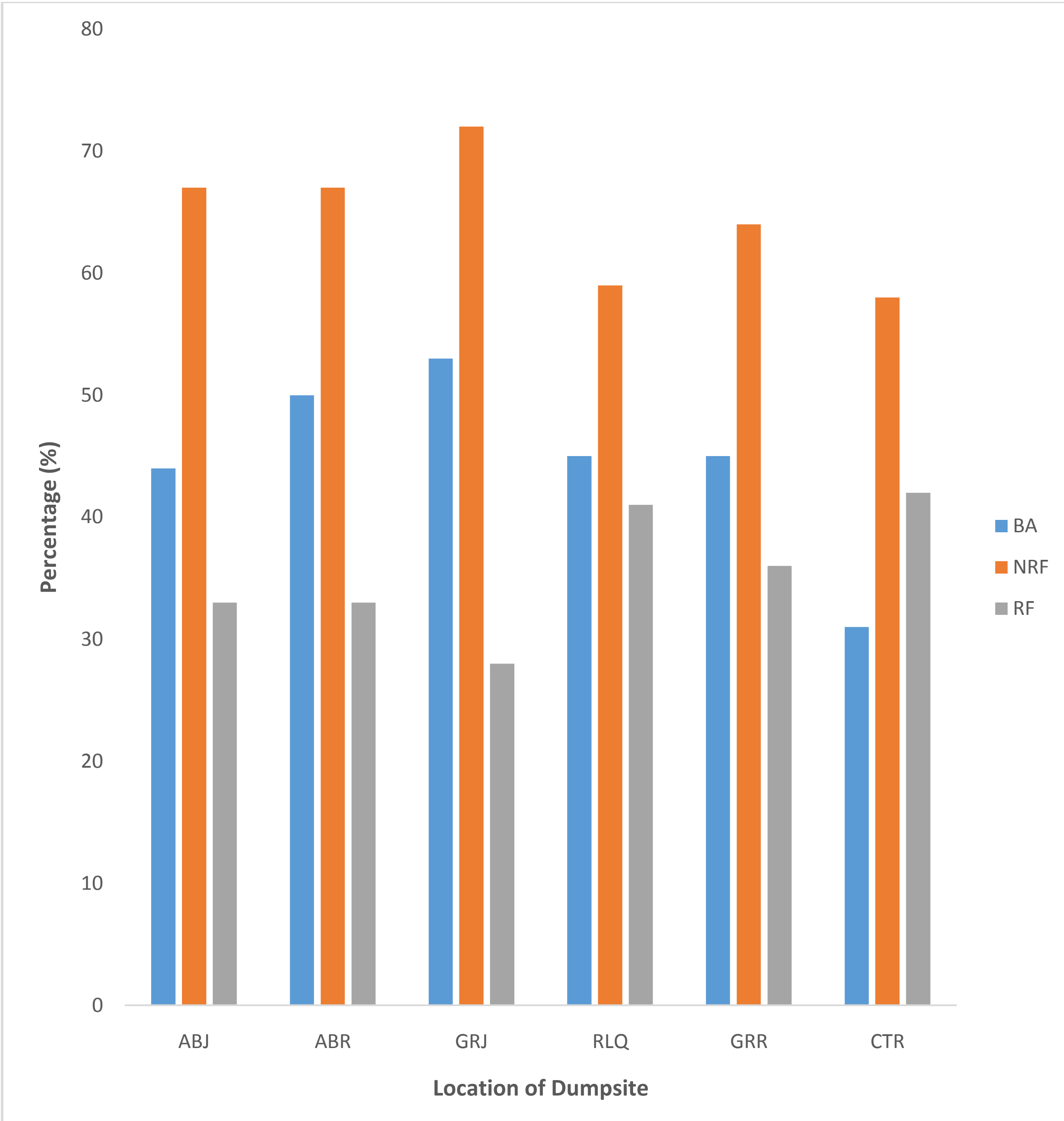

Figure 4.6: Percentage of the Bioavailable (BA), Residual (RF) and Non-residual (NRF) Copper in the Wet Season Dumpsite Soils from Kafanchan

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

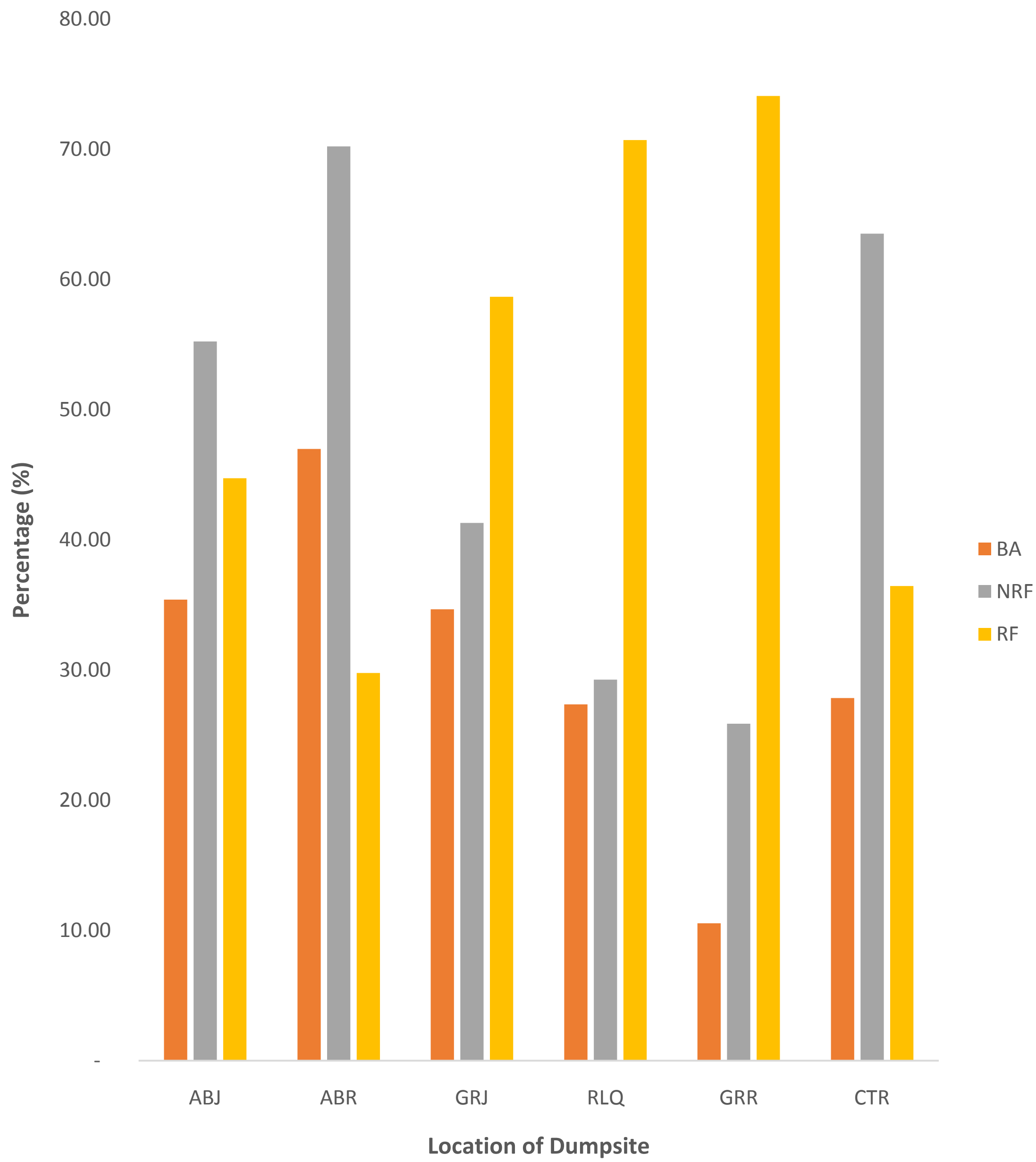

Figure 4.7: Percentage of the Bioavailable (BA), Residual (RF) and Non-residual (NRF) Copper in the Dry Season Dumpsite Soils from Kafanchan

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

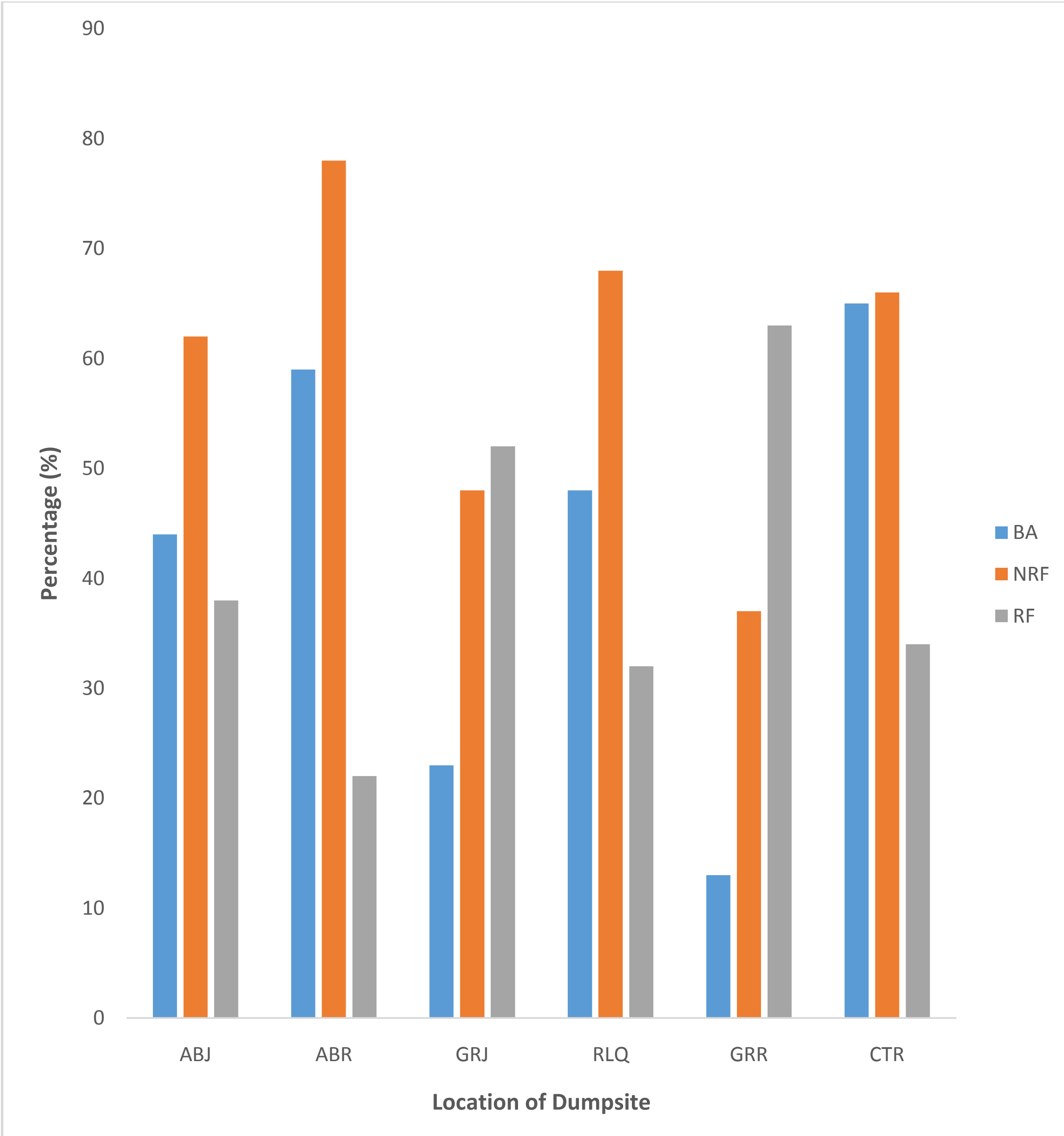

Figure 4.8: Percentage of the Bioavailable (BA), Residual (RF) and Non-residual (NRF) Chromium in the Wet Season Dumpsites Soils from Kafanchan

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

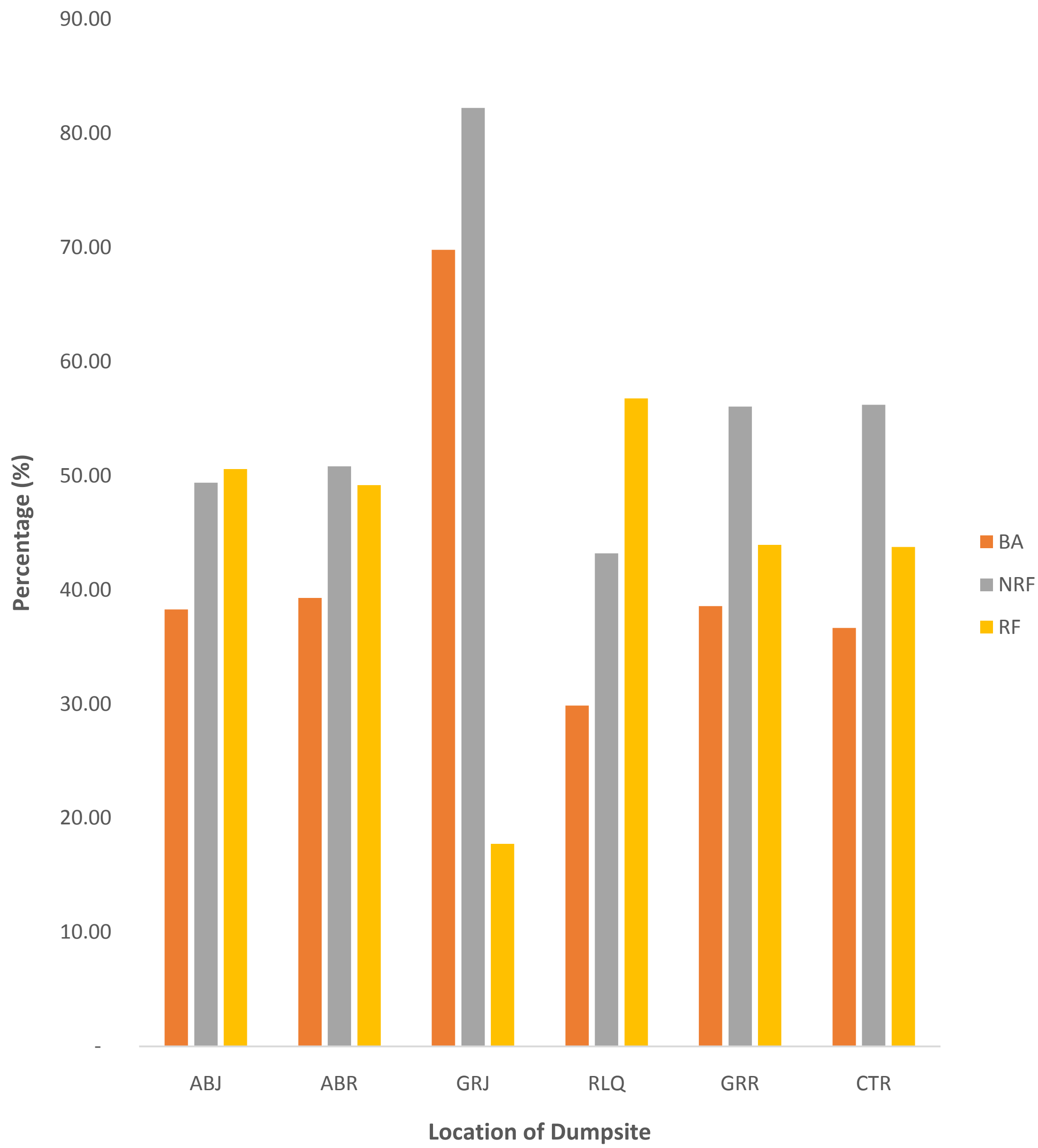

Figure 4.9: Percentage of the Bioavailable (BA), Residual (RF) and Non-residual (NRF) Chromium in the Dry Season Dumpsites Soils from Kafanchan

