DETERMINATION OF SOME HEAVY METALS UPTAKE IN *AMARANTUS HYBRIDUS* GROWN ON SOILS OBTAINED FROM THE BANK OF RIVER NIGER, LOKOJA, NIGERIA

BY

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Declaration

I declare that the work in this dissertation entitled "Determination of Some Heavy Metals in *Amarantus hybridus* Grown on Soils Obtained from the Bank of River Niger, Lokoja, Nigeria" has been carried out by me in the Department of Chemistry. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other institution.

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Certification

This dissertation entitled "DETERMINATION OF SOME HEAVY METALS IN *AMARANTUS HYBRIDUS*GROWN ON SOILS OBTAINED FROM THE BANK OF RIVER NIGER, LOKOJA, NIGERIA"by Mukhtar MUSTAPHA meets the regulation governing the award of the degree of Masters of Science in Analytical Chemistry of the 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 Almighty Allah who made it possible for me to be trained in this field of learning and to my lovely parent.

Abstract

The study was undertaken to assessed the accumulation of heavy metals (Cd, Cu, Mn, Ni, Pd and Zn) in riverside soils of River Niger and River Benue around their confluence and their uptake by *Amarantus hybridus*and *Corchorus olitorius L.*grown on these soils. Samples were collected in dry and rainy seasons of 2013 and 2014, samples were prepared, digested and taken for AAS analysis. The result shows thatthe concentrations of metals in the soil ranged from3.95-8.4for Cd; 11.6 - 20.2for Cu; 150.3-211.5 for Mn; 177.0 -281.0 forNi; 20.3-34.2 for Pb and 40.5-77.8mg/kg for Zn. Levels of nickel and cadmium were higher than the European Union Standards (2002).The levels of Ni, Zn, Pb and Cd in the vegetableswere higher than the WHO permissible value in plants.The total metal contents in *A. hybridus* and *C. olitorius L*grown on the riverside soils follow the order: Ni > Mn > Zn > Pb > Cu > Cd. The order of the percentage of extracted metal by EDTA to the total metal content was Pb > Zn > Cu > Ni > Mn > Cd. Geoaccumulation index showed that Cd and Ni were the major pollutants of the soil samples. Of all the metals studied, Pb had the highest bioaccumulation factor, 0.5691 and 0.6301 in the plant for *A. hybridus* and *Corchorus olitorius L*respectively.

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Abbreviations

N = Niger Riverside Soil,

B = Benue Riverside Soil,

CR = Right side Soil after Confluence,

CL = Left side Soil after Confluence.

EU, 2002 = European Union Standard Limits, 2002

WHO, 1996 = World Health Organization Permissible Limit, 1996

CEPA, 1995 = Chinese Environmental Protection Administration, 1995

CHAPTER ONE

1.0 INTRODUCTION

About ninety natural elements exist in the environment and are distributed through the environment in the geochemical and bio-chemical cycles (Kaim and Schwederski, 1994). Heavy metals are metallic chemical elements that have a relatively high density precisely greater than $5gcm^{-3}$. This classification includes transition metals and higher atomic weight metals of group IIIA to VA of the periodic table (Ademoroti, 1996a). Heavy metal contamination refers to the excessive deposition of toxic heavy metals in the soil caused by human activities. This includes some significant metals of biological toxicity, such as mercury, cadmium, lead, chromium, arsenic,zinc, copper, nickel, stannium, vanadium.

In recent years, with the development of the global industrialisation, both the type and content of heavy metals in the soil caused by human activities have gradually increased, resulting in the deterioration of the environment (Chao*et al.,* 2014). Heavy metals are highly hazardous to the environment and organisms. As heavy metals get into the ecosystem they can be enriched through the food chain. Once the soil accumulates heavy metal and is contaminated, it is difficult to get it remediated. In the past, soil contamination was not considered as important as air and water pollution, because soil contamination was not often and was more difficult to be controlled and taken care of than air and water pollution. However, in recent years soil contamination in developed countries has become an environmental concern(Chao*et al.*, 2014).

1.1 Characteristics of Heavy Metal Contaminated Soils

1.1.1 Wide distribution of heavy metals in soils

Excessive heavy metals in soils originate from many sources, which include atmospheric deposition, sewage, irrigation, improper stacking of the industrial solid waste, mining activities, the use of pesticides, fertilizers and so on (Zhang *et al*., 2011).

Arsenic (atomic number 33) is a silver-grey brittle crystalline solid with atomic weight of 74.9, specific gravity 5.73, melting point 817°C (at 28 atm), boiling point 613°C, and vapour pressure 1 mm Hg at 372°C. It is odourless and tasteless, Arsenic exists in the −3, 0, +3, and +5 valence oxidation states, and is in a variety of chemical forms in natural waters and sediments. The environmental forms include arsenious acids (H_3AsO_3, H_3AsO_3), arsenic acids (H_3AsO_4), arsenites, arsenates, methylarsenic acid, dimethylarsinic acid and arsine. The two most common forms in natural waters are arsenite (AsO_3^{3-}) and inorganic arsenate (AsO_4^{3-}), referred to as As^{3+} and As^{5+}. From both the biological and the toxicological points of view, arsenic compounds can be classified into three major groups. These groups are inorganic arsenic compounds, organic arsenic compounds and arsine gas.

Lead, with atomic number 82, atomic weight 207.19 and a specific gravity of 11.34 is a bluish or silvery-grey metal with a melting point of 327.5°C and a boiling point of 1740°C at atmospheric pressure. It has four naturally occurring isotopes with atomic weights 208, 206, 207 and 204 (in decreasing order of abundance). Despite the fact that lead has four electrons in its valence shell, its typical oxidation state is +2 rather than +4, since only two of the four electrons ionize easily due to inert pair effect.Apart from nitrate, chlorate and chloride, most of the inorganic salts of Pb^{2+} have poor solubility in water. Lead exists in many forms in the natural sources throughout the world and is now one of the most widely and evenly distributed trace

metals. Soil and plants can be contaminated by lead from car exhaust, dust and gases from various industrial sources.

Mercury is a naturally occurring metal that is present in several forms. Metallic mercury is shiny, silver-white, odourless liquid. It combines with other elements, such as chlorine, sulphuror oxygen, to form inorganic mercury compounds or salts, which are usually white powder or crystals. The element also combines with carbon to form organic mercury compounds. Mercury, which has the lowest melting point (−39°C) of all the pure metals, is the only pure metal that is liquid at room temperature. As any other metal, mercury could occur in the soil in various forms. It dissolves as free ion or soluble complex and is nonspecifically adsorbed by binding mainly due to the electrostatic forces, chelated, and precipitated as sulphide, carbonate, hydroxide, and phosphate. There are three soluble forms of Hg in the soil environment. The most reduced is Hg^{o} metal with the other two forms being ionic of mercurous ion(Hg_2^{2+}) and mercuric ion (Hg^{2+}), in oxidizing conditions especially at low pH. Hg^{+} ion is not stable under environmental conditions since it tranforms into Hg^{0} and Hg^{2+}. A second potential route for the conversion of mercury in the soil is methylation to methyl or dimethyl mercury by anaerobic bacteria.

1.1.2 Strong latency of heavy metals in soil

Heavy metal contamination of soil is difficult to notice, since the changes cannot be identified by colour or odour. The contamination does not explicitly damage the environment in a short period. Nevertheless, when it exceeds the environmental tolerance, or when environmental conditions have changed, heavy metals in the soil may be activated and cause serious ecological damage. So heavy metal contamination is usually termed chemicalTime Bombs (CTBs) (Wood, 1974).

1.1.3 Irreversibility and difficulty in the remediation of soil

If air and water are polluted, the pollution problem can be reversed certainly by dilution and self-purification after switching off from the sources of pollution. However, it is difficult to use dilution or self-purification techniques to eliminate heavy metal contamination and to get soils improved. Some soils contaminated by heavy metals are likely to take one or two hundred years to be remediated (Wood, 1974).Therefore, heavy metal contamination needs relatively high cost of remediation and the remediation cycle is relatively long.

1.1.4 Complexity of heavy metal contamination

In the past, soil contamination was mainly caused by a single heavy metal. However, in recent years more cases are found to be caused by a variety of heavy metals (Zhou, 1995). The complex contamination is caused by the presence of a variety of heavy metals,this always amplify the contamination of heavy metals compared to whenthey are separately present(Zhang *et al*., 2011).

1.2Pathways of Sewage and Solid Waste to Soil

Heavy metals in the atmosphere are mainly from gas and dust produced by energy, transport, metallurgy and production of construction materials. Except mercury, heavy metals basically go into the atmosphere in the form of aerosol and deposit to the soil through natural sedimentation and precipitation, etc. (Chao, *et al.*, 2014).

Wastewater can be divided into several categories, sanitary sewage, chemical wastewater, mining wastewater and urban mining mixed sewage, etc. Heavy metals from sewage are brought to the soil by irrigative sewage and are subsequently fixed in the soil in different ways. Indiscriminate passing of sewage to soil surface do cause heavy metal to continually accumulate

in the soil year by year. Irrigation using sewage is a feasible way to solve the problem of crop irrigation in arid area. However heavy metal contamination caused by sewage irrigation must be paid enough attention. Quality of irrigative sewage must be strictly controlled within the national quality standard for irrigation water (Chao, *et al.,* 2014).

There are a variety of solid wastes with complex composition. Of this mining and industrial solid waste contamination are the most serious. When these wastes are deposited on land or used as landfills, heavy metals leach into groundwater to the soil due to the facilitation of sunlight, raining and washing. The pollutant spread to the surrounding water and soils,which pose a serious environmental concern.

With the development of industry and the acceleration of urban environmental construction, technology for sewage treatment continue to be strengthened. China now has more than 80 sewage treatment plants, with an estimated 400 million tonnes of sludge production. Solid wastes can expand contamination scope easily with the help of wind and water.

1.2.1Pathway of agricultural supplies to soils

Fertilizers, pesticides and mulch are important agricultural inputs for agricultural production (Chao*et al.,* 2014). Nevertheless, the excessive application on a long term has resulted in the heavy metal contamination of soils. The vast majority of pesticides are organic compounds, and while a few are organic - inorganic compound or pure mineral; some pesticides contain Hg, As, Cu, Zn and other heavy metals (Arao *et al*., 2010).

Heavy metals are the most reported pollutants in fertilizers. However, heavy metal content is relatively low in nitrogen and potash fertilizers, while phosphoric fertilizers usually contain considerable toxic heavy metals. Heavy metals in compound fertilizers are mainly from master materials and manufacturing processes. The content of heavy metals in fertilizers is

generally in the following ranking: phosphoric fertilizer> compound fertilizer>potash fertilizer> nitrogen fertilizer (Boyd, 2010). Cd is an important heavy metal contaminant in the soil. Cd is brought to soils with the application of phosphoric fertilizers. Many studies have shown that, with the application of a large amount of phosphate fertilizers and compound fertilizers, the content of Cd in soils increases constantly, and Cd taken by plants increases accordingly.

In recent years, usage of mulch has been promoted and used in large areas, which results in white pollution of soils, because the heat stabilizers, which contain Cd and Pb, are always added in the production process of mulch. This increases heavy metal contamination of soils (Satarug *et al.,* 2003).

1.3 Impact of Heavy Metal Contamination of Soils

1.3.1 Impact on soil microorganisms and enzymatic activity

Microbial activity and enzymatic activity of soil can reflect the quality of the soil, Chao, *et al.*(2014) stated that microbial biomass of soil is an important indicator for determining the extent of soil contamination. Microbial activity is inhibited significantly in heavy metal contaminated soil. Kandeler *et al*. (1997) indicated that the microbial biomass in soil contaminated by Cu, Zn, Pb and other heavy metals are inhibited severely. The soil's microbial biomass near the mine was significantly lower than that far away from the mine. And the effects of different concentrations of heavy metals and different heavy metals on soil microbial biomass were different.

Chander *et al*. (1995) studied the effect of different concentrations of heavy metals on soil microbial biomass, and found out that it is only if the concentration of heavy metals in the soil is three times above the environmental standard, established by the European Union, that it could inhibit microbial biomass. Fliepbach *et al*. (1994) also discovered that low concentrations

of heavy metals could stimulate microbial growth and increase microbial biomass; while high concentrations could decrease soil microbial biomass significantly.

The enzymes in the soil play an important role in the process of organic matter decomposition and nutrient cycling. Studies have showed that the activities of enzymes in the soil are related to the heavy metal contamination. Chander *et al*. (1995) found that the activities of almost all enzymes in the soil are significantly reduced by 10 to 50 times with increase in the concentration of heavy metals.

1.3.2 Impact of heavy metals on the plants

Low concentration of soil heavy metals, regardless of whether it is necessary or unnecessary to plants, will not affect the growth of plants in a certain range. But if the concentration is too high, the content of heavy metals bioaccumulated by the plant exceeds its tolerance threshold, and thus the plant physiological composition is altered and it may even lead to death of the plant. In Florida, it was found that if the copper content in soil was more than 50 mg/kg, it would affect citrus seedlings; if soil copper content reached 200 mg/kg, wheat would wither (Zhang *et al.,* 1989). Research has indicated that the growth of cabbage and bean seedling under Cd concentration of 30 μmol/L was inhibited: the root length decreased, and the plant height and leaf area dropped (Qin *et al.,* 1994). Cd may interfere with crop photosynthesis and protein synthesis, and may cause membrane damage etc (Chao *et al.,* 2014).

1.3.3 Impact of heavy metals on humans

Cadmium may damage the metabolism of calcium, which will cause calcium deficiency and result in cartilage disease and bone fractures, etc. Agency for Toxic Substances Management Committee has listed Cd as the sixth most toxic substance that damages human health. Pb mainly enters human body through the digestive tract and respiratory tract, and then goes into the blood

circulation in the form of soluble salts, protein complexes or ions, etc. It is reported that 95% of the insoluble lead phosphate accumulates in bones. Pb is strongly pro-organizational, it affects and damages many of the body organs and systems, such as kidney, liver, reproductive system, nervous system, urinary system, immune system and the basic physiological processes of cells and gene expression. Cu, Zn and Ni are essential trace metals in the human body, but if the body takes excessive Cu, Zn and Ni from the outside environment, they will damage human health. Ni and Cu are tumour promoting factors, whose carcinogenesis effect has attracted global concerns. Workers who are in close contact with the nickel powder are more likely to suffer from respiratory cancer, and the content of Ni in the environment is positively correlated with nasopharyngeal carcinoma (Chen, 2011).

1.4 Soil Quality

Soil is a crucial component of rural and urban environments and in both places land management is the key to soil quality. Flooding, mining, manufacturing and the use of synthetic products such as pesticides, paints, batteries, industrial waste and domestic waste can result in heavy metal contamination of urban and agricultural soils (Chao*et al.,* 2014).

The quality of soil depends both on its physical properties (colour, texture, moisture content, pH)and chemical properties (cation exchange capacity, phosphate-phosphorous, sulphate-sulphur, nitrate and nitrite-nitrogen). The physical properties and chemical properties of soil largely determine the suitability of a soil for its planned use. The management requirements to keepsoil quality is worthwhile and should be intensified by all, since the benefits is unquantifiable.

1.4.1 Cation exchange capacity of soil

Cation exchange capacity of soil is the capacity of the soil to hold cations. Soil particles are composed of silicate and aluminosilicate clay. Cation exchange capacity therefore increases as the clay content increases and also as the organic matter increases in the soil (Frank, 2006). Cation exchange capacity also depends on the density of the negative charges on the surfaces of soil colloids and the relative charges on the metal species in solution and on the soil surface.

1.4.2 pH of soil

In agriculture, pH is probably the most important single property of the moisture associated with a soil, since that parameter reveals what crops will grow readily in the soil and what adjustments must be made to adapt it for growing any other crops. Acidic soils are often considered infertile and so they are for most conventional agricultural crops, although conifers and many species of shrub will not thrive in alkaline soil. As soil acidity increases so does the solubility of aluminium and manganese in the soil and many plants (including agricultural crops) will tolerate only slight quantities of these metals. Acid content of soil is however heightened by the decomposition of organic material (Andrew, 1990).

pH is generally acknowledged to be the principal factor governing concentration of soluble and plant available metals (Brallier *et al.*, 2001). As metal solubility tends to increase at lower pH and decrease at higher pH values (Garcia *et al.*, 2009).

1.4.3 Soil texture and soil colour

The colour of soil can give clues to its health, origin and long-term changes. It can also indicate the colour of the parent material. Subsoil colour can be a valuable indicator of how well

the subsoil drains, which can be influenced by topography. Dark colour in the soil usually indicate that the soil has a high organic matter content. The more humus the black the soil, it could mean that the parent from which soil developed was also rock (Frank, 2006).

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

1.5 Effects of Some Heavy Metals on the Environment

1.5.1 Arsenic

The toxicity of arsenic and its compounds varies widely, ranging from the exceedingly poisonous arsine and its organic derivatives to the elemental arsenic itself, which is relatively inert (Prett *et al*., 1995). Arsenical compounds in general are skin irritants, which easily cause dermatitis. Protection against inhalation of arsenic containing dusts is recommended, but most poisoning appears to come from ingestion (Yadav *et al*., 2000).

Arsenic is believed to exert its toxicity by combining with certain enzymes, thereby interfering with cellular metabolism. Individual susceptibility to arsenic poisoning varies widely; some persons have been known to develop a tolerance to doses that would kill others. Poisoning may result from a single large dose (acute poisoning) or from repeated small doses (chronic poisoning). Symptoms of acute poisoning from swallowing arsenic include nausea, vomiting, burning of the mouth and throat and severe abdominal pains (Heilman *et al.,* 2003).

With the exposure of human to arsenic compounds, circulatory collapse may occur and be followed by death within a few hours. In persons exposed to arsine, the outstanding effects are destruction of red blood cells and damage to the kidneys. With chronic exposure, the more common effects include gradual loss of strength; diarrhea or constipation; pigmentation and scaling of the skin, which may undergo malignant changes; nervous manifestations marked by paralysis and confusion; degeneration of fatty tissue, aneamia and the development of characteristic streaks across the fingernails (Revitt *et al*., 2009).

1.5.2 Cadmium

Cadmium occurs in a few minerals and in small quantities in other ores, especially zinc ores, from which it is produced as a by - product. Some lead ores also contain small quantities of cadmium and if it is present in sufficient quantity it is recovered by a cycle of operations similar to that used by zinc smelters.

The concentrations of cadmium in agricultural soils depend upon the amounts present in the parent rocks from which the soil is formed, the amounts added in the form of fertilizers and soil amendments, the amounts deposited onto soils from the atmosphere and the amounts removed by harvested crops and by leaching. On the average, sedimentary rocks contain greater concentrations of Cd than either igneous or metamorphic rocks and therefore, recent soils derived from sedimentary rock should contain greater concentrations of Cd than those derived from igneous or metamorphic rocks. Among the commercial fertilizers, phosphorus fertilizers contain somewhat elevated levels of Cd. Results show that the long - term use of phosphorus fertilizers will slightly increase the concentration of Cd in surface soils (Wedelpohl, 1998).

In acute cadmium poisoning by ingestion, irritation of the gastrointestinal tract is the major toxicity, causing nausea, vomiting, diarrhea and abdominal cramps. With chronic exposure

by inhalation, however, kidneys and lungs are the target organs. Cadmium compounds do damage many organs. They cause skin lesions, decrease heart contractility, damage blood vessel and injuries of the nervous system, kidney and liver. Cadmium compounds also produce skin and lung tumours in humans (Jenne *et al.,* 2011).

1.5.3 Copper

The major portion of copper produced in the world is used by electrical industries; most of the remainder is combined with other metals to form alloy. Important series of alloys in which copper is the chief constituent are brass (copper and zinc) and bronze (copper and tin) (Morse, 1994). Copper resists the action of the atmosphere and seawater on exposure for long periods to air, however, this results in the formation of a thin green protective coating (patina) that is a mixture of hydroxocarbonate, hydroxosulphate and small amounts of other compounds. Copper is a moderately noble metal, being unaffected by non-oxidizing or non-complexing dilute acids in the absence of air; it will however, dissolve readily in HNO_3 and in H_2SO_4 in the presence of oxygen (Frits *et al.,* 2000).

Copper is among heavy metals that are essential to life but could be toxic at elevated levels. It is toxic at low concentration in water and is known to cause brain damage in mammals. Elevated levels of this metal has however, been found to be toxic (Hukabee *et al.,* 2011). Toxicity of Copper in plants as a result of high level in sewage treated agricultural soil has been reported. Contribution of copper to environmental burden could be by atmospheric deposition from metal industries, dumpsites and power plants that burn fuels (Baryla *et al.,* 2011).

1.5.4 Lead

Lead is present in several minerals but all are of minor significance except the sulphide, PbS (galena), which is the major source of lead production throughout the world. Lead is also

found in anglesite ($PbSO_4$) and cerussite ($PbCO_3$). The elimination of lead from insecticides and paint pigments and the use of respirators and other protective devices in areas of exposure have reduced lead poisoning materially. The recognition that the use of tetraethyl lead [$Pb(C_2H_5)_4$] as an antiknock additive in gasoline was polluting the air and water led to the compound's elimination as a gasoline constituent in the 1980s (Taylor, 1995).

Lead and its compounds are toxic and are retained by the body, accumulating over a long period of time, a phenomenon known as cumulative poisoning until a lethal quantity is reached. The toxicity of lead compounds increases as their solubility increases. In children and adults the accumulation of lead may result in progressive renal disease. Symptoms of lead poisoning include abdominal pain and diarrhea followed by constipation, nausea, vomiting, dizziness, headache and general weakness. Elimination of contact with a lead source is normally sufficient to effect a cure (Leonard *et al.,* 1998).

In humans the main sources of lead are usually lead - based paint and drinking water carried through lead pipes; lead-based paints are especially harmful to children who chew on painted toys and furnishings and eat paint peelings from walls. Industries in which workers encounter lead-containing solids, dusts or fumes include the petroleum industry, mining, smelting, printing, cutlery, storage-battery manufacture, plumbing, gas fitting, paint and pigment manufactureand manufacture of ceramics, glass and ammunition. Other possible sources of lead poisoning include the agricultural use of insecticides containing lead compounds; the spraying of fruits and vegetables that may affect the workers and eventually, the consumers. In the mid-20th century, constant exposure to exhaust fumes of motor vehicles powered by fuel containing tetraethyl lead became a significant cause of lead poisoning, especially in children (Kersten *et al.*, 2003).

Symptoms of lead poisoning vary, they may develop gradually or appear suddenly after chronic exposure. The poisoning affects the entire body especially the nervous system, the gastrointestinal tract and the blood forming tissues. The victim usually becomes pallid, moody irritable and may complain of a metallic taste. Digestion is deranged, the appetite fails and there may be severe abdominal pain, with spasms of the abdominal muscles and constipation. A black line (lead line) may appear at the base of the gums. There is often anaemia, in later stages, headache, dizziness, confusion and visual disturbances may be noted. Peripheral nerve involvement results in a paralysis (lead palsy) that generally first affects the fingers, hands and wrists (wrist drop). The most serious effects are seen in children under the age of six, in whose brain and nervous system development is still occurring. In these children, even a small amount of lead can result in permanent damage and loss of function of the affected area of the brain. Complications may occur, such as learning disabilities, slowed growth, blindness, deafness, and, in extreme cases, convulsions and coma ending in death. Brain injury may also occur in adults after massive exposure (Sahu *et al.,* 2008).

1.5.5 Manganese

Manganese combined with other elements is widely distributed in the earth's crust. Manganese is second only to iron among the transition elements in its abundance in the earth's crust; it is roughly similar to iron in its physical and chemical properties but is harder and more brittle. It occurs in a number of substantial deposits, of which the most important ores (which are mainly oxides) consist primarily of manganese (IV) oxide (MnO_2) in the form of pyrolusite, romanechite and wad (Uba *etal.,* 2008).

Manganese is essential to plant growth and is involved in the reduction of nitrates in green plants and algae. It is an essential trace element in higher animals, where it participates in

the action of many enzymes. Deficiency of manganese do cause testicular atrophy. An excess of this element in plants and animals is toxic. Manganese always associates with iron deposits, known to block calcium channels. It is also an essential element to plants and animals as it aids in activating enzymes in man (Awwal, 2008). In some circumstances it can pose health risk to man when it is associated with steel, iron, battery manufacture and coal burning processes. The availability of this metal is highest in acidic soils but drops in calcareous soil (Lloyd *et al*., 2011).

1.5.6 Zinc

The major uses of zinc metal are in galvanizing iron and steel against corrosion and in making brass and alloys for die-casting. Zinc itself forms an impervious coating of its oxide on the surface when exposed to the atmosphere, and hence the metal is more resistant to ordinary atmosphere than iron and corrodes at a much lower rate. Zinc is an essential trace element in the human body, where it is found in high concentration in the red blood cells serving as an essential part of the enzyme carbonic anhydrase, which promotes many reactions related to carbon (IV) oxide metabolism. The zinc present in the pancreas may aid in the storage of insulin. Zinc is a component of some enzymes that digest protein in the gastrointestinal tract. Zinc deficiency in nut-bearing and fruit trees causes such diseases as pecan rosette, little leaf and mottle leaf (Noltze *et al*., 2003).

The toxicity of zinc is low, in drinking water zinc can be detected by taste only when it reaches a concentration of 15 mg/kg; water containing 40 mg/kg zinc has a definite metallic taste. Vomiting is induced when the zinc content exceeds 800 mg/kg. Cases of fatal poisoning have resulted through the ingestion of zinc chloride or sulphide, but these are rare. Both zinc and zinc salts are well tolerated by the human skin. Excessive inhalation of zinc compounds can

cause such toxic manifestations as fever, excessive salivation and a cough that may cause vomiting; but the effects are not permanent (Kline*et al*., 2010).

1.6 Justification for the Study

Irrigation on river side soils of River Niger and Benue help to provide vegetable crops for the people of Lokoja and the environs during the dry season and early part of the rainy season. Kogi State faced the problem of flooding in 2012, consequently, large items were washed into the water body, thus the level of heavy metals in both soils and plants grown on the river side soils are expected to be elevated beyond the threshold levels. It is worthy of note that these two rivers come from far distance, therefore, domestic industrial, mining, metallurgical and agricultural activities contribute to the heavy metal loading of the water and neighboured riverside soils being irrigated with water from the rivers. These activities lead to heavy metal loading of the soil, therefore the determination of the heavy metal levels of the riverside soils post flooding becomes imperative.

Determination of the heavy metal uptake is further justified, since these metals are taken up by plants and from here enter into the food chain where they may cause health hazards. The pollution indices of the riverside soil will help to determine the level of pollution loading after the flooding of 2012 when data is compared to that in literature before the flood.

1.7 Aims and Objectives of the Study

This study is aimed at determining the levels of some heavy metals in riverside soils of River Niger, River Benue and beyond the confluence point, and to assess the heavy metal uptake by spinach(*Amarantus hybridus*) called “aleyafu” in Hausa, “Inine” or “Opotoko” in Igbo and “Efo” in Yoruba and jute (*Corchorus olitorius L*.) called “Laalo” or “Malafia” in Hausa, “Arira”

or “Ahihara” in Igbo and “Oyoyo” or “Ewedu” in Yoruba,planted on the soils, for possible contamination.

The objectives set to achieve the aims include:

I. To determine the physico-chemical parameters of the river bank soils (pH, CEC, Organic matter, colour, textural class and so on);

II. To carry out characterization of the soil;

III. To determine the total metal content of the soil;

IV. To determine the EDTA-extractable heavy metals in samples of thefarmland soil near the rivers and control soil collected from farmland soil far away from the river, which is not in any way associated with the river;

V. To determine the concentration of heavy metals in the *Amarantus hybridus* and *Corchorus olitorius L.* grown on the soil samples obtained from the farmland near the river bank and the control soil;

VI. To assess the metal mobility and their availability to *Amarantus hybridus* and *Corchorus olitorius L.*;

VII. To establish and assess the level of heavy metal pollution of the riverside soil with seasonal variation and

VIII. To use some pollution indices to assess the level of the contamination or otherwise on the riverside soil used for agricultural activity.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Study Area

It was in Lokoja, that the name Nigeria was coined by Flora Shaw, the future wife of Baron Lugard, a British colonial administrator, while gazing out at the river that stretched before her in the late 19th century.Agriculture is the chief support of the economy in the state and the principal cash crops are many,which are notably coffee, cocoa, palm oil, cashews, groundnuts, maize, cassava, yam, rice and melon among others.The mineral resources found in Kogi State include coal, limestone, iron, petroleum and tin. The state is home to the largest iron and steel industry in Nigeria known as Ajaokuta Steel Complex.

Like many states in Nigeria, Kogi State faces problem of flooding in 2012, in that year the river extended its territory beyond its banks, thus sacking residents from their humble abodes. The disaster brought back the memories of 1998, when the river covered and threatened some of the buildings at the river bank, though the situation was however not as bad as the one experienced in 2012.

Consequently, the flood washed away a large amount of farm lands,thus the levels of heavy metals in both soils and plants grown within the metropolis are expected to be elevated beyond the threshold level.

2.2 Polluted Soils and the Environmental Impact

In recent years, studies have shown that the characteristics of heavy metal contamination in urban soils and agricultural soils are different (Babula *et al*., 2008). Heavy metals in urban soils may go into the body directly through ingestion, skin contact and so on. However, heavy metals in agricultural soils are absorbed and accumulated by crops. Ingesting heavy metals through the soil – crop system is a major way of damaging human health (Aeliona *et al*., 2008).

