EVALUATION OF LEVELS OF HEAVY METALS IN SOIL AND WELL WATER WITHIN SELECTED AUTOMOBILE MECHANIC WORKSHOPS IN LOKOJA, NIGERIA

BY

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BY

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DEPARTMENT OF CHEMISTRY,
FACULTY OF SCIENCE
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MAY, 2016

DECLARATION

I declare that the work in the dissertation entitled 'Evaluation of levels of Heavy Metals in Soil And Well Water Within Selected Automobile Mechanic Workshops in Lokoja, Nigeria**.**' has been performed by me in the department of chemistry, under the supervision of Professor E.B, Agbaji And Dr. H.Z, Omenesa. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this research was previously presented for another degree or diploma at any university or institution.

Moses YAHAYA

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Name of Student	Signature	Date

CERTIFICATION

This dissertation entitled "Evaluation of levels of Heavy Metals in Soil And Well Water Within Selected Automobile Mechanic Workshops in Lokoja, Nigeria" by Moses Yahaya meets the regulation governing the degree of MSc. analytical chemistry of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This dissertation is dedicated to God Almighty.

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ABSTRACT

Soil characterization and levels of heavy metals in two different soil depths (0 - 15 cm and 15 - 30 cm depth) and well water ofautomobile mechanic workshop soil at Zawangi, Crowther Memorial, Lokongoma Phase 1, Lokongoma Phase 2, Felele , and first 200 unit areas of Lokoja metropolis, Nigeria werecarried out between September and December, 2014.The physicochemical parameters of the soil such as pH, particle size, cation exchange capacity (CEC), organic matter (OM), electrical conductivity, phosphates and sulphates were determined. The soil samples were subjected to sequential extraction to ascertain the mobility of the metals in the soils. Statistical analysis on the data obtained was carried out using One- way ANOVA. The results indicated that the soils at the experimental and control sites were a mixture of sandy loam, clay and slightly acidic. The %OM and CEC for the experimental soils were higher than the soils of the Nigerian Savanna.The concentrations of the studied metals (Zn-64.00mg/kg, Pb-45.22mg/kg, Cd-2.84mg/kg, Fe-151.58mg/kg and Ni-16.06mg/kg) in the soils from experimental sites were higher than the corresponding values from the control site (Zn-5.75mg/kg, Pb-2.07mg/kg, Cd-1.90mg/kg, Fe-36.65mg/kg and Ni-2.1mg/kg), and also, higher than the recommended limits given by the World Health Organization (WHO). The soil samples showed remarkably high levels of all the metals (Ni, Fe, Zn and Pb) above background concentrations with most of them decreasing with decrease in soil depth. The distribution was in the following order Fe> Zn> Pb > Ni > Cd. Across the sampling locations and profiles, Fe and Cd gave the highest (154.58 mg/kg) and least (2.54 mg/kg) values respectively. Pollution load index (PLI) andgeoaccumulation index(*Igeo*) revealed overall high and moderate contamination respectively while theenrichment factors (EFs) for Zn and Ni were severe. The inter-elemental relationship revealed anidentical source of elements in the soils of the studied areas. The levels of metal in well water within the mechanic workshops at different distances of 20m and 30m away from each location were determined.The results indicated that, the levels of metal in well water were higher in 20m than 30m away from the mechanic workshops. At 20m, Zn was the highest in Lokongoma phase1 (14.03 mg/kg) and least at Zanwangi (1.16 mg/kg), Pb was highest in Lokongoma phase1(1.96mg/kg) and least in Crowther Memorial and Felele (1.56 mg/kg), Cd was the highest in Lokongoma Phase1(0.21 mg/kg) and least in Lokongoma Phase2(0.15mg/kg), Fe was the highest in Lokongoma Phase1 (1.73mg/kg) and least in Crowther Memorial and Felele (0.83mg/kg) and Ni was the highest in 200Unit (45.55 mg/kg) and least in Felele (0.07 mg/kg). While at 30m, Zn was the highest in Lokongoma Phase2 (6.34mg/kg) and least in Zanwangi(0.16mg/kg), Pb was highest in 200Unit and Felele (1.56mg/kg) and least in Lokongoma Phase1 (1.25mg/kg),Cd was highest in 200Unit and Felele (0.15 mg/kg) and least in Lokongoma Phase1, Lokongoma Phase2 and Zanwangi(0.13mg/kg), Fe was highest in 200Unit (1.54mg/kg) and least in Crowther Memorial and Felele (0.64 mg/kg) and Ni was highest in Lokongoma Phase1&2 (0.09 mg/kg) and least in Zanwangi (0.01mg/kg).The accuracy of the results has beencheeked using the standard reference material; SRM (PACS-2). The mechanic workshop soils represent potential sources of heavy metal pollution to the environment. The elevated levels of heavymetals in these soil profiles constitute a serious threat to humans live, surface and groundwater.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

The increase in automobile repairs/workshops and their activities in Nigeria are partly due to the ever-increasing demand for personal vehicles, most of which are used "Tokunbo" vehicles. These have contributed remarkably to the problem of soil contamination in most cities. Automobiles used oil (waste) contains oxidation products, sediments, water and metallic particles resulting from machinery wears, used batteries, organic and inorganic chemicals used in oil additives and metals (European Environment Agency, 2007). Soil Percolation of leachates from these materials poses threats to groundwater. Unfortunately, information on the impact of automobile mechanics' activities on the ecosystem is still very unavailable. The co-existence of toxic heavy metals and hydrocarbons (HCs) at many of the mechanics contaminated sites all over Nigeria and in other developing countries pose a severe threat to the environment. In fact, the presence of trace elements in soil is increasingly becoming an issue of global concern especially as soil constitutes a crucial component of rural and urban environment (United States Department of Agriculture 2001, Lim, 2008). Heavy metals such as cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn) which are often used as additives in some lubricants and gasoline are non-degradable in the soil. Some of them have been classified as priority pollutants by United State Environmental Protection Agency(United States Department of Agriculture 2001). At the moment, very few technologies, such as soil washing and bioremediation, are available to treat these mixed wastes (Sharma, 2004)

The problem of soil and vegetation pollution due to toxic metals in spent oil is cause for concern in most metropolitan cities (Vwioko *et al*., 2006). These toxic heavy metals entering the ecosystem may lead to bioaccumulation and bio magnifications (Wong *et al*., 2002). Spent oil soil pollution leads to the build-up of essential and non-essential elements in the soil and eventual translocation in plant tissues (Vwioko et al., 2006). Soil pollution by spent lubricating oil has been reported to cause growth retardation/ reduction in plants and this has been attributed to the presence of heavy metals at toxic concentrations in the soil (Anoliefo and Vwioko, 1995).

Due to the ever-increasing population and industrialization, most environments are to some extent polluted.

It is also estimated that the contributions of metals from anthropogenic sources in soil is higher than the contribution from natural ones, hence, the repeated evaluation of the contamination status of soils (Nriagu, 1988).

Nriagu (1978) reported that we may be experiencing a silent epidemic of environmental metal poisoning from the increasing amounts of metals released into the biosphere. Waste engine oil pollution is responsible for several environmental problems, including disruption of plant water relations having direct toxicity and indirect effects on plant metabolism (Racine, 1994). Edebiri and Nwanokwale (1981) found that metals present in spent lubricating oil are not necessarily the same as those present in unused lubricant. Heavy metals such as vanadium, lead, aluminium, nickel and iron which are low in unused engine oil gave higher concentrations in spent engine oil. Hall (2002) observed that heavy metals, such as copper and Zinc are essential for normal plant growth. There are researches in the Southern part of Nigeria onspent oil pollution of soil and vegetation, but not much has been done on spent oil pollution in the North Central region of the country.

Consequently, this work is initiated to study and evaluate soil pollution due to heavy metals in spent lubricating oil in the vicinity of some mechanic workshops in Lokoja Metropolis of North Central Nigeria.

1.2 Water

Water, after air, is the most essential commodity to the survival of life. Human life depends to a large extent, on water. It is used for an array of activities; chief among these being for drinking, food preparation, as well as for sanitation purposes. Inasmuch as safe drinking water is essential to health, a community lacking a good quality of this commodity will be saddled with a lot of health problems which could otherwise be avoided (Miller, 1997).

Water covers 70.9% of the Earth's surface, and is vital for all known forms of life. On Earth, it is found mostly in oceans and other large water bodies, with 1.6% of water below ground in aquifers and 0.001% in the air as vapor and precipitations. Oceans hold 97% of surface water, 2.4% for glaciers and polar ice caps, and, 0.6% for other land surface water such as rivers, lakes and ponds. A very small amount of the Earth’s water is contained within biological bodies and manufactured products (Wikipedia, 2010).

Groundwater is of major importance and is intensively exploited for private, domestic and industrial uses. According to Ajibade *et al*., (2011), 90% of the population in Nigeria depends largely on hand-dug wells and boreholes. Without water there can be life, Water is necessary for a sustainable economic development of a country. Hand-dug wells are used to complement the usually unavailable pipe-borne water in many communities in a country and this is an indication that water sustains life. Hand dugged wells have been the sources of water for people in Nigeria for ages. Some of this well is dugged in close proximity to rivers. And it is well known that rivers are the major transporting means for different contaminants into groundwater and lakes (Sina *et al., 2009).*

The preference of groundwater as a source of drinking water in rural areas is because of its relatively better quality than river water (Obiri-Danso*et al., 2009).* Historically rural settlement was being determined by water source such as stream, river and spring (Okeola*et al.*, 2010). The inhabitants of these settlements relied on underground water often within a few meters of the surface which they exploited in well digging.

Access to safe drinking water is a basic human need and a fundamental human right, crucial for poverty reduction and eradication. According to a report (United Nation, 2003), this situation forces people to consume water directly from the rivers and ponds and this represents a high risk to their health. According to World Health Organization (*WHO*, 2000), in the next thirty years alone, accessible water is unlikely to increase more than ten percent (10%) but the earth's population is projected to rise by approximately one-third. Unless the efficiency of water use rises, this imbalance will reduce quality water services, reduce the conditions of health of people and deteriorate the environment and the world.

1.3 Statement of Research problem

Lokoja is one of the largest towns in the north central part of Nigeria. It has a population of about 196,643 according to the 1996 population Census. Majority of the people engage in town services such as: Motor cycle, taxi and bus driving as their occupation which has led to the existence of many automobile mechanic workshops almost everywhere in Lokoja town, Also, indiscriminate disposal of their spent oil subjects the soil of thisenvironment to high risk of pollutionwith heavy metals and other harmful substances. Since heavy metals at elevated levels can be dangerous to lives and environment, there is need to check their concentration and mobility in this town. Lack of strict application of environmental protection legislation the need for better control of the pollution situation and absence of basic data about heavy metal pollution from automobile mechanic workshops in the town is the background for the present work.

1.4 Aim

The aim of this research is to evaluate the level of heavy metals and their mobility in the soil and well water of some selected automobile mechanic workshops in Lokoja metropolis, Nigeria. This aim would be achieved through the following objectives.

1.5 Objectives

i. Determination of some physicochemical parameters, such as pH, clay, silt, sand, Electrical conductivity, organic carbon, Cation Exchange Capacity, PO_4^{3-} and SO_4^{2-} in the soil sample.

ii. Determination of the concentration of Cd, Fe, Ni, Pb and Zn in the soil sample and well water located within the vicinity of these automobile mechanic workshops.

iii undertake speciation studies to determine the mobility of the above heavy metals in the vicinity automobile mechanic workshops.

1.6 Justification for the Research

Because of the pollution associated with heavy metal at elevated concentration to humans lives, surface water and underground water in the environment. There is need to ascertain the levels of the heavy metal in this environment.

The work is intended to give a base line data for future investigation of activities leading to temporary changes, in concentrations of heavy metals in the vicinity of automobile mechanic workshops in the areas studied (Lokoja). Since no known work of this nature has yet been done in this town.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Heavy Metals

The term ‘heavy metal’ refers to any metallic element that has a relatively high density (Lenutech, 2004, Duruibe *et al.*, 2007).

Heavy metals are commonly associated with pollution and toxicity problems. They occur in soil in minute amount without regard to their requirement by plants and animals. They are classified according to their effect into three categories: the toxic, the nutritive and the essential nutritive metals (Lenutech,2004).

However, according to report by expert committee on metals (WHO, 2000), all essential elements become toxic at high intake and the margin between levels that are beneficial and those that are harmful may be small. Copper, zinc, cobalt, nickel, chromium, manganese, iron, selenium, silicon, tin, fluorine, iodine, molybdenum and vanadium are essential trace elements, while lead, cadmium, mercury are non-essential. Heavy metals are natural component of the earth crust: they enter our bodies via food, drinking water and air(WHO, 2000). Some heavy metals (such as copper, selenium and zinc) are essential to maintain the metabolism of the human body. However at higher concentration they can lead to poisoning. Heavy metal poisoning could result, for instance from drinking contaminated water such as lead pipes, high ambient air concentration near emission sources, or intake via the food chain(WHO, 2000).

2.2 Soil Pollution

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

Materials that find their entry into the soil system persist and accumulate in toxic concentrations becoming sources of pollution in the soil (Misra and Mani, 2009). Among the pollutants that persist and accumulate in the soils include; inorganic toxic compounds for example fertilizers, organic wastes, organic pesticides and radio nucleides (Misra and Mani, 2009; Jia *et al.*, 2010).

2.3 Natural Occurrences

Heavy metalsoccur naturally as chemical elements in the earth's crust in varying concentration that may give rise to ore deposits in locations where they are highly concentrated. The levels in the earth's crust and common ore minerals of some heavy metals often used and discharged industrially are obtained from sulphide ores. As is a bye product of Cu ores, Bi is also a bye product of Pb ores, while Hg and Cd (dominantly) are bye products of Zn ores (Alloway, 1990).

Heavy metals are peculiar to all kinds of soils, sediments waters and living organisms in a range of normal background levels but when they exceed an optimum range of safe exposure then the term ''heavy metal pollution'' is used (Petrovic,*et* *al.,*1999). Thus, of concern are their emissions into the environments as a result of increase in industrial, agricultural and urban activities, which give rise to anomalous high concentration of the metals relative to the normal background levels. Hence many heavy metals are essential to life, but they can be toxic at high levels while Cd, Hg and Pb have been found to possess toxicity effect even at very low levels (Cook, 1979).

2.4 Origin of Heavy Metals in Soil

Two sources of heavy metals in soil are geochemical and anthropogenic, such as land disposal of municipal and industrial wastes and use of fertilizer and pesticides (Petrovic,*et al.,* 1999).

2.4.1 Geochemical Sources

Heavy metals occur as trace constituents of primary minerals in igneous rock, which erupt from the molten magma. They become incorporated into the crystal lattice as ores of the major elements at the time of crystallization. This substitution is governed by ionic charge, ionic radius and electro negativity of the major and trace elements replacing it, Substitution can occur when the radii of the major constituent ions and that of trace metals are within 15% of each other and when the charges differ by not more than a unit (Krauskopf, 1976). Weathering of the outcropping rock at the earth surface releases heavy metal constituents. The content depends upon the minerals, the matrix and levels of metals in water in which the sediments are deposited. The sediments from which they are formed have appreciable amount of organic matter which acts both as an adsorbent for heavy metals and as a substrate for micro-organisms (Krauskopf, 1976).

2.4.2 Anthropogenic sources

The conventional sources of heavy metal pollution are domestic sewage, spent oil lubricant, industrial waste, oil spills, mining operation, combustion emission, garbage dumps and metallurgical activities (Bryan 1976: Fporstner and Witmann, 1979). Metals have a wide range of uses from which they find their way into the soil. Raw materials used in the cottage industries where operations like welding, soldering are undertaken contain these metals. Input of heavy metals into the soil has increased over decades as a consequence of agricultural practices e.g (use of fertilizer and pesticides) disposal of sewage sludge and augmented atmospheric deposition (Adriano, 1986). The modification of natural cycle of heavy metals has led to input of the metals in the soils and the removal due to harvest of agricultural crops, losses due to leaching and volatization of metals (Udosen *et al.*, 2006). Therefore, soil acts as a sink or filter in which heavy metals accumulate but deplete slowly, unlike other environmental compartments such as water, heavy metals in soil are characterized by long residence time. Adriano (1986) reported that contamination of soil with respect to copper, lead and zinc appears to be permanent.

Some of the major anthropogenic sources include phosphate fertilizer and slag from iron manufacturing pesticides and herbicides contain various combinations of heavy metals either as impurities or active constituents. There is some indirect evidence of possible heavy metal build up in some agricultural soil in savannah region because of long term application of phosphate fertilizers (Agbenin and Felix-Henningson, 2001).

Another source is atmospheric pollution from motor vehicle. The use of leaded petrol hasbeen responsible for the global dispersion of lead aerosol. The use of lead in paints and organic Pb compounds in gasoline has caused lead to be wide spread in the environment (Oliver, 1997).

Combustion of fossil fuel leads to the dispersion of many elements in the air over a large area. The dispersal of urban and industrial waste can result in soil pollution from the deposition of aerosol particles emitted by the incineration of metal containing minerals. The unauthorized dumping or disposal of metal containing items, ranging from miniature dry cell batteries (Ni, Cd, and Hg) to abandoned cars can give rise to small areas of high metal concentration in the soil. The disposal of some domestic wastes by burning on garden bonfires, or burial add to the contents of metals, such as lead, in soils used for growing vegetables (Oliver, 1997).

Organic manure is a major anthropogenic source. For example pig and poultry manures which may contain high levels of Cu or As added to the feed to improve food conversion efficiency. Sewage slugs often contain high concentration of several metals especially those from industrial catchments (Alloway, 1990).

Metallurgical industries can contribute to soil pollution by emission of fumes and dust containing metals, which are transported in the air and eventually deposited into the soil and vegetation, by effluents during flood. Mining and smelting of non-ferrous metals has caused soil pollution dating back to the Roman time and in some places, like Germany (Alloway, 1990).

2.5 Water

Water is a liquid at ambient conditions, but it often co-exists on Earth with its solid state being ice, and gaseous state being water vapor or steam (Ameyibor *et al*, 1991). Human bodies are approximately 60% water, blood is at least 50% water andthe human brain made of 77% water (Stanistski *et al*., 2000).

The main sources of water supply in Nigeria include surface water, ground water and rain water. According to FAO (2005) as cited in (Stanistski *et al*., 2000), rainfall, although not reliable, has a mean ranging from 2150 mm in the south-western part to 800 mm in the south-eastern. Rainwater harvest is not so popular among urban settlers. Nevertheless, it provides a significant amount of domestic water in the southern rural areas particularly during the humid months of May, June, July and August (Stanistski *et al*., 2000). estimated total annual run-off as 56.4%.

(Sina *et al, 2009)*determine the effects of well depth on water quality, the wells up to 4 m. depth and 100 m. far from the river were selected in Isfahan, a total of 100 samples were taken and analyzed. Results of this study showed that Total Coliform, Fecal Coliform, COD, NO_3, Total Dissolved Solid and Electrical Conductivity showed a range of 3-460 and 0-29 MPN/100 mlShowed that NO_3, ElectricalConductivity and Total Dissolved Solid increased and Total Coliform, Fecal Coliform decreased with increasing well depth.

(Sina *et al, 2009)*. Study at the effect of depth on the microbial pollution of shallow wells in theThree floodplains of Makurdi metropolis of Benue State, Nigeria,The species isolated were Salmonella syphilis, Escherichia coli, Streptococcus faecalis, Proteus spp. and total coliform.The pollution of wells was found to increase with decrease in depth and decrease with increase in depth.The water table was found to vary from 4.3m (in wet season) to 6.4m (in dry season).All the wells studied do not meet the limit by World Health organization (WHO) for drinking water which is 0cfu/ml and 10cfu/ml by the

National Agency Food and Drugs Administration and Control, Nigeria (NAFDAC). This shows that wells must be up to 15m deep so as to be free from pollution.

(Obiri Danso et al., 2009)determined the relationships between water chemistry and depth of hand dug wells in a densely populated part of Ibadan, Nigeria.The Results of the multiple regression and correlation showed that Coliform count, pH, total hardness (TH), calcium (Ca+),magnesium (Mg+), iron (Fe+) and chloride (Cl-) increase with increasing depth while nitrate (NO^{3}-) and bicarbonate ($(CO^{3}-)_2$ reduce with depth.

2.5.1 Sources of Water

Water can be grouped into Surface water comprising of oceans, rivers, lakes, reservoirs, lagoons, streams and many others, Ground water which is considered mostly as purer than the surface water and lastly the rain water which falls as a result of condensation and precipitation of the clouds (Stanistski *et al*., 2000). Surface water frequently contains substances that must be removed before it can be used as drinking water while ground water is that which pumped from wells and boreholes that have been drilled from underground aquifers and is usually free from harmful contaminants.

2.5.2 Wells

A Well is an excavation or a structure created in the ground by digging, driving, boring or drilling to access groundwater in underground aquifers (Roger,1982).The well water may be drawn by an electric submersible pump, a vertical turbine pump, a hand pump or a mechanical pump (e.g. from a water-pumping windmill). It can also be drawn up using containers, such as buckets that are raised mechanically or by hand (Obiri Danso et al., 2009).Wells can vary greatly in depth, water volume and water quality. Well water typically contains more minerals in solution than surface water and may require treatment to soften the water. There are basically three types of wells. They include hand-dug wells, driven wells and drilled wells. Hand-dug wells are constructed by hacking at the ground with pick and shovel to dig until the water table is reached. If the ground is soft and the water table is shallow, then dug wells can work. The well is lined with stones, brick, tile, or other material to prevent collapse, and is either covered with a cap of wood, stone, metal or concrete (Roger, 1982). In Nigeria, many of the wells we find in our homes are excavated until reaching the water table and are described as shallow (Obiri Danso *et al.*, 2009) . The depth of the wells depends on how far the water table could be reached. Driven wells are built by driving a small-diameter pipe into soft earth, such as sand or gravel (Roger, 1982). A screen is usually attached to the bottom of the pipe to filter out sand and other particles. They can only tap shallow water, and because the source of the water is so close to the surface, contamination from surface pollutants can occur. Drilled wells require a fairly complicated and expensive drill rig. They use rotary drill bits that chew away at the rock, percussion bits that smash the rock. Drilled wells can be drilled more than 1,000 feet deep. Often a pump is placed at the bottom to push water up to the surface (Roger, 1982).

