SPECIATION AND BIOAVAILABILITY OF SOME HEAVY METALS IN SOILS AND VEGETABLES OF IRRIGATED LANDS AROUND KWAKWACI MECHNICAL WORKSHOPS, KANO STATE.

BY

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BEING AN MSc DISSERTATION SUBMITTED TO THE DEPARTMENT OF
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LAND RESOURCES (DEVELOPMENT).

AUGUST, 2019

DECLARATION

I hereby declare that this dissertation titled "Speciation and Bioavailability of Some Heavy Metals in Soil and Vegetables in Irrigated Lands around Kwakwaci Mechanical

Workshops, Kano State Nigeria is the product of my own research undertaking under the supervision of Dr. Mansir A. Mohammed and has not been presented elsewhere for the award of a degree or certificate. All sources consulted have been duly acknowledged.

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CERTIFICATION

This to certify that this dissertation titled *"Speciation and Bioavailability of Some Heavy Metals in soils and vegetables of irrigated lands Around Kwakwaci Mechanical*

Workshops, Kano State Nigeria” and the subsequent preparation of this dissertation by Yasira Abdullahi Adam (SPS\15\MLR\00012) were carried out under my supervision

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APPROVAL PAGE

“This dissertation has been examined and approved for the award of Masters Degree (LAND RESOURCES DEVELOPMENT) ”

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Yasira Abdullahi Adam

DEDICATION

This research work is dedicated to my late parents and my life partner who believed that the best wealth and legacy bequeath to a child is knowledge. Love you all, and may Allah protect you all and grant you Aljannatul Firdausi, Amen.

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ABSTRACT

The study examined the speciation and bioavailability of some heavy metals in soil and vegetables in irrigated land around Kwakwaci mechanical workshops in Kano metropolis. Due to increase import of reconditioned motor vehicles lead to increase on automobile workshops which are unregulated and contaminated surrounding soil and water which needs to be explored. The research aimed at assessing the speciation and bioavailability of heavy metals to plant in order to determine the background and anthropogenic level of the heavy metals in the area. Free traverse soil survey method was adopted where 8 soil samples were collected from 0-15cm depth using point sampling method, the soil samples and vegetables collected were kept inside polythene bags, level appropriate and then taking to the laboratory for the analysis of heavy metals (speciation) using AAS, pH, OC, clay and CEC using standard laboratory procedures. The laboratory results were subjected to statistical analysis using Microsoft excels to carry out descriptive statistics and inferential such as ANOVA, correlation and regression at $p>0.05$. The results showed that the mean concentrations Cd (0.92), Cu (0.73), Zn (4.48), Pb (46.38), Cr (2.92) and Ni (2.24) in the soil were found below E.U Values. The mean value of Cd: 2.71 and 2.74, Cu: 0.21 and 0.46, Zn: 1.31 and 1.39, Pb: 59.02 and 146.95, Cr: 0.38 and 0.36, and Ni: 100.22 and 25.3 for Amaranths and Lettuce respectively. The results also showed that Zn have the highest mobility level (78%), while Cd have the lowest mobility (1.96%) among the heavy metals under studies, however, Ni recorded the highest bioavailability (44.65) and Cr (6.13) been the lowest among the heavy metals. The results further revealed that pH, OC, CEC and clay were positively correlated with Cd, Cu, Zn, Pb, Cr, and Ni at $p= 0.05$. It was concluded that, there is gradual accumulation of Cd, Cu, Zn, Pb, Cr, and Ni in the soil of the area but may not pose ecological risk in the area. Reduction in aerial contamination of heavy metals by segregation of the automobile waste and dispose properly, and planting crops that may store bioaccumulated heavy metals in non edible parts were recommended in the area.

CHAPTER ONE

INTRODUCTION

1.1 BACK GROUND TO THE STUDY

Soil is the upper layer of the earth on which people live and plant grow on it. Soil consist of heterogeneous medium that comprises of decomposed rock fragments, clay minerals, oxides of Iron (Fe), Alminium (Al) and Manganise (Mn), organic materials, organo-metallic complexes and soil solutions (Alloway, 1995). It plays an important role in sustaining life, as the very survival of mankind is tied to its productivity (Kabata-Pendias and Murkherjee, 2007). Thus, the live of all living things on the earth depend either directly, or indirectly on the resources provided by the soil and indeed, the quality of soils rests upon its ability to supply nutrients essentials to plant growth and provide a healthy environment to entire ecosystem (Mohammed, 2015). Apart from being a medium for plant growth, it can also transmit pollutants including potentially toxic metals into the atmosphere, biosphere and water resources (Chen *et al.,* 1997). Heavy metals in soil exist in various forms and are associated with various components (Tack and Verloo, 1995).

Heavy metals emanating from anthropogenic sources are more dangerous because of their instability and solubility leading to high bioavailability (Fernanander and Henriques, 1991). They can enter the environment in a bio available form and are capable of transforming to other species that are more toxic (Wang *et al.,* 2003). Overload of metal ions in soil environment clearly poses a significant risk to the quality of soil, plant, waters and human health (Adriano, 2001). Total metal content of soils is useful for many geochemical applications but often the speciation, mobility and bioavailability of these metals is more of an interest agriculturally in terms of what is biologically extractable (Cottennie *et al.,* 1980). Speciation is defined as the identification and quantification of the different, defined species, forms, or phases in which an element occurs (Tack *et al.,* 1995). Thus, the chemical form is of great significance in the potential bioavailability and remobilization of the soil metals to other compartments such as water, plant and biota when physicochemical condition are favorable (Yusuf, 2007).

The mechanisms by which a heavy metal element changes from one form to another and the speed, at which it does so, is imperfect but improving. In general, the concentration of an element in the soil solution is believed to depend on the equilibrium between the soil solution and solid phase, with pH playing the decisive role (Lindsay, 1979). The soil's ability to immobilize heavy metals increases with rising pH and peaks under mildly alkaline conditions. The environmental and human adverse effects the heavy metal produces are connected with their availability, solubility and bio availability in soil which depend on the pH level, OC and CEC of the soil. Excessive amounts of available heavy metals in soils have been reported to produce negative effects on the ecosystem (Ghosh *et al.,* 2004; Shanker *et al.,* 2005). In humans, following exposure to high levels, heavy metal toxicity has been associated with various physiological disturbances. For example, Pb toxicity has been linked to various reproductive effects, developmental delay and mental retardation in children (WHO, 2006).

Heavy metals exist mainly in six different geochemical forms in soils as: Water soluble, Exchangeable, Carbonate bound, Fe-Mn oxide bound, Organic matter bound and Residual (Tessier *et al.,* 1979; Abollino *et al.,* 2006). The sum of the fractions with the exception of residual is termed non-residual fraction (Hickey and Kittrick, 1984).Heavy metals in the non-residual fractions are assumed to be more available than metals associated with residual fractions. The association between the heavy metals and soil components increases from water soluble to residual, thus making the water soluble and the exchangeable fractions the most soluble and mobile forms. Fractionation of heavy metals to residual and non-residual fractions in soil and smelting waste materials has been broadly documented (Sanghoon, 2006; Basta and Gradwohl, 2000; Kabala and Singh, 2001).

1.2 STATEMENT OF THE RESEARCH PROBLEM

Increased imports of reconditioned motor vehicle in Kano metropolis have led to an unprecedented mushrooming of automobile mechanical workshops in the area. Despite the toxic contaminations contained in mechanical wastes, these mechanical workshops have remained unregulated, and their effects to the surrounding soils and water bodies have not been adequately evaluated. These may accumulate in the soil in excessive quantities over a long-term use (Wufem *et al.,* 2013).

In Nigeria, soil pollution problems associated with spilling of automobile wastes has been reported (Onianwa *et al.,* 2001; Ipeaiyeda and Dawodu2008). It is commonly known that when an automobile is running, the engine oil, transmission oil and hydraulic fluid collect heavy metal debris containing some heavy metals such as Lead (Pb), Cadmium (Cd), Zinc (Zn), iron (Fe) and Cupper (Cu) due to frictional wears. The amount of frictional wear and tear, however, is expected to depend on the age and conditions of the engine and the transmission systems. Predominance of old motor vehicles and continuous engine and gear box recycling are responsible for the increased wear and tear or the concentration of heavy metals in the used oil (Ipeaiyeda and Dawodu 2008). Extensive trace metal pollution of soils within and around mechanical villages implies that water bodies (surface and groundwater) within and away from the vicinity of a mechanical village may equally be polluted with trace metals due to continuous interactions between soil and water and high dispersion rate by leaching and runoff (Virkutyte and Sillanpaa, 2006). One of the major sources of increase in heavy metal concentrations in the ecosystems in Nigeria is auto mechanic activities (Adewole and Uchegbu, 2010).

The soils of the area are mostly contaminated from domestic and mechanical activities (auto mechanical work and paint) as well as from some cottage manufacturing activities which contaminate the soil through eluviations. Mechanic wastes such as paintings and release of gasoline engine oils in to the soil are considered as sources of some heavy metals in soils. Currently, Irrigation activities are carried out around the area using water coming from Jakara stream. This stream contaminated by auto mobile workshops activities through leaching and seepage. Some of the crops grown in the area include Amaranth, Cabbage, Water Leaf, Lettuce, Moringa and Carrot.

Each of these activities generates various types of waste (gasoline, diesel, spent engine oil and paint) which are disposed of by simply dumping in nearby surrounding areas. Pollution effects of mechanic site activities in Nigeria have received limited attention even though these activities have been shown to produce harmful wastes. Therefore, there is need to continually monitor their nature, volume, direct harmful effects and current methods of disposal as well as potential impacts on the environment (Udousoro *et al.,* 2011).

Soil is the medium of plant growth, the habitat of various forms and types of living organisms and almost all living organisms on the earth depend, either directly or indirectly, on the resources provided by the soil (Brady and Weil 1999; Hall, 2008). Therefore, alteration of soil quality by contaminants may affect the capability and capacity of the soil to provide ecological services to the environment (Mohammed, 2015).

Mohammed *et al.,* (2014) evaluated the ecological risks of heavy metals in the effluent affected soils using Atomic absorption spectrometry (AAS) where ecological risks and pollution levels of heavy metals were determined using models. However, the forms in which heavy metals exist in soil were not considered. It is very important to explore the various forms in which heavy metals exist in the soil because heavy metals take part in biogeochemical cycles and are permanently fixed in the soil thus; speciation in soil is a key issue in many environmental qualities.

Some studies such as those of Mohammed (2010), Marinora (2003), and Kabir (2014) studies the concentration of heavy metals using A A S in Nigeria. The limitation with their studies is the scope because they only evaluate the heavy metals concentration without partitioning of the heavy metals into oxide form, exchangeable form and carbonate, organic and residual. However, it is important to assess the speciation of heavy metals in order to identify the background and anthropogenic form of heavy metals exists in soil. Also bioavailability and mobility of heavy metals were not considered in their study, to assess the level of bioavailability of heavy metals in plant the mobility of heavy metals have to be considered.

Some studies carried- out by Onweremadu and Doruigbo, (2007) assessed the concentration of heavy metals in soils around crude oil and municipal waste contaminated soil respectively. The heavy metal in soil varies with major activities carried-out in the area. These studies are limited in scope because the speciation of the heavy metals and how they are affected by chemical properties such as clay, pH, OC and CEC were not considered. However, the physicochemical properties of soil are very important to be considered for the understanding of the mobility and bioavailability of heavy metals in the soil. Therefore, identification and quantification of different forms of heavy metals in soils and some physicochemical properties of soils are very important in determine their bioavailability and mobility.

Katana *et al.,* (2013) assessed the speciation of Zinc and Copper in open-air automobile mechanical workshop soil in Ngara area, Nairobi so as to determine the concentration levels of Zn and Cu in the various form of soils in the area. One limitation of this study is the scope because they considered Zn and Cu while Cd, Cr, and Pb were not considered, furthermore, the mobility level of individual heavy metals in the soil were not considered.

Although an attempts was made by Wufem *et al.,* (2013) in Gombe state Nigeria where they assessed the speciation of some heavy metals in soil around a cement factory. However, the study is limited in scope because they only focused on geological and anthropogenic form of heavy metals which is not sufficient enough in determining the speciation of heavy metals in soil. There is need to consider all the five forms of heavy metal in order to determine their dominant forms and propose their background level of the heavy metal which will be use to settle the standard or threshold levels.

The distribution and forms of heavy metals in some agricultural soils were determined by Aydinal and Marinola (2003). However, the limitation of this study is that, they fail to consider the factors that affect the bioavailability and mobility of heavy metals in the soils. Despite of the large scale of mechanical activities around Kano metropolis, there was no much attempt in carrying out a research on the speciation and bioavailability of heavy metals in soil around auto mechanical sites. Even the study of Katana *et al.*, (2013) was carried out in Kenya where the geology, soil type and management differ which makes the heavy metals concentration to be differing.

The current study would generate and improve the data based on the forms of heavy metals and identify the anthropogenic and propose the background level of heavy metals in the study area. The data generated would be used for decision and policy making with regard to soil quality and management. In doing this, the study set out to seek answers to the following research questions.

1.3 RESEARCH QUESTIONS

i. What are the concentrations of heavy metals in different forms in soils of the area?

ii. What are the concentration levels of heavy metals in Amaranths and Lettuce grown in the area?

iii. What are the mobility and bioavailability levels of the selected heavy metals in the soils of the area?
iv. What are the factors affecting the bioavailability and mobility of the selected heavy metals in soils of the area?

1.4 AIM AND OBJECTIVES

The aim of this study was to evaluate the speciation and bioavailability of some selected heavy metals (Cu, Cd, Pb, Zn, Cr and Ni) in order to determine their background and anthropogenic level in the soils and vegetables grown on irrigated areas around mechanical workshops. The aim was achieved through the following objectives as to:

i. determine the concentration of heavy metals under different form in the soil of the area.
ii. determine the concentration of heavy metals in Amaranths and Lettuce grown around the area.
iii. evaluate the mobility and bioavailability level of the selected heavy metals in the soil of the area.
iv. evaluate the factors affecting the bioavailability and mobility of the selected heavy metals in the soils of the area.

1.5 SCOPE OF THE STUDY

This study was conducted along irrigated land around Kwakwaci mechanical workshops where wastewater is used for irrigation along Gidan Saadu Zungur across Normans land. The heavy metals considered are Cd, Cu, Zn, Pb, Cr, Pb, Cd, and Ni. These heavy metals were considered because mechanical activity is one of their major sources into the environment. Organic carbon, clay, pH and Cation Exchange Capacity were considered because they are the most important factors influencing bioavailability and mobility of heavy metals in soils to plants (Brady and Weill, 1999). Amaranths and lettuce are the vegetable considered in this research because they are the major vegetables cultivated in the area and they normally store heavy metals in their edible part such as leaves rather than roots or shoots. These vegetables are consumed by human beings (Mohammed, 2010).