Numerous studies indicated that the major sources of heavy metal contamination in urban soils include emissions from transport (exhaust, tire wear debris particles, particles formed by weathering street, etc.), industrial wastes (from power plants, coal combustion, metallurgical industry, automobile repair plants, chemical plants and so on), house garbage, building and weathered particles of sidewalk and precipitation in the atmosphere, among others. However, the major sources of heavy metal contamination in agricultural soils include the impact from the city, smelting minerals, waste treatment (such as landfill, etc.), sewage sludge, automobile exhaust, fertilizers, pesticides and so on (Montagne *et al*., 2007).

The range and mean concentrations (mg/kg) of some heavy metals in the sediments collected from River Niger via Ajaokuta Steel Company, North Central, Nigeria between 2004 and 2005 were Zn 36.64 – 96.23 (70.70 ± 10.68); Mn 4.97 to 21.77 (13.24 ± 2.04); Pb 8.84 to 17.52 (12.35 ± 1.14); Ni 2.65 to 18.61 (9.67 ± 2.91); Cu 0.89 to 8.21 (3.58 ± 1.32); and Cr 0.48 to 13.08 (3.38 ± 0.76) and Cd 0.07 to 0.62 (0.27 ± 0.07) (Olatunde and Oladele, 2003).Thermal neutrons

activation analysis technique (TNAA) indicated that some farmland soil in Lokoja contained Mg, K, Ca in large concentration; Na, Mn and V were present in minor concentration in all the samples; Al and Ti were present in minor concentration while Dy was present in relatively low concentration (Oladipo*et al.*,2012).

In recent years, heavy metal contamination in China's urban and agricultural soils is rapidly getting worse with the development of industrial activities. According to Bulletin on National Survey of Soil Contamination, jointly issued by the Ministry of Environmental Protection of China and the Ministry of Land Resources of China in recent time, nearly 4 million of hectares of arable land have been contaminated moderately or severely, which accounts for about 2.9% of China's arable lands. The proportion of soils that exceeds environmental standard is about 16.1%, of which the proportion for the slight, mild, moderate and severe contaminated are 11.2%, 2.3%, 1.5% and 1.1% respectively in China (Chao *et al.*, 2014). Most of the soil contamination is in the form of inorganic (82.8%), seconded by organic, and the third is complex contamination. Contamination of arable land soil exceeds the 19.4%, of which the proportion for the slight, mild, moderate and severe contamination is 13.7%, 2.8%, 1.8% and 1.1% respectively, and the most contaminants in the arable land of China include Cd, Ni, Cu, As, Hg, Pb, Dichlorodiphenyltrichloroethane (DDT) and polyaromatic hydrocarbons (PAHs).

Worldwide samples of urban and agricultural soils are mainly collected from depths of 10 cm to 20 cm. In urban soils, samples are collected from parks, green spaces and urban street. These samples are mixed, dried and screened out through a mesh of less than 2 mm, and then processed and cleared up through a mixed acid (such as HF, $HClO_4$, HNO_3, H_2O_2, H_2SO_4, etc.). Finally, the contents of the heavy metals (Cd, Cr, Cu, Ni, Pb, Zn, As, Hg, etc.) in the samples of

interest are measured using methods such as Inductive Couple Plasma (ICP), Inductive Couple Plasma Mass Spectrometry (ICP-MS), Inductive Couple Plasma Atomic Emission Spectrometry(ICP-AES), Inductive Couple Plasma Optical Emission Spectrometry(ICP-OES), Cold Vapour Atomic Absorption Spectrometry (CV-AAS),Atomic Absorption Spectrometry(AAS) or X-ray fluorescence(XRF) etc.

From a study of the content of heavy metals in agricultural soils of 11 regions of the world,the average contents of the heavy metals Cr, Cu, Pb, Zn, Ni, Cd, Hg and As in the agricultural soils of China are 46.69, 38.03, 51.19, 117.35, 26.12, 1.50, 0.28, 21.19 mg/kg respectively(Chao *et al.,* 2014).

2.3 Indices for Assessing Pollution of Soil

The level of heavy metal contamination in soil can be analyzed and determined by various indices such as geoaccumulation index (Igeo) and Bioaccumulation factor (BF). This method began to be widely used in the late 1960s (Muller, 1979).

Geoaccumulation index (Igeo) is obtained by comparing the contamination levels before contamination and present contamination. The computation of Igeo is:

$$Igeo = \log_2\left(\frac{C_n}{1.5Bn}\right) \quad \text{.....2.1}$$

Where Cn is the measured mass fraction of the metal ($mgkg^{-1}$). Bn is the background mass fraction of the metal (mg/kg). The Chinese Environmental Protection Administration(CEPA) environmental background values (Wang *et al.,* 2007)can be used to calculate Igeo. Muller's evaluation method (Muller, 1979) can also used to evaluate the level of heavy metal contamination in soils, as shown Table 2.1.

Table 2.1 Classification of Geoaccumulation Index

Geoaccumulation index	Classification	Level of contamination
5＜I geo≤10	6	Extremely serious
4＜I geo≤5	5	Strong to extremely serious
3＜I geo≤4	4	Strong
2＜I geo≤3	3	Moderate to strong
1＜I geo≤2	2	Moderate
0＜I geo≤1	1	Light to moderate
I geo≤0	0	Non contamination

Bioaccumulation factor (BF) is the concentration of metal in plant with respect to the soil also known as Tranfer Factor (TF), Transfer Coefficient (TC), Mobility Ratio (MR), Bioconcentration Factor (BCF) or Plant Soil coefficient. This is expressed by the following formula:

$$BF = \frac{C_{plant}}{C_{soil}} \quad \text{.....2.2}$$

where C_{plant} and C_{soil} represents the toxic metal concentration in extracts of plants and soils on dry weight basis, respectively.

This ratio indicates qualities of metal absorption by plants. When the value of the ratio is more than one, plants are termed as "accumulators", when the value is close or equal to one they are termed as "indicators" and when it is less than one, they are termed as "excluders".

2.4Analysis of Heavy Metal Contamination

Chao, *et al.*,(2014) showed that South Korea's agricultural soils are almost not polluted by heavy metals, and the Cd contamination in Spain, the United States and Xuzhou is more serious. Heavy metal contamination in the agricultural soils of Wuxi and Chengdu is relatively serious than other cities. Hg contamination in Guangzhou and Chengdu are relatively serious. Worldwide speaking, the contents of Cu and Hg in most agricultural soils reach light contamination, which is different from the Pb and Cd in cities' soil.

In Nigeriatoday several ways were identified through which specific heavy metal can be transmitted to living species. Continuous use of leaded gasoline has contributed greatly to the number of cases of childhood lead poisoning. Leaded gasoline in Nigeria contain lead in the concentration range of 0.65 to 0.74 g/L, the Clean Air Initiative is proposed to reduce the

concentration to 0.15 g/L and finally to zero level. However, numerous studies revealed that, the initiative is just on paper (Orisakwe, 2009) due to government negligence. The consequences have been severe environmental problems. Upon the combustion of the leaded petrol in the engine, the organic lead is oxidized to lead oxide (equation 2.3).

i.e. $2Pb(C_2H_5)_4 + 27O_2 \longrightarrow 2PbO + 16CO_2 + 20H_2O$……2.3

The lead oxide formed reacts with the halogen carriers to form lead halides like $PbCl_2$,$PbBr_2$, or PbClBr, which escapes in to the air through vehicles exhaust pipes. About 80% of lead in petrol was noticed to escape. Lead pollution from automobile emissions in Nigeria has been extensively studied and documented in various Nigerian and international publications. Nriagu *et al.* (1997) investigated blood lead levels in 87 children aged 1-6 years from Kaduna state. An average of 10.6 µg/dl was found, with some children having up to 30 µg/dl. The values exceed the maximum allowed limit of 10 µg/dl recommended by Centre for Disease Control (CDC) and correlated linearly with the distance of house from highly trafficking roads, as well as, whether a family owns a car or not. At the beginning of the 21stcentury, the Federal Environmental Protection Agency (FEPA) of Nigeria examined the lead concentrations in soils from roads, markets and motor parks of Lagos, Aba, Abuja, Ibadan, Kaduna and Port Harcourt. The results revealed elevated and health threatening concentrations. It could be seen that, the highly trafficking cities of Lagos, Ibadan and Kaduna recorded the highest lead levels. Sridhar *et al.*, (2011) reported high degree of contamination in different samples from Ibadan and Lagos. Drinking waters exhibited up to 2.16 mg/L, foods contained 18.5 mg/kg and soil samples from residential and mechanic areas showed 81.91-4060.7 and 140.0- 5454.6 mg/kg respectively. The highest concentrations in all cases correlated linearly with level of traffic and gasoline usage.

Human beings, animals and soil are the ultimate recipients of the lead particulate. It sometimes exists in soil as lead (II) sulphate ($PbSO_4$). Concentrations of about 100 to 1000 ppm have been recorded depending on the nature of the activities, carried out in a particular area (Galadima *et al.,* 2010; Garba *et al.,* 2010). Other anthropogenic sources include mining and metallurgic industries, manufacture of batteries, sheet, ammunition, pipe, cable sheeting, solder, saint and trash incineration. The principal route of exposure for people in the general population is food and lead in contaminated drinking water, working and hand to mouth activities of young children living in polluted environments and the lead dust brought home by industrial workers on their clothes and shoes.

Paints containing lead are the most common high dose sources of lead exposure for school and pre-school children. Most of them contain up to 50% of lead in the form of lead sulphide (PbS). Children can get seriously lead poisoned when renovations, modelling and construction activities take place ina house or class that contains lead paints. Inhalation or swallowing of debris of the paints during regular playing causes the accumulation of the metal in the children body.

Although industrial and commercial utilisation of mercury and mercury products is regulated, occupational exposure, contamination of rivers and agricultural farmland with mercury based chemicals are considered the major contributors to mercury poisonings in Nigeria. Most of the known mercury compounds are poisonous but with cases reported mainly due to Hg, CH_3Hg, HgCl and $HgCl_2$. Some skin whitening products contain the toxic HgCl as the active ingredient. When applied, the chemical readily absorbs through the skin into the blood stream. Recently, some products were discovered to contain between 9,000 and 60, 000 times the recommended international limit. Eating of exposed aquatic plants and animals like fishes.

Arsenic is another identified key contaminant for many decades that occurs in a variety of minerals including Arsenopyrite (FeAsS), Realgar (As_2S_2), Orpiment (As_2S_3), Arsenolite (As_4O_6), native Arsenic in ores of Copper, Lead, Cobalt, Nickel, Zinc, Silver, and Tin and also as nickel glance (NiAsS) or mispickel. Arsenic is chemically very similar to its pre-decessor phosphorus, so much that it will partly substitute for it in biochemical reactions and is thus poisonous. When heated it rapidly oxides to arsenous oxide, which has a garlic odour. Arsenic and some arsenic compounds can also be sublime upon heating, converting directly to a gaseous form. Elemental arsenic is found in two solid forms; yellow and grey metallic, with specific gravities of 1.97 and 5.73 respectively (Garba *et al*.,2010). The most toxic of arsenic compounds are those in which the element lost all its three 4p electrons,that is when it exist in the +3 oxidation state (As^{3+}). One of the major mechanism by which Arsenic exerts its toxic effect is through an impairment of cellular respiration by inhibition of various mitochondrial enzymes and the uncoupling of oxidative phosphorylation. The level of arsenic in natural waters varies between land2 mg/L. Concentrations may be elevated however, in areas containing natural sources value as high as 12 mg/L have been reported.

Chromium is one of those heavy metals whose concentration steadily increases due to industrial growth, especially the development of chemical and tanning industries. Cement producing plants and potential source of atmospheric chromium particulate that are deposited on land and water;and are eventually carried out to river by runoff water (DanAzumi and Bichi, 2010). Other Industrial sources of chromium include wastewater from chrome plating, metal finishing industries and textile industries. Other sources of chromium permeating the environment are air, water erosion of rocks, power plants on liquid fuels, brown and hard coal, industrial and municipal waste (Fatoki, 2003).

Cadmium is a by-product in the production of zinc and lead and the pyrometallurgy production of Zinc (Zn) is the most important anthropogenic source to the environment. Other major sources are fossil fuel combustion and waste incineration (Su and Wong,2003). Cadmium is used in a wide spectrum of applications including alloys, pigments, metal coatings, batteries and in the electronic industry. It is also a contaminant in chemical fertilizer, manure and sewage sludge (Ademoroti, 1996a; Ademoroti, 1996b; Ladigbolu and Balogun, 2011).

Nickel is a ubiquitous heavy metal and occurs in soil, water, air and in the biosphere. The average content in the earth's crust is about 0.008%. Farm soils contain between 3 and 1000 mg nickel/kg. Levels in natural waters have been found to range from 2 to 10 μg/L (fresh water) and from 0.2 to 0.7 μg/L (marine). Atmospheric nickel concentrations in remote areas range from <0.1 to 3 ng/m^3. Nickel from various industrial processes and other sources finally reach wastewater. Residues from wastewater treatment are disposed of by deep well injection, ocean dumping, land treatment and incineration. Effluents from wastewater treatment plants have been reported to contain up to 0.5 mg nickel/L. International Agencies havelegalised the allowed concentration of heavy metals in both domestic and industrial products and effluents (Ayodele and Gaya, 1994; Ladigbolu and Balogun, 2011).

The EU Directive 94/62/EC (amended by 2004/12/EC) on Packaging Waste sets out a maximum limit of 100 mg/kg for all Pb, Cd, Cr (VI), Cd and Hg in packaging materials. This limitation must be controlled for polymeric packaging materials and to calculate a possible heavy metal enrichment provoked by recycling processes of organic polymers. World Health Organisation sets a tolerance limit of 0.05, 0.05, 0.01, 0.05, 0.05, 1.0, 5.0 and 0.3 ppm for Mn, Pb, Cd, Cr, Ni, Cu, Zn and Fe in drinking water respectively. The Federal Environmental Protection Agency of Nigeria (FEPA) approved a maximum tolerance limit of 1.0, 1.0, 1.0, 5.0,

20 and 1.0 ppm for Pb, Cr, Cu, Mn, Fe and Zn for industrial effluents respectively (Galadima and Garba, 2011).

2.5 The Implication of Soils and Plants Polluted by Heavy Metals

The fate of various metals in the natural environment is of great concern particularly near mine sites, dumps, tailing piles and impoundments including urban areas and industrial centres. Soil, sediment, water and organic materials in these areas may contain higher than average abundances of heavy metals (Adriano, 1986). In order to estimate the effects and the potential risks associated with elevated elemental concentrations in soils, resulting from mineral deposits and anthropogenic activities, the fraction of the total elemental abundances in water, sediment and soil to the bioavailable amounts in soil need to be identified (Adriano, 1988).

Bioavailability is the proportion of total metals that are available for incorporation into the biota. The total metal concentrations do not necessarily correspond with metal bioavailability (Davies, 1994). The extent of bioavailability is largely controlled by elemental speciation, which determines the solubility of heavy metals in soils. A number of soil testing methods and partial or sequential chemical extraction techniques and methods are used to determine elemental behaviour (Elder, 1999).

Bioavailability of metals released from deposits is very complex and depends on many interrelated chemical, biological and environmental processes. These processes may vary overtime and among micro - organisms, plants and animals. Field and laboratory studies of some

particular sites using soil, plants and selective chemical extraction methods may enhance understanding of this concept which is of environmental concern (Joel*et al.,* 2001).

Okoronkwo *et al.* (2006) carried out a study on the risk and health implications of metals pollution of soils of urban Umuahia, capital of Abia State in Southern Nigeria presently used for cultivation of crops for crop production. The results of the analyses showed that there was heavy metal contamination of the soils of the flooded area. They concluded that there is higher risk of exposure to heavy metal as a result of the plant uptake of these toxic elements, this makes the use of polluted soils for agricultural purposes to be environmentally risky. Of all the five toxic elements studied, Okoronkwo *et al.* (2006) stated, the highest mean concentration ($mgkg^{-1}$)of 133.74 ± 10.60 for Pb followed by Cr (22.27 ± 3.03), Ni (8.14 ± 0.33) and As (5.97 ± 0.32) in the soils of urban Umuahia, capital of Abia State in Southern Nigeria presently used for cultivation of crops, while the least mean concentration of 1.64 ± 0.11 was recorded for Cd.

The toxic elements were examined for dependency upon some soil factors through the use of correlation analysis. Sand, organic matter and effective cation exchange capacity (CEC) correlated significantly and positively with Cr and Pb, indicating that these factors largely control the concentration of these elements in soils.

Abdulmojeed and Abdulrahman (2011) carried out analysis of heavy metals in vegetables from some cultivated irrigated gardens in Kano metropolis, Nigeria. Using atomic absorption spectrophotometry (AAS), the concentrations of Cr, Co, Cu, Ni, Pb and Zn were determined in four deferent vegetables, including, spinach, okra, onions and tomatoes, grown in effluent irrigated fields at Sharada, Kwakwaci and Jakara in Kano metropolis, Nigeria. Similar vegetable samples from another irrigated fields at Thomas Dam, in the remote part of Kano,

were used as control. Samples were collected during the dry and rainy seasons of 2011. The mean level of the metals obtained ranged widely from 0.28mg/kg Cr to 18.89 mg/kg Zn. Samples from Jakara garden had the highest mean level of Co (1.14±0.17mg/kg), Cu (7.50 ± 1.08 mg/kg), Zn (18.89 ± 1.93 mg/kg) and Cr (0.85 ± 0.10 mg/g), while those from Sharada recorded the highest levels of Ni (2.02 ± 0.35 mg/kg) and Pb (1.60 ± 0.53 mg/kg). Comparison of the results with the control showed significant levels ($P < 0.05$), onall the metals analyzed in the vegetable samples obtained from the effluent irrigated gardens at Kano, Nigeria, were within the National Agency for Food and Drug Administration and Control (NAFDAC) tolerable limits of 40 mg/kg for Cu, 2.0 mg/kg for Pb, 2.7 mg/kg for Ni, 50 mg/kg for Zn in fresh vegetables.

Chowdhury *et al*. (2010) carried out the assessment of the phytoavailable Cd, Pb and Zn using various extraction procedures. The phytoavailability of cadmium, lead and Zinc in the soils from Bangladesh was assessed. The uptake by *Ipomea aquatica and Oryza sativa* was measured and a range of extractants tested on the soils and plant tissue samples. The results of the study suggested that agricultural soils of Bangladesh in the vicinity of different industrial areas were at risk of heavy metal contamination/pollution. There was a strong correlation between the extractable metal fractions and the metal content in plants, which indicated the phytoavailability of the heavy metals. The assessment of the phytoavailability of the elements considered in this study was found to be dependent on the method of extraction, the crop and metal species, as well as the soil type. The present study indicates that a mild extractant such as 1M HCl can be used to assess the phytoavailability of the heavy metals Cd, Pb and Zn.

Sharma *et al.* (2005) determined the level of heavy metals in vegetables and soil of agricultural fields of Kathmandu valley, Kathmandu, Nepal.From the study the highest accumulation of copper was (65.5 mg/kg), lead 146.75 mg/kg) and cadmium (2 mg/kg) from

Shankhamul; nickel (29.25 mg/kg) from Nakhu; cobalt (15.25 mg/kg) and manganese (675 mg/kg) from Balkhu; chromium (73.75 mg/kg) from Banasthali; zinc (162 mg/kg) and iron (75636 mg/Kg) from the soil in Khusibun agricultural fields. The highest level of accumulations of Cu, Co and Zn were recorded in spinach and Pb in red radish; Ni, Cr and Fe was recorded in broad leaf mustard and the highest level of Mn in cress leaf. Concentration of non-essential but toxic metal like Pb were higher than the level in plants from unpolluted soil (0.1-10 mg/Kg) in all the vegetables (except potato) collected from the different sampling sites.

The seven steps sequential extraction method, developed for the analysis of heavy metals in soil, was applied to two hundred and thirty four soil samples covering the area of the Henan Province representative agricultural soil. On the average, the order of cadmium in each fraction was exchangeable (27.3%) > weakly bound to organic matter (22.7%) > strongly bound to organic matter (16.4%) > residual (15.1%) > carbonate (12.1%) > Fe-Mn oxide bound (4.5%) > Water soluble (2.0%). For Zn it was residual (66.3%) > Fe-Mn oxide bound (10.9%) > weakly bound to organic matter (9.4%) > exchangeable (6.0%) > strongly bound to organic matter (3.9%) > carbonate (2.9%) > water soluble (0.6%). The accuracy of the sequential extraction was judged by the relative error (RE). RE for cadmium ranged from 0 to 45% with mean 16.3%. RE for Zinc ranged from 0.1 - 11.4% with mean 3.4%. On the average, bioavailability index (BI) for cadmium and zinc was 39.1% and 9.0% respectively. The mobility of the elements in the order Cd > Zn (Sherifat *et al*., 2008).

Seasonal variation in the physiochemical properties and concentration of the heavy metals in road side soil in Yauri, Kebbi, were determined during the two major seasons of Nigeria in 2007/2008. The ranges of the levels of heavy metals obtained using atomic absorption spectrophotometer were 1.15 - 3.14, 0.14 - 7.0,1.64 - 22.36, 4.86 - 29.30, 2001 - 8091, 351.6 -

843.3, 35.9 - 306.7, and 79.6 - 202.4 μg/g for As, Cd, Cr, Cu, Fe, Ni, Pb and Zn in the dry season and not detected level(ND) – 13.04 μg/g, ND - 7.02, ND - 13.79, 0.99 - 23.72, 748 - 6000, 201.13 - 507.10, 24.00 - 316.14 and 33.84 - 131.06 μg/g for the wet season respectively. It was revealed that there were strong correlations between the dry and wet season values for all the metals with exception of Ni. Generally, higher mean heavy metal concentrations were recorded in the soil during the dry season than in wet season. In both the wet and dry seasons most of the heavy metals were above the natural heavy metals concentrations for surface soil, and calls for concern (Yahaya *et al*., 2009).

An assessment of the seasonal variations in concentrations of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in soil and crops from a farm near the refuse dump site of Obafemi Awolowo University, Ile-Ife, Nigeria in 2005/2006 was carried outand the soil from landfill in the wet and dry seasons have accumulated levels of Cd, Cu, Fe, Ni, Cr, Zn, Co and Pb being higher than the normal levels for a typical agricultural soil; but As (3.20 and 4.13 mg/kg) was found to be within the acceptable range while Mn values of 597.00 - 828.37 mg/kg was slightly above the background levels. The study showed that the highest concentrations of As (8.31 mg/kg), Cr (9.00 mg/kg) and Ni (40.00 mg/kg) in *Manihot esculenta* leaves; Cu (25.0 0 mg/kg) and Fe (176.00 mg/kg) in *Xantosoma mafaffa* tuber; Cd (14.50 mg/kg), Co (22.50 mg/kg), Mn (189.50 mg/kg), Pb (680.00 mg/kg) and Zn (440.59 mg/kg) in *Talinum triangulare*. In general, the levels of the heavy metals in the studied soil and crops were higher in the dry season than in the wet season (Oluyemi *et al*., 2008).

Shridast *et al.* (2010) investigated the soil pollution in downstream area of a landfill, in relation to changes in soil chemical characteristics and heavy metals concentrations. The landfill was located in the southwest of Babol, North of Iran. The soil samples were taken at three depths

(0 - 30, 30 - 60, 60 - 90 cm) from different locations; upstream (control), around and downstream of the landfill, in thedry and wet seasonsof the year. Samples were analyzed by atomic absorption spectrophotometry for Cd, Ni, Pb, Fe and Mn concentrations. Although in the soil Vadose zone, heavy metals were found to be in their typical and normal ranges and within the background concentrations, these concentrations were higher in wet season. Variation in the concentration with depth suggests movement of the heavy metals either from the leachate or from the naturally present sources of minerals in the soil.

Speciation of Cu, Cd, Pb, Ni, Zn, Mn, Fe, Cr and Hg was carried out on soil of Agbabu, Nigeria, with a sequential extraction procedure in the dry (March) and rainy (August) seasons of year 2008, using atomic absorption spectroscopy. Hg was not detected in any of the five geochemical fractions considered. In the dry season, Cr (37.13%) was mostly abundant in the exchangeable fraction, Zn (44.87%) was mostly abundant in the fraction bound to Iron and manganese oxides, Cu (51.33%) was mostly abundant in the fraction bound to organic matter and sulphide and the remaining metals were mostly abundant in the residual fraction.

In the rainy season, Cr (36%) was mostly abundant in the exchangeable fraction and Zn (46.80%) was mostly bound to the Iron and manganese oxides while the remaining metals were mostly abundant in the residual fraction. From the results of the two seasons, most of the metals had high abundance in residual fraction indicating lithogenic origin and low bioavailability of the metals considered. The average potential mobility was calculated for the metals in the two seasons giving the following order: Zn > Cr > Cu > Mn > Cd > Fe > Ni > Pb > Hg (Olanipekun *et al.*, 2010).

Concentrations of Cd, Hg, Pb, Cr, Fe, Co, Ni, Cu, Zn, Mo and As were determined in the soils and leaves of plants from refuse dumpsites and background soils in two cities, a municipality and a rural community in Ghana, using a ThermoFinnigan Element 2 high resolution inductively coupled plasma mass spectrometric (HR-ICP-MS) instrument. The refuse dump soils were classified between 'uncontaminated to moderate' and 'strongly contaminated'. Pollution levels for Cd (Igeo = 2.06 – 2.40) and Zn (Igeo = 2.95 – 3.36) were higher than that of the other metals. The refuse dump soil from the rural community was the least polluted with the stated metals. Fe and Ni loads in plants from the refuse dump soils in the cities and the municipality were beyond the normal ranges of 40–500 μg/g (Fe) and 0.02–5.00 μg/g (Ni). Transfer ratios for Cd, Hg, Cu, Zn and Pb and Fe of plants from the background soils were higher than those from the refuse dump soils, which might be due to the higher levels of organic matter, pH, phosphate, Ca and Mg in the refuse dump soils (Agyarko *et al*., 2010).

2.6 Chelation of Heavy Metals

Chelates are chemicals that form soluble, complex molecules with certain metal ions, inactivating the ions so that they cannot normally react with other elements or ions to produce precipitates or scale. A soil extractant is a solution made of solvent and a certain concentration of chemicals to extract nutrients from soil into solution. A soil test requires an extractant to determine the amount of plant nutrients in the soil. Chelates can be used as soil extractants as they extract soil nutrients and hinder them to precipitate. A comparison of the expected stability of a number of chelates under a variety of soil conditions was made by Sommers and Lindsay (1979). They reported that the common chelating agent EDTA (ethylenediaminetetraacetic acid), HEDTA (hydroxyethylethylenediamine-triacetic acid), NTA (nitrilotriacetic acid), and EGTA

(ethyleneglycol- bis(2-aminoethylether)tetraacetic acid) would have potential as chelating agents to extract microelements and heavy metals under most expected soil conditions.

However the choice among the chelating agents is extremely difficult because they have usually been evaluated under widely incomparable conditions. The incentive to adopt a new extractant is based on the analysis of saving time and cost. Multiple-element extractants may enable determination of other plant nutrients at little additional cost, thereby possibly improving the diagnostic value of soil testing. Results have indicated that chelating agents play an important role in overcoming the rate-limiting steps of solution and adsorbed phase diffusion which are mainly responsible for the movement of ions in alkaline and calcareous soils. Gupta and Mittal (1981) conducted an experiment to evaluate various extractants. They reported that the order of extractability by different extractants was 6N HCl > 0.1N HCl > EDTA $(NH4)_2$ CO_3> EDTA NH_4OAc > DTPA+ $CaCl_2$> 1M $MgCl_2$. They suggested that the use of 0.1N HCl would be much cheaper than DTPA and other extractants.

CHAPTER THREE

3.0 MATERIALS AND METHODS

The apparatus, equipment and reagents used for this study are listed in Appendix I. All the reagents used are of analytical grade.

3.1 Preparation of Stock Solutions

3.1.1 Arsenic solution of concentration 1000mgL^{-1}

This was prepared by dissolving 1.022 g of As_2O_5 in 5.00 cm^3 of water then 25.00 cm^{3}concentrated HNO_3 was added and made up to the 1000.00 cm^3 mark in a volumetric flaskusing distilled water to give 1000.00 mgL^{-1} arsenic solution.

3.1.2 Cadmium solution of concentration 1000mgL^{-1}

The solution was prepared by dissolving 2.744 g $Cd(NO_3)_2.4H_2O$ in 5.00 cm^3 concentrated HNO_3. The solution was then made up to 1000.00 cm^3 with distilled water in a volumetric flask giving 1000.00 mgL^{-1} cadmium solution.

3.1.3 Copper solution of concentration 1000mgL^{-1}

This was prepared by dissolving 3.803 g of $Cu(NO_3)_2.3H_2O$ in 5.00 cm^3 concentrated HNO_3 and made up to the 1000.00 cm^3 mark in a volumetric flask using distilled water to give 1000.00 mgL^{-1} copper solution.

3.1.4 Lead solution of concentration 1000mgL^{-1}

This was prepared by dissolving 1.599 g $Pb(NO_3)_2$ in distilled water and made up to the 1000.00cm^3 mark in a volumetric flask using distilled water to give 1000.00 mgL^{-1} lead solution.

