LEVEL OF HEAVY METALS AND THEIR BIOAVAILABILITY IN SOIL IN KAKURI INDUSTRIAL AREA OF KADUNA, NIGERIA

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AUGUST, 2014

DECLARATION

I hereby declare that this thesis entitled "LEVEL OF HEAVY METALS AND THEIR BIOAVAILABILITY IN SOILS IN KAKURI INDUSTRIAL AREA OF KADUNA*"* is a record of my research work under the supervision of Prof. E.B.Agbaji and Dr. S. E. ABECHI in the Department of Chemistry, Ahmadu Bello University, Zaria. All sources of information are duly acknowledged by references. No part of this thesis was previously presented for another degree or diploma at any university or institution.

EMMANUEL, Solomon Arome

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CERTIFICATION

This thesis entitled "LEVEL OF HEAVY METALS AND THEIR BIOAVAILABILITY IN SOILS IN KAKURI INDUSTRIAL AREA OF KADUNA" by Emmanuel Solomon Arome meets the regulations governing the award of degree of M.Sc. Analytical Chemistry of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This research work is dedicated to the Almighty God

ACKNOWLEDGMENT

My greatest thanks go to Almighty God for giving me the wisdom, strength and grace to bring this work to completion.

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ABSTRACT

This study investigated the level of heavy metal contamination in soils at 0 to 10cm and 10 to 20 cm depths from twelve (12) sample locations in Kakuri industrial area of Kaduna, Nigeria. The phisco-chemical parameters such as organic matter content (OM), soil pH, calcium carbonate and particle size distribution of the soil samples were determined. The total concentrations of Cu, Zn, Pb, Cr, Ni, Hg and V were also determined using XRF spectrophotometer with the results showing a mean concentrations (in $mgkg^{-1}$) of 100.5 ± 19.82, 60.02 ±3 .60, 26.25 ± 6.44, 42.42 ± 5.21, 32.00 ± 1.68, 28.80 ± 9.35 and 73.08 ± 3.52 respectively.Significant spatial variation in concentrations was observed for all metals across the locations as metal concentrations (mgkg-1) ranged: Zn, 20-420; Cu, 26-110; Ni, 9-72; Cr, 22-157; Pb, 27-34; Hg, 10-60 and V, 47-120. The degree of pollution varies with the level and proximity to industrial activities. The data was subjected to descriptive analysis to determine the Geo-accumulation index (Igeo) and contamination factor (Cf) with results indicating that the soils can be considered uncontaminated with Igeo ≤ 1 for virtually all the locations with the exception of KGW with 1 Igeo ≤ 2 indicating it is considerably contaminated according to the Igeo classification guideline. The contamination factor Cf also confirms the soil is uncontaminated having Cf values 1.31, 1.40 and 1.70 for Zn, Cu and Pb respectively which falls under the classification 1 ≤ Cf 3 meaning the soil is considerably contaminated. Correlation analysis shows Zn, Hg and Cu have common source(s) in the environment and also strongly correlated to pH and organic matter.Bioavailable concentrations of the studied soil were equally low due to basic soil pH and to high content of free calcium carbonate. The relative bioavailability followed the order of Zn>Cu>Hg>Pb>Ni>Cr>V.

TABLE OF CONTENTS

Cover page……..i

Fly leaf……...ii

Title page……..iii

Declaration……....iv

Certification……...v

Dedication…….....vi

Acknowledgment…….....vii

Abstract…….....viii

Table of Content……...ix

List of Tables……..….xv

List of Figures……...…..xvi

List of Appendices…….....xvii

Abbreviations……xviii

CHAPTER ONE

1.0 INTRODUCTION…….1

1.1 Background Study……...1

1.2 Justification for the Research…….....2

1.3 Aims and Objectives……4

CHAPTER TWO

2.0 LITERATURE REVIEW……..…….....6

2.1 Heavy Metals in Soil and Toxicity..……...…….5

2.2 Sources of Heavy Metals in Contaminated Soil…….....7

2.2.1 Metal Mining, Milling Processes and Industrial Waste…….……...8

2.2.2 Air Borne Sources…….……...……..9

2.2.3 Fertilizers…….…….…….....10

2.2.4 Pesticides……..10

2.2.5 Biosolids and Manures…….…….……...12

2.2.6 Wastewater……...13

2.3 Methods of Soil Analysis for Heavy Metals…….……15

2.4 Soil Chemistry and Potential Risks of some Heavy Metals……..……..19

2.4.1 Lead…… ..……..…….…….…….....19

2.4.2 Zinc……..…20

2.4.3 Chromium…….……..21

2.4.4 Copper…….…….……...22

2.4.5 Mercury…….……..23

2.4.6 Nickel……...…….……..24

2.4.7 Vanadium……..……...……....24

2.5 Bioavailability of Metals in Soil……..….....25

2.6 Influence of Plants on Mobility and Bioavailability of Heavy Metals in Soil.....28

2.7 Impacts of Heavy Metals on Soil Functions…….....29

2.8 Evaluation of Metal Ion Concentration in Soil……..……..…….…....30

CHAPTER THREE

3.0 MATERIALS AND METHOD……...35

3.1 Sample Collection……...35

3.2 Sample Treatment……..……38

3.3 Measurement of Physicochemical Parameters…….……...……38

3.3.1 pH Measurements……..…..…….38

3.3.2 Particle Size Distribution…….....38

3.3.3 Calculation of percent sand, silt and clay……40

3.3.4 Calcium Carbonate Determination…….....41

3.3.5 Organic Matter Measurement……...……43

3.4 Preparation of Reagents……..…….44

3.4.1 Preparation of Methyl Orange Indicator……...……..……44

3.4.2 Preparation of Calcimeter Bernard Filling Solution…….....…..42

3.4.3 Preparation of Solution of 4M HCl……..…...45

3.4.4 Preparation of 0.16moldm^{-3} Potassium Dichromate ($K_2Cr_2O_7$)…….....45

3.4.5 Preparation of 1.0moldm^{-3} Ferrous Sulphate ($FeSO_4.7H_2O$)…….....……45

3.4.6 Preparation of Ortho-phenanthroline Solution…….....…...45

3.5 Heavy Metal Content Measurement.……...……...46

3.5.1 Total Heavy Metal Content…….……...46

3.5.2 Theory of X- Ray Spectrophotometer…….……46

3.5.3 Bioavailable Metal Content……...……..……...47

CHAPTER FOUR

4.0 RESULTS ……..…….....49

CHAPTER FIVE

5.0 DISCUSSION…….59

5.1 Physicochemical Properties……...59

5.2 Total Heavy Metal Concentration……60

5.2.1 Zinc……61

5.2.2 Copper…….....….....62

5.2.3 Nickel……...…….…….62

5.2.4 Lead……..……..63

5.2.5 Vanadium……..…….64

5.2.6 Mercury…….……..64

5.2.7 Chromium……..…….65

5.3. Correlation Analysis of Heavy Metals, pH and Organic Matter…….……...65

5.4 Heavy Metals Contamination in Soil……...…….....66

5.4.1 Contamination Factor (Cf)……..…….,,….....67

5.4.2 Geo-accumulation Index (Igeo) …….……..68

5.5 Heavy Metals Concentration in Sample and Control Soil…….....69

5.6 Heavy Metal Concentration at 0 to 10cm and 10 to 20cm Depths…….….70

5.7 Bioavailability of Heavy Metals in Soil……..……...71

CHAPTER SIX

6.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS……..73

6.1 Summary and Conclusions……...73

6.2 Recommendations for Further studies…….....74

REFERENCES……...75

APPENDICES…….…...89

LIST OF TABLES

Tables **Pages**

2.1 Soil concentration ranges and regulatory guidelines for some heavy

For European soil…….…….....33

2.2 Target and intervention values for some soil heavy metals provided by the

Department of Petroleum Resources …….....34

3.1 Sample locations and common industrial activities…….....36

4.1 Physicochemical Parameters of Samples and Control Soils in Kakuri

Industrial Area.....49

4.2Statistical summary showing Mean±SD, median and Range of concentrations

of heavy metals in soil samples……..……...50

4.3 Correlation between heavy metals, pH and organic matter (O.M) in soil

Samples……..……..….....54

4.4 Mean Concentration, Baseline Data ($Mgkg^{-1}$), Average Shale ($Mgkg^{-1}$),

Geo-Accumulation Index (I_{geo}) Values and Enrichment Factor of Heavy Metals

in Soils in Kakuri Industrial Area……..……55

LIST OF FIGURES

Figures **Pages**

3.1 Map of Kakuri industrial layout indicating soil sample collection point..……..37

4.1 Concentrations of Zn, Cu and Ni at 10 to 20 cm depth of soil samples in comparison with average concentrations of control, DPR target and Intervention levels and RSGalert level……..…….....51

4.2 Concentrations of Pb and V at 10 to 20 cm depth of the soil samples in comparison with average concentrations of control samples, DPR target and Intervention levels and RSG alert level ……..…… ……...……52

4.3 Concentrations of Hg and Cr at 10 to 20 cm depth of the soil samples in comparison with average concentrations of control samples, DPR target and Intervention levels and RSG alert level ……..…… ……...……53

4.4 Comparison of average concentration of heavy metals in sample and control soil……...56

4.5 Comparison of heavy metals concentration at (0 to 10cm) and (10 to 20cm)

soil depths in Kakuri industrial area……..…….….....57

4.6 Total metals in soil in comparison with bioavailable metals available in the

soilsamples inKakuri industrial area……..…….…….58

LIST OF APPENDICES

Appendices **Pages**

A Concentration ($mgkg^{-1}$) of heavy metals in some soil samples at depths 0 to10 and 10 to 20cm……...……..……89

Concentration ($mgkg^{-1}$) of heavy metals in some soil samples at depths 0 to10 and 10 to 20cm(Continue).....……..…….90

B Heavy metals Concentration ($mgkg^{-1}$) in control samples……..…….....91

C Heavy metals distribution across sample locations in Kakuri industrial area……..…..……92

D Muller's Classification for the Geo-Accumulation Index…….…….…….93

E Standard Regulatory Limits/Background Levels of Metals in Soil…….…….94

F Contamination factor (C_f) and degree of contamination (Cd) of soil sample……...……...95

G Bioavailable heavy metals ($mgkg^{-1}$) in sample and control soils in Kakuri industrialarea at 10 – 20 cm depth…….…….…….96

H Bioavailable metal content as a percentage of the total metal content of

the soil in Kakuri industrial area……...97

I List of Apparatus and Equipments…….…….....98

ABBREVIATIONS AND SYMBOLS

AAS Atomic Absorption Spectrophotometer

AD Air Dry weight

ANOVA Analysis of Variance

AHT Ahmed Thalib

ART Arewa Textiles

C_f Contamination Factor

CCG Changchangi

DIC Defence Industries Corporation

DICON Defence Industries Corporation of Nigeria

DOC Dissolved Organic Carbon

DPR Department of Petroleum Resources

DTPA Diethylenetriamine Pent-acetic Acid

EDTA Ethylenediamine Tetra-acetic Acid

EDXRF Energy Dispersive X-Ray Fluorescence

EGASPIN Environmental Guidelines and Standards for the Petroleum Industry in Nigeria

EPA Environmental Protection Agency

f Correction Factor

FIAM Free-ion Activity Model

GARTAC Ground Water Remediation Technologies Analysis Center

I_{geo} Geo-accumulation Index

IBBI International Breweries and Beverage Industry

KTL Kaduna Textile Limited

NBC Nigerian Bottling Company

NCC Nocaco Cable Company

MCF Moisture Content Factor

OD Oven Dry weight

OM Organic Matter

PAN Peugeot Automobile Nigeria

PI Pollution Index

ppb Part Per Billion

ppm Part Per Million

PVC	Polyvinyl Chloride
RDQ	Down quarters
RSG	Romanian Soil Guideline
SNG	Sunglass
SPLP	Synthetic Precipitation Leaching Procedure
TCLP	Toxicity Characteristic Leaching Procedure
UNT	United Nigeria Textile
USEPA	United State Environmental Protection Agency
XRF	X-Ray Fluorescence

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background Study

Heavy metals are among the most common environmental pollutants and their occurrence in soils indicates the presence of natural or anthropogenic sources. The main natural sources of metals in soils are weathering of parent material and soil erosion (Yoon *et al*., 2007). The anthropogenic sources are associated mainly with industrial activities such as metal finishing, paint pigment and battery manufacturing, leather tanning, mining activities, foundries and smelters, diffuse sources e.g., piping, constituents of products, combustion by-products, traffic emissions and other human activities like urban composts and municipal waste water sludges depositions and use of pesticides and phosphate fertilizers (Omar and Al-Khashman, 2004., Boularbah *et al*., 2006).

Heavy metals constitute an ill-defined group of inorganic chemical hazards, and those most commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) (GWRTAC, 1997). Soils are the major sinks for heavy metals released into the environment by aforementioned anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation (Kirpichtchikova *et al*., 2006) and the total concentration of heavy metals in soil persist for a long time after their introduction (Adriano, 2003). Changes in their chemical forms (speciation) and bioavailability are, however, possible.

The presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants (Maslin and Maier, 2000). Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems (McLaughlin[1]*et al*., 2000 and Ling*et al*., 2007).

Adequate protection and restoration of soil ecosystems contaminated by heavy metals require their characterization and remediation. The high toxicity of these metals has drawn increasing interest in the development of techniques for their removal from waste water before they are disposed into the environment. Some of the techniques which have been used in the removal of metals from effluents include ion exchange, chemical precipitation, electro-dialysis, electrolytic extraction, reverse osmosis, and cementation. These methods are expensive and have the inability to remove metals at low concentration (Faur-brasquet*et al*., 2002; Bishnoi*et al*., 2004). Consequently, due to the high cost of treatment, many industries do not treat their waste properly but rather dispose them untreated. This practice goes a long way to cause damage to our environment (Okuo and Ozioka, 2001).

1.2 Justification for the Research

Heavy metals are usually present in wastewaters which are released into the soil environments from various industries as there is no clear demarcation between residential and industrial area in Nigeria. The adverse effects caused by these heavy metals are of great concern. Heavy metals are non-biodegradable and tend to accumulate in living organisms

thereby causing various diseases and disorders (Bailey *et al*., 1999). It is worthy of note that the major industrial activities in Kakuri industrial area has declined following the closure of some textiles industries. However there has been increase in population and vehicular traffic, as well as the creation of a variety of ancillary activities such as vehicle repairs, vulcanizer, welders, auto-electricians, battery chargers etc. Their activities could have resulted to heavy metals contamination of waterways and are subsequently deposited into nearby soils (Adefolalu, 1980; Mabogunje, 1980).

Several research works have been reported on heavy metals in soil and waterways in Kaduna and its environs in recent times. These include Chemical Fractionation of Heavy Metals in Soils around the Vicinity of Automobile Mechanic Workshops in Kaduna Metropolis (Achi *et al*., 2011), Levels of Toxic Metals in Soil from Irrigated Farmland in Kaduna Metropolis (Umoru, 2013), Assessment of Cd and Zn in Roadside Surface Soils and Vegetation along Some Roads of Kaduna Metropolis, Nigeria **(**Okunola *et al.*, 2008**);**Assessment of Heavy Metals Bioaccumulation by Eleusine indicafrom refuse dumpsites in Kaduna Metropolis, Nigeria **(**Mohammed*et al*,. 2012) and other similar works but none has been specific on soil of highly populated Kakuri industrial area.

Contemporary legislation in respect to environmental protection and public health, at both national and international levels, are based on data that characterize chemical properties of environmental phenomena (Zhao and Kaluarachchi, 2002). Soil characterization would provide an insight into heavy metal speciation and bioavailability. In addition, attempt at remediation of heavy metal contaminated soils would entail knowledge of the source

ofcontamination, basic chemistry, environmental and associated health effects (risks) of these heavy metals.

There is therefore need for a continuous monitoring of level of heavy metal in the area in order to keep a check on the environment and to provide data for future research works.

1.3 Aim and Objectives

The aim of this research is to determine the distribution of heavy metals and their bioavailability from soils in the vicinities of Kakuri industrial area of Kaduna state and to compare the soil heavy metal concentrations with regulatory standard values permitted by the Nigerian environmental guideline as well as international standards.