2.5.3 Well Contamination

Shallow pumping wells can often supply drinking water at a very low cost, but because impurities from the surface easily reach shallow sources, a greater risk of contamination occurs for these wells when they are compared to deeper wells. Contamination of the wells increases during the rainy seasons where the aquifer is “topped up” more rapidly and both vertical and horizontal migrations of water are accelerated (Roger, 1982). Dug and driven wells are easy to contaminate because they are relatively shallow.

The quality of the well water can be significantly increased by lining the well, sealing the well head, fitting a self-priming hand pump, constructing an apron, ensuring the area is kept clean and free from stagnant water and animals. Most of the bacteria, viruses, parasites, and fungi that contaminate well water come from faecal material from humans and other animals.

Ground water is considered the healthiest source of drinking water, but domestic, agricultural and industrial activities have led to the degradation of ground water quality in different parts of the world. Ground water is a resource found under the earth's surface as most ground water comes from rain and melting snow soaking into the ground. Ground water - its depth from the surface, quality for drinking water, and chance of being polluted - varies from place to place. Generally the deeper the well, the better the ground water, the amount of new water flowing into the area also affects ground water quality (Odukoya *et al*., 2010).

Even if no sources of anthropogenic contamination exists there is potential for natural levels of metals and other chemicals to be harmful to human health. This was highlighted in Bangladesh where natural levels of Arsenic in ground water were found to be causing harmful effects on the population (Odukoya *et al*., 2010).

Geochemical analyses of groundwater and streams flowing around abandoned and active mechanic workshops in Lagos, South western Nigeria were carried out by Odukoya *et al*.,(2010), while the water around most of the mechanic workshops areas exceeded the acute and chronic effect levels proposed by the United States Environmental Protection Agency in 2007 (Odukoya *et al*., 2010).

Geochemical implication of heavy metals was evaluated on groundwater surrounding mechanic workshops at Olusosun, site Lagos (Laniyan *et al*., 2011). The results revealed dominance of Pb, Fe and, Mn when compared with WHO and SON standard, while all the metals were found high in the leachates. Contamination assessment revealed Fe and Pb to be extremely contaminated in the groundwater, while geoaccumulation factor showed that farther away from the mechanic workshops contamination reduces. Thus, Pb, Fe and Mn if not checked could lead to major health problems like tooth decolouration, low mental development and kidney problems on the public (Laniyan *et al*., 2011).

2.6 Metal Speciation and Mobility in Soil

Metals are present in soils in different chemical and physical forms, which influence their mobility and bioavailability (Zauyah *et al,* 2004). The terms bioavailability and metal speciation (particularly the free ion species) are often used interchangeably. They are in fact separate concepts with the latter often assisting in determining the former. There is a consensus that the concept of metal bioavailability needs to be considered in environmental risk assessments (NEPM, 1999). Bioavailability is a qualitative term conveying the concept that often the total concentration of the chemical(s) of concern in environmental media is not a good predictor of acute toxicity to organisms (Zauyah *et al*, 2004).

Speciation of heavy metals in soil can also be defined as the determination of precise chemical forms or oxidation states of an element in soil solution or soil pore water by sequential extraction techniques. The extraction will usually be designed to extract the elements associated or bound to a particular soil phase but in practice the soil phase may be ill defined and the extract not specific to the phase. The use of selective extract ants to quantify the elemental content in a particular phase is illuminated by the concept of pool ions soil occur in various forms, each possessing different mobility and phytoavailability. Environmental hazard derived from heavy metals are linked to their movement in soil (Li and Shuman, 1996). The biological availability of an element and its ultimate effect on organism may depend on the chemical organism, and the chemical form in which the elements are encountered. Thus solubility properties, the oxidation state or the bonding characteristics in a particular compound may determine whether it will be inert, poisonous or detoxified by normal metabolic pathway (Sindhu, 2005).

Bioavailability is the proportion of total metals that are available for incorporation into biota. Total metal concentrations do not necessarily correspond to 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 are used to determine elemental behaviour (Elder, 1999).

Bioavailability of metals released from deposits is very complex and dependent 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 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).

Heavy metals in soil can be separated into defined fractions that are relevant to their physicochemical forms (Shuman, 1991). The water soluble forms include ions, inorganic and organic complexes in soil solution, the exchangeable form, the organic complexes and residual primary mineral lattice.

The first three fractions are considered to be plant available form in the environment and could have harmful impact on ground water. Studies of the forms of Cd, Cu, Pb and Zn in soil and their uptake by cereal crops, adoption of sequential extraction, into five fractions was used by Chlopecka (1996). The fractions include exchangeable, carbonate, Fe-Mn oxides, organic and residual. The residual was the most abundant fraction in untreated soil for metalsChlopecka (1996).

2.7 Forms of heavy metals in soil

Heavy metals are found in significant levels in sludge and are associated with soil solids in five major forms:

i. Exchangeable form: A small proportion is held in this form which is available for plant uptake e.g Cd, Ni and Cr.

ii. Organically bound form: This is bounded by organic materials inherent in the sludgeand is not readily available to plants but can be released over a period of time e.g Cu and Pb.

iii. Definite compound e.g metals carbonates phosphates and sulphides.

iv. Residual form: This is composed of sulphides and often insoluble compounds that are less available to plants than any other forms.

2.8 Effects of Heavy Metals on Humans and Animals

Plants derive some elements by uptake from the soil and through sorption of vapour and particulate from their surroundings. Some animals are dependent on plants for their elemental nutrient supply. The concept of soil-plant to man relationship shows a coordinated understanding of how a particular sequence of events may lead to an imbalance (toxicity or deficiency) in the nutritional quality of food for man(http://www.lenntech.com/heavy-metal.htm.

2.8.1Lead

Lead has a negative influence on both children and adults. For children, Pb reduces the physical growth and mental growth (Simeonov *et al*., 2010). The intelligent quotient of children is diminished and symptoms of irritability and fatigue could be observed. Chronic exposure can affect physical growth and can cause anemia, kidney damage, headache, hearing problems, speaking problems, fatigue or irritable mood (Simeonov *et al*., 2010). It has the ability to inactivate enzymes, compete with calcium for incorporation into bones and interfere with nerve transmission and brain development(Simeonov *et al*., 2010).

The main sources of Pb in the environment include, dust from leaded paints from older houses, leaded gasoline and tap water from soldered pipes (Simeonov *et al*., 2010). In the soils, the maximum allowable limits of lead in UK and USA are 100 mg/kg and 200mg/kg respectively (Mamtaz and Chowdhury, 2006).

2.8.2 Cadmium

Cd is a heavy metal characterized by high mobility in biological systems. It is emitted to the atmosphere in combustion processes, mainly in the form of oxides (Wieczorek *et al*., 2004). Cd uptake by plants is partly limited by presence of calcium, phosphorus and chelating compounds in the soil (Wieczorek *et al*., 2004). The exposure to Cd and especially chronic exposure can cause renal dysfunction, calcium metabolism disorders and increased incidence of some forms of cancer (Selinus and Alloway, 2005). In plants, it induces oxidative stress and inactivates some enzymes (Wieczorek *et al.*, 2004). Taken up by plants from the soil first accumulates in the roots, and then transported in smaller quantities to stems and seeds (Wieczorek *et al.*, 2004). Among the sources of Cd in the environment include; mining and smelting of metal ores, fossil fuel combustion and also phosphate fertilizers (Challa and Kumar, 2009). Farming practices such as tobacco growing also increases the level of Cd in the environment (Selinus and Alloway, 2005). The sources of in the urban areas are much less well defined than those of Pb, but metal plating were still being considered the likely sources (Jaradat and Momani, 1999). Cd is also found in lubricating oils as part of many additives and car tyres as a result of the vulcanization process. The other sources of Cd are industrial activities; the metal is widely used in electroplating, pigments, plastics, stabilizers and battery industries (Adeleken and Abegunde, 2011). Small quantities cause adverse changes in the arteries of human kidney. It also replaces zinc biochemically and causes high blood pressures and kidney damage (Adeleken and Abegunde, 2011). The recommended concentration of cadmium in soils 3kg/mg (EU 1986).

2.8.3 Chromium

Chromium is one of those heavy metals in the environment whose concentration is steadily increasing due to industrial growth, especially the development of metal, chemical and tanning industries (Adeleken and Abegunde, 2011). The most common forms of chromium are chromium (VI) and chromium (III) (Hilgenkamp, 2006). Chromium (III) is an important component of a balanced human and animal diet and its deficiency causes disturbance to the glucose and lipid metabolism in humans while chromium (VI) is carcinogenic (Hilgenkamp, 2006). Although chromium toxicity in the environment is rare, it still presents some risks to human health since it can be accumulated in skin, lungs, muscle, fat, in liver, hair, nails and placenta where it is traceable to various health problems (Adeleken and Abegunde, 2011).

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

The maximum allowable limit of chromium in the soil set by United Kingdom is 300 mg/kg (EU 1986)

2.8.4 Manganese

Manganese is essential for normal physiological functioning of humans and animals and exposure to low levels in the diet is considered nutritionally essential in humans. However chronic exposure to higher doses is detrimental to human health (Calkins, 2009). In higher doses its toxic and its toxicity varies with route of exposure, chemical species, age, sex and animal species (EPA, 2004). The nervous system has been determined to be the primary target organ with neurological effects generally observed (EPA, 2004). Syndrome called manganism may result from chronic exposure to higher levels of manganese (EPA, 2004; Calkins, 2009). Manganism is characterized among other symptoms with, weakness, tremors, a masklike face and psychological disturbance (Calkins, 2009). Human activities are also responsible for much of this manganese contamination in water in some areas (EPA, 2004). Sources of manganese due to human activities in the environment include; combustion of coal, residential combustion of wood, iron and steel production and power plants (Calkins, 2009). The primary sources in surface and ground water releases are industrial facility, effluent discharge, landfill and soil leaching (EPA, 2004).

2.8.5 Zinc

Zinc is an essential trace element for plants, animals and humans found in virtually all foods and potable water in the form of salts or organic complexes (Miculescu *et al*., 2011). The average adult body contains between 2-3 g of zinc Mebrahtu, G. and Zebrabruk, S. (2011). It is used in the formationof connective tissues like ligaments and tendons (Miculescu *et al*., 2011).

Zinc toxicity is rare but at concentrations of up to 40 mg/L, it may induce toxicity characterized by symptoms of irritability, muscular stiffness and pain (Al-Weher, 2008).

2.8.6 Copper

The major portion of copper produced in the world is used by the electrical industries; most of the remainder is combined with other metals to form alloys(Prusty, 1983). Important series of alloys in which copper is the chief constituent are brasses (copper and zinc) and bronze (copper and tin) (Morse, 1994). Copper resists the action of the atmosphere and seawater; exposure for long periods to air, however, 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 nitric and sulphuric acids 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 (Rogers *et al.*, 2009). Toxicity of Copper in plants as a result of high level in sewage treated agricultural soil has been reported and the 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).

Human biology is full of instances where heavy metal toxicity has led to mass deaths (Shrivastav, 2001). All heavy metals are toxic to living organisms at excessive concentrations, but some are essential for normal healthy growth and reproduction by plants at low but critical concentrations (Bose and Hemantaranjan,. 2005). The heavy metals essential to plants include Co, Cu, Fe, Mo and Zn and for animals are Cr, Ni and Sn. The heavy metals Cd, Hg and Pb have not been shown to be essential for either plants or animals (Misra and Mani, 2009).

Heavy metals are non-biodegradable and once they enter into an environment, they will stay there for a long time (Voet *et al.,* 2008).

Heavy metals occur in atmosphere basically in particulate form. Hence, the transfer of airborne particles to land or water surfaces by dry, wet and occult deposition constitutes the first stage of atmospheric heavy metals (Shrivastav, 2001).

2.9.0Soil Physicochemical Properties

2.9.1 Soil pH

The soil pH serves as a useful index of availability of nutrients, the potency of toxic substances present in the soil and the physical properties of the soil. Several studies have shown that availability of heavy metals is pH dependent (Iwegbue et al., 2006; Gonzalez-Fernandez et al., 2008).

Soil pH is an indication of the acidity or alkalinity of soil. pH is defined as the negative logarithm (base 10) of the activity of hydronium ions (H^+ or, more precisely, H_3O^+aq) in a solution.As the amount of hydrogen ions in the soil increases the soil pH decreases thus becoming more acidic.Soil pH controls many chemical processes that take place. It specifically affects plant nutrient availability by controlling the chemical forms of the nutrient. The optimum pH range for most plants is between 5.5 and 7.0 (Perry, 2012), however many plants have adapted to thrive at pH values outside this range

The solubility of most metals decreases with increasing pH, (Uba*et al*., 2008). Alkaline soils have a high saturation of base cations (K^+, Ca^{2+}, Mg^{2+} and Na^+). This is due to an accumulation of soluble salts which are classified as either saline soil, sodic soil, saline-sodic soil or alkaline soil. All saline and sodic soils have high salt concentrations, with saline soils being dominated by calcium and magnesium salts and sodic soils being dominated by sodium. Alkaline soils are characterized by the presence of carbonates. Soil in areas with limestone near the surface are alkaline from the calcium carbonate in limestone constantly mixing with the soil (Brandy and Weil, 2002).

Both macronutrient and micronutrient availability are affected by soil pH. In slightly to moderately alkaline soils, molybdenum and macronutrient (except for phosphorus) availability is increased, but P, Fe, Mn, Zn Cu, and Co levels are reduced and may adversely affect plant growth. In acidic soils, micronutrient availability (except for Mo and Bo) is increased (Hansson, 2011).

2.9.2 Organic Matter

The soil organic matter consists of a complex and varied mixture of organic substances. The organic matter is an important factor in adsorption and accumulation of heavy metals in soil (Alloway, 1995; Kabata-Pendias and pendias, 1999). Chemical elements in the soil are more adsorbed unto the finest soil particles (colloids) which are clay and humus; although they are small in size, colloids play a major influence on soil properties. Heavy metal cations are easily sorbed to the soil organic matter and other forms of humified natural organic matter. The type of sorption by the organic matter affects the fate of the heavy metal in the environment (Tan 1996).

2.9.3 Cation Exchange Capacity (CEC)

Cation exchange capacity of soil is the capacity of a soil for ion exchange of positive charged ions between the soil and the soil solution (Baryla *et al*., 2011). Soil particles are composed of silicate and alumina silicate clay. Cation exchange capacity therefore increases as the clay content increases (Baryla *et al*., 2011). The cation exchange capacity of a soil is simply a measure of the quantity ofsites on soil surfaces that can retain positivelycharged ions by electrostatic forces Cations retained electrostatic ally are easilyexchangeable with other cations in the soilsolution and are thus readily available forplant uptake (Mordi *et al*., 2002). Thus, CEC is important formattaining adequate quantities of plantavailable calcium (Ca^{2+}), magnesium (Mg^{2+})and potassium (K^{+}) in soils. Under acidconditions (pH <5.5), aluminium (Al^{3+}) may also be present as an exchangeable cation (Mordi *et al*., 2002).Soil CEC is normally expressed in units ofcharge per weight of soil. Commonly twosets of units are used: meq/100g (milliequivalents of charge per 100g of dry soil) or cmol /kg (centimoles ofcharge per kilogram of dry soil). While a soilwith a higher CEC may not necessarily bemore fertile, when combined with othermeasures of soil fertility, CEC is a goodindicator of soil quality and productivity.Cation exchange sites are found primarily on clay and organic matter surfaces (Krzystof *et al*., 2012). Normal CEC ranges in soils would be from < 3 cmol/kg, for sandy soils low in OM, to >25 cmol/kg for soils high in certaintypes of clay or OM. Soil OM will develop agreater CEC at near-neutral pH than underacidic conditions. Additions of an organicmaterial will likely increase a soil's CEC. SoilCEC may also decrease with time throughacidification and OM decomposition (Donald, 2000)

2.9.4 Particle Size Analysis

Particle size analysis is the determination (by weight) of the distribution of mineral particles. It is an operation that involves complete dissociation of soil material into individual particle and the total destruction of aggregates and broken aggregate (Agbenin, 1995).

All other analytical data cannot be validly interpreted without explicit reference to the particle size composition and particularly to the clay content which is the most active particle size fraction. This is because the fraction is associated with humified organic matter and/or iron, provides the essential cohesion in aggregates and fixes anions and cations on its exchange sites, retains water, swells and shrinks under certain condition (Agbenin, 1995).

2.10 Methods for Heavy Metal Analysis

Several techniques for the determination of heavy metal elements are currently in use. These include flame atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICP-AES) Begum *et al*. (2009), inductively coupled plasma – mass spectroscopy (ICP-MS) Begum *et al*. (2009), X-ray fluorescence and neutron activation analysis (Magdaleno *et al*., 2011). A lot of studies on heavy metals in water, soil plants and animals have used atomic absorption spectroscopy as the method of analysis for the heavy metals. A study by Begum *et al*. (2009) in the analysis of lead, iron, zinc, nickel and copper in soil and plants employed AAS for analysis. Similarly, Fong *et al*. (2008) used AAS to analyse copper, cadmium, manganese, lead and zinc in urban roadside soils. Other researchers who have employed atomic absorption spectroscopy in their analysis of heavy metals include, Mamtaz and Chowdhury (2006), Awokunmi *et al*. (2010), Mico *et al*., (2006), Al weher (2008), Wieczorek *et al*. (2005).

2.11 Sequential Extraction

Sequential chemical extraction procedures provides operationally defined soil fractions and numerous schemes have been described, particularly in the last two decades by researchers such as Welte *et al*, (1983), Tessier and Campbell, (1988); and Berti*et al*(1998). This shift may probably be due to the observation of Pickering who stated that the scientific community has recognized that assessment of health hazards, toxicity and bioavailability of soil metal levels must be based on concentration of specific chemical forms rather than on total elemental content.

The sequential method described by Sposito *et al* (1982) with slight modification by (Agbenin and Atin, 2003) was used to determine operationally-defined chemical species of the metals. Five operationally-defined fractions of metals were removed by this sequential extraction method

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Material

All the chemicals and Reagents used were of analytical grade (AR), manufactured by British Dry House Chemicals limited pool England or Merck Germany. No further purification of the reagents was carried out before use. **Distilled water was used throughout the research work.**

All glass wares, plastic containers, crucibles, mortar and pestle were washed thoroughly. Glasses were washed with liquid soap, rinsed with distilled water and then soaked in 10 % HNO_3 solution for 24 hours (Todorovi *et al.*, 2001). They were then washed with distilled water and dried in drying oven at 80 ^{0}C for 5 hrs.

Atomic Absorption Spectroscopy

3.2 Description of Study Area

The study area, Lokoja (Fig 3.1), is located between latitudes $7^0 46^1$ and $7^0 52^1$N and longitudes $6^0 38^1$ and $6^0 46^1$E. Lokoja is the capital city of Kogi State and the major confluence town in Nigeria. The area enjoys both wet and dry seasons with the total annual rainfall ranges between 804.5-1767.1mm (Audu, 2001). Mean annual temperature is about 27.7^{0}C with a relative humidity of 30% in dry season and 70% in wet season. Average daily wind speed is 89.9km/hr. Average daily vapour pressure is 26Hpa (Audu, 2001). The most important hydro-geological feature is the confluence Rivers, River Niger and River Benue (Audu, 2001). It is also found in Guinea Sananna with the presence of gallery forest along water courses (Audu, 2001). The land rises from about 300m along the Niger valley to between 300-900m above sea level in the uplands (Audu, 2001). In terms of population, Lokoja has a population of 82,483 in 1991 (National population commission, 1991). In 2006, the population of Lokoja stood at 196,643 (National population Commission, 2006).