3.1.5 Zinc solution of concentration 1000mgL^{-1}

This was prepared by dissolving 1.244 g of ZnO in 5.00 cm^3 of water then 25.00 cm^3 concentrated HNO_3 was added and made up to the 1000.00 cm^3 mark in a volumetric flask using distilled water to give 1000.00 mgL^{-1} Zinc solution.

3.1.6 Manganese solution of concentration 1000mgL^{-1}

This was prepared by dissolving 4.058 g $MnSO_4.4H_2O$ in 5.00 cm^3 of water, 1.00 cm^3 concentrated H_2SO_4 was then added and the solution made up to the 1000.00 cm^3 mark in a volumetric flask using distilled water to give 1000.00 mgL^{-1} manganese solution.

3.2 Description of the Study Area

Kogi State is found in the North Central region of Nigeria, it occupies 29,833 square kilometre, it lies on $7^0$30`N and $6^0$42`E, it has 21 of Nigeria's 774 Local Government Areas and share common borders with the Federal Capital Territory (Nigeria) to the north, Nasarawa State to the North East, Benue State to the east, Enugu State to the South East, Anambra State to the South, Edo State to the South West, Ondo and Ekiti States to the West, Kwara State to the North

West and Niger State to the North. It is popularly called the confluence state because the confluence of River Niger and Benue is at its capital, Lokoja, which is the first administrative capital of modern-day Nigeria. The sampling area is depicted in plate 3.1 and plate 3.2.

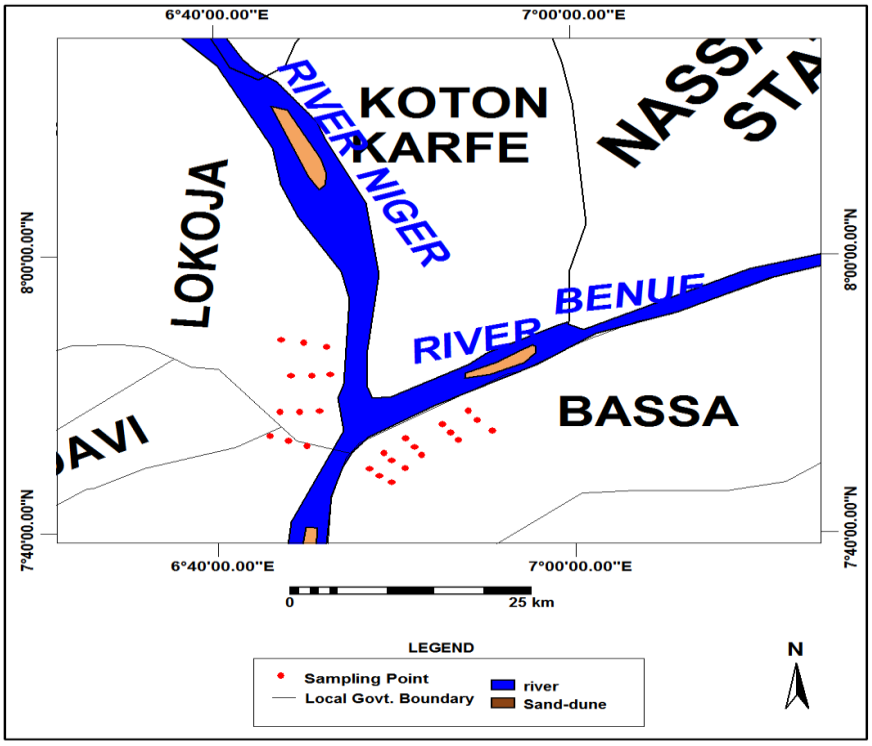

Plate 3.1: Site Map



Plate 3.2: The Two Rivers Approaching Confluence

3.3 The Sources of the Two Rivers

River Niger is the principal river of West Africa, extending about 4,180km. Its drainage basin is 2,117,700km^2 in area. Its source is in the guinea highlands in south eastern Guinea, it runs in a cresent through Mali, Niger, on the border with Benin and then through Nigeria meeting with the River Benue. It is the third-longest river in Africa, exceeded only by the Nile and the Congo River

The River Benue previously known as Chadda River or Tchadda is the major tributary of the Niger River. The river is approximately 1,400 kilometres long and almost entirely navigable during the summer months. It rises in the Adamawa Plateau of northern Cameroon, from where it flows west, and through the town of Garoua and Lagdo Reservoir, into Nigeria, south of the Mandara mountains, and through Jimeta, Ibi and Makurdi before meeting the Niger at Lokoja.

3.4Sample Collection

The river side soils for total metal determination were collected from the bank of River Niger, River Benue and beyond the confluence point at 0-15cm and 15-30cm depth (plate 3.3). The collection site was 50m away from the bank of the river and each point of collection was 10m away from the other (n=60).

Another set of soil samples (0-30cm) were collected at the dry season 50 m from the river bank (n=10) for pot culture experiment to determine the amounts of Cd, Cu, Mn, Ni, Pd and Zn absorbed by *Amarantus hybridus* and *Corchorus olitorius L*.

Soil sample for control experiment were collected from a farmland far away from the two riverssince this part is not affected by water from the river.



Plate 3.3: Sample Collection

The collected soil samples were placed in labeled polythene bags, and then taken to the laboratory for treatment and analysis. The sample collection was done for both the dry(March 2013; January 2014) and the early rainy seasons(June 2013and May 2014).

3.5 Pot Culture Experiment for the Plants

In order to study the phytoavailability of the Cd, Cu, Mn, Ni, Pd, Zn in the two plants, seeds of spinach(*Amarantus hybridus*) and jute (*Corchorus olitorius L*.)were planted separately on 5 kg of the soil in pots having no hole at the bottom. Three seedlings per pot after germination were plant cultured (watered twice a day, weeded manually, exposed to sunlight and with adequate plant protection measures). The pot culture experiment was carried out in a glass house at Crop Protection Department, Institute of Agricultural Research, Ahmadu Bello University, Zaria, Nigeria (plate 3.4). They were uprooted after six (6) weeks. Identification of the plant was done at the Herbarium of the Department of Biological Sciences, Ahmadu Bello University, Zaria, Nigeria. This was carried out in the Month of August 2014. The *Amarantus hybridus*was identified with Herbarium number; V/no.: 2400 and *Corchorus olitorius L*. with Herbarium number; V/no.: 2649.

3.6 Pre – Treatment of the Soil and Plant Samples

Soil samples from each site were homogenised in an agate mortar and pestle and then air dried overnight in circulating air in an oven at 30°C.It was then sieved through a 2 mm sieve. The sieved soils were placed in polythene bags and ready for analysis.



Plate3.4: Pot Culture Experiment for the Plants

The Plant samples(*Amarantus hybridus* and *Corchorus olitorius L*.) were properly rinsed with tap water and then with distilled water to remove any attached soil particles, they were then cut into smaller portions and then placed in large clean crucible where they were oven dried at 100°C for 48 h in order to remove moisture. The dried plant samples were ground into fine particles using a clean acid-washed agate mortar and pestle.

The glasswares were washed with liquid soap, rinsed with distilled water and then soaked in 10% HNO_3 solution for 24 h (Todorovi *et al.,* 2001). The wares were then rinsed with plenty distilled water and later dried in a Memmert drying oven at 80°C for 5 h.

3.7 Characterization of the Soil Collected from the Riverside

To ascertain the percentage composition of the soil types, known weight (1.00 kg) of the soil samples were prepared and weighed.

3.7.1 Measurement of the physico-chemical parameters of the soil samples

The following are the physicochemical properties that were measured in the soil samples collected from the confluence point at Lokoja in March, 2013, June, 2013; January, 2014 and May, 2014.

3.7.1.1*Determination ofpH*

To 20.00 g of a dried soil weighed into a 50.00 cm^3 beaker, 20.00 $cm^3$of distilled water was added. The mixture was then stirred with a glass rod and allowed to stand for 30 minutes. A pre-calibrated, Hanna pH meter (model H1991000) was then inserted into the slurry and the pH taken (Uba *et al.*, 2008).

3.7.1.2 *Determination of electrical conductivity*

To 25.00 g of the air-dried soil sample placed in a 250.00 cm^3 beaker, distilled water was added slowly and drop wise on the entire surface in a uniform pattern, until the soil appeared wet. A stainless steel spatula was then used to form a homogeneous soil paste. The beaker was then covered with a Petri – dish and 50.00 cm^3 of distilled water added, the mixture was shaken for 1 h. After this 40.00 cm^3 of the diluted extract was placed into 100.00 cm^3 beaker and the electrode of the conductivity meter inserted to the extract to record the electrical conductivity of the soil (Wilcox, 1950).

3.7.1.3*Determination of colourof the soil*

Riverside soil samples were determined using Munsell charts, where the soil sample in one hand travels through the chart to find the colour that matches the soil colour. Then the soil sample must be placed behind the apertures of the chart in order to find the most similar colour chip.

3.7.1.4*Organic carbon*

The organic carbon content of the collected soil sample was determined by wet oxidation method of Walkley and Black. In this method, organic carbon was oxidised by $K_2Cr_2O_7$ in the presence of H_2SO_4 leading to the formation of CO_2 according to equation 3.1 below:

$$2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2 \quad \ldots\ldots 3.1$$

$$3C + 3O_2 \rightarrow 3CO_2 \quad \ldots\ldots 3.2$$

The soil samples were sieved using a 0.50 mm sieve after which they were weighed in duplicate and transferred to a 250.00 cm^3 Erlenmeyer flask. Exactly 10.00 cm^3 of 1.00M potassium heptaoxodichromate(VI) was pipetted into each flask and swirled gently to dispose the soil followed by the addition of 20.00 cm^3 concentrated sulphuric acid. The flask was then swirled gently until the soil and reagents were thoroughly mixed. The mixture was allowed to stand for 30 minutes on a glass plate. Then100cm^3 of distilled water was added followed by addition of 3 to 4 drops of ferroin indicator, after which it was titrated with 0.50M ferrous sulphate solution. A blank titration was similarly carried out.

The percentage organic carbon is given by the equation:

$$\frac{meK_2Cr_2O_7 - meFeSO_4 \times 0.003 \times 100 \times F}{Mass(g)\ of\ soil\ (dried\ soil)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.3$$

F = Correction factor (1.33)

me = Molarity of solution transferred x ml of solution used

$$\%Organic\ matter\ in\ soil = \%Organic\ carbon\ x1.729 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.4$$

3.7.1.5*Determination of particle size distribution of the soil samples*

A 50.00 g sieved soil sample was placed in a 250.00 cm^3 plastic beaker, 100.00 cm^3 of 50% sodium hematophosphate (calgon) solution was then added to the soil mixture and stirred with a glass rod. After which 100.00 cm^3 of distilled water was added to the mixture, the mixture was stirred and allowed to stand for 30 min with occasional stirring. The mixture was then transferred into a 250.00 cm^3 plastic container and shaken on a mechanical shaker for 10 minutes and then into 1000.00 cm^3 measuring cylinder and made up to mark with a hand plunger and hydrometer. The temperature readings were taken after 40 seconds and 8 h respectively.

A blank consisting 0% calgon in 100.00 cm^3 of distilled water was made, it was then diluted to 1000.00 cm^3in a measuring cylinder and the hydrometer and temperature readings taken (Bouyocos, 1951).

$$\%Clays = \frac{(corrected\ 8\ hours\ reading - blank) \times 100}{Weight\ of\ soil\ sample\ taken} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

$$\%Silt = \frac{(corrected\ 40\ \text{sec}.\ readings - blank) \times 100 - \%clay}{Weight\ of\ soil\ sample\ taken} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.6$$

$$\%Sand = 100 - (\%Clay + \%Silt) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.7$$

$$Corrected\ readings\ (^{g}/_{l}) = (R - R_1) + 0.36 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.8$$

R = Hydrometer reading of soil suspension

R_1 = Balance readings

0.36 g/l is added to soil suspension readings for every degree above 20^0C

3.7.1.6*Determination of the textureof the soil samples*

Soil texture refers to the relative proportion of sand, silt and clay in a soil sample. Clay size particles are the smallest being less than 0.002 mm in size, while silt is the medium, between 0.002 and 0.05 mm in size. The largest particle is sand with diametres between 0.05 for fine sand, to 2.00 mm for very coarse sand. Based on the above values, the samples were classified according to the International System of Textural Classification (Jaiswal *et al*., 2004)

3.7.1.7*Determination of the cation exchange capacityof the soil*

A 10.00 g amount of the soil sample was weighed into a 100.00 cm^3 plastic beaker, 40.00 cm^3 of 1.00 $moldm^{-3}$ ammonium acetate solution (pH 7) was added and the suspension

was stirred with a glass rod and left overnight. The mixture was then filtered with light suction using 55 mm Buchner funnel (coning size No.40).

The residue from the filtration was leached with four 25.00 cm^3 portions of 1000 mol/dm^3 NH_4Cl solution (pH 7) and 25.00 cm^3 portion of a 0.25 $moldm^{-3}$ NH_4Cl (pH 7). The solution was discarded and the electrolyte was washed out of the sample with 150.00 cm^3 ethanol. The sample was then allowed to drain completely and leached gradually with acidified NaCl to a volume of 250.00 cm^3. A 50.00 $cm^3$of 2.00 v/v% boric acid was measured into a 250.00 cm^3 conical flask and 3 drops of the mixed indicator added. The leachate was distilled over the boric acid. 1.50Mammoniumborate distillate was titrated with standard 0.10 $moldm^{-3}$ HCl (Black, 1965).

$$CEC(C\ {}^{mol}\!/_{kg}) = \frac{(Titre - Blank) \times M \times 100}{Weight\ of\ sample\ (g)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.9$$

M = Molarity of acid

3.7.1.8*Determination of moisture content of the soil*

A 1.00g sieved soil sample collected from the river bank was weighed into a dry crucible. The crucible was then placed in an air circulated oven at 105^oC and dried to constant weight (for 6 h). The samples were cooled in desiccators and re-weighed. The percentage air - dried moisture from the lost weight was then calculated as follows (Uba, *et al.*,2008).

$$\%moisture\ content = \frac{loss\ in\ weight \times 100\,\%}{initial\ weight} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.10$$

3.8Digestion of Soil Samples

The samples of soil were digested in order to carry out heavy metal analysis on them using the method of Ogunfowokan *et al*. (2009). Each 1.0 g sample of the soil sample was digested in a Teflon cups with 30 cm^3 aqua-regia ($HCl:HNO_3$, 3:1) on a thermostatted hotplate at 150^0C. After about 2 h of digestion, the Teflon cup with its content was brought down from the hot-plate to simmer. Then, 5 cm^3HF was added to the mixture and heated further for 30 min. The Teflon cup with its content was then allowed to cool to room temperature and filtered. After which the filtrate was quantitatively transferred into 50 cm^3 volumetric flask and made to the mark with distilled water.

3.9 Calibration Curves for Determining the Concentrations of Heavy Metals

Six working standards were prepared in triplicates for each metal by serial dilution of the stock solution prepared in 3.1. These standards and the blank solution were aspirated in a PG–990 atomic absorption spectrophotometer. Then the absorbance from the calibration curves versus the corresponding concentrations of the metal in the samples were obtained.

A blank determination was carried out on distilled water without the sample. Then the As, Cd, Cu, Hg, Pb, Mn, and Zn concentrations in the samples were determined using Atomic Absorption Spectrophotometer (AAS) AA240FS, Varian, in 2014 at Ahmadu Bello University Multi-user Science Research Laboratory.

3.10Determination of EDTA-Extractable Heavy Metals in the Soil Samples

The experiment to determine the amount of the phytoavailable heavy metals in the soil was carried out, since this amount correlate with the bioavailable form of metal, which may subsequently circulate in the food chain.

A 20g amount of the 2mm sieved soil samples collected from Lokoja in May 2014 was put in twenty 100 cm^3 plastic bottles (n = 10), 40cm^3 of 0.05M ethylenediaminetetraacetic acid

(EDTA) solutions was then added and the bottles screw capped tightly. The mixture was then shaken on a mechanical shaker at 120 revolutions per minutes for two hours. The suspension was filtered using a Whatmann no. 2 filter paper. Then the level of Cd, Cu, Mn, Ni, Pd and Zn were determined using Atomic Absorption Spectrophotometer (AAS).

3.11 Digestion ofthe Plant Samples

The plant samples harvested after six weeks from the pot experiment conducted in the procedure 3.4.2 were digested according to Awofolu (2005). A 0.5 g dried plant sample each of *Amarantus hybridus*and *Corchorus olitorius L*was weighed into 100 cm^3 beaker, to this a mixture of 5 cm^3 concentrated HNO_3 and 2 cm^3 $HClO_4$ was added and digested at low heat ($<100^0C$) using a hot plate until the content was about 2 cm^3. The digest was allowed to cool and then filtered into 50 cm^3 standard flask. The beaker was then rinsed with about 2 cm^3 of distilled water using a washed bottleand then filtered into 100 cm^3 volumetric flask and made up to 20cm^3 mark. Each digest was carried together with the blank in triplicate for thedetermination of As, Cd, Cu, Mn, Pb and Zn contents using Atomic Absorption Spectrophotometer (AAS).

3.12AAS Determination of Metal Concentrations

3.12.1 Wavelength, current, burner height and slit width of measurement

Air-acetylene flame was used for the Atomic Absorption Spectrophotometer analysis. The characteristic wavelength of absorption of each metal used in the analysis and other instrumental parameters are given in Table 3.1

Table 3.1: Instrumental Parameters Used in the Spectrometer

Metal	Wavelength (nm)	Lamp current (mA)	Gas Mixture (2300°C)	Flow rate (l/min)	Slit width (mm)	Burner height(mm)
As	336.5	5	Acetylene	2.3	5	4
Cd	324.8	3	Acetylene	2.3	3	4
Cu	228.8	4	Acetylene	4.0	4	4
Mn	279.5	8	Acetylene	2.3	3	4
Pb	283.3	5	Acetylene	1.5	7	5
Zn	213.9	3	Acetylene	2.4	5	4

3.12.2 Steps employed in spectrophotometre measurement

1. Thecell holder was checked to be sure it was empty.
2. The spectrophotometer was turned on using the power switch on the left side of the back of the instrument.
3. The spectrophotometer was allowed to warm up for 30 minutes.
4. A/T/C was pressed to select the absorbance or %transmittance mode.
5. The wavelength was set to the desired value. Holding the key down will cause the wavelength to change more quickly.
6. The blank was inserted into the cell holder with the clear walls of the cuvette to the front and back of the instrument. The sample compartment was closed. The blank was used to zero absorbance readings due to imperfections in the cuvette and for the absorbance of light by the medium or carrier solution. The procedure used will contain specific instructions about the composition of the blank.
7. 0 ABS/100%T was pressed to blank the instrument.
8. The blank was removed from the cell holder, the sample inserted, and the sample compartment closed.
9. The instrument reading was recorded.
10. The sample was then removed from the sample compartment.

3.13 Determination of the Pollution Indices of the Farmland Soils

3.13.1Geoaccumulation indices (Igeo)

This allows for the assessment of metal contamination through a comparison of the metal concentration in the contaminated soil with its concentration prior to contamination (Loska *et. al*., 1997). Given as

$$Igeo = \log_2(\frac{C_n}{1.5Bn}) \quad \text{.....3.11}$$

where Cn is the measured mass fraction of the metal (mg/kg). Bn is the background mass fraction of the metal (mg/kg). The Chinese Environmental Protection Administration (CEPA) environmental background values was used to calculate Igeo in accordance to Wang *et al.*, (2007). Muller's evaluation method (Muller, 1969) was used to evaluate the level of heavy metal contamination in the soils collected from the farmland near River Niger and Benue in Lokoja in March 2013, June 2013, January 2014 and May 2014, as shown on Table 3.2.

3.13.2Bioaccumulation factor (BF)

Bioaccumulation factor for each of the metals, Cd, Cu, Mn, Ni, Pb and Zn would be calculated using the formula:

$$BF = \frac{C_{plant}}{C_{soil}} \quad \text{.....3.12}$$

where C_{plant} and C_{soil} represents the heavy metal concentration in extracts of plants and soils on dry weight basis, respectively.

The BF would help to ascertain the extent of contamination

Table 3.2 Classification of Geoaccumulation Index

Geoaccumulation index	Classification	Level of contamination
5＜I geo≤10	6	Extremely serious
4＜I geo≤5	5	Strong to extremely serious
3＜I geo≤4	4	Strong
2＜I geo≤3	3	Moderate to strong
1＜I geo≤2	2	Moderate
0＜I geo≤1	1	Light to moderate
I geo≤0	0	Non contamination

3.14 Statistical Analysis

3.14.1Students t-test

The variation in the levels of the metals accumulated in the soil and plant with respect to the timeof the year when the samples were collected was assessed using Students' t-test at $P < 0.01$.

3.14.2 Pearson correlation

The relationship between the levels of the metals in the soil in relation to the uptake amounts in the plants*Amarantus hybridus*and *Corchorus olitorius L*was assessed using Pearson correlation.

3.14.3 Analysis of variance (ANOVA)

This was used to evaluate the difference in the heavy metal uptake by *Amarantus hybridus*and *Corchorus olitorius L*.at $P < 0.01$. It was carried out using Microsoft Excel 2010.

CHAPTER FOUR

4.0 RESULTS

4.1 Physicochemical Parameters and Heavy Metal Contents of Riverside Soil of River Niger and Benue across the Seasons

Table 4.1a presents the physicochemical properties of the soils collected from River Niger, Benue and after the confluence points and the total concentrations of Cd, Cu, Mn, Ni, Pd and Zn in the soil samples collected during the dry (March) season of 2013.

Table 4.1b shows the physicochemical properties of the soils collected from River Niger, Benue and after the confluence points and the total concentrations of Cd, Cu, Mn, Ni, Pd and Zn in the soil samples collected during the early wet (June) season of 2013.

Table 4.1c highlighted the physicochemical properties of the soils collected from River Niger, Benue and after the confluence points and the total concentrations of Cd, Cu, Mn, Ni, Pd and Zn in the soil samples collected during the dry (January) season of 2014.

While, Table 4.1d presents the physicochemical properties of the soils collected from River Niger, Benue and after the confluence points and the total concentrations of Cd, Cu, Mn, Ni, Pd and Zn at different depths in the soil samples collected during the early wet (May) season of 2014.

4.2: Permissible Limits of Heavy Metals in Soils and Plant

Table 4.2 contain permissible limits of heavy metals in soils and plant that will be compared to the values gotten from this analysis to ascertain the level of contamination of both soil and plant samples.

Table 4.1a: Physicochemical Parameters and Heavy Metal Contents of Riverside Soil of River Niger and Benue in the Dry Season of 2013

Soil property	N soil (mg/kg)	B soil (mg/kg)	CR soil(mg/kg)	CL soil(mg/kg)
pH	6.7	7.1	6.9	6.9
% sand	84	50	62	76
% clay	6	34	26	10
%silt	10	16	12	14
Textural Class	Loamy sand	Sandy clay loam	Sandy loam	Sandy loam
Organic Carbon (%)	0.239	0.958	0.563	0.852
Organic Matter (%)	0.413	1.652	0.821	1.364
Moisture Content(%)	78.20 ± 0.01	71.20 ± 0.10	64.10 ± 0.12	68.00 ± 0.03
Total Cd (mg/kg)	4.50 ± 0.0009	4.15 ± 0.0003	4.25 ± 0.0003	3.95 ± 0.0005
Total Cu (mg/kg)	18.80 ± 0.0004	12.00 ± 0.0005	17.20 ± 0.0003	12.80 ± 0.0005
Total Mn (mg/kg)	172.30 ± 0.0036	176.20 ± 0.0041	163.40 ± 0.0032	150.30 ± 0.0028
Total Ni (mg/kg)	187.50 ± 0.0004	177.00 ± 0.0005	187.50 ± 0.0004	185.00 ± 0.0005
Total Pb (mg/kg)	34.20 ± 0.0002	29.00 ± 0.0003	33.30 ± 0.0006	21.10 ± 0.000
Total Zn (mg/kg)	58.80 ± 0.0025	50.70 ± 0.0012	40.50 ± 0.0014	44.50 ± 0.0026

Table 4.1b: Physicochemical Parameters and Heavy Metal Contents of Riverside Soil of River Niger and Benue in the Early Wet Season of 2013

Soil property	N soil(mg/Kg)	B soil(mg/Kg)	CR soil(mg/Kg)	CL soil(mg/Kg)
pH	6.7	6.9	6.6	6.7

% sand	84	50	62	76
% clay	6	34	26	10
%silt	10	16	12	14
Textural Class	Loamy sand	Sandy clay loam	Sandy loam	Sandy loam
Organic Carbon (%)	0.278	0.935	0.547	0.825
Organic Matter (%)	0.406	1.673	0.839	1.350
Moisture Content(%)	85.40 ± 0.01	77.3 ± 0.10	69.2 ± 0.12	73.3 ± 0.03
Total Cd (mg/kg)	5.60 ± 0.0009	5.80 ± 0.0003	5.80 ± 0.0003	5.50 ± 0.0005
Total Cu (mg/kg)	14.00 ± 0.0004	17.20 ± 0.0005	13.90 ± 0.0003	15.00 ± 0.0005
Total Mn (mg/kg)	192.20 ± 0.0036	181.30 ± 0.0041	211.50 ± 0.0032	150.30 ± 0.0028
Total Ni (mg/kg)	250.00 ± 0.0004	218.70 ± 0.0005	281.00 ± 0.0004	250.00 ± 0.0005
Total Pb (mg/kg)	26.50 ± 0.0002	26.50 ± 0.0003	20.30 ± 0.0006	20.30 ± 0.000
Total Zn (mg/kg)	66.20 ± 0.0025	56.50 ± 0.0012	61.60 ± 0.0014	50.80 ± 0.0026

Table 4.1c: Physicochemical Parameters and Heavy Metal Contents of Riverside Soil of River Niger and Benue in the Dry Season of 2014

Soil property	N soil(mg/Kg)	B soil(mg/Kg)	CR soil(mg/Kg)	CL soil(mg/Kg)
pH	6.5	6.7	6.6	7.2
% sand	84	50	62	76
% clay	6	34	26	10
%silt	10	16	12	14
Textural Class	Loamy sand	Sandy clay loam	Sandy loam	Sandy loam
Organic Carbon (%)	0.239	0.958	0.563	0.852
Organic Matter (%)	0.473	1.602	0.721	1.263
Moisture Content	75.20 ± 0.01	73.20 ± 0.10	62.10 ± 0.12	67.20 ± 0.03
Total Cd (mg/kg)	5.80 ± 0.0009	6.40 ± 0.0003	6.40 ± 0.0003	7.30 ± 0.0005
Total Cu (mg/kg)	17.40 ± 0.0004	20.00 ± 0.0005	18.60 ± 0.0003	17.50 ± 0.0005
Total Mn (mg/kg)	183.20 ± 0.0036	187.70 ± 0.0041	209.40 ± 0.0032	208.20 ± 0.0028
Total Ni (mg/kg)	223.00 ± 0.0004	243.70 ± 0.0005	209.40 ± 0.0004	221.80 ± 0.0005
Total Pb (mg/kg)	32.70 ± 0.0002	23.50 ± 0.0003	32.90 ± 0.0006	30.50 ± 0.000
Total Zn (mg/kg)	74.00 ± 0.0025	60.20 ± 0.0012	61.40 ± 0.0014	62.50 ± 0.0026

Table 4.1d:Physicochemical Parameters and Heavy Metal Contents of Riverside Soil of River Niger and Benue in the Early Wet Season of 2014

Soil property		N soil(mg/Kg)	B soil(mg/Kg)	CR soil(mg/Kg)	CL soil(mg/Kg)
pH		6.7	6.5	6.5	6.4
% sand		84	50	62	76
% clay		6	34	26	10
%silt		10	16	12	14
Textural Class		Loamy sand	Sandy clay loam	Sandy loam	Sandy loam
Organic Carbon (%)		0.249	0.958	0.563	0.822
Organic Matter (%)		0.533	1.859	1.311	1.034
Moisture Content		81.20 ± 0.01	73.50 ± 0.10	68.10 ± 0.12	73.75 ± 0.03
Total Cd (mg/kg)	15cm	7.3 ± 0.0009	8.4 ± 0.0003	7.6 ± 0.0003	8.4 ± 0.0005
	30cm	3.3 ± 0.0007	4.2 ± 0.0004	3.0 ± 0.0005	3.4 ± 0.0004
Total Cu (mg/kg)	15cm	11.60 ± 0.0004	20.20 ± 0.0005	18.30 ± 0.0003	18.00 ± 0.0005
	30cm	10.20 ± 0.0003	18.70 ± 0.0013	19.40 ± 0.0004	17.50 ± 0.0004
Total Mn (mg/kg)	15cm	179.30 ± 0.0036	205.20 ± 0.0041	195.20 ± 0.0032	171.00 ± 0.0028
	30cm	176.30 ± 0.0032	201.10 ± 0.0039	193.30 ± 0.0035	170.00 ± 0.0030
Total Ni (mg/kg)	15cm	269.40 ± 0.0004	267.40 ± 0.0005	201.00 ± 0.0004	220.80 ± 0.0005
	30cm	262.90 ± 0.0005	211.70 ± 0.0003	206.70 ± 0.0005	210.40 ± 0.0007
Total Pb (mg/kg)	15cm	23.5 ± 0.0002	33.4 ± 0.0003	24.6 ± 0.0006	28.1 ± 0.0002
	30cm	23.5 ± 0.0003	32.2 ± 0.0003	25.1 ± 0.0005	28.0 ± 0.0004
Total Zn (mg/kg)	15cm	63.10 ± 0.0025	77.80 ± 0.0012	50.00 ± 0.0014	51.60 ± 0.0026
	30cm	61.7 ± 0.0030	74.1 ± 0.0021	48.7 ± 0.0021	50.0 ± 0.0010

Table 4.2: Permissible Limits of Heavy Metals in Soils and Plant

Elements	*Threshold concentration in soil (mg/kg) (EU, 2002)	**Background concentration in soil (mg/kg) (CEPA, 1995)	#Permissible value in plants (mg/kg) (WHO, 1996)
Ni	75	26.9	10
Cu	140	22.6	10
Zn	300	74.2	20
Pb	300	26	2
Cd	3	0.097	0.2
Mn	2000	63.2	300

4.3 Mean Concentration of Heavy Metals in Riverside Soil of River Niger, Benue and Confluence withEU Limit

Figure 4.1a, presents theCd concentrations in the soil of the studied area. Where Cd concentration of 8.4mg/kg was obtained in both B and CLsampling sites in theearly wet season of 2014 (May, 2014) as the highest concentration; and Cd concentration of 3.95 mg/kg at N sampling site in the dry season of 2013 (March, 2013) was the lowest Cd concentration,though this was higher than that of European Union Standardlimit of 3mg/kg Cd (EU 2002).