The objectives set to achieve this aim include to:-

1. establish the spatial distribution and variability in concentrations of heavy metals for soils in Kakuri industrial area of Kaduna with reference to the activities in each of the sample sites.
2. investigate the dispersion of the heavy metal concentrations at two different soil depths of 0 - 10cm and 10 - 20cm.
3. investigate the influence of physicochemical parameters on the bioavailability of metals in soils around Kakuri industrial area.
4. assess the level and extent of contamination by comparing the results obtained with Nigerian environmental soil guidelines as well as international soil standards and also using soil contamination indices in order to identify any need for regular monitoring and/or remediation.

5. establishany correlation between the heavy metals in soils and the physicochemical parameters.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Heavy Metals in Soil and Toxicity

Heavy metals are defined as those metals whose density is above 5g/cm^3 (Pattabhi*et al.*, 2008). High concentration of heavy metals in the environment can be detrimental to a variety of living systems. Excessive ingestion of these metals by humans can causes poisoning, cancer, nervous system damage and ultimately death (Corapcioglu and Huang, 1987; Issabayeva *et al*., 2007).

The toxicity of heavy metals is due to their ability to bind to oxygen, nitrogen, and sulphur groups in proteins, resulting in alterations of enzymatic activity. Most organ/systems are affected by heavy metal toxicity; the most common include the hematopoietic, renal, and cardiovascular organs/systems. To a lesser extent, lead toxicity involves the musculoskeletal and reproductive systems. The organ/systems affected and the severity of the toxicity vary with the particular heavy metal involved, the chronicity and extent of the exposure, and the age of the individual (Schwartz and Hu, 2007). Main sources of heavy metal contamination include urban industrial aerosols, solid wastes from animals, mining activities, industrial and agricultural chemicals. Increasing concern by environmentalists and governments on the effects of heavy metals and an attempt to protect public health has resulted in upsurge researches in development of advanced technologies to remove heavy metals from waters and wastewaters (Karbassi and Nadjafpour, 1996; Bong *et al*., 2004; Shetty and Rajkumar, 2009).

The most common heavy metals found at contaminated sites, in order of abundance are Pb, Cr, As, Zn, Cd, Cu, and Hg (USEPA 1986). These metals are capable of decreasing crop production due to the risk of bioaccumulation and biomagnifications in the food chain. There is also the risk of superficial and groundwater contamination. The fate and transport of a heavy metal in soil depends significantly on the chemical form and speciation of the metal. Once heavy metals are adsorbed in the soil by initial fast reactions (minutes, hours), slow adsorption reactions occurs (days, years) resulting in the redistribution into different chemical forms with varying bioavailability, mobility, and toxicity (Shiowatana*et al.*,2001; Buekers, 2007). This distribution is believed to be controlled by reactions of heavy metals in soils such as mineral precipitation, dissolution, ion exchange, adsorption, desorption; aqueous complexation, biological immobilization, mobilization and plant uptake (Levy *et al*., 1992).

2.2 Sources of Heavy Metals in Contaminated Soils

Heavy metals occur naturally in the soil environment from the pedogenetic processes of weathering of parent materials at levels that are regarded as trace(<1000 mg/kg) and rarely toxic [(Kabata-Pendias and Pendias (2001), Pierzynski*et al*., (2000)]. Anthropogenic activities and acceleration of nature's slowly occurring geochemical cycle of metals by man resulted /caused most soils environments to have accumulated one or more of the heavy metals above defined background values high enough to cause risks to human health, plants, animals, ecosystems, or other media (D' Amore *et al*., 2005). The heavy metals essentially become contaminants in the soil environments for the following reasons:

i) Their rates of generation via manmade cycles are more rapid relative to natural ones,

ii) They become transferred from mines to random environmental locations where higher potentials of direct exposure occur.

iii) The concentrations of the metals in discarded products are relatively high compared to those in the receiving environment, and

iv)The chemical form (species) in which a metal is found in the receiving environmental system may render it more bioavailable (D' Amore *et al*., 2005)

Heavy metals in contaminated soil from anthropogenic sources tend to be more mobile, than the heavy metal contamination from natural sources. (Kuo*et al*., 1983;Kaasalainen and Yli-Halla., 2003). Metal-bearing solids at contaminated sites can originate from a wide variety of anthropogenic sources in the form of metal mine tailings, disposal of high metal wastes in improperly protected landfills, lead based paints, land application of fertilizer, animal manures, biosolids (sewage sludge), composts, pesticides, coal combustion residues, petrochemicals and atmospheric deposition (Khan *et al*., 2008. Zhang *et al*., 2010. Basta*et al*., 2005).

2.2.1 Metal mining, milling processes and industrial wastes

Mining and milling of metal ores coupled with industrial activities have left a legacy of wide distribution of metal contaminants in soil. During mining, tailings (heavier and larger particles settled at the bottom of the flotation cell during mining) are directly discharged into natural depressions, including onsite wetlands resulting in elevated concentrations (DeVolder*et al*., 2003). Extensive Pb and Zn ore mining and smelting have resulted in contamination of soil that poses risk to human and ecological health. Soil heavy metal environmental risk to humans is related to bioavailability. Assimilation pathways include

the ingestion of plant material grown in (food chain), or the direct ingestion (oral bioavailability) of, contaminated soil (Basta and Gradwohl,. 1998). Other materials are generated by a variety of industries such as textile, tanning, petrochemicals from accidental oil spills or utilization of petroleum-based products, pesticides, and pharmaceutical facilities and are highly variable in composition. Although some are disposed of on land, few have benefits to agriculture or forestry. In addition, many are potentially hazardous because of their contents of heavy metals (Cr, Pb, and Zn).

2.2.2 Air-borne source

Airborne sources of metals include stack or duct emissions of air, gas, or vapor streams, and fugitive emissions such as dust from storage areas or waste piles. Metals from airborne sources are generally released as particulates contained in the gas stream. Some metals such as As, Cd, and Pb can also volatilize during high-temperature processing. These metals will convert to oxides and condense as fine particulates unless a reducing atmosphere is maintained (Smith *et al*., 1995). Fugitive emissions are often distributed over a much smaller area because emissions are made near the ground.

In general, contaminant concentrations are lower in fugitive emissions compared to stack emissions. The type and concentration of metals emitted from both types of sources will depend on site-specific conditions. All solid particles in smoke from fires and in other emissions from factory chimneys are eventually deposited on land or sea; most forms of fossil fuels contain some heavy metals and this is, therefore, a form of contamination which has been continuing on a large scale since the industrial revolution began. For example, very high concentration of Cd, Pb, and Zn has been found in plants and soils adjacent to smelting

works. Another major source of soil contamination by metal is the aerial emission of Pb from the combustion of petrol containing tetraethyl lead; this contributes substantially to the content of Pb in soils in urban areas and in those adjacent to major roads. Zn and Cd may also be added to soils adjacent to roads, the sources being tyres, and lubricant oils (USEPA 1986).

2.2.3 Fertilizers.

Agriculture was the first major human influence on the soil (Scragg, 2006). To grow and complete the lifecycle, plants must acquire not only macronutrients (N, P, K, S, Ca, and Mg), but also essential micronutrients. Some soils are deficient in the heavy metals (such as Co, Cu, Fe, Mn, Mo, Ni, and Zn) that are essential for healthy plant growth (Lasat, 2000), The compounds used to supply these elements contain trace amounts of heavy metals (e.g.,Cd and Pb) as impurities, which, after continued fertilizer application may significantly increase their content in the soil (Jones *et al*., 1981). Application of certain phosphoric fertilizers inadvertently adds Cd and other potentially toxic elements to the soil, including F, Hg, and Pb (Raven *et al*., 1998).

2.2.4 Pesticides

Several common pesticides used fairly extensively in agriculture and horticulture in the past contained substantial concentrations of metals. Pesticides are applied widely to protect plants from disease, weeds, insect damage etc. Usually pesticides come into contact with soil where they undergo a variety of transformations that provide a complex pattern of metabolites. There is also increasing interest in their transformation products, because they

can be present at higher levels in soil than the parent pesticide itself. (Vicente and Yolanda, 2004).

The fate of pesticides in soil is controlled by chemical, biological and physical dynamics of this matrix (Sparks, 2003). These processes can be grouped into those that affect persistence, including chemical and microbial degradation, and those that affect mobility, involving sorption, plant uptake, volatilization, wind erosion, run-off and leaching. Pesticides are degraded by chemical and microbiological processes. Chemical degradation occurs through reactions such as photolysis, hydrolysis, oxidation and reduction (Kodaka *et al*., 2003).

In recent past, about 10% of the chemicals used as insecticides and fungicides in UK were based on compounds which contain Cu, Hg, Mn, Pb, or Zn. Examples of such pesticides are copper-containing fungicidal sprays such as *Bordeaux mixture* (copper sulphate) and copper oxychloride (Raven *et al.*, 1998). Lead arsenate was used in fruit orchards for many years to control some parasitic insects. Arsenic containing compounds were also used extensively to control cattle ticks and to control pests in banana in New Zealand and Australia, timbers have been preserved with formulations of Cu, Cr, and As (CCA), and there are now many derelict sites where soil concentrations of these elements greatly exceed background concentrations. Such contamination has the potential to cause problems, particularly if sites are redeveloped for other agricultural or nonagricultural purposes. Compared with fertilizers, the use of such materials has been more localized, being restricted to particular sites or crops (McLaughlin[2]*et al*., 2000).

2.2.5 Biosolids and manures.

The application of numerous biosolids (e.g., livestock manures, composts and municipal sewage sludge) to land inadvertently leads to the accumulation of heavy metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Ti and Sb in the soil (Basta*et al*., 2005). In most pig and poultry industry, Cu and Zn added to diets as growth promoters as well as As contained in poultry health products may also have the potential to cause heavy metals contamination of the soil (Chaney and Oliver, 1996; Sumner, 2000). The manures produced from animals on such diets contain high concentrations of As, Cu, and Zn and if repeatedly applied to restricted areas of land can cause considerable buildup of these metals in the soil in the long run.

Biosolids (sewage sludge) are primarily organic solid products produced by wastewater treatment processes that can be beneficially recycled (USEPA, 1997). The term *sewage sludge* is used in many references because of its wide recognition and its regulatory definition. However, the term biosolids is becoming more common as a replacement for sewage sludge because it is thought to reflect more accurately the beneficial characteristics inherent to sewage sludge (Silveira*et al*., 2003).

In the United States it is estimated that more than half of approximately 5.6 million dry tonnes of sewage sludge used or disposed of annually is utilized as biosolids in agricultural. In the European community, over 30% of the sewage sludge is used as fertilizer in agriculture (Silveira*et al*., 2003). In Australia over 175 000 tonnes of dry biosolids are produced each year by the major metropolitan authorities, and currently most biosolids

applied to agricultural land are used in arable cropping situations where they can be incorporated into the soil (McLaughlin, 2000).

Heavy metals most commonly found in biosolids are Pb, Ni, Cd, Cr, Cu, and Zn. These heavy metal concentrations are governed by the nature and the intensity of the industrial activity, as well as the type of process employed during the biosolids treatment (Mattigod and Page, 1983).

2.2.6 Wastewater.

In several Asian and African cities, studies suggest that agriculture based on wastewater irrigation accounts for 50 percent of the vegetable supply to urban areas (Bjuhr, 2007). Farmers generally are not bothered about environmental benefits or hazards and are primarily interested in maximizing their yields and profits. Although the metal concentrations in wastewater effluents discharged into rivers in comparison to the discharge points of industries and other sources are usually relatively low, long-term irrigation of land with such can eventually result in heavy metal accumulation in the soil (Raymond e*t al.,* 2011). Due to rapid population growth, urbanization andindustrialization, there has been an increase in the quantity of discharges into the aquatic environment which contain huge amount of heavy metals and adversely affect the physicochemical properties of the receiving water and consequently its biota. (FAO, 1991)

Nigeria generates over 500, 000 tons of waste annually (Itah, 1998) and a good percentage of this is being discharged into the water ways untreated. River Kaduna for instance receives over 500, 000 m^3/day of untreated effluent from various industries in Kaduna through 53

tributaries from domestic and industrial sources such as food and beverages, oil depot, numerous textiles companies such as Kaduna Textiles Limited (KTL), United Nigerian Textiles Limited (UNTL), Norspin, Nigerian Brewery Ltd (NBL) and Changchangi Oil Depot (Ali *et al*., 2005).

The re-use of wastewaters from either domestic or industrial processes for irrigation is a common phenomenon of most urban industrial centers of the world. In Pakistan farmers were able to grow high quality crops like vegetables with wastewater (van der Hoek, 2004).Reports from many studies have shown that large scale and long term application of wastewater on the soil in irrigation farming and other activities may lead to danger of insect infestation, pollution of groundwater and built up of heavy metals, salts and other toxicants in the soil [(Hussein *et al.,* 2001, Okpala 2002; Samaila 2005 and Sharma *et al.,* 2007)].

Domestic sewage and refuse also found their way into the river from many settlements along the river via leaching, direct discharge and surface run off. Thus, there is every possibility of contamination of water, sediments and fishes of river Kaduna by heavy metals since industrial effluents and municipal wastes are known to contain high amounts of heavy metals (Abul-Kashan and Singh 1999). According to Oladimeji (1986) there is presence of Cu, Cr, Fe, Mn, Ni, V and Zn in river Kaduna. In order to tame this ugly trend, studies have suggested proper management practices such as partial treatment of wastewater before its discharge into water recipient surfaces, the selection of tolerant crops, awareness campaigns on the danger in the direct use of untreated water for crop development and monitoring of the quality of surface water applied in irrigation should form integral components in

agricultural development schemes for urban and peri-urban industrial centers (Samaila *et al.,* 2011).

2.3 Methods of Soil Analysis for Heavy Metals

Studies on heavy metals in soil in and around Kaduna using different methods have been reported widely in the literature over the years. Umoru, (2013) investigated concentration of heavy metals in soil from an irrigated farmland in Kaduna metropolis; He determined the concentrations of Cd, Cr, Cu, Pb and Zn in (mg/kg) in topsoil fromIrrigated farmland around Kawo area in Kaduna, a town in Northern Nigeria usingAtomic Absorption Spectrophotometer (AAS). Soil pHranged from 6.50-7.90 while the soil percentage organic matterranged from 0.80-1.86%. Concentration of Cd, Cr, Cu, Pb and Zn in all the soils samplesranged from 0.1-4.5, 0.50-30.50, 3.2-13.5, 4.0-28.00 and 5.5- 49.7mg/kg dry weight,respectively. The mean concentrations of soil samples studied were found to follow thedecreasing orders; Zn > Pb > Cr > Cu > Cd. He also discovered a correlation between soil physicochemicalparameters and metals such as Cu and Pb in the soil samples. It was also reported that the concentrations of heavy metals were within tolerable levels except for Cd. The slightlyhigh level of Cd was ascribed to lubricating oils as well as the burning of old tyresthat are frequently dumped close to the site. The results indicated that the soil had slightly high levels of Cd while the levels ofsoil Cr, Cu, Pb and Zn were within tolerable levels. However, the obtained meanvalues of heavy metals in the site studied are higher than that found in the control site.

Achi*et al*., (2011) carried out chemical fractionation of heavy metals in soils in the vicinity of automobile mechanic workshops inKaduna metropolis, Nigeria and reported that metal

toxicity depends on chemical associations in soils. It was suggested that determining thechemical form of a metal in soils was important to evaluate its mobility and bioavailability. Sequential extraction was therefore, used to fractionate seven heavy metals (Cd, Cu, Ni, Zn, Cr, Fe and Pb) fromten contaminated soils into six operationally defined groups: water soluble, exchangeable, carbonate, Fe-Mn oxide, organic, and residual. The residual fraction was the most abundant pool for all the metalsexamined. A significant amount (2.00 to 73.47, 1.77 to 17.78, 9.76 to 58.54 and 1.71 to 54.11%respectively) of Cu, Cd, Cr and Pb was present in the potentially available fraction to the non-residualfraction. Contamination of Zn, Ni and Fe in these soils was not as severe as Cu, Cd, Cr and Pb. Overall,the order of contamination was Cu >Cr> Pb > Cd > Ni > Zn > Fe. The study indicated that the possiblepollution of soils of this environment was as a result of anthropogenic activities.