1.6 JUSTIFICATION FOR THE RESEARCH

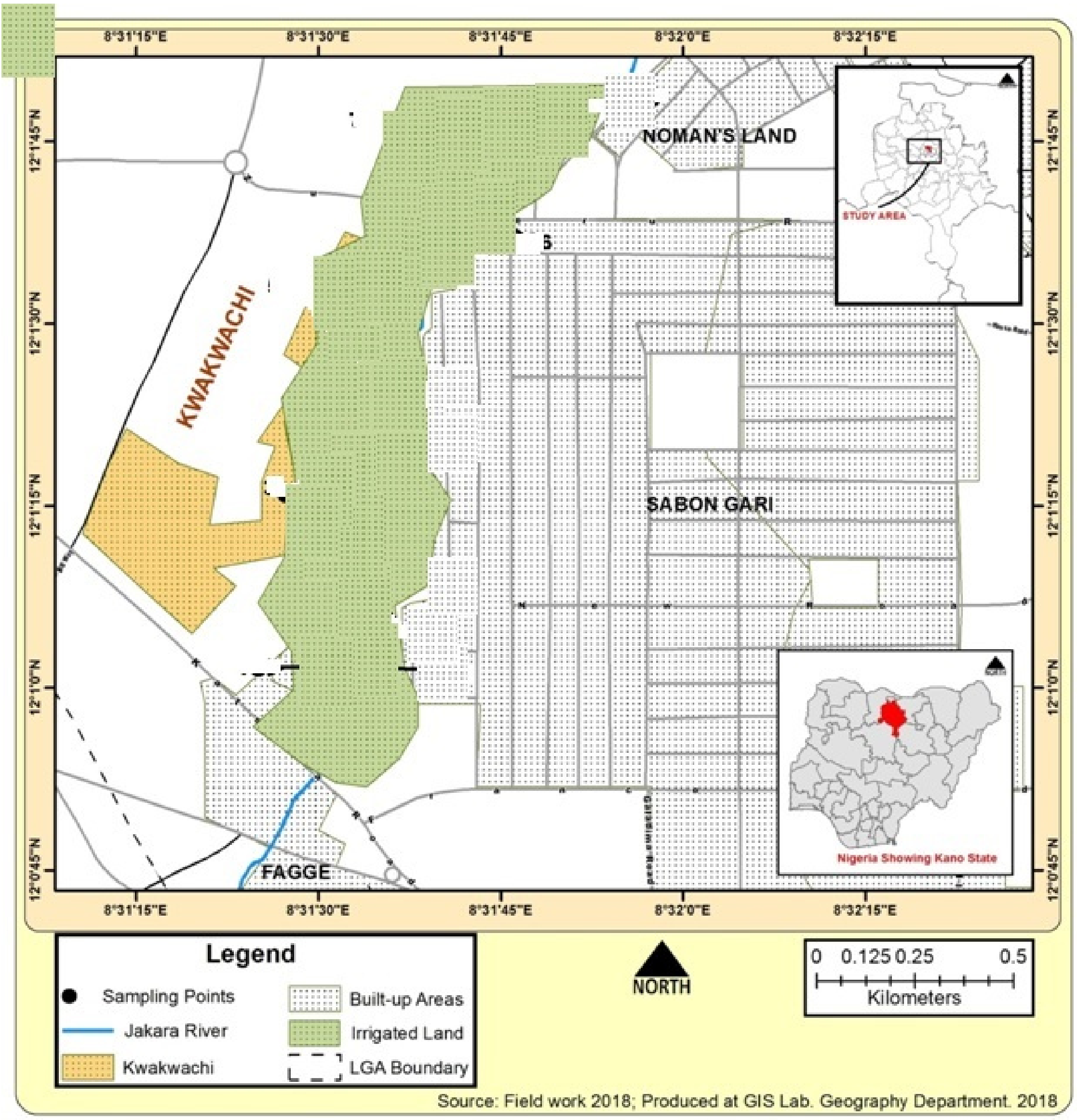
The research is worth conducting going by the level of environmental problems caused by heavy metals from automobile mechanical workshop in the study area (Mohammed, 2010). The study would generate and improve the data base on the forms of heavy metals and also identify the anthropogenic and propose the background level of heavy metals the study area. The data generated may also be used for decision and policy making with regard to soil quality and management.

1.7 THE STUDY AREA

The study area is described in terms of Location, Climate, Geology, Relief and Landforms, Soil, Vegetation, topography, Hydrology and Drainage, as well as Land use, which are presented in the following section:

1.7.1 Location and Extent of the Area

The auto mechanical workshop is located within Fagge Local Government Area in Kano state, which lies between Latitude $12^{\circ}1^{'}11^{''}$ N to $12\ ^{\circ}1^{'}23^{''}$ N and Longitudes $8^{\circ}\ 31^{'}\ 25^{''}$ E to $8^{\circ}31^{'}35^{''}$ E (Fig. 1). The study area started from Gidan Saadu Zungur to Nman’s Land and covers an area of approximately 14.2km^2 (Fig.1).



Source: Field work 2018; Produced at GIS Lab. Geography Department. 2018

Fig. Study area Showing Kwakwachi Mechanical workshop

Source: GIS Lab Geography Department, BUK (May, 2018)

1.7.2 Climate

Kano has a typical Sahelian climate with relatively wide and rapid changes. Temperature and humidity have very wide range. The mean daily Maximum and Minimum temperatures of the year are 43^0 C and 15.85^0 C respectively. The year is divided into wet and dry seasons, the dry season last from October to May. During the months of December and January the harmattan is at its peak with blowing dusts accumulated from the Sahara, and at this time temperature can fall below 15^0 C. From March to May however, the dry cold air turns hot, rising to about 32^0 C (Ahmed, 2010).

Rainfall is concentrated from June to September which is preceded by violent dust storms mainly during the month of May. The average annual rainfall is 870 mm (about 58% of this falls in July and August) and varies considerably from year to year, ranging from 635 mm to 889 mm (Ahmed, 2010).

The climate of the area is tropical wet and dry type, coded as Aw by Koppen, although climate changes are believed to have occurred in the past (Ayoade, 1983). The climate of the study area is influenced by the movement of the two air masses, dry desiccating air mass emanating from Sahara desert and the maritime air mass originating over Atlantic Ocean. These two air masses meet at Inter Tropical Convergence Zone (I.T.C.Z) and it is the seasonal movement of this front that determines the climate of the area.

1.7.2.1 *Rainfall**:*** Rainfall is a very important element because of its deficiency during the dry season in a normal year. The annual rainfall of Kano metropolis is about 800mm and there is great temporal variation in the amount of rainfall received in the area (i.e. no two consecutive years record the same amount)and average calculated for any two periods are never the same (Olofin, 1987). The rainfall in the area normally starts around June and last till around October (i.e. wet season is just 3-4 Months approximately) and dry season which has longer duration and leads to decrease in the growth of vegetation and crops to greater part of the year. The duration of wet season restrict the crops that can grow or limit the yield obtainable (Mohammed, 2004). Mostly the rain comes in heavy showers which splash away surface of the soil and help in mixing the soils with other toxic substances. The rains dissolve heavy metals from auto mechanic activities around their vicinity and dispose them through runoff and leaching into the environment.

1.7.2.2 *Temperature:* The temperature of the study area is warm to hot throughout the year even though there is a slightly cool period between November and February. The mean annual temperature is about 26^{o}C, but mean monthly values range between 21^{o}C in coolest months (December/January) and 31 ^{o}C in the hottest months (April/May) and temporal variation from one year to the other are very marginal (Olofin, 1987).

1.7.3 Geology, Relief and Landforms

Kano is characterized by four different landform types, but in general terms, about 60% of the land surface may be classified as plains. The four landforms according to Olofin, (1987) are:

Dissected hilly land, Plains with grouped hills, Alluvial channel complexes and Drift plains pediplain.

The larger section of the state to the south and North West is under taken by rocks of the basement complex type with intrusions of younger granite in the extreme southern parts. The area of the basement complex rock is separated from others by a zone recognized as the hydro-geological divide. The basement complex is pre-Cambrian in origin and consists of metamorphic and igneous rock types. They have been exposed to weathering, consequently, resulting in the formation of clay rich regolith. The younger granite is Jurassic intrusions that also form parts of the geology of Kano occurring at the southern tip of the state (Olofin, 1989). The soils largely reflect the influence of parent materials. Intensive use of the soil and addition of manure and chemical fertilizers have altered their character, profile, texture, structure and chemical characteristics. Olofin, (1987) state that the geology of an area influences the inherent chemical properties of the soil in the area.

1.7.4 Soils

The soil of Kano is said to be greatly influenced by basement complex rock that consequently resulted to mature soils occupying the plains, but immature soils are found in hill slopes, foot slopes and valley bottoms. Soil types include *hydromorphic* soils that occur in depressions on the old terrace and abandoned parts of channels. Another variety of *hydromorphic* soils-*vertisol* is common in areas which stay under flood water for about four months a year. Together, the *hydromorphic* soils are referred to as *fadama* soils (Adamu, 2014). Regosols also occupy the bed of the active channels and gully floors while *lithosols* occur on hill slopes and foot hills. *Lathosols* occupy the upland plains where they are well drained and brown to reddish brown in colour. They are deep except where they are exposed. Similar soils occur at the outer section of the high terrace but soil at the inner section are derived from regolith due to erosion and may also be ferruginous (Adamu, 2014).

The factors of soil formation in the study areas are not different from the factors elsewhere. However, the role of parent materials has great influence in the study area appears to pull a greated influence than climate. The soil in Kano metropolis is ferruginous tropical soil type whose equivalent to nitro sols according to Food and Agriculture Organization (FAO, 1991) and they are also equivalent to Ultisol and Alfisol according to United State Department of Agriculture (USDA, 1987). Variety of hydromorphic soils occur in depressions on the low terrace and abandoned parts of channels which are referred to as *fadama* soils. The soil in the metropolis is well drained and is often fine sandy to sandy loam, very permeable and good for both rainfed and irrigation farming. The soils are formed through several alternate wet - dry conditions (Oguntoyinbo 1978).

1.7.5 Hydrology and Drainage

The hydrology and drainage of the study area are influenced by rock structure, climate, relief and human activities. The climate of the study area controls the amount of water that is available both on the surface and sub-surface. The more humid the micro-climatic zone, the more water is had. Kano metropolis fall within the zone of high surface water discharge and retention which coincides with the zone of Basement Complex structure and have limited groundwater (Olofin, 1987). The unmodified stream in the study area is characterized by flash lows, storm discharges and seasonality. Surface water is not available during the dry season and ground water level falls rapidly through seepage, extraction by man and high evapotranspiration (Tanko, 2004). The quality of water is variable, but it has been found that ground water, particularly water within sub-surface channel sands, is suitable for human consumption without treatment and such water is low in total dissolved solids, usually less than 20ppm (Nabegu, 2010). However, untreated surface water is not suitable for human consumption because of the occurrences of water-borne diseases, particularly bilharzia and contaminations from domestic activities in the area (Mohammed, 2010).

The drainage of the study area is part of the inland drainage system of the Chad Basin and it is influenced by the rock structure, climate and human activities. The study area drains northeastwards to Lake Chad and the headstreams rise from southeast, south, southwest and west. Two major type of surface drainage were identified in the study area such as through-flow which drain southeast, south and southwest section of the area and disappearing flows which rise and flow freely over the Basement Complex section and lose their channels at short distance east of the hydrological divide into the unconsolidated sediments of the Chad formation (Olofin, 1987).

1.7.6 Vegetation

The natural vegetation of the area is Sudan savanna type within the Sudan Savannah type which is the typical vegetation type of the Kano region and is considered as farm parkland (Ahmed, 2008). The nature of the vegetation is, to a considerable extent, controlled by the climate, soil and topography which are the principled factors for agricultural potentials as well as fertility levels of the soils (Olofin, 1987). The vegetation is composed over an expanse of grassland. The trees are usually characterized by broad canopies and they are hardly taller than 20 meters. The Baobab, *(Adonsonia digitata)* is a peculiar tree which is larger than the others and is common in all landscape of the study site. There are various types of Acacia such as *Acacia seyal, nilotica, albida* and many more, occasionally forming woodlands and Neam trees *(Azadirachta indica)* are found in all the areas as part of artificial vegetation while, the dominant shrub species include *Guera senegalesis. Typhacae* grasses of various species are also found especially along stream channels (Mohammed, 2010).

1.7.7 LandUse

The major land use in the study area comprise of mechanical works, where auto mechanical take place. Irrigation activities are carried-out around the area using water coming from the Jakara stream. Dry season cultivation along the river bed, municipal household drains and low terrace depression that retain water are exploited for production of vegetables and other crops which include Amaranthus, Cabbage, Water leaf, Lettuce, Moringa and Carrot among others also, bore holes, hand dug wells, wash bore and shadeof are used to convey the available water to irrigate the farms (Lewcork, 1994).

CHAPTER TWO

CONCEPTUAL FRAMEWORK AND LITERATURE REVIEW

2.1 CONCEPTUAL FRAME WORK

Conceptual framework help in understanding problems and bringing out the hypothesis and guides to the identification of appropriate concepts for analyses. Two relevant concepts that give good reasons for identification of key points of problems are analyzed below:

2.1.1 Concept of Sustainable Development

Human beings have made a very impressive economic progress, especially during the 18th Century in creating material and luxuries of life style. This progress has been achieved at a tremendous cost to the environment. Ever increasing exploitation of natural resources coupled with environmental degradation has reached a point that now threatens the well being and future of mankind. Environmentalist and even the common man around the world are seeking answers to this question of how can we keep up industrial and economic development without depleting or degrading our natural resources? The answer to this question will explain the "concept of sustainable development" (Mohammed, 2017).

According to the concepts provided by the Department of Energy/Her Majesty's Stationary Office, (DoE/HMSO, 1994) majority of communities strive for economic development to guarantee better living standards for the present and the future generations. These communities also strive to protect and improve the environment at present and for their children - and sustainable development actually tries to combine these two tasks. In 1992 the World Bank described sustainable development with a laconic phrase as the "development that continues (World Development Report, 1992). Human greed must be controlled and human wants and needs must be restricted. We must treat our environment and resources with respect and stop their reckless exploitation of natural resources. Sustainable development emphasizes the rate of consumption/use and management of natural resources should balance. The rate at which these resources can be either substituted or replaced stressed, economic and industrial development must go on in such a way that no irreparable damage be done to the environment (Remigijus, Jolita and Bronislovas, 2009). Ghosh (2008) presents the concept of sustainable development as a geometric shape that is a triangle encompassing three main areas: economic, social, and environmental. Mahatma Gandhi's principle of "enoughness" in his saying "the earth provides enough to satisfy every person's need, but not for every person's greed" is perhaps more relevant at present time than when it was propounded (Remigijus, Jolita and Bronislovas, 2009). We have been bitten by the bug "consumerisms". We desperately want to possess all the goods and services, no matter what environmental price we have to pay for that (Remigijus, Jolita and Bronislovas, 2009).

2.1.2 Concept of Ecology and Ecosystem

Ecosystem is maintained through the cyclical processes of nature. In its naturally undisturbed state there is always equilibrium between inputs and outputs, which ensures the sustainability of the total environment. The balance in the input-output equation is achieved through such processes as diffusion, transmission, migration, decomposition, evaporation, weathering, succession, leaching and changes occurring in the three states of matter which are Solid, Liquid and Gaseous forms (Tanko, 2004). The balance leading to sustainability is only achieved when these processes are not disturbed or altered. However, where the natural state is disturbed, altered or modified by man's activities in the physical environment, the equilibrium is lost and attendant consequences set in. Few human activities pose such enormous threat to the natural equilibrium of the environment as industrialization does. The reason is because industrial development, especially in the developing countries, hardly considers the nature of the interactions among several elements operating in the environment. With increases in the drive for industrial development, pollution rate and consequently environmental problems also escalate (Mohammed, 2017).

As a result of the rapid growth of human population and the rapid advances in technology, the speed of industrialization in terms of global coverage and technological innovation increases in a faster rate. However, when considered along with the legitimate demands of this growing population for reasonable living standards, the situation demands a balanced approach that would accommodate the human needs and at the same time, not jeopardize the natural setting of the environmental system. This awareness has led and generated the environmental movements of the 1960's and early 1970's among the academics (Axel, 2011).

These concepts reviewed are relevant in environmental protection and conservation vis-a-vis industrial development like the sustainable development concept particularly with regard to this research. The concept of sustainable development was adopted in this research because of the need to manage our resources (Soil/ Water and Land) for the future use. There is urgent need for environmental monitoring and analyses so as to ensure the sustainability of both the natural environment and human development in Kano metropolis. This research is based on the concept of sustainable development considering Kano metropolis as an area with high population growth which led to the over exploitation of natural resources without considering the environmental consequences due to high population and developmental activities such as industrialization which affect the quality of our environment.

2.2 LITERATURE REVIEW

2.2.1 Heavy Metals in Soil, Water and Sediments

Heavy metals refer to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentration. Heavy metals occur naturally in the ecosystem with large variations in concentration (Hall, 2008). Nowadays, anthropogenic sources of heavy metals i.e. pollution, have been introduced to the ecosystem. These metals are a caus1e of environmental pollution (heavy-metal pollution) from a number of sources, including lead in petrol, industrial effluents and leaching of metal ions from the soil into water bodies by acid rain (Hussein *et al.,* 2013).

Toxic metals can be present in industrial, municipal and urban runoff, and by definition they are harmful to humans and aquatic biota. Increased urbanization and industrialization have increased the levels of trace metals, especially heavy metals in waterways (Misra and Mani, 1991). There are over 50 elements that can be classified as heavy metals, but only 17 are considered to be both very toxic and relatively accessible. Mercury, Lead, Arsenic, Cadmium, Selenium, Copper, Zinc, Nickel and Chromium, however, should be given particular attention in terms of water pollution and discharge effects. Toxicity levels depend on the type of metals, its biological role, and the type of organisms that are exposed to it (Akan *et al.,* 2010).

2.2.2 Sources of Heavy Metals Contaminants in Soils

Soils may become contaminated by the accumulation of heavy metals and metalloids through emissions from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition, (Khan *et al.,* 2008) . Soils are the major sinks for heavy metals released into the environment by aforementioned anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation (Kirpichikova *et al.,* 2006) and their total concentration in soils persists for a long time after their introduction (Adriano, 2001). Changes in their chemical forms (speciation) and bioavailability are, however, possible. The presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants (Mikanova, 2006). Heavy metal contamination of soil may pose risk and hazards to human and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal), drinking of contaminated water, reduction in food quality (safety and marketability) via phytotoxity, reduction in usability for agricultural production causing food insecurity, and land tenure problems (Mclaughin *et al.,* 2000). The metals are classified as "heavy metals" if in their standard state they have a specific gravity more than 5mg/m^3 (Wild, 1996). Heavy metals get accumulated over time in soils and plants and could have a negative influence on physiological activities of plants, determining the reduction in plant growth, dry matter accumulation and yield Devkota and Schmidt, 2010).