Figure 4.1b reportedthe copper content to be lower than that of European Union Standard limit (EU 2002) of 140mg/kg Copper had relatively low values ranging from 11.6 of the soil at N (early wet season of 2014) to 20.2mgkg^{-1} in B (early wet season of 2014).

As seen in Figure 4.1c, manganese concentration in the soil is generally higher than all the other metals recorded but it is generally lower than the European Union Standard limit of about 2000mg/kg (EU, 2002). It recorded the highest value (211.5 mgkg^{-1}) at CR of early wet (June) season of 2013 and the lowest (150.3 mgkg^{-1}) at CL of both dry (March, 2013) and early wet (June, 2013) season of 2013 (Figure 4.1c).

As presented in Figure 4.1d, Ni concentrations in the soil samples of the studied area of River Niger and Benue had the level in the soil being generally higher than theEuropean Union Standard limit (EU 2002) of 75mg/kg. The highest value (281 mgkg^{-1}) was at CR on the early wet (June) season of 2013 and the lowest (177.0 mgkg^{-1}) wasin the soil at B collected in the dry season (March, 2013) of 2013.

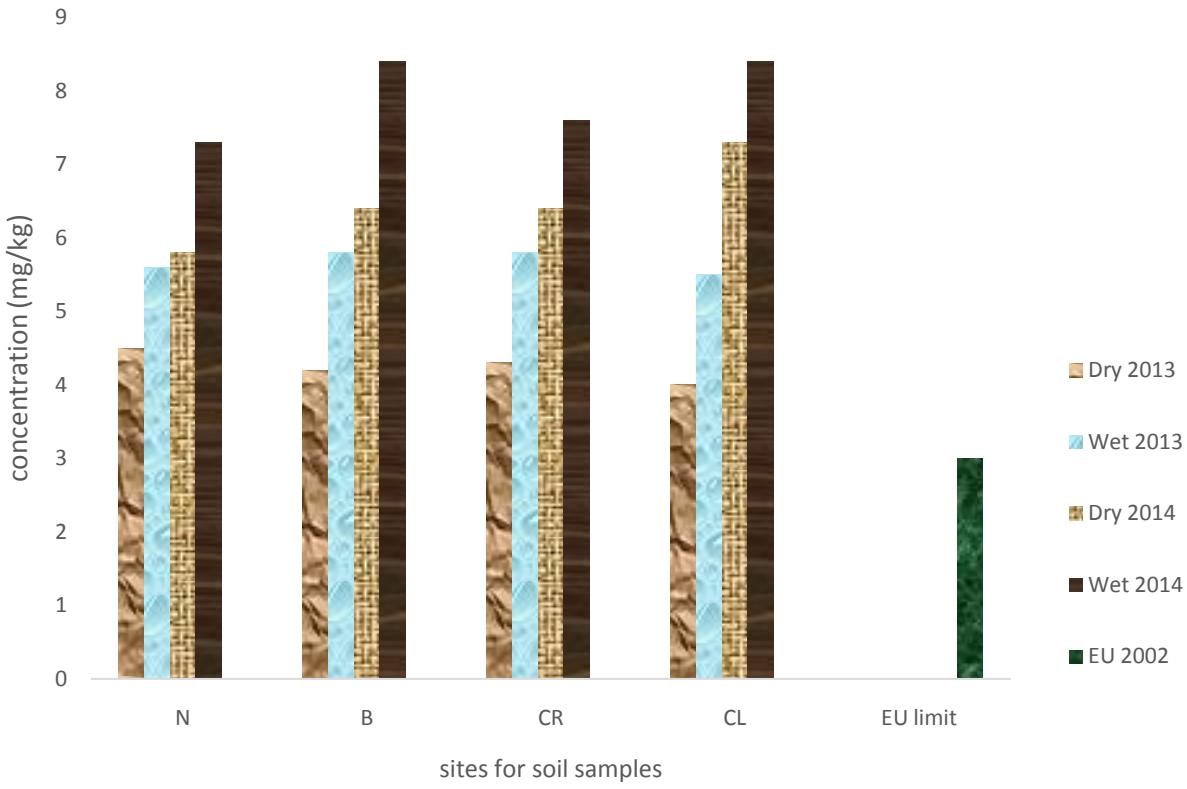

Figure 4.1a: **Mean Concentration of Cd in Riverside Soil of River Niger, Benue and Confluence withEU Limit**

Key

N = Niger riverside soil, B = Benue Riverside soil, CR = Right side soil after confluence,

CL = Left side soil after confluence, EU = limit as giving by EU, 2002 in figure 4.1a above.

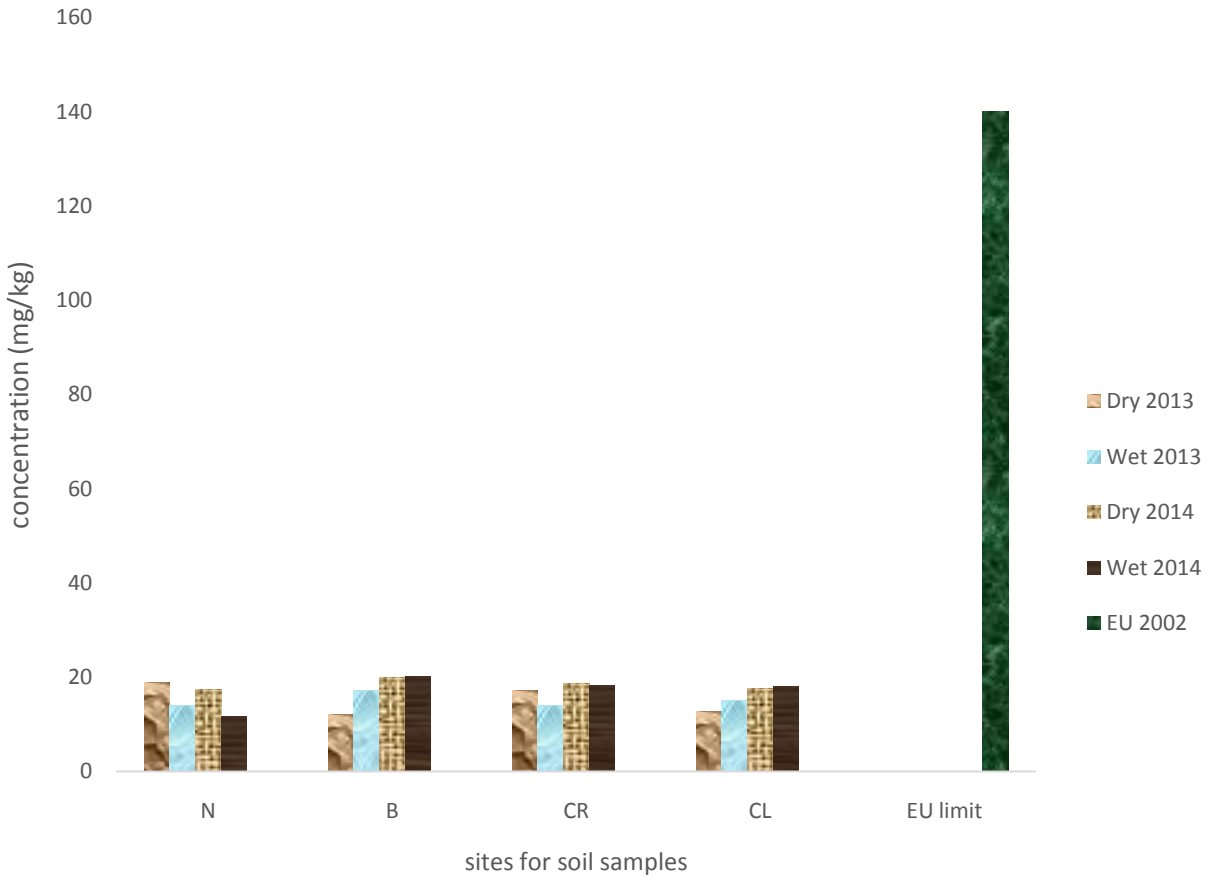

Figure 4.1b: **Mean Concentration of Cu inRiverside Soil of River Niger, Benue and Confluence withEU Limit**

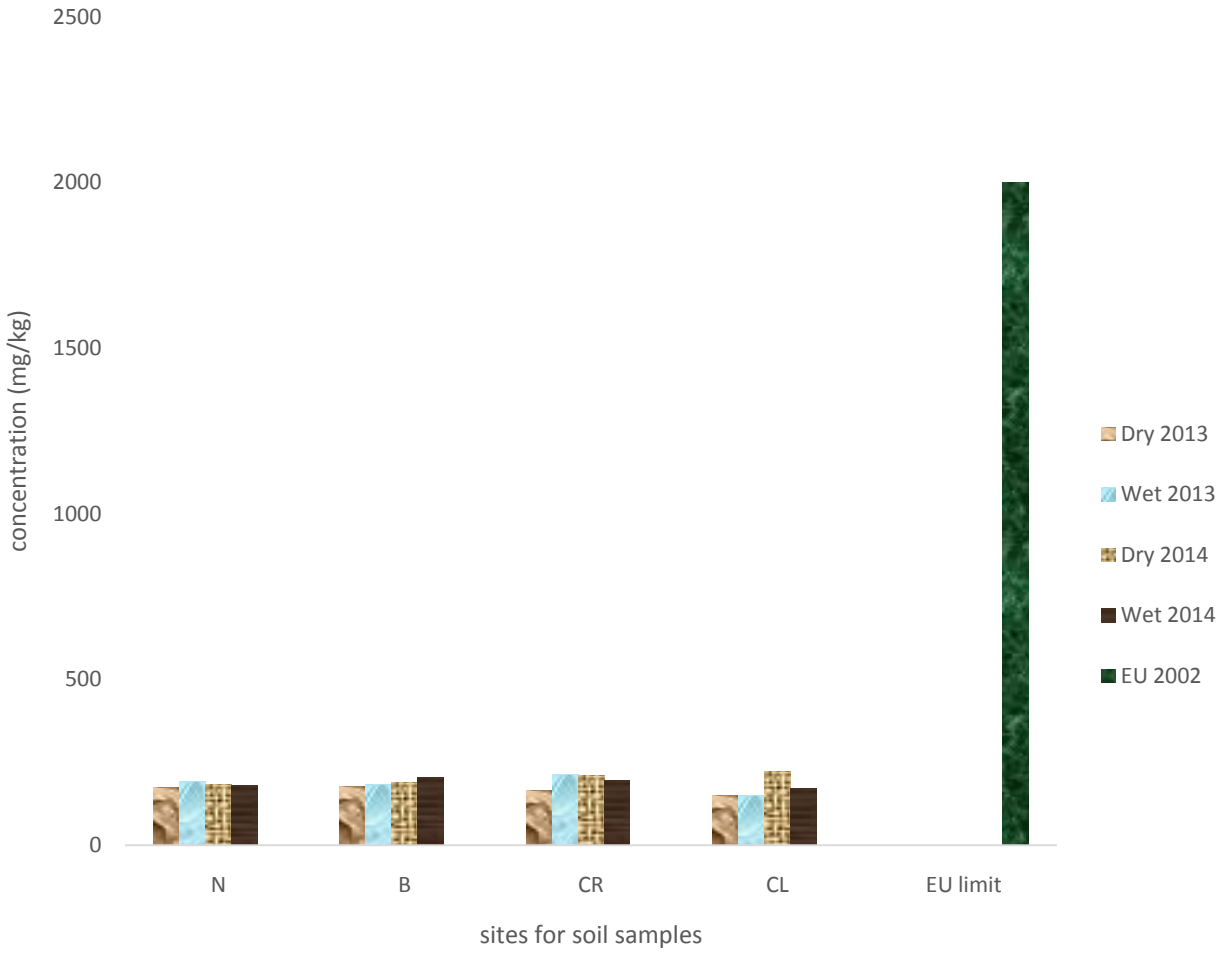

Figure 4.1c: **Mean Concentration of Mn inRiverside Soil of River Niger, Benue and Confluence withEU Limit**

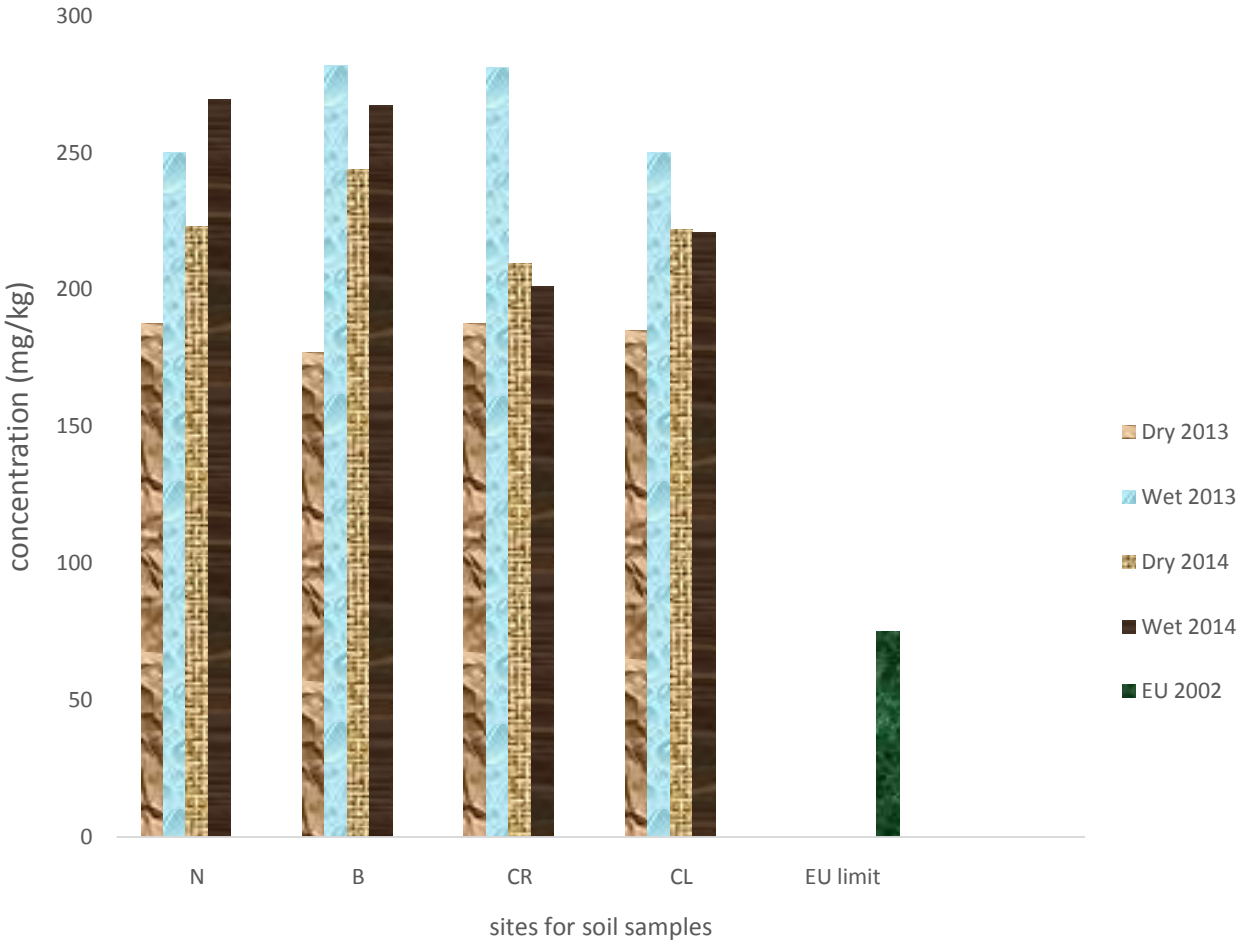

Figure 4.1d: **Mean Concentration of Ni inRiverside Soil of River Niger, Benue and Confluence withEU Limit**

Lead contents as depicted in Figure 4.1ewere found to record the highest (34.2mgkg^{-1}) level in the soil sample from N collected in the dry season (March, 2013)of 2013 and lowest at (20.3mgkg^{-1}) at both CR and CL during theearly wet (June, 2013) season of 2013. The value of Pb in the soil samples were generally low compared to the European Union Standard limit of about 300mg/kg(EU 2002).

Zn contents as presented in Figure 4.1f, indicated that the soil samples in CR of the dry (March) season in 2013 (40.5 mgkg^{-1}) was the lowest while the sample at B in theearly wet (May) season of 2014 (77.8 mgkg^{-1}) had the highest Zn concentration, Zn concentrations of the studied area of River Niger, Benue and beyond the confluence pointhad Zn amount being lower than the European Union Standard limit of 300mg/kg.

4.4 Geoaccumulation Index of theFarmland Soils

Table 4.3a presents the Geoaccumulation index for Cd, Cu, Mn, Ni, Pd and Zn in the soils collected from River Niger, Benue and after the confluence points during the dry (March, 2013) season of 2013.

Table 4.3b shows the Geoaccumulation index for Cd, Cu, Mn, Ni, Pd and Zn in the soils collected from River Niger, Benue and after the confluence points during the early wet (June) season of 2013.

Table 4.3c highlighted the Geoaccumulation index for Cd, Cu, Mn, Ni, Pd and Zn in the soils collected from River Niger, Benue and after the confluence points during the dry season (January) of 2014.

And Table 4.3d presents the Geoaccumulation index for Cd, Cu, Mn, Ni, Pd and Zn in the soils collected from River Niger, Benue and after the confluence points during the early wet (May, 2014) season of 2014.

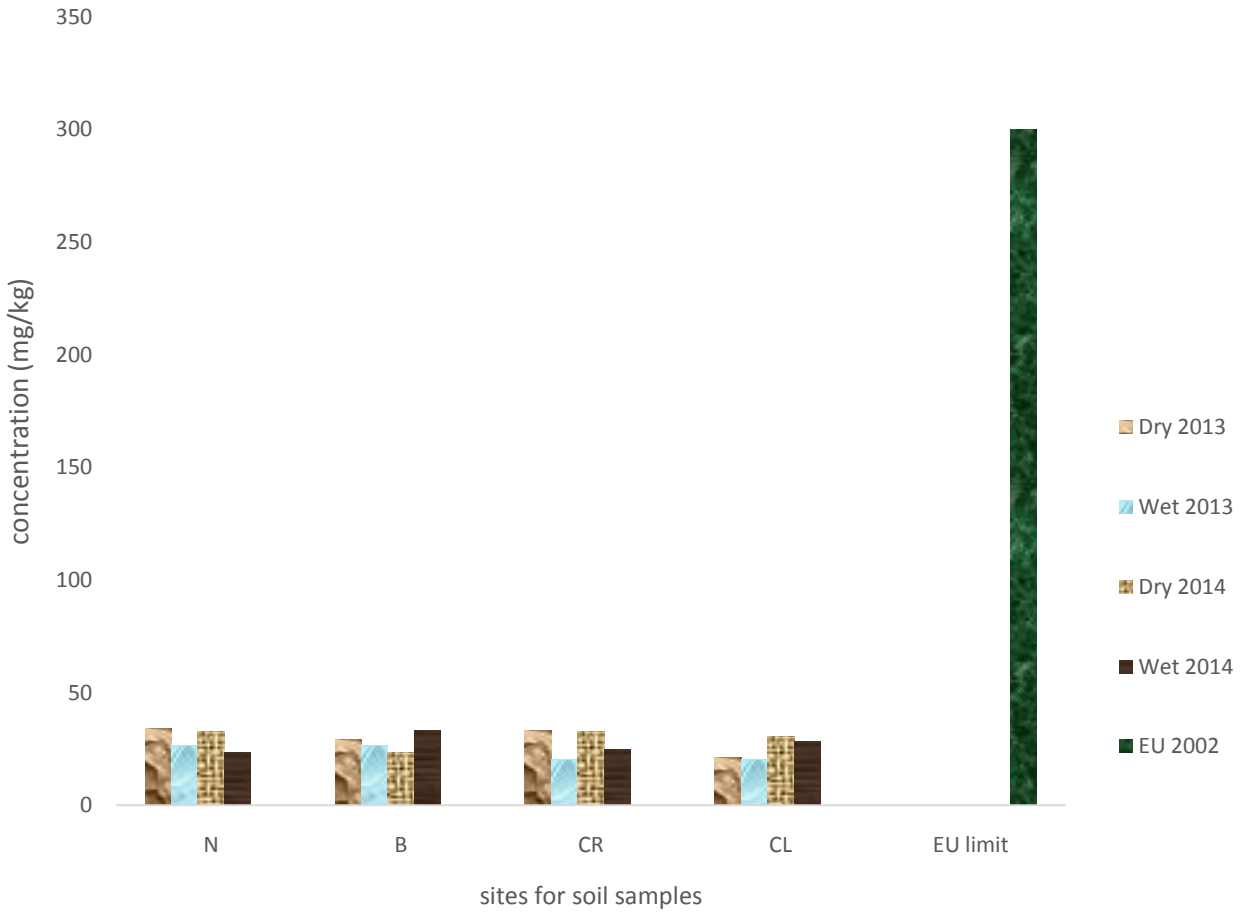

Figure 4.1e: **Mean Concentration of Pb inRiverside Soil of River Niger, Benue and Confluence withEU Limit**

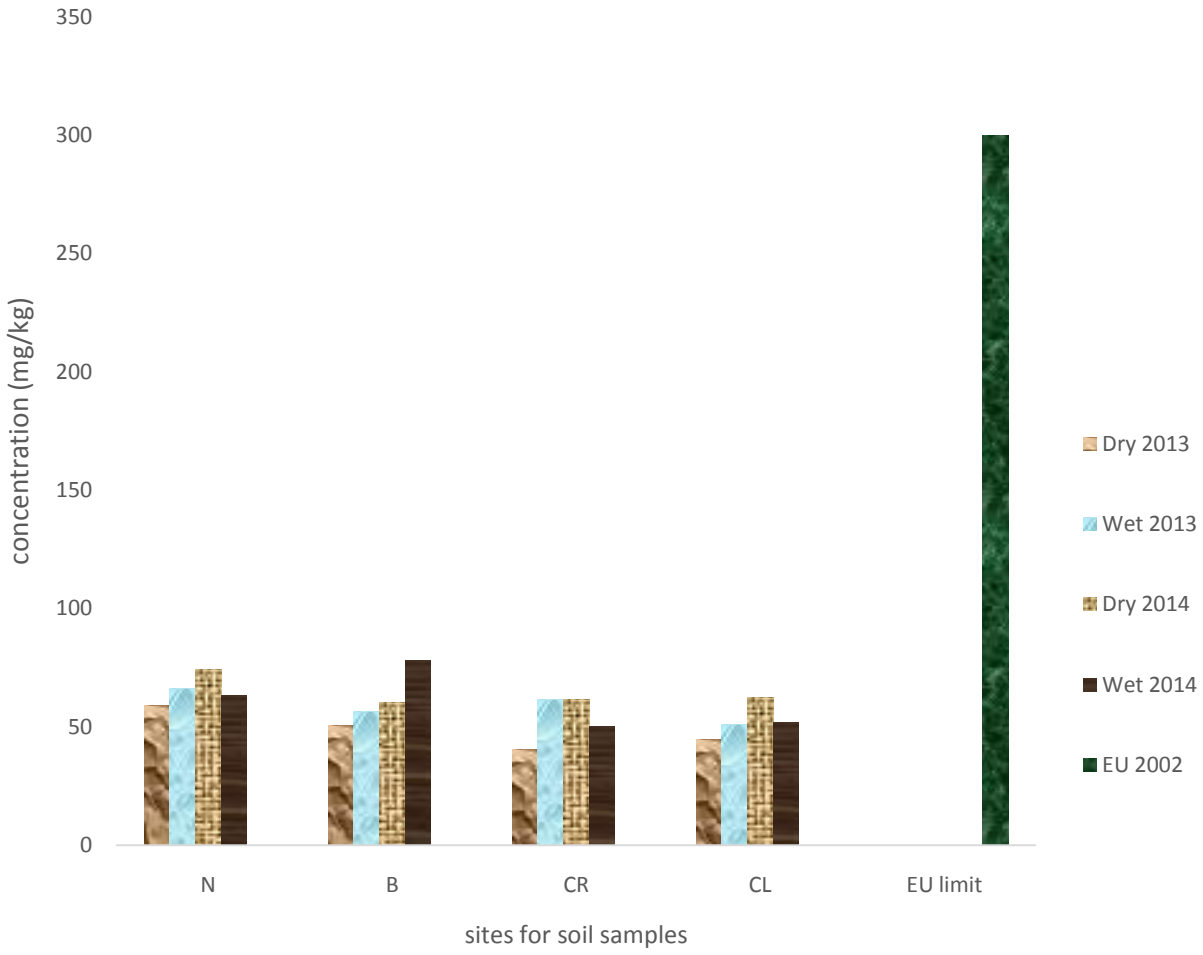

Figure 4.1f: **Mean Concentration of Zn inRiverside Soil of River Niger, Benue and Confluence withEU Limit**

Table 4.3a: **Geoaccumulation Index of theFarmland Soils Collected in the Dry Season of 2013**

Metal	N	B	CR	CL
Cd	4.949	4.832	4.868	4.763
Cu	-0.862	-1.514	-0.971	-1.395
Mn	0.864	0.895	0.782	0.678
Ni	2.217	2.137	2.217	2.195
Pb	-0.201	-0.434	-0.234	-0.889
Zn	-0.915	-1.120	-1.473	-1.321

Table 4.3b: **Geoaccumulation Index of theSoils Collected in the Early Wet Season of 2013**

Metal	N	B	CR	CL
Cd	5.266	5.315	5.315	5.240
Cu	-1.286	-0.971	-1.276	-1.184
Mn	1.021	0.933	1.157	0.678
Ni	2.632	2.438	2.799	2.632
Pb	-0.556	-0556	-0.943	-0.943
Zn	-0.761	-0.971	-0.863	-1.120

Table 4.3c: **Geoaccumulation Index of the Riverside Soils of River Niger and Benue Collected inDry Season of 2014**

Metal	N	B	CR	CL
Cd	5.317	5.458	5.458	5.648

Cu	-0.971	-0.761	-0.862	-0.943
Mn	0.948	0.985	1.144	1.137
Ni	2.467	2.594	2.378	2.459
Pb	-0.251	-0.737	-0.252	-0.358
Zn	-0.599	-0.889	-0.863	-0.836

Table 4.3d: **Geoaccumulation Index of the Riverside Soils of River Niger and Benue Collected in Early Wet Season of 2014**

Metal	N	B	CR	CL
Cd	5.649	5.851	5.707	5.851
Cu	-1.556s	-0.761	-0.889	-0.916
Mn	0.918	1.111	1.043	0.848

Ni	2.737	2.729	2.316	2.452
Pb	-0.737	-0.234	-0.666	-0.474
Zn	-0.811	-0.515	-1.152	-1.120

4.5 Heavy Metals Concentration in Farmland Soils beside River Niger, Benue and Confluence at Different Depths

Figure 4.2a-f depicts the results of the heavy metal concentration at the surface depth (15cm) of the riverside soils collected in May 2014 and the level at 30 cm depth. There were generally higher amount of Cd, Cu, Mn, Ni, Pd and Znin the soil at 15 cm depth than the sub-surface layers at 30 cm depth.

4.6 Result of t-test Analysis for Metal Ion Concentrations at 15cm and 30 cm Depth of the Soil Samples

Statistical test of significance using the Student t-test (Table 4.4) showed that there is no significant difference(95% level of confidence) in the concentrations ofCd, Cu, Mn, Ni, Pd and Znat 15cm and 30cm depth of the soil samples obtained from the river sides of River Niger, Benue and beyond the the confluence point in Lokoja-Nigeria for the samples collected in May, 2014.