In another study of heavy metals in soil around Kaduna,Mohammed*et al*.,(2012) carried out a research work on Assessment of Zn Bioavailability in Dumpsites of Kaduna Metropolis,Nigeria with the objective of this research being to investigate the chemical fractionation; mobility and bioavailability of Zn in refuse wastesoils of some dumpsites. The metal in the waste soil samples was sequentially extracted and measuredusing atomic absorption spectrometry, while the total concentration of the metal was determined using Energy Dispersive XRayFluorescence (EDXRF) techniques. The soil pH was also determined. The results showed that Kurmin Mashi hadthe highest total concentration of Zn. From the ANOVA ($P=0.005<0.05$) it was established that there is a significantdifference in the total Zn concentrations across the three locations. From the results it was also found out that the metal wasdistributed between oxide, carbonate and carbonate/organically bound

fractions and that EDTA extracted the highest Znconcentration across the dumpsites. Similarly, the ANOVA ($p=0.000<0.05$) indicated a significant difference in the Znextracted by the three extraction media.

Christopher and Therese (2010) studied Heavy Metal Contamination of Surface Soil in Relationship to Land Use Patterns in Benue State to assess soil environmental quality. Results revealed that metals levels were generally high in mineralized and urban soils and lower in agricultural soils whilst forest soils were polluted by anthropogenic sources. Mineralized soils developed from weathered sulphides were rich in lead (Pb), zinc (Zn), and cadmium (Cd). Urban soils accumulated Cu, Zn, and Cd most probably from refuse dumps, gasoline combustion and farming. Agricultural soils were enriched in arsenic (As) and to a lesser degree Pb and Cd originating most probably from the application of pesticides, manure and fertilizers. A pollution index (PI) based on plant-tolerant contamination levels, indicates that multi-element contamination in soils is low and implies that the sampled soils could be cultivated for crop production especially away from point sources of pollution. The degree of anthropogenic pollution was high for as (80%), and Pb (54%), moderate for Zn (47%), Cd (40%), and low for Cu (27%). Correlations (r) are significant between Zn- Pb (0.7), Cu-As (0.6) in mineralized soils, between Zn-Cu (0.64), Zn-Cd (0.5), Cu-Cd (0.6), in urban soils, As-Cd (0.61), in agricultural soils and Zn-Pb (0.82) in forest soils. These distinct relationships indicated a common source or similar geochemical control. Based on the overall evaluation, recommendation in respect of contamination, control and monitoring strategies as well as land use planning in the study area were presented.

Tamunobereton-ari*et al*., (2011) studied heavy metal speciation in contaminated soils of an abandoned hydrocarbon exploration field camp and workshop site in part of the Niger Delta, Nigeria and reported that the chemical mobility of heavy metals is fundamental to the understanding of their environmentalaccessibility, toxicity and geochemical behavior. In this work seven elements were investigated (Cr,Cu, Fe, Mn, Ni, Pb, and Zn), the EDXRF was used to analyse the total content of the metals. TheCommunity Bureau of References Extraction Scheme was employed (three-step sequential extractionscheme) to determine the bioavailability and mobile chemical forms of the metals in the samples. The results of thetotal contents of the metals in the area showed that the concentration values of the metals were reasonablyhigher in the test samples than the controlled samples. However, theresults of the extraction schemes showed relatively low bioavailability and mobility potential of the metals with more proportions retained in the residual fractions (inert state), and as such, poses little or nodanger to the environment and human in the short term.

Papafilippaki*et al* (2008) investigated the heavy metal contamination in topsoils from the industrial area ofHeraklion-Crete, Greece. The total and bioavailable forms of Cu, Zn, Pb, Cd and Ni weredetermined after their extraction with boiling Aqua Regia and DTPA respectively. Totalconcentration data according to Dutch classification scheme indicated that the soils can be considered uncontaminated with Cu, Zn and Pb, andmedium polluted with Cd and Ni. The bioavailable concentrations of the studied metals were low, due to basic soil nature and to high content of free calcium carbonate. The relativebioavailability reported followed the order of Cu>Zn≈Pb>Cd>Ni.

2.4 Soil Chemistry and Potential Risks of Some Heavy Metals

2.4.1 Lead

Lead (Pb) is usually found as a mineral combined with other elements, such as sulphur (PbS, $PbSO_4$), or oxygen ($PbCO_3$). Typical mean Pb concentration for surface soils worldwide averages 32 mg/kg and ranges from 10 to 67 mg/kg (Kabata-Pendias and Pendias, 2001). About half of the Pb used in the U.S. goes for the manufacture of Pb storage batteries. Other uses include solders, bearings, cable covers, ammunition, plumbing, pigments, and caulking.Ionic lead, Pb(II), lead oxides and hydroxides, and lead-metal oxyanion complexes are the general forms of Pb that are released into the soil, groundwater, and surface waters.

The most stable forms of lead are Pb(II) and lead-hydroxy complexes. Pb(II) is the most common and reactive form of Pb, forming mononuclear and polynuclear oxides and hydroxides (GWRTAC, 1997). The predominant insoluble Pb compounds are lead phosphates, lead carbonates (form when the pH is above 6), and lead hydroxides (Raskin and Ensley, 2000). Lead sulfide (PbS) is the most stable solid form within the soil matrix and forms under reducing conditions. Lead(II) compounds are predominantly ionic (e.g., Pb_2+ SO_4^{2-}), whereas Pb(IV) compounds tend to be covalent [e.g., tetraethyl lead, $Pb(C_2H_5)_4$]. Some Pb(IV) compounds, such as PbO_2, are strong oxidants.

Inhalation and ingestion are the two routes of exposure, and the effects from both are the same. Pb accumulates in the body organs such as the brain may lead to lead poisoning (plumbism) or even death. The gastrointestinal tract, kidneys, and central nervous system

are also affected by the presence of lead. Children exposed to lead are at risk for impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration.

Lead is not an essential element and can cause serious injury to the brain, nervous system, red blood cells and kidneys (Rosen, 2000). Acute lead poisoning in human causes severe dysfunction in the kidneys, reproductive system, liver, brain and the central nervous system. Lead poisoning from environmental exposure is thought to have caused mental retardation in many children. Mild lead poisoning causes anaemia. The victims may have headaches and sore muscles and may feel generally fatigued and irritable (Baldwin and Marshall, 1999).

2.4.2 Zinc

Zinc concentrations are rising unnaturally, due to anthropogenic activities such as mining coal, waste combustion and steel processing. Many foodstuffs contain certain concentrations of Zn. Drinking water also contains certain amounts of Zn, which may be higher when it is stored in metal tanks. Industrial sources or toxic waste sites may cause the concentrations of Zn in drinking water to reach levels that can cause health problems. Zinc is a trace element that is essential for human health. Zinc shortages can cause birth defects.

The world's Zn production is still on the rise which means that more and more Zn ends up in the environment. Plants often have a Zn uptake that their systems cannot handle, due to the accumulation of Zn in soils. Finally, Zn can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter (Campbell, 2006).

2.4.3 Chromium

Chromium is one of the less common elements and does not occur naturally in elemental form, but only in the form of compounds. Chromium is mined as a primary ore product in the form of the mineral chromite, $FeCr_2O_4$. Major sources of Cr-contamination include releases from electroplating processes and the disposal of Cr containing wastes (Smith *et al*., 1995). Chromium (VI) is the form of Cr commonly found at contaminated sites. Chromium can also occur in the +III oxidation state, depending on pH and redox conditions. Chromium (VI) is the dominant form of Cr in shallow aquifers where aerobic conditions exist. Chromium (VI) can be reduced to Cr(III) by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions often encountered in deeper groundwater. Major Cr(VI) species include chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) which precipitate readily in the presence of metal cations (especially Ba^{2+} , Pb^{2+}, and Ag^{+}). Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides. Chromium (III) is the dominant form of Cr at low pH (<4). Cr^{3+} forms solution complexes with NH_3, OH^-, Cl^-, F^-, CN^-, SO_4^{2-}, and soluble organic ligands. Chromium (VI) is the more toxic form of chromium and is also more mobile. Chromium (III) mobility is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5 due to the formation of $Cr(OH)_3$ (Bodek*et al*., 1988).

Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content, and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and un-adsorbed chromium complexes can leach from soil into groundwater. The leachability of

Cr(VI) increases as soil pH increases. Most of Cr released into natural waters is particle associated, however, and is ultimately deposited into the sediment (Smith *et al*., 1995). Chromium is associated with allergic dermatitis in humans (Scragg, 2006).

2.4.4 Copper

Copper is the third most used metal in the world (Eriksson *et al*., 1997). Copper is an essential micronutrient required for the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. Research shows that most Cu introduced into the environment is, or rapidly becomes, stable and results in a form which does not pose a risk to the environment unlike some man-made materials. In the soil, Cu strongly complexes with organic, implying that only a small fraction of copper will be found in solution as ionic copper, Cu(II). The solubility of Cu is drastically increased at pH 5.5 which is rather close to the ideal farmland pH of 6.0–6.5. (Franklin *et al*., 2004).

Soils contaminated with trace metals may pose both direct and indirect threats: direct, through negative effects of metals on crop growth and yield, and indirect, by entering the human food chain with a potentially negative impact on human health. Even a reduction of crop yield by a few percent could lead to a significant long-term loss in production and income. Some food importers are now specifying acceptable maximum contents of metals in food, which might limit the possibility for the farmers to export their contaminated crops (Bjuhr, 2007).

2.4.5 Mercury

Mercury is usually recovered as a byproduct of ore processing (Smith *et al*., 1995). Release of Hg from coal combustion is a major source of Hg contamination. Releases from manometers at pressure-measuring stations along gas/oil pipelines also contribute to Hg contamination. After release to the environment, Hg usually exists in mercuric (Hg^{2+}), mercurous (Hg_2^{2+}), elemental (HgO), or alkylated form (methyl/ethyl mercury).

The redox potential and pH of the system determine the stable forms of Hg that will be present in the soil. Mercurous and mercuric mercury are more stable under oxidizing conditions. When mildly reducing conditions exist, organic or inorganic Hg may be reduced to elemental Hg, which may then be converted to alkylated forms by biotic or abiotic processes. Mercury is most toxic in its alkylated forms which are soluble in water and volatile in air (Smith *et al*., 1995). Sorption to soils, sediments, and humic materials is an important mechanism for the removal of Hg from solution. Sorption is pH dependent and increases as pH increases. Mercury may also be removed from soil solution by coprecipitation with sulphides. Under anaerobic conditions, both organic and inorganic forms of Hg may be converted to alkylated forms by microbial activity of sulfur-reducing bacteria. Elemental mercury may also be formed under anaerobic conditions by de-methylation of methyl mercury, or by reduction of Hg(II). Acidic conditions (pH < 4) also favors the formation of methyl mercury, whereas higher pH values favor precipitation of HgS(s) (Smith *et al*., 1995). Mercury is associated with kidney damage (Scragg, 2006).

2.4.6 Nickel

Nickel exists in form of the stable nickelo-nickelic oxide, Ni_3O_4that is soluble in acid solutions. Other nickel oxide such as nickelic oxide, $Ni_2O_3$is unstable in alkaline solutions and decompose by giving off oxygen. In acidic media, however, these solids dissolve producing Ni^{2+} (EGASPIN, 2002). Nickel is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer on different sites within the bodies of animals. The most common application of Ni is in the formation of alloy.

The major sources of nickel contamination in the soil are metal plating industries, combustion of fossil fuels, and nickel mining and electroplating (Tessier*et al*., 1979). Nickel is released into the air by power plants and trash incinerators and settles to the ground after undergoing precipitation reactions. The larger part of all Ni compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result. In acidic soils, however, Ni becomes more mobile and often leaches down to the adjacent groundwater. Microorganisms can also suffer from growth decline due to the presence of Ni, but they usually develop resistance to Ni after a while.

2.4.7 Vanadium

Vanadium is widely used in industry but in small amounts. Most of the anthropogenic vanadium input into the environment is from the combustion of fossil fuels, fly-ash, sewage sludges and phosphate fertilizers. Vanadium is the major trace metal in petroleum products

and certain oils attain concentrations as high as 1400 $^{mg/kg}$ (Alloway, 1990). On combustion a fair amount of vanadium, estimated at 1 ton per 1000 tons is released to the atmosphere as V_2O_5(Alloway, 1990).Combustion of heavy fuels, especially in oil-fired power plants, refineries, industrial boilers, and coal are the major source of anthropogenic emissions of vanadium into the atmosphere (Mamane and Pirrone, 1998; Sepe*et al*., 2003).

Global anthropogenic atmospheric emission of vanadium has been estimated to be $2.1x10^5$ metric tons (MT)/year, 3 times higher than vanadium releases due to natural sources. Although anthropogenic releases to water and sediments are far smaller than natural sources (Van Zinderen Bakker and Jaworski, 1980). Such sources of vanadium in water may include leaching from the residue of ores and clays, vanadium-enriched slags, urban sewage sludge, and certain fertilizers, all of which are subjected to rain and groundwater drainage, as well as leachate from ash ponds and coal preparation wastes (Van Zinderen Bakker and Jaworski, 1980).

The transport and partitioning of vanadium in water and soil is influenced by pH, redox potential, and the presence of particulate. In fresh water, vanadium generally exists in solution as the vanadyl ion (V^{4+}) under reducing conditions and the vanadate ion (V^{5+}) under oxidizing conditions, or as an integral part of, or adsorbed onto, particulate matter (Wehrli and Stumm, 1989).

2.5Bioavailability of Heavy Metals in Soil

Bioavailability is the extent to which a contaminant in a source is free for uptake. In many definitions, especially those associated with pharmacology or mammalian toxicology,

bioavailability of a contaminant implies the degree to which the contaminant is free to be taken up and to cause an effect at the site of action (Newman and Unger, 2003). Whether or not the organism is exposed to the contaminant concentration will depend on whether it comes within close proximity of the media containing the contaminant. The organism must be in appropriate contact in order to absorb, ingest, imbibe, or inhale the contaminated material. Whether or not this contact results in a realized dose in the organism will depend on a wide range of factors that collectively determine bioavailability (Newman and Clements, 2008).

Metals of major interest in bioavailability studies, as listed by the U.S. Environmental Protection Agency (EPA), are Al, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Sb (McKinney and Rogers, 1992). Other metals that are presently of lesser interest to the EPA are Ag, Ba, Co, Mn, Mo, Na, Ti, V, and Zn. These metals were selected because of their potential for human exposure and increased health risk.

Metals can be dispersed in soil, water, air and atmosphere by natural geochemical cycling,microbial activities and by anthropogenic processes such as smelting and burning leaded gasoline and coal. These metal fluxes must be considered in overall metal bioavailability studies. Bioaccumulation of metals by biota in surface water and by plants and animals in terrestrial environments can adversely affect humans.

In surface and ground water, sediment and air, bioavailability is a complex function of many factors including total concentration and speciation (physical-chemical forms) of metals, mineralogy, pH, redox potential, temperature, total organic content (both particulate and dissolved fractions), and suspended particulate content, as well as volume of water, water

velocity, and duration of water availability, particularly in arid and semi-arid environments. In addition, wind transport and removal from the atmosphere by rainfall must be considered. Many of these factors vary seasonally and temporally, and most factors are interrelated. Consequently, changing one factor may affect several others. In addition, generally poorly understood biological factors seem to strongly influence bioaccumulation of metals and severely inhibit prediction of metal bioavailability (Luoma, 1989).

In order to understand bioavailability, plant materials and selective chemical leaches of soil must be analyzed and the results compared. Elemental suites for which analyses are performed and the type of selective leaches utilized must be tailored to bedrock and soil types, and to suspected anthropogenic inputs. Soil pH, organic matter, and sulfur and carbonate contents should be determined to enable accurate assessment of elemental reservoirs, mobility and bioavailability.

The solubility of heavy metals in soils is governed by pH, redox conditions, and the ionic composition of the soil solution as well as the nature of the soil's solid phase (Alloway, 1990; Adriano, 2003). The solubility of most heavy metals increases with decreasing pH. Reducing conditions can lead to the dissolution of oxides and the subsequent liberation of sorbed, occluded and co-precipitated heavy metals into solution while on the other hand oxidising conditions can lead to the oxidation and dissolution of insoluble sulphide minerals.