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

As shown in Figure 4.10 and 4.11 in the wet and dry seasons, the level of Pb in the chemical fractionated dumpsite soil was dominantly in the non-residual fraction. The non-residual fractions ranged from 60% in the sample from ABJ and ABR to 95% in GRR, the residual fraction ranged from 5 (GRR) to 40% in ABJ and ABR, while the mobile fraction contained 27 (GRR) to 56% (GRJ) Pb. From the results the control site had Pb being 54, 46 and 37% in the non-residual, residual and bioavailable fraction respectively in the wet season of 2015, while in the dry season, the non-residual fraction ranged from 54 (RLQ) to 78% (ABR), the residual fractions ranged from 21 (ABR) to 45% (RLQ), and the mobile fraction contained 36 (GRR) to 54% Pb (GRJ). The control samples had Pb levels of 72%, 28%, and 29% in the non-residual, residual and bioavailable fraction respectively (Appendix VII to XVIII).

Figures 4.12 and 4.13 showed the percentages of the bioavailable, residual and non-residual components of Ni in the dumpsite soil collected from Kafanchan in the wet and dry seasons of 2015. Ni in the bioavailable, non-residual and residual fraction ranged from 42 (RLQ) to 57% (ABR), 58 (ABJ) to 76% in ABR and RLQ, 24 in ABR and RLQ to 42% in ABJ respectively in the wet season samples. Also Ni in the bioavailable, non-residual and residual fraction ranged from 14 (GRJ) to 34% (ABJ), 40 (GRJ) to 65% (RLQ), 35 (RLQ) to 59% (GRJ) respectively in the dry season. The percentages of Ni in the bioavailable, non-residual and residual fractions of the control samples were 26, 46 and 54 respectively in the wet season while the dry season samples had percentages of the bioavailable, the non-residual and residual fractions in the control samples being 26, 46 and 54% respectively (Appendix VII – XVII).

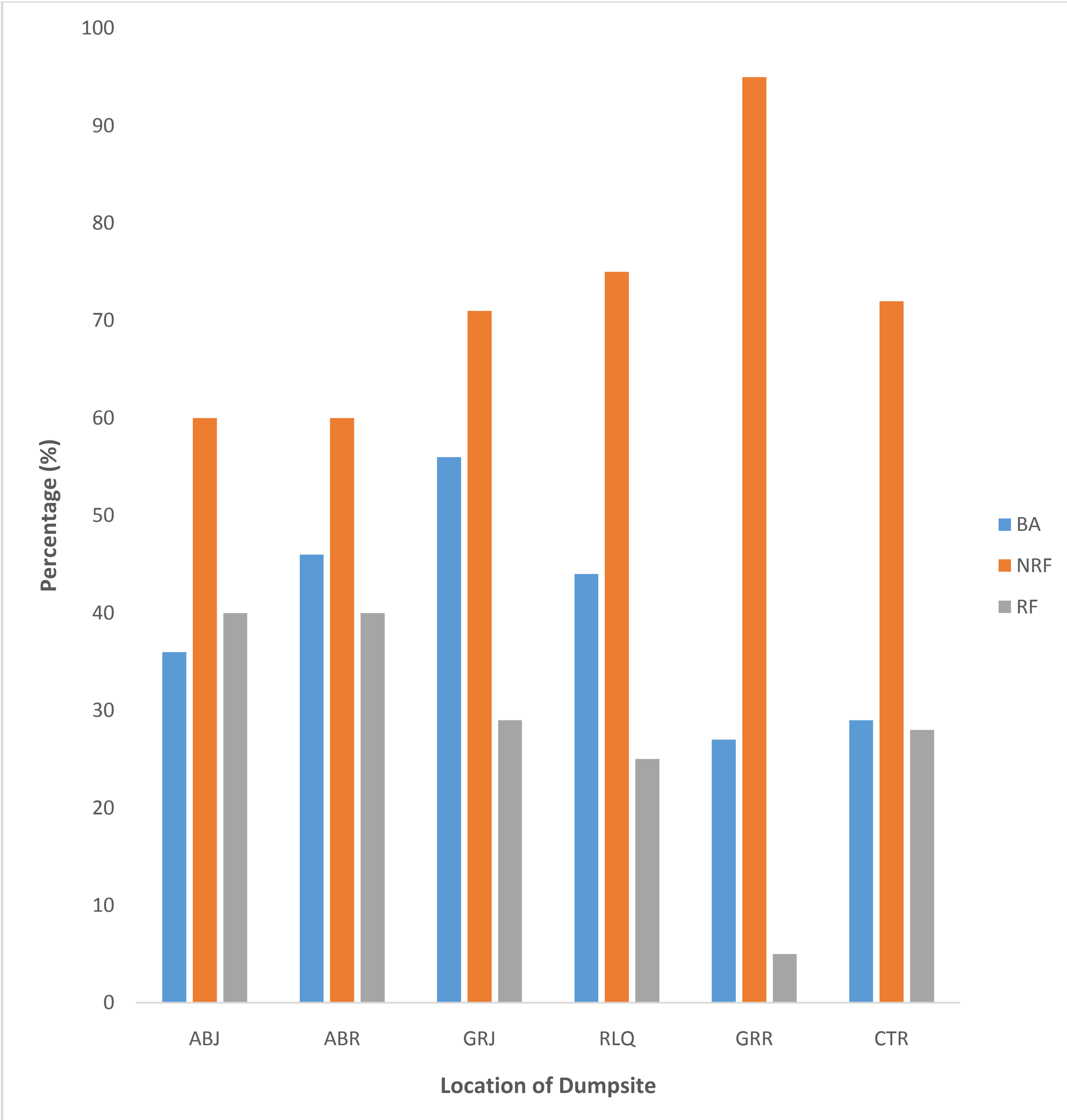

Figure 4.10: Percentage of the Bioavailable (BA), Residual (RF) and Non-residual (NRF) Lead in the Wet Season Dumpsites Soils from Kafanchan

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

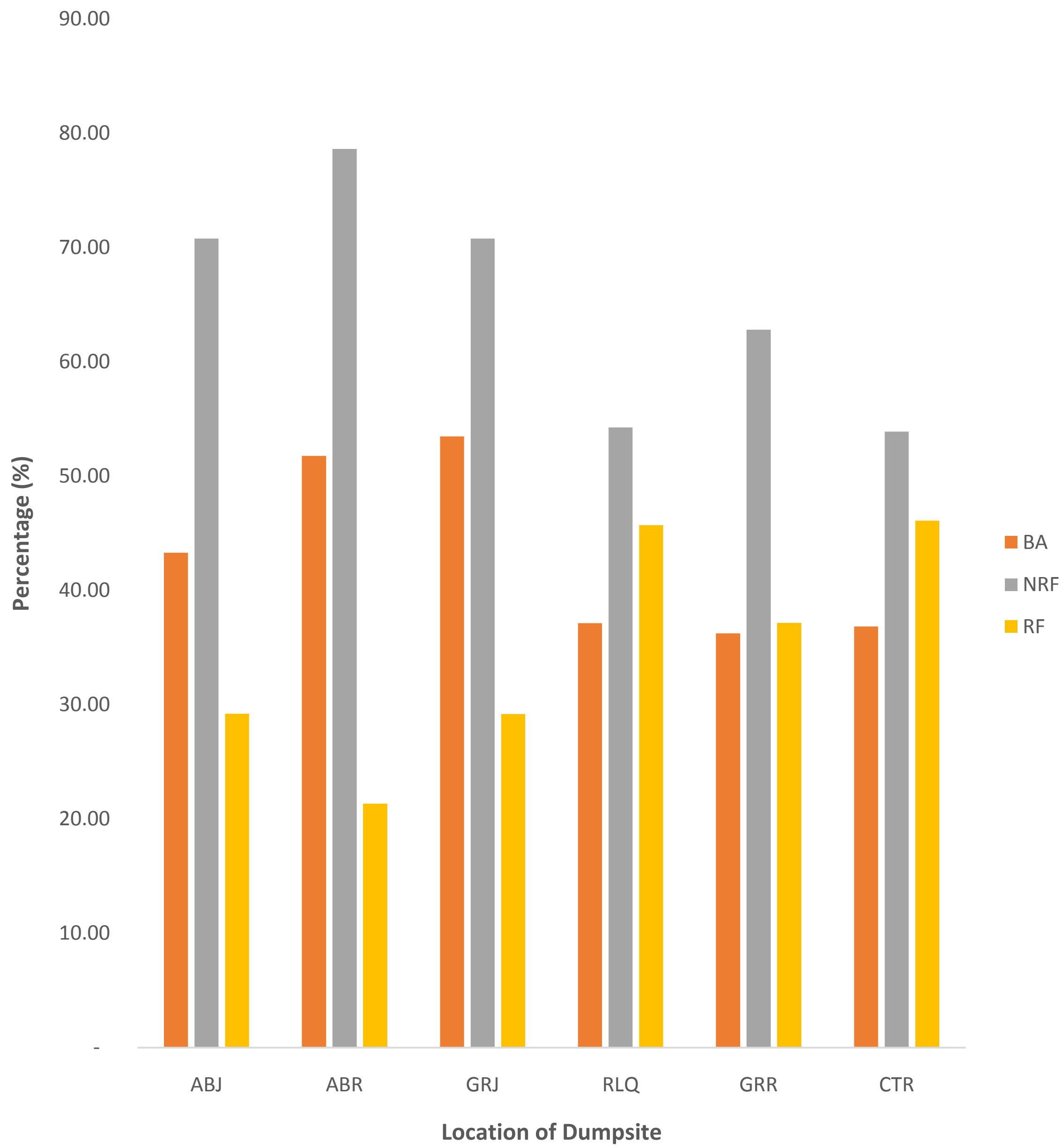

Figure 4.11: Percentage of the Bioavailable (BA), Residual (RF) and Non-residual (NRF) Lead in the Dry Season Dumpsites Soils from Kafanchan

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

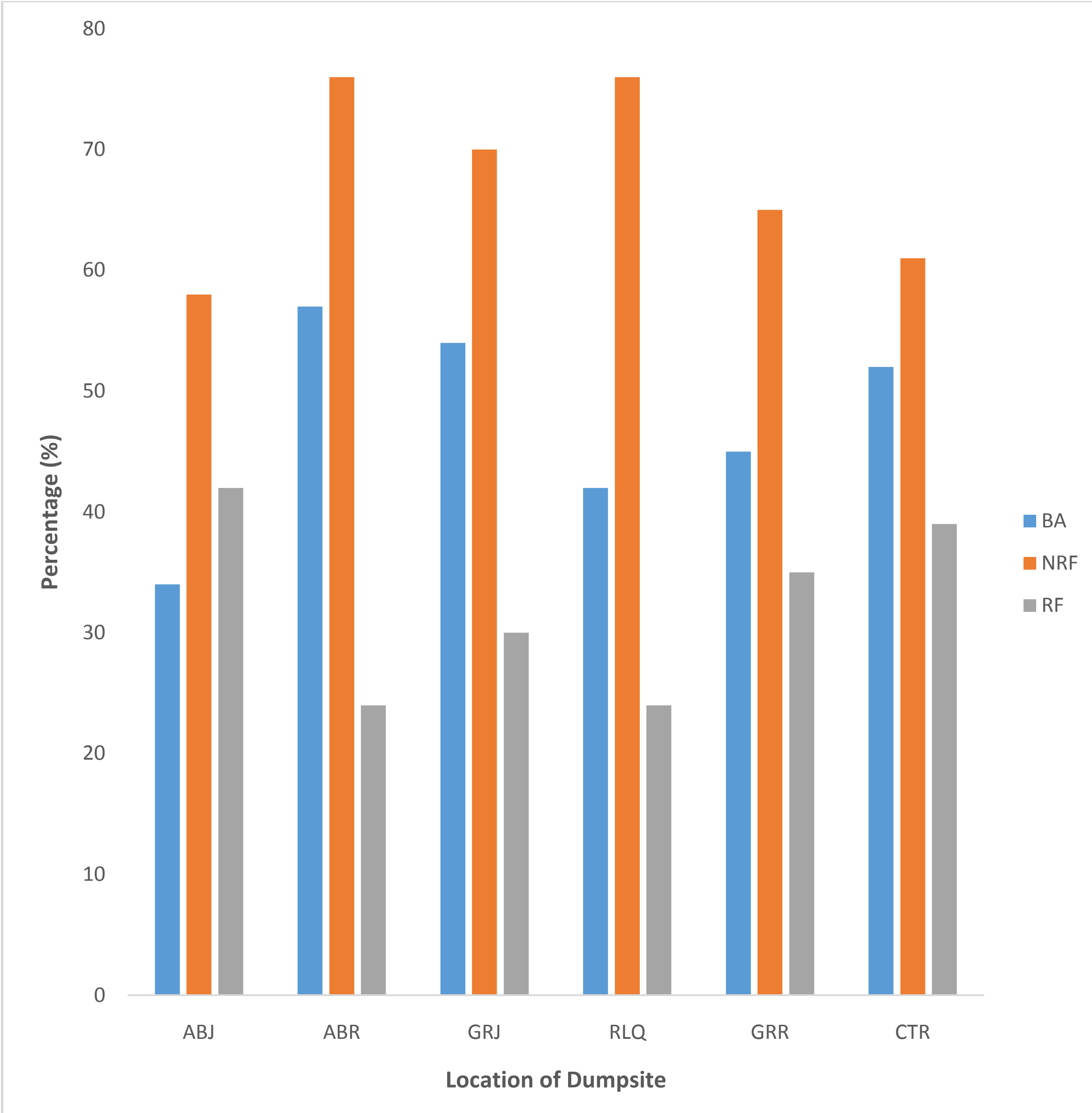

Figure 4.12: Percentage of the Bioavailable (BA), Residual (RF) and Non-residual (NRF) Nickel in the Wet Season Dumpsites Soils from Kafanchan