4.7 Mean Concentration of EDTA Available Fractions for Heavy Metals in the Riverside Soils of River Niger and Benue Collected in May 2014

As shown in Table 4.5 and Figure 4.3, the percentage of the total amounts of heavy metal extracted in the soil by EDTA differ among elements. Lead was the highest extracted relative to the total metal content (58.7%), zinc (36.4%), copper (31.2%) nickel (24.2%), manganese (21.5%) and cadmium (15%).

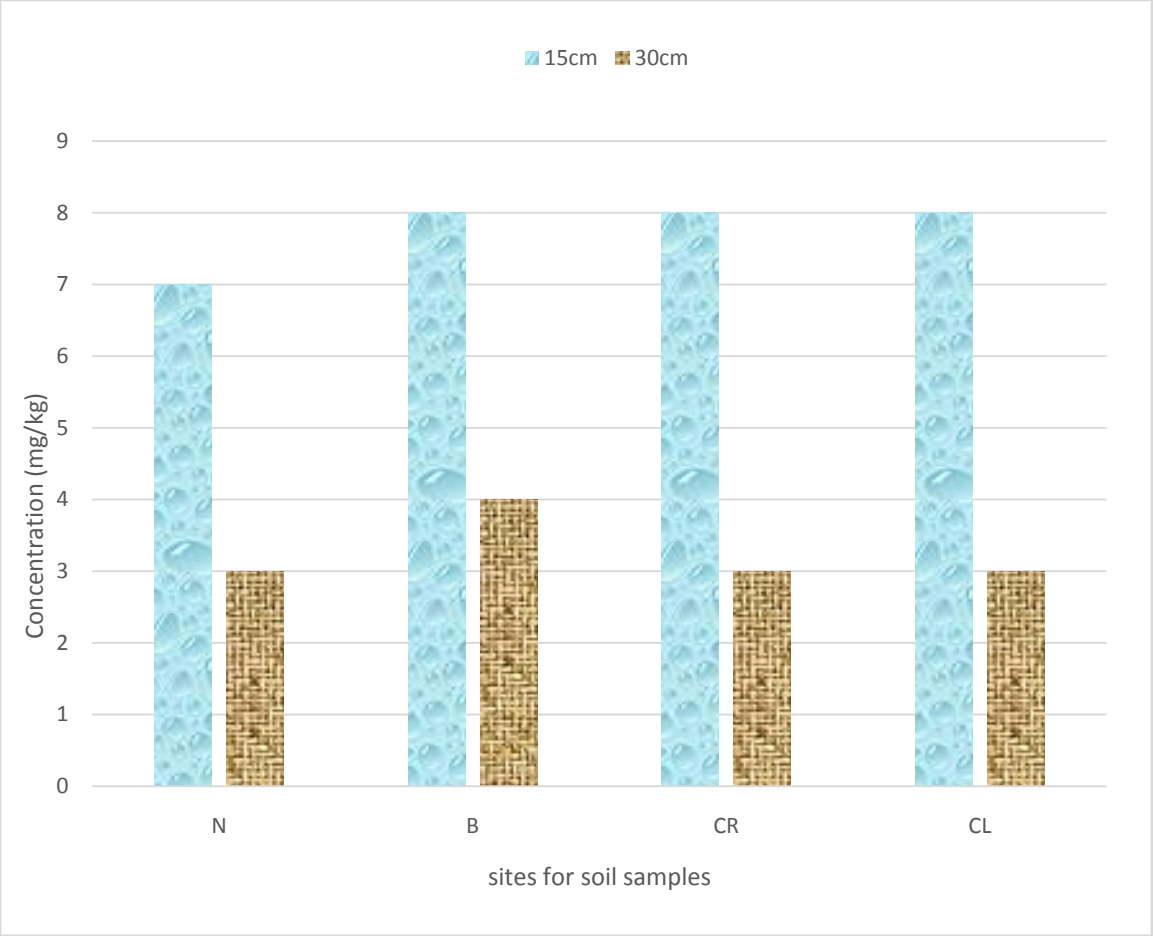

Figure 4.2a: CadmiumConcentration in Farmland Soils beside River Niger, Benue and Confluenceat Different Depths

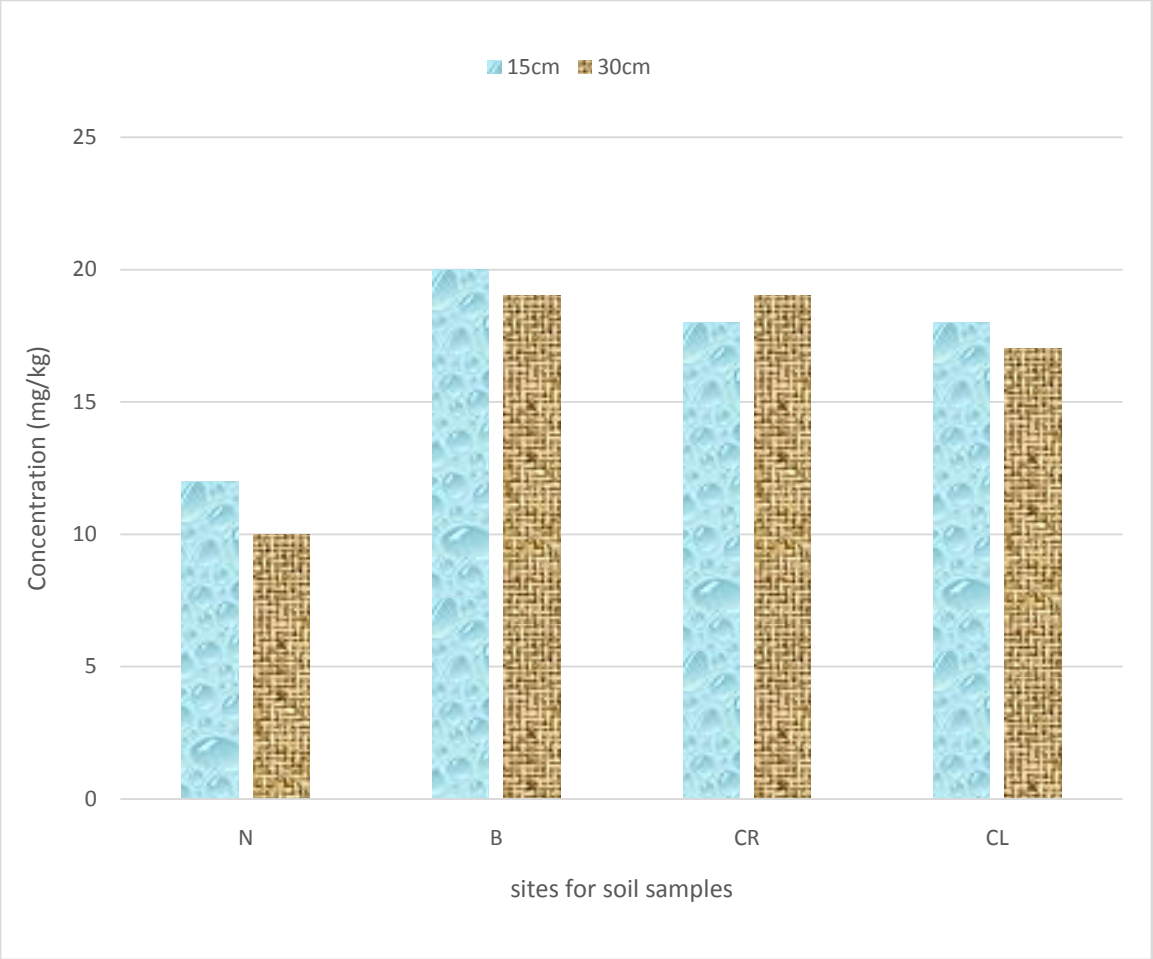

Figure 4.2b: CopperConcentration in Farmland Soils beside River Niger, Benue and Confluence at Different Depths

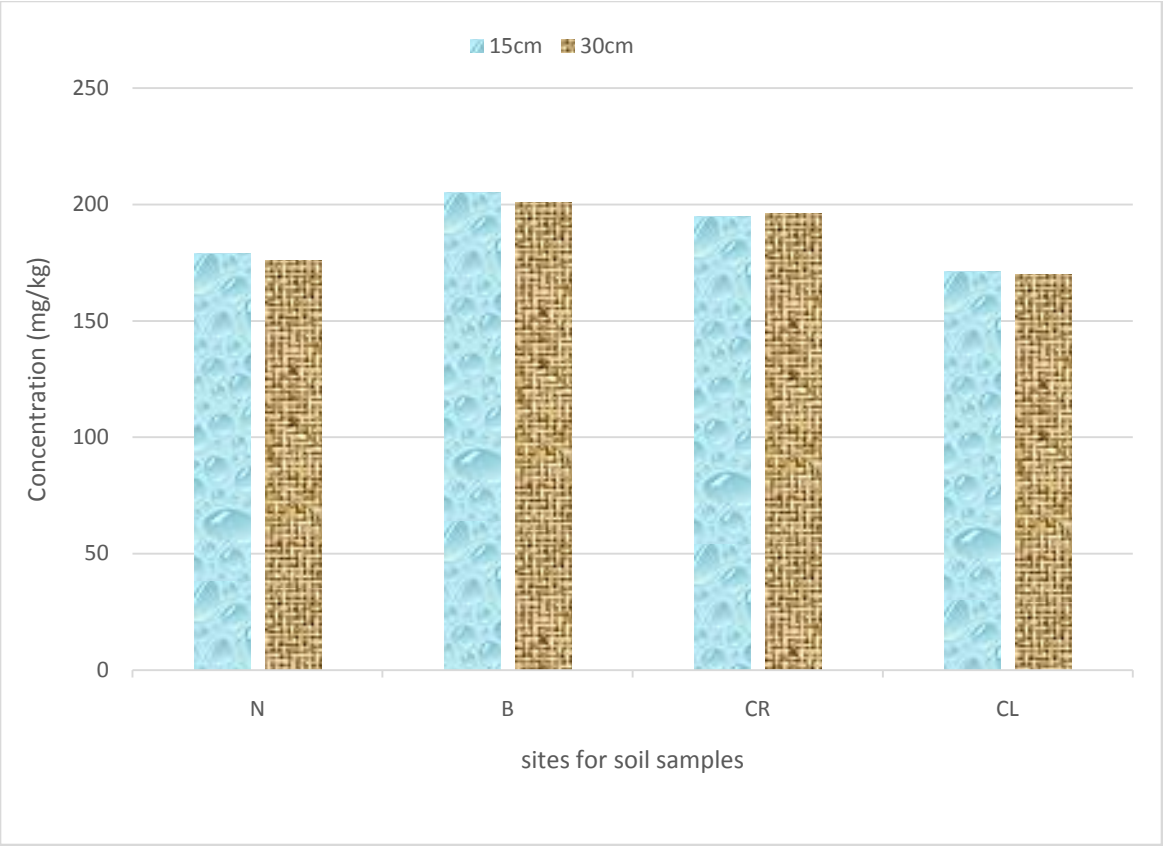

Figure 4.2c: Manganese Concentration in Farmland Soils beside River Niger, Benue and Confluence at Different Depths

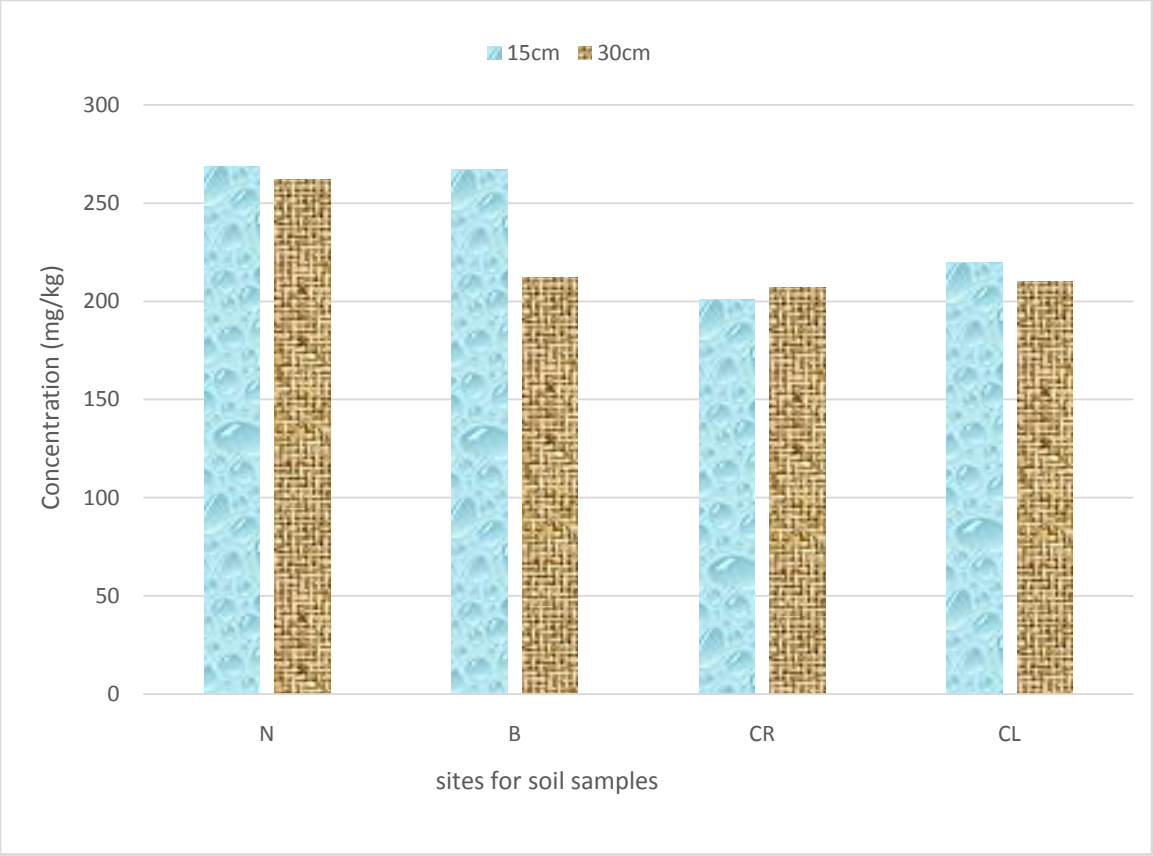

Figure 4.2d: NickelConcentration in Farmland Soils beside River Niger, Benue and Confluence at Different Depths

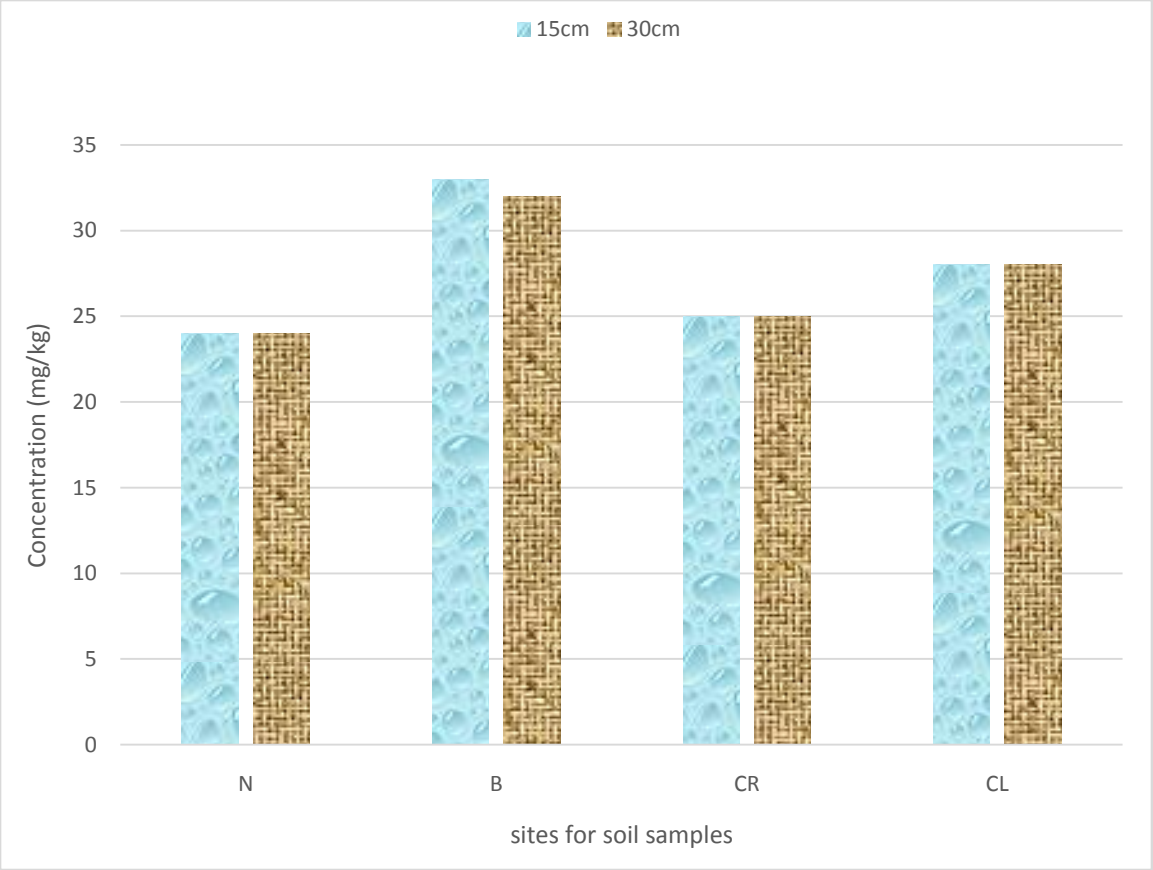

Figure 4.2e: LeadConcentration in Farmland Soils beside River Niger, Benue and Confluence at Different Depths

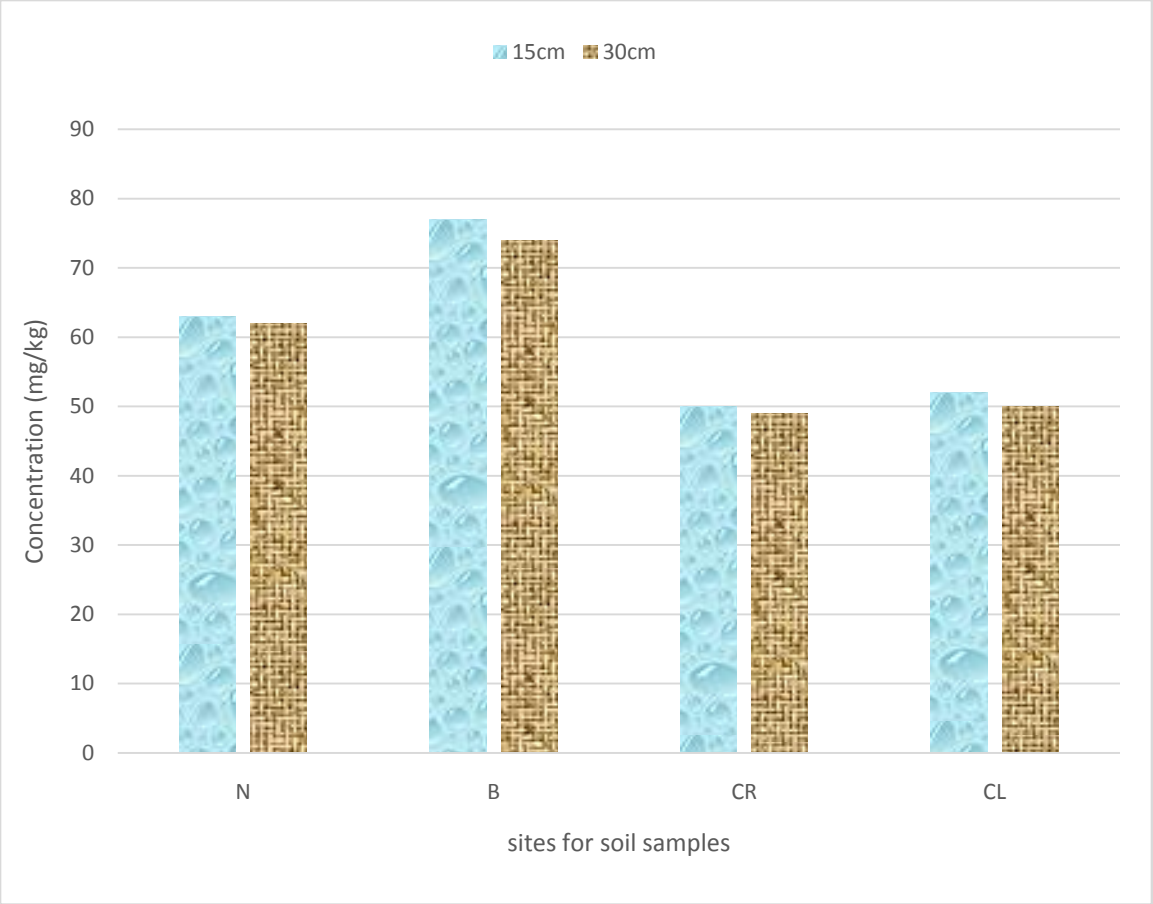

Figure 4.2f: ZincConcentration in Farmland Soils beside River Niger, Benue and Confluence at Different Depths

Table 4.4: Result of t-test Analysis for Metal Ion Concentrations at 15cm and 30 cm Depth of the Soil Samples

Metal	p-value	t-value
Cd	0.0003	3.1824
Cu	0.4099	3.1824
Mn	0.0338	3.1824
Ni	0.3016	3.1824
Pb	0.6156	3.1824
Zn	0.0392	3.1824

Table 4.5: Mean Concentration of EDTA Available Fractions for Heavy Metals in the Riverside Soils of River Niger and Benue Collected in May 2014

Metal	N (mg/kg)	B (mg/kg)	CR (mg/kg)	CL (mg/kg)	Control(mg/kg)	%total content
Cd	1.20±0.001	1.70±0.001	1.40±0.001	1.50±0.001	0.92±0.001	15
Cu	4.70±0.001	7.00±0.001	4.20±0.001	5.20±0.002	8.30±0.001	31.2

Mn	45.00±0.004	38.80±0.002	40.60±0.004	37.70±0.007	58.00±0.010	21.5
Ni	41.00±0.001	67.00±0.001	64.00±0.001	60.00±0.001	22.30±0.001	24.2
Pb	12.90±0.001	18.70±0.001	14.50±0.001	18.30±0.001	11.20±0.001	58.7
Zn	20.40±0.003	21.30±0.004	24.90±0.003	22.20±0.005	24.70±0.004	36.4

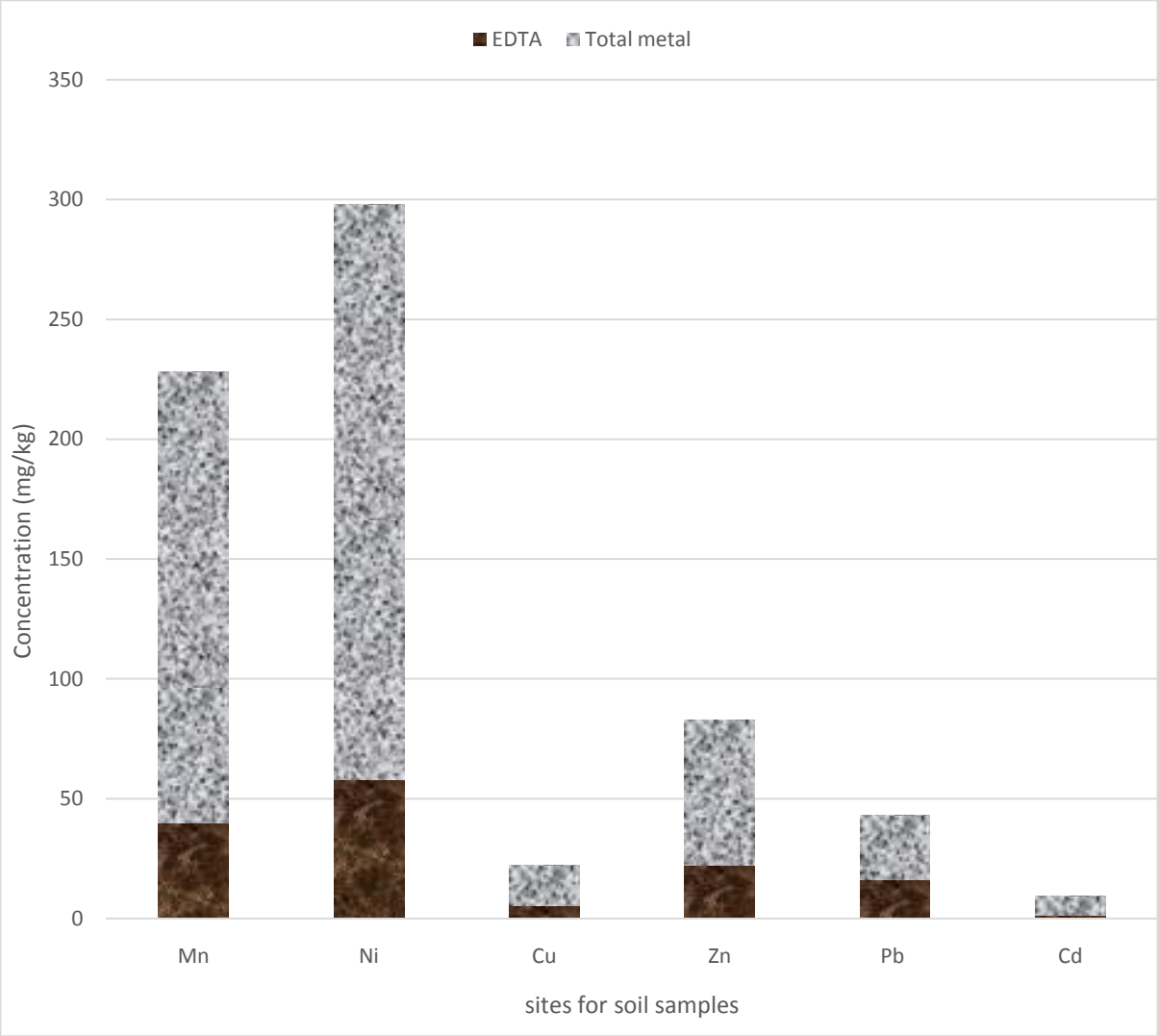

Figure 4.3 EDTA-Extractable Concentration of Heavy Metals in Soil versus the Total Metal Content in the Riverside Soilsof River Niger and Benue

4.8 Levels of Some Heavy Metals in*Amarantus hybridus*and *Corchorus olitorius L.* Planted in the Pot Experiment

The mean metal content in*A. hybridus* (mg/kg) as presented inTable 4.6a has Cd ranging from 1.0mg/kg in N and CR sites to 1.4 mg/kg in B and CL sites; Cu from 4.10mg/kg in CR to

6.00mg/kg in B; Mn from 30.60mg/kg in CL to 37.40mg/kg in N; Ni from 36.70mg/kg in CR to 51.20mg/kg in B site soil; Pb from 12.5mg/kg in N to 14.0mg/kg in CR; and Zn in the plant from on CL soil was 17.40mg/kg in B to 18.90mg/kg in the ones planted on CL and CR.

The mean metal content in*Corchorus olitorius L.* (mg/kg) as presented inTable 4.6b had Cd ranging from 1.0mg/kg in N and CL sites to 1.7 mg/kg in site B; Cu from 3.20mg/kg in site CL to 6.20mg/kg in site B, Mn from 30.30mg/kg in CR to 37.12mg/kg in N; Ni from 28.00mg/kg in CL to 40.30mg/kg in B; Pb from 12.30mg/kg in N to 15.70mg/kg in CL and Zn from 16.20mg/kg in B to 17.40mg/kg in N.

Concentrations of cadmium (Figure 4.4a) in*A. hybridus* was found to be lowest ($1.0mgkg^{-1}$) in the plant from N and CR soil and was highest ($1.4mgkg^{-1}$) in the *A. hybridus* planted onsite B and CL soil samples, while in *Corchorus olitorius L*. the lowest Cd concentration was $1.0mgkg^{-1}$in the crop planted on soils from N and CL, however, the highest level of Cd was $1.7mgkg^{-1}$ in the *C.olitorius L*. planted on B soil sample.

Copper contents in the two plants of the pot experiment as presented in Figure 4.4b, the level of Cu ranged from 4.1 $mgkg^{1}$ in the *A. hybridus* harvested from CR to 6.0 $mgkg^{1}$ in the plant obtained from B soil, while in *Corchorus olitorius L*, the level of Cu ranged from 3.2 in CL to $6.2mgkg^{-1}$ in the crop harvested from B soil.