The complexation of sorbed metal species by soluble low molecular weight organic ligands in the soil solution such as dissolved organic carbon (DOC) can enhance the mobilization of many heavy metals. Variations in ionic composition of the soil solution can influence the

degree of competition for sorption sites, the formation of soluble or insoluble compounds.Increase in ionic strength can result in reduced sorption and enhanced desorption from soil surface sites. Once soluble, heavy metals can become mobile and leach through the soil profile and eventually to the groundwater.

The speciation of a metal, which refers to the distribution of this metal amongst its chemical species, also depends on the above mentioned soil factors.Both the solubility and speciation of heavy metals govern the bioavailability and thus the toxicity of heavy metals to organisms. In order to be bioavailable, a metal needs to be mobile and to come in contact with the organism in a form in which it can be taken up and react with its metabolic machinery (Campbell, 1995). According to the free-ion activity model (FIAM), metal uptake into cells is a function of the activity of the free metal ions in solution, independent of the total concentration or of other species (Brezonik*et al*., 1991). The validity of the model is supported in plant nutrition where plant response generally correlates best with the activity of the free, uncomplexed metal ions in solution (Parker *et al*,. 1995).

2.6 Influence of Plants on Mobility and Bioavailability of Metals in Soil.

Plants have an important influence on the physicochemical conditions that determine the mobility and the bioavailability of heavy metals in soil. (McLaughlin[3]*et al*., 1998) specifically printed out the following factors and processes:

(i) Plant uptake may reduce ion activity and desorbs contaminants from surfaces.

(ii) Plant-induced changes in soil solution chemistry can affect sorption, e.g. by altering pH, E_h and ionic strength.

(iii) Plants excrete organic ligands that may increase or decrease the total concentration of contaminant in solution.

(iv) Living or dead plant materials in the rhizosphere can act as sorbing surfaces for contaminants,

(v) Microbial activity, stimulated by plants, can also alter soil solution chemistry and, thus, affect contaminant behavior. Some plants can take up high amounts of heavy metals or release compounds that render these metals less soluble or even insoluble. For these reasons phytoremediation has been proposed as a cost-effective technology for the treatment of contaminated soil (Lasat, 2000).

2.7 Impact of Heavy Metals on Soil Functions

Plant roots and most soil organisms depend on energy derived from assimilates produced above ground by photosynthesis. The mineralization of organic residues by bacteria and fungi, i.e. "microorganisms", releases inorganic nutrients such as nitrate, sulphate and phosphate that can then be utilized again by plants and other organisms. Microbial biomass and activity are generally much higher in the rhizosphere than in the bulk soil due to the much larger availability of substrates such as root exudates (Brimecombe*et al*., 2001). Because of their role in organic matter decomposition, microorganisms are of utmost importance for the fertility of soil as well as for the recycling of nutrient elements. Poisoning of soil microorganisms can thus have dramatic consequences for the functioning of the entire ecosystem.

Soil contamination by heavy metals is one of the problems threatening soil fertility and element cycling most seriously in many areas. If present in sufficiently high concentrations,

heavy metals have been found to reduce the size of the microbial populations, to destruct their community structure and to reduce their activity (Kandeler*et al*., 2000; Chander*et al*., 2001; Wang *et al*., 2004). Heavy metal pollution may therefore result in severe ecosystem disturbance.

2.8 Evaluation of Metal Ion Concentration in Soil

The operation that occurred at a site is directly related to the specific type of metal contamination that will be found in a contaminated soil around that site. The range of contaminant concentrations as well as the physical and chemical forms of contaminants will also depend on these activities, effluent treatment and disposal patterns for contaminated wastes on the environment. Other factors that may influence the form, concentration and distribution of metal contaminants include soil and ground-water chemistry and local transport mechanisms (GWRTAC, 1997). Resultof soil metal determination usually comes with interferences as soils may contain metals in the solid, gaseous, or liquid phases. The most common method for determining the concentration of metals contaminants in soil is via total elemental analysis (USEPA Method 3050) but for the analysis of environmental samples XRF has the advantage of being a rapid and inexpensive method with a simple sample preparation making the results consistent and accurate (Kulshreshtha *et al*., 2005). Quantitative and qualitative analyses are performed without acid digestion processes and a great number of elements can be determined simultaneously in a short time and without any significant interference (Kuo*et al*., 1983). The level of metal contamination determined by earlier method is expressed as mg metal kg^{-1} soil. This analysis does not specify

requirements for the moisture content of the soil and may therefore include soil water. This measurement may also be reported on a dry soil basis.

The level of contamination may also be reported as leachable metals as determined by leach tests, such as the toxicity characteristic leaching procedure (TCLP) (USEPA Method 1311) or the synthetic precipitation leaching procedure, or SPLP test (USEPA Method 1312). These procedures measure the concentration of metals in leachate from soil contacted with an acetic acid solution (TCLP) [EGASPIN, 2002] or a dilute solution of sulphuric and nitric acid (SPLP). In this case, metal contamination is expressed in mg/L of the leachable metal.

Sequential procedures contact the solid with a series of extractant solutions that are designed to dissolve different fractions of the associated metal. These tests may provide insight into the different forms in which metal contamination present exist in the collected soil samples. The metal concentrations are most commonly expressed as total dissolved metals in mass concentrations (mgL^{-1} or gL^{-1}) or in molar concentrations($molL^{-1}$). In dilute solutions.mgL^{-1} is equivalent to one part per million (ppm) and g/L is equivalent to one part per billion (ppb) (Riley *et al*. 1992).

Nigeria Environmental Protection Agency has not provided suitable parameters for the classification of heavy metals but in the interim the Department of Petroleum Resources has provided recommended guidelines on remediation of contaminated land based on two parameters (EGASPIN, 2002) namely:

1. Target value: This is the accepted value for quality soil recommended for plant and animal sustainability.

2. Intervention value: This value indicates the quality for which the soil functionality for plant and animal life is being threatened and the soil requires urgent attention.

Table 2.1: Soil concentration ranges and regulatory guidelines of some heavy metals for European soil (Romanian guideline, 1997)

Metal	Soil concentration range ($mgkg^{-1}$)	Regulatory limits ($mgkg^{-1}$)
Pb	1.00–69 000	600
Cd	0.10–345	100
Cr	0.05–3 950	100
Hg	<0.01–1 800	270
Zn	150–5 000	1 500

Table 2.2: Target and intervention values for some soil heavy metals provided by the Department of Petroleum Resources (DPR-EGASPIN, 2002)

Metal	Target value ($mgkg^{-1}$)	Intervention value ($mgkg^{-1}$)
Ni	140.00	720.00
Cu	0.30	10.00
Zn	150.00	1000.00
Cd	100.00	380.00
Pb	35.00	210.00
As	200.00	625.00
Cr	20.00	240.00
Hg	85.00	530.00

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Sample Collection

Soil samples were collected from twelve (12) selected locations at two different depths well mapped around Kakuri industrial area in Kaduna state Nigeria. Table 3.1 shows the sample locations as well as the industrial activities common in each of the locations while Figure 3.1 shows the sample collection points on the map of Kakuri industrial area.

The surface of the soil was cleared with a hand trowel and samples at 0-10cm depth were collected with the aid of a stainless spoon. After every collection, the hand trowel and spoon were washed with soap and rinsed with distilled water to avoid sample contamination (Awofolu, 2005). Five soil samples from each sampling location were randomly collected. The collected sub-samples were then pooled together to form a composite from each location. Hand trowel was used to dig approximately 10cm to 20cm depth and measured with a measuring tape before the sample was collected using a stainless steel spoon to represent the 10 to 20cm depth sample.Control samples were collected from two locations to validate the heavy metal concentration in soil. Control sample A and B were collected mainly from residential area with low traffic volume and industrial activities. A total of twenty eight (28) soil samples were collected on the same day. The collected samples were stored in polyethylene bag and labeled properlyand taken to the laboratory where the pH was immediately measured and recorded using digital analyzer model 61A pH-meter at Defence Industries Corporation of Nigeria Kaduna.

Table 3.1: Sample locations and common industrial activities

S/No	Sample Location	Abbreviation	Zone/Location	Industrial Activity(ies)
1	United Textile road	UNT	Nassarawa	Chemical and allied
2	Down quarters	RDQ	Down quarters	Textile
3	Changchangi area	CCG	Kakuri	Breweries
4	K.T.L. road	KTL	Kakuri	Textile and metal smelting
5	Arewa Textiles road	ART	Kurmin Gwari	Textile and machine
6	Ahmed Thalib road	AHT	Kakuri	Aluminumsmelting and plastics
7	D.I.C. area	KGW	Kurmin Gwari	Explosives and metal smelting
8	NBC road	NBC	Kakuri	Drinks and beverages
9	Peugeot automobile	PGA	Kakuri	Machine and leather works
10	Nocaco road	NCC	Trikania	Cable and chemicals
11	IBBI Area	IBB	Express bypass	Food and beverages, traffic
12	Sunglass avenue	SGA	Kudenda	Smelting and glassware

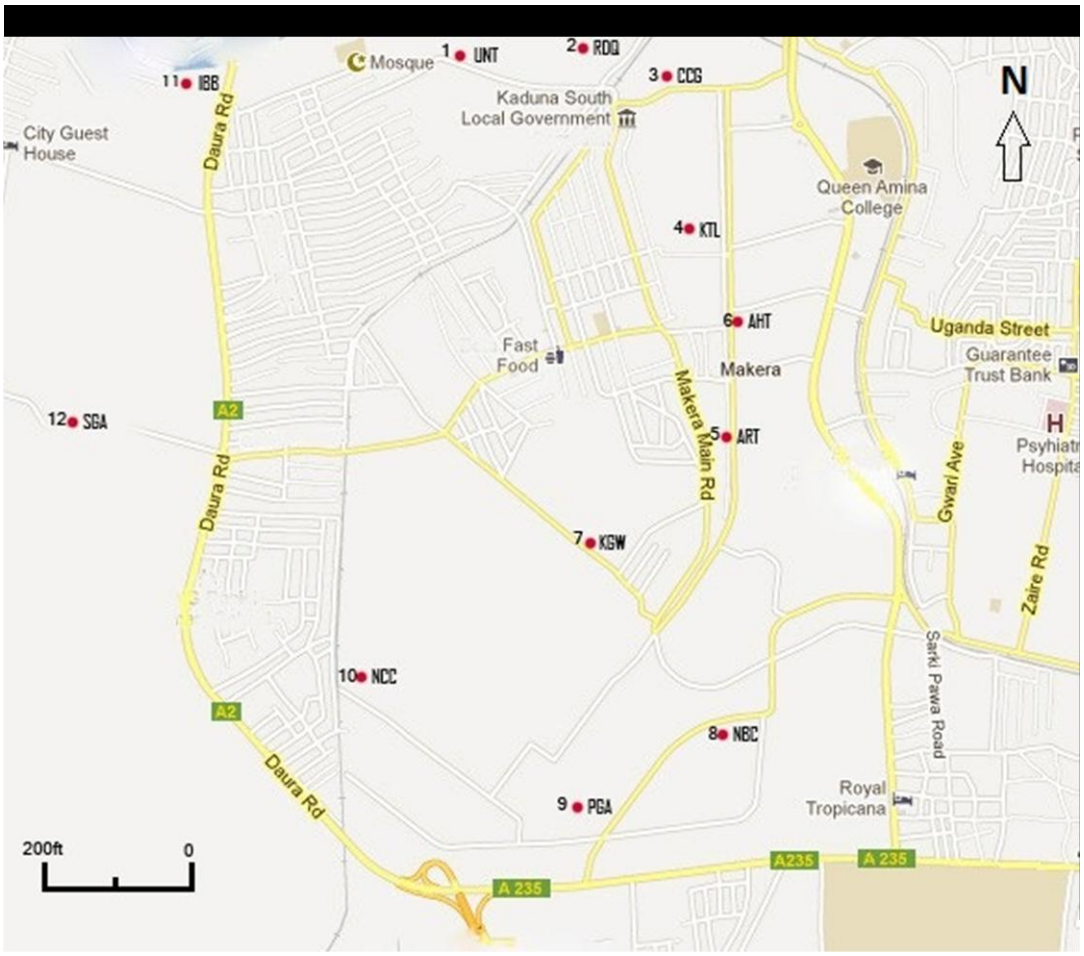


Figure 3.1: Map of Kakuri industrial layout indicating soil sample collection points

3.2Sample Treatment

The collected soil samples were dried at 150 °C for 2 hours in an oven. The samples were then divided into two sets. The first set for the physicochemical parameters test and the second set for the heavy metal concentration and bioavailability test. Rocks, pebbles, or twigs were removed before grounding with a mortar and pestle and passed through a 10-mesh (2 mm) sieve to achieve uniform particle size. Sample grinding continued until at least 90 percent of the original sample passed through the sieve. After passing through the 10-mesh sieve, the samples were further ground with a mortar and pestle to further reduce the particle size and screened through a 60-mesh (250 micron) sieve. Once again, at least 90 percent of the original sample passed through the sieve before further test were carried out (Antoaneta *et al*., 2009).

3.3 Measurement of Physicochemical Parameters

3.3.1 pH measurement

A 1% solution of the sample was made using distilled water and was subjected to vigorous shaking. The pH of the supernatant was obtained after 1 hour using an Electric pH Meter with a direct readout and the results were recorded accordingly (McLean., 1982).

3.3.2 Particle size distribution (Bouyoucos 1951)

The particle size distribution was determined using hygrometer as described by Bouyoucos (1951) at the Institute of Agriculture Research Laboratory, Ahmadu Bello University, Samaru, Zaria, Nigeria.

Principles and Procedure

A dispersed sample of soil was thoroughly mixed with 100 $cm^3$of water in a tall glass cylinder on a shaker followed by an addition of 2.0g of sodium metaphosphate (or sodium hexametaphosphate), which is a dispersant added to break up any aggregates in the soil sample. This ensures that smaller silt and clay particles will not bind to each other therefore allowing them to settle as if they were sand particles. After selected settling times, the density of the suspension was measured with a Bouyoucos hydrometer. Bouyoucos hydrometers are calibrated to measure grams of particles per liter of soil suspension. After a settling time of 40 seconds, the buoyant force on the hydrometer is due to a concentration of clay and silt. Because sand particles are the largest, any sand in the soil sample settled after 40 seconds leaving only clay and silt suspended in the water. The silt particles settled at the bottom of the cylinder after 2 hours.

The buoyancy on the hydrometer was determined by a concentration of particles equal to that of the clay particles throughout the suspension at time zero. The hydrometer was calibrated at 20 degrees (68 degrees Fahrenheit).Hydrometer readings were corrected for variations in temperature because of the viscosity of water and, to a lesser extent, the density of water changed as the temperature changes. The measurements were taken and data treated to obtain the results.

Soil moisture correction:

A weight of 10 grams of soil sample was oven dried for 24 hours at a temperature of 105^0C. The weight of the dried soil sample was taken after it was slightly cooled. The relationship below was used for correcting the weight of soil added to the system:

MCF = 1 – [(AD – OD) ÷ AD]

Where: MCF = Moisture Correction Factor

AD = air-dry weight

OD = oven-dry weight

3.3.3 Calculation of percent sand, silt and clay

$$\% \, clay = \frac{corrected \; 2 - hour \; hydrometr \; reading \; \text{x} \; 100}{Oven - dry \; weight \; of \; soil}$$

$$\% \text{ silt plus clay } = \frac{corrected \; 40 - \; second \; hydrometre \; reading \; \text{x} \; 100}{Oven - \; dry \; weight \; of \; soil}$$

$$\% \text{ sand } = 100 - \% \text{ silt plus clay}$$

Correcting Hydrometer Reading

For temperatures above 20 degrees C:

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

For temperatures below 20 degrees C:

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

To correct the hydrometer readings for temperature, a0.36 gram/liter was added for every1 degree C above 20 degrees C and subtracted 0.36 gram/liter for every 1 degree C below 20 degrees Celsius.

3.3.4 Calcium carbonate determination (Muller and Gatsner 1971)

Calcium carbonate was determined by a volumetric method according to Calcimeter Bernard Method**.**Percentage of calcium carbonate, $CaCO_3$ (%), is defined as the total carbonates which is contained in 100 g of dry soil. Carbonates; $CaCO_3$, $MgCO_3$etc. are expressed as $CaCO_3$.