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

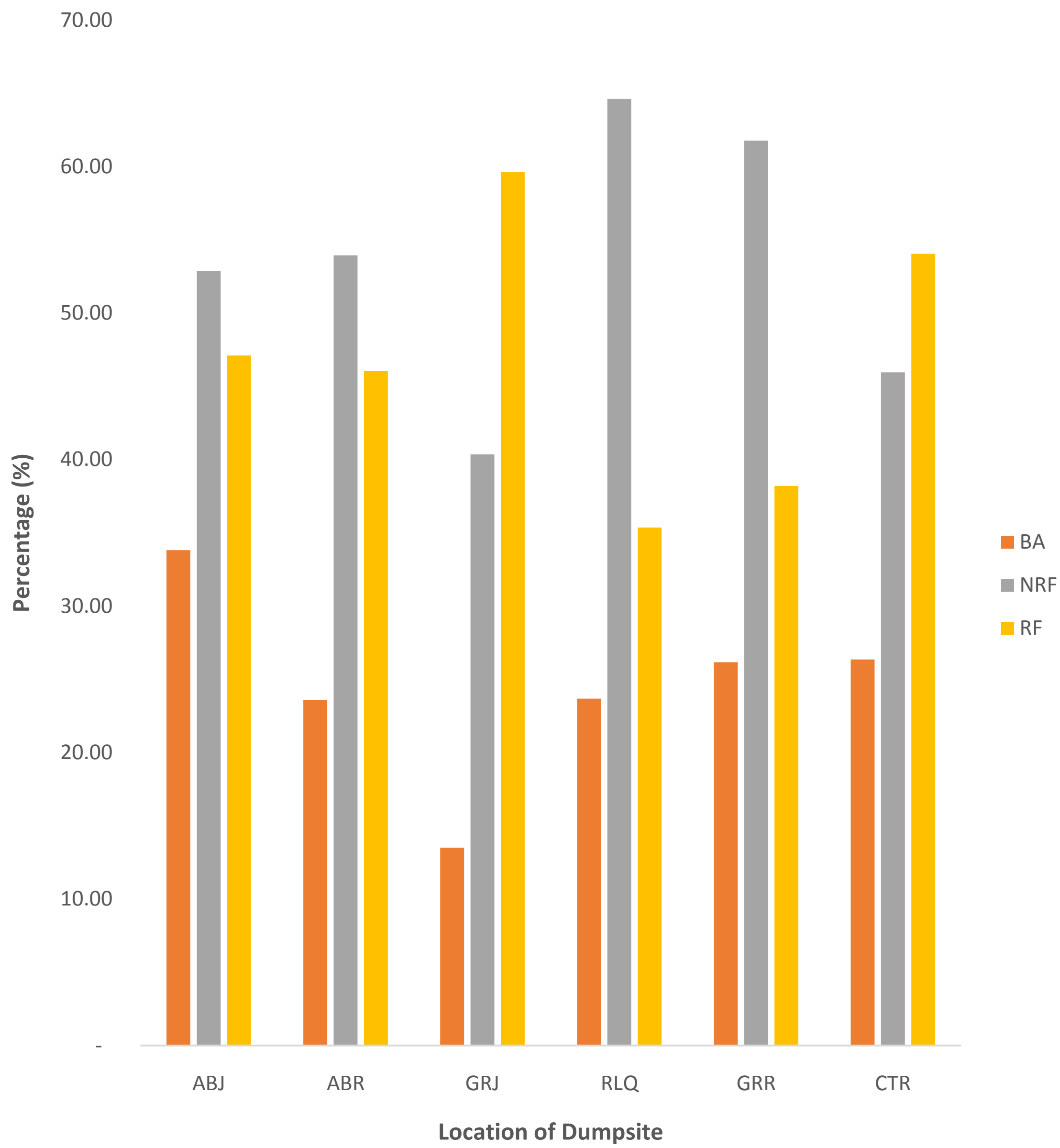

Figure 4.13: Percentage of the Bioavailable (BA), Residual (RF) and Non-residual (NRF) Nickel in the Dry Season Dumpsites Soils from Kafanchan

ABJ = Abuja Street dumpsite; ABR = Albarka Street dumpsite; GRJ = Garaje dumpsite; RLQ = Railway quarters dumpsite; GRR = Gurara Street dumpsite; CTR = Control site

4.6 Statistical Data Analysis

4.6.1 Analysis of variance (ANOVA)

The results of two-factor ANOVA as presented in Table 4.5 indicated that there was a significant difference in the mean concentrations of the metals studied across the dumpsites and the seasons at $P < 0.05$. Likewise, Table 4.6 present a one way ANOVA $P < 0.05$ indicating a significant difference in the mean concentrations of the metals studied in the *Abelmoschus esculentus* fruit across the sites.

4.6.2 Correlation analysis

Tables 4.7 and 4.8 presents the correlation coefficients obtained to explain the extent of the association between Cd, Cr, Cu, Ni and Pb in the dumpsite soils obtained from Kafanchan, Kaduna State, Nigeria. The results indicated that a strong positive correlation existed between Cu in the soil (Cu_s) and Ni_s, Pb_s, Cu_p, also a strong relationship existed between Cr_s and Ni_s, Ni_f, Pb_f. Furthermore, strong correlation existed between Ni_s and Pb_s, Cu_f, Ni_f, and also, there was strong relationship between Pb_f and Cu_f,Ni_f. Similarly, strong relationship existed between Cu_f and Ni_f, Pb_f, and between Ni_f, and Pb_f in the dry season of 2015. A two-step correlation analysis was carried out to determine the association between the metal concentrations in the dumpsite soil and *Abelmoschus esculentus*fruitsamples collected from the various sampling locations. In the wet season, strong relationship existed between Cd and Cu and also between Cr and Ni, Pb (Table 4.7).

Table 4.5: Results of the ANOVA for Metals in the Dumpsite Soils

Samples	*Source ofVariation*	*SS*	*df*	*MS*	*P-value*
Soil	[1]Seasons	2057.30	1	2,057.30	0.05[a]
	[2]Metals	9807.45	4	2,451.86	0.00[a]
	[3]Interaction	18762.39	4	4,690.60	0.00[a]
	Within	26100.33	50	522.0066	
	Total	56727.48	59		

SS sum of squares, df degree of freedom, MS mean of squares; [a] $p \leq 0.05$, reject H_0

The results of the tests of the null hypotheses stated in 3.9 are presented in Appendix XIX.

Table 4.6: One-way ANOVA Results for the Heavy Metals in the *Abelmoschus esculentus* Samples Collected in the Dry Season

Source of Variation	*SS*	*df*	*MS*	*P-value*
Between Groups	296.87	4	74.22	0.06
Within Groups	730.65	25	29.23	
Total	1027.52	29		

SS sum of squares,df degree of freedom, MS mean of squares; [a] $p \leq 0.05$, reject H_0

Table 4.7: Correlation of Total Metal Concentrations in the Dumpsite Soils and *Abelmoschus esculentus* Fruit in the Dry Season of 2015

	Cd_s	Cu_s	Cr_s	Ni_s	Pb_s	Cd_f	Cr_f	Cu_f	Ni_f	Pb_f
Cd_s	1									
Cu_s	-0.620	1								
Cr_s	0.161	0.360	1							
Ni_s	-0.299	0.914	0.660	1						
Pb_s	-0.592	0.974	0.534	0.944	1					
Cd_f	0.245	-0.483	-0.180	-0.439	-0.467	1				
Cr_f	-0.343	0.305	-0.019	0.137	0.242	-0.347	1			
Cu_f	-0.196	0.716	0.438	0.776	0.702	0.169	0.091	1		
Ni_f	-0.224	0.548	0.769	0.670	0.659	0.131	0.273	0.757	1	
Pb_f	-0.200	0.515	0.687	0.599	0.594	-0.006	0.571	0.655	0.938	1

Cd_s = cadmium in soil, Cu_s = copper in soil, Cr_s = chromium in soil, Ni_s = nickel in soil, Pb_s= lead in soil, Cd_f= cadmium in fruit, Cr_f= chromium in fruit, Cu_f= copper in fruit, Ni_f= nickel in fruit, Pb_f= lead in fruit

Table 4.8: Correlation of Total Metal Concentrations in the Dumpsite Soils in the Dry Season of 2015

	Cd	*Cu*	*Cr*	*Ni*	*Pb*
Cd	1				
Cu	0.733	1			
Cr	0.281	0.131	1		
Ni	0.207	-0.048	0.781	1	
Pb	0.316	0.295	0.919	0.584	1

4.7 Contamination Factor and Pollution Load Index of the Dumpsite Soil from Kafanchan

The contamination factor (CF) of the dumpsite soil of Kafanchan collected in the wet and dry seasons of 2015 are presented in Tables 4.9 and 4.10 respectively. At Abuja Street (ABJ) refuse site, the contamination factors (CF) ranged from 0.71 (Cd) to 4.54 (Cu) in the wet season and 1.70 (Cr) to 4.14 (Pb) in the dry season.

In the Albarka Street refuse site soil (ABR), the CF ranged from 1.22 (Cd) to 3.93 (Ni) in the wet season and 1.21 (Cu) to 2.63 (Pb) in the dry season. However, in the Garaje dumpsite soil, the CF values ranged from 0.76 (Cd) to 5.38 (Cu) in the wet season and 1.18 (Cr) to 3.61 (Pb) in the dry season. At Railway Quarters refuse site (RLQ) the lowest CF for the soil was for Cd (0.75) in the dry season and the lowest CF was for Cu (0.96) in the wet season; while the highest CF was for Cu (2.20) in the dry season and the highest CF was for Pb (1.90) in the wet season. At GRR, the lowest CF was for Cd being 0.59 in the dry season, and 0.90 in the wet season, while the CF was highest in the soils for Cu with the value 5.78 in the dry season and the highest for Pb with CF 4.55 in the wet season. At the control site however, the CF value was 1.00 for all the heavy metals in the wet and dry season.

The pollution load index (PLI) for the soils in the wet and dry season were 1.73 and 1.95 respectively (Table 4.9 and 4.10).

Table 4.9: Contamination Factor and Pollution Load Index of the Dumpsite Soils of Kafanchan in the Wet Season

Location	Cd	Cu	Ni	Pb	Cr
Abuja Street	2.41	1.76	1.87	4.14	1.70
Albarka Street	1.73	1.21	1.45	2.63	1.95
Garaje	1.52	1.88	3.33	3.61	1.18
Railway Quarters	1.36	0.96	1.35	1.90	1.13
Garara Street	0.90	1.79	1.81	4.55	1.19
Control	1.00	1.00	1.00	1.00	1.00
	***PLI**	= 1.95			

PLI = Pollution load index in the entire Kafanchan metropolis for the wet season

Table 4.10: Contamination Factor and Pollution Load Index of the Dumpsite Soils of Kafanchan in the Dry Season

Location	Cd	Cu	Ni	Pb	Cr
Abuja Street	-0.75	1.11	1.00	0.33	0.61
Albarka Street	1.12	3.35	3.93	1.70	2.62
Garaje	0.76	5.36	4.02	1.98	1.33
Railway Quarters	0.75	2.20	1.27	1.32	1.06
Garara Street	0.59	5.78	4.43	2.23	1.61
Control	1.00	1.00	1.00	1.00	1.00
	***PLI**	= 1.73			

PLI = Pollution load index in the entire Kafanchan metropolis for the dry season

4.8 Geo-Accumulation Index of the Dumpsite Soils of Kafanchan

The Geo-accumulation indices (I-geo) of the soils in the wet and dry seasons are presented in Tables 4.11 and 4.12 respectively. The Abuja Street dumpsite (ABJ) soil had (I-geo) ranging from 0.13 (Cr) to 1.02 (Pb) in the wet season, and I-geo was -0.75 (Cd) to 1.11 (Cu) in the dry season. On the other hand, at Albarka Street dumpsite soil (ABR), the (I-geo) ranged from -0.03 (Ni) to 0.56 (Pb) in the wet season and -0.29 (Cd) to 0.96 (Ni) in the dry season while at Garaje dumpsite (GRJ), the (I-geo) was -0.24 (Cr) to 0.88 (Pb) in the wet season and -0.68 (Cd) to 1.28 (Cu) in the dry season.