The sources of contamination of soils are mainly from domestic waste disposal, industries, discharges from industries and finally get into rivers that are usually utilized in various ways including irrigation, exhausts of motorized machines and vehicles are also of great concerned in metropolitan, organic waste and corrosive metal waste. These metallic wastes get into difference phase as gaseous, liquid or solid forms (Tudun Wada *et al.,* 2007). The waste disposal among the anthropogenic sources in which during wet season leaches substances are washed down to the stream and also ground water, these water are use directly or indirectly for crops production which are already contaminated (Yusuf, 2001).

Heavy metals are toxic when they found in large concentration or above the threshold level. Toxic metals exert their toxicity in a number of ways including the displacement of essential metals from their normal binding sites on biological molecules, inhibition of enzymatic functioning and disruption of nucleic acid structure (Wild, 1996). Heavy metals play an important role in biological life as essential and micro-elements, yet high concentration might be a threat to human health and biological life (Chen *et al.,* 1997). Environmental and occupational exposure to heavy metals such as Cadmium, Mercury and Lead results in severe health hazards including prenatal and development defects (Abollino *et al.,* 2006). Heavy metals at elevated concentrations are known to affect soils microbial population and their associated activities, which may directly influence the soil fertility (Mohammed, 2010).

2.2.3 Effects of Heavy Metals on Soils

The contamination of soils by heavy metals is a significant problem which leads to negative influence on soil characteristics and limitation of productive and environmental functions. The soil microbial community has a fundamental role in the process of organic matter degradation and mineralization, which allows the recycling of nutrients (Castaldi *et al.,* 2004). Heavy metals affect the number, diversity and microbial activity of soil microorganisms. They can cause slow down the speed of growth and reproduction of microorganisms in the soil then prevail slower growing microorganisms with lower diversity and higher resistance to heavy metals, but decreased biological activity (Simon, 1999). Concern about heavy metals in soil derives not only for their toxicity to living organisms inhabiting soil, but also for their immobilization within different organic and inorganic colloids. In the immobilized form, they can persist for long time before being again available to living organisms including plants (Nannipieri *et al.,* 1997).

Baath, (1989) found-out that Monitoring methods characterizing microbiological and biochemical soil properties are successfully used to evaluate the intensity of the soil contamination. They are more sensitive and their reaction to soil contamination is faster in comparison with the monitoring of the chemical and physical properties of soil which are manifested after a long time (months to years). The toxicity of heavy metals for the soil micro flora depends on the pH, temperature, inorganic anions and cations, clay minerals, hydrous metal oxides, organic matter form and amount, chemical forms in which metals occurs, etc. Hence, there are differences between many studies. Some of them confirm the negative influence of heavy metals on the soil microbiology activities; others show that there is no evidence of correlation between soil microbial properties and increasing heavy metal pollution (Castaldi *et al.,* 2004).

2.2.4 Effects of Heavy Metals on Plants

Heavy metals are natural components that cannot be degraded or destroyed biologically. Life can't develop and survive without the metal ions as life is as much inorganic as organic (Simmon 1999). The elementary constituents of plant, animal and human life may be classified as major and trace elements, the latter group comprising both essential and non-essential element (including toxic elements) (Ambika *et al.,* 2016).

The heavy metals available for plant uptake are those present as soluble components in the soil solution or those solubilised by root exudates (Blaylock and Huang 2000). Plants require certain heavy metals for their growth and upkeep. Excessive amounts of these metals can become toxic to plants and the ability of plants to accumulate essential metals equally enables them to acquire other nonessential metals (Djingova and kuleff 2000). As heavy metals cannot be broken down, when concentrations within the plant exceed optimal levels, they adversely affect the plant both directly and indirectly and some of the direct toxic effects caused by high heavy metal concentration include inhibition of cytoplasmic enzymes and damage to cell structures due to high metal concentration which may lead to decrease in organic matter decomposition leading to a less fertility of soil. Enzyme activities are very much useful for plant metabolism, hampered because of their heavy metal interference with activities of soil microorganisms. These toxic effects (both direct and indirect) lead to a decrease in plant growth which finally results in the death of plant (Schaller and Diez 1991).

The effect of heavy metal toxicity on the growth and development of plants differs according to the particular heavy metal for that process. Heavy metals such as Pb, Cd, Hg, and As which do not play any beneficial role in plant growth, adverse effects have been recorded at very low concentrations of these metals in the growth medium. (Kibra, 2008) noticed significant reduction in height of rice plant growing on the soil contaminated with 1 mg Hg/Kg with reduction in tiller and panicle formation. For Cd toxicity which reduces the shoot and root growth in wheat plants when Cd as low as 5mg/L in the soil (Ahmad *et al.,* 2012). Most of the record reduction in the growth parameters of plants growing on polluted soils can be attributed to reduced photosynthetic activities, plant mineral nutrition, and reduced activity of some enzymes. (Kabata- Pendias, 2001) reported that like every living organisms, plants are often sensitive both to the deficiency and to the excess availability of some heavy metal ions as essential micronutrient, while the same at higher concentrations and even ions such as Cd, Hg as are strongly poisonous to the metabolic activities. Research has been conducted throughout the world to determine the effect of toxic heavy metal on plants (Kabir *et al*., 2009). Contamination of agricultural soil by heavy metal has become a critical environmental concern due to their potential adverse ecological effects. Such toxic elements are considered as soil pollutants due to their widespread occurrence and their acute and chronic toxic effect on plants grown of such soils (Sanghoon 2006).

2.2.5 Effects of Some Selected Heavy Metals on the Environment

Cadmium (Cd): Cadmium is one of the heavy metals found in soil and water samples. It is a by-product of the mining and smelting of lead and zinc. It is used in nickel cadmium batteries, PVC plastic and paint pigments. It can be found in soils because insecticides, fungicides sludge, and commercial fertilizers that use cadmium are used in agriculture. Inhalation accounts for 15-20% of absorption through the respiratory system; 2-7% of ingested cadmium is absorbed in the gastrointestinal system. Cadmium toxicity is generally indicated when urine levels exceed 10 μg/dl and blood levels exceed 50 μg/dl. Cadmium sulphide and selenide are commonly used as pigments in plastics (Eaton, 2005). Cadmium toxicity can affect the environment either directly or indirectly by disrupting ecological systems that exist in rivers, lake, oceans, streams, wetlands, estuaries and other ecosystems (Atakan and Ayse 2009). It is known that Cadmium input to the environment through discharge of industrials waste, surface run off and deposition of Cadmium also strongly absorbed onto sediments and soils (Rauret, 1998).

Zinc (Zn): Zinc is one of the numbers of trace elements considered essential to plant growth and the physiological function of organism. The permissible limit for zinc in portable water is 5.0ppm. At the concentrations above, 5.0ppm, Zinc can cause a bitter, astringent taste and turbidity in alkaline waters. Zinc requirements of human vary because individuals zinc in adults ranges from 2-3μg. The highest concentrations are found in the urethra tract and the prostrate (ATSDR, 1994). Zinc cannot only be a threat to cattle, but also to plant species. Plants often have a zinc uptake that their systems cannot handle, due to the accumulation of zinc in soils (Ajayi, 1990). Zinc can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms and the breakdown of organic matter may seriously slow down because of this interruption (Axel, 2011).

Copper (Cu): Copper is an essential metal for normal plant growth and development, although it is also potentially toxic. Copper (Cu) is considered as a micronutrient for plants (Kabir, *et al.,* 2009) and plays important role in Co_2 assimilation and ATP synthesis(Mohnish and Kumar 2015). Cu is also added to soils from different human activities including mining and smelting of Cu containing ores. Mining activities generate a large amount of waste rocks and tailings, which get deposited at the surface. Excess of Cu in soil plays a cytotoxic role, induces stress and causes injury to plants.

Chromium (Cr): Chromium is fairly abundant. The only important Cr ore is chromite, a mineral of the spinel group (Council Directive 1986). The ore contains chromic oxide and ferrous oxide. It can exist in a variety of oxidation states, but commonly occurs as trivalent and hexavalent. The important Cr ions are chromates and dichromate, which are easily reduced to trivalent Cr in acid solution and in the presence of organic matter (Council Directive 1986). High Cr content has been associated with infertility of some soils. Chromium is an essential nutrient that helps the body use sugar, protein and fat. Deficiency result in impaired growth and longevity, and disturbances in glucose, lipid, and protein metabolism (Castaldi *et al.,* 2004).it reduce renal failure, anemia, haemolysis and liver failure (UK Food Standards Agency, 2003).

Lead (Pb): The primary form of Pb in the natural state is the insoluble sulphate ore, galena, PbS (Bennett, 1981).lead can be found as other compounds including PbO_2, PbCO3 and $PbSO_4$.The Pb contents in soils are typically in the range 10 to 150mg/kg (Nriagu, 1984).it is generally higher in urban and industrial area compared to rural areas. Lead has many different uses. It is used to make batteries, ammunition (lead shot), metal products (solder and pipes),and devices to shield X-rays.the uses of Pb can result in sources of transfer to humans, such as from improperly disposed of industrial waste into agricultural soils, air and water.

The immobilization of lead in soil is greatest in soils of high cation exchange capacity (Bennett, 1981).lead enters the plants by root uptake from soil or by direct deposition from air. The natural Pb levels in plants, animals and humans are very low.

2.2.6 Forms of Heavy Metals in Soils

The five forms in which heavy metals exist in soils are presented below.

2.2.6.1 Exchangeable Form

This fraction involves weakly adsorbed metals retained on the solid surfaces by relatively weak electrostatic interaction and metals that can be released by ion-exchangeable processes (Tessier *et al.,* 1979). Remobilization of metals can occur in this fraction due to adsorption desorption reactions and lowering of pH (Narwal *et al.,* 1999). Exchangeable metals are measures of those trace metals which are released most readily to the environment. Corresponding metals in the exchangeable fraction represent a small fraction of the total metal content in soil, sewage sludge and sediments and can be replaced by neutral salts (Rauret, 1998). This fraction generally account for less than 2% of the total metals in soils presents. The exceptions to this are K, Ca, and Mn (Emmerson *et al.,* 2000). Exchangeable fraction is also known as non-specifically adsorbed fraction, it can be released by the action of cations such as K, Ca, and Mg or (NH_4) displacing metals weakly bond electrostatistically organic or inorganic sites (Beckett, 1989). The common reagents used for the extraction of metals in this fraction are $MgCl_2$, Sodium acetate (pH 5.4) by Acetic acid (Tessier *et al.,* 1979). Reagents used for this purpose are electrolytes in aqueous solution, such as salts of strong acids and bases or salts of weak acids and bases at pH 7. Other reagents showing similar properties have seldom been used, such as Nitrate salts (to avoid complexation that is too strong) or Calcium salts (Ca^{2+} being more effective than Mg^{2+} or NH^{4+} in removing exchangeable ions). Results obtained with these reagents give good correlation with plant uptake (Gleyzes *et al.,* 2002).

2.2.6.2 Carbonate Form

Carbonate tends to be a major adsorbent for many metals when there is reduction of Fe-Mn oxides and organic matter in the aquatic system. The most popular use reagent for the extraction of trace metals from Carbonates phases in soils and sediments is 1M Sodium acetate adjusted to pH 5.0 with acetic acid (Tessier *et al.,* 1979). The carbonate fraction is a loosely bound phase and bound to changes with environmental factors such as pH (Beck *et al.,* 2001). The time lag for the complete solubilisation of carbonates depends on some factors such as the type and amount of the carbonate in the sample, particle size of the solid (Beck *et al.,* 2001). Extraction of metals from carbonates phases enhances the leaching of metals specifically sorbed to organic and inorganic substrates (Tessier *et al.,* 1979). In general, this fraction is sensitive to pH changes, and metal release is achieved through dissolution of a fraction of the solid material at pH close to 5.0 (Gleyzes *et al.,* 2002).

2.2.6.3 Iron and Manganese Oxides Form

This is referred to as sink for heavy metals, scavenging by these secondary oxides, present as coating on mineral surfaces or as fine discrete particles. This can occur as a combination of the precipitation, adsorption, surface complex formation and ion exchange (Hall and Pelchat 1999). There is a variation accounted, 0.1M release metal mainly from amorphous manganese oxide phases with less attack on the iron oxide phase (Shuman, 1983). Extract with 0.5M gives effective attack on the iron oxide phase while still release metals from manganese oxide phase. Different reagents have been used for metal extraction in Fe-Mg oxide phases amongst are Sodium dithionate in combination with Sodium citrate and Sodium bicarbonate in a varying concentration range (Beckett, 1989). Extraction with Ascorbic acid / Ammonium oxalate reagent offers great merits over others because high purity degree is achieved and it does not attack silicates. However, the most successful reagents for evaluating the total amount of metal ion associated with these minerals contain both a reducing reagent and a liable to retain released ions in a soluble form, the efficiency of the reagent being determined by its reduction potential and its ability to attack the different crystalline forms of Fe and Mn oxide hydroxides. Hydroxylamine, oxalic acid and dithionite are the most commonly used reagents (Gleyzes *et al.,* 2002).

2.2.6.4 Organic Form

The bioaccumulation or complexation process being the primary source in which trace metal get associated with organic materials such as living organisms, etc. In aquatic systems, organic substances tends to have high degree of selectivity for individual ions compared to monovalents ions into organic matter being Hg > Cu > Pb > Zn > Ni > Co (Filgueiras *et al.,* 2002). In organic phase, metallic pollutant bound to this phase are assumed to stay in the soil for longer periods but may be immobilized by decomposition process (Kendall *et al.,* 2001). Under oxidizing conditions, degradation of organic matter can lead to a release of soluble trace metals bound to this component. The extracts obtained during this step are metals bound to sulphides (Marin *et al.,* 1997). The organic fraction released in the oxidisable step is considered not to be bioavailable due to the fact that it is thought to be associated with stable high molecular weight humic substances that release small amounts of metals in a slow manner (Filgueiras *et al.,* 2002). The most commonly used reagent for the extraction of metals in organic phases is hydrogen peroxide with ammonium acetate for re-adsorption or precipitation of released metals (Barber, 1995). Other reagents such as Hydrogen ferioxide Ascorbic acid or HNO_3 + HCl have been used to dissolve Sulphides with enhanced selectivity, but on the other hand, silicates are attacked to some extent (Klock *et al.,* 1986). Oxidation with Sodium hypochlorite has also been recommended, (Shuman, 1983) but fractions of organically bond metals released showed considerable variability in different soil horizons (Papp *et al.,* 1991).

2.2.6.5 Residual Form

Residual phase serve as a useful tool in the assessment of the long-term potential risk of heavy metal or toxic metals entering the biosphere. Digestion in strong acid such as nitric acid, hydrochloric acid that do not dissolve the silicate matrix have been commonly used to leach out the re-resistant metals that are bound to the sediment in the residual phase. Residual phase give an estimate of the maximum amount of elements that are potentially mobilisable with changes in environmental conditions (ISO, 1999) digestion procedure is a known well procedure with a legal backing in some European countries and had been used as a standard reference material of soil and sediments. Moreover, primary and secondary minerals containing heavy metals in the crystalline lattice constitute the bulk of this fraction (Ure *et al.,* 1995). Its destruction is achieved by digestion with strong acids, such as HF, $HClO_4$, HCl and HNO_3. The amounts of associated metals are also associated by some authors as the difference between the total concentration and the sum of the fractions of the metals extracted during the previous steps (Gleyzes *et al.,* 2002).

2.2.7 Metal Species, Mobility and Bioavailability in Soils

It is generally accepted that total metal content in soils is not a good indicator of exposure or risk to plants or humans (Marisa, 2007). Only a portion of the total quantity of pollutant present in soil is potentially available for uptake by organisms. This concept is referred to as the biological availability (or bioavailability) of a chemical (Kendall *et al.,* 2001). Peijnenburg and Jager, (2003) have defined bioavailability fraction as the fraction of the total amount of a chemical present in a specific environment compartment that, within a given time span, is either available or can be made available for uptake by (micro) organisms or plant, or by ingestion in food.

In the soil environment, the mobility and the fate of metals is regulated through their partitioning between the soils and soil solution (Likluionyuu *et al.,* 2007).in other words, metals bioavailability in soil is largely dependent on the partition of the metals between the solid and solution phase. Various species of the metals can exist in solution either as free ions or as complexes associated with organic (i.e. functional group such as carboxyl and phenolic) or organic (e.g. anion) (Marisa, 2007).