Principle

The determination of percentage $CaCO_3$ is based on the volumetric analysis of the carbon dioxide CO_2, which is liberated during the application of hydrochloric acid solution HCl 4 N in soil's carbonates and is described with the following reaction:

$$CaCO_3 + 2\ HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow$$

During the application of the acid into the soil sample a characteristically foaming is observed, evidence of carbon dioxide's liberation and the existence of carbonate salts consequently water was addedand made up to 1000 cm^3 in a volumetric flask.

Procedure:

A 2.0 g weight of the sample was taken and transferred into the Bernard apparatusconical flask. The glass of the apparatus was then filled with 4M HCl solution until it was three-quarter of the height of the apparatus before it was placed into the conical flask. Care should be taken and make sure the tubule and the acid inside it stays upright.

The solution in the conical flask was capped and then the level of the filling solution zerorized. The left hand was used to bring the pear shaped glass container next to the graduated column for the fluids both in the pear shaped container and in the graduated tube stand in the same level and was shaken in order for the 4M HCl to come in contact with the prepared soil sample making the filling solution of graduated column to descend due to the pressure of liberated CO_2. At the same time, the pear shaped container was lowered for its fluid level to remain in the same level with the fluid of the column. This way the hydrostatic pressure equalized. When the liberation of the $CO_2$was finished, the agitation was stopped and the column's reading was noted and recorded.

Calibration:

The correction factor ***f*** of the instrument was determined as follow:

About 0.10 g $CaCO_3$ was dried for two hours at 104^{o}Ctransferred into the Bernard apparatus conical flask and the same procedure described above was followed.

$$f = \frac{W \times T}{122 \times V}$$

Where: *W*= weight (g) of $CaCO_3$

T = Temperature of measurement, in K

V= Volume (cm^3) of produced CO_2.

3.3.5 Organic matter measurement

Organic matter was determined by the Walkley–Black procedure (Nelson and Sommers, 1982). This procedure is based on the principle of oxidation of organic matter with dichromate in a strong sulphuric acid medium.

Procedure and Principle

The soil sample (1.0g) was weighed into a 250-mL wide mouth graduated Erlenmeyer flask. Two blanks were titrated without the soil sample before titration with the soil samples in order to standardize Ferrous Sulfate solution.

Potassium dichromatesolution (1N 10.0 mL) was pipette into each flask containing soil samples and mixed carefully by rotating the flask to wet all of the soil after which 20 mL of concentrated sulfuric acid was added to each flask and mix gently under a fume hood. The flasks were allowed to stand for 5 min under the fume hood and was made up to a final volume of 125-mL with distilled water.

The solution was allowed to cool in 30 minutes after which the volume was checked and recorded. Ten drops of diphenylamineindicator was added and immediately titrated with 0.5N ferrous ammonium sulphate solution. As the titration proceeded the solution changed from dull green to turbid blue and later changed abruptly to a brilliant green when the endpoint of the titration was reached. The volumetric reading at this point was recorded.

Calculations

Organic matter (%) of sample = (1 - S / B) x 10 x 0.68

Where:

S = volume of ferrous ammonium sulphate solution required to titrate the sample, in mL.

B = average volume of ferrous ammonium sulphate solution required to titrate the Two blanks, in mL.

10 =conversion factor for units.

0.68 = a factor derived from the conversion of % organic carbon to % organic matter.

3.4 Preparation of Reagents

3.4.1 Preparation of methyl orange indicator

Methyl orange sodium salt (50mg) was dissolved in 100cm^3 H_2O which contain 15.2 $cm^3$of 0.01 $moldm^{-3}$HCl solutions. The solution was heated mildly and allowed to cool before it was filtered.

3.4.2 Preparation of Calcimeter Bernard Filling solution

A 200 g of $CaCl_2$**.**$6H_2O$ was dissolved in 100 cm^3 distilled water followed by the addition of 3 drops methyl orange indicator and some drops of non-concentrated solution of hydrochloric acid was added until the solution became red-orange.

3.4.3 Preparation of solution of 4M HCl

A known volume (340 cm^3) of concentrated $HCl_{(aq)}$(37% w/v) with specific gravity of 1.19$g/cm^3$was diluted with distilled.

3.4.4. Preparation of 0.16moldm^{-3} Potassium dichromate ($K_2Cr_2O_7$)

Potassium dichromate (0.16*moldm*$^{-3}$) was prepared by dissolving *98.08g of* oven-dry/desiccated Potassium dichromate in approximately 1500 cm^3 of distilled water and diluted to 2 L. The prepared solution was transferred to a clean glass bottle for use with a repipette which dispenses solution with a very high accuracy.

3.4.5 Preparation of 1.0 moldm^{-3} Ferrous Sulphate ($FeSO_4 \cdot 7H_2O$)

Ferrous Sulfate (556.04 g) was dissolved in approximately 1500 cm^3 of distilled water and 30 cm^3 of concentrated Sulphuric acid was carefully mixed, cooled and diluted to 2 L. After preparation, this solution was transferred to a clean 8-L plastic carboy. The tubing, stopcock and attachments to the burette were rinsed three times with new ferrous sulphate solution before titrating blanks or samples.

3.4.6 Preparation of Ortho-Phenanthroline Ferrous Complex Indicator

A weight of 3.71 g of o-phenanthroline and 1.74 g of $FeSO_4 \cdot 7H_2O$ was slowly dissolved in 250 mL of water.

3.5Heavy Metal Measurement

3.5.1 Total heavy metal content

The total heavy metal content was determined using XRF spectrophotometer according to (Constantinescu, *et al* 2009) at Defence Industries Corporation of Nigeria, Research and Development Laboratory Kaduna. An aliquot (portion of sample) of finely grounded soil was placed in a sample analysis cup. The sample cup was filled to three-quarters. The sample cup was then covered with a Mylar film before it was placed in the XRF machine. The entire data set of the analysis was made available on the monitor, displayed in percentage before it was converted to mg/kg.

3.5.2 Theory of X-ray Spectrophotometer

XRF is an analytical method for determining the chemical composition of all kinds of materials; solid, liquid, powder, filtered or in other forms. In XRF, x-ray is produced by a source to irradiate the sample; the elements present in the sample will emit fluorescent x-ray radiation with discrete energies that are characteristic for these elements. Coupled with a detector and multi-channel analyzers, it is possible to measure the energies of the radiations emitted by the sample to determine which element is present and by measuring the intensities of the emitted energies it is possible to determine how much of each element is present in the sample. The method is fast, accurate and non-destructive and usually requires only a minimum of sample preparation. The applications of XRF are very broad and include the metal analysis. The range of elements that can be analyzed is wide (Be-U). The concentration range goes from sub-ppm levels to 100%. Elements with high atomic numbers have better detection limits than lighter elements. The precision and reproducibility of XRF analysis is very high, very accurate results are possible when good standard specimens are available, but also in application where no specific standard can be found.

A compact energy dispersive X-ray Spectrometer designed for elemental analysis of a wide range of samples known as the Mini Pal was used for this analysis. The system is controlled by a PC running the dedicated Mini Pal analytical software.

The Mini Pal 4 version in use is PW 4030 X-ray Spectrometer, which is an energy dispersive microprocessor controlled analytical instrument designed for the detection and measurement of elements in a sample (solids, powders and liquids), from sodium to uranium. The sample for analysis is weighed and ground in an agate morta and a binder (PVC) dissolve in Toluene) is added to the sample, carefully mixed and pressed in a hydraulic press into a pellet.

The pallet is loaded in the sample chamber of the spectrometer and voltage (30kV maximum and a current (1mA maximum) is applied to produce the X-rays to excite the sample for a preset time (10 minutes in this case). The spectrum from the sample is now analyzed to determine the concentration of the element in the sample.

3.5.3 Bioavailable metal content

The available metal contents were determined by extraction of the soils with 0.005M diethylenetriaminepenta-acetic acid DTPA (pH=7.3). Exactly 20 cm^3 of DTPA solution were added to 10g of soil sample placed in polypropylene bottles. The bottles were shaken on a rotating shaker for 2 hours and then centrifuged for 10 min at 3000 rpm (Lindsay *and* Norvell, 1978). The concentrations of total and available metals in the supernatant liquid were measured using XRF spectrophotometer (Constantinescu*et al.*, 2009).

CHAPTER FOUR

4.0 RESULTS

Table 4.1: Physicochemical Parameters of Samples and Control Soil in Kakuri Industrial Area

Site	Sand	Silt	Clay	pH	Calcium Carbonate(%)	Organic Matter(%)
UNT	63	24	13	7.50	56.12	4.80
RDQ	57	30	13	7.90	76.33	3.29
CCG	61	26	13	7.80	46.50	4.30
KTL	65	28	07	7.80	50.12	4.80
ART	60	25	15	7.80	56.20	4.45
AHT	61	24	15	7.90	55.12	5.20
KGW	59	30	11	7.70	50.20	4.10
NBC	69	20	11	7.30	65.10	3.10
PGA	58	32	10	7.45	67.12	3.30
NCC	63	24	13	7.40	58.20	4.00
IBB	72	20	08	8.00	57.10	4.02
SGA	68	21	11	7.90	60.12	3.10
Cont. A	71	21	08	7.60	60.20	3.20
Cont. B	72	21	07	7.55	49.82	3.80

Table 4.2: Statistical summary showing Mean±SD, median and Range of concentrations of heavy metals in soil samples.

No of samples	Metals	Median	Range (mg/kg)	Mean± S.D

12	Zn	69.00	20-420	100.5 ± 19.82
12	Cu	61.00	26-110	60.02 ±3 .60
12	Ni	17.00	9-72	26.25 ± 6.44
12	Cr	38.00	22-157	42.42 ± 5.21
12	Pb	33.50	27-34	32.00 ± 1.68
12	Hg	20.00	10-60	28.80 ± 9.35
12	V	71.00	47-120	73.08 ± 3.52

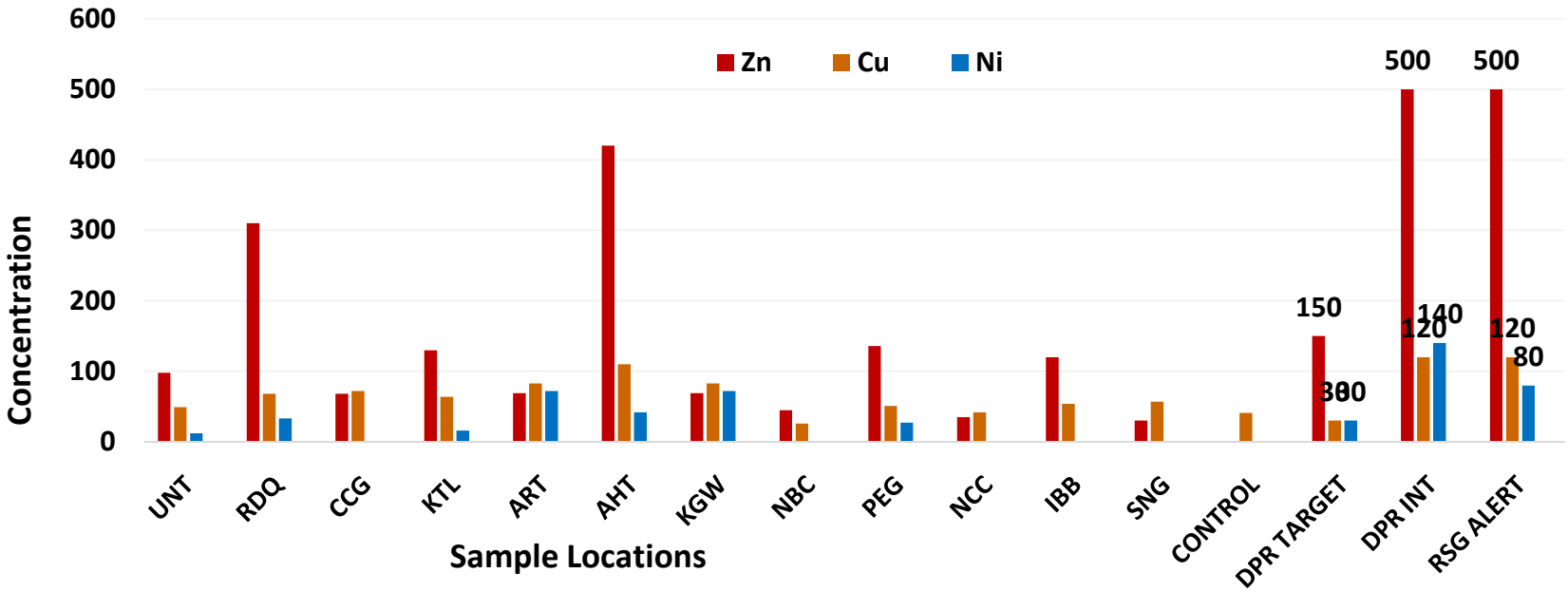


Figure 4.1: Concentrations of Zn, Cu and Ni at 10 to 20 cm depth of soil samples in comparison with average concentrations of control, DPR target and Intervention levels and RSG alert level.

DPR TARGET: Department of Petroleum Resources Target Value

DPR INT: Department of Petroleum Resources Intervention Value

RSG ALERT: Romanian Soil Guideline Alert Level

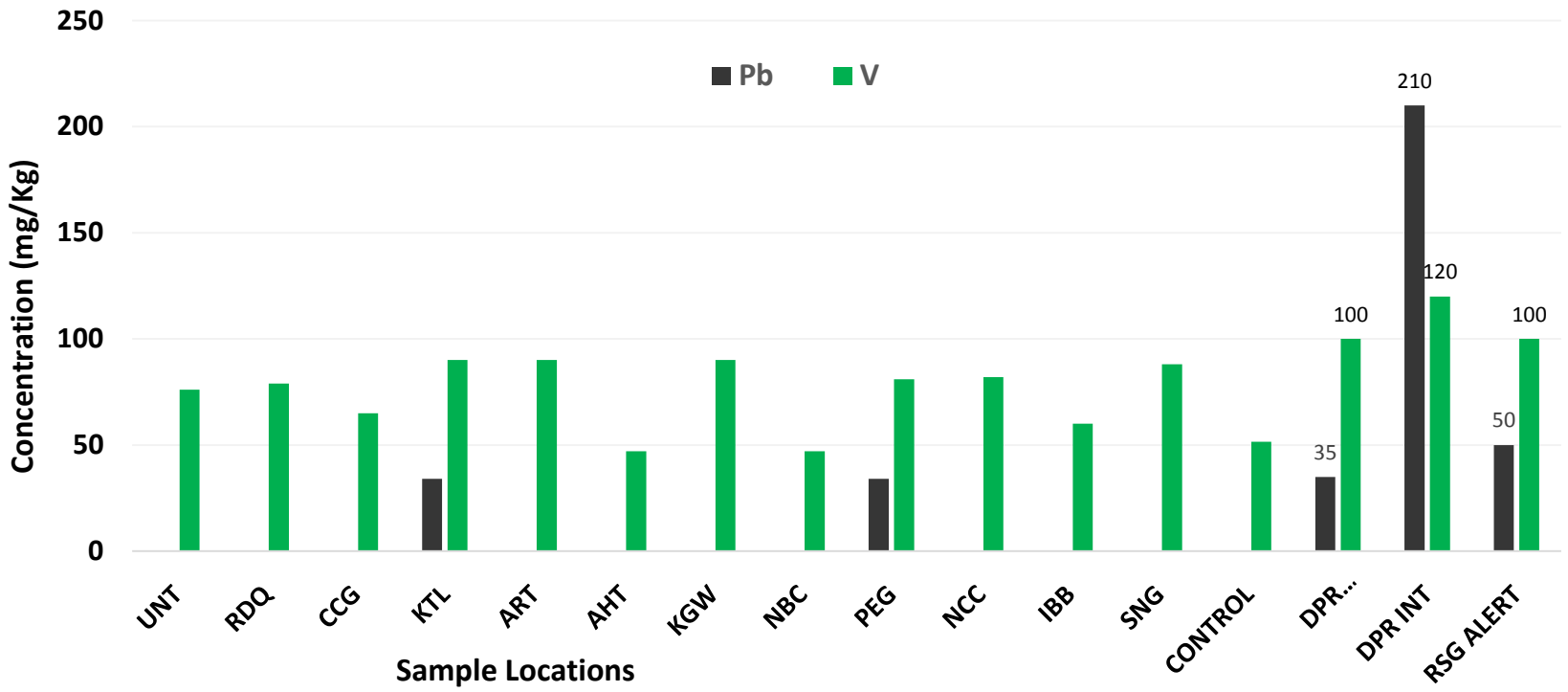


Figure 4.2: Concentrations of Pb and V at 10 to 20 cm depth of soil samples in comparison with average concentrations of control sample, DPR target and Intervention levels and RSG alert level.