At Railway Quarters (RLQ) soil, Cu had the lowest (I-geo) of -0.45 (wet season) and -0.70 in the dry season, while Pb had the highest (I-geo) of value 0.23 in the wet season and 0.38 in the dry season. The Gurara Street (GRR) dumpsite soil had the lowest I-geo being for Cd with value -0.51 in the wet season and the lowest value of -0.92 was obtained in the dry season of 2015. The highest I-geo value in the wet season was obtained for Pb (1.11) and for Cu with the value 1.35 in the dry season of 2015. On the other hand, the control site soil had I-geo values of -0.41 for both the wet and dry season of 2015.

4.9 Transfer Factor of the Heavy Metals

The transfer factor (TF) of the dumpsite soil of Kafanchan collected in the wet and dry seasons of 2015 is presented in Tables 4.13. From the results below, Cadmium had highest transfer factor of 0.72 (ABJ) and lowest ratio of 0.23 (RLQ) for the *A. esculentus*fruit grown near the dumpsite. GRJ had highest transfer ratios for lead (0.17), nickel (0.25) and copper (0.86) though Cu recorded least transfer ratio at ABR (0.34), GRR had the least ratio for Pb (0.08), Ni (0.19) and Cr (0.04).

Table 4.11: Geo-Accumulation Index of Dumpsite Soils and Control Site in the Wet Season

Location	Cd	Cu	Ni	Pb	Cr
Abuja Street	0.47	0.16	0.22	1.02	0.13
Albarka Street	0.14	-0.21	-0.03	0.56	0.26
Garaje	0.01	0.23	0.80	0.88	-0.24
Railway quarters	-0.10	-0.45	-0.10	0.23	-0.28
Gurara Street	-0.51	0.17	0.20	1.11	-0.24
Control	-0.41	-0.41	-0.41	-0.41	-0.41

Table 4.12: Geo-Accumulation Index of Dumpsite Soils and Control Site in the Dry Season

Location	Cd	Cu	Ni	Pb	Cr
Abuja Street	-0.75	1.11	1.00	0.33	0.61
Albarka Street	-0.29	0.80	0.96	0.12	0.56
Garaje	-0.68	1.28	0.99	0.28	-0.12
Railway quarters	-0.70	0.38	-0.17	-0.13	-0.34
Gurara Street	-0.92	1.35	1.08	0.40	0.07
Control	-0.41	-0.41	-0.41	-0.41	-0.41

The transfer of Cr from the soil to the fruit at the dumpsite was highest recording 0.13 at ABJ and ABR. The transfer factor for the control site was relatively high with highest ratio observed for cadmium (0.90) with the least ratio for Pb (0.10).

Table 4.13: Transfer Factor of Heavy Metals into *Abelmochus esculentus*Fruit.

Location	Cd	Cr	Cu	Ni	Pb
Abuja Street	0.72	0.13	0.39	0.24	0.15
Albarka Street	0.26	0.13	0.34	0.24	0.13
Garaje	0.29	0.08	0.86	0.25	0.17
Railway Qaurters	0.23	0.05	0.37	0.19	0.17
Gurara Street	0.63	0.04	0.67	0.19	0.08
Control	0.90	0.35	0.59	0.17	0.10

Where TF = Transfer factor

CHAPTER FIVE

5.0 DISCUSSION

5.1 Quality Assurance of the Spectrophotometer

The mean percentage recovery was 87.66 ± 3.00% to 94.32±1.00% (Table 4.1), the efficiency of the atomic absorption spectrophotometer is therefore validated.

5.2 Particle Size Characterization

The results of the particle size distribution (Table 4.1) shows that the textures of soil were predominantly loamy sand. The sand fraction was generally higher compared to the other fractions. However, high percentage of sand on the topsoil is of advantage as it would encourage seepage (Uba *et al.,* 2008). However, loamy sand texture was recommended (Loughry, 1974) as being suitable for waste disposal sites, since they are highly permeable. Excessive drainage of sandy soil can encourage leaching of major cations and anions to the deeper layers. This will increase the possibility of ground water pollution. Nevertheless, Brady and Weil (1999) observed that sandy soils of the humid tropics were unsuitable for waste disposal as they encourage surface flooding and pollution. Osazee *et al*., (2013) reported a range of 56.4 – 70.4, 13.6 – 23.0, 13.5 – 20.6 % for sand, silt and clay respectively in the study of microbiological and physicochemical analyses of top soils obtained from four municipal waste dumpsites in Benin City, Nigeria; while Finzgar *et al*., (2007) reported a range of 10.5 – 70.7 %, 20.2 – 71.6% and 6.9 – 35.9 % for sand, silt and clay respectively in the study of the relationship of soil properties to fractionation, bioavailability and mobility of lead and zinc in soil in Celje region, Slovenia, which were in agreement with the report from this study.

The high range of sand contents in soils from the vicinities of municipal waste dumpsites could permit the usage of these open waste dumpsites as landfill sites. Ogbonna *et al*., (2006), reported that dumpsites with low sand fractions (< 40%) are not suitable for waste land filling since they are rapidly permeable and could allow large quantities of leachate from the wastes to invade the deposited refuse and finally to the groundwater resources. The mean sand content of the dumpsite studied in Kafanchan, Nigeria was from 78.00 to 84.00 %. This implies that they are suitable for waste land filling.

5.3 Physicochemical Parameters of the Dumpsites Soils from Kafanchan, Nigeria

5.3.1 pH of the dumpsite soil

pH is among several properties which affect the availability, retention and mobility of nutrients and heavy metals in soils. The pH values (Tables 4.3 and 4.4) ranged from acidic (6.67) in the soil sample collected from GRR, neutral (7.01) in ABJ and alkaline (7.98) in RLQ in the dry season of 2015. However, in the wet season all the dumpsite soil sample were alkaline (pH 7.10 to 8.90). These might be as a results of the sorption of metals in the soil (Lee and Saunders, 2003). Alkaline soil enhances soil fertility and plant growth. The pH values obtained in this study are similar to that reported for dumpsites by other researchers (Uba *et al*., 2008; Elaigwu *et al*., 2007; Gupta and Sinha, 2006).

Micronutrient cations are the most soluble and available under acidic condition (Uwumarongie *et al.*, 2008). The degree of acidity and/or alkalinity is considered a master variable that affects nearly all soil physico-chemical properties. Some organisms are unaffected by a rather broad range of pH values, while others exhibit considerable intolerance to even minor variations in pH (Ogbonna *et al*., (2006). pH can affect the accumulation factor of soil among others. It was observed that the accumulation factors for metals vary inversely with pH of soil, having great effects on solute concentration and absorption in soil. At low pH, metals are more bioavailable to plants, and hence could pose severe toxicity problems compared to alkaline soils (Oluyemi *et al*., 2005).

5.3.2 Electrical conductivity of the dumpsite soil

The electrical conductivity values were found to vary significantly across the sites; 0.50 μScm^{-1} (GRR) to 2.05 μScm^{-1} (RLQ), and 0.40 μScm^{-1} (ABJ) to 1.75 μScm^{-1} (RLQ) in the wet and dry seasons of 2015 respectively. The variation observed in electrical conductivity between sites could be attributed to soluble salts in the soil samples. The results of electrical conductivity were quite high with values ranging from 0.40 – 2.05µs/cm especially RLQ (1.75) and (2.05) in the wet and dry season. These values were higher than the values reported by Osakwe and Otuya (2008) and Oviasogie and Omoruyi (2007).

The high electrical conductivity of soils is an indicator of high or significant presence of ions. The observed electrical conductivity values in the dumpsite soils of Kafanchan could be attributed to the reactions between some deposits containing acids such as batteries of transistor radios and some metals from vehicular scraps, resulting to availability of some soluble and ionizable inorganic salts in the soils.

5.3.3 Nitrate – nitrogen (NO_3^--N %) content of the dumpsite soil

As shown in Table 4.3 and 4.4 the NO_3^--N % contents of the dumpsite soils were significantly low across the sites, the control site has a value of 0.309%. The nitrate contents in this research is lower than that reported by Uba *et al*., (2008) which ranged from 4.17 to 11.33 % for dumpsite soil of dumpsites in Zaria Metropolis, Nigeria. However, the results reported by Osazee *et al.,* (2013) had the range 3.476 to 4.522 %

which is also significantly higher than the concentration reported in this research. According to Godson, 1953, the presence of higher levels of nitrite and nitrate nitrogen in the soil is a clear indication of humus rich nitrogenous substances which could be favourable to plant growth, but it may have implication for the ground water quality. Therefore, the low nitrate level in this research implies that the soil might not be favourable for plant growth.

5.3.4 Phosphate (PO_4_P) of the dumpsite soil

The extractable phosphate of the dumpsite soils ranged from 42.53 mg/kg to 105.60 mg/kg during the wet season and 48.68 to 102.45 mg/kg in the dry season (Table 4.3 and 4.4). However, variation was generally observed in the PO_4-P values of the study sites and the control site which recorded much lower values of 18.03 mg/kg in the wet season and 19.23 mg/kg in the dry season. The high concentration of phosphorous in most of the dumpsites studied contributes to good growth of plants (Uba *et al*., 2008).

5.3.5 Organic matter content of the dumpsite soil

Following from Table 4.3 and 4.4, the highest organic matter content of the soil in the wet and dry season of 2015 were recorded as ABJ (6.80 $mgkg^{-1}$) and (6.21 $mgkg^{-1}$) respectively, while the lowest values in both seasons were 3.85 $mgkg^{-1}$ and 4.15 $mgkg^{-1}$ at ABR. Higher organic matter contents of the dumpsite soils was observed in the dry season compared to the wet, this could be due to the lower soil moisture contents during the dry season which retards the activities of the micro - organisms involved in the organic matter decomposition, thereby accumulating more organic matter in the dry season. The organic matter contents of the soil plays an important role in absorption reaction in the soil, hence prevent a pollutants from reaching the ground water sources (Alloway and Aryes, 1997)

5.3.6 Cl^- content of the dumpsite soil

The Cl^- content of the dumpsite soils ranged from 2.75 mg/kg GRJ dumpsite to 12.54 mg/kg ABJ dumpsite in the wet season and 2.54 mg/kg (RLQ) to 8.24 mg/kg (ABJ) in the dry season of 2015. The control site on the other hand had the values of 1.73 mg/kg and 2.12 mg/kg in the wet and dry seasons. The range reported for Kafanchan dumpsite soil in this study is not in agreement with the range (71.71 to 889.63 mg/kg) reported by Uba *et al*., (2008) for dumpsites of Zaria Metropolis, Nigeria. Chloride is found in soil as chloride ion, being an anion, it is fully mobile except when held by soil anion exchange sites (Uba *et al*., 2008).

5.3.7 Cation exchange capacity (CEC) of the dumpsite soil

As shown in Table 4.3 and 4.4 the mean level of CEC in the control site was low (6.00 Cmol/kg and 6.11 Cmol/kg) in wet and dry season, Cation exchange of heavy metals depends on the density of ionic strength of the surfaces of soil colloids and on the relative charges of metal species in soil solution. The surface negative charge may be pH dependent (soil organic matter) (Evans, 1989). Cations are less bioavailable because they have less competition from H^+ for available binding sites. According to Awode *et al*. (2008), CEC of soil is more greatly influenced by organic matter than by the concentration of clays, hence CEC tends to be higher in the study sites than in the control sites.

5.4 Total Heavy Metal Concentration of Dumpsites Soil

5.4.1 Mean Cd concentrations in the dumpsite soils and control site

The levels of cadmium in the dumpsite soil is presented in Figure, 4.1 and 4.2 and Appendix II and III. Cadmium is generally low though it is higher in the wet season (21.86 - 58.27 mg/kg) than in the dry season (13.00 - 24.60 mg/kg). The mean level of Cd in the dumpsite soils of the study areas ranged from 21.86 – 58.27 mg/kg in wet season and from 24.60 – 13.00 mg/kg in dry season, while the control values for wet and dry season were 24.18 and 21.93 respectively, high values of Cd were recorded in control (Appendix II and III).

The mean Cd value obtained for the dumpsite soils studied were higher than those reported by Omoniyi *et al* (2013); Yahaya *et al* (2009); Ukpong *et al* (2013) and Adelekan and Alawode (2011). But the results of this study were lower than those reported by Awokunmi *et al*. (2010) with 219 – 330 mg/kg.

From the results, the level of Cd in the soils may lead to environmental hazard. The high concentration of cadmium in the study areas could be likened to the location of the dumpsite and the nature of the waste been dumped. Human activity can also contribute to increased Cd level as a result of urban-industrial activity or agricultural practices (Mico *et al*., 2006). Cadmium concentrations in the soils were above the standard limits (0.01 mg/kg) set by Federal Environmental Protection Agency (FEPA) 1991 and (3.0 mg/kg) set by European Commission (1986).

5.4.2 Mean Cr concentrations in the dumpsite soils and control site

The mean level of Cr in the dumpsite soils ranged from 25.86 mg/kg – 44.69 mg/kg in the wet season and 20.34 – 52.89 mg/kg in the dry season. However higher values were obtained in the dry season compared to the wet, this could be due to leaching effect on chromium containing compounds in the wet season. Chromium concentration in the refuse soils were generally above standard limits (0.03 mg/kg) set by Federal Environmental Protection Agency (FEPA) 1991 and (50 mg/kg) set by European commission (1986).

Sources of Cr in the soils could be due to automobiles, coloured polythene bags, discarded plastic materials, empty paint containers and electronic waste (Jung and Casher, 2006)

The concentration range reported in this study for the Cr was within the range of values reported by Adelekan and Alawode (2011) being (13.15 – 75.55 mg/kg). The levels of Cr recorded in this study were lower than those recorded by Awokunmi *et al*. (2010) (212.00 – 2020.00 mg/kg); Oluyemi *et al*., (2008) (107.50 - 181.25 mg/kg) and Ukpong *et al* (2013) with range (1.00 – 4.50 mg/kg). The mean Cr values in the control site studied in Kafanchan, Nigeria were generally lower than those in the studied areas.