Heavy metals are metals and metalloids which are stable and have density greater than $5g/cm^3$ (Mohammed, 2010). Some of these heavy metals are essential to life in trace quantities and are described as micronutrients; vital and needed for body metabolism, to facilitate growth and proper functioning of the living organism, but when the concentrations exceed the target or permissive level in the environment, they become hazardous to human health, harmful to the ecosystem, cause damage to structures or interfere with legitimate uses of the environment (Alloway and Ayres, 1997; Patterson and Passino, 1990). Total metal content of soils is useful for many geochemical applications but often the speciation (bioavailability) of these metals is more of an interest agriculturally in terms of what is biologically extractable (Cottenie *et al,*1980). In terms of bioavailability various species of metals are more biologically available in the ecosystem (Nelson and Donkin, 1985). Bioavailability and the mobility of metals are also related to each other, the higher the concentration of mobile toxic metal in the soil column which increases the potential for plant uptake, and animal/human consumption the higher the availability (Lund, 1990).

Chemical speciation is the process of identifying and quantifying different species, forms, or phases in which an elements occurs (Tessier *et al.,* 1979). Speciation is defined as the identification and quantification of the different, defined species, forms, or phases in which an element occurs (Tack *et al.,* 1995) and is essentially a function of the mineralogy and chemistry of the soil sample examined (Tessier *et al,* 1979). Quantification is typically done using chemical solutions of varying but specific strengths and reactivity to release metals from the different fractions of the examined soil (Ramos *et al,* 1994). In terms of bioavailability, various species of metals are more biologically available in the ecosystem Nelson and Donkin, 1985). Heavy metal pollution in soil within and around automobile village, cause deterioration to plants and water bodies (surface and groundwater) in the vicinity and beyond (Behera and Reddy, 2002). The interactions between metals and solid phases of soils, soil water, and air within and above soil depend on a variety of chemical factors which consequently determine the heavy metal transport and fate (Joan and Bert, 1992). Heavy metals may have toxic and hazardous effects on human health, and ecosystem especially Cadmium and Lead (Bakirdere and Yaman, 2008). This deleterious effect may be through direct ingestion (eating of raw fruits and leaves or the use of tree barks for medical purposes), physical contact (skin) and the food chain (soil-plant-human or soil-plant-animal-human), consumption of contaminated groundwater, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems (Nor *et al.,* 2012).The non-biodegradability and tendency to bioaccumulation in the living cell, make the heavy metals more daring (Majolagbe *et al.,* 2010).

2.2.8 Factor Affecting Heavy Metals Mobility and Bioavailability

The bioavailability of metals in soils depends on their forms and concentrations in the parent material and their input through fertilizers, sewage sludge and aerial deposition (Antoniadis, 1998). It is also affected by leaching processes, adsorption and desorption from the solid phase and mineralization of the organic properties which regulate these processes. Generally, conditions resulting in less fixation of metal in soil lead to greater bioavailability to living organisms. Influential soil properties include pH, Organic matter content, Cation exchange capacity, Redox reactions and other ions (Alloway, 1995). The main factors are discussed below:

2.2.8.1 Soil pH

Soil pH is a determination of the soil solutions acidity and alkalinity. By definition, pH is the negative Logarithm (Base 10) of the Hydrogen ion concentration in a solution. Hydrogen ions are strongly attached to the surface negative charges, and they have the power to replace most cations (Alloway, 1995). Soil pH is probably the most important factor governing metals speciation, solubility from mineral surfaces, transport, and eventual bioavailability of metals in aqueous solutions (Haney *et al.,* 2001).

Evan, (1989) explained that pH has a significant effect on metals dynamics because it controls adsorption and precipitation, which are the main mechanisms of metal retention in soils.

Metal solubility tends to increase at lower pH. With the exception of Mo, Se and As, the mobility of trace elements is reduced with increasing soil pH because of the precipitation as insoluble hydroxides, carbonates and organic complexes (Silveire *et al.,* 2003). In a typical temperate environment, such as the UK, soils normally have a pH in range 4-8 (Alloway, 1995).

2.2.8.2 Organic Matter

Soil organic matter refers to the non-living organic material in the soil, which makes up by far the major portion of the total organic component (Bigham, 1996). Hence, it can be of plant, animals or microbial origin and may be relatively fresh or highly decomposed and transformed. In physical terms, organic matter improve the stability of soil aggregates resulting in better aeration of the soil and better water retention. It also contributes, in chemical terms, to the increase of the adsorption sites as it increases the solid phase of the soil (Froster, 1985). In general, the composition of soil organic matter is dominated by large molecular weight humid and humic acid compound and lower molecular weight folic acid (Ross, 1994). It tends to be highly reactive toward ionic and polar contaminants because ionisable functional groups within natural organic matter have a propensity to bind metal ions and form stable complexes (National Research Council of the National Academies, 2003). The amount of organic matter found in soil significantly influences metal bioavailability. It is considered as the most important soil constituent that retains heavy metals. Generally, fulvic-metal complexes are soluble, while humic-metal complexes are insoluble (McLaughlin *et al.,* 1995). Depending on the complexes solubility, metal-organic complex can be found either in the liquid or in the solid phase (Silveira *et al.,* 2003).

Several studies have investigated the influence of soil organic matter content on metal mobility and bioavailability. Schaecke *et al*., (1991) evaluated biosolid application rates (equivalent 82-330 tons of dry matter per hectare) incorporated in 0-25cm depth of a haplic *chernozem* site in the dry belt of Central Germany. Different doses of sewage sludge had been applied in 1982, 1983, and 1985. The aim of the investigation was to study the fate of heavy metals, (Zn, Cd, Cu, Ni, Pb and Cr) and to determine their concentration in the different soil fractions. Eleven years after the last application, metals supplied with the sludge had moved as far as 50cm in depth. Concentrations of Zn, Cd, Cu, Ni and Cr in the saturation extract of the sampled soil layers were closely correlated to concentrations of dissolved organic carbon (i.e the heavy metal displacement was partly linked to the dissolved organic carbon movement in soil. Halim *et al.,* (2003) evaluated the influence of soil amendment with an exogenous humic material on the environmental mobility and potential availability of Cd, Cu, Pb, Ni and Zn. the results showed that addition of Humic acid generally reduced the extractability of the soluble and exchangeable forms of metals. The effect was directly related to the amount of added humic acid and increased with ageing.

2.2.8.3 Cation Exchange Capacity

Cation exchangeable capacity of the soil is the sum total of the exchangeable cation that a soil can adsorb. The CEC level in soil depends on the organic matter, soil pH, soil texture and, nature and type of the clay (Hall, 1999). There are always sufficient cations held by electrostatic forces on soil particle surfaces to balance the surface negative charge known as the cation exchange capacity or CEC (Rowell, 1994). The determination of exchangeable ions in soil requires that ions on soil exchange sites be forced into solution in which they can be effectively measured. However, the measurement of CEC is complicated by the fact that it is affected by both pH and ionic strength of the soil solution, especially in highly weathered soils and other soils rich in Al and Fe oxide, hydroxide, and amorphous clays (Roberts *et al.,* 1999).

Most heavy metals exist mainly as cation in the soil solution, and their adsorption therefore depends on the density of negative charges on the surfaces of the soil colloids (Alloway, 1995). In order to maintain electro neutrality, the surface negative charge is balanced by an equal quantity of cations from the soil solution, and this cation exchange, between the balance and solution cations, is reversible (Brown, 1969 cited in Alloway, 1995). The cation from weak, electrostatic bonds with the soil surface and are easily exchanged with other similarly adsorbed cations (Evan, 1989). Soils with significant negative charge have high cation exchange capacity and low cation mobility (Kelley *et al.,* 2002). Soils with high organic matter or clay content tend to have a high CEC .Whereas sandy soils have a relatively low CEC. The CEC varied from 10mmol/kg for coarse-textured soils to 500 to 600mmol/kg for fine-textured soils containing large amounts of 2:1 layer silicate minerals and organic matter (Bohn *et al.,* 2001).

CHAPTER THREE

MATERIAL AND METHODS

3.0 INTRODUCTION

This Chapter presents the research design, nature and sources of data, data collection techniques, Laboratory procedures for the determination of heavy metals through sequential extraction and statistical analysis.

3.1 RECONNAISSANCE SURVEY

A reconnaissance survey was carried out by visiting the area to locate, familiarize and observe the activities going-on in the studying area. The possible ways by which heavy metals can contaminate the soils and subsequently pollute the vegetable of the area.

3.2 MATERIALS

The materials used in this work include soil auger and spade for collecting soil samples, pH meter for pH determination, Global Position System (GPS) for recording the coordinates of sampling point, polythene bags for storing soils samples collected, marker for labeling the samples collected, measuring tape for measuring distances and Atomic Absorption Spectrometry (AAS) were used for sequential extraction of heavy metals in the study area.

3.3 NATURE AND SOURCES OF DATA

This research depends completely on quantitative data generated from the field and laboratory analyses of some selected heavy metals (Cd, Cu, Zn, Pb, Cr and Ni), speciation and bioavailability of these heavy metals in the soil and vegetables (Amaranths and Lettuce) because they stored must of these heavy metals in there edible part . The Achieves sources were generated from careful, selection of relevant materials such as books, proceedings and Journals.

3.4 SAMPLE COLLECTION TECHNIQUES

Free traverse soil sampling method was adopted because of the morphology of the sampling area (strip shape of the area along the channel). Base map extracted from goggle earth was used. The traverse lines were drawn along the irrigated land and sampling points were established, along the traverse line at about 500m intervals (Fig. 2). Eight sampling point were established on the traverse line and in each of the sampling point established a quadrant of $10m^2$ was constructed and five soil and vegetables samples were collected from 0-15cm depth using soil auger i.e one in each corner of the quadrant and one at the center were we have a total of 40 soils and vegetables sampled. The samples collected were fine mixed and subsamples of about 1/2kg were taken. The samples collected were taken into polythene bags leveled appropriate and then taken to the laboratory for further analysis. The vegetables which are 3 weeks after planting/ age (Amaranths and Lettuce) were collected using hand freely at each quadrant established and kept in polythene bags for the laboratory analysis.

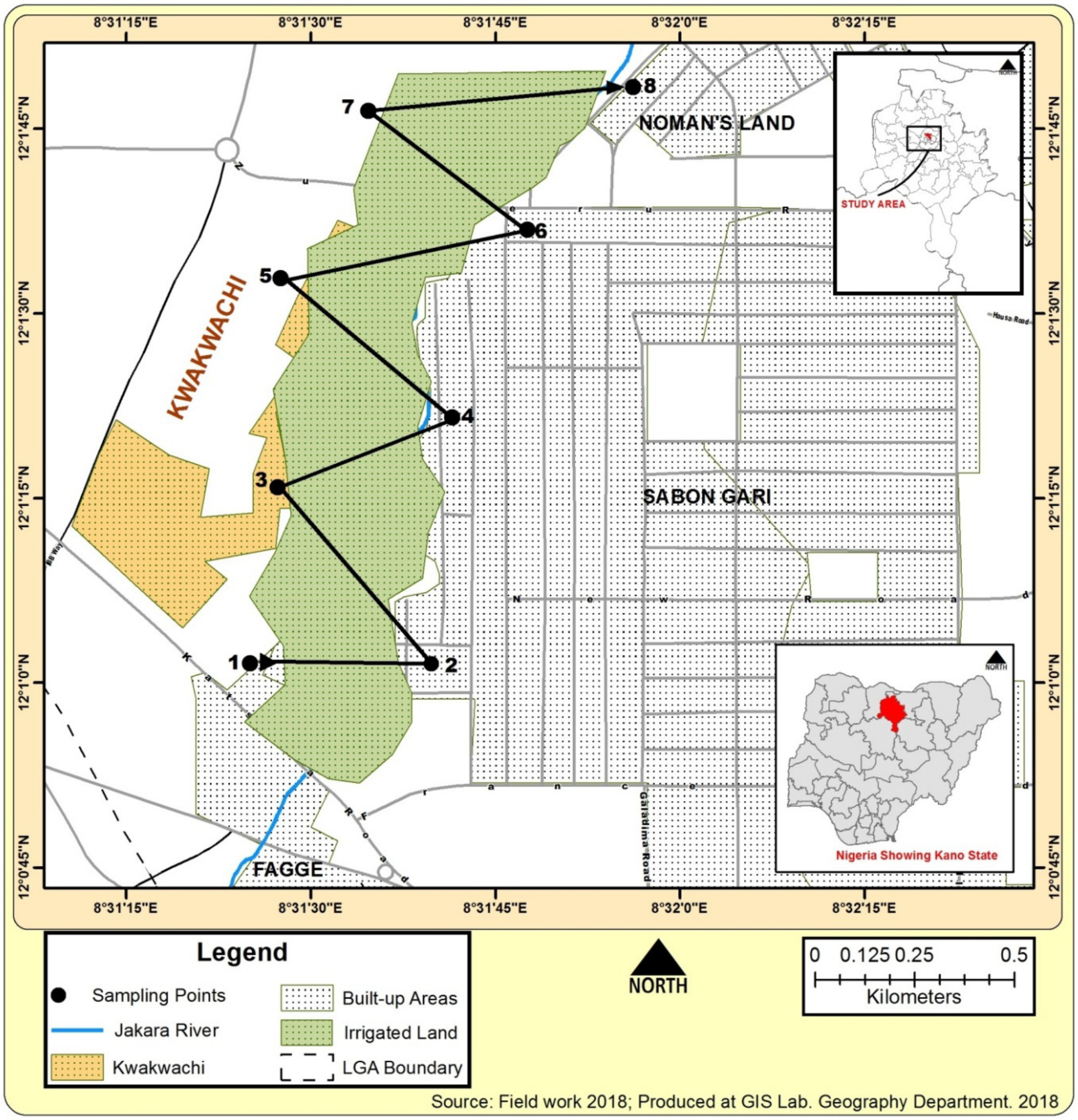


Figure 2: Study area showing soil sampling points
Source: GIS Lab Geography Department, BUK (May, 2018)

3.5 LABORATORY ANALYSIS

The soil and vegetables (Amaranths and lettuce) samples collected were analyzed in the laboratory using standard laboratory procedures as presented below.

3.5.1 Heavy Metals Sequential Extraction

The selected heavy metals (Cd, Cu, Zn, Pb, Cr and Ni) under investigation were extracted using the five forms of sequential extraction as described by Tessier *et al.,* (1979).

Exchangeable fraction. 1g of soil was extracted at room temperature for 1 hour with 16ml of magnesium chloride solution (1M $MgCl_2$) at pH of 7.0. Soil and extraction solution was thoroughly agitated throughout the extraction. This is mainly an adsorption-desorption process. Metals extracted in the exchangeable fraction include weakly adsorbed metals that can be released by ion-exchange process.

Bound to Carbonates. The metals bound to carbonate form are affected by ion exchange and changes of pH. The residues of exchangeable fraction were extracted with 16ml of 1M sodium acetate/acetic acid buffer at pH 5.0 for 5 hours at room temperature. The residual soils were used for the next extraction.

Bound to Oxides. The residues from bound to carbonates were extracted under mild reducing conditions. 13.9g of hydroxyl amine hydrochloride ($NH_20H.HCL$) was dissolved in 500ml of distilled water to prepare 0.4M $NH_2OH.HCl$ in 25% (v/v) acetic acid with agitation at 96^oC in a water bath for 6 hours. The extracted metal solutions were decanted from the residual soils which were used for the next extraction.

Bound to Organics: Trace metals may be bound by various forms of organic matter, living organisms, and coating on mineral particles through complexation or bioaccumulation. These substances may be degraded by oxidation leading to a release of soluble metals. The residues from bound to oxides were oxidized as follows: three milliliters (3mL) of 0.02M HNO_3 and 5mL of 30% (v/v) Hydrogen peroxide, which were adjusted to pH 2.0, were added to the residue from bound of oxides. The mixture was heated to 85^0 C in a water bath for 2 hours with occasional agitation and allowed to cool down. Another 3mL of 30% hydrogen peroxide, adjusted to pH 2.0 with HNO_3 was then added. The mixture were heated again at

85◦C for 3hour with occasional agitation and allowed to cool down. Then 5mL of 3.2M Ammonium acetate in 20% (v/v) Nitric acid was added, followed by dilution to a final volume of 20mL with deionized water. The extracted metal solutions were decanted from the residual soils which were used for the next extraction.

Residual or inert fraction: Residues from bound of organics were oven dried at 105^0c. Digestion were carried out with a mixture of 5mL conc. HNO_3 (HNO_3, 70% w/w), 10mL of Hydrofluoric acid (HF, 40% w/w) and 10mL of Perchloric acid ($HClO_4$, 60% w/w).

The extraction solution was aspirated with Atomic Absorption Spectrum where the reading was displaced in readout panel.

3.6 METHOD OF DATA ANALYSIS.

The results of laboratory analysis were analyzed using mean to determine the mean concentration of heavy metals and standard deviation. The mobility of the selected heavy metals in soil were evaluate using mobility factor(MF) which is defined as the ratio of an element in the mobile fraction to that in the inert fraction as shown in equation 1.

$$mf = \frac{s_1+s_2}{s_3+s_4+s_5} \text{---} (1)$$

Where S_1 is the Exchangeable fraction, S_2 is the Carbonate fraction, S_3 Oxide fraction, S_4 Organic fraction and S_5 is the Residual fraction (Kabala and Singh, 2001). The bioavailability level of the heavy metals were evaluated by bi-concentration factor (FB) which is ratio of metals concentration in plant to metals concentration in soil, calculated using equation 2.

$$bf = \frac{x}{y} \text{---} (2)$$

Where *bf* is the biconcentration factor, *x* is the concentration of selected heavy metals (Cd, Cu, Zn, Pb, Cr and Ni) in plant and *y* is the concentration of selected Heavy metals (Cd, Cu, Zn, Pb, Cr and Ni) in soil.