DPR TARGET: Department of Petroleum Resources Target Value

DPR INT: Department of Petroleum Resources Intervention Value

RSG ALERT: Romanian Soil Guideline Alert Level

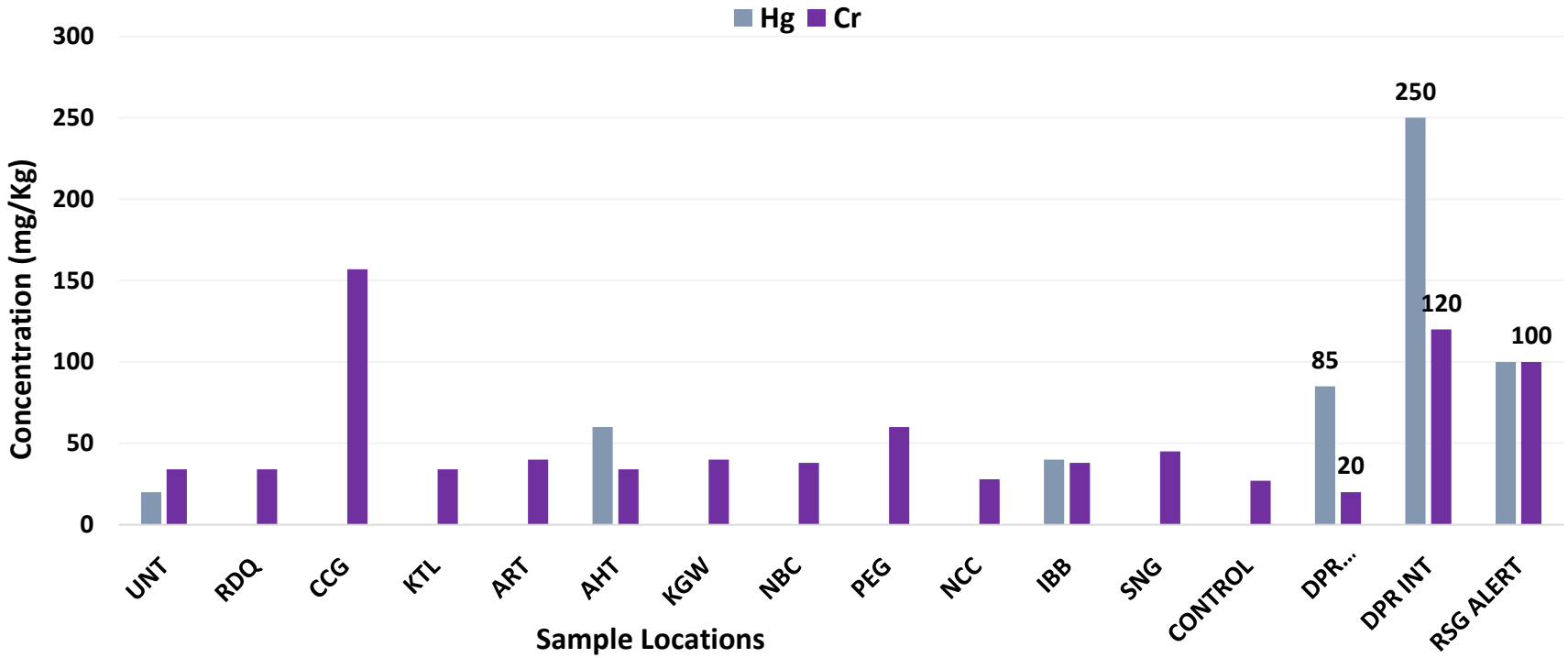


Figure 4.3: Concentrations of Hg and Cr at 10 to 20 cm depth of the soil samples in comparison with average concentrations of control samples, DPR target and Intervention levels and RSG alert level.

DPR TARGET: Department of Petroleum Resources Target Value

DPR INT: Department of Petroleum Resources Intervention Value

RSG ALERT: Romanian Soil Guideline Alert Level

Table 4.3: Correlation Matrix between heavy metals, pH and organic matter (O.M) in Soil Samples

	Zn	Cu	Ni	Cr	Pb	Hg	V	pH	O.M
Zn	1								
Cu	0.6142*	1							
Ni	0.2766	0.6779*	1						
Cr	-0.1893	0.1016	-0.2299	1					
Pb	0.0216	-0.1214	-0.0230	-0.0200	1				
Hg	0.6377*	0.4418	0.0034	-0.2047	-0.2335	1			
V	-0.3839	0.0231	0.3431	-0.1440	0.3175	-0.6255**	1		
pH	0.4164	0.6445*	0.1951	0.1036	-0.1593	0.3820	0.0664	1	
O.M	0.3274	0.5920*	0.2793	0.0069	0.0076	0.5355*	-0.0728	0.2478	1

* Strong positive correlation

** Strong negative correlation

O.M - Organic matter

Table 4.4: Mean Concentration, Baseline Data (Mg/kg), Average Shale (Mg/kg), Geo-Accumulation Index (I_{geo}) Values and Enrichment Factor of Heavy Metals in Soils in Kakuri Industrial Area

	Zn	Cu	Ni	Cr	Pb	V
Mean (mg/kg)	127.5	63.25	39.14	48.5	34	74.58
Baseline data (mg/kg)	29.2 - 115	7.1 – 33.5	11.6 – 36.6	14.8 – 35.2	12.1 – 27.3	82 - 131
Average Shale (mg/kg)	95	45	68	90	20	131
I_{geo} Values	< 0	< 0	< 0	< 0	< 0	< 0
I_{geo} Classification	Uncontaminated	Uncontaminated	Uncontaminated	Uncontaminated	Uncontaminated	Uncontaminated
EF	1.34	1.40	0.57	0.53	1.7	0.57
Degree of contamination	Slightly contaminated	Slightly contaminated	Uncontaminated	Uncontaminated	Slightly contaminated	Uncontaminated

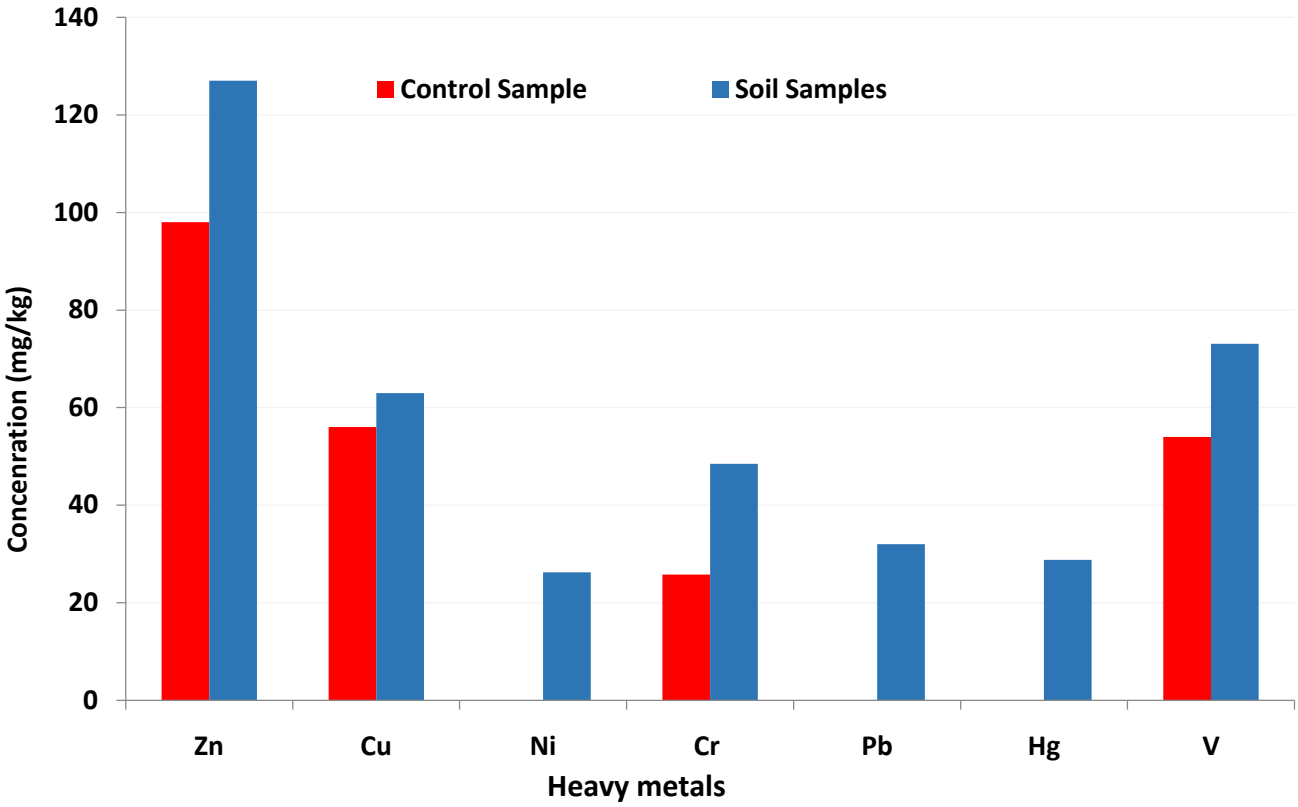


Figure 4.4: Comparison of heavy metal average concentration (mg/kg) in soil samples and control soil

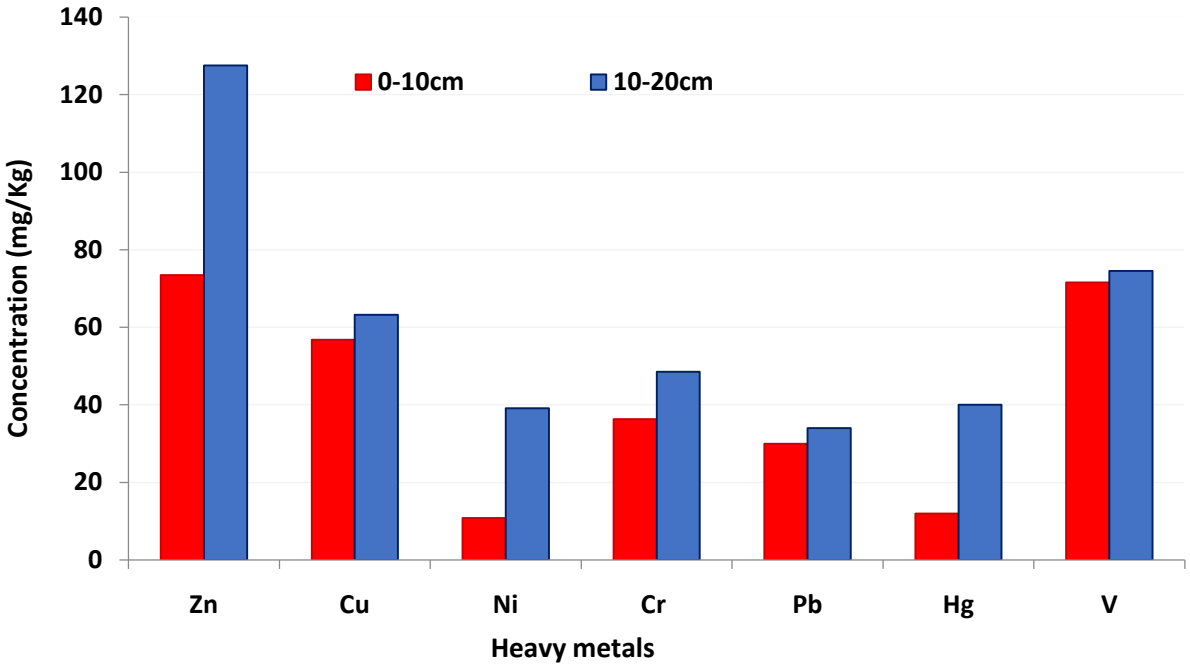


Figure 4.5: Comparison of the average heavy metals concentrations (mg/kg) at 0 to 10cm and 10 to 20cm soil depths

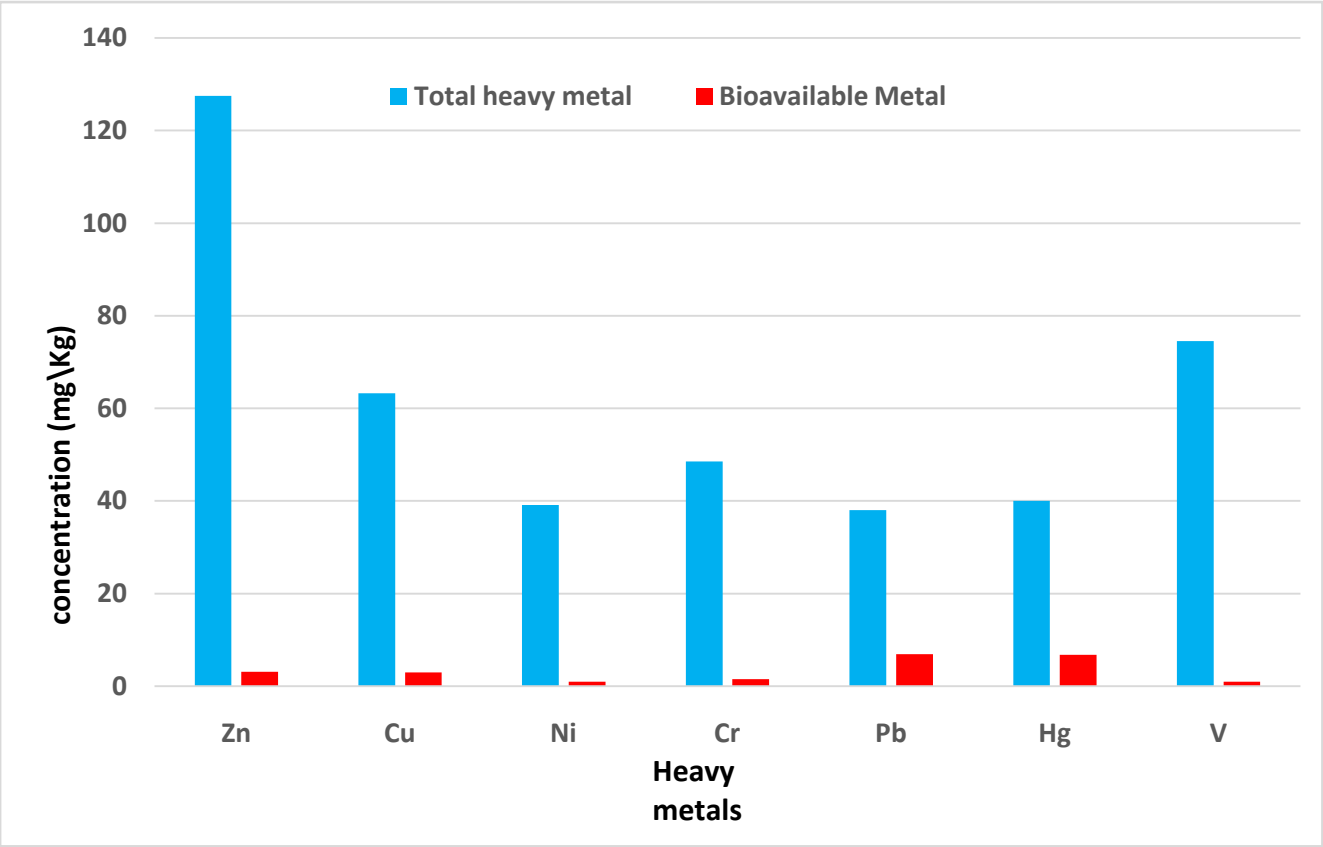


Figure 4.6: **Total metals in soil in comparison with bioavailable metals available in the soil samples in Kakuri industrial area**

CHAPTER FIVE

5.0 DISCUSSIONS

5.1 Physicochemical Properties

The results of the physicochemical analysis of soils from Kakuri industrial area are shown in Tables 4.1.The percentages of particle size distribution in the sample soil werein the range 7 to 15, 21 to 30and 57 to 72% for clay, silt and sand respectively. Generally the soils were found to be sandy loam in majority of the areas and sandy in locations like IBB and SGA.