5.4.3 Mean Cu concentrations in the dumpsite soils and control site

Copper concentration was generally higher than all other elements studied. The lowest Cu concentration in the wet season was 41.33 (RLQ) and the highest was 81.21 in GRJ dumpsite, while in the dry season the lowest Cu level was 61.45 (RLQ) and the highest was 161.30 in GRR dumpsite soil. Copper concentration in the dumpsite were above standard limits (140 mg/kg) set by European Commission (1986) in the dry season but was below the standard limits in the dry season of 2015. There was a sharp increase in the Cu contents of the dumpsite soil in the dry season, this could probably be due to the nature of the solid wastes deposited in the dumpsites during the wet season. The extremely high value obtained in GRR site during the dry season could be due to the decomposition of solid wastes containing high copper contents.

The levels of Cu recorded in this study were higher than the levels reported by Opaluwa *et al* (2012) with range (0.82 – 0.91 mg/kg). On the other hand, the concentration range of 1.70 – 446 mg/kg was reported by Oluyemi *et al* (2008) were higher than the concentration reported in this study, showing that the dumpsites in Kafanchan were not as polluted as those studied by these researchers. The mean copper values in the control site were lower than those in the study areas in the dry season but higher than RLQ in the wet season.

5.4.4 Mean Ni concentrations in the dumpsite soils and control site

Nickel concentration in the refuse soils were generally above the standard limits (0.1 mg/kg) set by Federal Environmental Protection Agency (FEPA) 1991 and the 75 mg/kg limit set by European Commission (1986), thus implying that the soil was contaminated with Ni. Global input of nickel to the human environment is from natural and anthropogenic sources including emissions from fossil fuel consumption, industrial production, use and disposal of nickel compounds and its alloys (Kasprzak *et al*., 2003).

The concentration range reported in this study was higher than the concentration range reported by Adelekan and Alawode (2011) being 4.35 – 49.80 mg/kg, and the range (1.50 – 54.80 mg/kg) reported by Ukpong *et al* (2013), Opaluwa *et al* (2012) (0.21 – 0.31 mg/kg) and range (7.10 – 14.90 mg/kg) reported by Akpofure (2012). However, the concentrations of Ni reported in this study were lower than the concentration range reported by Awokunmi *et al*. (2010) and Oluyemi *et* al (2008). The concentration of nickel in the control site was higher in the wet season than the dry season.

5.4.5 Mean Pb concentrations in the dumpsite soils and control site

Lead had values ranging from 23.62 mg/kg to 56.63 mg/kg in the wet season and 42.70 mg/kg to 72.13 mg/kg in the dry season. The high levels of lead in the soils could be attributed to the dumpsite. This is because in the past lead was used in gasoline and hence a major contributor to lead in soil and automotive exhaust emitted when gasoline contained lead.Lead is released into the air during the burning oil or waste. Lead is gotten rid from the air by rain and by particles falling to land or into surface water, once lead falls onto soil, it sticks strongly to soil particles and remains in the upper layer of soil (ATSDR, 2007).

The levels of Pb recorded in this study were lower than the range of 35.7 – 635.31 mg/kg reported by Yahaya *et al* (2009), Ukpong *et al* (2013) with a range of (3.00 – 117.50 mg/kg) and Adelekan and Alawode (2011)(45.00 – 624.50 mg/kg). On the other hand, the concentrations of Pb reported in this study were higher than those reported by Opaluwa *et al* (2012) with range 0.90 – 4.20 mg/kg. Higher values were recorded for lead in this study, which were found to be above the 0.05 mg/kg limit of Pb in soil as recommended by Federal Environmental Protection Agency (FEPA) 1991, but were below the standard limit set by European Commission (1986) being 100 mg/kg, though they are within the tolerance limit set by EU, Pb levels should be cautiously minimised to prevent health hazard on man and the entire environment.

In general, the ranking of the average metal contents in the study area was Cr>Ni>Pb>Cd>Cu for the wet season and Cu>Ni>Pb>Cr>Cd for the dry season; the concentrations of the metals found in the soils of the study areas were higher than the control site while the concentration of metals increased from the wet to dry season. Analysis of variance (ANOVA) indicated that the levels of the studied heavy metals in the soils of the dumpsites compared to the control sites were significantly different ($P < 0.05$) (Appendix II and III).

5.5 Total Heavy Metal Concentration in the Fruit Samples (mg/kg)

Heavy metal concentrations in *Abelmoschus esculentus* friut planted on the dumpsite and collected in the wet and dry seasons, of 2015 were found to be mostly lower than those of the soils(Figure 4.3, and Appendix IV).

5.5.1 Mean concentrations of the selected metals in *Abelmoschus esculentus*fruit obtained from the dumpsites and control soils

Cadmium concentration in the fruit ranged from 8.53±0.03 mg/kg (ABR) to 21.15±0.12 mg/kg (ABJ). Cd concentrations in the fruit were above the standard limit of 0.2 mg/kg set by FAO/WHO (2001). The high concentration obtained may be due to atmospheric deposition of the metal from non – ferrous metal activities, combustion, etc. which can be absorbed into foliage and translocated through the plant. Studies have shown that Cd is easily translocated to plants (Alloway, 1996).

The levels of cadmium recorded in this study was however much higher than the values of 0.01 – 0.03 mg/kg reported by Fatoba *et al* (2012) and was also higher than the highest mean values of 0.08 mg/kg reported by Amusan *et al* (2005). Toxic effects of cadmium on plants include reduced shoot growth and inhibition of root growth (Wang *et al.*, 2004).

Similarly, the concentration of Cr in the fruit samples had the higher levels being 14.29±0.01 mg/kg (GRJ) and lowest 7.98±0.01 (GRR). Chromium content of the fruit were generally above the standard limit of 2.30 mg/kg set by FAO/WHO (2001).

From Figure 4.3 the level of copper reported for *Abelmochus esculentus* fruit was highest at GRJ (18.80±0.01 mg/kg) and lowest (7.35±0.02 mg/kg) at RLQ. Cu concentrations in the friut from most of the study sites were generally below the standard limit of 73.3 mg/kg set by FAO/WHO (2001). Results obtained from this study was lower than the values of 18.75 – 21.90 mg/kg reported by Amusan *et al* (2005) for okro fruit planted on dumpsites in Obafemi Awolowo University, Ile-Ife, Nigeria; but was higher than the values reported by Akpofure (2012) for*Hibiscus esculentus* grown on abandoned dumpsites in Effurun, Nigeria.

When copper ends up in soils, it strongly attaches to organic matter and minerals. As a result, it does not travel very far after release and consequently copper tends to accumulate in soil (Slooff *et al.,* 1989). Perhaps, this might explain why the soil had high levels of copper while the fruits had lower levels. High toxicity of copper in plants tends to lead to a reduction in root growth, seed growth and biomasss which could eventually lead to plant mortality (Sheldon and Menzies, 2005).

Nickel concentrations in *Abelmoschus esculentus* fruit obtained from the dumpsite soils in Kafanchan were below the standard limit of 67.90 mg/kg set by FAO/WHO (2001). Nickel in the plant is highly mobile and is likely to accumulate in both leaves and seeds (Sengar *et al*., 2008). Intake of very large quantities of nickel by humans from plants grown on nickel rich soils has higher chances of inducing the development of cancers of the lung, nose, larynx and prostrate, as well as inducing respiratory failures, birth defects and heart disorders (Duda-Chodak and Blaszczyk, 2008). The results obtained in this study however, was higher than the value reported by Akpofure (2012) for*Hibiscus esculentus* grown on abandoned dump sites in Effurun, Nigeria.

The concentrations of Pb in the fruit in this study were above the standard limit of 0.3 mg/kg set by FAO/WHO (2001). The levels of lead recorded in this study was much higher than the values of 0.01 – 0.03 mg/kg reported by Fatoba *et al* (2012), and 1.50 –

3.40 mg/kg by Amusan *et al* (2005). Lead has no beneficial biological function and is known to accumulate in the body (Ellen *et al*., 1990; Yargholi and Azimi, 2008).

In general, the concentrations of the metals found in the plants at the study areas were higher than the control site, analysis of variance (ANOVA) indicated significant elevation the heavy metals in the plants from the dumpsites areas compared to the control sites ($P < 0.05$) (Appendix XIX).

5.6 Chemical Fractionation of the Heavy Metals in the Dumpsite Soils from Kafanchan

Chemical speciation carried out by sequential extraction of the metals is in order to access the mobility and bioavailability of Cd, Cr, Cu, Ni and Pb in the dumpsite soils from Kafanchan, Nigeria. Figures 4.5 to 4.18 showed the fractionation phases and the percentages of the bioavailable, residual and the non-residual fraction obtained for Cd, Cr, Cu, Ni and Pb. The results obtained showed the amounts of the heavy metals extracted into each fraction for the various dumpsite soils (Appendix VII to XVIII). Elemental speciation information is crucial today because the toxicity and biological activity of many elements depend not only on their quantities but also on their chemical forms (He *et al.,* 2005).

5.6.1 Chemical fractionation and percentage bioavailability of cadmium

Figures 4.4 - 4.5 revealed the concentration of cadmium in the extractable fractions and its percentage bioavailability in the dumpsites for the wet and dry seasons. From the results presented, the total extractable cadmium (F1+F2+F3+F4+F5+F6) was found to be above the recommended limit of 3.0 mg/kg for agricultural soils by Federal Environmental Protection Agency (FEPA) 1991 and European Commission (1986) for the wet and dry seasons samples. The highest concentrations of Cd were recorded in the residual fractions

(F6) in both seasons for all the dumpsite soils, this shows that the Cd would be released into the environment only under very harsh conditions. Association of Cd in the residual fraction does not generally constitute an environmental risk. This is due to the stable nature of the compound and the fact that the metals are bounded firmly within a mineral lattice that restricts the bioavailability of this metal (Abu-Kukati, 2001).

By comparing the levels of Cd in the residual and non-residual fractions in both seasons across the sites, the non-residual fractions constituted the highest percentage (75%), the high amount of Cd associated with the non – residual fractions shows that cadmium would be readily available for contamination.

The findings in this investigation is in agreement with the observations of Gupta and Sinha (2006) and Obasi *et al* (2013), who reported similar Cd concentration levels in soils from tannery (Uttar Pradesh, India) and from dumpsites (Okigwe, Nigeria) respectively. The bioavailability values for Cd ranged from 51% at ABR to 40% at GRR in the wet season and from 50% at RLQ to 33% at ABJ in the dry season. The percentages of bioavailable Cd across the sites were relatively high ($\geq$ 40 %) and this may suggest that Cd in the refuse soil is bioavailable for plant uptake (Uba *et al*., 2008).

The mean value of Cd in the *Abelmoschus esculentus*fruit (15.60 mg/kg) was lower than the mean concentration of Cd in the soil, the mean was Cd 35.93 mg/kg and 18.00 mg/kg respectively in the wet and dry season respectively.

5.6.2 Chemical fractionation and percentage bioavailability of chromium

Figures 4.9 - 4.10 (Appendix VIII to XVIII) show the concentration of chromium in the extractable fractions (F1+F2+F3+F4+F5+F6) and its percentage bioavailability in the dumpsites. The highest concentrations of Cr in the dumpsite soil in both the wet and dry seasons across the dumpsites were recorded in the residual fraction (F6) with the exceptions of GRJ (13.04 and 4.80 mg/kg respectively) and ABR (8.43 and 20.47 mg/kg respectively) that recorded high values in the exchangeable fractions (F2) in both seasons. In F2, heavy metals are held together by electrostatic adsorption (Uzairu *et al.,* 2013). Exchangeable fractions can cause environmental toxicity during mobility (Karbassi and Shankar, 2005).

According to Venkateswaran *et al.*,(2007), the leaching of Cr to the environment may not occur easily. Cr (VI) is a highly toxic metal that has been linked to cancer in humans following prolonged inhalation, and is toxic to plants at relatively low concentrations (USEPA, 1998). The extractable fractions (F1+F2+F3+F4+F5+F6) contained chromium in amounts that were above the critical level which is 0.03 mg/kg for soil recommended by FEPA (1991) and also, 50 mg/kg for soil permissible level by European Commission (1986).

The Cr content of the soil fractions was strongly associated with the residual which is in agreement with those reported by Alvarez *et al*., (2002) but however differ from those reported by Gupta and Sinha (2006).

The levels of Cr in the residual fraction was greater in percentage than the non-residual with exceptions in GRJ (48%) and GRR (37%) in the wet seasons across the sites, indicating bioavailability of the heavy metal. The highest bioavailability values were 70% at GRJ and 59% at ABR, while the lowest values observed were 21% at RLQ and 13% at GRR both the wet and dry seasons respectively. However, in the dry season, high percentages were recorded in the non-residual, this means that Cr is bioavailable but is also loosely bound in the crystal lattice.

The mean value of Cr in *Abelmoschus esculentus*fruit (10.53 mg/kg) was lower than the mean Cr concentration in the soil(61.94 mg/kg and 33.13 mg/kg) in the wet and dry season respectively.

5.6.3 Chemical fractionation and percentage bioavailability of copper

Appendix VII to XVI show the concentration of copper in the extractable fractions (F1+F2+F3+F4+F5+F6) and its percentage bioavailability in the dumpsites. The highest concentration of Cu in the six fractions obtained for the wet and dry seasons in 2015 was in the residual fraction (24.03 and 85.35)This means that the amount of Cu in the residual fraction reflects greater tendency for Cu to be less mobile in the soil. Presence of a metal in the residual fraction indicates that it is largely embedded in the crystal lattice of the soil (Uba *et al*., 2008).

By comparing the concentration of Cu in the residual (RF) and the non-residual (NRF) fractions, high percentage of Cu in the non-residual was recorded during the wet season (72 %), while in the dry season high percentage of Cu dominated the residual (74.12 %) with exceptions at ABR (29.78 %) and ABJ (44.75 %). The highest percentage of Cu in the residual fraction (74.12 %) in the dry season shows vividly that Cu metal would not be readily released into the environment to cause contamination except under harsh conditions. The high amount of Cu being associated with the non – residual fraction (72 %) in the wet season shows that Cu may be easily transferred into the food chain through water reservoirs, uptake by plants growing on the dumpsite soils may therefore have potentially negative impact on the environment and consequently on human health. The total extractable concentrations of copper in all the dumpsite soils was above the toxic limit of 140 mg/kg set by (EU 1986) in the dry season samples but was below the toxic limit in the wet season (Appendix VII to XVI).