Analysis of variance (ANOVA) was used to determining whether there is variation or not among the selected heavy metals, (Cd, Cu, Zn, Pb, Cr and Ni). Correlation analyses was carried out to determine the nature of the relationship between selected heavy metals and factors (OC, pH and CEC) influencing bioavailability and mobility of heavy metals. Also regression analyses was used to determine the extent of the relationship that exist between the selected heavy metals and the factors that affect bioavailability and mobility of the selected heavy metals (Cd, Cu, Zn, Pb, Cr and Ni), in soil and vegetables of the area.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 INTRODUCTION

This chapter presents the Laboratory results of the sequential extraction of the selected heavy metals concentrations in vegetables (Amaranths and lettuce), mobility, bioavailability of heavy metals and factors affecting the mobility and bioavailability of the heavy metals were evaluated and presented.

4.1 FORMS OF HEAVY METALS IN SOIL SAMPLES

Five forms of heavy metal that exist in the soil of the area which consist of exchangeable, carbonate, Fe-Mn Oxide, organic and residual form, were evaluated and presented in table 1

Table 1: Form of heavy Metal in soil samples

		Heavy metals in (mg/kg)				
	Cd	Cu	Zn	Pb	Cr	Ni
Exchangeable form 7.53%						
Mean	0.04	0.05	0.24	3.52	0.21	0.41
Sd	0.01	0.02	0.35	2.30	0.12	0.38
Cv	36.32	47.75	147.66	65.45	58.04	92.26
Carbonate bond form 63.57%						
Mean	0.05	0.04	0.52	4.05	0.42	0.37
Sd	0.01	0.04	0.69	1.88	0.74	0.44
Cv	25.09	98.59	133.80	46.55	175.01	116.40
Fe-Mn oxide form 9.39%						
Mean	0.09	0.18	0.57	3.23	0.39	0.25
Sd	0.07	0.27	0.61	2.17	0.19	0.30
Cv	17.94	148.07	107.60	67.34	48.55	123.58
Organic form 8.12%						
Mean	0.37	0.10	0.56	5.14	0.18	0.30
Sd	0.05	0.07	0.76	4.16	0.27	0.37
Cv	14.31	72.63	134.88	80.99	148.89	124.20
Residual form 11.46%						
Mean	0.37	0.36	2.59	30.90	1.73	0.91
Sd	0.24	0.18	2.04	13.71	0.76	1.17
Cv	64.31	49.29	79.01	44.39	43.75	128.41
Sum of the mean	0.92	0.73	4.48	46.83	2.92	2.24
Mean pH(1.25CaCl)	6.08					

Source: Laboratory Analysis (2017)

The mean values of Pb (46.83mg/kg) is found to be higher than all the selected heavy metals under investigation with Cu (0.73mg/kg) being the lowest among the heavy metals (Table 1).

The order of heavy metals is $Pb > Zn > Cr > Ni > Cd > Cu$ in decreasing order. High mean values of Pb in the soil of the area may probably be attributing to the mechanical waste and waste combustion in the area. This is contended by Barry and Rayment (2007) who reported that waste combustion is the major source of Pb in the soil. Similarly the percentage of the fractions followed the order: Carbonate bond (63.57%) > Residual form (11.46%) > Fe-Mn oxide form (9.39%) >organically form (8.12%) >Exchangeable form (7.53%) in decreasing order. From the forms of heavy metals evaluated, it was observed that 88.54% of the heavy metals which composed of the percentage of Exchangeable (7.53%), Carbonate bond (63.57%), Fe-Mn oxide (9.39%) and Organically (8.12%) is 88.54% making the percentage concentration of heavy metals from anthropogenic forms while 11.46% is for geological compose of the soil which form the background level of heavy metals in the soil of the area.

The concentration of heavy metals in the area were evaluated by summing each individual heavy metals in all the five forms to form the concentration of each individual heavy metals in the soil of the area as presented in Figure 3.

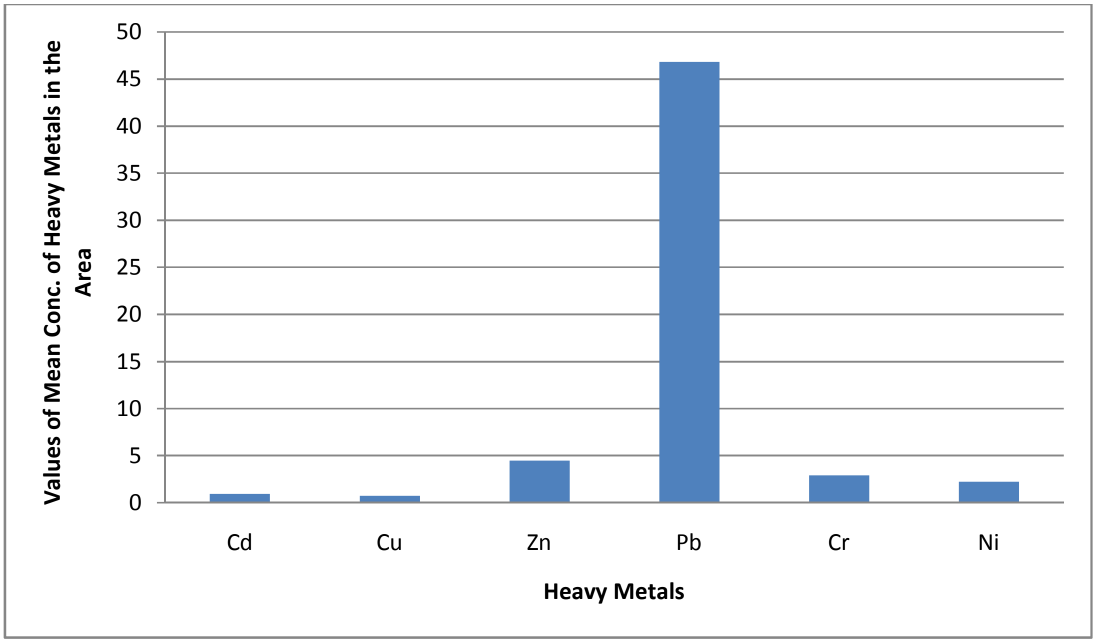


Fig. 3: Mean Concentration of Heavy Metals in soil of the Area

Source: Laboratory Analyses 2017

The mean concentration of heavy metals in (Figure 3) shows that Pb is found to be high in the study area than the other heavy metals under investigation while, Cu is found to have low mean value in the area. These may be attributed to the waste combustion in the area.

In exchangeable forms (figure 4) show that Pb (3.52mg/kg) is found to be high followed by Ni (0.41mg/kg), which shows that Pb has high concentration in exchangeable form than Cd (0.04mg/mg), Cu (0.05mg/kg), Zn (0.24mg/mg), Cr (0.21mg/kg) and Ni (0.41mg/kg). This implies that Pb can easily be absorb and exchanged with cation present in the soil colloid and then absorb by plant grown in the area. In exchangeable forms the mean value of heavy metals followed the order: $Pb(3.52) > Ni(0.41) > Zn(0.24) > Cr(0.21) > Cu(0.05) > Cd(0.04)$.

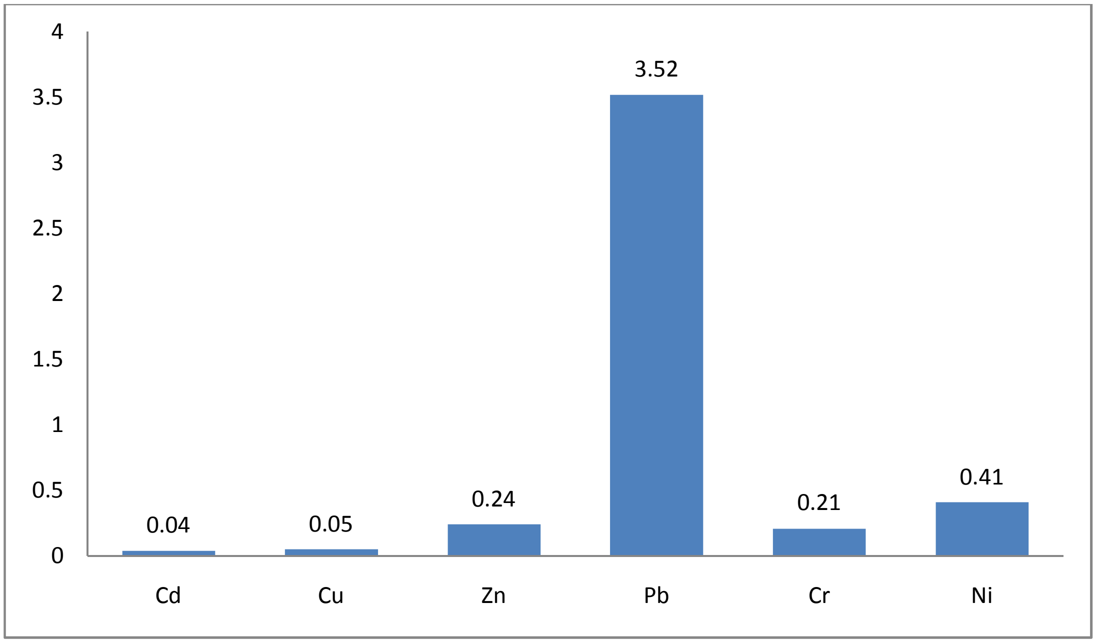


Fig. 4: Mean Concentration of Heavy Metals in Exchangeable Form

Source: Laboratory Analysis 2017

The carbonate bond forms of heavy metals in (Figure 5) shows that, Cu (0.04mg/kg) has the lowest concentration, while Pb (4.05mg/kg) recorded highest mean values. The concentration level of heavy metals for the entire fraction followed order as: $Pb > Zn > Cr > Ni > Cd > Cu$. High concentrations of Pb in carbonate form indicate that Pb is highly bioavailable to the soil microbes and plant in the area. This is contended by Katana *et al.,* (2013) that heavy metals bond to carbonate is naturally available to soil microbes and plant. Carbonate bond heavy metals have the highest percentage (63.51%) among the five forms of heavy metals. High percentage of heavy metals in carbonate form indicates that, 63.51% of the concentration of the selected heavy metals is available to be use by soil microbes and plant grown in the area. This may lead to high concentration of heavy metals in vegetation of the area which may consequently cause ecological risks to the consumers.

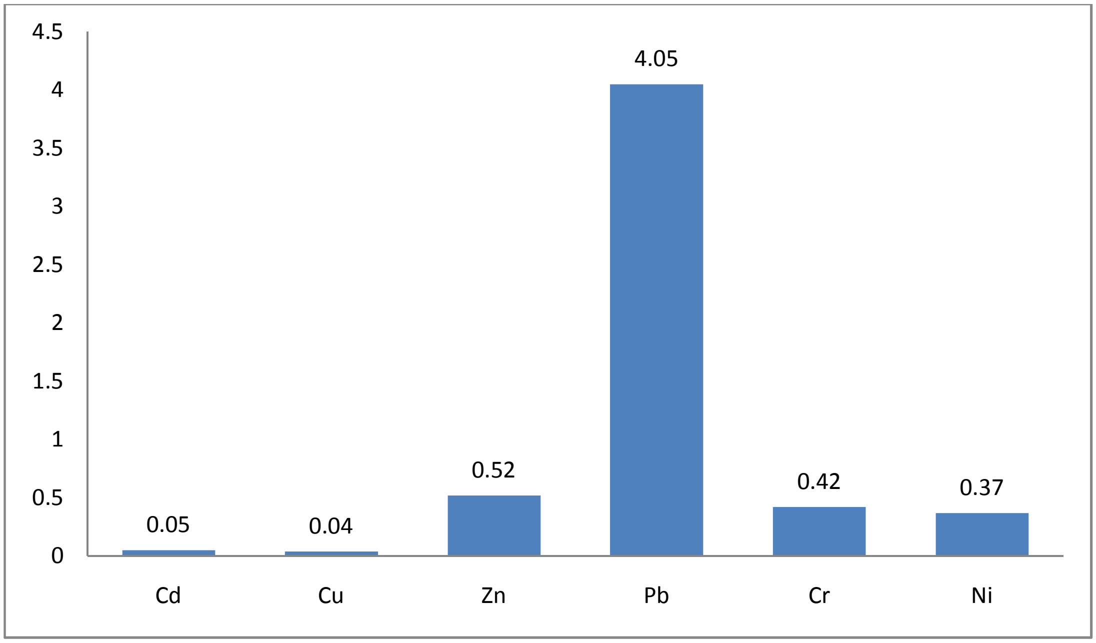


Fig. 5: Mean Concentration of Heavy Metals in Carbonate Bond Form

Source: Laboratory Analysis 2017

The oxide form (Figure 6) shows that, Pb (3.23mg/kg) has the highest concentration with low values in Cd (0.09mg/kg). This form has 9.39% among the form of heavy metals. The Pb in oxide form has been reported as the major heavy metals under reducible condition. High Pb concentration in oxide form can be indicating the high anthropogenic source of Pb in the area. This is supported by Surthland *et al.,* (2000) who reported that high proportion of heavy metals in oxide form is an indication of anthropogenic pollution. The concentration level of heavy metals in oxide form followed the order as: $Pb > Zn > Cr > Ni > Cu > Cd.$ High concentration of Pb in oxide form also implies that Pb can easily be released and then mobilized in the ecosystem. This is supported by Katana *et al.,* (2013) who explained that high concentration of heavy metals in oxide form implies that the heavy metals can easily be released into the ecosystem particularly under oxidation condition which determine its mobility rate.

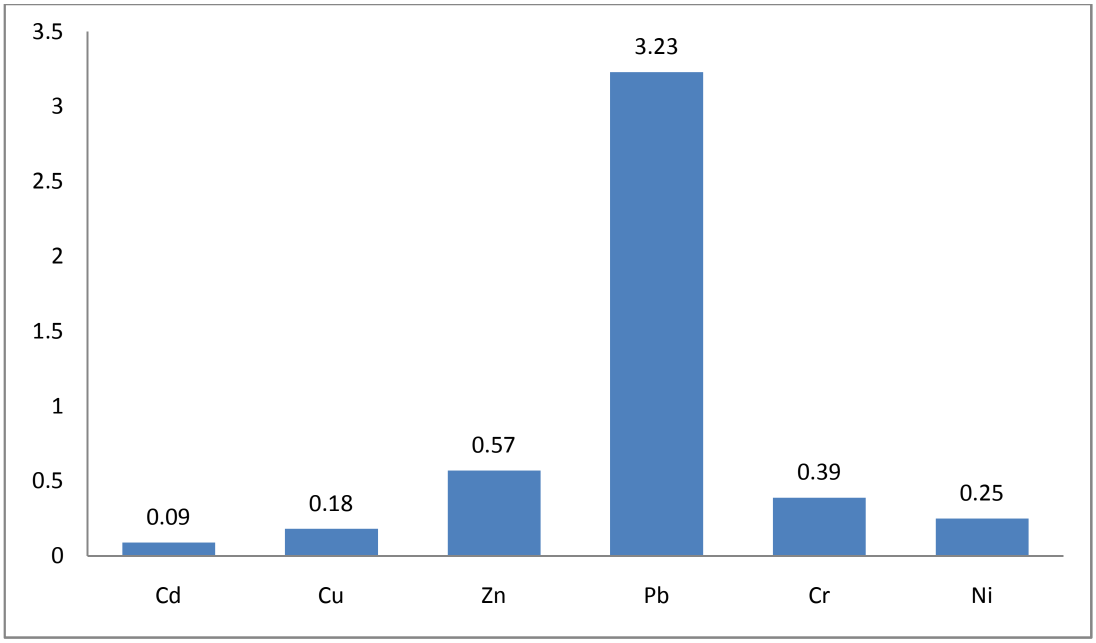


Fig. 6: Mean Concentration of Heavy Metals in Oxide Form

Source: Laboratory Analysis 2017

The organic bond (Figure7) shows that, Pb (5.14mg/kg) recorded the highest mean valued with Cu (0.10mg/kg) having low mean value and the concentration level of heavy metals under organic form followed the order as: $Pb > Zn > Cd > Ni > Cr > Cu.$ the Organic bond has 8.12% among the form of heavy metals in the soil.