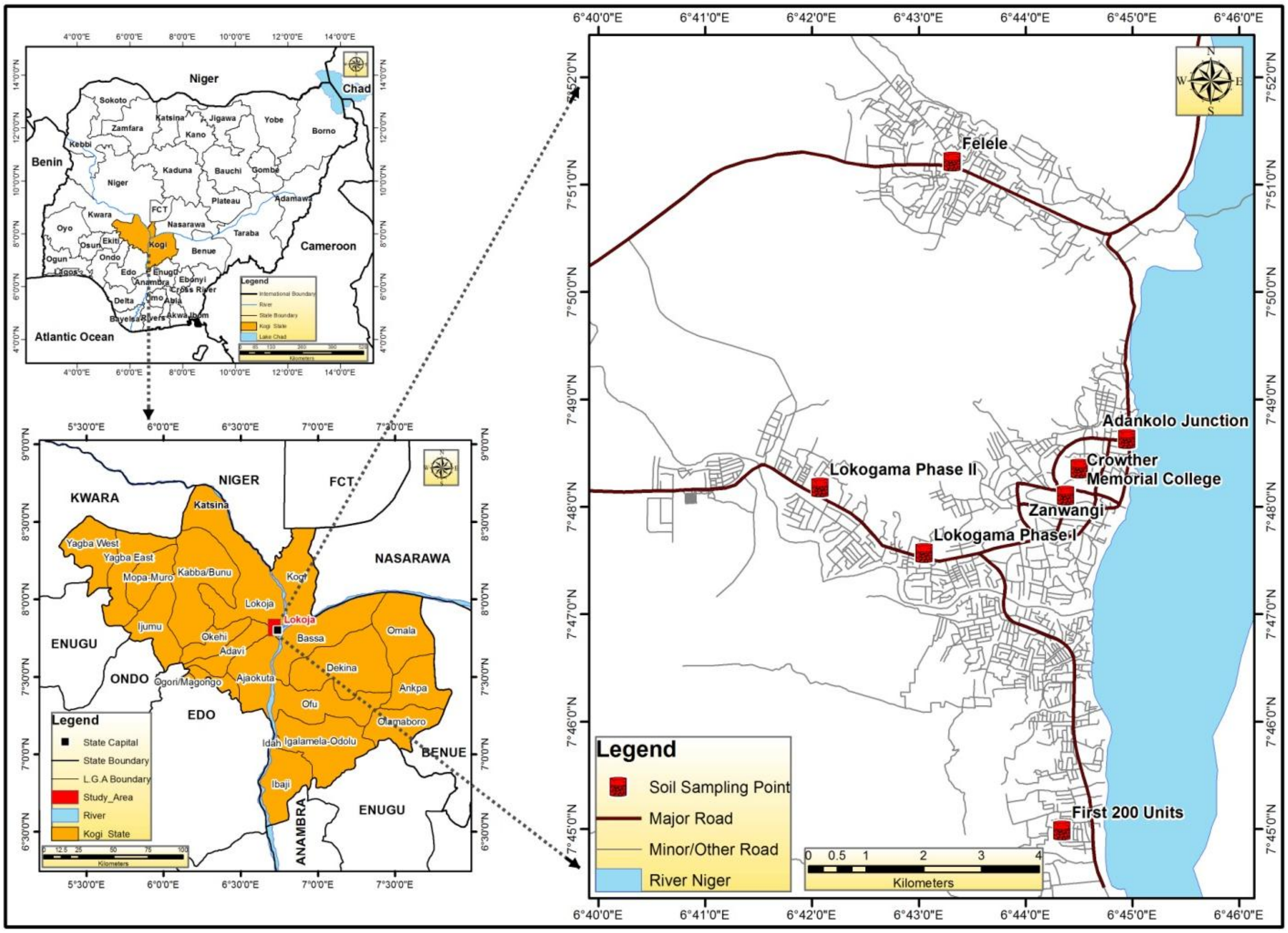

Figure 3. 1: Map of Lokoja showing Soil Sampling Points

Source: Modified from the Administrative Map of Lokoja L.G.A

3.3 Sample collection

Soil and well water samples from six (6) automobile mechanic workshops were collected from Zawangi (ZW), Crowther Memorial (CM), Lokongoma Phase 1 (LP1), Lokongoma Phase 2 (LP2), Felele (FL), and first 200 unit (2U) areas of Lokoja town. Soil samples were collected from two sampling depths of 0-15cm, and 15-30cm; within a location samples were collected from three different point at a depthof 0 -15cm and 15 -30cm which is referred to as top soil and sub-soil respectively (Awofolu, 2005). One control sample was collected from Adam-kolo Junction where no human activities such as those of auto mechanics ever existed.

The collected soil samples were crushed with porcelain mortar with pestle, air- dried for one week to remove moisture, and sieved through a 2mm sieve made of stainless (Dikko and Ibrahim, 1999). The soil samples were then stored in labeled polythene bags ready for analysis (Ayodele and Gaya, 1998).

All extractions or digestions were conducted in acid – washed (5% HNO_3) apparatus.

3.4 Determination of Physicochemical properties of soil

3.4.1 pH

0.01M Calcium Chloride ($CaCl_2$); 1.1g of salt was dissolved in distilled water and made up to a litre. (Hendershot *et al*., 1993)

3.4.2 Procedure

To 10.0 g of air-dried soil in a 100ml beaker was added 10ml of distilled water and the suspension formed was allowed to stand for 15minutes with frequent stirring with a glass rod. Prior to use, the pH meter was calibrated with pH 4.0 and 7.0 buffers. The electrode of the pH meter was then immersed into the partly settled suspension and the pH was measured. The above was repeated using 0.01M calcium chloride solution (which was prepared by dissolving 1.1 g of calcium chloride salt in 1000ml of distilled water) and the pH was measured.

3.4.3 Determination of Electrical conductivity

Preparation of Reagents

To 5g of an air-dried soil sample placed in a 250.00 ml beaker, distilled water was added slowly and drop wise over the entire soil surface in a uniform pattern, until the soil appeared wet. A stainless steel spatula was used to make a homogeneous soil paste. The beaker was then covered with a Petri - dish, 50.00 ml of distilled water was added and shaken for 1 hour. 40.00 ml of the diluted extract was placed into 100.00 ml beaker and the electrode of the conductivity meter inserted to record the electrical conductivity of the soil(Pierzynski *et al*., 2011).

3.4.4 Determination of Organic carbon in soil(Agbenin and Atin, 2003)

Preparation of Reagents

Potassium dichromate ($K_2Cr_2O_7$)49.04g of $K_2Cr_2O_7$ was dissolvedin distilled water and diluted to 1 litre.

Concentrated sulphuric acid (H_2SO_4).

Ferrous sulphate (0.5N) -140g of $FeSO_4.7H_2O$ was dissolved in water and 15ml conc. H_2SO_4, was added cooled and diluted to 1 litre with distilled water.

Indicator – Phenolphthalein.

3.4.5 Procedures

1g of dried soil sample (passed through 2 mm sieve) was weighted into 250ml Erlenmeyer flask. 10ml of $K_2Cr_2O_2$ solution was accurately measured into the flask, and the soil was dispersed by swirling gently. 20ml concentrated H_2SO_4 was added rapidly by the use of an automatic pipette,sand swirled gently until the soil and the reagents were mixed, then continuous swirling of the flask was maintained for one more minute. The flask was swirled again, and allowed to stand on a sheet of asbestos for about 30minutes, after which 100ml of distilled water was added. Then 3-4 drops of indicator (phelnolphthaline)was added and titration was carried out with 0.5M $FeSO_4$ solution. As the end-point was approached, the solution took on a greenish cast and then changed to dark green. Then, the ferrous sulphate was added drop wise until the colour changed sharply from blue to red (maroon colour) in reflected light against a white background. The blank titration was done in the same manner without the soil sample to standardize the dichromate.

Calculations:

Organic carbon in soil (%) = 10-MeFeSO$_4$) X 0.003 X 100 (f)

Weight of air dried soil

Where f = correction factor = 1.33

Me = molarity of gtitrant X ml of titrant used 3.1

1g of air-dried soil

3.4.6 Determination of Particle Size Distribution (Agbenin, 1995).

Preparation of Reagents

Calgon (Sodium hexametaphosphate) 37g/dm^3

3.4.7 PROCEDURE

50 g of air-dried soil (passed through 2 mm sieve) was weighed into a 250ml plastic beaker then 100ml of 50% calgon and 100ml distilled H_2O were added and stirred with a glass rod. The soil suspension was left to stand for about 30 minutes with occasional stirring, then it was shaken on a reciprocating shaker for 20 minutes, after which, it was transferred to an end to end shaker and shaken for 10 minutes. Which was then transferred into a 1000ml measuring cylinder, and the contents in the container were washed completely into a 1000ml measuring cylinder and made up to mark with distilled water. Before hydrometer reading, the suspension was vigorously mixed by long handle plunger and the sediment at the bottom was thoroughly disturbed. Hydrometer was immediately placed into suspension until it was floating. 40 seconds after that it was then removed and the temperature of the suspension was recorded with a thermometer. After the suspension was allowed to stand for 2 hours, the second hydrometer reading and the temperature were taken.

Calculations

The corrected hydrometer reading C (g/dm^3) are obtained by subtracting the blank reading RL (g/dm^3) from the hydrometer reading in the soil suspensions R (g/dm^3) and adding 0.36 g/dm^3 for every degree above 20^oC.

C = R – RL + (0.36T)

Where T = Room temperature minus 20

The percentages by weight of the SILT + CLAY and SAND fractions are given by:

$$\% \text{ clay} = \frac{\text{Corrected 2hrs reading – Blank x 100}}{\text{Weight of soil taken}} \quad 3.2$$

$$\% \text{ Silt} = \frac{\text{Corrected 40 sec reading – Blank x 100 -\% clay}}{\text{Weight of soil taken}} \quad 3.3$$

% Sand = 100 – (% clay + % silt) 3.4

3.4.8Cation Exchange Capacity(Baryla *et al*., 2011).

Preparation of Reagents

Isoppropyl alcohol 99%

1N- Ammonium Chloride (NH_4Cl); adjusted to pH 7.0 with NH_4OH

0.25N Ammonium chloride, adjusted to pH7.0 with NH_4OH. Ammonium oxalate $(NH_4)_2 (SO_4.H_2O)$, 10%

Dilute ammonium hydroxide (NH_4OH): Add 1 unit volume of concentrated NH_4OH to equal volume of water. 0.10N silver nitrate ($AgNO_3$); 0.02N H_2SO_4; 2% Boric acid (H_3BO_3)

1N Sodium hydroxide (NaOH); Bromocresol green- methylred mixed indicator.

3.4.9 Procedure

10g of soil sample was put into 100ml. Erlenmeyer flask, 50ml of concentrated ammonium acetate solution was added and the suspension was shaken and left over night. It was filtered through whatman No. 42 filter paper. The soil was leached with more ammonium acetate solution to remove all exchangeable bases and saturate exchange sites of the colloid with NH_4^+ ion. 30ml of 99% isopropyl alcohol was added to the sample and shaken after which it was centrifuged to remove excess ammonium acetate. This was repeated three times. Soil samples were filtered and transferred into a 500mlkjeldhal flask with addition of 200ml distilled water, and10ml of sodium hydroxide was added. This was distilled into 50ml of 2%boric acid. The distillate was titrated with NH4- borate to determine the ammonium ion concentration. A blank titration was carried out using same procedure without soil.

CEC C mol/100g was calculated

$$CEC = \frac{Titre - Blank \times N \times 100}{Weight\ of\ soil\ sample} \qquad 3.5$$

Where N = Normality of acid used

3.4.10 Determination of Phosphate concentration in soil (Pierzynski *et al.,* 2011)
Reagents:

Concentrated sulphuric acid (AR), 98% v/v

Ammonium molybdate, $(NH_4)_6$ $M_{O7}O_{24}.4H_2O$ (0.01M): 40g of the solid salt was dissolved in 800 ml of water in a $1dm^3$ volumetric flask and made up to the mark with the water

Ascorbic acid solid (vitamin C)

Ammonium sulphate solid, $(NH_4)_2$ $SO_{4,}$ BDH (AR)

Potassium dihydrogen Phosphate, KH_2PO_4 (AR)

Soil-extract

3.4.11 Procedure

0.75g of dried ammonium sulphate was accurately weighed and dissolved in 50ml of distilled water. 5ml of concentrated sulphuric acid was then added slowly. The solution was allowed to cool and then diluted to 250ml with distilled water. To 10g of dry soil sample, 200ml of sulphuric acid/ammonium sulphate mixture was added and shaken occasionally for 30 minutes then filtered through a Whatman No. 42 filter paper.

Preparation of standard phosphate stock Solution (100ppm)

Standard phosphate solution (100ppm) was prepared by dissolving 0.220g of solid KH_2PO_4 in 160 ml of water in a 500 ml volumetric flask, and diluted to the mark.

Working standard phosphate solution (5ppm)

5ml of the standard phosphate stock solution was transferred into a 100ml volumetric flasks and diluted to the mark. A set of standard phosphate solutions of 0 ml, 0.5ml, 1.0ml, 2.0ml, 3.0ml, 4.0ml and 5.0ml were pipetted into separate 50mlvolumetric flasks and made up to the mark with distilled water in each case. These solutions with concentrations of 0, 0.1,0.2, 0.4, 0.6, 0.8 and 1.0ppm respectively were taken in separate test-tubes, 4.0mlof 0.01mol /dm^3 molybdate reagent and a spatula ascorbic (Vitamin C) crystals were added to each. The solutions were heated slowly to boiling, until a deep blue or green color developed and then it was allowed to cool.

The wavelength region of maximum absorbance (λmax) of the coloured substance was determined. Absorbance of the various solutions of standard phosphate were measured at λmax and corrected with a blank. This data was used to construct a calibration curve.

Preparation of sample solution

5ml of the soil extract was pipetted into a 25ml volumetric flask and 10 ml of distilled water was added, followed by 4ml of molybdate solution and one spatula of ascorbic acid (Vitamins C) crystals. The mixture was shaken and made up to the mark with distilled water. The solution was transferred into a 150 ml conical flask and heated slowly to boiling, until a deep blue or green coloured developed and was allowed to cool. The absorbance was measured at λmax and the phosphate concentration was calculated from the calibration curve.

Calculation

$$PO_4\text{-}P\ (mg/kg) = \frac{\text{conc.of } PO_4^{2-} \times 1000}{\text{Weight of sample (g)}} \qquad 3.6$$

3.4.12 Determination of Sulphate in Soil (Agbenin, 1995)

Soil – Extraction: (KH_2PO_4 Extraction method)

KH_2PO_4 solution (0.016mol/dm^3): 2.14g of KH_2PO_4 was dissolved in distilled water and then made up to 1 dm^3 in a standard volumetric flask. This solution was used as the extracting solution to extract both soluble and adsorbed sulphate.

5g of air – dried soil sample was weighed into an Erlenmeyer flask, 25ml of the extracting solution was added and the flask was shaken on a mechanical shaker for 30 minutes. The suspension was filtered through a Whatman No. 42 filter paper.

Preparation of Reagent

Barium chloride solution (5% w/v): 5g of $BaCl_2$ was dissolved in distilled water and then made up to 100 ml.

Hydrochloric Acid (2.0mol/dm^3): 168cm^3 of concentrated HCl (37% v/v, sp gr. 1.18) was measured into 1dm^3 volumetric flask containing some little amount of water. After a thorough shaking, the solution was made up to mark with distilled water.

Sulphate stock solution (100mg/l): 0.181g of K_2SO_4 was dissolved in distilled water in a 1 dm^3volumetric flask and made up to the mark with distilled water.

Procedure

Separate volumes of 0ml, 2.0ml, 4.0ml, 6.0ml, and 8ml of the stock solution were pipetted into separate 50 ml volumetric flasks and made up to the mark with water in each case. These solutions had the concentrations of 1.0, 2.0, 3.0, 4.0 and 5.0mg/dm^{3}respectively. A portion of each of these solutions was taken in a separate test-tube, then 1cm^3 of the 5% m/v $BaCl_2$ solution followed by 1cm^3 of the 2mol/dm^{3}of HCl solution were added into each test-tube. The solution was allowed to stand for 30minutes.

The concentration of the unknown was determined by construction of calibration curve of absorbance against concentration of standard solution.

Calculation

$$SO_4^{2-}(\text{mg/kg}) = \frac{\text{R} \times \text{VE} \times \text{DF}}{\text{W}} \qquad 3.7$$

where R = sample concentration from calibration curve ,VE = volume of Extraction solution (25 ml), DF = dilution factor and W = weight of sample.

3.6.9 Determination of the total metal content (USEPA, 1986)

Preparation of Reagents

The method developed by the United state Environmental Protection Agency for (total absorbed) heavy metals in soils, sediments and sludge (USEPA SW-846, Method 3050) was used in the preparation of the soil samples for the determination of total metal content in this study. The reagents used were 15ml concentrated HNO_3, 17 ml distilled water and 5ml concentrated HCl per soil sample.

3.6.10 Procedure

1g of air-dried soil sample was accurately weighed into 125ml conical flask. 10ml of 1:1 HNO_3 was added, and the slurry was mixed and covered with a watch glass. This was heated on a hot plate at 95^{o}C, until the solution reduced to about 5ml without boiling (by only partially covering the beaker). The sample was allowed to cool then 2ml of distilled water along with 3ml of 30% H_2O_2 were added. With the beaker covered, the sample was heated gently to start the peroxides reaction. A continuous addition of 30% H_2O_2 in 1ml increments was done, followed by gently heating until reaction with peroxide was minimal (or effervescence subsided) or sample appeared unchanged. 5ml of concentrated HCl along with 10ml of distilled water was added, and with the beaker cover reflux was repeated for an additional 15minutes without boiling. The sample was allowed to cool and filter papers were rinsed with small volumes of 1:1HCl, and the filtrate was made up to mark of 60ml with distilled water.

3.6.11 Determination of Cd, Fe, Ni, Pb and Zn by Atomic Absorption Spectrometry

Preparation of Standard Solution

Digestion of Sample

Concentration of Cd**,** Fe, Ni, Pb and Zn in the filtrate were determined by AAS.

3.6.12 Sequential Extraction of Metals (Agbenin and Atin, 2003)

Preparation of Reagents

0.25M of K_2SO_4 Solution; 0.5M NaOH Solution; 0.05M Na_2EDTA solution. The solution was prepared by weighing 1.86g of Na_2EDTA a 1 dm^3 capacity beaker to which 200ml of distilled water was added. $HClO_4$-HNO_3-H_2SO_4.

3.6.13 Procedure

5g of air-dried soil sample was accurately weighted into 25 ml polypropylene centrifuge tube, and the following extractions were made sequentially.

Water soluble, F1

Five grams of air-dried 2mm sieved soil sample was weighed into a pre-weighed centrifuge tube, and 25ml of distilled water was added. The suspension was shaken for 2 hours, centrifuged at 3500rpm for 10min and filtered through Whatman No. 42 filter paper under vacuum into a 100 ml vial. The fraction was designated SOL.

Exchangeable, F2

The residue from F1 was extracted by adding 25ml of 0.25M K_2SO_4. The suspension was shaken for 16hours, centrifuged for 10mins at 3500 rpm and filtered into a 100 ml vial through Whatman No. 42 filter paper. The fraction was designated EXCH.

Carbonate- Bound, F3

The residue from F2 was extracted by adding 25ml of 0.05M Na_2EDTA. The suspension was shaken for 8 hours, centrifuged for 10mins at 3500rpm and filtered through Whatman No. 42 filter paper into a 100ml vial. This fraction was designated CARBON.

Organic- Bound (Oxidizable) F4

25ml of 0.5M NaOH solution was added to the soil residue from F3 and then shaken for 16hours, centrifuged at 3500rpm for 10mins. The supernatant was then filtered into a 100ml vial through Whatman No. 42 filter paper and was designated ORG.

Residual F5

The residual fractions of the metals was computed by subtracting the sum of fraction F1-F4 from the respective total metal concentration (Bell et al., 1991, Alva et al., 2000) determined by $HClO_4$-HNO_3-H_2SO_4 digestion (Agbenin, 1995).

At the end of extraction period, the individual metals in the filtrates were determined by AAS.

3.6.14 Determination of Heavy Metal in the Well Water (Agbenin, 1995)

Preparation of Reagents

HNO_3; distilled water.

3.6.15 Procedure

50ml of the well water was accurately measured into 125ml conical flask.10ml of concentratedHNO_3 was added mixed and covered with a watch glass. Heating was done on a hot plate at 95^{o}C. The solution was reduced to 30ml. The sample was allowed to cool, made up to 50ml with distilled water, and filtered through what man No. 42 filter paper.The metals in the filtrate was determined by AAS.

Indices of Pollution

Pollution Load Index

The PLI is obtained as a contamination factor (CF) of each metal with respect to the natural background value in the soil Angulo (1996) and Usero, *et al.,* (2000) by using Equations (3.8) and (3.9);

$$CF = Csample / Cbackground \qquad 3.8$$

$$PLI = [CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n]^{1/n} \qquad 3.9$$

where,

CF: contamination factor, n = number of metals = 5;

Csample: mean metal concentrate of polluted soils;

Cbackground: mean natural background value of that metal.

Enrichment Factor(EF) and Geo-Accumulations Index (Igeo)

The extent of soil contamination was assessed using enrichment factor (EF) and geoaccumulation index(*I*geo) Woitke *et al.,* 2003 and Selvaraj, (2004). EF was used in the study to assess the relative contributions of natural and anthropogenic heavy metal inputs to soil Adamo et al (2005) and Valdes J., (2005). EF has also been used to indicate the degree of pollution or contamination or both, Feng, H, (2004). Data from samples taken from the control site were used to establish metal-normalizer relationships to which the data generated from various mechanic workshops are compared. According to this technique, metal concentrations were normalized to the textural characteristic of soil. Most commonly used reference elements include Sc, Mn, Al and Fe Loska et al (1997). In this study, Fe was chosen as the geochemical normalizer because of its conservative nature Chapman, and Wang (2001). Moreover, soils in Nigeria have been reported to be rich in Fe, Ololade, I.A., (2007) and Kakulu, S.E., (1985). Based on Rubio *et al*., (2000). EF is defined as:

$$EF = (X/Fe)_{soil}\ (X/Fe)_{background} \qquad 3.10$$

where $(X/Fe)_{soil}$ is the ratio of heavy metal (X) to Fe in the soil from mechanic workshops, and$(X/Fe)_{background}$ is the natural background value of the metal-Fe ratio.

The EF values close to unity indicate crusted origin, those less than 1.0 suggest a possible mobilization or depletion of metals, whereas EF > 1.0 indicates that the element is of anthropogenic origin, Zsefer et al (1996). Five contamination categories are recognized and interpretedas suggested by Birth, G.A. (2003). EF < 1 indicates no enrichment, EF < 3 is minor enrichment, EF = 3 - 5 ismoderate enrichment, EF = 5 - 10 is moderately severe enrichment, EF = 10 - 25 is severe enrichment, EF = 25 -50 is very severe enrichment and EF > 50 is extremely severe enrichment.

Geoaccumulation Index

The geoaccumulation index (*I*geo) as defined by Equation (3.11) was used to quantify the extent of heavy metal contamination associated with the soils from the various mechanic workshops. The *I*geo values were calculated using the Birth, G.A. (2003)expression:

$$I\text{geo}=\log_2 Cm/1.5B_n \quad 3.11$$

Where Cm = measured total concentration of metals in soils (mg/kg);

Bn= geochemical background values of metals (mg/kg);

1.5 = the background matrix correction factor due to lithogenic effects.

The *I*geo scale consists of seven grades (0 - 6) ranging from uncontaminated to very highly contaminated.