Table 4.6a. Levels of Some Heavy Metals in*Amarantus hybridus*Planted in the Pot Experiment

Metal	N(mg/kg)	B(mg/kg)	CR(mg/kg)	CL(mg/kg)	Control(mg/kg)

Cd	1.00±0.001	1.40±0.001	1.00±0.001	1.40±0.001	0.70±0.001
Cu	4.50±0.001	6.00±0.001	4.10±0.001	4.30±0.001	7.50±0.001
Mn	37.40±0.002	32.80±0.003	32.60±0.002	30.60±0.001	48.60±0.002
Ni	42.10±0.001	51.20±0.001	36.70±0.001	40.50±0.001	16.20±0.001
Pb	12.50±0.002	13.20±0.003	14.00±0.001	14.00±0.002	9.50±0.002
Zn	18.90±0.002	17.40±0.003	18.80±0.001	18.90±0.002	21.00±0.002

Table 4.6b: Levels of Some Heavy Metals in*Corchorus olitorius L*Planted in the Pot Experiment

Metal	N(mg/kg)	B(mg/kg)	CR(mg/kg)	CL(mg/kg)	Control(mg/kg)
Cd	1.0±0.001	1.7±0.001	1.5±0.001	1.0±0.001	0.6±0.001
Cu	4.5±0.001	6.2±0.001	4.3±0.001	3.2±0.001	7.1±0.001

Mn	37.12±0.002	37.8±0.003	30.3±0.001	32.4±0.002	47.7±0.003
Ni	40.3±0.001	37.7±0.001	36.2±0.001	28±0.001	16.7±0.001
Pb	12.3±0.003	12.4±0.002	15.5±0.002	15.7±0.002	9.5±0.001
Zn	17.4±0.002	16.2±0.003	16.5±0.001	16.4±0.001	20.5±0.002

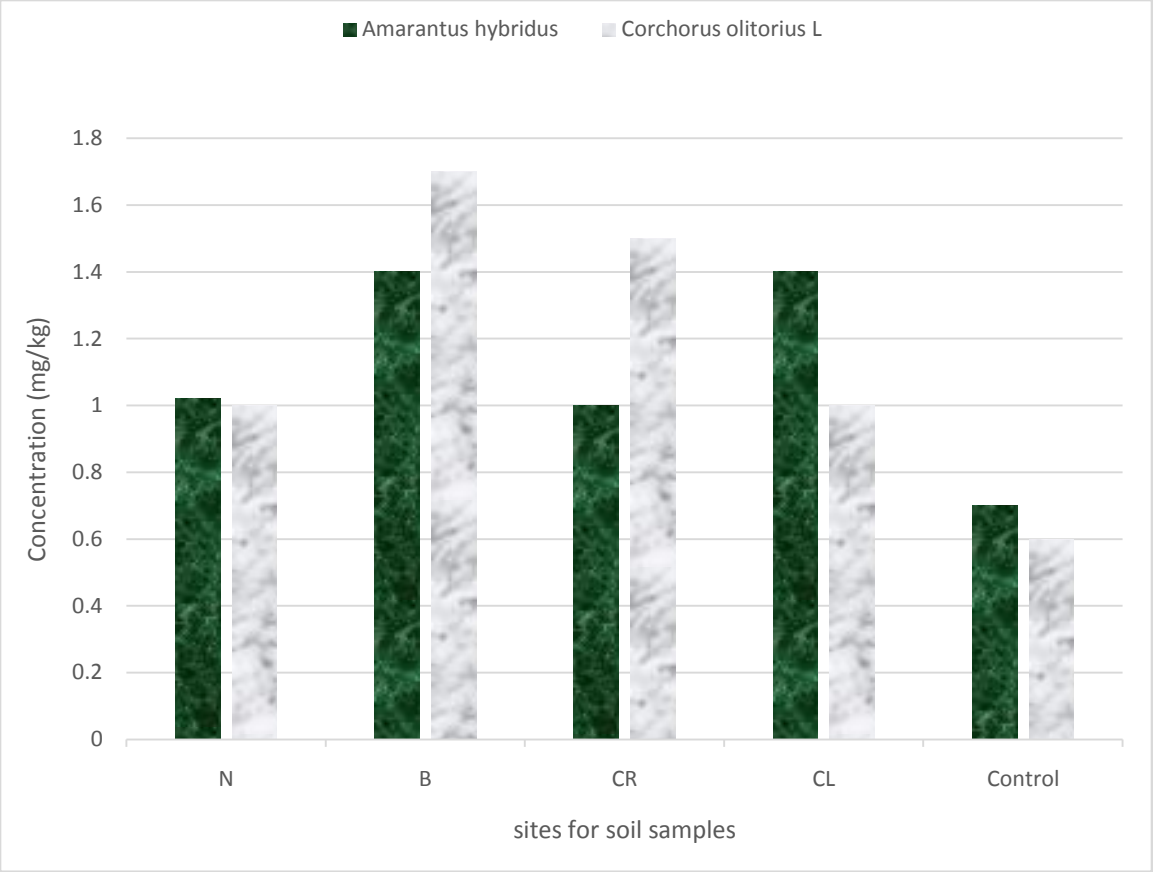

Figure 4.4a: CadmiumContent in the Two Plants Grown on Riverside Soils in the Pot Experiment

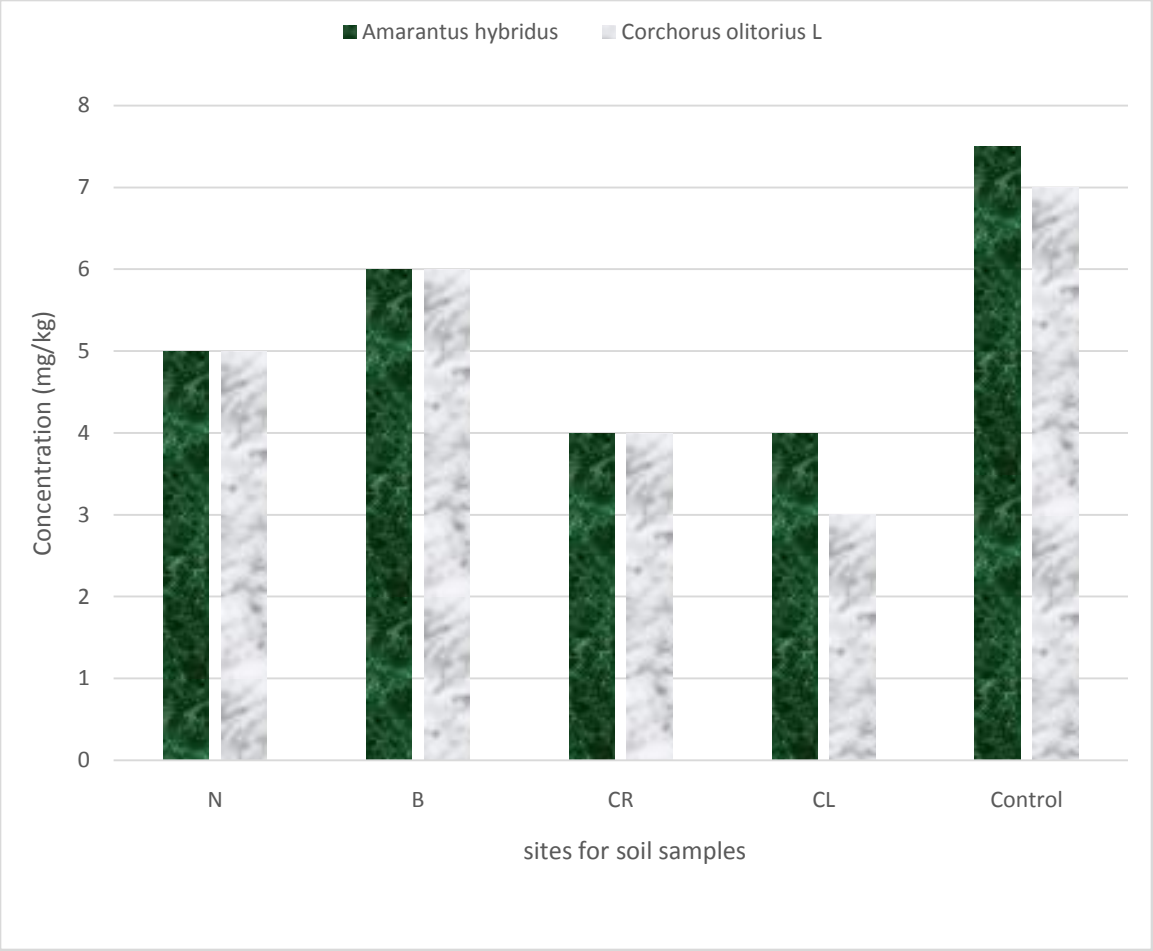

Figure 4.4b: CopperContent in the Two Plants Grown on Riverside Soils in the Pot Experiment

Concentrations of manganese (Figure 4.4c) in*A. hybridus* was found to be lowest (30.60 $mgkg^{-l}$) in the plant from CL soil and was highest (37.40 $mgkg^{-l}$) in the *A. hybridus* planted onN soil samples; while in *Corchorus olitorius L*., the lowest Mn concentration was30.30$mgkg^{-l}$in the

crop planted on CR soil and the highest level of Mn was 37.8mgkg^{-1} in the *C.olitorius L*., planted on B soil sample.

Nickel contents (Figure 4.4d) was relatively higher than manganese, andwas the highest level recorded among all the metals studied. The concentrations of Ni (Figure 4.4d) in*A. hybridus* was found to be lowest (36.70 mgkg^{-1}) in the plant collected from CR soil and was highest (51.2 mgkg^{-1}) in the *A. hybridus* planted on B soil samples. On the other hand, in *Corchorus olitorius L*. the lowest Ni level was 28.00 mgkg^{-1}in the crop planted from CL and the highest level of Ni was 40.3 mgkg^{-1} in the *C.olitorius L*. planted on N soil sample.

Lead contents (Figure 4.4e) in the two plants of the pot experiment was lowest in *A. hybridus* planted on the soil of N site (12.5 mgkg^{-1}) and the value was highest in the plant harvested from CL and CRsoils (14 mgkg^{-1}). For *Corchorus olitorius L*, the lowest level of Pb was 12.3mgkg^{-1}obtained in the plant from N. The highest amount of Pb (15.7 mgkg^{-1}) was recorded in the plant from CL.

Zinc contents (Figure 4.4f) in*A. hybridus* planted on the riverside soil of River Niger, Benue and beyond the confluence point ranged from 17.4 in the soil from B to 18.9mgkg^{-1} in the soil from N and CL; while in *Corchorus olitorius L*Zn level ranged from 16.2mgkg^{-1} in the sample of *C. olitorius L.* planted on B to 17.4mgkg^{-1} in the soil from N site.

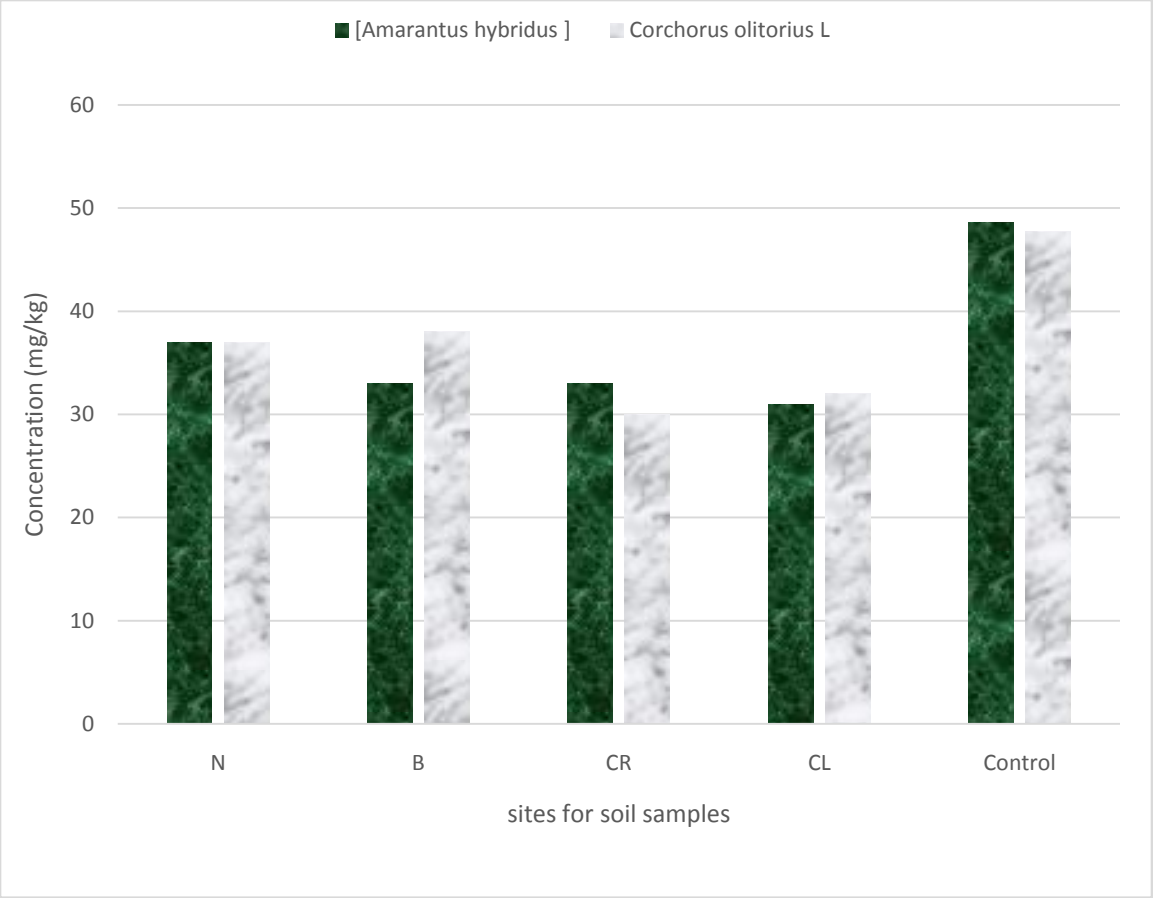

Figure 4.4c: Manganese Content in the Two Plants Grown on Riverside Soils in the Pot Experiment

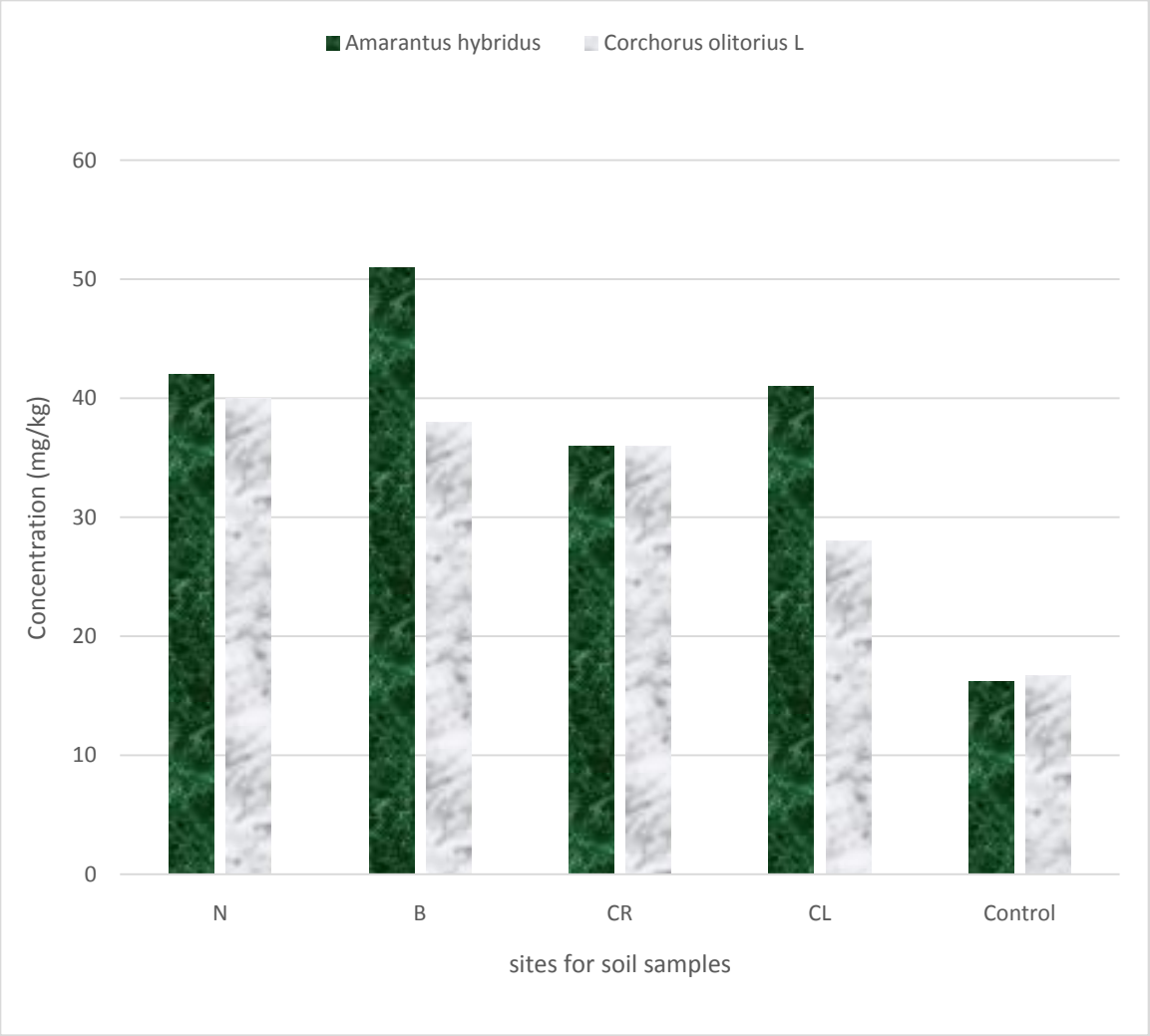

Figure 4.4d: NikelContent in the Two Plants Grown on Riverside Soils in the Pot Experiment

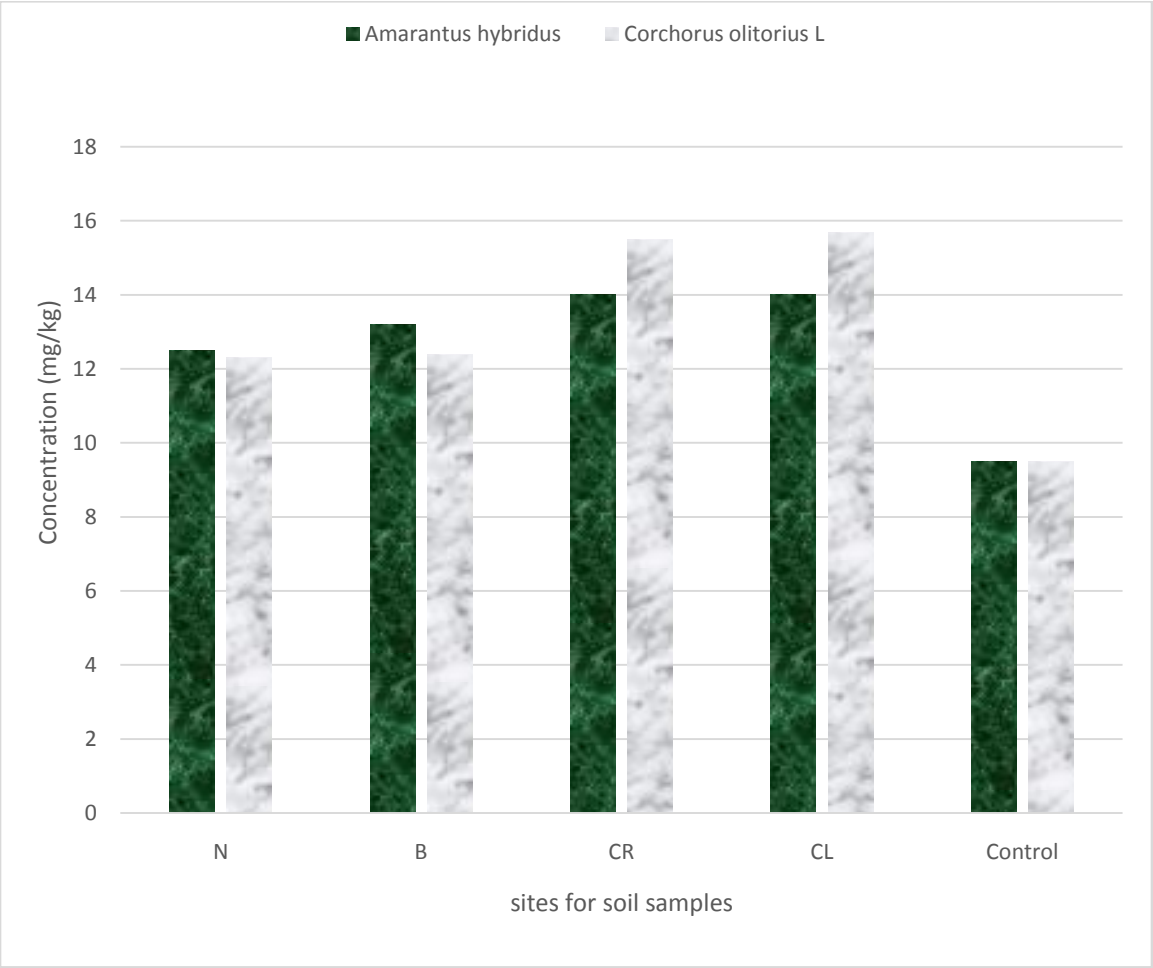

Figure 4.4e: LeadContent in the Two Plants Grown on Riverside Soils in the Pot Experiment

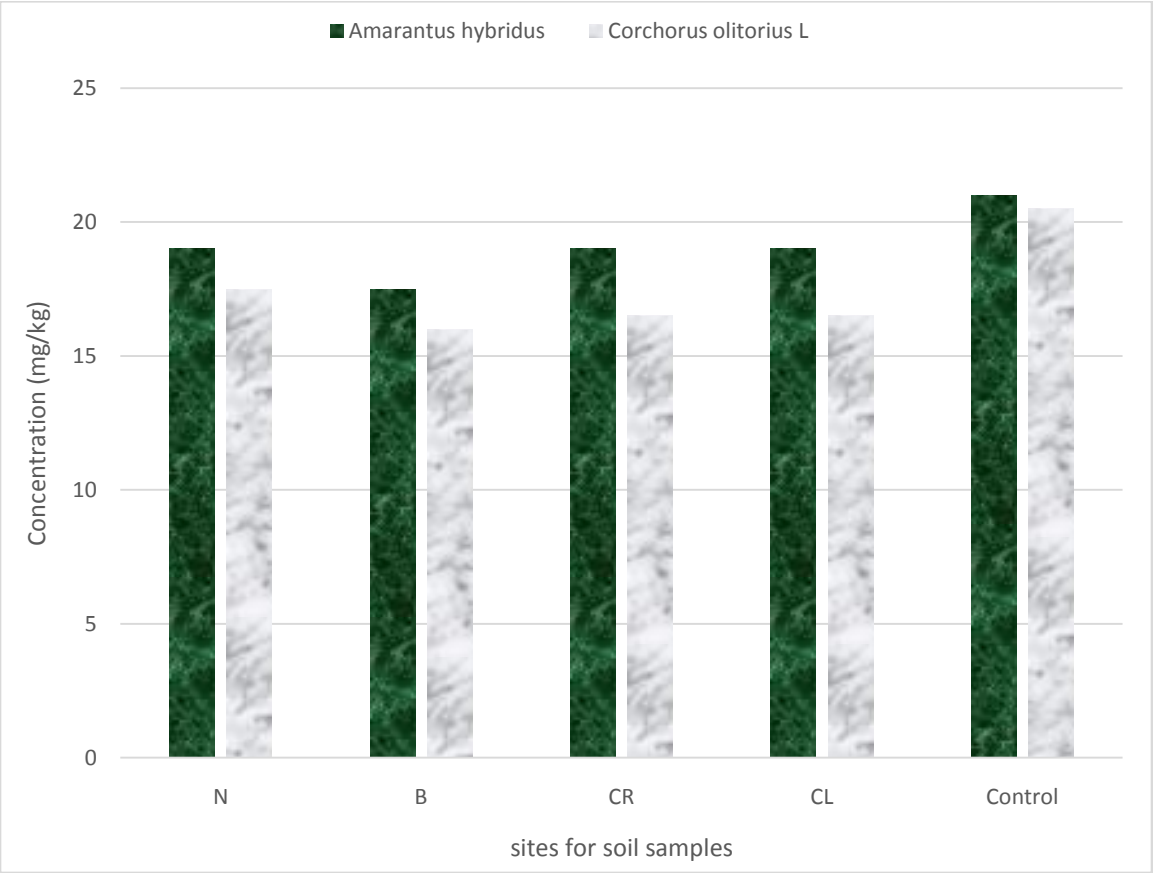

Figure 4.4f: ZincContent in the Two Plants Grown on Riverside Soils in the Pot Experiment

4.9 Bioaccumulation Factor (BF) of the Heavy Metals in *Amarantus hybridus*and *Corchorus olitorius L.*

Table 4.7a presents the Bioaccumulation Factor (BF) for *Amarantus hybridus* planted on the riverside soil of River Niger, Benue and beyond the confluence point. BF varied significantly among the soil species of the heavy metals, with Cd ranging from 0.1316 to 0.1667; Cu from 0.2240 to 0.3879, Mn from 0.1598 to 0.2086; Ni from 0.1268 to 0.1801; Pb from 0.3952 to 0.5691 and Zn from 0.2236 to 0.3760.

Table 4.7b presents the BF for *Corchorus olitorius L*. planted on the riverside soil of River Niger, Benue and beyond the confluence point. Thebioaccumulation factor (BF) varied significantly among the soil the heavy metals ($P < 0.01$), with Cd ranging from 0.1190 to 0.2024, Cu from 0.1778 to 0.3879, Mn from 0.1552 to 0.2070, Ni from 0.1268 to 0.1801, Pb from 0.3712 to 0.6301 and Zn from 0.2082 to 0.3300.

4.10 Correlation between the Total Metal Content, EDTA Fraction Content of Soil and Metal Ion Levels in*A. hybridus* and *Corchorus olitorius L.*

As shown in Table 4.8a and 4.8b, the Ni, Cu and Cd contents of the *A. hybridus* and *Corchorus olitorius L.*showed high significant ($P <0.01$) positive correlations with the total heavy metals and EDTA extractable fractions of the metals in the soil, Zn showed relatively poor or insignificantly negative correlations while the relationship for Mn and Pb were rather irregular (Table 4.8a and b).

Table 4.7a: Bioaccumulation Factor (BF) of the Heavy Metals in *Amarantus hybridus*

Metal	N	B	CR	CL
Cd	0.1370	0.1667	0.1316	0.1667
Cu	0.3879	0.2970	0.2240	0.2389
Mn	0.2086	0.1598	0.1670	0.1789
Ni	0.1496	0.1410	0.1801	0.1268
Pb	0.5319	0.3952	0.5691	0.4982
Zn	0.2995	0.2236	0.3760	0.3663

Table 4.7b: Bioaccumulation Factor (BF) of the Heavy Metals in *Corchorus olitorius L*.

Metal	**N**	**B**	**CR**	**CL**

Cd	0.1370	0.2024	0.1974	0.1190
Cu	0.3879	0.3069	0.2350	0.1778
Mn	0.2070	0.1842	0.1552	0.1895
Ni	0.1496	0.1410	0.1801	0.1268
Pb	0.5234	0.3712	0.6301	0.5587
Zn	0.2757	0.2082	0.3300	0.3178

Table 4.8a: Correlation between the Total Metal Content, EDTA Fraction Content of Soil and Metal ion Levels in *Amarantus hybridus*

Metal	**Total Metal content in soils versus*Amarantus hybridus* metal content**	**EDTA fraction content in soils versus*A. hybridus*metal content**
Cd	0.976	0.832

Cu	0.417	0.957
Mn	-0.025	0.966
Ni	0.779	0.215
Pb	0.109	0.440
Zn	-0.872	0.252

Table 4.8b: Correlation between the Total Metal Content,EDTAFraction Content of Soil and Metal Ion Levels in *Corchorus olitorius L*.

Metal	**Total Metal Content in Soils versus*Corchorus olitorius L*Metal Content**	**EDTA Fraction Content in Soils versus*Corchorus olitorius L*. Metal Content**
Cd	0.653	0.670
Cu	0.678	0.715
Mn	0.234	0.332

Ni	0.584	0.890
Pb	-0.238	0.163
Zn	-0.099	-0.435

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physicochemical Parameters of the Farmland Soils near River Niger, Benue and Beyond Confluence point

The mean concentrations for the physicochemical properties of the farmland soils in thedry(March 2013, January, 2014) and early rainy seasons (June 2013, May, 2014) are presented in Tables 4.1a-d. The soil pH ranged from 6.4 to 7.2 for the farmland soils of River Niger, Benue and beyond the confluence for the contaminated soils, in the dry (March) season of 2013 the River Benue side (B) had the highest pH of 7.1 and River Niger side (N) had the least (6.7) (Table 4.1a). However, in the early wet (June) season of 2013site B had the highest (6.9)

and soil beyond the confluence on the right side (CR) the least (pH 6.6)as presented in Table 4.1b.

On the other hand, in the dry (January) season 2014, soil collected beyond the confluence on the left side (CL) had the highest pH of 7.2 and N had the least pH (6.5) (Table 4.1c). In the early wet (May) season of 2014 soil from N had the highest pH (6.7) and CL the least (6.4) (Table 4.1d). The pH range obtained in this study is close to 6.41 – 6.73 recorded for some farmland soils in Lokoja, Nigeria by Oladipo *et al*. (2012). The lower pH values recorded may be attributed to acid effluent coming from industrial discharges upstream of the rivers, as well as high organic content. At low pH, metals are more soluble in the soil solution, thus more bioavailable to plants, and hence pose severe toxicity problems in acidic than in alkaline soil (Oluyemi *et al*., 2005). The pH range was in conformity with the findings of Enokela and salifu (2012) who evaluated the quality of water at the bank of River Niger in the confluence town of Lokoja used for irrigation on Sarki-noma fadama farm,the pH recorded ranged from 6.9 – 7.2.