The bioavailability of copper was from 11% (GRR) to 47% (ABR) in the wet season and 44% (ABJ) to 53% (GRJ) in the dry season. The value of the total extractable fraction obtained for Cu indicates that it will be readily bioavailable to the environment. However, some of the dumpsite had percentages of the total extractable fractions in the mobile phase (F1+F2+F3+F4+F5 >28%), indicating that these metals are readily bio-available to the environment (Uzairu *et al*., 2013).

The mean value of Cu in the *Abelmoschus esculentus*fruit (14.43 mg/kg) was lower than the mean concentration for Cu in the soil (31.10 mg/kg and 103.48 mg/kg) in the wet and dry season respectively.

5.6.4 Chemical fractionation and percentage bioavailability of nickel

Figures 4.5 - 4.6 (Appendix VIII – XVIII) show the concentration of nickel in the extractable fractions (F1+F2+F3+F4+F5+F6) and its percentage bioavailability in the dumpsites. The highest value of the extractable fractions of Ni was 70.69 mg/kg at GRJ and the lowest was 31.45 mg/kg at RLQ for wet season, while for the dry season the highest level was 76.68 mg/kg while 32.75 mg/kg was the lowest. The values of Ni in the dumpsite soils were above the Federal Environmental Protection Agency (FEPA) 1991 and European Commission (1986) maximum permissible limit of 3.0 mg/kg. High concentrations of nickel in both seasons were dominated in residual fraction F6, with some exceptions in ABR (8.43 mg/g) which is predominantly found in the water soluble phase (F1) during the wet season. The water soluble fraction is the most biologically active. The water soluble fraction has the highest potential of contamination of food chain, surface water and ground water (Leita and De-Nobility, 1991).

By comparing the concentrations of Ni in the residual (F6) and non-residual (F1+F2+F3+F4+F5) fractions across the dumpsites in the wet and dry season, the study showed that the non-residual constituted high percentage of the total extractable fractions (F1+F2+F3+F4+F5+F6) across the dumpsites soils in the dry season with exceptions GRJ (40.4%), while in the wet season, the highest percentage of Ni was found in the non-residual (F1+F2+F3+F4+F5) across all the dumpsites, this indicates that Ni would be released to the environment for contamination throughout the seasons except in the soil of GRJ (40.4%) in the dry season. The high association of Ni in the residual fraction (F6) of the dumpsite soils may be attributed to the alkaline stabilization process of the soils (Su and Wong, 2003). Similar results have been reported by Gupta and Sinha (2006).

The percentage bioavailability of nickel in the dumpsite soils were relatively high with ABJ (34%) and ABR (57%) having the highest values while GRJ (13%) and ABJ (34%) had the lowest values for the wet and dry seasons samples respectively. Thus indicating that Ni would be readily bioavailable to the environment for contamination and can cause environmental toxicity during mobility, especially during the wet season. The mean value of the Ni in *Abelmoschus esculentus*fruit (7.09 mg/kg) was lower than the mean content of Ni in the soil (41.91 mg/kg and 56.26 mg/kg) in the wet and dry season.

5.6.5 Chemical fractionation and percentage bioavailability of lead

Figures 4.7 - 4.8 (Appendix VIII to XVIII) show the concentration of lead in the extractable fractions (F1+F2+F3+F4+F5+F6) and its percentage bioavailability in the dumpsite soils. The highest concentration of lead in both seasons across the dumpsites existed in the residual fraction (F6) with GRR (31.6) having the highest value. The residual fractions represents the level of metals that are embedded in the crystal lattice of the soil and are readily bioavailable for contamination only under harsh conditions (Uba *et al*., 2008). All the dumpsite soils had Pb levels that exceeded the toxic limit of 0.05 mg/kg set by Federal Environmental Protection Agency (FEPA) 1991 but did not exceed the toxic limit of 100 mg/kg set by (European Commission 1986) in both seasons.

The levels of Pb in the non-residual was higher than in the non-residual for both seasons, indicating bioavailability of the heavy metal in wet and dry season. The highest bioavailability values were 85% at GRR and 56% at GRJ while the lowest values were 46% at RLQ and 27% at GRR for the wet and dry season respectively. This finding is in agreement with what was reported by Kabata-Pendias and Pendias (1992) who reported that there was a strong association of Pb with organic matter. Pb metals have toxic effects on living organisms because they are not required nutrient elements (He *et al.*, 2005).

The mean value of Pb in *Abelmoschus esculentus*fruit (6.62mg/kg) was lower than the mean concentration of Pb in the soil (55.55 mg/kg and 36.99 mg/kg) in the wet and dry seasons respectively.

5.7 Analysis of the Metal Content of the Dumpsite soils and *Abelmochus esculentus*Fruit

The results of the ANOVA of this study(Table 4.5 and 4.6; Appendix XIX). The study indicated that a significant difference existed in the mean concentrations of the metals studied across the dumpsites and the seasons at $P < 0.05$. Seasonal change affects the pollution levels of the dumpsites by the metals studied. This can be attributed to the mobility and accumulation of leachable metals on soil surface by seasonal rainfall and wind. Aerial deposition of these metals could be another source (Onianwa, 2001; Yusuf *et* *al*., 2003). Table 4.5 showed that a significant difference ($\alpha = 0.05$) in the concentration of metals in both the wet and the dry seasons of 2015 for the dumpsite soils collected from Kafanchan, Nigeria. Also, there was a significant difference ($P < 0.05$) in the distribution of all the studied metals in the dumpsites, irrespective of the season ($\alpha = 0.05$). Those differences could be attributed to differences in the physicochemical characteristics of the soil and the background levels of each metal in the dumpsite. A similar trend was observed for the soil profiles of automobile waste dumps in Nigeria (Iwegbue *et al*., 2006) and soil profiles in the vicinity of a copper smelter in Poland (Kabala and Singh, 2001). The results further showed that there was an interaction between the metal levels with seasons of collection ($\alpha = 0.05$) indicating that $P < 0.05$; so a significant difference in the metals levels. Therefore, seasonal changes have a significant effect on the distribution of metals in the soils samples, and this factor interacts positively with the metal type (Table 4.6).

Likewise, there was a significant difference in the mean concentrations of the metals studied in the fruit of*Abelmoschus esculentus* across the sites, (one way ANOVA $P< 0.05$). The resultshowes no significant difference in the levels of the metals studied in the fruit samples ($\alpha = 0.06$) with $P > 0.05$ (Table 4.6).

5.8 Correlation Analysis of the Total Metal Concentrations in the Dumpsite Soils and *Abelmoschus esculentus* Fruit

Correlation analyses performed by Pearson's Product Moment Correlation are presented in Table 4.7. This shows significant positive correlations between the soil and plant. On the contrary, the results of cadmium in plants varied negatively with the metal concentrations of all soil samples (except cadmium in soil). The most significant correlation values ($r > 0.75$) were found in the correlation of Cu_s vs Pb_s ($r = 0.909$), Ni_s vs

Pb_s (r = 0.944), Cu_s vs Ni_s (r = 0.914), Ni_s vs Cu_p (r = 0.776), Cr_s vs Ni_p (r = 0.769), Cu_p vs Ni_p (r = 0.757). The positive correlation between the metals across the sites suggests a common source of pollution. The high concentrations recorded at the sites may not be unconnected with dumpsite constituents where copper containing waste formed most of the constituents.

Table 4.8 showed the degree of association of the metal ions, the variables showed significant positive correlations with each other, except for the result of copper. Cadmium is toxic when inhaled even in trace amount in dust/particulates during incineration/burning at dumpsite because of its carcinogenicity (Aiyesanmi *et al*., 2011). The positive correlation between the metals across the sites suggests a common source of pollution. The high concentrations recorded in the sites may not be unconnected with dumpsite constituents where copper containing waste are mostly the constituents.

5.9 Evaluation of Heavy Metal Contamination in Dumpsites

In order to have an idea about the levels of contamination of the dumpsite soil, data obtained were compared with the background values. The background value of an element is the maximum level of the element in an environment beyond which the environment is said to be polluted with the element (Puyate *et al*., 2007).

5.9.1 Contamination factor (CF)

Contamination Factor (CF) determines the level ofcontamination of soils in terms of anthropogenic input.The calculated results for the contamination factors of the heavy metals in the refuse soils are presentedin Tables 4.9 and 4.10 for the wet and dry seasons. CF is classified into four categories as follows: CF < 1, low contamination factor; 1 < CF < 3, moderate contamination factor; 3 < CF < 6, considerable contamination factor. The dumpsite soils were considerablycontaminated in the wet season by Ni at GRJ (3.33), and also by Pb at ABJ (4.14) GRJ (3.61) and GRR (4.55); while in the dry season the soil was considerablycontaminated by Cu at all the dumpsites with the exceptions at RLQ (2.20) and by Ni at ABJ (4.07), GRJ (4.02), GRR (4.43), and moderately contaminated by all the five heavy metals in both seasons (Table 4.9 and 4.10).

Equally the dumpsite soil had low contamination by Cd and Cu at GRR (0.90) and RLQ (0.96) in the wet season; while in the dry season at ABJ (0.71), GRJ (0.76), RLQ (0.75), and GRR (0.59) by Cd. Thecontamination of the soil by the metals studied decreased in the order: Cu>Ni>Cr>Pb>Cd in the dry season, while in the wet season it was Pb>Ni>Cd>Cr>Cu.

5.9.2 Transfer factors (TF) of Heavy Metals into *Abelmoschusesculentus*fruit

Transfer factor (TF) is the ratio of the concentration of heavy metal in a fruit to the concentration of heavy metal in soil. It signifies the amount of heavy metals in the soil that ended up in the vegetable crop site (Chamberlain, 1983; Harrison and Chirgawi, 1989; Smith *et al*., 1996). The transfer of copper from the soils to *Abelmoschus esculentus*fruit in this study was highest at GRJ (0.86), but it is relatively low compared to the high mean value of Cu in the dumpsite soil (161.30 mg/kg) and in the fruit (18.80 mg/kg). This could be because copper contents do not mobilize in fruit and remain stagnant in roots, which would explain the lower content of the metal in fruit as compared to the soils (Bakare *et al*., 1994). Yang *et al*., (2002) showed that copper mainly accumulated in roots while a small fraction (10%) of absorbed copper was transported to the shoots. Chromium had lowest transfer factor in this study at GRR (0.04), and had low transfer factor across site compared to the mean values in the soil (52.89 mg/kg) and in the plant (14.29 mg/kg).

The transfer factor of nickel from the soil to the okro fruit was high (0.19 – 0.25); but relatively lower than the mean value of Cd in the soil (22.88 – 79.85 mg/kg) and in the plant (1.33 – 16.75 mg/kg). Although literature shows that nickel in plants is highly mobile and is likely to accumulate in both leaves and seeds.

The transfer of cadmium (0.23 - 0.73) from the soil to the fruit was higher than that of nickel (0.19 – 0.25); but lower than its mean value in the soil (13.00 – 24.60 mg/kg) and in the fruit (8.51 – 21.15 mg/kg). The high transfer factor of cadmium in the study may be as a result of cadmium contamination from the dumpsite. Cadmium is a highly mobile metal that is easily absorbed by plants through the root surface and moves to the wood tissue and transfers to upper parts of plants growing on dumpsites (Romera *et al*., 2005). The transfer factor of lead was between 0.08 – 0.17 this could explain why *Abelmoschus esculentus*fruit and the soil had higher mean values than permissible levels of 0.3 mg/kg set by FAO/WHO (2001) for lead and Federal Environmental Protection Agency (FEPA) 1991. The levels of lead in the soil of this study could be attributed to the indiscriminate disposal of lead containing wastes on the dumpsite. Lead accumulation in many plants can exceed several hundred times the threshold of maximum level permissible for human (Wierzbicka, 1995).

TF is one of the key component of human exposure to heavy metals through the food chain.Transfer factors in this study were seen to be relatively high in the control site, this is in agreement with observations made by Amusan *et al*. (2005) in his study of characterization and characteristics of soil and crop uptake of metals in municipal waste dumpsites in some Nigeria cities. It was also observed that the transfer factor values recorded for the metals show reverse trend compared to the total metal content. According to Udosen *et al*. (2006) some factors such as pH, exchange binding capacities, climate change and morphology of the plant might have contributed to some of the low transfer factor values obtained in the dumpsites. The prolonged human consumption of *A.esculentus* and the transfer of these heavy metals into the human body system could pose serious human health problems.

5.9.3 Geo-accumulation index (I-geo)

Pb and Cu had the highest I-geo values of 1.11 and 1.35 at GRR in the wet and dry season while Cd had the least I-geo in both seasons (Table 4.11 and 4.12). From the values recorded, the contamination status of the refuse soil in this study area indicated that it is practically uncontaminated to slightly contaminated in both season, the control sites values in the two seasons had I-geo being -0.41, this implies that the control site was not polluted.

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATION

6.1 Conclusion

The results of the physiochemical parameters of the dumpsites revealed that the dumpsite soils were rich in fruits nutrients (wet and dry season). The heavy metal concentration in the dumpsite soil in Kafanchan metropolis varied significantly by sampling sites and metal type. The order of the total metal contents of the dumpsite soil for the wet and dry seasons was Cu > Ni > Pb > Cr > Cd and Cr > Ni > Pb > Cd > Cu however, the order of total metal in the fruits was Cd > Cu > Cr > Ni > Pb. Among all the metals analysed, Cu had the highest concentration in both seasons while Cr was the least in the wet and Cd was least in the dry season. The results show relatively low transfer factor for *Abelmoschus esculentus* fruit which accounts for the low metal contents found in *Abelmoschus esculentus*fruit compared to the metal level in the dumpsite soil in the wet and dry seasons.