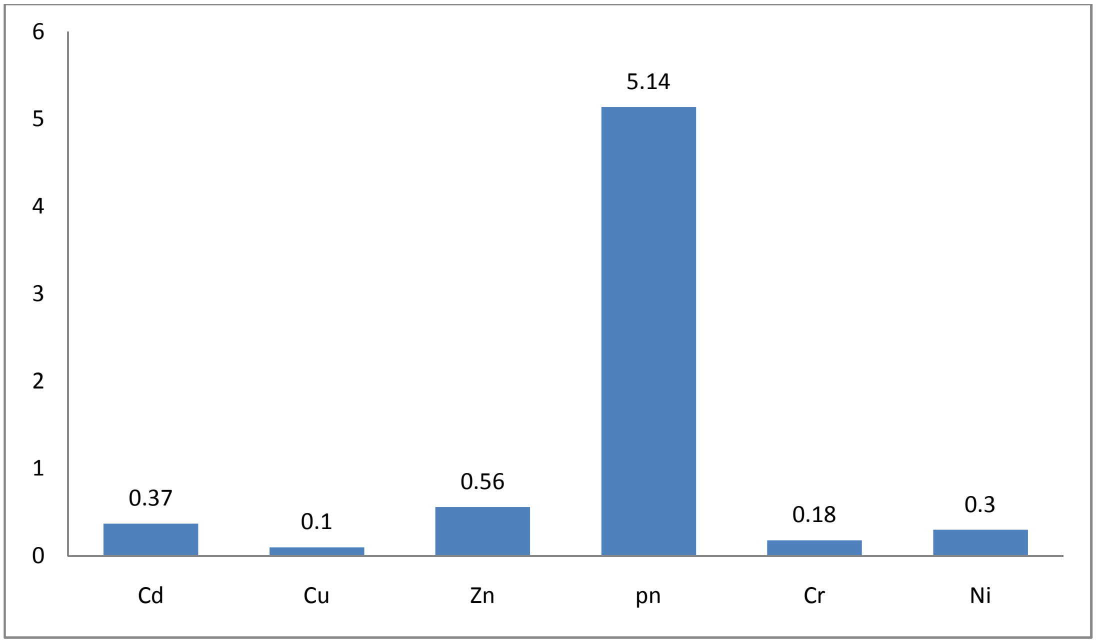


Fig. 7: The Mean Concentration of Heavy Metals in Organic Form
Source: Laboratory Analysis 2017

The residual form (figure 8) shows that Cu (0.36) has the lowest mean value, with Pb (30.90) having the highest concentration level. This implies that all the selected heavy metals level under residual forms was inert or non mobile which are not available to plant and soil microbes. This residual form is the background level of heavy metals which can be used to set as standed. This was explained by Ogundiran and Osinbajo, (2009) that concentration levels of heavy metals in residual form are not easily released into the environment because are firmly bonded with the crystal structure of the soil mineral, hence, they have low mobility. The residual forms also have 11.46% among the form of heavy metals in the area which is the second highest among the forms of the selected heavy metals.

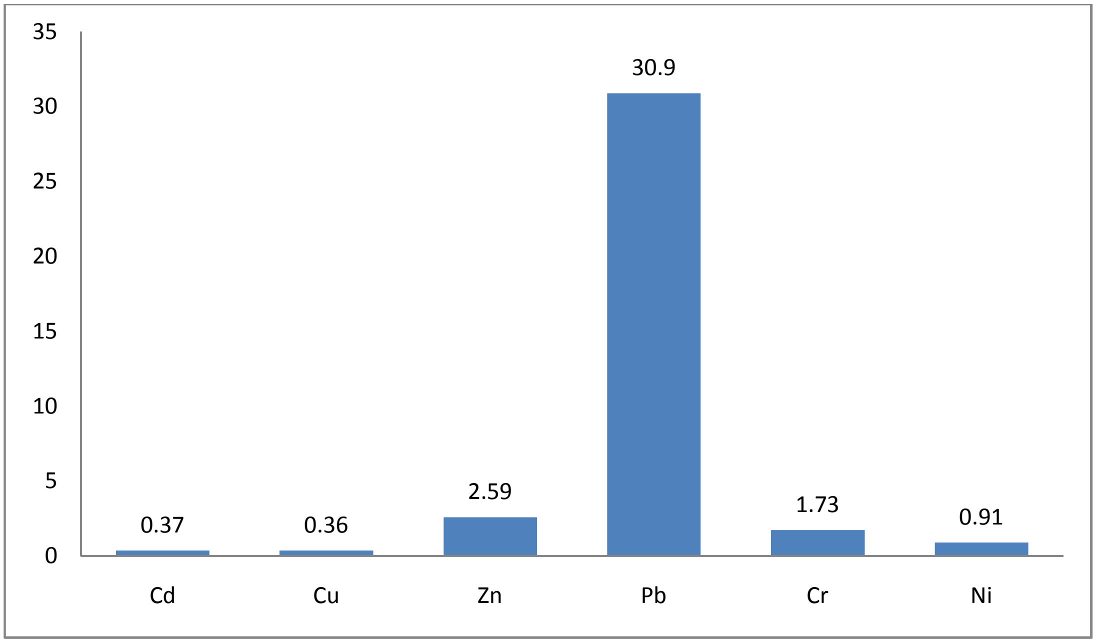


Fig 8: Mean Concentration of Heavy Metals in Residual Form
Source: Laboratory Analysis 2017

The residual form is the form of the selected heavy metals derived mostly from the geological or parent material of the soil and could be used as background level i.e. any additional of values of heavy metals may considered as anthropogenic in origin. The residual value can be considered as background level of heavy metals in the soil of irrigated land along Kwakwaci mechanical workshop.

4.2. COMPARISON OF HEAVY METALS WITH E.U VALUES

The mean values of the selected heavy metals were evaluated and then compared with E.U value as presented in Table 2

Result shows that, all the selected heavy metals in soil of the study area were found to be lower than the E.U values, (Table 2) this indicates that, the level of the heavy metals is not within the level that may pose an ecological hazard in the area. Because all the values obtained are below the E.U. Values. The result obtained in this research is in line with the result obtained by Mohammed (2010) who discovered that Cd, Pb, Cu, Mo, and Zn was found to be lower than E.U value. Despite the low mean values of all the heavy metals compared to E.U values these heavy metals (Cd, Cu, Zn, Pb, Cr and Ni) may cause ecological risk by their gradual accumulation and bioavailability in the soil of the area.

Table: 2 Comparison of Heavy Metal of the Area with EU Values

Heavy Metals	Mean Values (mg/kg)	EU Values
Cd	0.92	3
Cu	0.73	140
Zn	0.280	300
Pb	46.84	400
Cr	2.92	180
Ni	2.24	75

Source: Field (2017) and Ferguson, (1990)

Analysis of variance was carried out to determine whether there is significant difference among the heavy metals under investigation (Table 3)

Table 3: Analysis of variance of heavy metals in the area

ANOVA

Sources	*SS*	*Df*	*MS*	*F*	*P value*	*F crit*	*RMSSE*	*Omega Sq*
Between Groups	531.4308	5	106.2862	7.598612	3.7E-05	2.437693	0.97459	0.407357
Within Groups	587.4782	42	13.98758					
Total	1118.909	47	23.80658					

Source: Field and Analysis 2017

Table 3: shows that, there is significant difference in the mean values of the heavy metals in the area with P-value (3.7E-05) which is less than (0.05) (Table 3).This show that each heavy metal has different values in the soil of the area which is probably due to the nature of the metals and their concentration in the pollutants, this is also because some heavy metals are found abundantly in nature, while some area are as well as their amount present in the pollutant.

4.3. CONCENTRATION OF HEAVY METALS IN VEGETABLE SAMPLES

The mean concentration of heavy metals in Amaranth and Lettuce were evaluated in Table 4.

The mean value of Ni (100.02mg/kg) in Amaranths was found to be higher than all the selected heavy metals under investigation with Cu (0.21mg/kg) being the lowest among the heavy metals (Table 4). The order of heavy metals follow as: $Ni > Pb > Cd > Zn > Cr > Cu$. The mean value of heavy metals in the lettuce, Pb (146.95mg/kg) is found to be higher than the remaining heavy metals under investigation, where as Cr (0.36mg/kg) has the lowest mean value among the other (Tableb 4). The order of heavy metals follows as: Pb >Ni>Cd>Zn>Cu>Cr.

Table 4. Mean concentration of heavy metals in Vegetable samples

Heavy Metals	Amaranths(mg/kg)	Lettuce(mg/kg)
Cd	2.71	2.74
Cu	0.21	0.46
Zn	1.31	1.89
Pb	59.02	146.95
Cr	0.38	0.36
Ni	100.02	25.3

Source: Field and Laboratory Analysis 2017

High mean values of Ni (100.02mg/kg) in Amaranths and Pb (146.95mg/kg) in Lettuce indicates that these vegetables have high bioavailability of these heavy metals (Ni and Pb for Amaranths and Lettuce respectively). This implies that the consumers of these vegetable may likely be at risk of the Ni and Pb hazard due to their bioavailability levels. Taken up by plants, heavy metals may enter the food chain in significant amounts. Hence, people could be at risk of adverse health effect from consuming vegetables grown in soils containing elevated metals concentrations. For instance, it is estimated that approximately half of human Pb intake is through food, with around half originating from plants (Nasreddine and Parent-Massin, 2002). According to the Environmental Protection Agency (EPA), Pb is the most common heavy metal contaminant in the environment (Watanabe, 1997) and may be toxic to organisms even when absorbed in small amounts. Cadmium and Lead are the elements of most concern because of their potential for toxicity or accumulation in plants such as (Lettuce and cabbage) and animals (Wolnik *et al.,* 1983). Although metals such as Zn and Cu are essential trace elements for plants and animals, they can also be dangerous at high exposure levels. For example, poisoning incident with symptoms of gastrointestinal distress, nausea and diarrhea have been reported after a single or short-term exposure to concentrations of Zn in water and beverages of 1000-2500mg/L (WHO, 2001). At high doses of certain metal compounds, of the order of several grams, chronic toxicity as well as fatality may occur.

4.4 MOBILITY AND BIOAVAILABILITY LEVELS OF HEAVY METALS IN SOIL SAMPLES

The bioavailability and mobility of the of heavy metals from the soil to the vegetables were evaluated using Equations (1) and (2) as described by Kabala and Singh, (2001).

4.4.1 Mobility of the selected heavy metals

The mobility level of heavy metals shows that, Zn (4.42mg/kg) has the highest mobility level, while Cd; (0.11mg/kg) recorded the lower mobility level. This implies that Zn have the highest potential of been mobile and be available to plants and soil microbes in the soil, Zn can also be dangerous at high exposure levels. This is supported by Ogundiran and Osibanjo, (2008) who explained that the potential capacity and ability of heavy metals to be mobilized in the soil and to be available for soil microbes and crops grown in the soil is associated with the high level of mobility factors. The mobility factor of the heavy metals in the area followed the order as:$Zn > Ni > Cr > Cu > Pb > Cd$.

Table 5: Mobility Level of Heavy Metals in soil samples (mg/kg)

Heavy Metals	Mobility Level	Mobility Level in%
Cd	0.11	1.96
Cu	0.14	2.5
Zn	4.42	78.78
Pb	0.12	2.14
Cr	0.29	5.17
Ni	0.53	9.45

Source: Field and Laboratory Analysis 2017

The high mobility factor of Zn indicates that, Zn originated from anthropogenic sources which can be mobile rather than inert form. This is supported by Councils Directive (1986) and Chao, (1984) who explained that heavy metal with high mobility factor is an indication of an anthropogenic origin. This was contended by Mohammed (2010), who further explained that tine wear, wastes and effluents, pesticides and fertilizers are the major, anthropogenic sources of Zn into the ecosystem. This coincides with the activities taking place in the studies area where the major land use of the area is auto mechanical activities , use of pesticide and fertilizer as well as high traffic volume along the Katsina road, airport road and Nman's-land all contributed to high concentration of Zn in the area.

Low mobility level of Cr (0.29mg/kg) in the soil of the area is probably attributed to the pH level (6.08) of the soil of the area because at high pH the hydrogen ion dissociate themselves so that the solubility and availability will decrease in the area because mobility increase with an increase in pH level. This is collaborated by Brady and Weil, (1999) who explained that, the availability; solubility and mobility of heavy metals depend on the pH level normally (6.5) and mobility increase with increase of pH.

However, low mobility factor of Cd, Cu and Pb indicates that these heavy metals were found in the soil in immobile form so that they are available and mobile in the soil at very low rate. This is explained by Ogundiran and Osibanjo, (2009) who reported that low mobility factor of heavy metals is associated with ion mobile nature of heavy metals.

4.4.2 Bioavailability level of heavy metals in plant sample

The bioavailability level is the total amount of metals present in a specific environment compartment within a given time span, is either available or can be available for uptake by microorganisms or plants, or by ingestion of food (Peijnenburg and Jager, 2003).

a) Bioavailability of heavy metals in Amaranthus samples

The bioavailability of Cd, Cu, Zn, Pb, Cr and Ni were evaluated using equation (2) and presented in Table.

Table 6: Mean Bioavailability level of heavy metals in Amaranthus and Soil samples

Heavy Metals	Amaranths(mg/kg)	Soil (mg/kg)	Bioavailability Factors
Cd	2.71	0.92	2.95
Cu	0.21	0.73	0.29
Zn	1.31	4.48	0.29
Pb	59.02	46.83	1.26
Cr	0.38	2.92	0.13
Ni	100.02	2.24	44.65

Source: Laboratory Analysis 2017

Table 6 shows that Ni (44.65mg/kg) has the highest mean value of bioavailability followed by Cd (2.95mg/kg) and Pb (1.26mg/kg). Whereas Zn (0.29mg/kg) and Cu (0.29mg/kg) have the same value, while Cr (0.13mg/kg) has the lowest value. This implies that Ni is more available or can be available for uptake by soil microbes and plant and high level of Ni in humans is associated with a variety of clinical symptoms and signs including nausea, vomiting, diarrhea and headache. The UK Food Standard Agency, (2003) state that chronic inhalation of Ni and its compounds is associated with an increased risk of lung cancer. The bioavailability of heavy metals follows the order as: Ni>Cd>Pb>Zn& Cu>Cr in decreasing order.

b) Bioavailability of heavy metals in Lettuce

The bioavailability of Cd, CU, Zn, Pb, Cr and Ni were evaluated using equation (2) and are tabulated in Table 7.

Table 7: Bioavailability level of heavy metals in Lettuce and soil samples

Heavy Metals	Lettuce (mg/kg)	Soil (mg/kg)	Bioavailability Factors
Cd	2.74	0.92	2.98
Cu	0.46	0.73	0.01
Zn	1.89	4.48	0.42
Pb	146.95	46.83	3.14
Cr	0.36	2.92	0.12
Ni	25.30	2.24	11.29

Source: Laboratory Analysis 2017

The bioavailability level of heavy metals in the lettuce samples were evaluated and presented in (Table 7) which shows that Ni, (11.29mg/kg) has the highest value, then Pb, (3.14mg/kg) and Cd, (2.98mg/kg) respectively, while Cu, (0.01mg/kg) has the lowest value. High bioavailability level of Ni implies that Ni is more available for plant and soil microbes' uptake and high availability of Ni may cause visual disturbances and headache to humans (The UK Food Standard Agency, 2003). The heavy metals follow the order as: Ni>Pb>Cd>Zn>Cr>Cu in decreasing order.

4.5 DETERMINED FACTORS AFFECTING BIOAVAILABILITY AND MOBILITY OF HEAVY METALS IN SAMPLE SOILS

The factors affecting bioavailability and mobility of heavy metals (CEC, pH, Clay and OC) were evaluated and presented in Table 8. The mean value of pH is 6.08 which is slightly acidic and is ideal for most crops. The pH value obtained in this work is within the range where the availability, solubility of soil nutrient is favored. This collaborates the work by Mohammed, (2010) who explained that pH level of 6-6.5 are the pH that influence the availability and solubility of some soil nutrients such as N, P and K.

Table 8: Mean Values of the factors affecting the bioavailability and mobility of heavy metals

Factors in the sample soils	Mean values
CEC (Cmol/kg)	15.55
pH ($CaCL_2$)	6.08
Clay (%)	8.00
OC (%)	1.07

Source: Laboratory Analyze 2017

The mean value of organic carbon content is 1.07% and is considered low based on the ranking of London, (1991). The value of organic carbon obtained in this work is lower than the mean values (3.83%) obtained by Mohammed, (2010). This shows that there is gradual decrease in Organic Carbon in the soil of the study locations which may probably be attributed to the crops mining, leaching and runoff which will result to infertility of the soil and reduction in crop yield in the study area. This is contended by Brady and Weill (1999) who found-out that the major source of OC loss from soil is leaching, crop uptake and runoff.

The mean value of CEC in the sample soil of the area is 5.55cmol/kg and the value (5.55cmol/kg) is ranked low based on the ranking of London, (1991). The low level of CEC in the soil of the area is probably due to the low OC in the soil of the area. This is supported by Tan, (2009) who explained that low CEC in soils indicates that the soil have low clay and organic colloids. The value of CEC obtained in this work is higher than values obtained by Mohammed (2010) and Adamu, (2014). This indicates that there is gradual increase in the exchangeable cation due to the pH level in the soil of the area. This is explained by Brady and Weil (1999) that cation exchange capacity of the soil increases with increase of exchangeable cation and exchangeable acidity.