Values calculated based on soil layer 0 - 15 cm only. Normalizing element, Fe, with natural background value of 154.58 mg/kg

> 5, extremely contaminated; 4 - 5, strongly to extremely strongly contaminated; 3 - 4, strongly contaminated; 2 - 3, moderately to strongly contaminated; 1 - 2, moderately contaminated; 0 - 1, uncontaminated to moderately contaminated; <0, practically uncontaminated (Forstner *et al*., 1993).

3.6.17 Quality assurance validation

Validation of the technique for the metal determination was conducted on digested plant and soil samples. This was done by spiking the pre-digested samples with multi-element standard solution (0.5mg/l of Cd, Fe, Ni, Pb and Zn) as reported by Awofolu (2005).

3.6.17 Preparation of multi-element standard solution (MESS)

1 mg/dm^3$Cd(NO_3)_2.4H_2O$: 0.0027g of salt was dissolved in 2 ml of 2M HNO_3 in a beaker and then transferred into 1dm^3 standard volumetric flask. The beaker was rinsed thoroughly with distilled water into the flask. Similarly, 0.0049gof $Fe(NO_3)_2.6H_2O$, 0.0050g of $Ni(NO_3)_2.6H_2O$, 0.0016g of $Pb(NO_3)_2$, and0.0012g ZnO were separately dissolved in 2ml of 2M HNO_3 in a beaker and then transferred into 1dm^{3}standard volumetric flask. The solution in the flask was made up to the mark with the distilled water to give 1mg/dm^{3}of the multi-element standard solution which was used in the spiking experiment.

3.6.19 Spiking experiment

Multi-element standard solution (20ml) was pipetted to spike to two different samples. These were digested and filtered and their metal concentrations were determined from the filtrate by AAS. The concentration of metals in the spiked and their corresponding unspiked samples were used to calculate the percentage recovery in order to validate the method.

Calculation:

Amount of metal used to spike sample =

$$\frac{\text{vol. of MESS used x conc.of metal in MESS(mg/L)}}{1000} = Xmg \quad 3.12$$

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

=Ymg3.13

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

= Zmg 3.14

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

% recovery = $\frac{Y-Z}{X}$ x 100 3.15

3.6.20. Atomic Absorption Spectroscopy

Atomic absorption spectroscopy is based on the absorption of ultraviolet or visible light by gaseous atoms. The sample is converted into vapour by spraying the solution into a flame. A hollow cathode lamp composed of the element to be determined is used as the light source: this makes the method relatively free from spectral or radiation interferences. The atoms of this element in the flame absorbs at precise wavelength. The absorption in the flame is proportional to the concentration of the elements in the sample.

3.6.21 Statistical Analysis

All treatments were replicated three times in the experiments. The means and standard deviations (SD) were calculated by the Microsoft Excel 2003. One-way analysis of variance (ANOVA) was carried out with SPSS version 21.0. when a significant ($p<0.05$) difference was observed between treatments.

CHAPTER FOUR

4.0 RESULTS

4.1 General characteristics of mechanic workshop soil

The mean values and standard deviations of pH, organic matter (%), exchangeable cations (mg/kg), and particle size distribution (*i.e.* percentages of sand, silt and clay) in soil samples from the areas under study (0-15 and 15-30cm) are shown in Table 4.1 and 4.2.

In the study area, extractable sulphate content ranged from 0.91 to 1.30 mg/kg while the sulphate in samples from the control area was 0.63 mg/kg. Significant variation was observed between the sulphate level in the study and control areas. This could be due to the activities of battery chargers within the study area, an indication of soil contamination within this area. The level of extractable PO_4^{3-} in soil samples ranged from 4.60 – 17.90 mg/kg in the study area while in the control area, the PO_4^{3-} was 6.15 mg/kg. Similar to sulphate, phosphate level in the study area was mostly greater than the level in the control area. For similar reasons, sulphate could be responsible for high phosphate within these sites.

4.2 Quality assurance validation

The results for validation of the technique for the metal determination conducted on digested water and soil samples. The percentage recovery of the studied metals for the two samples were as follows:

Sample 1:Cd-80%, Ni-67%, Pb-82%, Zn-75.5% and Fe-77%. (water)

Sample 2:Cd-89%, Ni-75.5%, Pb-94.1%, Zn-85% and Fe-95.5%. (soil)

Table 4.1: Physicochemical parameters of all the study areas (0-15cm)

Location	Water pH	pH ($CaCl_2$)	OC (%)	CEC (Meq/100g of soil)	EC(µScm-1)	Ext PO_4(mg/kg)	Ext SO_4(mg/kg)	Sand (%)	Silt (%)	Clay (%)
Zanwangi	6.35 ± 0.05^{ab}	6.10 ± 0.00^{b}	0.16 ± 0.01^{ab}	26.00 ± 2.00^{a}	0.30 ± 0.10^{a}	3.15 ± 0.35^{c}	1.22 ± 0.11^{a}	65.00 ± 3.00^{b}	17.00 ± 1.00^{a}	18.00 ± 2.00^{a}
Lokongoma Phase I	6.25 ± 0.05^{ab}	6.00 ± 0.10^{bcd}	0.13 ± 0.01^{abc}	7.60 ± 0.40^{bc}	0.60 ± 0.25^{a}	17.90 ± 5.40^{a}	1.30 ± 0.03^{a}	80.00 ± 2.00^{ab}	9.00 ± 1.00^{a}	11.00 ± 1.00^{b}
Lokongoma Phase 2	6.15 ± 0.05^{ab}	5.65 ± 0.05^{d}	0.10 ± 0.03^{c}	9.25 ± 0.55^{bc}	0.60 ± 0.03^{a}	5.15 ± 0.45^{bc}	0.91 ± 0.00^{a}	74.00 ± 2.00^{ab}	13.00 ± 1.00^{a}	13.00 ± 1.00^{b}
Crowther Memorial	5.65 ± 0.65^{b}	6.05 ± 0.15^{bc}	0.12 ± 0.01^{bc}	13.10 ± 2.30^{b}	0.43 ± 0.08^{a}	4.60 ± 0.00^{bc}	0.92 ± 0.35^{a}	75.00 ± 9.00^{ab}	15.00 ± 7.00^{a}	10.00 ± 2.00^{b}
200 Unit	6.20 ± 0.00^{ab}	5.70 ± 0.10^{cd}	0.17 ± 0.01^{a}	9.60 ± 3.60^{bc}	0.53 ± 0.13^{a}	11.65 ± 2.35^{ab}	0.92 ± 0.35^{a}	78.00 ± 4.00^{ab}	10.00 ± 4.00^{a}	12.00 ± 0.00^{b}
Felele	6.85 ± 0.05^{a}	6.25 ± 0.15^{b}	0.11 ± 0.01^{c}	9.15 ± 3.35^{bc}	0.48 ± 0.23^{a}	16.70 ± 1.50^{a}	1.03 ± 0.31^{a}	81.00 ± 3.00^{a}	9.00 ± 3.00^{a}	10.00 ± 0.00^{b}
Control	6.75 ± 0.05^{a}	6.70 ± 0.10^{a}	0.04 ± 0.02^{d}	5.00 ± 0.90^{c}	0.13 ± 0.20^{a}	6.15 ± 0.45^{bc}	0.63 ± 0.09^{a}	77.00 ± 1.00^{ab}	10.00 ± 0.00^{a}	13.00 ± 1.00^{b}
P value	**0.120ns**	**0.003****	**0.004****	**0.004****	**0.434ns**	**0.011***	**0.511ns**	**0.272ns**	**0.531ns**	**0.029***

Means with the same superscript alphabet(s) along column are not significantly different

(P>0.05)

Means with different superscript alphabet(s) along the same column are significantly different (P<0.05)

*Means significantly different (P<0.05)

Ns Means not significantly different (P<0.05)

Table 4. 2: Physicochemical parameters of all the study areas (15-30cm)

Location	Water pH	pH ($CaCl_2$)	OC (%)	CEC (Meq/100g of soil)	EC (µScm-1)	Ext PO_4 (mg/kg)	Ext SO_4(mg/kg)	Sand (%)	Silt (%)	Clay (%)
Zanwangi	6.20±0.05^{ab}	6.00±0.00^{b}	0.10±0.01^{ab}	22.00±2.00^{a}	0.18±0.10^{a}	3.10±0.35^{c}	1.18±0.11^{a}	65.09±3.00^{b}	17.00±1.00^{a}	18.03s±2.00^{a}
Lokongoma Phase I	6.20±0.05^{ab}	6.00±0.10^{bcd}	0.11±0.01^{abc}	6.75±0.40^{bc}	0.50±0.25^{a}	17.67±5.40^{a}	1.23±0.03^{a}	80.08±2.00^{ab}	9.03±1.00^{a}	11.00±1.00^{b}
Lokongoma Phase 2	6.10±0.05^{ab}	5.37±0.05^{d}	0.10±0.03^{c}	8.65±0.55^{bc}	0.55±0.03^{a}	5.10±0.45^{bc}	0.84±0.00^{a}	74.00±2.00^{ab}	13.05±1.00^{a}	13.02±1.00^{b}
Crowther Memorial	5.60±0.65^{b}	5.05±0.15^{bc}	0.10±0.01^{bc}	13.13±2.30^{b}	0.38±0.08^{a}	4.60±0.00^{bc}	0.70±0.35^{a}	75.07±9.00^{ab}	15.00±7.00^{a}	10.03±2.00^{b}
200 Unit	6.15±0.00^{ab}	5.70±0.10^{cd}	0.15±0.01^{a}	8.75±3.60^{bc}	0.45±0.13^{a}	11.55±2.35^{ab}	0.92±0.35^{a}	78.23±4.00^{ab}	10.04±4.00^{a}	12.08±0.00^{b}
Felele	6.70±0.05^{a}	6.20±0.15^{b}	0.09±0.01^{c}	9.20±3.35^{bc}	0.40±0.23^{a}	16.55±1.50^{a}	1.00±0.31^{a}	81.05±3.00^{a}	9.02±3.00^{a}	10.06±0.00^{b}
Control	6.65±0.05^{a}	6.55±0.10^{a}	0.04±0.02^{d}	5.05±0.90^{c}	0.11±0.20^{a}	6.10±0.45^{bc}	0.57±0.09^{a}	77.06±1.00^{ab}	10.00±0.00^{a}	13.00±1.00^{b}
P value	**0.120ns**	**0.003****	**0.004****	**0.004****	**0.434ns**	**0.011***	**0.511ns**	**0.272ns**	**0.531ns**	**0.029***

Means with the same superscript alphabet(s) along column are not significantly different (P>0.05)

Means with different superscript alphabet(s) along the same column are significantly different (P<0.05)

*Means significantly different (P<0.05)

Ns Means not significantly different (P<0.05)

The values of physicochemical parameters in different depths in all the locations are shown in Figure 4.1 and 4.2. The pH (water) values was 6.43 (0 - 15 cm) and 6.20 (15 - 30 cm). The pH ($CaCl_2$) values ranged from 6.13 (0- 15cm) and 6.00 (15- 30cm) the soils are moderately acidic.

Electrical Conductivity (EC) values was 0.46 and 0.41 µscm-^{1}at 0-15 and 15-30cm respectively in the study area. Also, variation observed in electrical conductivity between sites could be due to the content of available soluble salts.

The total organic matter (TOM) content in the samples ranged from 0. 13%- 0.17% (0 - 15 cm), 0.4% - 0.10% (15 - 30 cm). Based on total soils examined, the CEC (in cmol·kg.1) ranged from 7.60 - 26.00 (0 - 15 cm) and 5.0 - 13.10 (15 - 30 cm) across all studied soils in decreasing order down the profiles at each sample location.

The organic matter decreases down the soil depth from 0-15 to 15-30 in all the locations. The range in organic matter content of the control area (1.00% - 3.3%) is much higher than the range (0.10% - 0.17%) of any of the samples from auto-mechanic workshops.

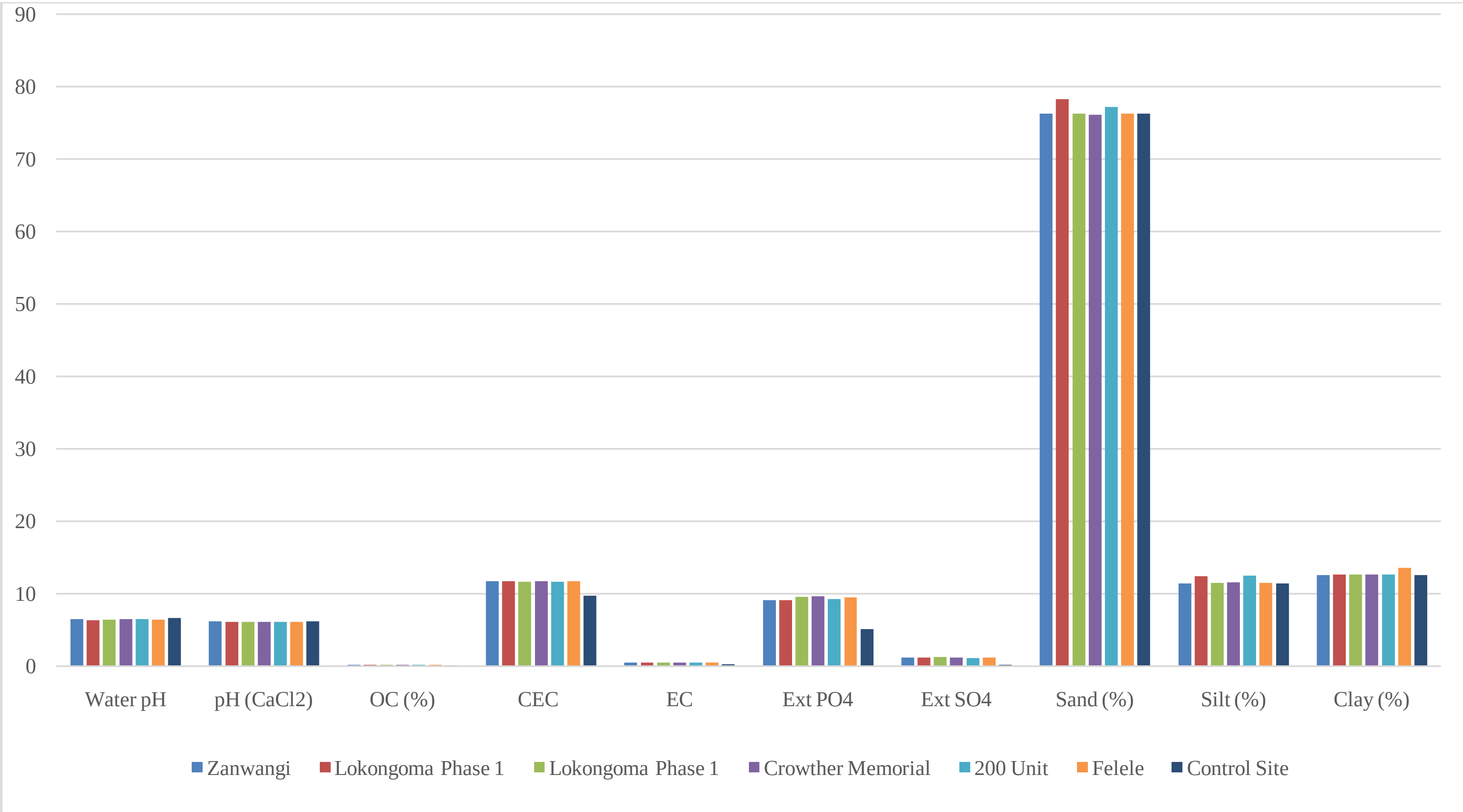

Figure 4. 1: Physico-chemical parameters at 0 -15cm in all the locations

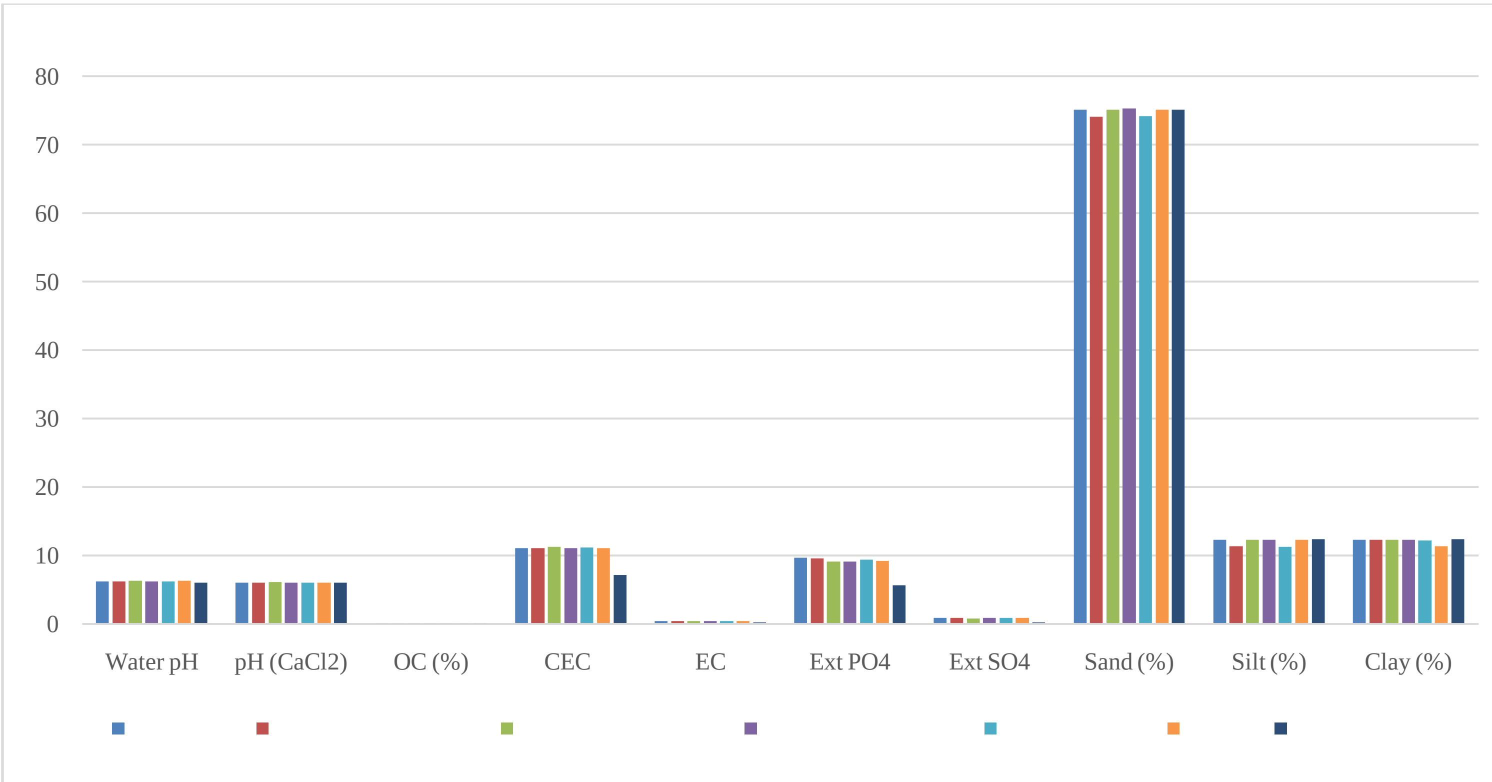

Figure 4. 2:Physicochemical parameters at 15 -30cm in all the locations

4.3 Level of metal concentrations

Total metal concentrations are shown Table 4.3 and Table 4.4, which indicated that all the metals in the study areas were higher than the control site. This is as a result of automobile activities in the study areas. While the concentrations generally decreased with the depth.

All the metals in the soluble fraction extraction of depth 0 – 15cm is shown in Table 4.5. In this fraction, zinc was found in only one of the locationslead and iron were found in all the locations, cadmium was not detected in any of the locations, while nickel was only detected in the control site.

The concentration of metals in the water soluble of depth 15 – 30cm in all the locations is shown in Table 4.6. This shows high concentration metal (Zn, Pb, Fe and Ni) at this depth than at 0 – 15cm.

The amount of metals in the Exchangeable fraction in all the locations of 0 – 15cm is shown in the Table 4.7. In this fraction, all the metals were found in all the locations but not is such significantly higher concentrations than they were in the control sample.

The amount of metals in Organic carbon fraction across all the locations at depth 0 -15 and 15 – 30cm, are shown in Table 4.8 and Table 4.9: which show that the concentration of the metals decrease with depth except for cadmium and nickel that increase with depth indicate that these metals have potential for mobility and can cause environmental pollution.

The amount of metals in carbonate fraction across all the locations of 0 -15 and 15 – 30cm, are shown in Table 4.10 and Table 4.11: which show that the concentration of the metals decrease with depth except for Iron that increases with depth.