Sequential extraction was used to fractionate Cd, Cr, Cu, Ni and Pb present in the dumpsite soils and control site located 2.0 km away from the dumpsites, the result infers that the amount of heavy metal bound to each fraction in the dumpsite soil differed according to metal type, dumpsites and across the seasons.

In the wet season, the ranking of the metals in the various fractions were:

Cd - Residual > water soluble > oxidisable > exchangeable > acid soluble > reducible

Cr - Residual > exchangeable > acid soluble > water soluble > reducible > oxidisable

Cu - Residual > water soluble > acid soluble > exchangeable > reducible > oxidisable

Ni - Residual > water soluble > reducible > acid soluble > exchangeable > oxidisable

Pb - Residual > oxidisable > water soluble > acid soluble > reducible > exchangeable

On the other hand,

In the wet season, the ranking of the metals in the various fractions were:

Cd - Residual > acid soluble > water soluble > exchangeable > reducible > oxidisable

Cr - Residual > exchangeable > acid soluble > reducible > oxidisable > water soluble

Cu - Residual > water soluble > acid soluble > reducible > oxidisable > exchangeable

Ni - Residual > reducible > oxidisable > water soluble > acid soluble > exchangeable

Pb - Residual > acid soluble > reducible > exchangeable > water soluble > oxidisable

The heavy metals were retained predominantly by the residual fraction (F6), indicating that these metals would be potentially unavailable in most of the dumpsites. In addition, the non - residual fraction (NRF) was found to retain higher amount of (Cd, Cr, Cu, Ni, and Pb) in most of the dumpsites, hence indiscriminate dumping of refuse should be discouraged especially near household and commercial areas. The most polluted dumpsite in the wet season was Abuja Street dumpsite; while in the dry season the most polluted dumpsite was Gurara Street (GRR) dumpsite, and the least polluted dumpsite was Railway quarters (RLQ) for both the wet and dry season.

These results imply that pollution of an environment by dumpsites has human health and ecological risks and that plants that are cultivated on dumpsite or the use of dumpsite as soil manure resulted to significant bioaccumulation of the heavy metals studied by sampling site ($P < 0.05$). Therefore, dumpsites in Kafanchan metropolis that were studied are potential sources of heavy metal in plants and the environment; this prompt the suggestion of the use of incinerators for waste collection and enlightenment on the risks growing crops on dumpsites.

6.2 Recommendation

Phytoremediation of these heavy metals is necessary for clean-up of the environment from these toxic metals. It is further recommended that speciation of other toxic metals be carried out at various depth in these dumpsites and other major ones in Kafanchan metropolis, so as to obtain a thorough and broad database for elucidating the environmental impact of heavy metals in the dumpsites of Kafanchan metropolis.

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APPENDICES

Appendix I: List of Apparatus and Equipment

1. Conical flask – 12 ml, 250 ml
2. Beaker – 50 ml, 100 ml, 250 ml
3. Volumetric flask – 50 ml, 100 ml, 250 ml, 1000 ml
4. Measuring cylinder – 100 ml, 10 ml, 5 ml
5. Plastic bottles for digest – 50 ml
6. Polythene bags
7. Wash bottles
8. Funnel
9. Forceps
10. Filter paper – whatman no. 42 grades
11. Mortar and pestle
12. Nose guard
13. Eye goggles
14. Drying oven
15. Desiccators
16. Hot plates
17. Analytical balance
18. Centrifuge tubes (50 ml)
19. Fume cupboard
20. HANNA pH/conductivity meter
21. Steam bath

22. Stainless steel spoon

23. Crucibles

24. Centrifuge

25. Furnace

26. Glass rod

27. Pipette – 1ml, 5ml, and 10ml

28. Hydrometer

29. Butchner funnel

30. Erlenmeyer flask

31. Teflon Cup

32. 2mm sieve

33. Spatula

34. Petri-dish

List of Reagents and Chemicals (Analar Grade)

1. $AgNO_3$ – Silver Nitrate
2. $BaCl_2$ – Barium Chloride
3. $Cd(NO_3)_2$ – Cadmium nitrate
4. $Cu(NO_3)_2 .3H_2O$ – Hydrated Copper nitrate
5. HCl – Hydrochloric acid
6. HClO4 – Per chloric acid
7. HF – Hydrofluoric acid
8. HNO_3 –Nitric acid
9. $HONH_3Cl$ – Hydoxylammonium Chloride
10. H_2O_2 – Hydrogen peroxide

11. H_2SO_4 – Sulphuric acid

12. KCl – Potassium Chloride

13. $K_2Cr_2O_7$ – Potassium Dichromate

14. K_2CrO_4 – Potassium Chromate

15. KH_2PO_4 – Potassium hydrogen phosphate

16. K_2SO_4 – Potassium sulphate

17. $MgSO_4$ – Magnesium sulfate

18. $Mg(NO_3)_2$ – Magnesium nitrate

19. $SnCl_2$ – Stannous chloride

20. NaCl – Sodium Chloride

21. NH_4F –Ammonium Flouride

22. NH_4OAc –Ammonium acetate

23. NaOH –Sodium hydroxide

24. NH_4Cl –Ammonium Chloride

25. NaOAc – Sodium Acetate

26. As_2O_5 –Arsenic pentoxide.

27. Pb $(NO_3)_2$- Lead nitrate

28. Distilled water

Appendix II: Mean Concentration of Heavy Metals (mg/kg) in the Dumpsite Soils and the Control site in the wet season

Location	Cd	Cr	Cu	Ni	Pb
ABJ	58.27 ± 0.04	39.04 ± 0.05	76.15 ± 0.02	43.43 ± 0.01	51.54 ± 0.22
ABR	41.73 ± 0.15	44.69 ± 0.20	52.39 ± 0.04	33.75 ± 0.03	32.75 ± 0.11
GRJ	36.63 ± 0.13	26.96 ± 0.08	81.21 ± 0.02	77.44 ± 0.01	44.95 ± 0.16
RLQ	32.90 ± 0.13	25.86 ± 0.01	41.33 ± 0.03	31.44 ± 0.02	23.62 ± 0.15
GRR	21.86 ± 0.22	27.16 ± 0.05	77.35 ± 0.07	42.18 ± 0.01	56.63 ± 0.02
CTR	24.18 ± 0.02	22.90 ± 0.01	43.23 ± 0.04	23.23 ± 0.01	12.45 ± 0.04

Appendix III: Mean Concentration of Heavy Metals (mg/kg) in the Dumpsite Soils and the Control site in the dry season

Location	Cd	Cu	Cr	Pb	Ni
ABJ	15.53 ± 0.18	126.68 ± 1.56	52.89 ± 0.22	67.58 ± 0.71	73.43 ± 0.60
ABR	24.60 ± 0.07	93.55 ± 0.07	50.16 ± 0.13	54.83 ± 0.18	70.85 ± 2.33
GRJ	16.60 ± 0.14	149.98 ± 31.82	25.48 ± 0.19	63.83 ± 0.35	72.55 ± 1.80
RLQ	16.35 ± 2.93	61.45 ± 0.21	20.34 ± 0.27	42.70 ± 0.53	22.88 ± 1.17
GRR	13.00 ± 0.18	161.30 ± 0.25	30.81 ± 0.12	72.13 ± 0.46	79.85 ± 3.11
CTR	21.93 ± 0.46	27.90 ± 0.07	19.13 ± 0.29	32.28 ± 0.42	18.03 ± 2.44

Appendix IV: Mean Concentration of Heavy Metals (mg/kg) in *Abelmoschus esculentus*Fruit planted on the Dumpsite soils and the control site

Location	Cd	Cr	Cu	Ni	Pb
ABJ	21.15 ± 0.12	11.66 ± 0.01	17.75 ± 0.01	16.75 ± 0.06	12.63 ± 0.04
ABR	8.51 ± 0.03	9.26 ± 0.06	14.03 ± 0.01	7.03 ± 0.02	6.75 ± 0.06
GRJ	14.36 ± 0.43	14.29 ± 0.01	18.80 ± 0.01	8.80 ± 0.08	9.23 ± 0.02
RLQ	8.63 ± 0.30	12.98 ± 0.04	7.35 ± 0.02	1.33 ± 0.02	4.30 ± 0.10

GRR	8.96 ± 0.30	7.98 ± 0.01	15.70 ± 0.00	5.70 ± 0.00	4.08 ± 0.25
CTR	31.97 ± 0.20	7.00 ± 0.00	12.95 ± 0.03	2.95 ± 0.03	2.75 ± 0.02

Appendix V: Descriptive Statistics of Selected Metals in Soil across Sampling Locations

	Dry Season					*Wet Season*				
	Cd	*Cu*	*Cr*	*Ni*	*Pb*	*Cd*	*Cu*	*Cr*	*Ni*	*Pb*
Mean	18.00	103.48	33.13	56.26	55.55	35.93	31.10	61.94	41.91	36.99
Median	16.48	110.11	28.14	71.70	59.33	34.77	27.06	64.27	37.96	38.85
SD	4.35	52.19	14.86	27.95	15.46	13.25	8.66	18.31	18.92	17.09
Variance	18.95	2724.08	220.82	781.17	239.04	175.67	74.98	335.34	358.04	291.97
Minimum	13.00	27.90	19.13	18.03	32.28	21.86	22.90	41.33	23.23	12.45
Maximum	24.60	161.30	52.89	79.85	72.13	58.27	44.69	81.21	77.44	56.63
Sum	108.00	620.85	198.81	337.58	333.33	215.57	186.61	371.65	251.46	221.93

Appendix VI: Descriptive Statistics of Selected Metals in Plants Found in Sampling Locations

	Dry Season				
	Cd	*Cr*	*Cu*	*Ni*	*Pb*
Mean	15.60	10.53	14.43	7.09	6.62
S. Error	3.84	1.18	1.68	2.22	1.52
Median	11.66	10.46	14.86	6.36	5.53
SD	9.42	2.90	4.10	5.45	3.73
Variance	88.67	8.41	16.84	29.69	13.94
Range	23.46	7.30	11.45	15.42	9.88
Minimum	8.51	7.00	7.35	1.33	2.75
Maximum	31.97	14.29	18.80	16.75	12.63
Sum	93.59	63.17	86.58	42.56	39.73

Appendix VII: Mean Concentrations of the Individual Metals in the Soil Fractions (Abuja Street Dumpsite) in Wet Season

	F1	F2	F3	F4	F5	F6	Sum	BA	MF	NRF	RF
Cd	11.47	5.36	2.67	7.17	12.68	20.37	59.72	0.33	33	66	34
Cr	9.62	4.03	3.58	5.22	1.68	14.62	38.75	0.44	44	62	38
Cu	11.93	8.95	11.26	6.68	9.80	24.03	72.65	0.44	44	67	33
Ni	9.03	4.95	1.22	3.38	7.39	18.93	44.9	0.34	34	58	42
Pb	10.58	1.23	7.23	3.38	9.08	20.70	52.2	0.36	36	60	40

F1’- F6 represents Fractions 1 to 6 of the sequential extraction procedures; F1 = water soluble, F2 = exchangeable, F3 = Carbonate bound; F4 = Fe – MnO; F5 = organic bound; F6 = residual; Sum = Σ of all fraction; BA = bioavailability of metals in samples; MF= mobility factor; NRF = non – residual fraction; RF = residual fraction.

Appendix VIII: Mean Concentrations of the Individual Metals in the Soil Fractions (Abuja Street Dumpsite) in Dry Season

	F1	F2	F3	F4	F5	F6	Sum	MF	BA	NRF	RF
Cd	3.38	2.15	2.9	0.63	3.73	4.08	16.87	0.5	50	75.8	24.2
Cu	13	13.5	19.95	11.9	14.13	58.7	131.18	0.35	35.4	55.3	44.7
Cr	8.75	5.04	5.44	2.44	3.14	25.41	50.22	0.38	38.3	49.4	50.6
Pb	10.3	20.48	4	13.08	8.98	23.45	80.29	0.43	43.3	70.8	29.2
Ni	16.28	3.58	3.88	9.9	3.48	33.05	70.17	0.34	33.8	52.9	47.1

F1’- F6 represents Fractions 1 to 6 of the sequential extraction procedures; F1 = water soluble, F2 = exchangeable, F3 = Carbonate bound; F4 = Fe – MnO; F5 = organic bound; F6 = residual; Sum = Σ of all fraction; BA = bioavailability of metals in samples; MF= mobility factor; NRF = non – residual fraction; RF = residual fraction.

Appendix IX: Mean Concentrations of the Individual Metals in the Soil Fractions (Albarka Street Dumpsite) in Wet season

	F1	F2	F3	F4	F5	F6	Sum	BA	MF	NRF	RF
Cd	8.77	4.66	5.74	1.54	7.92	9.36	37.99	0.50	50	75	25
Cr	5.02	10.98	8.50	3.41	4.82	9.02	41.75	0.59	59	78	22
Cu	14.80	5.48	4.58	6.48	2.28	16.43	50.05	0.50	50	67	33
Ni	8.83	0.48	10.58	4.48	2.28	8.43	35.08	0.57	57	76	24
Pb	10.70	1.43	2.85	1.80	2.98	13.15	32.91	0.46	46	60	40

F1’- F6 represents Fractions 1 to 6 of the sequential extraction procedures; F1 = water soluble, F2 = exchangeable, F3 = Carbonate bound; F4 = Fe – MnO; F5 = organic bound; F6 = residual; Sum = Σ of all fraction; BA = bioavailability of metals in samples; MF= mobility factor; NRF = non – residual fraction; RF = residual fraction.