4.5.1 Relationship between Heavy Metals and Factor Affecting Mobility and Bioavailability

The relationship between heavy metals and factors that affect mobility and bioavailability (pH OC and CEC) were evaluated and present in Tables 9-12.

The correlation analysis between the heavy metals and pH shows that pH was positively correlated with all the heavy metals under investigation. This implies that increase in soil pH will increase the availability and mobility of all the heavy metals under investigation because pH values influence other chemical and biological properties in the soil. This is adduced by Brady and Weil (1999) who explained that soil pH influenced the chemical and biological properties of soil and their solubility and availability depend on the pH level. It was also revealed that (Table 9) the mobility and bioavailability of Cd ($r = 0.6$) and Ni ($r = 0.53$) were strongly related with soil pH.

Table 9: Relationship Between Heavy Metals and pH

Heavy metals	R	R^2	p-values
Cd	0.596	0.355	0.118
Cu	0.03	0	0.94
Zn	0.28	0.08	0.499
Pb	0.351	0.123	0.394
Cr	0.378	0.143	0.386
Ni	0.53	0.281	0.176

Source: Laboratory Analysis 2017

The coefficient of determination (r^2) show that the variation in bioavailability and mobility of heavy metals in the study area were explained by 36.2%, 0%, 8.2%, 12.53%, 14.8% and 28.22% for Cd, Cu, Zn, Pb, Cr, and Ni respectively by heavy metal leaving the remaining percentage to explain by other factors as shown on Appendix I. This indicates that Cd (r^2=0.35) and Ni (r^2= 0.28) are the heavy metals with high effect on bioavailability and mobility than Cu, Zn, Pb and Cr in the soil of the area.

The correlation analysis between heavy metals and organic carbon content (Table 10) shows that organic carbon was positively correlated with all the heavy metals. Also there is strong relationship between organic carbon and Ni, The coefficient of determination (r^2) show that the variation in bioavailability and mobility of heavy metals in the study area were explained by 0.4%, 9%, 18.3%, 23.1%, 18.5% and 30.4% for Cd, Cu, Zn, Pb, Cr, and Ni respectively leaving the remaining percentage to explain by other factors as shown on Appendix II. This indicates that Ni (r^2 = 0.304) and Pb (r^2 = 23.1%) are the heavy metals with high effect on bioavailability and mobility than Cu, Zn, Pb and Cr in the soil of the area and the OC would be considered as indicator of heavy metals in the soil of the study area.

Table 10: Relationship Between Heavy Metals and Organic carbon

Heavy metals	R	R^2	p-values
Cd	0.065	0.004	0.879
Cu	0.3	0.09	0.47
Zn	0.428	0.183	0.29
Pb	0.48	0.231	0.228
Cr	0.433	0.188	0.284
Ni	0.551	0.304	0.157

Source: Laboratory Analysis 2017

The correlation analysis between heavy metals and clay (Table 11) shows that clay was positively correlated with all the heavy metals and also there is strong correlation between Cd (0.596) and Ni (0.53) with clay. The coefficient of determination (r^2) show that the variation in bioavailability and mobility of heavy metals in the study area were explained by 36.2%, 0.10%, 8.04%, 12.53%, 14.8% and 28.62% for Cd, Cu, Zn, Pb, Cr, and Ni respectively as shown on Appendix III. This indicates that Cd (r^2 = 0.355) and Ni (r^2 = 0.28) are the heavy metals with high effect on bioavailability and mobility than Cu, Zn, Pb and Cr in the soil of the area. The coefficient of determination (r^2) values (Table11) show that the variation of Cd and Ni in the area could be explained by OC with 36.2% and 28.62% respectively leaves the remaining percentage to explain by other factor.

Table 11: Relationship Between Heavy Metals and Clay

Heavy metals	R	R^2	p-values
Cd	0.596	0.355	0.118
Cu	0.031	0.001	0.942
Zn	0.282	0.079	0.499
Pb	0.351	0.123	0.394
Cr	0.378	0.143	0.356
Ni	0.53	0.281	0.176

Source: Laboratory Analysis 2017

The correlation analysis between heavy metals (Cd, Cu, Zn, Pb, Cr and Ni) and CEC shows that CEC was positively correlated with all the heavy metals which indicate that their increase would increase the heavy metals activity as shown on Appendix IV. This implies that CEC of the soil affect the heavy metals activity. This is supported by Kertesz and Mirleau, (2004) who reported in their finding that the higher the rate of CEC, the greater the reduction in heavy metals activity. The coefficient of determination (r^2) show that the variation in bioavailability and mobility of heavy metals in the study area were explained by 1.7%, 0.18%, 0.3%, 0.14%, 0.3% and 7.770E-0.7 for Cd, Cu, Zn, Pb, Cr, and Ni respectively. This indicates that, the coefficient of determination (r^2) values (Table12) shows that Cd (0.366) accounted for 1.7%, while the rest heavy metals were found to be negligible.

Table 12: Relation Between Heavy Metals and CEC

Heavy metals	R	R^2	p-values
Cd	0.366	0.134	0.372
Cu	0.254	0.065	0.543
Zn	0.167	0.021	0.694
Pb	0.103	0.011	0.808
Cr	0.144	0.021	0.733
Ni	0.001	7.770E-07	0.998

Source: Laboratory Analysis 2017

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 SUMMARY OF THE MAJOR FINDINGS

The finding revealed that all the selected heavy metals investigated Pb has the highest mean value in all the five forms identified. Whereas Cu being the lowest among the heavy metals. The mean values of Cd, Cu, Zn, Pb, Cr and Ni in the area were found to be below the European Union regulatory values (EU Standard). The ANOVA shows that there is significant variation in the mean values of heavy metals in the study area .

The percentage of mobility factor revealed that Zn has the highest mobility, while Cd has the lowest mobility, indicating that Zn is potentially mobile and would be highly available for the soil microbes and crop to absorb since the percentage of mobility factor is above 10%. It was also observed that, the bioavailability level of the heavy metals in both Amaranths and Lettuces indicate that Ni has the highest value, while Cr has the lowest value. This implies that Ni is highly available for uptake by plants or soils microbes. The mean value of pH in the area indicate that the soil is slightly acidic which is ideal for most crops, while the Organic carbon content is low indicating that there is decrease in Organic Carbon accumulation in the soil of the area. The CEC value is found to be high which is probably attributed to the pH value of the soil. The correlation analysis between heavy metals and the factors affecting bioavailability and mobility of the heavy metals revealed that, there is positive correlation between the Cd, Cu, Zn, Pb, Cr and Ni and pH, OC, CEC and Clay, however strong correlation is discovered between Cd and Ni with pH. The variation of the bioavailability factor and mobility of the Cd, Cu, Zn, Pb, Cr and Ni, were explained by pH, OC, CEC and Clay.

5.2 CONCLUSION

The study established that there is gradual accumulation of some heavy metals that may not pose health hazard, however their gradual accumulation via ingestion may cause health related problem such as gastrointestinal cancer, liver problem lung cancer, among others. Also the mobility of Zn in the area indicates the anthropogenic origin of the heavy metal and the bioavailability show that Ni has the highest value and is more available to plants and soil microbes. This may pose ecological risk to humans. There is positive correlation between the heavy metals studies and factors that affect the bioavailability and mobility of the heavy metals which influence, their solubility and availability in the soil of the study area.

5.3 RECOMMENDATIONS

Based on the findings, the following suggestions were recommended in the area.

1. Segregating the automobile waste and then dispose properly away from irrigated land, in order to avoid further contamination from automobile waste.
2. Change of cropping pattern from growing the crops that can bioaccumulate heavy metals into their edible plant (such as carrot, onion, amaranths and lettuce) to crops that can store the bioaccumulated heavy metals into non-edible plant (shoot) such as morringa, tomatoes, pepper and pumpkin.
3. Construction of better drainage by government or workshop stakeholder to avoid releasing the workshop waste directly into the river to avoid direct contact of waste emanating from workshop to the stream channel.
4. Groundwater sources such as boreholes, tube well and hand dugs wells should be use to avoid direct application of contaminated water for irrigation, because soil can serve as filter to the groundwater source.

v. The levels determined may be used as standards for the determination of further anthropogenic level of some heavy metals contamination in the area.

REFERENCES

Abollino, O., Giacomino, A., Malandrino, M., Mentasti, E., Aceto, M. and Barberis, R. (2006). Assessment of metal availability in a contaminated soil by sequential extraction. *Plant Soil,* 265 (1–2): 243–252

Adamu, G. K. (2014). *An assessment of the characteristics and the potentials of Fadam soils in the reaches of two major streams in Kano state, Nigeria,* Unpublished Ph.D Thesis, department of Geography, Bayero University Kano, Nigeria. 6-19.

Adamu, G. K. and Aliyu, A.K. (2012). Determination of the influence of texture and organic matter on soil water holding capacity in and around Tomas irrigation scheme, Dambatta local government area Kano state, *Journal of Environmental and Earth Science,* I4 (12): 1038-7881

Adewole, M.B, and Uchegbu, L.U. (2010). Properties of Soils and plants uptake within the vicinity of selected Automobile workshops in Ile-Ife Southwestern, Nigeria. *Ethiopian J. Environ.* 7 (2): 347-358

Adriano, D. C. (2000). Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals Springer, New York, NY, USA, 2nd edition, 2003. P.

Adriano, D.C. (2001). Trace Metals in Terrestrial Environment: Biochemistry, Bioavailability and Risk of Metals. Springer-Verlag, New York. 879

Agbenin, J. O. and Latifatu, A. O. (2004), Competitive adsorption of copper and zinc by a Bt horizon of a savanna Alfisol as influenced by pH and selective removal of hydrous oxides and organic matter. *Geoderma,* 119: 85-95

Ahmad, M.J. Akthar, Z. Zahir, A. and Jamil, A. (2012). "Effect of cadmim on seed germination and seedling growth of four wheat (Triticum aestivum L) cultivars". *Pakistan journal of botany,* 44 (5): 1569-1574

Ahmed, K. (2010) 'The Kano Physical Environment'. Chapter 1 in *Perspectives on Kano,* Produced ByInuwar Jama'ar Kano. Published by Tellettes Consulting Coy Ltd. Nigeria.

Ajayi J.O (1990), The Price of Land with Distances from Rural-Urban Fringes of Kano. *Tambari Kano Journal of Education,* 5 (2): 88-98

Ajibola, V.O. and Ozigis, I. (2005) Lead, Nickel, Vanadium, Cobail, Cupper and Manganese Distribution in Intensively Cultivated Floodplain in Soil of Croos River Nigeria. *J. Chem. Soc. Nig.,* 30 (1): 62– 66

Akan, J. C., Abdurrahman, F. I., Sodipo, O. A., Ochanya, A. E. and Askira, Y. K. (2010). Heavy metals in Sediments from River Ngada*,* Maiduguri Metropolid, Borno State, Nigeria*. J. Environ Chem EcoToxicol* 2: 131-140

Alloway, B. J. (1995). *Heavy metals in soil,* Blackie Academic and Professional, an imprint of Chapman and Hall, London, 11-37

Alloway, B. J. and Ayres, D. C. (1997). *Chemical Principles of Environmental Pollution,* 2nd Ed. Blackie Academic and Professional, UK, 190-217

Ambika, A., Mohnish, P. and Kumal, N (2016). Effect of Heavy Metals on Plant: An Over view. *International Journal of Application or Innovation in Engineering and Management* (IJAIEMz13excv) 5 (3): 57-58

Antoniadis, V. (1998), *Heavy Metal Availability and mobility in sewage sludge-Treated soils,* PhD Thesis, The University of Reading, Department of Soil Science.

Areola, O., Irueghe O., Ahmed, K., Adeleke, B., and Leong, G.O (1992). *Physical and Human Geography* University press plc Ibadan.

Ataka, W. and Ayse, H. (2009) Environmental Toxicity of Cadmium and Health Effect, *Journal of Environmental Protection and Ecology* 10 (1): 84-93

ATSDR, (1994). US Department of Health and Human Service, *Toxicological profile for zinc,* US Department of Health and Human Service, Public Health Service 205: 88–608

Axel, K. (2011). How does the earth system generate and maintain thermodynamic Disequilibriu and what does it imply for the future of the planet, *physiological transaction of the royal society,* 2-8.

Aydinal, C. and Marinola, S. (2003). The Distribution and Forms of Heavy Metals in Some Agricultural Soils, *Polish Journal of Environmental Studies,* 12 (5): 629-633

Ayoade, J. A. (1983). *Introduction to Climatology of the Tropics*; Spectrum Book Limited Sunshine House, Oluyole Industrial Estate Ibadan-Nigeria.

Baath, E. (1989). Effects of heavy metals in soil on microbial processes and populations (a review). *Water, Air and Soil Pollution*, 47: 335–379

Bakirdere, S. and Yaman, M. (2008). Determination of lead, cadmium and copper in roadside soil and plants in Elizig Turkey, *Environmental Monitoring and Assessment*, (136) 401-410

Barber, S. A. (1995). Soil nutrients bioavailability; a mechanical approach, (2nd Ed.) Johgn Wiley and Sons Inc, 605, Third Avenue, New York N,C. 181-289

Basta, N. and Gradwohl, R. (2000). Estimation of Cd, Pb and Zn bioavailability in smelter-contaminated soils by a sequential extraction procedure, *J. Soil Contam.* 9 (2): 149–164

Beck, J.N., Gauthreaux, K. and Sneddon, J. (2001). Abstracts of Papers, 221st ACS National Meeting, San Diego, CA, United States, April 1 - 5. 103

Beckett, P. H. T. (1989). The use of extraction in studies on trace metals in soils, sewage sludge, a sludge-treated soils. *Advances in soil science* 9: 143-146

Behera, B., and Reddy, V. R. (2002). Environment and accountability: Impact of industrial pollution on rural communities. *Economic and Political Weekly*, 37 (3): 257-265

Bennett, J. M. (1981).*'Exposure Commitment Assessments of Environmental Pollutants Vol 1.No.1'*.London: University of London. (MARC Report Number 23).

Bigham, J. M. (1996). Methods of Soil Analysis Part 3 Chemical Methods Spark D.L., Page, A.L., Helmke, P. A., and Summer, M. E. (Ed) Wisconsin: Soil Science Society of America. Inc.

Blaylock M. J. and Huang J. W. (2000). "Phytoextraction of metals," in Phytoremediation of Toxic Metals: UsingPlants to Clean up the Environment. Wiley, New York, 193-229

Bohn, H. L., McNeal, B. L., and O`Connor, G. A. (2001). *Soil Chemistry.* 3rd Ed. New York: John Wiley and Sons.

Brady, N. C. and Weil R. R. (1999). *Nature and properties of soils,* 14th Edition, Pearson Education Inc, Upper Saddle River, New Jersey.

Brown, E. (1969). Metal Tolerance, Accumulation, and Detoxification in Plant with Emphasis on Arsenic in Terrestrial Plant, American Chemical Society. Available at: http//Iqma.ifas.edu/Publication/Cai-02.pdf (Accessed: 12 March 2007).

Castaldi S., Rutigliano F.A., Virzo De Santo A. (2004): Suitabilityof soil microbial parameters as indicators of heavy metal pollution. Water, Air and Soil Pollution. 158: 21-35

Chao, T. T. (1984).Use of partial dissolution techniques in exploration geochemistry: *journal of Geochemical Exploration* 20:101-135

Chen, T.B., Wong, W.J.C., Zhou, H.Y., Wong, M.H., (1997). Assessment of trace metal distribution and contamination in surface soil of Hong Kong. *Environmental Pollution* 96: 61-68

Chude, V. O., Malgwi, W. B., Amapu I. Y. and Ano , A. O. (2011). Manuel on soil fertility assessment, workshop paper on soil fertility interpretations and fertilizer recommendation. *African Journal of Agricultural research* 7 (47): 6204-6214

Cottenie, A., Verloo, M. and Dhaese, A. (1980). "Fractionation and determination of trace elements in plants, soils and sediments," *Pure and Applied Chemistry,* 52 (1): 45–53

Council Directive 86/278/EEC. (1986). On the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. European Commission Official Journal 181

Dawaki, M. U., Yusuf, M.A. and Adamu, G. K. (2007). Quality assessment of soils under irrigation along the Jakara Stream in Kano Metrpolis *International journal of pure and applied science,* 1 (3): 37-42

Djingova, R. and Kuleff, I. (2000). "Instrumental techniques for trace analysis," in Trace Elements: Their Distribution and Effects in the Environment, as in: Vernet, J.P. and Elsevier, E.D, London, UK

DoE/HMSO (1994). Department of Energy/Her Majesty's stationary Office, *sustainable Development-the Uk Strategy.*

Eaton, A. D. (2005). Standard Method for the Examination of Water and Wastes Water. 21st Edn. *American Public Health Association*, Washington 21:343-453

Emmerson, R.H., Birkett, J.W., Scrimshaw, M. and Lester, J.N. (2000). Solid phase partitioning of metals in managed retreat soils: field changes over the first year of tidal inundation. *Sci Total Environ* 254: 75-92

Esu, I., E. (1999). *Fundamental of padelogy,* stirling-Horden Publisher, Nigeria Limited, 42: 68-69

Evan, L. J. (1989). Chemistry of metal retention by soil, environmental science and technology 23:1046-1056

Ferguson, J. E. (1990). The Heavy Metals Element: Chemistry ,Environmental Impact and Health Effects: pergamon press: Oxford, UK

Fernandes, J. C, Henriques, FS (1991). Biochemical, physiological and structural effects of excess copper in plants. *Bot Rev* 57:247–273

Fernandez-CalviNo, D., Soler-rovira, P. Polo, A. Diaz-Ravina, M. Arias-Estevez, M. amd Plaza, C. (2010). Enzyme activities in Vineyard Soils Long-term treated with copper-based fungicides, soil biology and biochemistry, 42:2119-2127.