Table 4. 3:Total Heavy Metal Concentrations (mg/kg) from some Mechanic Workshops in Lokoja Metropolis (0-15cm)

	Zn	Pb	Cd	Fe	Ni
Zanwangi	54.44	32.33	2.89	154.58	16.06
Lokongoma Phase 1	64.37	31.07	2.19	118.83	7.93
Lokongoma Phase 2	15.27	24.25	2.19	115.09	5.03
Crowther Memorial	49.64	39.04	2.59	145.08	4.31
200 Unit	19.02	26.28	2.54	131.17	5.05
Felele	26.22	45.22	2.19	131.92	7.83
Control	**5.75**	**2.8**	**1.94**	**36.65**	**2.1**

Table 4. 4: Total Heavy Metal Concentrations (mg/kg) fromsome Mechanic Workshops in Lokoja Metropolis (15- 30cm)

Location	Zn	Pb	Cd	Fe	Ni
Zanwangi	54.10	32.23	2.84	151.58	16.06
Lokongoma Phase 1	64.00	30.09	2.13	114.83	7.93
Lokongoma Phase 2	14.40	24.00	2.14	112.09	5.03
Crowther Memorial	49.25	38.40	2.49	141.05	4.31
200 Unit	18.2	25.28	2.34	129.17	4.08
Felele	26.00	45.22	2.14	130.92	7.60
Control	**5.75**	**2.07**	**1.90**	**36.65**	**2.1**

Table4. 5: Heavy Metal concentration (mg/kg) in the water soluble fraction at 0-15cm in all Locations

Location	Zn	Pb	Cd	Fe	Ni
Zanwangi	$0.00{\pm}0.00^{b}$	$1.72{\pm}0.02^{e}$	$0.00{\pm}0.00$	$15.07{\pm}0.04^{g}$	$0.00{\pm}0.00^{b}$
Lokongoma Phase I	$0.00{\pm}0.00^{b}$	$2.73{\pm}0.02^{b}$	$0.00{\pm}0.00$	$20.15{\pm}0.05^{f}$	$0.00{\pm}0.00^{b}$
Lokongoma Phase 2	$0.00{\pm}0.00^{b}$	$3.23{\pm}0.03^{c}$	$0.00{\pm}0.00$	$22.52{\pm}0.11^{e}$	$0.00{\pm}0.00^{b}$
Crowther Memorial	$0.00{\pm}0.00^{b}$	$2.22{\pm}0.08^{d}$	$0.00{\pm}0.00$	$35.73{\pm}0.01^{b}$	$0.00{\pm}0.00^{b}$
200 Unit	$1.64{\pm}0.01^{a}$	$2.73{\pm}0.00^{c}$	$0.00{\pm}0.00$	$33.75{\pm}0.01^{c}$	$0.00{\pm}0.00^{b}$
Felele	$0.00{\pm}0.00^{b}$	$2.73{\pm}0.00^{c}$	$0.00{\pm}0.00$	$28.17{\pm}0.03^{d}$	$0.00{\pm}0.00^{b}$
Control	$0.00{\pm}0.00^{b}$	$0.74{\pm}0.01^{a}$	$0.00{\pm}0.00$	$8.56{\pm}0.04^{a}$	$0.86{\pm}0.01^{a}$
P value	0.000*	0.000**		0.000**	0.000**

Table 4. 6: Heavy Metal concentration (mg/kg)in the water soluble fraction at 0-15cm in all Locations

Location	Zn	Pb	Cd	Fe	Ni
Zanwangi	$7.20{\pm}0.00^{d}$	$2.73{\pm}0.02^{c}$	0.00±0.00	$44.55{\pm}0.03^{d}$	$3.07{\pm}0.00^{c}$
Lokongoma Phase I	$7.52{\pm}0.02^{a}$	$2.73{\pm}0.01^{c}$	0.00±0.00	$30.24{\pm}0.09^{f}$	$1.90{\pm}0.00^{c}$
Lokongoma Phase 2	$2.00{\pm}0.00^{d}$	$3.23{\pm}0.10^{b}$	0.00±0.00	$45.73{\pm}0.03^{b}$	$2.10{\pm}0.00^{c}$
Crowther Memorial	$3.09{=}0{\pm}0.00^{d}$	$2.73{\pm}0.00^{c}$	0.00±0.00	$44.25{\pm}0.05^{e}$	$5.01{\pm}0.00^{c}$
200 Unit	$5.60{\pm}0.00^{d}$	$3.23{\pm}0.02^{b}$	0.00±0.00	$50.12{\pm}0.01^{a}$	$1.74{\pm}0.02^{a}$
Felele	$6.34{\pm}0.08^{b}$	$3.23{\pm}0.02^{b}$	0.00±0.00	$27.66{\pm}0.01^{g}$	$2.00{\pm}0.00^{c}$
Control	$1.00{\pm}0.01^{c}$	$0.74{\pm}0.01^{a}$	0.00±0.00	$4.77{\pm}0.01^{c}$	$0.40{\pm}0.01^{b}$
P value	0.000**	0.000**		0.000**	0.000**

Means with the same superscript alphabet(s) along column are not significantly different ($P>0.05$)

Means with different superscript alphabet(s) along the same column are significantly different ($P<0.05$)

Table 4. 7: Heavy Metal concentration (mg/kg in exchangeable fraction at 0-15cm in all Locations

Location	Zn	Pb	Cd	Fe	Ni
Zanwangi	1.74 ± 0.01^{b}	5.26 ± 0.10^{a}	0.67 ± 0.03^{b}	3.96 ± 0.01^{e}	1.65 ± 0.01^{c}
Lokongoma Phase I	1.03 ± 0.01^{e}	4.75 ± 0.00^{a}	0.67 ± 0.03^{b}	1.28 ± 0.02^{d}	1.52 ± 0.01^{d}
Lokongoma Phase 2	1.23 ± 0.02^{d}	5.26 ± 0.04^{a}	0.77 ± 0.01^{a}	1.61 ± 0.01^{c}	2.17 ± 0.00^{a}
Crowther Memorial	1.03 ± 0.01^{e}	5.76 ± 0.00^{a}	0.67 ± 0.00^{b}	1.93 ± 0.01^{b}	1.65 ± 0.01^{c}
200 Unit	1.74 ± 0.01^{b}	2.65 ± 2.65^{a}	0.77 ± 0.01^{a}	1.28 ± 0.01^{d}	1.65 ± 0.01^{c}
Felele	2.04 ± 0.00^{a}	5.26 ± 0.04^{a}	0.57 ± 0.00^{c}	1.28 ± 0.01^{d}	2.99 ± 0.00^{e}
Control	0.54 ± 0.00^{c}	1.76 ± 0.00^{a}	0.57 ± 0.00^{c}	0.25 ± 0.00^{a}	0.78 ± 0.03^{b}
P value	**0.000****	**0.425ns**	**0.000****	**0.000****	**0.000****

Table 4. 8: Heavy Metal concentration (mg/kg in exchangeable fraction at 15-30cm in all Locations

Location	Zn	Pb	Cd	Fe	Ni
Zanwangi	5.44±0.01[c]	4.75±0.00[c]	0.67±0.03[c]	1.96±0.01[d]	1.91±0.01[d]
Lokongoma Phase I	2.84±0.00[a]	5.26±0.04[b]	0.77±0.01[c]	1.28±0.01[c]	2.17±0.00[b]
Lokongoma Phase 2	4.93±0.01[e]	5.26±0.04[b]	0.67±0.00[b]	1.28±0.01[c]	1.78±0.03[e]
Crowther Memorial	6.63±0.01[f]	5.76±0.00[a]	0.77±0.01[b]	1.61±0.01[b]	2.04±0.01[c]
200 Unit	4.23±0.02[d]	5.26±0.04[b]	0.87±0.00[a]	1.61±0.01[b]	2.17±0.00[b]
Felele	9.94±0.00[b]	5.76±0.00[a]	0.67±0.00[c]	1.93±0.01[a]	2.57±0.00[a]
Control	1.23±0.02[d]	0.26±0.04[b]	0.17±0.00[c]	0.13±0.01[a]	1.25±0.01[f]
P value	0.000**	0.000**	0.000**	0.000**	0.000**

Means with the same superscript alphabet(s) along column are not significantly different (P>0.05)Means with different superscript alphabet(s) along the same column are significantly different (P<0.05)

Table 4. 9:Heavy Metal concentration (mg/kg) inOrganic Carbon fraction at 0 – 15 cm

Location	Zn	Pb	Cd	Fe	Ni
Zanwangi	4.84 ± 0.01^{d}	4.75 ± 0.00^{c}	0.47 ± 0.00^{b}	42.63 ± 0.01^{b}	1.78 ± 0.03^{b}
Lokongoma Phase I	25.58 ± 0.01^{a}	5.26 ± 0.04^{b}	0.47 ± 0.00^{b}	21.16 ± 0.01^{d}	1.78 ± 0.03^{b}
Lokongoma Phase 2	8.83 ± 0.10^{g}	4.75 ± 0.01^{d}	0.47 ± 0.00^{b}	21.80 ± 0.01^{c}	1.38 ± 0.01^{c}
Crowther Memorial	15.80 ± 0.01^{b}	5.76 ± 0.00^{a}	0.76 ± 0.00^{c}	12.04 ± 0.01^{f}	1.12 ± 0.01^{d}
200 Unit	5.74 ± 0.01^{c}	4.75 ± 0.00^{c}	0.47 ± 0.00^{b}	17.02 ± 0.00^{g}	1.12 ± 0.01^{d}
Felele	2.04 ± 0.00^{e}	4.75 ± 0.00^{c}	0.47 ± 0.00^{b}	58.98 ± 0.00^{a}	2.17 ± 0.00^{a}
Control	0.30 ± 0.01^{f}	1.24 ± 0.00^{c}	0.18 ± 0.01^{a}	7.31 ± 0.01^{e}	0.59 ± 0.00^{e}
P value	**0.000****	**0.000****	**0.000****	**0.000****	**0.000****

Table 4. 10: Heavy Metal concentration (mg/kg) inOrganic Carbon fraction at 15 – 30 cm

Location	Zn	Pb	Cd	Fe	Ni
Zanwangi	$1.23{\pm}0.02^{c}$	$4.75{\pm}0.00^{b}$	$0.40{\pm}0.00^{d}$	$9.62{\pm}0.00^{d}$	$1.65{\pm}0.01^{b}$
Lokongoma Phase I	$2.64{\pm}0.01^{b}$	$4.24{\pm}0.01^{c}$	$0.47{\pm}0.00^{c}$	$35.58{\pm}0.00^{a}$	$2.04{\pm}0.01^{a}$
Lokongoma Phase 2	$3.00{\pm}0.00^{f}$	$4.24{\pm}0.01^{c}$	$0.47{\pm}0.00^{c}$	$5.41{\pm}0.99^{e}$	$1.25{\pm}0.01^{d}$
Crowther Memorial	$13.26{\pm}0.04^{a}$	$5.26{\pm}0.04^{a}$	$0.77{\pm}0.00^{d}$	$24.36{\pm}0.01^{c}$	$1.65{\pm}0.01^{b}$
200 Unit	$1.26{\pm}0.14^{c}$	$4.75{\pm}0.00^{b}$	$0.76{\pm}0.01^{a}$	$26.28{\pm}0.01^{b}$	$1.52{\pm}0.01^{c}$
Felele	$1.23{\pm}0.02^{e}$	$4.75{\pm}0.00^{b}$	$0.57{\pm}0.00^{b}$	$5.89{\pm}0.01^{f}$	$1.52{\pm}0.01^{c}$
Control	$0.33{\pm}0.01^{d}$	$1.26{\pm}0.04^{a}$	$0.14{\pm}0.01^{a}$	$2.45{\pm}0.01^{e}$	$0.59{\pm}0.00^{e}$
P value	0.000**	0.000**	0.000**	0.000**	0.000**

Means with the same superscript alphabet(s) along column are not significantly different

Means with different superscript alphabet(s) along the same column are significantly different (P<0.05)

Table 4. 11:Heavy Metal concentration (mg/kg) inCarbonate fraction at 0 – 15 cm

Location	Zn	Pb	Cd	Fe	Ni
Zanwangi	27.89±0.00^{b}	12.33±0.00^{d}	0.28±0.00^{b}	32.63±0.00^{b}	0.73±0.00^{d}
Lokongoma Phase I	37.21±0.00^{a}	14.35±0.00^{c}	0.28±0.00^{b}	33.72±0.00^{g}	0.20±0.00^{f}
Lokongoma Phase 2	4.04±0.00^{g}	7.78±0.00^{g}	0.20±0.00^{c}	16.15±0.00^{e}	3.09±0.00^{a}
Crowther Memorial	17.97±0.00^{d}	26.46±0.00^{b}	0.28±0.00^{b}	18.65±0.00^{d}	1.12±0.00^{c}
200 Unit	14.46±0.00^{e}	6.77±0.00^{f}	0.18±0.00^{c}	14.23±0.00^{f}	1.65±0.00^{b}
Felele	23.28±0.00^{c}	35.05±0.00^{a}	0.38±0.00^{a}	25.51±0.00^{c}	0.46±0.00^{e}
Control	3.64±0.00^{f}	5.26±0.00^{e}	0.14±0.00^{a}	11.46±0.00^{a}	0.00±0.00^{g}
P value	**0.000****	**0.000****	**0.000****	**0.000****	**0.000****

Table 4. 12: Heavy Metal concentration (mg/kg) inCarbonate fraction at 15 – 30 cm

Location	Zn	Pb	Cd	Fe	Ni
Zanwangi	23.68 ± 0.00^{a}	9.30 ± 0.00^{a}	0.28 ± 0.00^{b}	36.47 ± 0.00^{b}	2.83 ± 0.00^{a}
Lokongoma Phase I	11.46 ± 0.00^{c}	7.78 ± 0.00^{b}	0.18 ± 0.00^{c}	64.22 ± 0.00^{g}	0.07 ± 0.00^{e}
Lokongoma Phase 2	2.84 ± 0.00^{g}	6.77 ± 0.00^{d}	0.23±0.05b	26.60 ± 0.00^{d}	0.33 ± 0.00^{c}
Crowther Memorial	16.77 ± 0.00^{b}	7.78 ± 0.00^{b}	0.38 ± 0.00^{c}	23.59 ± 0.00^{f}	0.46 ± 0.00^{b}
200 Unit	3.64 ± 0.00^{d}	5.80 ± 0.00^{d}	0.28 ± 0.00^{b}	35.06 ± 0.00^{c}	0.20 ± 0.00^{d}
Felele	3.44 ± 0.00^{e}	7.78 ± 0.00^{b}	0.47 ± 0.00^{a}	24.94 ± 0.00^{e}	0.20 ± 0.00^{d}
Control	1.74 ± 0.00^{f}	1.73 ± 0.00^{c}	0.08 ± 0.00^{b}	16.37 ± 0.00^{a}	0.00 ± 0.00^{f}
P value	0.000**	0.000**	0.000**	0.000**	0.000**

Means with the same superscript alphabet(s) along column are not significantly different (P>0.05)Means with different superscript alphabet(s) along the same column are significantly different (P<0.05)

The concentration of metal in residual phase across all the locations of 0 -15 and 15 – 30cm, are presented in Table 4.13 and Table 4.14: which show high concentration of the metals than all the phases in a sequential extraction and decrease with depth except for Cadmium that increases with depth, this is because the bidding parameters do not support the mobility of metal in the study areas. Hence, the metals are more concentrated in the residual phase and give overall behaviors of metal in the soil. While the control site has the least of all the metals concentration.

Table 4. 13: Heavy Metal concentration (mg/kg) inResidual fraction at 0 – 15 cm

Location	Zn	Pb	Cd	Fe	Ni
Zanwangi	27.89±0.00^{b}	9.30±0.00^{b}	1.65±0.00^{a}	65.45±0.00^{b}	9.67±0.00^{a}
Lokongoma Phase I	36.51±0.00^{a}	7.78±0.00^{c}	1.06±0.00^{c}	55.19±0.00^{e}	8.09±0.00^{b}
Lokongoma Phase 2	2.14±0.00^{f}	6.27±0.00^{e}	0.57±0.00^{d}	34.10±0.00^{f}	0.59±0.00^{e}
Crowther Memorial	6.14±0.00^{e}	7.28±0.00^{d}	1.26±0.00^{b}	60.32±0.00^{d}	0.00±0.00^{f}
200 Unit	10.45±0.00d	7.28±0.00d	0.38±0.00e	65.77±0.00a	2.70±0.00d
Felele	19.47±0.00^{c}	13.84±0.00^{a}	0.57±0.10^{d}	62.18±0.00^{c}	5.99±0.00^{c}
Control	0.00±0.00^{g}	6.27±0.00^{e}	0.47±0.00^{de}	28.59±0.00^{g}	0.00±0.00^{f}
P value	**0.000****	**0.000****	**0.000****	**0.000****	**0.000****

Table 4. 14: Heavy Metal concentration (mg/kg) inResidual fraction at 15 – 30 cm

Location	Zn	Pb	Cd	Fe	Ni
Zanwangi	20.17±0.00^{b}	9.80±0.01^{a}	1.36±0.00^{b}	60.83±0.00^{a}	11.91±0.01^{a}
Lokongoma Phase I	9.65±0.00^{c}	7.28±0.00^{b}	0.57±0.00^{c}	42.82±0.00^{d}	0.00±0.00^{d}
Lokongoma Phase 2	0.83±0.00^{d}	5.76±0.00^{e}	0.47±0.00^{d}	53.97±0.00^{c}	0.00±0.00^{d}
Crowther Memorial	27.69±0.00^{a}	9.80±0.01^{a}	1.36±0.00^{b}	55.51±0.00^{b}	0.59±0.00^{c}
200 Unit	0.00±0.00^{c}	6.77±0.00^{c}	1.46±0.00^{a}	26.22±0.00^{g}	0.00±0.00^{d}
Felele	0.00±0.00^{c}	7.28±0.00^{b}	0.57±0.00^{c}	30.32±0.00^{e}	1.78±0.00^{b}
Control	0.00±0.00^{c}	1.27±0.00^{d}	0.17±0.00^{d}	9.59±0.00^{f}	0.00±0.00^{d}
P value	0.000**	0.000**	0.000**	0.000**	0.000**

Means with the same superscript alphabet(s) along column are not significantly different (P>0.05)Means with different superscript alphabet(s) along the same column are significantly different (P<0.05)

The metal concentration in the well water at different distances of 20m and 30m away from each location are shown in Table 4.15 and Table 4.16. Table 4.15 shows that at a distance of 20m, the following concentrations of metals were observed; Zn had the highest in Lokongoma phase1 (14.03 mg/dm^3) and least in Zanwangi (1.16 mg/dm^3), Pb had highest in Lokongoma phase1(1.96mg/dm^3) and least in Crowther Memorial and Felele (1.56 mg/dm^3), Cd had the highest in Lokongoma Phase1(0.21 mg/dm^3) and least in Lokongoma Phase2(0.15mg/dm^3), Fe had the highest in Lokongoma Phase1 (1.73mg/dm^3) and least in Crowther Memorial and Felele (0.83mg/dm^3) and Ni had the highest in 200Unit (45.55 mg/dm^3) and least in Felele (0.07 mg/dm^3). While in 30m, the following concentrations was observed Zn had the highest in Lokongoma Phase2 (6.34mg/dm^3) and least in Zanwangi(0.16mg/dm^3), Pb had highest in 200Unit and Felele (1.56mg/dm^3) and least in Lokongoma Phase1 (1.25mg/dm^3),Cd had the highest in 200Unit and Felele (0.15 mg/dm^3) and least in Lokongoma Phase1, Lokongoma Phase2 and Zanwangi(0.13mg/dm^3), Fe had the highest in 200Unit (1.54mg/dm^3) and least in Crowther Memorial and Felele (0.64 mg/dm^3) and Ni had the highest in Lokongoma Phase1&2 (0.09 mg/dm^3) and least in Zanwangi (0.01mg/dm^3). Generally the concentration of metals decreased with distance which indicated low or decreased mobility of the metal ionsin the environment. Also, the lower concentration of metals in the control sample confirm that the metals in the vicinity are from the mechanic workshops.

Table 4.17. Shows a summary of the concentrations of heavy metals in well water at both distances of 20m and 30m from mechanic workshops. The table shows lower metalconcentration at longer distance from the mechanic workshops which indicate

decreased mobility of the metal ions from the mechanic workshops with increasing distance.

Table 4. 15: MetalConcentration in Well Water in all locations at 20m away from Mechanic workshop

Location	Zn	Pb	Cd	Fe	Ni
Zanwangi	1.61±0.00^{e}	1.66±0.00^{c}	0.17±0.00^{b}	1.60±0.00^{b}	0.12±0.00^{a}
Lokongoma Phase I	14.03±0.00^{a}	1.96±0.00^{a}	0.21±0.00^{a}	2.73±0.00^{a}	0.15±0.00^{a}
Lokongoma Phase 2	4.38±0.00^{c}	1.66±0.00^{c}	0.15±0.00^{c}	1.09±0.00^{c}	0.07±0.00^{a}
Crowther Memorial	2.23±0.00^{f}	1.56±0.00^{d}	0.17±0.00^{b}	0.83±0.00^{e}	0.09±0.00^{a}
200 Unit	12.41±0.00^{b}	1.76±0.00^{b}	0.17±0.00^{b}	0.90±0.00^{d}	45.55±000^{a}
Felele	2.24±0.00^{f}	1.56±0.00^{d}	0.17±0.00^{b}	0.83±0.00^{e}	0.07±0.00^{a}
Control	0.79±0.00^{d}	0.09±0.00^{c}	0.06±0.00^{b}	0.08±0.00^{d}	0.02±0.00^{a}
P value	0.000**	0.000**	0.000**	0.000**	0.492ns

Table 4. 16: MetalConcentration in Well Water in all locations at 30m away from Mechanic workshop

Location	Zn	**Pb**	**Cd**	**Fe**	**Ni**
Zanwangi	2.79±0.00^{c}	1.35±0.00^{d}	0.13±0.00^{c}	1.03±0.00^{c}	0.04±0.00^{d}
Lokongoma Phase I	4.61±0.00^{c}	1.25±0.00^{e}	0.13±0.00^{c}	0.83±0.00^{e}	0.09±0.00^{a}
Lokongoma Phase 2	6.34±0.00^{a}	1.35±0.00^{d}	0.13±0.00c	0.71±0.00^{f}	0.09±0.00^{a}
Crowther Memorial	3.51±0.00^{b}	1.46±0.00^{c}	0.17±0.00^{b}	0.64±0.00^{g}	0.04±0.00^{c}
200 Unit	2.24±0.00^{c}	1.56±0.00^{b}	0.15±0.00^{b}	1.54±0.00^{a}	0.07±0.00^{b}
Felele	1.23±0.00^{d}	1.56±0.00^{b}	0.15±0.00^{b}	1.28±0.00^{b}	0.07±0.00^{b}
Control	0.16±0.00^{c}	0.07±0.00^{a}	0.02±0.00^{a}	0.08±0.00^{d}	0.01±0.00^{c}
P value	0.000**	**0.000****	**0.000****	**0.000****	**0.000****

Means with the same superscript alphabet(s) along column are not significantly different (P>0.05) means with different superscript alphabet(s) along the same column are significantly different (P<0.05)

Table 4. 17: Summary of the Concentration of Heavy Metals in Well Water at two distances away from Mechanic workshops

Distance	Zn	Pb	Cd	Fe	Ni
20 m	4.89±2.24	1.69±0.05	0.18±0.01	1.13±0.14	0.09±0.01
30 m	1.98±0.90	1.46±0.05	0.15±0.01	0.99±0.12	0.06±0.01
Total	**3.44±1.23**	**1.57±0.05**	**0.16±0.01**	**1.06±0.09**	**0.07±0.01**
P value	**0.252ns**	**0.010****	**0.020***	**0.480ns**	**0.109ns**

*Means significantly different (P<0.05)

Ns Means not significantly different (P<0.05)

The variations of metal concentration with depths in all the locations is shown Figure 4.3 and 4.4.