The pH result indicates the soil samples were slightly alkaline with values in the range 7.30 to 8.00 which is consistent with the value of 7.00 to 8.00 reported by Achi *et al*. (2011) in their studies of some mechanic workshops in Kaduna metropolis. Soil pHserves as a useful index of availability of nutrients, thepotency of toxic substances present in the soil as well as thephysical properties of the soil. Several studies haveshown that availability of heavy metals is pH dependent and their mobility in soil decreases with increased soil pH and vice versa (Iwegbue*et al*., 2006; Gonzalez-Fernandez *et al*., 2008). The high soil pH values suggest that heavy metals availability for plant uptake is low in the sample soils.

The percent organic matter content was found to be in the range of 3.10 to 5.20 across the sample locations which is also consistent with the range 2.77 to 6.32 reported by Abdullah *et al*., (2012) but was higher than the average value of 3.50 percent in the control samples. Hence, the relativelyhigh total organic carbon content in samples soil as compared to control samples couldbe due to the high organic content of usedlubricants that were discharged from heavy duty machines,

mechanic workshops in the areas (Akoto*et al*., 2008) as well as indiscriminate disposal of organic waste into the environment as the industrial area is crowed by residential houses with no proper waste disposal systems. The presence of organic matter has asignificant effect on the mobility and bioavailability of heavy metals (De la Rosa *et al*. 2003; Weng *et al*. 2004). Furthermore, it has also been reported that about 50% of the total heavy metals in organic rich soils are retained with organic substances. (Smagunova *et al*. 2004) but these values across the locations does not give an indication of a high tendency of heavy metals availability and retention in the soils around Kakuri industrial area.

The average percentage calcium carbonate value of 58.01% was slightly lower than the average value of 60.01% in the control samples. This is because humic substances contain a highly complex mixture offunctional groups. Binding of metals to organic matterinvolves a continuum of reactive sites, ranging from weakforces of attraction to formation of strong chemical bonds. Soilorganic matter can be the main source of soil cation exchangecapacity, contributing >200meq/100 g of organic matter insurface mineral soils. Organic matter content, however,decreases with depth, so that the mineral constituents of soilwill become a more important surface for sorption as theorganic matter content of the soil diminishes. The high values of calcium carbonate indicates that heavy metals mobility in the sample soil will be low.

5.2 Total Heavy Metal Concentration

X-ray fluorescence (XRF) analysis results obtained for the collected soil samples shows presence of Zinc (Zn), Copper (Cu), Nickel (Ni), Chromium (Cr),

Lead (Pb), Mercury (Hg) and Vanadium (V) for all the samples at both 0 to 10 cm and 10 to 20cm soil depths. The average concentrations of heavy metals Cr, Cu, Ni, Pb, V, Hgand Zn for five measurements of each of the soil samples at 0 to 10cm and 10 to 20cm depths are given in Appendix A and Appendix B. Statistical summary of the heavy metals concentrations in sample soils is displayed in Table 4.2.

5.2.1 Zinc

Zinc was detected in all the sample locations and depths across Kakuri Industrial layout with average concentration of 100.5±19.82 mg/kg(Table 4.2) which is similar to the average value 108.6mg/kgreported by Achi *et al*. (2008).These values are greater than the permissible value 100 mg/kgof European standard (Romanian Guideline, 1997) but less than the target and intervention values prescribed by Nigeria Department of Petroleum Resources (EGASPIN, 2002) as displayed in Figure 4.1.

The presence of Zn in all the sample locations may be due to natural occurrence of zinc in soil with about 70 mg/kg in crustal rocks(Mason and Moore, 1982) and also as a result of indiscriminate disposal and combustion of zinc containing materials by resident across the sample locations. Zn concentrations in most locations (UNT, AHT, RDQ, KTL, IBB and PAN) at both depths were found to be above 100 mg/kg, with the exception of UNT where it was below 100 mg/kg at 0 to 10 cm depth. AHT had the highest Zn concentration (420 mg/kg) as a result of several smelting activities in these areas as well as pollutions from tyres and lubricant oils from high vehicular traffic along these locations.RDQ also shows high concentration of 320 mg/kgsuggesting that its soil serves as drain for the industries

around and also heavy metal pollution from old railway yard housing several welding, foundry and mechanic workshops.

5.2.2 Copper

Copper (Cu) was present in all the sample locations. Its concentrations were greater than the permissible value (20 mg/kg) of European standards (Romanian Guideline.1997) for all studied sites and depths including the control sites.Cu has an average value of 60.02 ± 3.60 mg/kg (Table 4.2) across the twelve (12) sample locations. Copper distribution across the sample location was equally high with a wide range of 26 to 110mg/kgbutlower than the value of 98.00 ± 2.00mg/kg reported by Achi *et al*(2011)The highest concentration values were observed at AHT and KGW area (110 and 131mg/kgrespectively)but did not exceed the DPR alert level of 120 mg/kgas displayed in Figure 4.1.

High concentration of Cu in AHT was due to higher stability constant of Cucomplexes with organic matter where the organic matter content was highest (Venkateswaran *et al*., 2007) indicating that it is mainly oflithogenic origin (Xuelu *et al*., 2008) and also high volume of heavy duty trucks fluid leakages, diesel combustion, brake pads and other copper materials disposed in the environment by mechanic workshops.

5.2.3 Nickel

Nickel (Ni) was detected in UNT, RDQ, KTL, AHT, ART, KGW and PGA locations with an average concentration of 26.25 ± 6.44 mg/kg (Table 4.2) across the twelve (12) sample locations. All the concentrations were greater than the permissible values 5 mg/kg for Ni according to the Romanian soil guidelines

(Romanian Guideline, 1997) but by far below 140.00 mg/kgpermissible levels provided by Nigeria Department of Petroleum Resources (EGASPIN 2002). The highest concentration of Ni was observed around KGW area and ART (Figure 4.1) due to activities around these locations which include Nickel plating in Kaduna machine and Defence Industries Corporation of Nigeria (DICON). Machines and power plants as well as trash incinerators also contributed to the presence of Ni in other locations across the industrial area.

5.2.4 Lead

Lead was detected only at KTL and PAN vicinity with an average concentration of 32.00 ± 1.68 mg/kgin the two areas which is higher than the mean values 20.02±12.43mg/kg obtained by Umoru (2013) from their study of irrigated farmlands in Kaduna. The concentrations in both locations were greater than the permissible value 20 mg/kgat 0 - 10 cm and 10 – 20 cm depths (Figure 4.2) but below the alert level of 50 mg/kgof European standards. (Romanian Guideline, 1997). The concentrations were also slightly below the target value of 35 mg/kg and well below the value 210 mg/kg intervention values by the Department of Petroleum Resources (EGASPIN, 2002). The availability of lea in this area could be attributed to the presence of UNTL, breweries and the mechanic workshops around the vicinity as well as several battery chargers discharges waste into the environment.

5.2.5 Vanadium

Vanadium was present in all the sample locations with an average concentration of 73.08 ± 3.52 mg/kg which is greater than the permissible value 50 mg/kg (Romanian Guideline.1997) for all studied sites and depths with the exception of AHT and NBC drive at 10 to 20cm depth with 47 mg/kg each (Figure 4.2). None of the locations exceeded the intervention level of 120 mg/kg as prescribed by Department of Petroleum Resources (EGASPIN 2002). Vanadium was also widely distributed across the twelve locations with a range of 47 to 120mg/kg as it is known to have a natural occurrence average concentration of 135 mg/kg(Mason and Moore, 1982; Adriano, 1986) coupled with the several anthropogenic activities such as textiles and high vehicular traffic. Vanadium also has tendency to bind strongly with soil particles and sediments.

5.2.6 Mercury

Mercury was detected in only three sample locations, UNT, AHT and IBB with concentrations is in the range 10 to 60 mg/kg. The highest concentration was detected in AHT with an average of 60 mg/kg(Figure 4.2) which may be due to the release of mercury from manometer at pressure measuring site and hydraulic lifts attached to trucks along AHT road. The average values of Mercury in UNT and IBB were 18mg/kgand 25 mg/kgrespectively (Figure 4.2).The concentrations of mercury in the three locations were found to be greater than the permissible level of 4 mg/kgspecified in European guideline (Romanian Guideline.1997) but below the target value of 85 mg/kgstipulated by Department of Petroleum Resources (EGASPIN 2002).

5.2.7 Chromium

Chromium concentrations across the sample locations averaged 42.42 ± 5.2 mg/kg greater which is less than the value of 93 mg/kg reported by Achi *et al*., (2010) but greater than the permissible value 30 mg/kg (Romanian Guideline, 1997) for all studied sites and depths with the exception of UNT and AHT at 5cm depth with a concentration of 22 mg/kg and 26 mg/kg respectively.. The highest concentration of 74 mg/kg was observed at CCG and KGW area due to the presence of DICON that engages in industrial activities such as heat and surface treatment that involves electroplating such as etching process and chrome plating (Dan-Azumi and Bichi, 2010). The concentrations at all locations and level exceeded the target level of 20 mg/kgbut lower than the intervention level of 100 mg/kg of the Department of Petroleum Resources soil classification (EGASPIN, 2002) as displayed on Figure 4.2.

5.3 Correlation Analysis of Heavy Metals, pH and Organic Matter

Correlation coefficient measures the strength of a linear relationship between any two variables on a scale of -1 (perfect inverse relation) through 0 (no relation) to +1 (perfect sympathetic relation). In this study, the raw data was used in calculating the correlation coefficient using the Microsoft Excel computer software package (Microsoft corp., 2013 version). The correlation analysis between heavy metals in sample soils, pH and organic matter (O.M) are shown in Table 4.3.

Zn and Cu correlated positively with pH with values +0.41643 and +0.64447 respectively. This is an indication that pH accounts for the availability of Zn and Cu in the soil samples which is evident from their availability in all the sample locations due to similar soil pH in the range of 7.30 to 8.00. A positive correlation was also observed between Zn and Cu (+0.6142) and also Zn and Hg (+0.6377)

indicating that Zn have the same source(s) in the sample soils with Hg and Cu as the results shows that metal and aluminum smelting, mechanic workshops, battery chargers, heavy duty machines and vehicle traffic in areas such as AHT, KGW, RDQ, KTL and ART accounts for have high concentrations of Zn, Cu and Hg. Humified organic matter is also involved in the formation of soluble complexes especially with Zn and Cu which during organic mineralization become more available for the plants. This explains the higher availability of Cu in the studied soils as predicted by a strong correlation (+0.5920) with organic matter in relation to the other metals other than Zn (Andreu and Garcia 1999).

Mercury (Hg) was only detected in locations where the O.M contents were highest and this is justified by the strong positive correlation value of +0.5355. Furthermore, a strong negative correlation (-0.6255) between Hg and V was observed which indicate different anthropogenic sources of metals in soil or biogeochemical behaviours (Okunola*et al*., 2008).

5.4 Heavy Metal Contamination in Soil

Assessments of heavy metals contamination in the sample soil were carried out using geo-accumulation and contamination factor pollution indexes. The average crustal abundance and levels of metals obtained from this study were used as "background values'' and "present background" values in order to give a comparative idea about the quality and degree of heavy metal contamination of soils in Kakuri industrial area of Kaduna.

5.4.1 Contamination factor (C_f)

This is an assessment according to contamination factor (C_f) or enrichment ratio (ER) and the degree of contamination (C_d). The contamination factors are calculated according to the equation 2. The degree of contamination (C_d) was defined as the sum of all contamination factors. Calculated contamination factor (C_f) and degree of contamination (Cd) for this study is shown in Appendix F.

$$C_f = \frac{[M]}{[M_b]} \quad \text{..... (2)}$$

Where [M] = Concentration of heavy metal in the studied area

$[M_B]$ = Background concentration levels of metals in soil

Background value of the metal is equal to world surfacerock average given by Martin and Meybeck (1979).The Enrichment Factor (EF) values between 0.5 and 1.5 indicates that the metals are entirely from the coastal materials whereas EF values greater than 1.5 indicates that the sources are most likely to be anthropogenic activities (Zhang and Liu, 2002). The different levels of degree of contamination based on the EF values are shown in Appendix G. Standard regulatory limits/ background levels of metals in soil values are given in appendix H.

From the results obtained as displayed in Table 4.4, the studied area can be said to be moderately contaminated with Zn, Cu and Pb with mean values of 1.31, 1.40 and 1.70 respectively which falls under the classification $1 \leq C_f < 3$. The highest contamination of Zn (considerable contamination) was observed at KGW and RDQ for Zn with values of 4.46 and 3.36 respectively which is a clear indication of heavy metal pollution from metal/aluminum smelting, welding activities and indiscriminate dumping and burning of materials by DICON, Kaduna

machine works, Railways yard, welding and foundry activities by road side workshops in these areas. Pb was undetected in most of the sample locations with the exception of KTL and PAN with the same value of 1.7 which can be classified as moderate contamination with its direct source being that that area is a hub for battery chargers workshops.

On the basis of mean value of C_f, the soils are enriched for metals in the following order Cu > Pb > Zn > Ni > Cr. Standard regulatory limits / background levels of metals in soil values are shown in Appendix E.

5.4.2 Geo-accumulation Index (I_{geo})

This index allows the estimation of the enrichment of heavy metals concentration in soil above baseline concentration using an equation proposed by Muller (1981).

$$I_{geo} = log_2\left(\frac{[M]}{1.5[M_b]}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where [M] = Measured concentration of heavy metals in sample soil

$[M_b]$ = Geochemical background value of heavy metals in soil

The geochemical background value concentrations of heavy metals in soil are the average concentration of the metals in the shale (Turekian and Wedepohi, 1961) and displayed in Appendix D. The I_{geo}index consists of seven grades (0-6) ranging fromuncontaminated to highly severely contaminated and shown in Appendix E.

The results obtained from the studied areas indicates that the soil around Kakuri industrial area is generally uncontaminated with all the $I_{geo} \leq 1$ with the exception of KGW with I_{geo}value of 1.561 for Zn which falls under the

classification $1 < I_{geo} \leq 2$ (heavily contaminated). This confirms the results of C_f index calculation and the pollution could be attributed to activities of large number of welding and machine works by Kaduna machine works, DICON and a market over a long period of time.

5.5 Heavy Metals Concentrations in Collected Soil Samples and Control Samples

X-ray fluorescence (XRF) analysis results of the sample and control soils shows the presence ofZn, Cu, Ni, Cr, Pb, Hg and V in allsamples analyzed but only Zn, Cu, Cr and V were detected in control samples with average concentrations of 98.5 mg/kg, 56 mg/kg, 25.8 mg/kg and 54mg/kgrespectively as Ni, Pb and Hg were below detection limits in the control samples.

The concentrations of heavy metals in the control samples were below that of the sample soils with the exception of Cu which is the same for both control and sample soils with a concentration of 60.25 mg/kg (Figure 4.4). This exceeds the permissible level of 20mg/kg but still lie below the intervention level of 120 mg/kg stated in Department of Petroleum Resources (DPR) and Romanian Soil Guidelines (RSG). The concentrations of heavy metals in the sample soilsas compared to the control samples suggests that industrial activities of these factories and small scale industries around the sample locations contributed greatly to the level of heavy metals in the soil (Ayodele and Abubakar, 2001; Ibeto andOkoye, 2010).

The availability of Zn, Cu, Cr and V in control samples shows that apart from direct discharge of heavy metals into the soil in the sample locations from anthropogenic sources, other activities in these areas such as burning of waste,

metal disposal, burning of wood and application of fertilizer and pesticides/insecticides in small farms and gardens in these vicinities where the control samples were collected from account for the presence of heavy metals in these environments because heavy metals tends to persist in soil for a very long time due to their non-biodegradable nature.

5.6 Heavy Metals at 0 to 10cm and 10 to 20cm Depths

Soil physicochemical properties, soil chemistry of metals in soil and depth play a big role in the retention capacity and mobility of metals in soil. A comparison of the concentrations of heavy at depths 0 to 10 cm (depth 1) and 10 to 20 cm (depth 2) showsclearly that heavy metals concentration at depth 2 were higher than depth 1 across all the sample locations (Figure 4.5). Heavy metals have the tendencies of accumulating at increased depth as reported by Hu *et al.*, (2008). This may also be as a result of soil metals leaching through the top soil and settling at greater depths due to the soil porosity as the physicochemical parameters shows the soil samples are mostly sandy loam.