The lowest organic matter content in the dry (March) season of 2013 was recorded at N soil sample (0.413gkg^{-1}) and the highest at B(1.652 gkg^{-1}) (Table 4.1a) while in the early wet (June) seasonof 2013, the organic matter content ranged from 0.406 gkg^{-1} at N to1.673gkg^{-1} at B (Table 4.1b). The lowest organic matter content in the dry season (January) of 2014 was recorded at N soil sample (0.473gkg^{-1}) while the highest was in B(1.602gkg^{-1}) (Table 4.1c). On the other hand, in the early wet (May) season of 2014 organic matter ranged from 0.533gkg^{-1} at N site to1.859gkg^{-1} at site B. The significantly higher organic matter contents of the farmland soil in the dry season compared to early wet season could be due to the lower soil moisture contents during the dry season which retards the activities of the micro - organisms involved in the organic matter decomposition, thereby accumulating more organic matter in the dry season.

The organic matter content was low as a result of intensive use of these soils and the rapid mineralization of organic matter under semiarid conditions. The organic matter contents of the soil plays an important role in absorption reaction in the soil, hence preventing pollutants from reaching ground water sources (Alloway *et. al*, 1995).

Moisture content which is directly proportional to the water holding capacity of the farmland soil collected from the farmland soils of River Niger, Benue and beyond the confluence ranged from 64.1 to 85.4% (Table 4.1a to 4.1d), soil of N on the early wet (June) season of 2013have the highest value (85.4%) while sample from CR on the dry (March) season 2013 have the least value (64.1%). The higher moisture contents in the wet season explain why plants grow healthily compared to dry season.

There was no remarkable difference in the mean values of most parameters across the seasons, as the values were similar for both wet and dry season. Analysis of Variance (ANOVA) shows that pH, organic matter, and moisture content were positively correlated (Appendix 2).

5.2Heavy Metal Content in the Riverside Soil Samples Used for Agricultural Purposes

The soil distribution of Cd, Cu, Mn, Ni, Pd and Zn in the farmland soils collected from the riverside of River Niger, Benue and beyond the confluence is presented in Figures 4.1a-f (dry and early wet seasons of 2013 to 2014) and Table 4.1a (dry season/March 2013), Table 4.1b (early wet season/June 2013), Table 4.1c (dry season/January2014), Table 4.1d (early wet season/May2014).

Cd concentrations of the studied area as shown in Figure 4.1a and Table 4.1a to 4.1d, indicated that Cd concentrationof value 8.4mg/kg obtained in both site B and CLin theearly wet

(May) season of 2014 was the highest concentration; while the Cd concentration (3.95mg/kg) at N sampling site in the dry (March) season of 2013 was the lowest. The Cd concentrations obtainedwere higher than the European Union Standards of 3mg/kg(EU, 2002).

Cadmium is regarded as one of the most toxic trace elements in the environment. It occurs naturally in soils as a result of the weathering of the parent rock (Alloway, 1995). Although most natural soils contain less than 1 $mgkg^{-1}$ cadmium from the weathering of parent materials, those developed on black shales and those associated with mineralised deposits can have much higher levels (Alloway, 1995). Anthropogenic sources of cadmium are much more significant than natural emissions and account for its ubiquitous presence in soil (Alloway, 1995; ECB, 2007; ATSDR, 2008).

Cadmium is a trace element in phosphatic fertilizers. Atmospheric deposition is also an important source of cadmium pollution (Alloway, 1995; ECB, 2007; ATSDR, 2008). Cadmium is much less mobile in soils than in air and water. Cadmium is strongly adsorbed to organic matter in soils. When cadmium is present in soils it can be extremely dangerous, as the uptake through food will increase. Sedimentary rocks contain greater concentrations of Cd than either igneous or metamorphic rocks, and therefore, recent soils derived from sedimentary rock should contain greater concentrations of Cd than those derived from igneous or metamorphic rocks. Among the commercial fertilizers, phosphorus fertilizers contain somewhat high levels of Cd. The fact that highly weathered soils are somewhat depleted in Cd suggest that greater quantities of Cd are removed by crops and leaching than are added through fertilization and atmospheric deposition. Surface soils commonly contain higher concentrations of Cd than subsurface horizons. The higher concentrations of Cd in surface horizons are probably due to the cycling of Cd from lower depths to the surface by plants Page *et al.,* (1987). Cadmium is higher in the

studied area, this could be due to the use of phosphatic fertilizers, irrigation by untreated water of the river and due to the soil of the study area being from deposits of the flooding of year 2012; and the soil have been derived from sediments (sand, silt and clay) of the River Niger and Benue.

Analysis of Variance (ANOVA)of Cd shows that there was remarkable difference in the mean values of most parameters across the seasons, with p-value (4.82×10^{-7}) which is far less than the significance level of (α) 0.05 (Appendix III).

Copper content was reported (Figure 4.1b and Table 4.1a-d) to be lower than that of European Union Standard limit (EU 2002) of 140mg/kg. Copper had relatively low values ranging from 11.6mgkg^{-1} in the soil at N (early wet season/May 2014) to 20.2mgkg^{-1} in B (early wet season/May 2014). Most copper compounds will settle and be bound to water, sediments or soil particles. The concentrations of copper are higher in some soil samples due to the irrigation of agricultural lands with untreated river water which could lead to the accumulation of Cu in soils. The Cu concentrations are lower due to the continuous removal of heavy metals by the food crops grown in this area and also due to leaching of heavy metals into the deeper layer of the soil and to the ground water.

Analysis of Variance (ANOVA) of Cu shows that there was no remarkable difference in the mean values of most parameters across the seasons, with p-value (0.287976) which is greater than the significance level (α) of 0.05 (APPENDIX III).

As seen in Figure 4.1c, manganese concentration in the soil is generally higher than all the other metals recorded but it is generally lower than the European Union Standards of about 2000mg/kg (EU, 2002). It the recorded highest value (211.5 mgkg^{-1}) at site CRin theearly wet (June) season of 2013 and was lowest (150.3 mgkg^{-1}) at site CL of both dry (March) and early

wet (July) seasons of 2013 (Figure 4.1c). The Mn content obtained for the studied soil, however was generally lower than the 354 – 394 $mgkg^{-1}$ reported using neutron activation analysis for some farmland soils from Lokoja metropolis, Nigeria (Oladipo *et al*., 2012). The observed large concentration of Mn in the soil samples might have been due to background concentration of Mn in the soil and sediment of the river. Dara (1993) reported that manganese may be found in most soil since it is one of the elements in the earth crust.

Analysis of Variance (ANOVA) of Mn shows that there was no remarkable difference in the mean values of most parameters across the seasons, with p-value (0.132966) which is greater than the significance level (α) of 0.05 (Appendix III).

As presented in Figure 4.1d, Ni concentrations in the soil samples of the studied area of River Niger and Benuewas generally higher than that of European Union Standards (EU 2002) of 75mg/kg. The highest value (281 $mgkg^{-1}$) obtained at site CR in the early wet (March) season of 2013 and was lowest (177.0 $mgkg^{-1}$) in the soil at site B soil collected in the dry (June) season of2013. Nickel occurs naturally in soils as a result of the weathering of the parent rock (McGrath, 1995).The underlying geology and soilforming processes strongly influence the amount of nickel in soils with higher median concentrations reported in clays, silts and fine grained loams relative to coarser grained loams, sandy and peaty soils (Mohamed, 2014). Agricultural fertilisers, especially phosphates, are also a significant source of nickel in soil but it is unlikely to build-up in soil in the long term from their use (McGrath, 1995). The irrigation of the farmland near River Niger and Benue by the river water and use of agricultural fertilizersmay account for the increase in Ni concentrations of the farmland soil.

Analysis of Variance (ANOVA) of Ni shows that there was remarkable difference in the mean values of most parameters across the seasons, with p-value (0.007273) which is less than the significance level (α) of 0.05 (Appendix III).

Lead contents (Figure 4.1e and Table 4.1a-d) were found to be highest (34.2mgkg^{-1}) in the soil sample from N collected in dry (March) season of 2013and lowest at (20.3mgkg^{-1}) at both CR and CL during theearly wet (June) season of 2013. The value of Pb in the soil samples were generally low compared to the European Union Standards of about 300mg/kg(EU 2002).

When lead is deposited in soil from anthropogenic sources, it does not biodegrade or decay and is not rapidly absorbed by plants, so it remains in the soil at elevated levels. Lead is toxic to humans, and poisoning can occur either through ingestion of lead or by breathing in lead dust. Both long-term low-dose and short-term high-dose exposure can permanently damage the nervous, renal (kidney) and hematopoietic (blood-forming) systems.

Analysis of Variance (ANOVA) of Pb shows that there was no remarkable difference in the mean values of most parameters across the seasons, with p-value (0.243233)being greater than the significance level (α) of 0.05 (Appendix III).

Zn contents as presented in Figure 4.1f, indicated that the soil samples in site CR of the dry season(March) in 2013 (40.5 mgkg^{-1}) was the lowest while the sample from B in theearly wet (May) season of 2014 (77.8 mgkg^{-1}) recordedthe highest Zn concentration. Zn concentrations in the studied area of River Niger, Benue and beyond the confluence pointhad Zn amount being lower than that of European Union Standards of 300mg/kg. Zn is released to the environment from both natural and anthropogenic sources; however, releases from anthropogenic sources are greater than those from natural sources. The most important sources of anthropogenic zinc in soil come from discharges of smelter slags and wastes, mine tailings, coal

and bottom fly ash, and the use of commercial products such as fertilizers and wood preservatives that contain zinc. Zinc does not volatilize from soil. Zinc usually remains adsorbed to soil, although leaching has been reported. The lower concentrations Zn in this study below the safe limits of EU at most sites might be due to the continuous removal of heavy metals by the food crops grown in this area, and also due to leaching of heavy metals into the deeper layer of the soil and to the ground water.

Analysis of Variance (ANOVA) of Zn shows that there was no remarkable difference in the mean values of most parameters across the seasons, with p-value (0.124333) which is greater than the significance level (α) of 0.05 (Appendix III).

5.3 Geoaccumulation Index (Igeo) of the Soils of the Farmland from River Niger and Benue

Table 4.3a-d present the Igeo values for the heavy metals studied. The Igeo values for Ni in all the sampling siteswere greater than 2 (moderately to strongly contaminated). The Igeo values obtained for Cdwere greater than 4, this varied with the range 4.763-5.649, indicating highly to extremely contaminated. Geoaccumulation index showed that Cd and Ni were the major pollutant of the soil samplessoils of riveside soil of River Niger, Benue and beyond the confluence point in Lokoja, Nigeria, although Cd was seen to pollute virtually all the riverside soils, being highest in the early wet (May) season of 2014 (5.649) and lowest in the dry (March) seasonof 2013 (4.763).

I-geo for Mn was generally above zero in all the riverside soils and across the seasons, an indication of Mn pollution in most of the sites. The highest I-geo value obtained for Mn was in early wet (June) season 2013 (I-geo = 1.157) at CR, which shows a relative pollution by Mn, while lowest I-geo value was 0.678 at site CL in both the dry (March) and early wet (June) season of 2013, this values indicate moderate pollution.

However, Cu, Zn and Pb were seen not to pollute the riverside soils even across the seasons; this could be accounted for by the nature of the solid wastes deposited into the rivers upstream, as there are different kinds of activities around River Niger and Benue from the source to the different water courses.Cu, Zn and Pd were in class 0 (uncontaminated); Mn is in class 1 (except for the soil samples collected from CR in the wet season of March 2013 and both the dry (January) and wet (May) seasons in 2014 had the Igeo>1 for all the riverside soils. This indicates that the soil in these riverside are uncontaminated to moderate contamination by Cu, Mn, Pd and Zn.

5.4 Statistical Analysis on the Concentration of Metals at 15cm and 30 cm Depth of Soil Samples

Figure 4.2a-f depicted the results of the heavy metal concentration at the surface depth (15cm) of the riverside soils and the level at 30cm depth. There were generally higher amount of Cd, Cu, Mn, Ni, Pb and Znin the soil at 15cm depth than the subsurface layers 30cm depth.

Statistical test of significance using the Student t-test (Table 4.4) showed that there was no significant differences(95% level of confidence) in the concentrations of Cu, Ni andPbat 15cm and 30cm depth of the soil samples obtained from the river sides of River Niger, Benue

and beyond the confluence point in Lokoja-Nigeria. But there was a significant difference in the concentration of Cd, Mn and Zn (Table 4.4).

5.5 Concentraion of the Available Essential Heavy Metals Extracted by EDTA from the Soil

Heavy metals extracted by ethylenediaminetetraacetic acid(EDTA) should be the fraction available for plants. Hence, these amounts of heavy metals are significantly lower than total amounts in soils as shown in Table 4.5. The percentage of the total amounts of heavy metal extracted in the soil by EDTA differ among elements. Lead was the highest extracted relative to the total metal content (58.7%), zinc (36.4%), copper (31.2%) nickel (24.2%), manganese(21.5%) and cadmium (15%). The result indicated thatlead had the highest extractabilityby EDTA, followed by manganese, then copper, cadmium, zinc, while nickel had the least EDTA extractable amount. Similar results were reported for the EDTA extraction in a farmland soil in Croatia, (Lončarić *et al*. 2008) with lead, copper and zinc recording higher percentage extractability than for nickel, cadmium and least for Mn.

5.6 Level of Heavy Metal in *Amarantus hybridus* and *Corchorus olitorius L.*

Heavy metal concentrations in spinach(*Amarantus hybridus*) and jute (*Corchorus olitorius L.*)were found to be generally lower than that levels of each of the heavy metals in the soil, as shown in Figures 4.4a-f and Table 4.6a and b for *Amarantus hybridus* and *Corchorus olitorius .L*respectively.

The mean metal content in*A. hybridus* (mg/kg) as presented inTable 4.6a which ranged from 1.0mg/kg in sites N and CR to 1.4mg/kg in sites B and CL;4.10mg/kg in site CR to

6.00mg/kg in B; 30.60mg/kg in CL to 37.40mg/kg in N; 36.70mg/kg in CR to 51.20mg/kg in B; 12.5mg/kg in N to 14.0mg/kg in sites CR and CL; 17.40mg/kg in site B to 18.90mg/kg in sites CL and CR for Cd, Cu, Mn, Ni, Pb and Zn respectively. The control area has the mean metal concentration:Cd0.7,Cu 7.5, Mn 48.6, Ni 16.2, Pb 9.5, Zn 21.0. The order of the amount of these metals in*A. hybridus* planted on soil of the riverside of River Niger, Benue and beyond the confluence point is in the ranking: Ni > Mn > Zn >Pb>Cu>Cd; while the pattern in *A. hybridus*planted on the soil obtained from the control site was Mn>Zn>Ni>Pb>Cu>Cd.

The mean metal content in*Corchorus olitorius L.* (mg/kg) as presented inTable 4.6b ranged from 1.0mg/kg in sites N and CL to 1.7mg/kg in site B; 3.20mg/kg in CL to 6.20mg/kg in B; 30.30mg/kg in CR to 37.12mg/kg in N; 28.00mg/kg in CL to 40.30mg/kg in B; 12.30mg/kg in N to 15.70mg/kg in CL; 16.20mg/kg in B to 17.40mg/kg in site N for Cd, Cu, Mn, Ni, Pb and Zn respectively. The control area has the mean metal concentration:Cd 0.60mg/kg,Cu 7.10mg/kg, Mn 47.70mg/kg, Ni 16.70mg/kg, Pb 9.50mg/kg, Zn 21.50mg/kg. The order of the amount of these metals in*Corchorus olitorius L.* planted on the farmland soil near River Niger, Benue and beyond the confluence point is: Ni > Mn > Zn >Pb>Cu>Cd, while the pattern in *A. hybridus*planted on the soil obtained from the control site was Mn>Zn>Ni>Pb>Cu>Cd.

The metal content of nickel, lead and cadmium in *A. hybridus* and *Corchorus olitorius L*were higher than the WHO permissible value in plants 10 mg/kg, 2 mg/kg and 0.2 mg/kg respectively(WHO, 1996). However, zinc,manganese and copper were below the WHO permissible values of20mg/kg, 300mg/kg and 10mg/kg respectively. When the values obtained were compared to the control, manganese, copper and zinc were in amounts being higher than that in the control counterpart.

Concentrations of cadmium (Figure 4.4a) in*A. hybridus* was found to be lowest (1.0mgkg^{-1}) in the plant from N and CR, and was highest (1.4mgkg^{-1}) in the crop planted on B and CL soil samples. For *Corchorus olitorius L.*,the lowest Cd level was 1.0mgkg^{-1}in the plant from N and CL and the highest level was 1.7mgkg^{-1} in the crop planted on site B soil sample. The plant in the control soil had relatively lower value both for*A. hybridus* and *Corchorus olitorius L.* compared to the experimental soils. There was significant difference in the values recordedin *A. hybridus* compared to*Corchorus olitorius L*as presented in Appendix IV.

Copper contents in *A. hybridus*as presented in Figure 4.4b ranged from 4.1 in the crop harvested from CR to 6.0 mgkg^{l} in the plant from site B;while in *Corchorus olitorius L,* it ranged from 3.2 in CL to 6.2mgkg^{-1} in B. The extremely high value obtained in site B both in*A. hybridus* and *Corchorus olitorius L,* could be due to the decomposition of solid wastes containing high copper contents, which are drain into the rivers and subsequently in the soil. In the control sites very low values were recorded in both the *A. hybridus* and *Corchorus olitorius L*. This could be due to the fact that the site is not affected by the untreated water of the river. These values are however above the tolerance limit (10 mgkg^{l})set by WHO, (1996). There was no significant difference in the values recordedin *A. hybridus* compared to*Corchorus olitorius L*as seen in Appendix IV.

Manganese contents as presented in Figure 4.4c, had the lowest value in *A. hybridus* planted on the soil ofsite CL(30.6 mgkg^{-1}) and was highestin the plant harvested from the soil of N (37.4 mgkg^{-1}). On the other hand,for *Corchorus olitorius L*.the lowest level of Mn was 30.3 mgkg^{-1}for the ones from CR soil and 37.8mgkg^{-1} the highest Mn level recorded in the plant from B soil sample. From the Figure 4.4c, it is indicated that the plant from the control site had relatively high level of Mn for both*A. hybridus* and *Corchorus olitorius L,* which is as expected.

In addition, there was little significant difference in the values obtained for both*A. hybridus* and *Corchorus olitorius L* (Appendix III).

Nickel contents (Figure 4.4d) was relatively higher than manganese, andwas the highest level recorded among all the metals studied, the lowest value of Ni in *A. hybridus* was recorded inthe ones planted on the soil from CR (36.7 $mgkg^{-l}$) and the highest Ni was recorded in the plant harvested from the soil of B (51.2 $mgkg^{-l}$). For *Corchorus olitorius L*. 28 $mgkg^{-l}$ was the lowest level of Ni in the crop fromsite CL and 40.3$mgkg^{-l}$was the highest Ni level recorded in the plant harvested fromsite N soil. Figure 4.4d indicated that the plant from the control site had relatively low level of Ni in both the *A. hybridus* and *Corchorus olitorius L*. In addition, there was no significant difference in the values obtained for both*A. hybridus* and *Corchorus olitorius L*(Appendix III).

Lead contents (Figure 4.4e) measured was lowest in *A. hybridus* planted on the soil from N (12.5 $mgkg^{-l}$) and was highest in the plant from CL and CR soils (14 $mgkg^{-l}$). For *Corchorus olitorius* .the lowest level of Pb was 12.3$mgkg^{-l}$obtained in the plant from N soil. The highest amount of Pb was 15.7 $mgkg^{-1}$ recorded in the plant from CL soil. The control plant had relatively lower value both for*A. hybridus* and *Corchorus olitorius L*compared to the experimental plants. There was no significant difference in the values recordedin *A. hybridus* compared to*Corchorus olitorius L*(Appendix III).

Zinc contents (Figure 4.4f) in*A. hybridus* planted on the soil ranged from 17.4 in soil from B to 18.9$mgkg^{-l}$ in the soils from N and CL; for *Corchorus olitorius L*, Zn level ranged from 16.2 in the sample planted on B soil to 17.4$mgkg^{-l}$ in the one from N. The concentration of zinc in the control site was higher than those in the sample area, this could be attributed to the

background zinc present in the soil (Dara, 1993). These zinc values recorded in the experimental plant are above the tolerance limit of zinc in plant and could be harmful to man if accumulated over time through the food chain. There was significant difference in the values recordedin *A. hybridus* compared to*Corchorus olitorius L*as seen in Appendix IV.

The ranking of these metalsin*A. hybridus* and *Corchorus olitorius L*planted on the riverside soils is in the order: Ni>Mn>Zinc>Pb>Cu>Cd, while the pattern in the control site was Mn>Zn>Ni>Pb>Cu>Cd.

5.7 Bioaccumulation Factor (BF)of the Heavy Metals in *A. hybridus* and *Corchorus olitorius L.*

In order to determine the extent of contamination content of the heavy metals in soil, an enrichment factor was computed called the transfer factor or bioaccumulation factor (BF). This was expressed as the ratio of the concentration of the metals in the plants to that in the soil (Oyedele *et al*., 1995). Table 4.7a presents the BF for *Amarantus hybridus*, while Table 4.7b presents for *Corchorus olitorius L*.The bioaccumulation factor (BF) varied significantly among the soil species of the heavy metals. Of all the metals studied, the BFfor Pb from the soil to the plant was highest, this being 0.5691 (soil from CR to*A. hybridus)*and 0.6301 (soil from CR to*Corchorus olitorius L.)*respectively.

The BF obtained for Ni withrespect to*A. hybridus* and *Corchorus olitorius L* was the lowest, with the exception of soil from CR (0.1801). Similar trend was observed for Cd except in*Corchorus olitorius L.*for thesoil from B (0.2024) where transfer factor was relatively high. These results indicate that *A. hybridus* and *Corchorus olitorius L*. have potential to accumulate more of Pb and Cu from the riverside soilcompared to Ni and Cd. There is tendency of Pb and Cu in the soil of the farmland from River Niger and Benue in Lokoja to be transferred into the

food chain through the consumption of edible plants on the site by either animals or man. Hence consumptions of these plants overtime may cause some health hazards as reported by Uba *et al*., (2008). It was also observed that the transfer factor or bioaccumulation factor values recorded for the metals show reverse trend compared to the total metal content obtained across the seasons Pb >Cu > Zn > Mn > Cd > Ni. According to Udosen *et al*. (2006) some factors such as pH, exchange binding capacities, climate change and morphology of the plant might have contributed to low transfer factor values obtained in the riverside soils to the plant.

5.8: Correlation of the Heavy Metals in the Soil of River Niger and Benue to the Planted Vegetables

As shown in Table 4.8a and 4.8b the Ni, Cu and Cd contents of the *A. hybridus* and *Corchorus olitorius L,* showed highly significant ($P < 0.01$) positive correlations with the total heavy metals and EDTA extractable fractions of the metals in the soil. This indicated that the metal level in the soils is the major factor governing the heavy metal contents in the plants studied. Zn showed relatively poor or insignificantly negative correlations while the relationship for Mn and Pb were rather irregular (Table 4.8a and b). The correlation values were observed to be better for EDTA extractable elements in most cases. Most of the correlation values between each of the total and EDTA extractable fractions and the metal contents in plants were found to be positive but not significant. The positive relationships among the soil and plant metal contents could be related to heavy metal toxicities in both plants and animals through their entry into the food chain. Poor and negative correlations observed among the soil and plant metal contents might be due to differences in soil types, the nature of the plants concerned, the extent and type of industrial effluents, etc.

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

From the findings there was no remarkable difference in the mean values of most parameters across the seasons as the values were similar for both the dry and early wet season. Correlation analysis showed that pH, organic matter, and moisture content were positively correlated.The abundance of heavy metals measured in these soils decreases as follows: Ni > Mn > Zn > Pb > Cu > Cd.Geoaccumulation index showed that Cd and Ni were the major pollutants, with Cd having I-geo values from 4.763 to 5.649 and Ni from 2.137 to 2.799; although Cd was seen to pollute virtually all the riverside soils. I-geo for Mn were generally above zero in all the riverside soils and across the seasons, an indication of Mn pollution in most of the sites and the I-geo values for Cu, Zn and Pd were in class 0 (uncontaminated).Percentage of total metal extracted by EDTA differ among elements, lead was extracted in the highest absolute amounts (58.7%), followed by zinc (36.4%), then copper (31.2%), nickel (24.2%), manganese (21.5%) and cadmium (15%)was in the lowest relative amount.

The order of availability of these metals in the vegetables planted on the riverside soils is in the ranking: Ni>Mn> Zn >Pb>Cu>Cd, while the pattern in the control site was Mn>Zn>Ni>Pb>Cu>Cd.The result of transfer factor indicated that *A. hybridus* and *C. olitorius L*, had the potential for accumulating more of Pb and Cu from the soil at some selected riverside soils; which implies thatthere is a high tendency of these metals in the soils to be transferred into the food chain through the consumption of edible plants from the site by either animals or man.The Ni, Cu and Cd contents of the *A. hybridus* and *Corchorus olitorius L*, showed high significant ($P<0.01$) positive correlations with the total and EDTA extractable fraction of heavy metals in the soils. This indicated that the metal level in the soil is the major factor governing the heavy metal contents in the plants studied. Zn in *A. hybridus* and *Corchorus olitorius L*. showed relatively poor or insignificant negative correlationsto the total and EDTA extractable fractions

in the soils, while the relationship for Mn and Pb were rather irregular compared to the other metals.

From the present study,it can be concluded that in the agricultural fields the concentration of Ni and Cd are above the normal soil value and reflect the possibility of soil pollution. Accumulation of nickel (28.0 – 51.2 mg/kg), lead (12.30 – 15.70 mg/kg) and cadmium (1.00 – 1.70 mg/kg)in the vegetablesin both *A. hybridus* and *Corchorus olitorius L.*were higher than the WHO permissible value for plants 10 mg/kg, 2 mg/kg and 0.2 mg/kg respectively for the stated elements. This indicated that the highly toxic Pb has been entering the food chain through vegetables planted on the riverside soil of River Niger and River Benue in Lokoja, Nigeria. Although the green vegetables are the good sources of Zn, Cu, Fe necessary for our good health, but accumulation of toxic metals like Ni, Pb and Cd in the crop could decrease the availability of some essential micronutrientsin the food to the consumers (Sharma *et al.,* 2005).

6.2 Recommendations

1. Research should be carried out regularly to ascertain the level of pollution of heavy metals in the farmland soils near River Niger and River Benue.
2. Study of heavy metals in the farmland soils near River Niger and River Benue should be carried out at varying depths.
3. In heavy metal contaminated areas, leafy vegetables which are good accumulator of heavy metals should not be cultivated; for commercial farming the cultivation of poor-accumulators of heavy metals like sweet potato is recommended.
4. Waste water from industries should be treated and re-used for industrial purposes. For this purpose existing environmental lawsshould be enforced by government obliging big industries to establish their own waste water treatmentplants, while small

industries should be grouped into clusters to establish common waste water treatment plants.And factories should not be allowed to dispose their waste water into the canals without proper treatment.

REFERENCES

Abdulmojeed O. L., Abdulrahman A. A. (2011). Analysis of heavy metals in vegetables from some cultivated irrigated gardens in the Kano metropolis, Nigeria. *Journal of Environmental Chemistry and Ecotoxycology,Vol. 3*(6), pp. 142-148.

Ademoroti, C.M.A. (1996a). Levels of trace heavy metals on bark and fruit of trees in Benin city, Nigeria. *International Journal of Environmental pollution (Senci B), UK*, *4*; 241-253.

Ademoroti, C. M.A. (1996b). Environmental Chemistry and Toxicology. Foludex press Ltd, Ibadan.

Ademoroti, C.M.A. (1996b). Environmental chemistry and toxicology. *Foluedex Press ltd, Ibadan.* P 162-181.

Adriano, D. C. (1986). Trace elements in the terrestrial environment.*New York, Springer*, P. 533.

Adriano, D. C. (1988). Natural remediation processes.*New York, Springer*. P. 441.

Aeliona C. M., Davisa H. T., McDermottb S. (2008). Metal concentrations in rural topsoil in South Carolina: potential for human health impact. *Science of the Total Environment*, ` *402*: 149-156.

Agyarko, K., Darteh, E. and Berlinger, B. (2010). Metal levels in some refuse dump soil and plants in Ghana. *Plant and Soil Environmental Journal*. 56 (5): 244-251.

Alloway, B. J. and Ayres, D. C. (1997). Chemical principles of environmental pollution. *Blackie Academy and Professional*, P. 353-359.

Alloway, B.J. (1995). Cadmium inHeavy Metals in Soils (2nd edn.) (ed. B.J. Alloway). London: *Blackie Academic & Professional.*

Andrew, N. (1990). Organic and conventional management effects on biologically active soil organic matter pools. *Soil Science Society of American. Journal*, *58*: 1130-1139.

Arao T., Ishikawa S., Murakam I. M. (2010). Heavy metal contamination of agricultural soil and counter measures in Japan. *Paddy and Water Environment*, *8*(3): 247-257.