In Zanwangi all the metals decrease with depth except Ni which increases with depth, in Lokongoma Phase1 all the metals decrease with depth except Fe that increases with depth, also, in Lokongoma Phase2 all the elements decrease with the depth except Pb that has the same concentration in both depth, in Crowther Memorial Zn, Fe and Ni increase with the depth, Pb decreases with depth while Cd shows the same concentration in both depth. In 200 Unit Cd and Fe increase with the depth while Zn, Pb and Ni decrease with depth. In Felele all the metals decrease with the depth, while Cd increases with the depth. In the Control site all the metals decrease with the depth, except Cd that increases with depth. Generally most metals tend to decrease with depth in almost all locations.

The metal fraction concentration in the sequential phases are shown in Figure 4.5 and 4.6.

The water soluble fraction all the metals increase with depth except Cd, which is not detected in both depths. In the exchangeable fraction Zn decreases with depth, Cd and Ni increase with depth, while Pb and Fe indicate the same concentration in both the depth. In Organic phase Zn, Pb and Fe decrease with depth while Cd and Ni increase with the depth. In Carbonate all the metals decrease with depth except Fe, which increases with the depth. In Residual all the metals decrease with depth, but Cd increases with the depth. In summary most of the metals decrease with the depth in some of sequential phases. Hence, low mobility of metal ions in study areas.

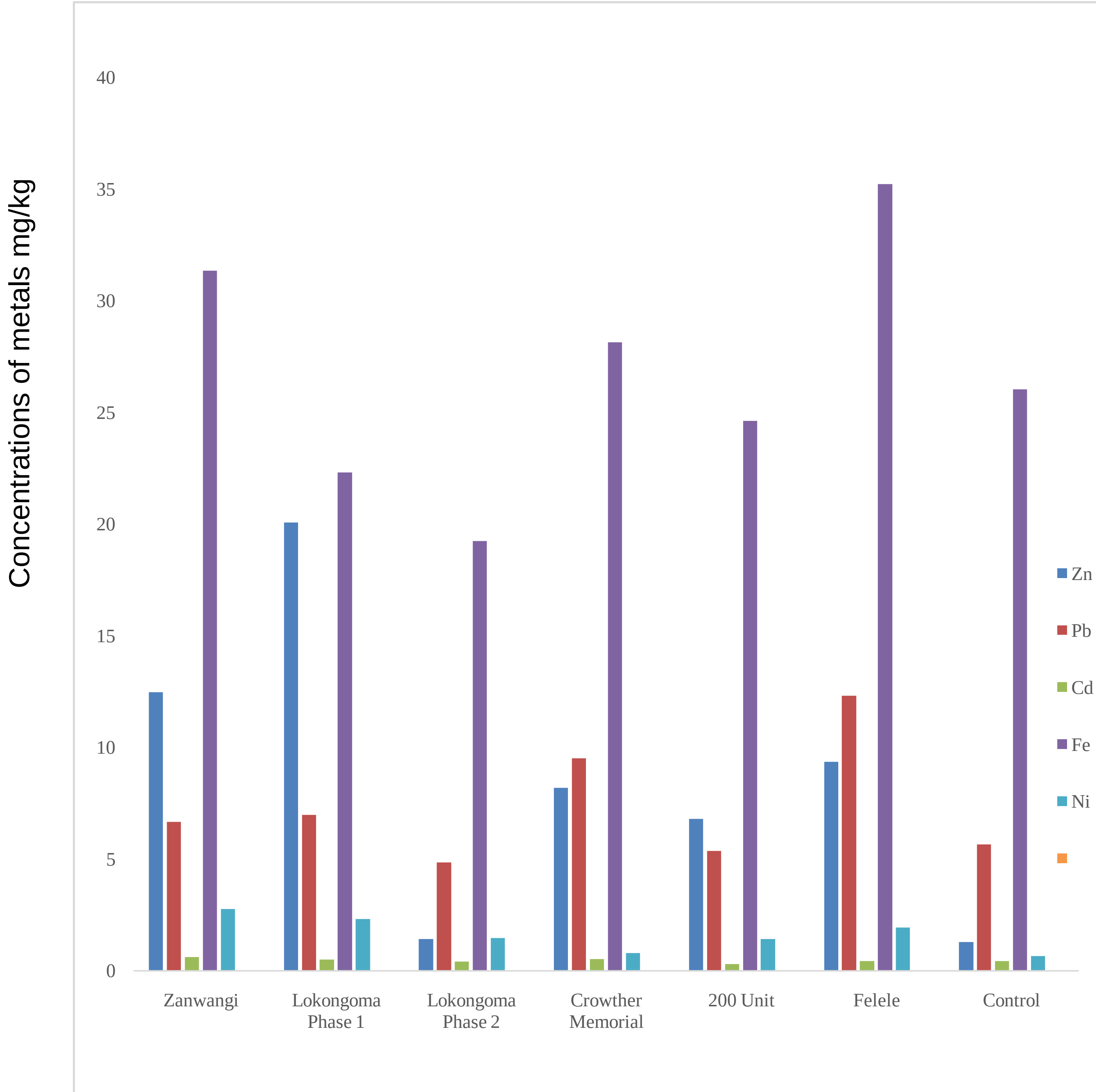

Figure 4. 3: Metal levels at 0-15cm 1n all the location

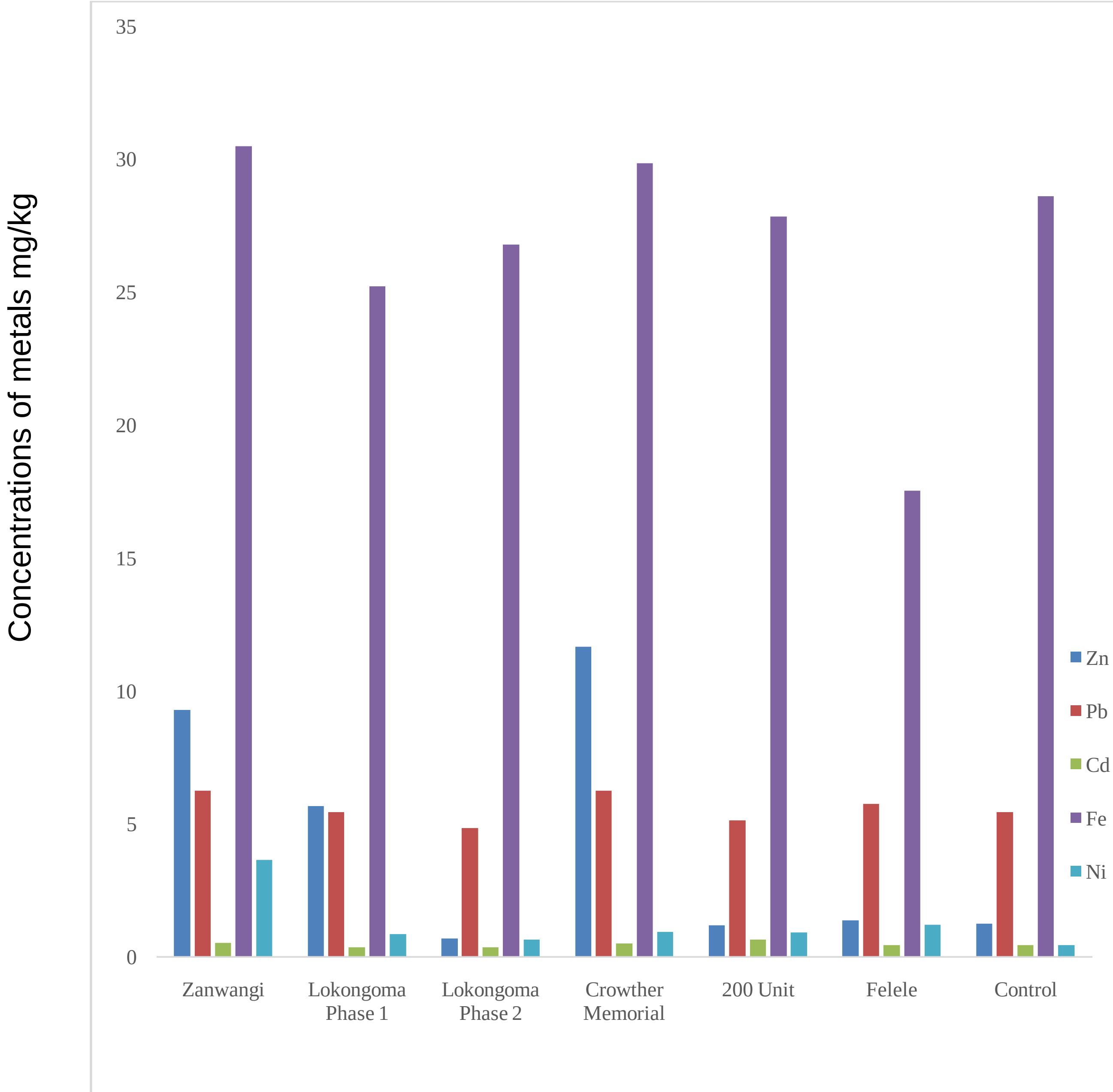

Figure 4. 4: Metal levels at 15-30cm in all the locations

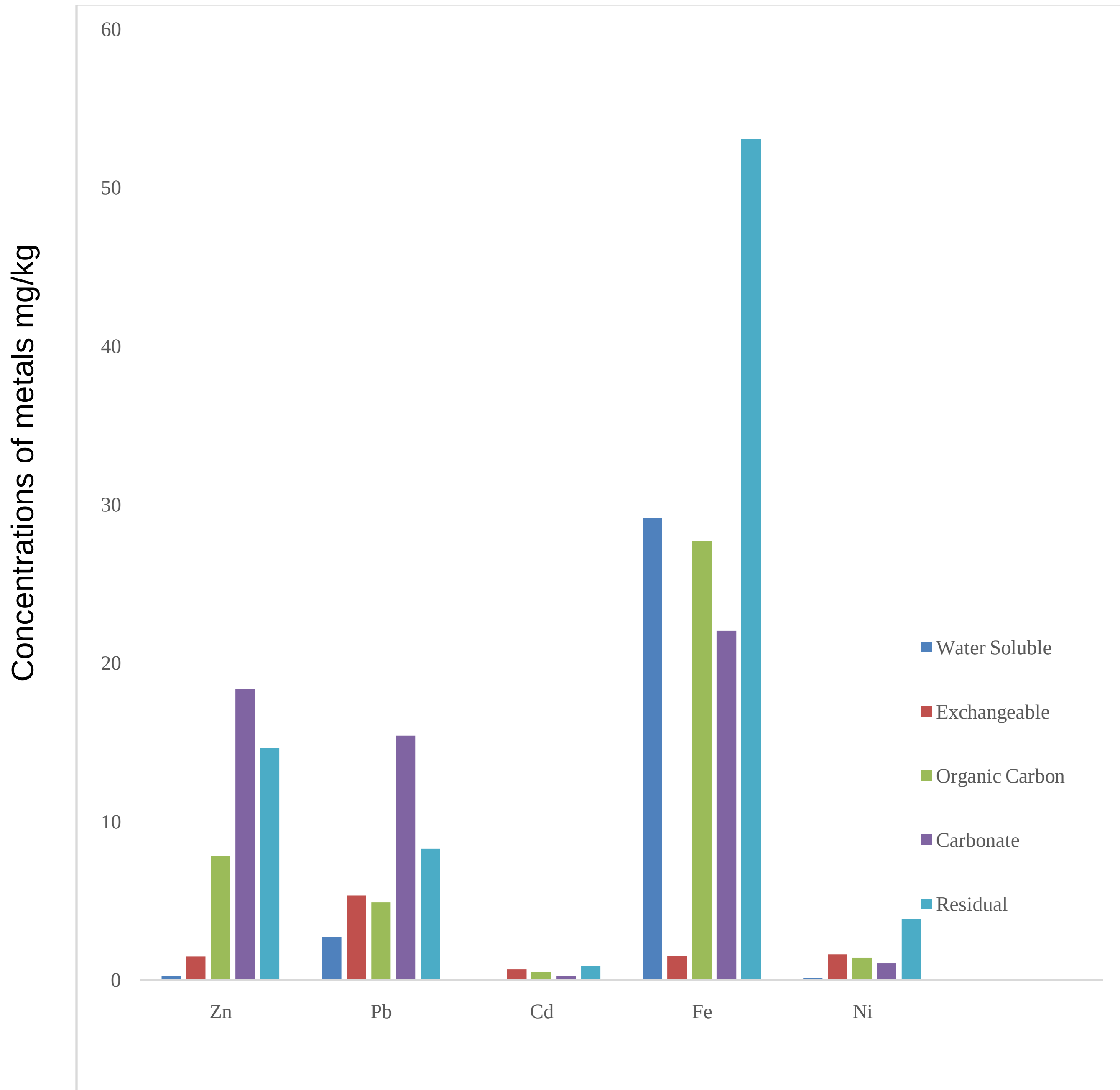

Figure 4. 5: Metal fraction levels at 0 -15cm

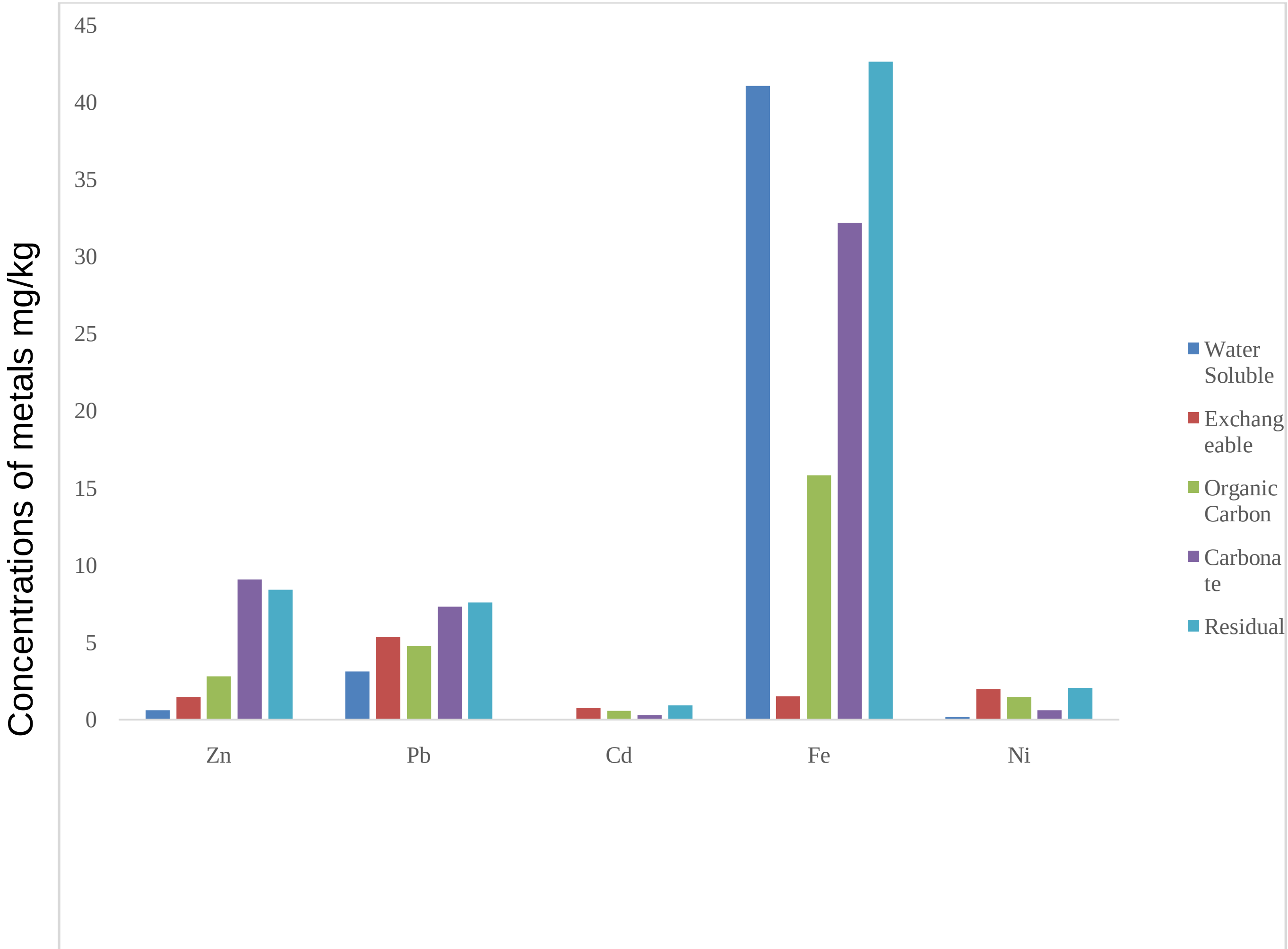

Figure 4. 6: Metal fraction levels at 15 – 30cm

4.4 Pollution Load Index (PLI)

In order to give proper assessment of the degree of contamination, attempts were made to calculate the PLI (Fig: 4.7) using the Tomlinson's*et al.,* approach (1980). The PLI represents the number of times by which the metal content in the soil exceeds the average natural background concentration, and gives a summative indication of the overall level of heavy metal toxicity in a particular sample. The control samples were taken to represent natural background according to Angulo (1996). PLI is able to give an estimate of the metal contamination status and the necessary action that should be taken.

4.5 Enrichment Factor and Geo-Accumulations Index

The extent of soils contamination was assessed using the enrichment factor (EF) and geoaccumulation index(*I*geo) (Woitke *et al* (2003 and Selvaraj,*et al.,* (2004). EF was used in the study to assess the relative contributions of natural and anthropogenic heavy metal inputs to soils Adamo *et al.,*(2005) and Valdes, *et al.,*(2005). It (EF) has also been used to indicate the degree of pollution or contamination or both, Feng,*et al.,* (2004). Data from samples taken from the control site were used to establish metal-normalizer relationships to which the data generated from various mechanic workshops are compared. According to this technique metal concentrations were normalized to the textural characteristic of soils.

4.6 Correlation Matrix

The results of correlation between the various metals were calculated using the data from the results. Table 4.25 and Table 4.26 show the correlation of two depths (0-15 and 15-30 cm).