Appendix X: Mean Concentrations of the Individual Metals in the Soil Fractions (Albarka Street Dumpsite) in Dry season

	F1	F2	F3	F4	F5	F6	Sum	MF	BA	NRF	RF
Cd	3.23	3.05	6.3	3.3	1.78	6.88	24.54	0.51	51.3	72	28
Cu	23.93	3.93	21.55	10.78	13.65	31.3	105.14	0.47	47	70.2	29.8
Cr	-	8.84	7.52	3.07	1.73	20.47	41.63	0.39	39.3	50.8	49.2
Pb	13.5	4.88	11.4	6.13	9.33	12.28	57.52	0.52	51.8	78.7	21.3
Ni	5.8	3.7	7.1	14.1	7.25	32.4	70.35	0.24	23.6	53.9	46.1

F1'- F6 represents Fractions 1 to 6 of the sequential extraction procedures; F1 = water soluble, F2 = exchangeable, F3 = Carbonate bound; F4 = Fe – MnO; F5 = organic bound; F6 = residual; Sum = Σ of all fraction; BA = bioavailability of metals in samples; MF= mobility factor; NRF = non – residual fraction; RF = residual fraction.

Appendix XI: Mean Concentrations of the Individual Metals in the Soil Fractions (Garaje Dumpsite) in Wet season

	F1	F2	F3	F4	F5	F6	Sum	BA	MF	NRF	RF
Cd	9.72	1.00	3.18	7.81	2.18	13.65	37.54	0.37	37	64	36
Cr	0.55	3.96	1.18	5.36	1.07	13.04	25.16	0.23	23	48	52
Cu	17.35	13.05	11.78	6.48	9.13	22.28	80.07	0.53	53	72	28
Ni	11.35	14.05	12.78	7.48	3.75	21.28	70.69	0.54	54	70	30
Pb	8.98	8.28	6.48	1.63	4.78	12.30	42.45	0.56	56	71	29

F1'- F6 represents Fractions 1 to 6 of the sequential extraction procedures; F1 = water soluble, F2 = exchangeable, F3 = Carbonate bound; F4 = Fe – MnO; F5 = organic bound; F6 = residual; Sum = Σ of all fraction; BA = bioavailability of metals in samples; MF= mobility factor; NRF = non – residual fraction; RF = residual fraction.

Appendix XII: Mean Concentrations of the Individual Metals in the Soil Fractions (Garaje Dumpsite) in Dry season

	F1	F2	F3	F4	F5	F6	Sum	MF	BA	NRF	RF
Cd	3.58	3.9	1.45	1.5	3.13	5.43	18.99	0.47	47	71.4	28.6
Cu	25.5	8.1	16.83	3.18	6.48	85.35	145.44	0.35	34.7	41.3	58.7
Cr	-	12.67	6.18	1.55	1.8	4.8	27	0.7	69.8	82.2	17.8
Pb	9.3	13.95	19.98	7.88	6.1	23.6	80.81	0.53	53.5	70.8	29.2
Ni	4.68	0.63	6.3	9.6	11	45.73	76.68	0.13	13.5	40.4	59.6

F1'- F6 represents Fractions 1 to 6 of the sequential extraction procedures; F1 = water soluble, F2 = exchangeable, F3 = Carbonate bound; F4 = Fe – MnO; F5 = organic bound;

F6 = residual; Sum = Σ of all fraction; BA = bioavailability of metals in samples; MF= mobility factor; NRF = non – residual fraction; RF = residual fraction.

Appendix XIII: Mean Concentrations of the Individual Metals in the Soil Fractions (Railway Quarters Dumpsite) in Wet season

	F1	F2	F3	F4	F5	F6	Sum	BA	MF	NRF	RF
Cd	7.80	9.82	4.50	3.17	7.28	12.09	44.66	0.50	50	73	27
Cr	1.30	6.05	5.63	1.15	4.11	8.63	26.87	0.48	48	68	32
Cu	5.46	5.33	7.38	4.58	1.23	16.58	40.56	0.45	45	59	41
Ni	5.35	5.33	2.38	7.58	3.23	7.58	31.45	0.42	42	76	24
Pb	4.78	3.55	1.40	5.75	1.18	5.55	22.21	0.44	44	75	25

F1'- F6 represents Fractions 1 to 6 of the sequential extraction procedures; F1 = water soluble, F2 = exchangeable, F3 = Carbonate bound; F4 = Fe – MnO; F5 = organic bound; F6 = residual; Sum = Σ of all fraction; BA = bioavailability of metals in samples; MF= mobility factor; NRF = non – residual fraction; RF = residual fraction.

Appendix XIV: Mean Concentrations of the Individual Metals in the Soil Fractions (Railway Quarters Dumpsite) in Dry season

	F1	F2	F3	F4	F5	F6	Sum	MF	BA	NRF	RF
Cd	1.8	2.58	3.95	2.58	1.25	7.13	19.29	0.43	43.2	63	37
Cu	13.5	3.35	1.68	0.4	0.9	47.88	67.71	0.27	27.4	29.3	70.7
Cr	-	2.79	3.48	1.71	1.09	11.92	20.99	0.3	29.9	43.2	56.8
Pb	1.7	2.55	12.88	7.1	0.8	21.08	46.11	0.37	37.1	54.3	45.7
Ni	2.38	0.98	4.4	7.83	5.58	11.58	32.75	0.24	23.7	64.6	35.4

F1'- F6 represents Fractions 1 to 6 of the sequential extraction procedures; F1 = water soluble, F2 = exchangeable, F3 = Carbonate bound; F4 = Fe – MnO; F5 = organic bound;

F6 = residual; Sum = Σ of all fraction; BA = bioavailability of metals in samples; MF= mobility factor; NRF = non – residual fraction; RF = residual fraction.

Appendix XV: Mean Concentrations of the Individual Metals in the Soil Fractions (Gurara Street Dumpsite) in Wet season

	F1	F2	F3	F4	F5	F6	Sum	BA	MF	NRF	Res
Cd	3.21	4.59	0.67	1.61	1.19	11.45	22.72	0.37	37	50	50
Cr	1.41	1.19	0.19	1.44	3.55	13.24	21.02	0.13	13	37	63
Cu	14.09	5.33	9.43	8.08	4.23	23.18	64.34	0.45	45	64	36
Ni	7.56	5.33	5.43	6.08	2.23	14.18	40.81	0.45	45	65	35
Pb	2.23	5.45	11.50	13.23	34.58	3.18	70.17	0.27	27	95	5

F1'-F6 represents Fractions 1 to 6 of the sequential extraction procedures; Sum = Σ of all fraction of the F1'-F6 represents Fractions 1 to 6 of the sequential extraction procedures; BA = Bioavailability of metals in samples; MF= mobility factor; NRF = Non Residual fractions; RF = Residual Fractions

Appendix XVI: Mean Concentrations of the Individual Metals in the Soil Fractions (Gurara Street Dumpsite) in Dry season

	F1	F2	F3	F4	F5	F6	Sum	MF	BA	NRF	RF
Cd	0.28	2.01	2.73	0.55	1.11	5.8	12.48	0.4	40.2	53.5	46.5
Cu	6.1	5.68	7.08	21.08	6.33	132.37	178.64	0.11	10.6	25.9	74.1
Cr	1.14	6.15	5.93	4.7	1.29	15.06	34.27	0.39	38.6	56.1	43.9
Pb	5.58	4.7	20.58	19.05	3.55	31.63	85.09	0.36	36.3	62.8	37.2
Ni	4.38	4.05	6.85	10.93	9.85	22.3	58.36	0.26	26.2	61.8	38.2

F1'- F6 represents Fractions 1 to 6 of the sequential extraction procedures; F1 = water soluble, F2 = exchangeable, F3 = Carbonate bound; F4 = Fe – MnO; F5 = organic bound; F6 = residual; Sum = Σ of all fraction; BA = bioavailability of metals in samples; MF= mobility factor; NRF = non – residual fraction; RF = residual fraction.

Appendix XVII: Mean Concentrations of the Individual Metals in the Soil Fractions (Control) in Wet season

	F1D6	F2D6	F3D6	F4D6	F5D6	F6D6	Sum	BA	MF	NRF	Res

Cd	0.55	3.46	5.77	0.03	1.91	14.55	26.27	0.37	37	45	55
Cr	2.00	1.10	7.55	0.10	0.03	5.67	16.45	0.65	65	66	34
Cu	6.57	2.65	6.11	4.83	8.75	20.98	49.89	0.31	31	58	42
Ni	6.57	3.65	4.68	0.83	1.75	10.98	28.46	0.52	52	61	39
Pb	0.58	2.625	0.88	2.56	3.65	3.93	14.25	0.29	29	72	28

F1'- F6 represents Fractions 1 to 6 of the sequential extraction procedures; F1 = water soluble, F2 = exchangeable, F3 = Carbonate bound; F4 = Fe – MnO; F5 = organic bound; F6 = residual; Sum = Σ of all fraction; BA = bioavailability of metals in samples; MF= mobility factor; NRF = non – residual fraction; RF = residual fraction

Appendix XVIII: Mean Concentrations of the Individual Metals in the Soil Fractions (Control) in Dry season

	F1D6	F2D6	F3D6	F4D6	F5D6	F6D6	Sum	MF	BA	NRF	RF
Cd	3.13	1.5	3.95	6.28	1.8	9.4	26.06	0.33	32.9	63.9	36.1
Cu	1.28	4.5	3.05	7.75	3.55	11.55	31.68	0.28	27.9	63.5	36.5
Cr	-	2.79	3.84	1.84	1.7	7.91	18.08	0.37	36.7	56.2	43.8
Pb	3.6	5.33	4.9	6.4	-	17.3	37.53	0.37	36.8	53.9	46.1
Ni	3.8	-	1.58	2.48	1.53	11.03	20.42	0.26	26.3	46	54

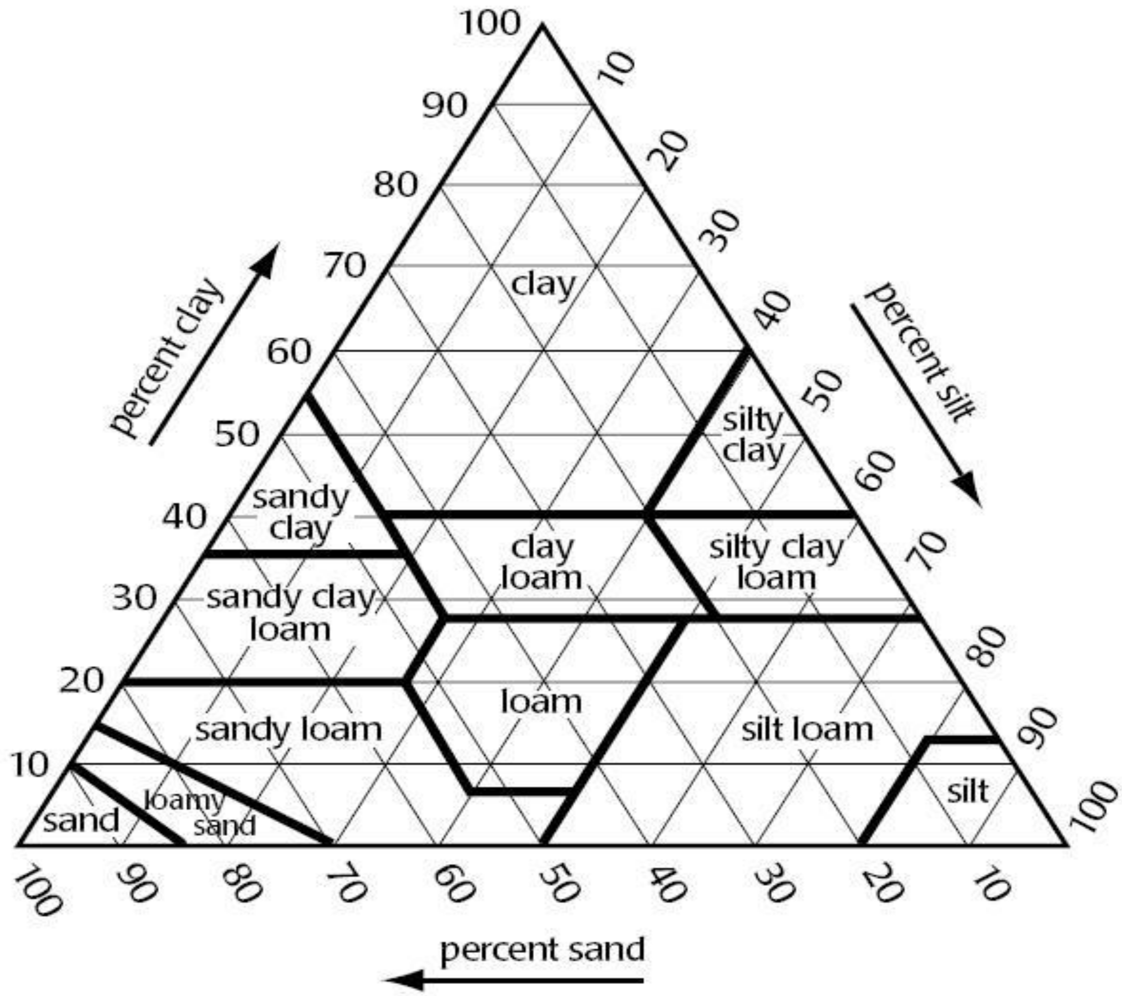
F1'- F6 represents Fractions 1 to 6 of the sequential extraction procedures; F1 = water soluble, F2 = exchangeable, F3 = Carbonate bound; F4 = Fe – MnO; F5 = organic bound; F6 = residual; Sum = Σ of all fraction; BA = bioavailability of metals in samples; MF= mobility factor; NRF = non – residual fraction; RF = residual fraction.

Appendix XIX: ANOVA Summary for Heavy Metals in *Abelmoschus esculentus* *S*amples obtained in the Dry Season

Groups	*Count*	*Sum*	*Average*	*Variance*
Cd	6	54.04	9.01	34.42
Cr	6	60.36	10.06	22.61

Cu	6	98.80	16.47	33.85
Ni	6	75.21	12.53	47.19
Pb	6	44.84	7.47	8.06

Appendix XX: Soil Texture Triangle



Appendix XXI: Gurara Street Dumpsite

Appendix XXII: Abuja Street Dumpsite

Appendix XXIII: Railway Quarters Dumpsite

Appendix XXIV: Albarka Street Dumpsite

Appendix XXV: Garaje Dumpsite

Appendix XXVI: Control

Appendix XXVI: Control