ATSDR (Agency for Toxic Substances and Disease Registry), (2008). Draft toxicological profile for cadmium Atlanta: *US Department of Health and Human Services, Agency for*

Toxic Substances and Disease Registry. Available from: http://www.atsdr.cdc.gov/toxprofiles/tp5-p.pdf [Accessed June 2009].

Awofolu, O. R. (2005). A Survey of Trace Metals in Vegetation, Soil and Lower Animals along Some Selected Major Roads in Metropolitan City of Lagos. *Environmental Monitoring and Assessment, 105*: 431-447.

Awwal, R. (2008). Manganese as a micronutrient. *British Medical Bulletin*, P. 13-15.

Ayodele, J. T. and Mohammed, S. S. (2011). Speciation of Nickel in soils and cereal. *Research Journal of Applied Science and Engineering Technology, 3*(3): 202-209.

Ayodele, J.T. and Gaya, U.M. (1994). Determination of lead in street dust to index its pollution in Kano municipal. *Spectrum Journal*, (1 and 2): 92 – 96.

Babula P, Adam V, (2008). Uncommon heavy metals, metalloids and their plant toxicity: A review. *Environmental Chemical Letter*, *6*: 189-213.

Baryla, G., Genel, A. and Gary, R. (2011). Chemical partitioning of cadmium, copper, nickel and zinc in the soil and sediments containing high levels of heavy metals. *Journal of environmental Quality,4*(8): 45-49.

Bolan, V., Ralph, S. and Perka, D. (2009). Importance of phosphorus in living organisms.*CRC press Inc. Boca Raton* (ed), P. 26-45.

Boyd R. S. (2010). Heavy metal pollutants and chemical ecology: Exploring new frontiers. *Journal of Chemical Ecology, 36*: 46-58

Brallier, C., Clark, T. and Paul, J. (2001). Heavy metals in soil. *Halsted press, John Wiley and Sons, London*, P. 221-237.

Cambier. D., Feel, C. and Booke, K. (2001). Heavy metal poisoning.*Gale Encyclopaedia of alternative medicine, Farmington Hills*, P. 31-32.

CEPA (Chinese Environmental Protection Administration). (1990). Elemental Background Values of Soils in China. *Environmental Science Press of China, Beijing, China*.

CEPA (Chinese Environmental Protection Administration). 1995. Environmental Quality Standard for Soils (GB15618-1995). *Environmental Science Press of China, Beijing, China.*

Chander, K., Brookes, P.C., Harding S.A. (1995). Microbial biomass dynamics following addition of metal-enriched sewage sludge to a sandy loam. *Soil Biology and Biochemistry,* 27(11): 1409-1421.

Chowdhury M.T.A., L. Nesa, M.A. Kashem and S.M. Imamul Huq (2010). Assessment of the Phytoavailability of Cd, Pb and Zn using Various Extraction Procedures. *Pedologist* 80-95

Chao S., LiQin J., WenJun Z., (2014). A review on heavy metal contamination in the soil worldwide: Situation, impact and remediation techniques. *Environmental Skeptics and Critics,2014, 3*(2): 24-38.

Chen Y. F. (2011). Review of the research on heavy metal contamination of China's city soil and its treatment method. *China Population, Resources and Environment, 2011, 21*(3): 536-539.

Dan-Azumi S. and M.H. Bichi (2010). Industrial Pollution and Heavy Metals Profile of Challawa River in Kano, Nigeria. *Journal of Applied Sciences in Environmental Sanitation, 5*(1): 23-29, January-March, 2010.

Dara, S.S. (1993). A text of environmental chemistry and pollution control. *S. Chand and Company Ltd. Ram Nagar, New Delhi,* 110055.

Davies, B. E. (1994). Trace element pollution. In B. E. Davies. (Ed). Applied soil trace elements. *Wiley and Sons, New York*, P. 287-251.

David, N., Benjamin, L. and Patrick, Y. (2009). Some physico-chemical and heavy metal levels in soils of waste dumpsites in Port Harcourt municipality and environs. *Journal of Applied Environmental Management*. *13*(4): 65-70.

Ding Y. (2000). The management of polluted soils by heavy metal. *Environment and Development,15*(2): 25-28.

Dolk, M. (1997). Residents near waste landfill sites and risk of non-chromosal congenital malfunctions. *Eurohazcon: Collaboration study group, New York*.

ECB (Environmental Control Board), (2007). European Union Risk Assessment Report. Cadmium oxide and cadmium metal, Part 1 – environment. Volume 72. EUR 22919EN. Luxembourg: Office for Official *Publications of the European Communities*. Available from:http://ecb.jrc.ec.europa.eu/documents/ExistingChemicals/RISK_ASSESSMENT/REPORT/cdmetal_cdo xideENVreport302.pdf [Accessed June 2009].

Edwin, O.A. (2011). Metal fractionation in soil profiles in Umutu Oil field, Northwest Niger Delta Nigeria. *International Journal of Chemistry*. *Canadian centre of Science and Education, 3*(1): 57- 67.

Elder, M. C. (1999). Chemical speciation and fractionation in soil and sediment: heavy metal analysis. A review. *International. Journal of Environmental Analytical. Chemistry.* 59: 225-236.

Essaku, S., Obuli, P., Kurian, J. and Nagendran, R. (2010). Heavy metal fractionation and leachability studies on fresh and partially decomposed municipal solid waste. *Environmental Monitoring and Assessment42*: 161-173.

European Union, (2002). Heavy Metals in Wastes, *European Commission on Environmen*t. http://ec.europa.eu/environment/waste/studies/pdf/ heavymetalsreport.pdf.

Fatoki, O.S. (2003). Lead, Cadmium and Zinc Accumulation on soil and vegetation along some selected major roads of Eastern Cape. *International Journal of Environmental Studies,60* (2): 199 – 204.

Federal Environmental Protection Agency (FEPA) (1989). *Corporal profile. Metro prints Ltd, Port Harcourt. P*. 68-75.

Fliepbach, A., Martens, R., Reber, H. (1994). Soil microbial biomass and activity in soils treated with heavy metal contaminated sewage sludge. *Soil Biology and Biochemistry*, *26*: 1201-1205.

Frank R. Spellman (2006). Chemistry for nonchemist: Principles and Application for Environmental Practitioners. *Government institute an imprint of the screcrew press, inc.*

Frits, R., Vega, G. and Perez, L. (2000). Important chemical properties of metals. *CRC press Inc. Boca Raton.* P. 22-25.

Galadima, A., Muhammad, N.U. and Z.N. Garba (2010) Spectroscopic investigation of heavy metals in waste waterfrom University students' halls of residence. *International Journal of Chemistry*, Vol. 20, No. 4, (2010) 239-244.

Galadima, A, Garba, Z.N. (2011). Recent Issues in Environemntal Science. "Including incidencesand reports from Nigeria". *Lap Lambert Academic Publishers, Germany, ISBN: 978-3- 8454-2915-1*, 100p.

Garba, Z.N., Hamza, S.A. and Galadima, A. (2010). Arsenic Level Speciation in Fresh Water from Karaye Local Government, Kano State, Nigeria. *International Journal of Chemistry*, *20* (2): 113-117.

Garcia, K., Powell, R. and Hill, G. (2009). Chelates in agriculture. *Fertilizer Research*, 25, P. 127-131.

Gupta, V. K., and S. B. Mittal. 1981. Evaluation of chemical methods for estimating available Zn and response of green gram (phaseolus Aureus Roxb) to applied Zn in non-calcareous soils. *Plant and soil.* 63 (3): 477-484.

Heilman, M., Johnson, P. and Raulet, Y. (2003). Symptoms of acute arsenic poisoning in Man. *British Medical Bulletin*, *10*(7): 12-15.

Hukabee, D., Mark, S. and Kirk, T. (2011). Copper in soil and plants. Sydney, *Academic Press*, P. 265-285.

Jackson, M. L. (1962). Soil Chemical Analysis. *Prentise Hall, New, York*, P. 26-29.

Jais, T., Turner, M. and Black, F. (2011). Decomposition in terrestrial ecosystems. *Oxford, U.K, Blackwell Scientific Publications.* P. 18-28.

Jaiswal, P. C. (2004). Soil, Plants and Water Analysis. P. 403.

Jenne, H., Rubio, V. and Gibson, K. (2011). Heavy metal poisoning. *Gale Encyclopaedia of alternative medicine, Farmington Hills.* P. 68- 82.

Joel, F. E. and Siepak, J. H. (2001). Speciation of heavy metals in bottom sediments of Lakes. *Pollution Journal of Environmental Studies,8*(5): 331-338.

Kandeler E, Lurienegger G, Schwarz S. (1997). Influence of heavy metals on the functional diversity of soil microbial communities. *Biology and Fertility of Soils*, *23*: 299-306

Kaim, W. and Schwederski, B. (1994). Bioinorganic chemistry: Inorganic elements in the chemistry of life. *Wiley, Chichester, U.K.* P. 359 – 361.

Kaslo, Y., Rette, B. and Raily, E.(1962). Relative abundance of nitrogen in air. *Mc Graw-Hill, Companies Inc., U.S.A.* P. 21-23.

Kersten, B., Sommers, D. and Morgan, N. (2003). Environmental toxicology and chemistry. *Academic press, London.* P. 22-25.

Ladigbolu, I. A. and Balogun, K.J (2011). Distribution of Heavy Metals in Sediments of Selected Streams in Ibadan Metropolis, Nigeria. *International journal of environmental sciences*, *1*, (6).

Leonard, T., Pocock, S. and Bisson, G. (1998). Heavy metal poisoning.*Gale encyclopaedia of alternative medicine, Farmington Hills*. P. 30-33.

Li, K. (1955). Evapotranspiration rate and how it affects planning of irrigation schemes.*Journal of sustainable tropical agricultural research, 2*(3): 31-36.

Lloyd, D., Wall, J., and Clerk, L. (2011). Heavy metal Poisoning. *Gale Encyclopaedia of alternative medicine, Farmington Hills.* P. 20-24.

Lončarić Z., Karalić K., Popović B., Rastija D. and Vukobratović M. (2008). Total and plant available micronutrients in acidic and calcareous soils in Croatia. *Cereal Research Communications 36*, 331-334.

Loska, K., Cebula, J., Pelczar, J., Wiechula, D. and Kwapulinski, J. (1997). Use of enrichment and contamination factors together with geoaccumulation indices to evaluate the content of Cd, Cu and Ni in the Rybnik water reservoir in Poland. *Journal of Air and Soil Pollution,93*: 347-365.

Matsuno, R. (2011). Nitrate fluctuations in tropical soils. *Journal of Agricultural Science*, *50*: 82–92.

McGrath, S. P. (1995). Nickel. In Heavy Metals in Soils (2nd edn.) (ed. B.J. Alloway). *London: Blackie Academic & Professional*.

Montagne, D., Cornu, S., Bourennane H. (2007). Effect agricultural practices on trace-element distribution in soil. *Communications in Soil Science and Plant Analysis*, 38: 473-491.

Morse, L.(1994). Brass and bronze 'The important copper alloys'. *Cambridge University press, Cambridge*. P. 12-15.

Mohamed S.M. EL-Bady (2014). Spatial Distribution of some Important Heavy Metals in the Soils South of Manzala Lake in Bahr El-Baqar Region, Egypt. *Nova Journal of Engineering and Applied Sciences*, *2*(3), Mar 2014: 1-15.

Muller, G. (1979). Schwermetalle in den sedimenten des Rheins-veranderungen seit. *Umschall, 79*, P. 778-783.

Noltze, V., Welt, A. and Montel, S. (2003). Influence of dietary zinc on lead toxicity in rats. *Toxicology Letter*,*1*: 227-234.

Nriagu, J., Oleru, N.T., Cudjoe, C., Chine, A. (1997). Lead poisoning of children in Africa, III. Kaduna, Nigeria. *The Science of the Total Environment, 197*, 13-19.

Oladipo, M.O.A., Njinga, R.L. Achi, S.S., Ogunleye, P. O., Alfa , B. and Ibrahim, A.A. (2012). Analysis of savannah and rainforest soils of Nigeria using thermal neutron activation analysis technique. *International Journal of Science and Technology*,*2*(8): 583 – 589.

Olatunde S. O. and Oladele O. (2003). Eco-partitioning and indices of heavy metal accumulation in sediment and *Tilapia zillii* fish in water catchment of River Niger at Ajaokuta, North Central Nigeria. *International Journal of Physical Sciences*, *8*(20): 1111-1117.

Ogunfowakan, A. O., Oyekunle, J. A. O., Dorosinmi, L. M., Akinjokun, A. I. and Gabriel, O.D. (2009). Speciation study of lead and manganese in roadside dusts from major roads in Ile-Ife, South Western Nigeria. *Journal of Chemistry and Ecology*, *25*(6): 405-415.

Okoronkwo, N. E., Odemelam, S. A. and Anon, O.A. (2006). Levels of Toxic Elements in soils of Abandoned Waste Dumpsites. *Journal of Environmental Pollution*, *5*(13): 1241-1244.

Okunola, O. J., Uzairu, A. and Ndukwe, G. (2007). Levels of trace metals in soil and vegetation along major and minor roads in metropolitan city of Kaduna, Nigeria. *African. Journal of Biotechnology*, *6*(14): 1703 – 1709.

Okunola, O.J., Uzairu, A., Gimba, C.E., Kagbu, J. A. (2011). Geochemical partitioning of heavy metals on roadside surface soil of different grain size along major roads in Kano metropolis, Nigeria. *British Journal of Applied Science and Technology,1*(3): 94-115.

Olanipekun, E. O., Fagbote, E. O. (2010). Speciation of heavy metals in soil of bitumen deposit impacted area of western Nigeria. *European Journal of Scientific Research, Eurojournals publishing Inc. 47*(2): 265-277.

Oluyemi, E. A., Feuyit, G., Oyekunle, J. A. O. and Ogunfowokan, A. O. (2008). Seasonal variations in heavy metal concentrations in soil and some selected crops at a landfill in Nigeria. *African Journal of Environmental Science and Technology,2*(5): 89-96.

Enokela, S. O. and Salifu, E. (2012). Evaluation of Ground water Quality for Fadama Irrigation Land in River Niger – Benue Confluence Point of Lokoja, Nigeria. *International Journal of scientific and research publication,2* (9).

Orisakwe, O.E (2009) Environmental pollution and blood lead levels in Nigeria: Who is unexposed. *International Journal of Occupational and Environmental Health, 15*(3): 315-317.

Oyedele, D. J., Obioh, I.B., Adejumo, J.A., Aina, P. O. and Aubiojo, O.L. (1995). Lead contamin ation of soil and vegetation in the vicinity of a lead smelter in Nigeria. *Science of Total Environment Journal*, 1732: 189 - 195.

Page, A.L.; Chang, A.C. and EL-Amamy, M. (1987). Cadmium Levels in Soils and Crops in the United States (Chapter 10). *Dept.of Soil and Environmental Sciences, University of California, Riverside*, CA 92521.

Prett, T., Howell, R. and Kloke, N. (1995). Environmental chemistry and Toxicology. *Foludex press Ltd.* P. 100-110.

Qin T. C, Wu Y. S., Wang H. X. (1994). Effect of cadmium, lead and their interactions on the physiological and biochemical characteristics of Brassica chinensis. *Acta Ecologica Sinica,14*(1): 46-49.

Qin, Y.S., Zhao, J., Liu, Z.Q. (2008). Study on the influences of combined pollution of heavy metals Cu and Pb on soil respiration. *Journal of Anhui Agricultural Sciences,36*(3): 1117-1128.

Sahu, H., Kwan, G. and Kucera, T. (2008). Metal toxicity in children. *In: Training manual on paediatric Environmental Health*. P. 5-8.

Satarug, S., Baker, J.R., Urbenjapol, S. (2003). A global perspective on cadmium pollution and toxicity in non-occupationally exposed population. *Toxicology Letters*, *137*: 65-83

Sharma, B., M.K., Chettri. (2005). Monitoring of heavy metals in vegetables and soil of agricultural fields of Kathmandu valley. *Ecoprint Vol* 12.

Sherifat, I., Kolo, M. T. and Olarinoye, I. O. (2008). Heavy metal content of soil samples from two major dumpsites in Minna. *Natural and Applied Sciences Journal*, 11(1): 1-5.

Shirdast, M., Hosseini, M and Sarmadiyan, F. (2010). Variation in soil heavy metal concentrations around downstream of a municipal waste landfill. *Paper presented in 19th World Congress of Soil Science. Brisbane, Australia*. P. 225-230

Su, D.C. and Wong, J.W.C. (2003); Chemical speciation and Phyto availability of Zn, Cu, Ni and Cd in soil amended with fly ash stabilized sewage sludge. Environmental International, *29*: 895 – 898.

Plant and Soil Sciences E-Library (2015).Soils - Part 5: Nitrogen As A Nutrient.

Sommers, L. A., and W. L. Lindsay. 1979. Effect of pH and redox on predicted heavy metal-chelate equilibria in soils. *Soil Sci. Soc. Am. J. 43*: 39.

Sridhar M.K.C, Olawuyi, J.F., Adogame, L.A., Okekearu, I.R., Osajie, C.O and Aborkar, L (2011). Lead in the Nigerian Environment: Problems and Prospects. Available from; ` www.cprm.gov.br/pgagem/Manuscripts/sridharm.htm accessed 09/08/2011.

Taylor, B.(1995). Pollution prevention: fundamentals and practice. *Mc Graw-Hill, Companies Inc., U.S.A.* P. 25-28.

Todorovi, Z., Poli, P., Djerdjevi, D. and Antonijevi, S. (2001). Lead distribution in water and its association with sediment constituents of the Barje Lake (Leskovae, Yugoslavia) *Journal of Serbaria Chemical Society*. *66*(10): 697-708.

Uba, S., Uzairu, A., Harrison, G. F. S., Balarabe, M. L. and Okunola, O. J. (2008). Assessment of heavy metals bioavailability in Dumpsites of Zaria Metropolis, Nigeria. *African Journal of Biotechnology*, *7*(2), P. 122-130.

Udosen, E. D., Benson, N. U. Essien, J. P. and Ebong, G. A. (2006). Relation between aqua-ragia extractable heavy metals in soils and *Manihot utilisima* within municipal dumpsites. *International Journal Soil of Science*,*1*: 27-32.

Vaskorg, H., Walky, V. and Fagg, M. (2010). Soil and the environment: An introduction. *Cambridge University press*. P. 13-20.

Wail, C. (1843). Moisture in soil and weight correction. *National water bulletin*: 12-13.

Wang, D.D., Li, H.X., Hu, F.G.(2007). Role of earthworm-straw interactions on phytoremediation of Cu contaminated soil by ryegrass. *Acta Ecologica Sinica*, *27*(4): 1292-1299.

Wedepohl, K. H. (1998). Origin and distribution of elements. In Ahrens, L. H. (Ed). International Symposium on the Origin and Distribution of the Elements.*Pergamon Press, New York*, P. 999.

World Health Organization,(1996). *Permissible limits of heavy metals in soil and plants*. (Geneva: World Health Organization), Switzerland (1996).

Wilcox, L. V. (1950). Electrical conductivity. *American Water Works Association Journal*, 42: 775-776.

Wong, M. T. F., Van der Kruijs, A. C. B. M. and Juo, A.S.R. (2005). Leaching loss of calcium, magnesium, potassium and nitrate derived from soil, lime and fertilizers as influenced by urea applied to undisturbed lysimeters in south-east Nigeria. *Nutrient Cycling in Agro ecosystems*, 31, P. 281-289.

Wood J. M. (1974). Biological cycles for toxic elements in the environment. *Science*, 183: 1049-1052

Yadav, W., Fisher, G. and Hooder, R. (2000). Heavy metals in North Carolina soils, occurrence and significance. *North Carolina Department of Agric and consumer Services, Agronomic Division.* P. 27-35.

Yahaya, M. I., Mohammad, S. and Abdullah, B. K. (2009). Seasonal variations of heavy metals concentration in abattoir dumping site soil in Nigeria. *Journal ofApplied Sciences and Environmental Management, 13*(4): 9-13.

Yang, Y.B., Sun, L.B. (2009). Status and control countermeasures of heavy metal pollution in urban soil. *Environmental Protection Science, 35*(4): 79-81.

Zhang, W.J., Jiang, F.B., Ou, J.F. (2011). Global pesticide consumption and pollution: with China as a focus. *Proceedings of the International Academy of Ecology and Environmental Sciences,1*(2): 125-144.

Zhang, Z.J., Lu, Q.F., Fang, F. (1989). Effect of mecury on the growth and physiological function of wheat seedlings. *Chinese Journal of Environmental Science*, *10*(4): l0-13.

Zhou, Q.X.,(1995). Ecology of Compound Pollution. *China Environmental Science Press, Beijing, China.*

APPENDICES

APPENDIX I

List of Apparatus and Equipments

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

22. Stainless steel spoon
23. Crucibles
24. Centrifuge
25. Furnace
26. Glass rod
27. Pipette – 1ml, 5ml, and 10ml
28. Hydrometer
29. Butchner funnel
30. Erlenmeyer flask
31. Teflon Cup
32. 2mm sieve
33. Spatula
34. Petri-dish

List of Reagents and Chemicals (Analar Grade)

1. $BaCl_2$ – Barium Chloride
2. $Cd(NO_3)_2$ – Cadmium nitrate
3. $Cu(NO_3)_2.3H_2O$ – Hydrated Copper nitrate
4. HCl – Hydrochloric acid
5. HClO4 – Per chloric acid
6. HF – Hydrofluoric acid
7. HNO_3 –Nitric acid
8. H_2O_2 – Hydrogen peroxide
9. H_2SO_4 – Sulphuric acid
10. KCl – Potassium Chloride
11. K_2CrO_4 – Potassium Dichromate
12. KH_2PO_4 – Potassium hydrogen phosphate
13. $AgNO_3$ – Silver nitrate
14. K_2SO_4 – Potassium sulphate
15. $Mg(NO_3)$ – Magnesium nitrate
16. $SnCl_2$ – Stannous chloride
17. NaCl – Sodium Chloride
18. NH_4OAc –Ammonium acetate
19. NaOH –Sodium hydroxide
20. NH_4Cl –Ammonium Chloride
21. NaOAc – Sodium Acetate
22. As_2O_5 –Arsenic pentoxide.

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

24. Distilled water

25. 0.05M ethylenediaminetetraacetic acid (EDTA) solutions

APPENDIX II

Test of Statistical Significant Difference for some Physicochemical Parameters

Analysis of variance for pH of the soils collected from River Niger, Benue and after the confluence points

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Dry 2013	4	27.6	6.9	0.026667
Wet 2013	4	26.9	6.725	0.015833
Dry 2014	4	27	6.75	0.096667
Wet 2014	4	26.1	6.525	0.015833

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.285	3	0.095	2.451613	0.11367	3.490295
Within Groups	0.465	12	0.03875			
Total	0.75	15				

Analysis of variance for organic matter content of the soils collected from River Niger, Benue and after the confluence points

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Dry 2013	4	4.25	1.0625	0.306195
Wet 2013	4	3.451	0.86275	0.322083
Dry 2014	4	4.059	1.01475	0.262091
Wet 2014	4	4.737	1.18425	0.306018

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.2122	3	0.070733	0.236489	0.869219	3.490295
Within Groups	3.589161	12	0.299097			
Total	3.801361	15				

Analysis of variance for moisture content of the soils collected from River Niger, Benue and after the confluence points

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Dry 2013	4	281.5	70.375	35.6425
Wet 2013	4	305.2	76.3	47.74
Dry 2014	4	277.8	69.45	35.65667
Wet 2014	4	296.55	74.1375	28.96229

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	123.6892	3	41.22974	1.114306	0.381675	3.490295
Within Groups	444.0044	12	37.00036			
Total	567.6936	15				

APPENDIX III

Test of Statistical Significant Difference for Heavy metals Across the Season

Analysis of variance for Cd content of the soils collected from River Niger, Benue and after the confluence points

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	4	16.85	4.2125	0.052292
Column 2	4	22.7	5.675	0.0225
Column 3	4	25.9	6.475	0.3825
Column 4	4	31.7	7.925	0.315833

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	28.84547	3	9.615156	49.74697	4.82E-07	3.490295
Within Groups	2.319375	12	0.193281			
Total	31.16484	15				

Analysis of variance for Cu content of the soils collected from River Niger, Benue and after the confluence points

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	4	60.8	15.2	10.98667
Column 2	4	60.1	15.025	2.349167
Column 3	4	73.5	18.375	1.469167
Column 4	4	68.1	17.025	14.02917

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	30.48688	3	10.16229	1.409757	0.287976	3.490295
Within Groups	86.5025	12	7.208542			
Total	116.9894	15				

Analysis of variance for Mn content of the soils collected from River Niger, Benue and after the confluence points

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	4	663.2	165.8	136.8067
Column 2	4	735.3	183.825	655.4492
Column 3	4	788.5	197.125	185.3558
Column 4	4	750.7	187.675	237.3158

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2065.687	3	688.5623	2.267007	0.132966	3.490295
Within Groups	3644.783	12	303.7319			
Total	5710.469	15				

Analysis of variance forNi content of the soils collected from River Niger, Benue and after the confluence points

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	4	737	184.25	24.75
Column 2	4	999.7	249.925	646.8892
Column 3	4	897.9	224.475	202.0625
Column 4	4	958.6	239.65	1168.09

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	9983.975	3	3327.992	6.519748	0.007273	3.490295
Within Groups	6125.375	12	510.4479			
Total	16109.35	15				

Analysis of variance forPb content of the soils collected from River Niger, Benue and after the confluence points

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	4	117.6	29.4	35.76667
Column 2	4	93.6	23.4	12.81333
Column 3	4	119.6	29.9	19.38667
Column 4	4	109.6	27.4	19.84667

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	104.75	3	34.91667	1.590495	0.243233	3.490295
Within Groups	263.44	12	21.95333			
Total	368.19	15				

Analysis of variance forZn content of the soils collected from River

Niger, Benue and after the confluence points

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	4	194.5	48.625	63.6225
Column 2	4	235.1	58.775	43.9625
Column 3	4	258.1	64.525	40.7825
Column 4	4	242.5	60.625	165.1492

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	551.5275	3	183.8425	2.345553	0.124333	3.490295
Within Groups	940.55	12	78.37917			
Total	1492.078	15				

APPENDIX IV

Test of Statistical Significant Difference between*A. hybridus* and *Corchorus olitorius L,*

t-Test: Paired Two Sample for Cadmium content in the two plants grown on riverside soils in the pot experiment

	Variable 1	*Variable 2*
Mean	1.025	1.3
Variance	0.0825	0.126667
Observations	4	4
Pearson Correlation	0.815193	
Hypothesized Mean Difference	0	
Df	3	
t Stat	-2.66789	
P(T<=t) one-tail	0.037913	
t Critical one-tail	2.353363	
P(T<=t) two-tail	0.075826	
t Critical two-tail	3.182446	

t-Test: Paired Two Sample for Copper content in the two plants grown on

riverside soils in the pot experiment

	Variable 1	*Variable 2*	
Mean	4.725		4.55
Variance	0.749167		1.536667
Observations	4		4
Pearson Correlation	0.883857		
Hypothesized Mean Difference	0		
Df	3		
t Stat	0.561048		
P(T<=t) one-tail	0.306971		
t Critical one-tail	2.353363		
P(T<=t) two-tail	0.613943		
t Critical two-tail	3.182446		

t-Test: Paired Two Sample for Manganese content in the two plants grown on

riverside soils in the pot experiment

	Variable 1	*Variable 2*	
Mean	33.35		34.405
Variance	8.276667		13.2561
Observations	4		4
Pearson Correlation	0.563938		
Hypothesized Mean Difference	0		
df	3		
t Stat	-0.67683		
P(T<=t) one-tail	0.273516		
t Critical one-tail	2.353363		
P(T<=t) two-tail	0.547032		
t Critical two-tail	3.182446		

t-Test: Paired Two Sample for Nickel content in the two plants grown on

riverside soils in the pot experiment

	Variable 1	*Variable 2*	
Mean	42.625		35.55
Variance	37.80917		28.20333
Observations	4		4
Pearson Correlation	0.287195		
Hypothesized Mean Difference	0		
df	3		
t Stat	2.058395		
P(T<=t) one-tail	0.065849		
t Critical one-tail	2.353363		
P(T<=t) two-tail	0.131698		
t Critical two-tail	3.182446		

t-Test: Paired Two Sample for Lead content in the two plants grown on

riverside soils in the pot experiment

	Variable 1	*Variable 2*	
Mean	13.425		13.975
Variance	0.5225		3.529167
Observations	4		4
Pearson Correlation	0.926038		
Hypothesized Mean Difference	0		
df	3		
t Stat	-0.88737		
P(T<=t) one-tail	0.220122		
t Critical one-tail	2.353363		
P(T<=t) two-tail	0.440244		
t Critical two-tail	3.182446		

t-Test: Paired Two Sample for Zinc content in the two plants grown on

riverside soils in the pot experiment

	Variable 1	*Variable 2*	
Mean	18.5		16.625
Variance	0.54		0.2825
Observations	4		4
Pearson Correlation	0.554736		
Hypothesized Mean Difference	0		
df	3		
t Stat	6.011231		
P(T<=t) one-tail	0.004612		
t Critical one-tail	2.353363		
P(T<=t) two-tail	0.009224		
t Critical two-tail	3.182446		