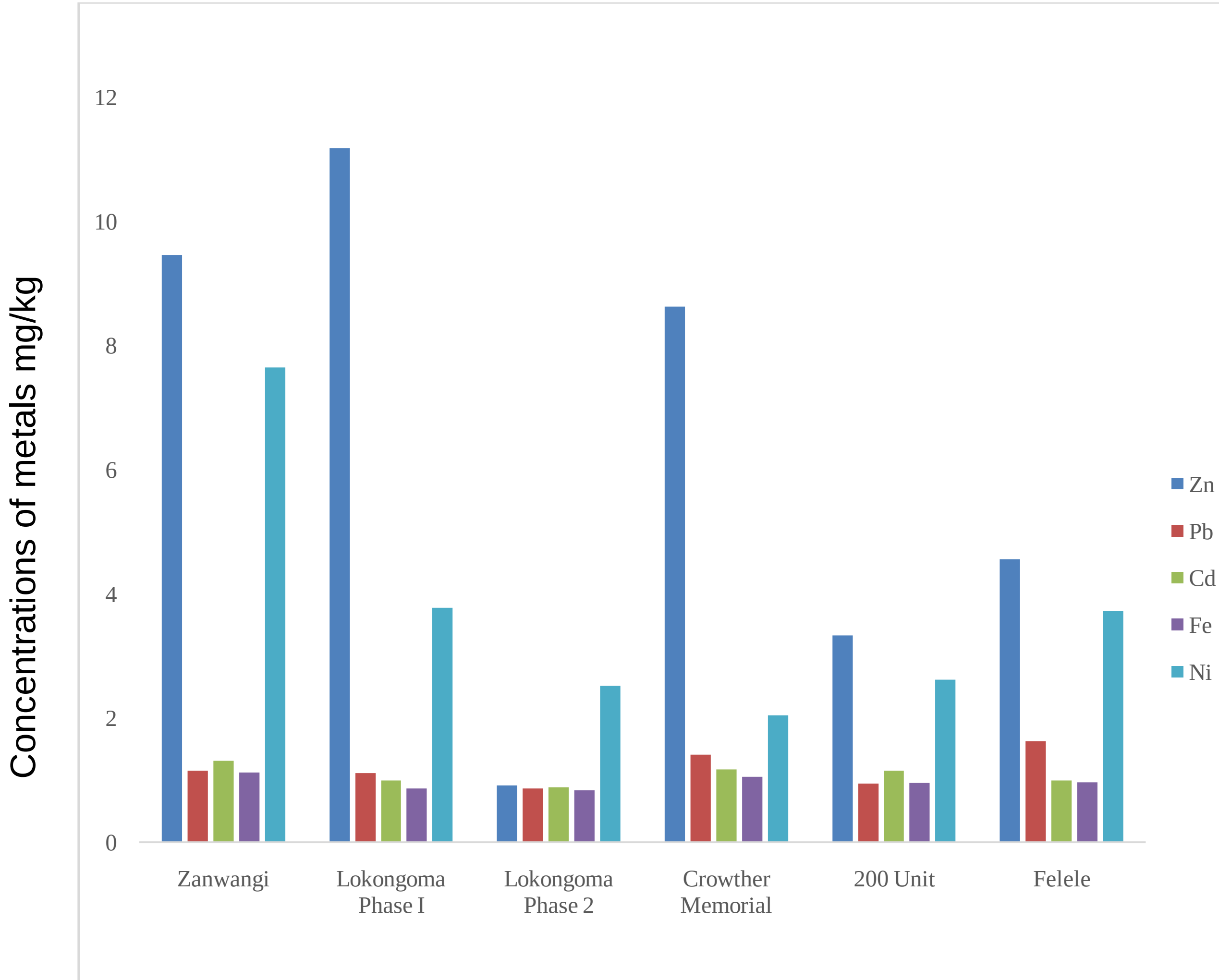

Figure 4. 7: Contamination Factor Heavy Metals in all the locations

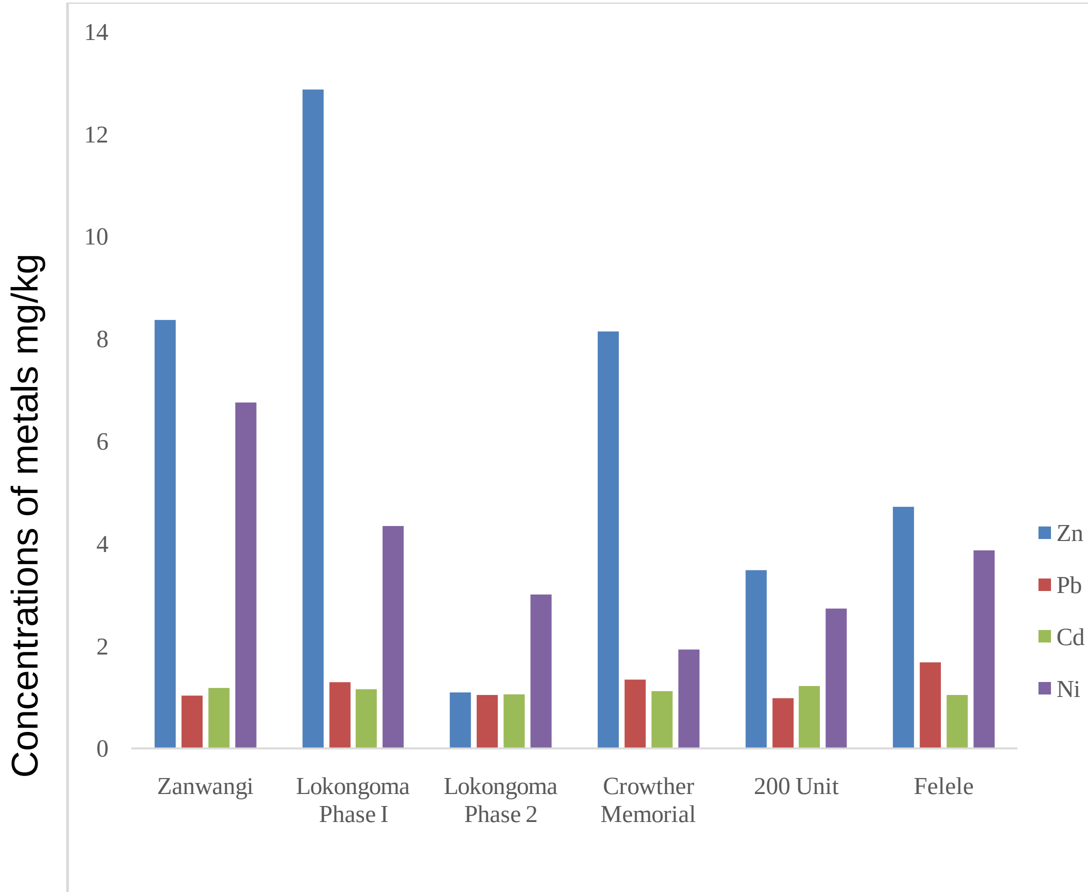

Figure 4. 8: Enrichment Factor Heavy Metals in all the locations

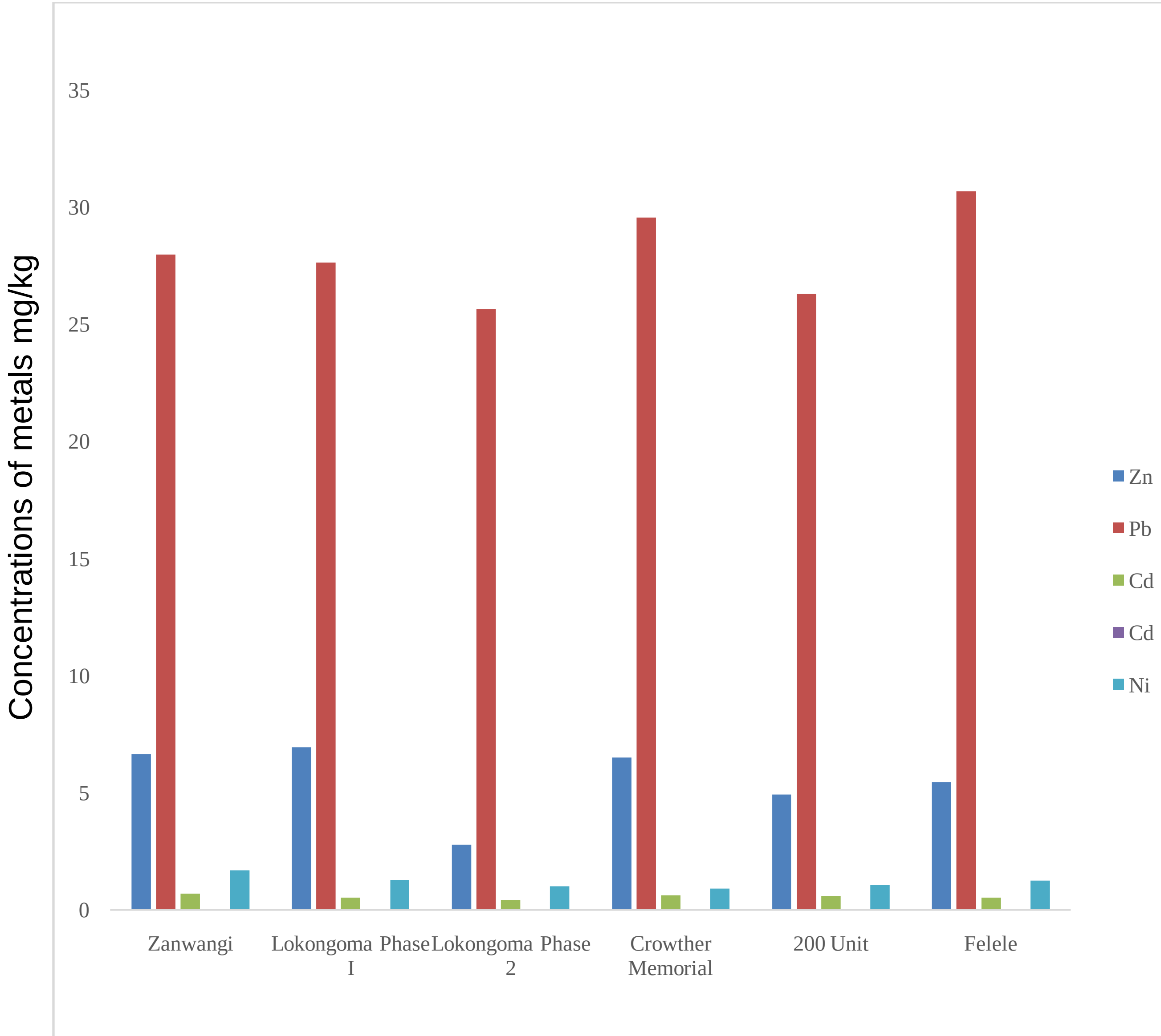

Figure 4. 9: Geo-Accumulation Index Heavy Metals in all the locations

Table 4. 18: Correlation Matrix of 0- 15cm(P>0.05)

Z	Zn	Pb	Cd	Fe	Ni	Water pH	pH ($CaCl_2$)	OC (%)	**CEC (Meq/100g of soil)**	**EC (µScm-1)**	**Ext PO_4 (mg/kg)**	**Ext SO_4(mg/kg)**	Sand (%)	Silt (%)	
Zn	1														
Pb	0.39	1													
Cd	0.53*	0.19	1												
Fe	0.33	0.36	0.87*	1											
Ni	0.58*	0.18	0.59*	0.44	1										
Water Ph	-0.38	0.13	-0.31	-0.06	0.08	1									
pH (CaCl2)	-0.07	0.32	-0.01	0.40	-0.15	0.59*	1								
OC (%)	0.53*	0.04	0.63*	0.20	0.62*	-0.40	-0.68*	1							
CEC	0.24	0.15	0.78*	0.78*	0.72*	-0.18	-0.10	0.46	1						
EC	0.18	0.19	0.03	0.04	-0.32	0.30	0.52*	-0.15	-0.54*	1					
Ext PO4	0.20	0.31	-0.37	-0.52*	-0.06	0.37	-0.04	0.14	-0.63*	0.57*	1				
Ext SO4	0.82*	0.23	0.30	0.00	0.77*	-0.15	-0.37	0.68*	0.23	-0.08	0.39	1			
Sand (%)	-0.21	0.21	-0.63*	-0.62*	-0.65*	0.25	0.09	-0.28	-0.88	0.61*	0.79*	-0.19	1		
Silt (%)	0.30	0.00	0.63*	0.64*	0.50*	-0.53*	-0.18	0.29	0.86*	-0.65*	-0.82*	0.16	-0.91*	1	
Clay (%)	0.06	-0.41	0.49	0.47	0.68*	0.12	0.03	0.22	0.71*	-0.42	-0.58*	0.19	-0.88*	0.61*	1

Table 4. 19: Correlation Matrix of 15 – 30cm(P>0.05)

Z	Zn	Pb	Cd	Fe	Ni	Water pH	pH ($CaCl_2$)	OC (%)	**CEC (Meq/100g of soil)**	**EC (µScm-1)**	**Ext PO_4 (mg/kg)**	**Ext SO_4(mg/kg)**	Sand (%)	Silt (%)	
Zn	1														
Pb	0.39	1													
Cd	0.48*	0.19	1												
Fe	0.33	0.36	0.68	1											
Ni	0.58*	0.18	0.48*	0.44	1										
Water Ph	-0.38	0.13	-0.31	-0.06	0.08	1									
pH (CaCl2)	-0.07	0.32	-0.01	0.40	-0.15	0.59*	1								
OC (%)	0.53*	0.04	0.63*	0.20	0.62*	-0.40	-0.68*	1							
CEC	0.24	0.15	0.65*	0.65*	0.68*	-0.18	-0.10	0.46	1						
EC	0.18	0.19	0.03	0.04	-0.32	0.30	0.52*	-0.15	-0.45*	1					
Ext PO4	0.20	0.31	-0.37	-0.42*	-0.06	0.37	-0.04	0.14	-0.53*	0.57*	1				
Ext SO4	0.80*	0.23	0.30	0.00	0.77*	-0.15	-0.37	0.68*	0.23	-0.08	0.39	1			
Sand (%)	-0.21	0.21	-0.63*	-0.62*	-0.65*	0.25	0.09	-0.28	-0.88	0.61*	0.79*	-0.19	1		
Silt (%)	0.30	0.00	0.61*	0.62*	0.50*	-0.53*	-0.18	0.29	0.86*	-0.65*	-0.82*	0.16	-0.91*	1	
Clay (%)	0.06	-0.40	0.45	0.43	0.58*	0.11	0.03	0.20	0.68*	-0.40	-0.52*	0.19	-0.84*	0.60*	1

CHAPTER FIVE

5.0 DISCUSSION

Most of the soil pH values of the study areas did not indicate the availability of these metals which could indicate low metal uptake by plants. Electrical Conductivity (EC) decreases from the study areas to control site. The electrical conductivity values (0.30 to 0.60) were higher than those values (0.07 to 0.09) obtained by Iwegbue et al. (2006) but much lower than those values (1.32 to 2.7) by Osakwe and Otuya (2008).

In the study area, extractable sulphate content ranged from 0.91 to 1.30 mg/kg while those samples from the control area ranged between 0.57mg/kg to 0.63 mg/kg. Significant variation was observed between the extractable sulphate level in the samples (0.91 to 1.30 mg/kg) and control (0.63 mg/kg). This could be due to the activities of battery chargers within the study area, which is an indication of soil contamination within this area. The level of extractable PO_4^{3} in soil samples ranged from 4.60 – 17.90 mg/kg in the study areas while in the control area, the PO_4^{3-} level was 3.30 mg/kgwhich was less than in the former for similar reasons, since the presence of sulphate could be responsible for high phosphate level within these sites. Extractable phosphates in the study area had a mean of 9.33mg/kg which is lower than the value (16.23 mg/kg) reported by Iwegbue et al. (2006).

The soil samples show a variable mixture of sand, silt and clay.

Results show that sand (>65%) was the main component of all soil samples, with a mean range from 65% to 71%. Mean clay contents were in the range of 12% to 18% and silt in the range of 11% to 17%.

The distribution pattern of the metals across all the sampling locations and depths, Fe and Cd showed the highest (151.58mg/kg) to (112.09mg/kg), and for Fe (2.84mg/kg) and to

(2.13mg/kg) for Cd respectively. In terms of concentration value across the various profiles, the highest mean concentration for Zn (20.06mg/kg and Pb (12.32mg/kg) were recorded in the top soil samples (0 - 15 cm depth) with decreasing order down the soil depths. However, the highest for Cd (0.66mg/kg) and Ni (3.66mg/kg) were recorded in the 15 - 30 cm depth which decreasedwith soil depth which showed decreased mobility of these metals.

The data in Table 4.1**3**Shows that the pH across the entire study area ranged in a narrow interval. Top soils (0 – 15cm) and sub-soil (15 - 30 cm) across the studied area and this suggest slightly acidic soil condition. pH plays significant role in solute concentration and in sorption and desorption of contaminants in soil Gillman (1981), and Elliot., *et at* (1986). However, based on the data in Table 4.1, the pH levels are very close at each soil layer which may suggest that, all other factors being equal, the effects of pH on the metal's bioavailability is insignificant.

The CEC is high in all top soils. The reduction in CEC down the soil profile makes the soil less suitable for tap rooted crops. The reduction in CEC of the studied soil over that of the control is a reflection of nutrient depleting wastes or displacement by toxic metals which are indirectly introduced through indiscriminate disposal of auto mechanic wastes. However, there are no significant mean differences ($p < 0.05$) in levels of CEC obtained at each soil layer from the various sampling locations.

The organic carbon decreases down the soil profile from 0-15 to 15-30 cm in all the locations displaying the highest and least percentagesrespectively. The range in organic matter content of the control area (1.00% - 3.3%) is much higher than the range (0.10% - 0.17%) in any of the samples from the auto-mechanic workshops. The significant difference in the organic carbon content of control and mechanic workshops sample indicated depletion of soil nutrients by wasteswhich are indiscriminately disposed within an automobile mechanic workshops. Previous studies have found that higher organic carbon (>3.0%) levels are typically associated with fine soils and lower organic carbon levels with coarse soils,Kamaruzzaman et al., (2009).

The mobility and availability of heavy metals in soils depend on how the metals are associated with the components of the soil, and the measure of the mobility and availability of metals serves topredict the behavior of heavy metals in the soil.

The metals are bound to the soil through phases such as water soluble, exchangeable, carbonate, oxides and hydroxides and organics. The selective sequential extraction of heavy metals provides detailed insight on how the metals are associated with the components of the soil. Tables 4.5 to 4.14 present total and sequentially fractionated metal (Cd, Zn, Fe, Ni and Pb) concentrations in soil, and the heavy metal percentage for each fraction calculated for the sampled areas of Lokoja soil.

Analysis of variance between heavy metals across sites revealed significant differences ($p < 0.05$). A correlation matrix for heavy metals in the soil of the different sites was calculated to see if some metals were interrelated with each other and the results are presented in Table 4.25 and 4. 26. Negative correlation was especially found between themetals in the study areas, Cd: Ni and Pb; Pb: Cr; and Pb: Cd, though not significantly ($p > 0.05$).However, others showed significant ($p < 0.05$)positive correlation between Cr: Zn and Fe. Also, Table 25 and Table 26. Showed the correlation between heavy metals in soils and the soil physicochemical parameters which revealed significant positive correlation($p < 0.05$) between Zn: clay, silt, and extractable $SO_{4,}^{2-}$ and Cu: andextractable

SO_4^{2-}. Hence, positive correlation between metal concentration and physicochemical parameters could imply a significant effect on the heavy metals in the soil, since the mobility and bioavailability of metals present in soils depend on physicochemical properties of both the metal and the soil (McEldowney *et al*., 1993). In the study sites the distribution pattern of metals in the five geochemical phases of the soil showed differences. As shown in the results, the highest percentage of metals was found in the residual fractions while the water soluble fraction had the least percentage.

5.2 Heavy Metal Distribution

Metals in soils of the auto-repair workshop are not all retained within the profile depth of 0 - 15 cm.

Average concentrations of Pb, Zn and Fe obtained from this study generally decreased vertically with soil depth while Cd and Ni increased with depth. This illustrates the mobility potential of heavy metals down the soil profile. The enhanced concentrations of some of the metals may be attributed to the presence of additives (consisting of metals in various proportions) in lubricants used by auto mechanics. Slight variation exists between the levels of individual metal across all sampling locations but without any significant mean differences ($\alpha \geq 0.95$). The variation may be due to factors such as age of the mechanic workshops, volume of work done on each site, types of automobile service or repairs, type of lubricant commonly used, mode of wastes disposal and type of soil. However, significant variation and mean differences occur between levels of individual metals ($p < 0.05$).Comparing metal concentrations with the permissible level of heavy metal in the soil by Department of Petroleum Resources (DPR,1991). Cadmium value (2.89mg/kg) of the study areas was above the Cd, value (0.8mg/kg) of the (DPR, 1991).For metals like cadmium that has no biological function, this calls for public concern, Tchenitchin, et al., (1998) and Martnez, et al., (1997). The elevated levels of these metals in the soil profiles constitute a serious threat to both surface and ground water. Some of the metals correlated significantly with percent organic carbon with decreasing soil depth. The total metal concentrations in the present study were compared to other studies, particularly in Nigeria. As noted earlier, the very few studies were based on top 0 - 15 cm soil depth. Apart from Pb (24.00 to 45.22mg/kg) which was found within the range (23.04 to 47.11mg/kg) reported by Fakayode*et al.,* (2003), mean concentrations of all the other metals were above levels (09.15 to 11.04mg/kg) recorded in literature by Adeniyi and Afolabi (2002) and Ogunfowokan *et al., (*2009).

The levels of metal in well water within the mechanic workshops at different distance of 20m and 30m away from each location were determined.The results indicated that, the levels of metal in well water are higher at 20m away from the mechanic workshops than at 30m away. This showed that, there could be greater pollution as a results of automobile workshops activities in the immediate vicinity of these workshops.

5.3 Indices of Pollutions

In this study, the enrichment factor (EF), contamination factor (CF) and pollution load index (PLI) was applied to assess heavy metal contamination in soil located within some automobile mechanic workshops.

In the study, the contamination factor and pollution load index are presented in Table 4.31.The CFs for the five metals in the different soil depths and are indeed very high, ranging from 1.34 (Fe) to 1.83 (Zn). The trend is such that highest CFs was observed in Zn and Ni and least in Fe. In general, the increasing order was CFs is Fe < Cd <Pb< Ni <Zn. The CFs values decreased down the soil depth for Fe and Pb but increased down the soil depths for Ni and Cd. The pattern in Zn was irregular. The very high values of the

CFs (>1) in all the metals can be due to influence of mechanic activities such as indiscriminate disposal of metal containing compounds such as used engine oil, vehicle spare parts, welding activities etc. The data on PLI of all the soil Samples (Table 4.31) were far greater than unity (>1). Consequently, soils from the mechanic workshops (as representatives of other workshops) are considered to be of pollution concern in view of indiscriminate disposal of used oils, vehicle spare parts and other wastes from their workshops.

5.4 Enrichment Factor and Geo-Accumulation Index

Details of the EF values of the metals studied with respect to the natural background concentration are presented in Table 4.32. Variation occurs in the EFs of Zn occurring at levels ≥ 9 while Ni occur, at values EF =5-10 Thus, based on Birth, *et al.,* (2003) interpretation, the EFs for Ni indicated moderately severe enrichment which suggested a possible mobilization of metals while Pb and Cd at < 3 indicate minor enrichment. All the auto-mechanic workshops are seen to be severely enriched with Zn (1.09 to 12.87mg/kg). Do these truly represent anthropogenic input? In a recent report, it has been shown that high EFs do not provide a reliable indication of the degree of human interference with the global environment, Sucharova *et al.,* (2012). In the report carried out in Czech Republic where five different elements were used as reference, the sequence of the EFs does not reflect the relative importance of the elements determined. It was concluded that other factors, such as the choice of reference element may be responsible for high EFs. The variation in EFs from site to site may also reflect the age of establishment of the various workshops and indicative of the number of services each workshops rendered.

5.5 Geoaccumulation Index

Unlike the EFs, the six metals fall within two *I*geo class based on Muller's Sucharova *et al* (2012) interpretation; Cd and Ni were moderately contaminated while Pb and Ni were extremely contaminated. This contamination can only result from anthropogenic activities considered to emanate from mechanic workshop activities.