The difference in concentration of V at both depths did not quite give an obvious difference as V has the ability to bind to particles and sediments therefore slowing down the rate at which the metals move in the soil even with the high porosity effect observed in other heavy metals.

There was however a large variation in the concentrations of Cu, Cr, V, Zn and Ni the investigated soils in at both depths around UNT, AHT, ART and KGW which may be as a result of different industrial activities such as fertilizer blending company along UNT, Agro miller industry, machine works, aluminum Industries

and other small scale industries like dyeing, metal smelting, printing, paints as well as fuel stations discharging effluents into the waterways along KGW, AHT and ART deposited around these areasthrough various means. High human and vehicular traffic in these areas can also account for these pollutions.

5.7 Bioavailability of Heavy Metals in Soil

The determination of total heavy metal concentrations in soils might be useful to predict the potential environmental risk posed by these metals, but do not always provide a good indication of metals' labile fraction available for plant uptake (Gasparatos *et al*., 2001). The severity of pollution depends not only on total heavy metal content of the soil, but also on the proportion of their mobile and bioavailable proceedings of these metals in the soil. Figure 4.6 shows the concentrations (mg/kg) of bioavailable metals in soil samples at depth 10 to 20 cm. Bioavailability test on samples at depth 1 (0 to 10cm) were below detection limit indicating that bioavailable metals are hardly available for plant uptake in top soils.

Heavy metals are potentially available for plant uptake if the bioavailability percentage is above 10% (Ullrich *et al*., 1999). The bioavailable content as a percentage of the total metal content from this study was found to be generally very low. Despite the high total concentration of the heavy metals in some of the studied soil, the proportion available for plant uptake is relatively small and does not raise any environmental safety concern.

The studied soil shows they are strongly calcareous in nature and this leads to a high presence of free calcium carbonate and this affects the retention capacity of the soil

(Pichering, 1982; Gasparatos *et al*., 2001). This property of the soil explains the low bioavailable heavy metals in the sample soils.

Basic soil pH due to the presence of free calcium carbonate affects the bioavailability of the heavy metals. The adsorptive capacity of soils is usually increased by high soil pH. (Papadopoulos and Rowell, 1988). Zn has the highest bioavailable metal value as a percentage of the total heavy metal of 10.0% at PA where the soil physicochemical properties favors heavy metal retention in soil followed by 8.7% and 6.2% for Zn and Cu respectively around NCC drive with relatively lower soil pH and high organic matter which improves heavy metals mobility in soil. There bioavailability could also be as a result of their high concentrations in soil around these areas due to closeness to several aluminum smelting and machine industries. Generally heavy metals across the industrial area are still within the tolerable level and are not available for plant uptake.

CHAPTER SIX

6.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary and Conclusions

An assessment of the soils metals (Zn, Cu, Ni, Cr, Pb, Hg and V) from the twelve selected locations in Kakuri industrial area was carried out in comparison with the control soil samples and the environmental soil guidelines. The results reveal that the locations UNT, RDQ, KTL, ART, AHT, KGW and PAN were considerably polluted with heavy metals but still have heavy metal concentrations below the intervention/alert level provided by the environmental protection agencies. The results also shows that heavy metal availability and distribution pattern varies with industrial activities and this is indicated by the wide range of concentrationvalues observed for virtually all the heavy metals in the soils analyzed across the sample locations. Soil pollution assessment using C_f and I_{geo} indexes confirmed the soils are uncontaminated. Therefore soils in Kakuri industrial area can be considered uncontaminated.

The total heavy metals availability as compared to the mobility of the studied metals in the soils in Kakuri industrial area followed the order of Zn>Cu>Hg>Pb>Ni>Cr>V. The bioavailability result indicate that the heavy metals available in the soils are not available for plant uptake as the bioavailable metal contents as a percentage of the total metal were below 10% of the total heavy metals in the soil. These low values could be as a result of basic soil pH and high content of free calcium carbonate in the soils. Therefore the soils in and around Kakuri industrial area are healthy for plants sustainability and animal survival.

6.2 Recommendations on Further Studies

With the increase in human and vehicular traffic in Kakuri industrial area as well as other small scale industrial activities such as vehicle repairs, vulcanizer, welders, auto-electricians, battery chargers etc. there is bound to be increase in environmental pollution especially heavy metals as they tend to accumulate due to their non-biodegradable nature in the soil. Therefore it is recommendations that:

1. Research should be carried out regularly to ascertain the level of pollution of heavy metals in the environment.
2. Further research on the bioavailability in plants around Kakuri Industrial area should be done to find out the level of plant uptake of heavy metals.
3. Research on soil heavy metals should be done at greater soil depths.

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APPENDICES

Appendix A: Concentration (mg/kg) of heavy metals in some soil samples at depths 0 to10 and 10 to 20

Sample Location	Depth (cm)	Zn	Cu	Ni	Cr	Pb	Hg	V
UNT	1	106	58	0	22	BDL	14	58
	2	98	49	12	34	BDL	20	76
RDQ	1	230	48	20	48	BDL	BDL	65
	2	310	68	33	34	BDL	BDL	79
CCD	1	58	61	BDL	43	BDL	BDL	63
	2	68	72	BDL	157	BDL	BDL	65
KTL	1	130	66	BDL	39	27	BDL	61
	2	130	64	16	34	34	BDL	90
ART	1	20	61	9	33	BDL	BDL	56
	2	69	83	72	40	BDL	BDL	90
AHT	1	85	61	17	28	BDL	BDL	78
	2	420	110	42	34	BDL	60	47
KGW	1	20	61	9	33	BDL	BDL	56
	2	69	83	72	40	BDL	BDL	90

Appendix A Continue: Concentration (mg/kg) of heavy metals in some soil samples atdepths 0 to10 and 10 to 20.

Sample Location	Depth	Zn	Cu	Ni	Cr	Pb	Hg	V
NBC	1	20	38	BDL	36	BDL	BDL	61
	2	45	26	BDL	38	BDL	BDL	47
PA	1	53	44	10	40	33	BDL	120
	2	136	51	27	60	34	BDL	81
NC	1	30	41	BDL	32	BDL	BDL	91
	2	35	42	BDL	28	BDL	BDL	82
IBB	1	110	64	BDL	41	BDL	10	66
	2	120	54	BDL	38	BDL	40	60
SG	1	20	79	BDL	41	BDL	BDL	84
	2	30	57	BDL	45	BDL	BDL	88

Depth 1: 0 to 10 cm

Depth 2: 10 to 20 cm

BDL: Below Detection Limit

Appendix B: Heavy metals Concentration (mg/kg) in controlsamples

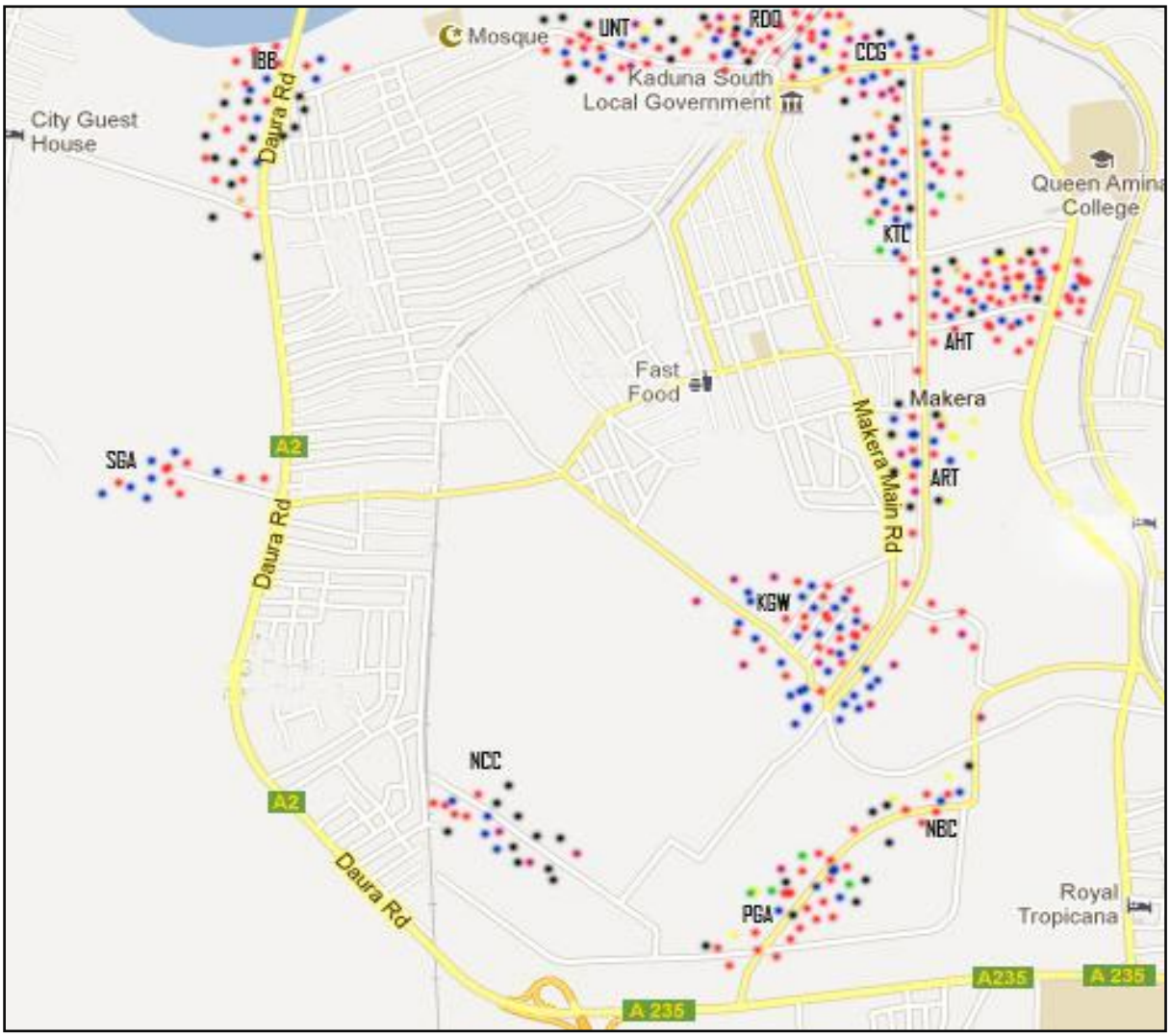
Control Sample	Depth	Zn	Cu	Ni	Cr	Pb	Hg	V
A	1	76	70	BDL	17	BDL	BDL	52
	2	98	22	BDL	20	BDL	BDL	43
B	1	100	72	BDL	32	BDL	BDL	61
	2	120	60	BDL	34	BDL	BDL	60

Depth 1: 0 to 10 cm

Depth 2: 10 to 20 cm

BDL: Below Detection Limit

Appendix C: Heavy metals distribution across sample locations in Kakuri industrial area



Zinc
Copper
Nickel
Chromium
Vanadium
Mercury
Lead

Appendix D: Muller's Classification for the Geo-Accumulation Index (Martin and Meybeck, 1979)

Igeo Value	Class	Sediment Quality
≤0	0	Unpolluted polluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
>6	6	Extremely polluted

Appendix E: Standard Regulatory Limits/Background Levels of Metals in Soil. (Turekian and Wedepohi 1961).

Metals	Concentration (mg/kg)
Pb	20
Zn	90
Cr	100
Ni	40
V	131
Cu	30
Hg	0.18

Appendix F: Contamination factor (Cf) and degree of contamination (Cd) of soil sample

Sample Location	Enrichment Ratio or Contamination Factor (C_f)							Degree of Contamination
	Zn	Cu	Ni	Cr	Pb	Hg	V	
UNT	1.03	1.09	0.17	0.38	-	-	0.58	3.25
RDQ	3.36	1.51	0.49	0.38	-	-	0.60	6.36
CCG	0.72	1.60	-	1.74	-	-	0.5	4.56
KTL	0.71	1.42	0.23	0.38	1.7	-	0.69	5.13
ART	1.36	1.84	1.06	0.44	-	-	0.69	5.39
AHT	0.73	2.44	0.62	0.38	-	-	0.36	4.53
KGW	4.46	1.84	1.05	0.44	-	-	0.69	8.48
NBC	0.73	0.57	-	0.42	-	-	0.36	2.08
PAN	0.47	1.13	0.40	0.66	1.7	-	0.62	4.98
NCC	1.43	0.93	-	0.31	-	-	0.63	3.30
IBB	0.37	1.20	-	0.42	-	-	0.46	2.45
SNG	0.32	1.27	-	0.50	-	-	0.68	2.77
Mean	1.31	1.40	0.57	0.53	1.70		0.57	6.08

Appendix G: Bioavailable heavy metals (mg/kg) in sample and control soils in Kakuri industrial area at 10 – 20 cm depth

Samples	Zn	Cu	Ni	Cr	Pb	Hg	V
UNT	2.30	2.22	0.16	0.41	BDL	2.80	0.40
RDQ	3.10	1.26	0.46	0.71	1.00	1.20	BDL
CCG	0.89	2.82	BDL	1.61	1.20	2.10	BDL
KTL	6.30	3.10	0.30	0.58	1.80	5.10	BDL
ART	1.60	1.92	0.38	0.72	5.20	1.20	0.60
AHT	5.60	1.92	0.37	0.92	1.60	3.50	0.70
KGW	4.20	1.18	0.81	0.64	4.10	1.80	BDL
NBC	2.10	1.62	0.21	0.66	1.60	3.40	BDL
PAN	13.6	1.58	0.41	0.78	4.00	1.20	BDL
NCC	2.56	2.41	0.28	0.56	0.80	3.90	BDL
IBB	5.20	1.01	BDL	0.51	BDL	1.50	0.50
SNG	0.45	1.32	BDL	0.62	BDL	4.80	BDL
Cont. A	0.09	0.08	BDL	0.03	BDL	BDL	BDL
Cont. B	0.09	0.08	BDL	0.04	BDL	BDL	BDL

BDL - Below Detection Limit

Cont. A– Control site A

Cont. B – Control site B

Appendix H: Bioavailable metal content as a percentage of the total metal content of the soilin Kakuri industrial area

Sample Sites	Zn (%)	Cu (%)	Ni (%)	Cr (%)	Pb (%)	Hg (%)	V (%)
UNT	2.37	4.90	1.30	1.20	BDL	BDL	0.50
RDQ	1.37	2.60	2.30	1.50	1.00	BDL	BDL
CCG	1.31	3.90	ND	2.82	1.20	BDL	BDL
KTL	4.85	4.80	3.00	1.70	5.20	BDL	BDL
ART	2.30	2.30	0.53	1.80	5.20	BDL	0.60
AHT	1.30	1.70	0.89	2.70	1.60	5.80	1.40
KGW	1.90	0.90	0.81	0.86	4.10	BDL	BDL
NBC	8.40	6.20	2.60	1.70	1.60	BDL	BDL
PAN	10.0	3.00	1.50	1.30	1.18	BDL	BDL
NCC	7.31	5.80	0.28	2.00	0.80	BDL	BDL
IBB	1.18	2.00	BDL	1.34	BDL	6.20	0.80
SGL	1.5	2.30	BDL	1.38	BDL	8.00	BDL

Appendix I: List of Apparatus and Equipment's

1. Bernard apparatus
2. Centrifuge
3. Beaker – 50 ml, 100 ml, 250 ml
4. Conical flask – 12 ml, 250 ml
5. Cylinder
6. Electric oven
7. Electric pH meter
8. Funnel
9. Erlenmeyer flask
10. Glass bottle
11. Hand trowel
12. Hygrometer
13. Measuring cylinder – 100 ml, 10 ml, 5 ml
14. Mortar and pestle
15. Myler film
16. Pipette – 1ml, 5ml, and 10ml, 25ml.
17. Plastic bottles for digest – 50 ml Polythene bags
18. Rotating shaker
19. Shaker
20. Sieve
21. Weighing balance
22. X-ray fluorescence spectrophotometer