5.6 Correlation Matrix

A correlation matrix for heavy metals in the soil of the different sites was calculated to see if some metals were interrelated with each other and the results are presented in Table 4.33. Positive correlation was especially found between the metals in the study areas, Cd: Pb and Pb; Zn: Fe; and Pb: Fe, ($p > 0.05$) though not significantly present. However, others showed significant ($p < 0.05$) positive correlation between Cd: Zn and Fe;Ni Also, Table 4.33 shows the correlation between heavy metals in soils and the soil physicochemical parameters, ($p < 0.05$). A positive correlation between Zn: clay silt and extractable SO_4^{2-} and Pb: extractable PO_4^{3-}. Hence, positive correlation between metal concentration and physicochemical parameters could imply a significant effect on the amount of heavy metals in the soil, since the mobility and bioavailability of metals present in soils depend on physicochemical properties of both the metal and the soil (McEldowney *et al.,* 1993).

The correlation coefficients between the concentrations of the different metals indicate strong links between them, which probably reflects their related origin. The wastes which are indiscriminately disposed within the various workshops are possible sources of these metals.

CHAPTER SIX

6.1 Conclusion

This survey determinedthe levels of some important heavy metals at two different depths of the soils sampled. The combined use of different approaches for evaluating soil metal contamination facilitates a comprehensive interpretation of the soil characteristics in terms of the background influences. The mechanic workshop environment is getting polluted, particularly with Pb, Ni and Cd based on the enrichment factor. This is a reflection of anthropogenic contribution which might partly result from the use of metal-containing additives as lubricants. Based on the geoaccumulation index data, the soils can generally be classified as “moderately contaminated” by these heavy metals although the pollution index load indicate that the entire mechanic workshop soils are considered to be of pollution concern. There was an indication of an uneven distribution of the metals in soils from various locations, though there was no significant difference in metal distributions between them.The levels of heavy metal determined in the well water at 20m away from the mechanic workshops indicated leaching of heavy metals from automobile workshop activities.

6.2 Recommendations

This study assessed the extent of heavy metal contamination in soils and well water within some selected mechanic workshops using some pollution indices. Consequent upon our findings, it is recommended that government should provide appropriate places that will serve as automobile village where auto repairs are kept at safe distances from human habitation. This may not be necessary in developed countries where measures are already put in place to legislate against deposition of metal pollutants. Education and legislation on management of wastes in place such as auto-mechanic workshops should be intensified to forestall the effects of heavy metal related wastes on the environment, particularly on groundwater. Also, modern waste disposal facilities should be acquired by relevant authorities and appropriate waste disposal sites be chosen to avoid the injurious effects of indiscriminate disposal of used oils/lubricants, scrap metals etc. In addition, continuous monitoring and further studies on the level of these heavy metals should be carried out in the near future and at intervals to ascertain long-term effects of this anthropogenic impact. This should also involve larger coverage with studies on ground water around such locations.

In addition, metals speciation should be carried out so that the form and extent of metal bioavailability can be further evaluated.

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APPENDICES

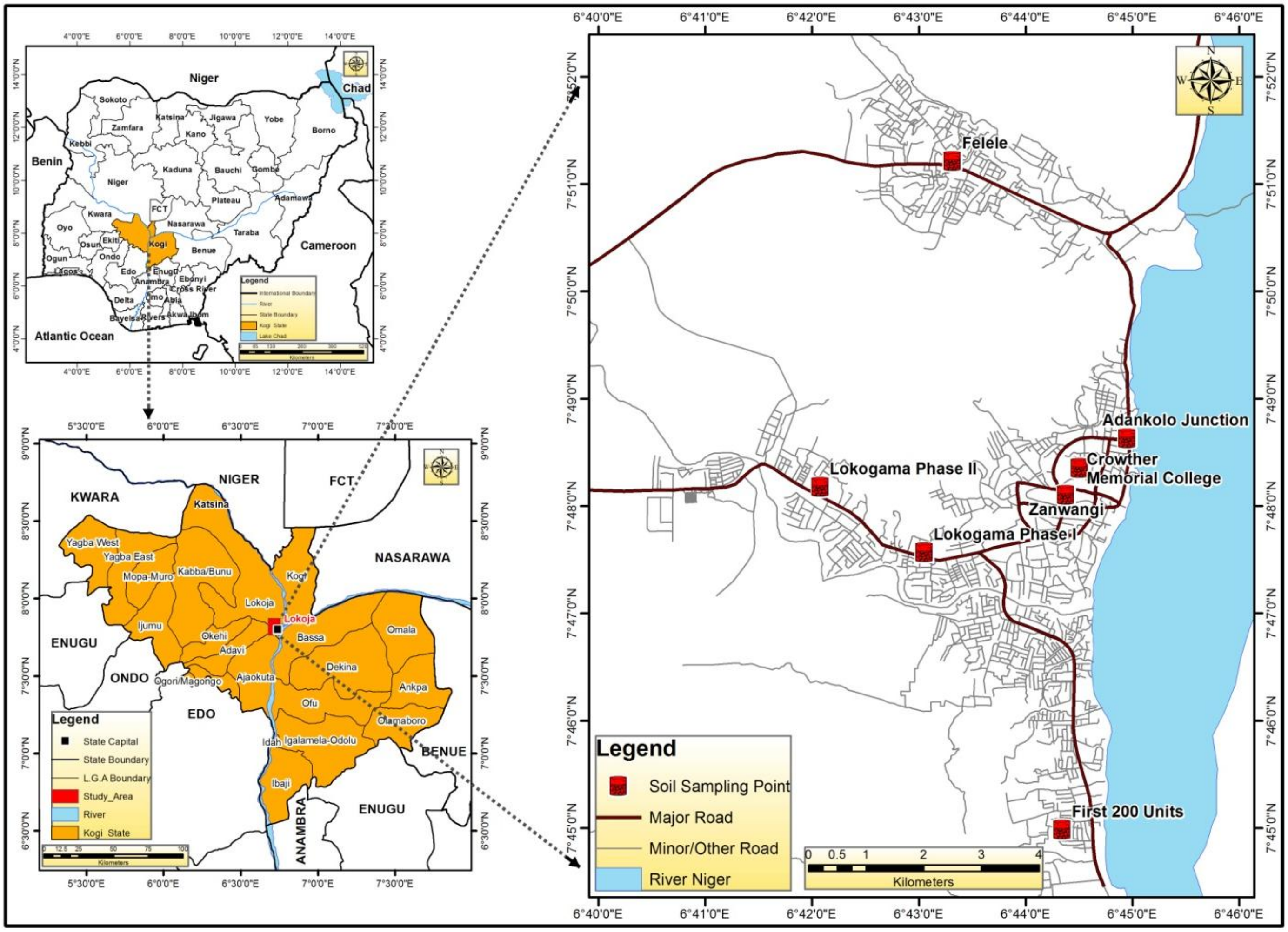
Appendix I: Department of Petroleum Resources (DPR, 1991) target and intervention values for metals in soil.

Metals	Target values (μg·g−1)	Intervention values(μg·g−1)
Cadmium	0.8	17
Chromium	100.0	380
Copper	36.0	190
Lead	85.0	530
Nickel	35.0	210
Zinc	140.0	720

The soil samples collected were pre-treated and digested accordAwofolu (2005). Glass electrode pH meter was used to measure the soil pH in 1:1 soil water suspension and 0.01M $CaCl_2$ suspension by Hendershot et al. (1993); organic carbon was determined by the method of Walkeley and Black (1934); Cation Exchange Capacity (CEO) was determined by Herdershot et al. (1993); while particle size distribution was determined by the hydrometer method as described by Bougousos (1951). Extractable Sulphate (SO_4^{2-}) and Phosphate (PO_4^{3-}) were determined by methods described by Allen et al. (1974). Sequential extraction method described by Sposito et al (1982) with slight modification (Agbenin and Atin, 2003) was used to determined five operationally defined fractions of the sequential extraction. With the following modification (i) water soluble was first of all extracted, (ii) Exchangeable: the soil soil residue from water extraction was sequentially extarcated by adding 25ml of 25ml of 0.25M K_2SO_4 (iii) Organicallly bound; 25ml of 0.5M NaOH was added to the soil residue after the extraction of the organic bound. (v) Residue: The residue fraction of the metals were computed by substracting the sum of fractions (i)-(iv) from the respective total metal concentration (Bell et al., 1991: Alva et al., 2000) determine by $HClO_4$-HNO_3-H_2SO_4 digestion (Agbenin, 1995).

At the end of each extraction period, the individual metals in the filtrates were determined by AAS and corrections were made for the concentration of metals in solution.

The distribution pattern of metals in a sequential phases in Zanwangi Mechanic Workshop is shown in Table 4.23.
Zn: Carbonate > Residual >Organic > Exchangeable > Water Soluble
Pb: Carbonate > Residual > Exchangeable > Organic > Water Soluble
Cd: Residual > Exchangeable > Organic > Carbonate > Water Soluble
Fe: Residual >Carbonate > Water Soluble > Organic > Exchangeable
Ni: Residual > Carbonate = Exchangeable > Organic > Water Soluble
The phases are significantly different at (($\alpha \geq 0.95$) except Fe.
The distribution pattern of metals in a sequential phases in Lokongoma Phase1 Mechanic Workshop is shown in Table 4.25.
Zn: Carbonate > Residual > Organic > Exchangeable > Water Soluble
Pb: Carbonate > Residual > Exchangeable > Organic > Water Soluble
Cd: Residual > Exchangeable > Organic > Carbonate > Water Soluble
Fe: Residual > Organic> Water Soluble> Carbonate > Exchangeable
Ni: Residual > Organic > Exchangeable > Carbonate> Water Soluble
The phases are significantly different at (($\alpha \geq 0.95$) except Zn, Pb and Ni.



Map of Lokoja showing Soil Sampling Points

Source: Modified from the Administrative Map of Lokoja L.G.A

3.4 Contamination Control

The distribution pattern of metals in a sequential phases in Lokongoma Phase2 Mechanic Workshop is shown in Table 4.26.

Zn: Carbonate > Residual > Exchangeable > Organic > Water Soluble
Pb: Residual > Carbonate >Exchangeable > Organic > Water Soluble
Cd: Exchangeable> Residual> Organic > Carbonate > Water Soluble
Fe: Residual >Water Soluble >Carbonate > Organic > Exchangeable
Ni: Exchangeable > Carbonate > Organic > Residual > Water Soluble
The phases are significantly different at (($\alpha \geq 0.95$) except Zn, Fe and Ni.

The distribution pattern of metals in a sequential phases in Crowther Memorial Mechanic Workshop is shown in Table 4.28.

Zn: Carbonate > Residual > Organic >Exchangeable > Water Soluble
Pb: Carbonate > Residual > Exchangeable > Organic > Water Soluble
Cd: Residual > Exchangeable > Organic > Carbonate > Water Soluble
Fe: Residual > Water Soluble > Organic > Carbonate > Exchangeable
Ni: Exchangeable >Organic > Carbonate > Residual > Water Soluble
The phases are significantly different at (($\alpha \geq 0.95$) except Zn and Pb.

The distribution pattern of metals in a sequential phases in 200 Unit Mechanic Workshop is shown in Table 4.30.

Zn: Carbonate > Residual > Organic >Exchangeable > Water Soluble
Pb: Residual > Carbonate > Exchangeable > Organic > Water Soluble
Cd: Residual > Exchangeable > Organic > Carbonate > Water Soluble
Fe: Residual > Water Soluble > Carbonate> Organic >Exchangeable
Ni: Exchangeable > Residual > Organic > Carbonate > Water Soluble
But no significant different at (($\alpha \geq 0.95$) except.

The distribution pattern of metals in a sequential phases in Felele Mechanic Workshop is shown in Table 4.31.

Zn: Carbonate > Residual >Exchangeable > Organic > Water Soluble
Pb: Carbonate > Residual > Exchangeable > Organic > Water Soluble
Cd: Residual = Exchangeable > Organic > Carbonate > Water Soluble
Fe: Residual > Organic > Water Soluble > Carbonate >Exchangeable
Ni: Residual > Organic > Exchangeable > Carbonate > Water Soluble
But no significant different at (($\alpha \geq 0.95$) except Cd.

The Table 4.33 Shows the distribution pattern of metals in a sequential phases in Felele Mechanic Workshop.
Zn: Carbonate >Exchangeable > Organic > Water Soluble > Residual
Pb: Carbonate > Residual > Exchangeable > Organic > Water Soluble
Cd: Organic > Exchangeable > Residual > Carbonate > Water Soluble
Fe: Carbonate > Water Soluble > Residual> Organic > Exchangeable
Ni: Exchangeable > Water Soluble > Organic > Carbonate = Residual
With significant different at (($\alpha \geq 0.95$).

Table 4. 20: **Concentration of Metals in Different Depth in Water Soluble Phase**

Depth	Zn	Pb	Cd	Fe	Ni
0 - 15 cm	0.23±0.23	02.73±0.25	0.00±0.00	029.14±04.27	0.12±0.12
15 - 30 cm	0.59±0.28	03.09±0.14	0.00±0.00	041.05±03.22	0.17±0.11
Total	**0.41±0.18**	**02.91±0.15**	**0.00±0.00**	**035.09±03.06**	**0.15±0.08**
P value	**0.351ns**	**0.230ns**		**0.046***	**0.783ns**

Table 4. 21: Concentration of Metals in Different Depth in Exchangeable Phase

Depth	Zn	Pb	Cd	Fe	Ni
0 - 15 cm	1.48±0.15	5.33±0.13	0.67±0.03	1.51±0.17	1.63±0.13
15 - 30 cm	1.46±0.28	5.33±0.13	0.73±0.03	1.51±0.14	1.98±0.15
Total	**1.47±0.15**	**5.33±0.09**	**0.70±0.02**	**1.51±0.10**	**1.80±0.11**
P value	**0.963ns**	**1.000ns**	**0.207ns**	**0.997ns**	**0.105ns**

Table 4. 22: Concentration of Metals in Different Depth in Organic Carbon Phase

Depth	Zn	Pb	Cd	Fe	Ni
0 - 15 cm	7.84±3.57	4.89±0.18	0.49±0.03	27.70±6.52	1.42±0.20
15 - 30 cm	2.79±1.77	4.75±0.16	0.53±0.06	15.80±4.82	1.46±0.17
Total	**5.31±2.04**	**4.82±0.12**	**0.51±0.03**	**21.75±4.23**	**1.44±0.13**
P value	**0.229ns**	**0.560ns**	**0.509ns**	**0.168ns**	**0.886ns**

Table 4. 23: Concentration of Metals in Different Depth in Carbonate Phase

Depth	Zn	Pb	Cd	Fe	Ni
0 - 15 cm	18.35±4.65	15.43±4.24	0.28±0.03	22.05±3.20	1.03±0.40
15 - 30 cm	9.08±3.21	7.28±0.48	0.26±0.05	32.18±5.67	0.58±0.38
Total	**13.71±3.00**	**11.35±2.34**	**0.27±0.03**	**27.12±3.43**	**0.81±0.27**
P value	**0.126ns**	**0.080ns**	**0.806ns**	**0.146ns**	**0.430ns**

Table 4. 24: Concentration of Metals in Different Depth in Residual Phase

Depth	Zn	Pb	Cd	Fe	Ni
0 - 15 cm	14.66±5.20	8.29±1.00	0.87±0.18	53.09±5.80	3.86±1.53
15 - 30 cm	8.38±4.31	7.56±0.61	0.89±0.18	42.61±5.44	2.04±1.66
Total	**11.52±3.36**	**7.92±0.57**	**0.88±0.12**	**47.85±4.09**	**2.95±1.11**
P value	**0.371ns**	**0.551ns**	**0.911ns**	**0.212ns**	**0.436ns**

The highest percentage fractions obtained by the sequential extraction procedure shows the following metal distribution pattern:

In 0- 15cm Depth

Cd:Residual>Exchangeable>Organic>Carbonate>WaterSoluble

Zn:Carbonate>Residual>Organic>Exchangeable>WaterSoluble

Fe: Residual > Organic > Carbonate>Exchangeable> Water Soluble

Ni:Residual>Exchangeable > Organic>Carbonate>WaterSoluble

Pb: Carbonate > Residual > Exchangeable > Organic >Water Soluble.

In 15- 30cm Depth

Cd: Residual>Exchangeable>Organic>Carbonate>Water Soluble

Zn: Carbonate>Residual>Organic>Exchangeable>Water Soluble

Fe: Residual>Carbonate>Organic>Exchangeable>Water Soluble

Ni: Residual>Exchangeable>Organic>Carbonate>WaterSoluble

Pb: Residual > Carbonate > Exchangeable>Organic>Water Soluble.

Table 4. 25: Concentration of Metals in Different Depth in all the Locations

Location	**Depth**	**Zn**	**Pb**	**Cd**	**Fe**	**Ni**
Zanwangi	0 - 15 cm	12.47±6.34	6.67±1.86	0.61±0.28	31.35±11.14	2.76±1.76
	15 - 30 cm	9.30±5.19	6.26±1.39	0.54±0.23	30.49±11.09	3.66±2.11
	Total	**10.89±3.90**	**6.46±1.10**	**0.58±0.17**	**30.92±7.41**	**3.21±1.30**
	P value	**0.709ns**	**0.866ns**	**0.840ns**	**0.958ns**	**0.753ns**
Lokongoma Phase 1	0 - 15 cm	20.06±8.24	6.97±2.01	0.50±0.18	22.30±8.95	2.32±1.49
	15 - 30 cm	5.68±2.08	5.46±0.94	0.38±0.15	25.23±7.40	0.86±0.51
	Total	**12.87±4.67**	**6.21±1.08**	**0.44±0.11**	**23.76±5.50**	**1.59±0.78**
	P value	**0.129ns**	**0.514ns**	**0.624ns**	**0.807ns**	**0.380ns**
Lokongoma Phase 2	0 - 15 cm	1.41±0.69	4.85±0.52	0.40±0.14	19.24±5.29	1.45±0.55
	15 - 30 cm	0.70±0.33	4.85±0.49	0.38±0.11	26.80±10.40	0.67±0.36
	Total	1.05±0.38	4.85±0.34	0.39±0.08	23.02±5.64	1.06±0.34
	P value	**0.379ns**	**1.000ns**	**0.913ns**	**0.535ns**	**0.272ns**
Crowther Memorial	0 - 15 cm	8.19±3.71	9.50±4.32	0.52±0.21	28.13±9.71	0.78±0.33
	15 - 30 cm	11.67±5.21	6.26±1.20	0.52±0.25	29.86±9.31	0.95±0.38
	Total	**9.93±3.07**	**7.88±2.18**	**0.52±0.16**	**29.00±6.35**	**0.86±0.24**
	P value	**0.601ns**	**0.492ns**	**1.000ns**	**0.901ns**	**0.746ns**
200 Unit	0 - 15 cm	6.80±2.50	5.35±0.81	0.36±0.13	24.61±11.63	1.42±0.44
	15 - 30 cm	1.20±0.66	5.15±0.59	0.66±0.25	27.86±7.88	0.92±0.41
	Total	**4.00±1.54**	**5.25±0.47**	**0.51±0.14**	**26.23±6.64**	**1.17±0.29**
	P value	**0.062ns**	**0.844ns**	**0.327ns**	**0.823ns**	**0.427ns**
Felele	0 - 15 cm	9.36±4.95	12.32±5.99	0.42±0.12	35.22±11.37	1.92±1.08
	15 - 30 cm	1.39±0.62	5.76±0.83	0.46±0.12	17.55±6.24	1.21±0.49
	Total	**5.38±2.70**	**9.04±3.05**	**0.44±0.08**	**26.38±6.79**	**1.57±0.57**
	P value	**0.149ns**	**0.310ns**	**0.824ns**	**0.210ns**	**0.565ns**
Control	0 - 15 cm	1.28±0.75	5.66±0.69	0.42±0.12	26.03±7.78	0.64±0.33
	15 - 30 cm	1.27±0.45	5.46±0.52	0.46±0.13	28.62±11.51	0.46±0.23
	Total	1.27±0.41	5.56±0.41	0.44±0.08	27.33±6.56	0.55±0.19
	P value	**0.986ns**	**0.821ns**	**0.826ns**	**0.857ns**	**0.659ns**

Means with the same superscript alphabet(s) along column are not significantly different (P>0.05)Means with different superscript alphabet(s) along the same column are significantly different (P<0.05)

Table 4. 26: Elemental contamination factors (CFs) of soils and Pollution Load index (PLI) of metals in different soil layers.

Location	Contamination Factor				
	Zn	Pb	Cd	Fe	Ni
Zanwangi	9.47	1.16	1.32	1.13	7.65
Lokongoma Phase I	11.19	1.12	1.00	0.87	3.78
Lokongoma Phase 2	0.92	0.87	0.89	0.84	2.52
Crowther Memorial	8.63	1.42	1.18	1.06	2.05
200 Unit	3.34	0.95	1.16	0.96	2.62
Felele	4.56	1.63	1.00	0.97	3.73
Pollution Load Index (PLI)	**1.83**	**1.39**	**1.37**	**1.34**	**1.68**

Average natural background concentration (±SD, n = 6) obtained in the study.

Table 4. 27: Enrichment Factor

Location	Enrichment Factor			
	Zn	Pb	Cd	Ni
Zanwangi	8.37	1.03	1.17	6.76
Lokongoma Phase I	12.87	1.29	1.15	4.34
Lokongoma Phase 2	1.09	1.04	1.05	3.00
Crowther Memorial	8.14	1.34	1.11	1.93
200 Unit	3.48	0.98	1.21	2.73
Felele	4.72	1.68	1.04	3.86

Table 4. 28: Geoaccumulation Factor

Location	Geo-Accumulation Index			
	Zn	**Pb**	**Cd**	**Ni**
Zanwangi	6.65	27.98	0.67	1.69
Lokongoma Phase I	6.93	27.66	0.50	1.26
Lokongoma Phase 2	2.77	25.66	0.42	1.01
Crowther Memorial	6.50	29.57	0.60	0.89
200 Unit	4.92	26.31	0.59	1.04
Felele	5.44	30.68	0.50	1.25