Filgueiras, A.V., Lavilla, I.and Bendicho, C. (2002). Chemical sequential extraction for metal Partitioning in environmental solid samples. *J of Environ Monit* 106 (4): 823-857

Kennedy, H., Sanchez, A.L., Oughton, D.H., Rowland, A.P. (1997). Use of single and Sequential chemical extractants to assess radionuclide and heavy metal availability from soils for root uptake. *Analyst* 122: 89-100

Friedlva, M. (2010). The influence of heavy metals on soil biological nd chemical properties crop science institute Czech Republic, *journal of water and soil resources,* 5 (10): 21-22

Froster, U. (1985). In: Leschber, R., Davis, R.D. and Hermite (eds), *Chemical methods for assessing bioavailable metals in sludges and soils,* 1–30. Elsevier, London.

Garcia-Magarraya, J. and Sosa, M.S. (1994). *Water, Air Soil Int. J. Envirn. Pollut*. 77: 141–149

GEM, P. and Pelchat, P. (1999).Water, Air, and Soil Pollution 112: 141–153

Ghosh, A.K., Bhattacharyya, P. and Pal, R. (2004). Effect of arsenic contamination on microbial biomass and its activities in arsenic contaminated soils of Gangetic West Bengal, *India. Environ. Int.,* 30: 491–499

Ghosh, N. (2008). The road from economic growth to sustainable development; how was it traversed, http://papers.ssrm.com/sol3/papers.cfm?abstract_id=1082686, Retrieved on 2nd March, 2015.

Giller, K.E., Rowe, E.C., de Ridder, N., van Keulen, H., (1998). Wheat yield and soil bulk-density response to some tillage systems on an Oxisol. *Soil Till. Res.* 18:37-45

Gleyzes, C. Tellier, S. M. and Astruc, M. (2002). Fractionation studies of trace elements in Contaminated soils and Sediments: a review of sequential extraction procedure. Trend *Analytical Chemistry* 21: 451-467

Hailm, M., Conte, P., Piccolo, A. (2003). Potential Availability of Heavy Metal to Phytoextraction from Contaminated soil induced by exogenous humic substance, *chemosphere*, 32:265-275

Haliru, A. H., Law, P. L. AND suhaiza, S.O. (2014). Heavy Metals Concentration Levels in Soil at Lake Geriyo irrigation site, Yola, Adamawa state, Northern Eastern Nigeria, *international journal of environmental monitori and analysis,* 2 (2): 106-111

Hall, G.E.M. P and Pelchat, P. (1999). Water, Air, and Soil Pollution 112 (104): 141–153

Hall, R. (2008). Soil essentials: managing your farms primary asset, landlink press, 150 Oxford street Collingwood, C16, 3066 Australia.

Haney, R. L., Franzluebbers, A.J., Hons, F.M., Hossner, L.R., and Zuberer, D.A. (2001). Molar concentration of K_2SO_4 and soil pH effect estimation of extractable C with chloroform fumigation extractiomn, *soil biology and biochemistry, 33: 1501-1507*

Haung,J., Haung,R. Jiao, J.J and Chen, K. (2007). "Speciation and mobility of heavy metals in mud, in coastal reclamation areas in Chenzhen, China," *Environment Geology,* 53 (1): 221–228

Hickey, M.G. and Kittrick, J.A. (1984). Chemical partitioning of cadmium, copper, nickel, and zinc in soils and sediments containing high levels of heavy metals. *J. Environ. Qual.,* (13): 372–376

Hickey, M. G. and Kittrick, J.A. (1984). Chemical partitioning of cadmium, copper, nickel and zinc in soils and sediments containing high level of heavy metals. *J. Environ. Qual.,* (13): 372-376

Horsfall, M. and Spiff, A. (2005). Equilibrium Sorption of Al, Co and Ag in Aqueous solution by fluted pumpkin (Telfairia Occidentalis Hook f). *West Biomass. Acc Chim.Slov.,* 52: 174 181

Hu, C., Chao, M., Wu, K., Chang-Chien, G., Lee, W., Chang, L., and W.S. Lee, (2003). Characterization of multiple airborne particulate metals in the surrounding of a waste incinerator in Taiwan, *Atmospheric Environment*, 37: 2845-2852

Hussein, A., Abbas, N. and Arshad, F. (2013). "Effects of diverse doses of lead (Pb) on different growth attributes of Zea mays L.," Agricultural Sciences, 4 (5): 262–265

Hussein, K.O., Olalekan, S.F., Falahan, A.A., Bhenkemusa, J.X. and Reinette, G.S. (2012). *A Review of sequential Extraction Procedures for Heavy Metals in Soil and Sediments*

Impelliteri, C. A., Allen, H.E., Yin, Y., You, S., and Saxe, J.K. (2001). Soil Properties Controlling Metal Partitioning. In “Heavy Metals Released in soils” *Environ. Toxical. Chem.* 22 (6): 1380-1386

International Standard Organization (1995). Soil Quality: Extraction of Trace Elements Solubles in Aqua Regia, ISO 11466

Ipeaiyeda, A. R. and Dawodu, M. (2008). Heavy metals Contamination of Topsoil and Dispersion in the vicinities of reclaimed auto-repair workshops in Iwo Nigeria. Bull. *Chem. Soc. Ethiopia,* 22 (3): 339-348

Iwegbue, C. M. A., Nwajei, G.E., Egauvoen, I.O and Ogala,J.E. (2007). Chemical Fraction of some Heavy Metal in Soil Profiles in the Vicinity of scarp Dumps in Warri, Nigeria. *Chemical Speciation and Bioavailability,*

Joan, E. M. and Bert, E. B. (1992). *Behaviour of Metals in soils.* Ground Water Issue United State Environmental Protection Agency EPA/540/S-92/018

Kabala, C. and Singh, B.R. (2001). Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. *J. Environ. Qual.,* (30): 485–492

Kabata-Pendias, A. (2001). “Trace Elements in Soils and Plants”, CRC Press, *Boca Raton, FL.* 9

Kabata-Pendias, A., and Murkherjee, A.B. (2007). Trace Element from Soil to Human: Springer-Verlag, Berlin. https://doi.org//10.1007/978-3-54g32714-i

Kabir, M., Iqbal, M. Z. and Shafiq, M. (2009). “Effects of lead on seedling growth of the specie populnea L., “*Advance in Environmental Biology* , 3 (2): 184-190

Kabiru, S. (2014). Assessment of Heavy Metals Concentrations in the Soil Bagega mining processing Environment, Zamfara State.

Katana, C., Jane, M., Harun, M. (2013). Speciation of Zinc and Copper in Open-Air Automobile Mechanic Workshop Soils in Area-Nairobi Kenya, *Resources and Environmental,* 3 (5): 145-154

Katare, J., Pichhode, M. and Nikhil, K. (2015). “Growth of Terminalia bellirica (gaertn) roxb on the malanjkhand copper mine overburden dump spoil material,” International Journal of Research – Granthaalayah, 3: 14-24

Kelly,M. E., Branuning, S. E., Schoof, R. A. and Ruby, M. V. (2002). Assessing Oral Bioavailability of Metal in Soil. Ohio: Battlle press.

Kendall, R.J., Anderson, T. A., Baker, R. J., Bens, C. M., Carr, J. A., Chiodo, L. A., Dickerson, R. L., Dixon, K. R., Frame, L. T., Hooper, M. J., Martin, C. F., McMurry, S. T., Patino, R., Smith, E. E., and Theodorakis, C. W. (2001). 'Ecotoxicology', in Klaassen, C.D. (Ed.) Toxicology. *The basic science of poisons.* New York:McGraw-Hill.

Kertesz, M. and Mirleau, P. (2004).The role of soil microbes in plant sulfur nutriention, *Journal of Experimental Botany,* 55 (404): 1939-1945

Khan, S., Cao, Q., Zheng, Y. M., Huang, Y. Z. and Zhu, Y. G. (2008). *"Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China,"* Environmental Pollution, 152 (3):686–692

Kibra, M.G. (2008). "Effects of mercury on some growth parameters of rice (*Oryza sativa L*)" soil and environment pollution, 27 (1): 23-28

Kirpichtchikova, T. A., Manceau, A., Spadini, L., Panfili, F. Marcus, M.A. and T.Jacquet, (2006). "Speciation and solubility of heavy metals in contaminated soil using X-ray micro fluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling," Geochimica et Cosmochimica Acta, 70 (9): 2163–2190

Klock, P.R., Czamanske, G.K., Foose, M.J. and Pesek, J. (1986). Selective chemical Dissolution of sulphides: An evaluation of six methods applicable to assaying Sulphide-bound nickel. *Chemical Geology* 54: 157-163

Kolay, A. k. (2002). *Basic concept of soil science,* 2nd ed., New age International Publisher, 48 35/24 Asari Road, Deryagnj, New Delhi, 91-137

Kotoky, P., Bora, B. J., Baruah, N. K., Baruah, J., Baruah, P. and Borah, G.C. (2003). Chemical fractionation of heavy metals in soils around oil installations, Assam. *Chem. Speciat. Bioavail.,* 15 (4):115–126

Kuo, S., Heilman, P. E. and Baker, A. S. (1983). Distribution and forms of copper, zinc, cadmium, iron, and manganese in soils near a copper smelter. *Soil Sci.,* 135 (2):101–109

Lewcork,C.P. (1994) *Study of the Use Of Urban Weste By Near Urban Farmers of Kano Metropolis* :QA 354 NRV UK.

Likluionyuu, C., Zhang, Y., Zhang, F., Zhang, S., Yin, M., Ye, H., Hou, H., Dong, H., Zhang, M., Jiang, J.,and Pei, L. (2007). Assessing pollutions of soil and plant by municipal waste dump. *Environ. Geol.,* 52 (4): 641-651

Lindsay, W.L. (1979). *Chemical Equilibrium in Soils.* John, Wiley and sons New York, NY

London, J. R. (1991). *Booker tropical soil mnual.* John Wiley and Sons Inc., New York, 465

Lund, W. (1990). Speciation Analysis-Why and How? Frensenius' *Journal of Analytical Chemistry,* 337 (5): 557-564

Majolagbe, A. O., Paramole, A. A, Majolagbe, H. O., Oyewole, O. and Sowemimo, M. O. (2010). Concentration of heavy metals in tree barks as indicator of atmospheric pollution in Oyo Town, southwest, Nigeria Achieves of applied science Research, 2 (3):170-178

Marin, B., Valladon ,M., Polve, M. and Monaco, A. (1997). Reproducibility testing of a sequential extraction scheme for the determination of trace metal speciation in a marine reference sediment by inductively coupled plasma-mass spectrometry. *Anal Chim Acta* 342: 91-112

Marisa, I (2007). Uptake of heavy metals by vegetable plants grown on contaminated soils, their bioavailability and speciation. http://nr/.northumbria.ac.uk/policies:html (Accessed: 1 August 2007).

McLaughlin, M.J.; Zarcinas, B.A; Stevens, D.P. and Cook, N. (2000). Soil Testing for Heavy Metals. Commun. *Soil Science Plant Anal*. 31: 11 – 14

Melero, S., Porras, J.C.R., Herencia, J.F. and Madejon, E. (2005). Chemical and biochemical properties in a silty loam soil under conventional and organic management, *Soil tillage and resources,* 90: 162-170

Ming, W., Genxing, P., and Ping,C. (2005). *The distribution and speciation of heavy metals in urban soils in Nanjing City:* In Urban Dimensions of Environmental Change, Science Press USA Inc., 25-33

Mohammed, M. A. (2010). *An Assessment of Heavy Metals Pollution of Soils Under Urban and Peri-Urbarn Irrigation* in Kano Metropolis Unpublished Msc, dissertation Geography Department BUK

Mohammed, M. A. (2004). *Assessment of fertility levels of different upland cultivated lands and fadama soils; a case study of Dambatta Tomas Dam*; Unpublished Bsc. Long Essay; department of Geography; BUK.

Mohammed, M.A. (2015). An Assessment of Heavy Metals Pollution of Soils under Urban and Peri – Urban Irrigation System in Kano Metropolis. *International Journal of Environmental Monitoring and Protection* 2 (1): 9-14

Mohammed, M.A. (2017). An Assessment of Heavy Metals Pollution of Soils under Urban and Peri – Urban Irrigation System in Kano Metropolis. *International Journal of Environmental Monitoring and Protection* 2 (1): 9-14

Mohammed, M.A., Yusif, M.A., Mukhtar, S. and Zubir, S.M. (2014). Ecological risk assessment of heavy metals pollution on irrigated soil along Salanta river valley Kano Nigeria Bayaro J*ournal of pure and applied sciences* (BAJOPAS) 8 (1):160-166

Mohnish, P. and Kumar, N. (2015). "Effect of Copper Mining Dust on the Soil and Vegetation in India: A Critical Review," *International Journal of Modern Sciences and Engineering Technology* (IJMSET), 2 : 73-76

Nabegu, A. B. (2010). *The Impact of Urbanization on the Morphology of Jakara Stream Channel,* unpublished Ph D. Thesis, Department of Geography, Bayero University Kano. Nigeria

Nannipieri P., Badalucco L., Landi L., and Pietramellara G. (1997): *Measurement in Assessing the Risk of Chemicals to the soil ecosystem. In: Zelikoff J.T.* (ed.): Ecotoxicology: Responses, Biomarkers and Risk Assessment. OECD Workshop. SOS Publ. Fair Haven, New York, 507–534.

Narwal, R. P., Singh, B. R. and Salbu, B. (1999). Communications in Soil Science and Plant Analysis 30: 1209-1230

Nasreddine, L. and Parent-Massin, D. (2002).'Food Contamination by Metals and Pesticides in the European Union. Should We Worry?' Toxicology Lettters, 127:29-41

National Research Council of National Academies (2003). *Bioavailability of Contaminant in Soils and Sediment: process, Tools, and Applications.* Washington D.C.: The National Academic Press.

Nelson A. and Donkin P. (1985). "Processes of bioaccumulation: the importance of chemical speciation," *Marine Pollution* Bulletin*,* 16 (4): 164–169

Nor, W. A., Zainon, N., Syakirah, A. M., Saffaatul, H. I. and Wan, A. A. (2012). Assessment of heavy metals in soil due to Human Activities in Kangar, Perlis, Malasia. *International Journal a of Civil and Environmental Engineering*, (12): 6

Nriagu, J .O.(1984).*Changing Metal Cycles and Human Health.* Berlin: Springer-Verlag, (28): 1-6

National special programme for food security and food and agricultural organization (2005). map of Nigeria showing different exchangeable potassium fertility classes for the top soil, national special programme for food security , Abuja Nigeria.

Ogundiran, M.B. and Osibanjo, O. (2008). Heavy metal concentrations in soils and accumulation in plants growing in a deserted slag dumpsite in Nigeria *Afr. J. Biotechnol.,* 7(17): 3050–3060

Ogundiran, M.B. and Osibanjo,O. (2009). Mobility and speciation of heavy metals in soils impacted by hazardous waste in Nigeria *Afr. J. Biotechnol.,* 21(2):59-69

Oguntoyinbo J.S (ed) 1978), *A Geography of Nigerian Development*, University Press plc Ibadan: Heinemen, Educational Book (Nig.)

Olofin E. A. (1987). *Some Aspect of Physical Geography of Kano Region*: Departmental of Geography Lecture Series BUK: Dabis Standard Printers 73A, Zaria Road Kano.

Olofin, E. A. (1989): "Human Responses to the Natural Environment in the Kano Environment in Kano Region". Article in *Kano and some of her Neighbours*. Edited by Barkindo, B.M. published for the Department of History, Bayero University by ABU Press Limited Zaria, Nigeria.

Onianwa, P. C., Jaiyeola, O. M. and Egekenze, R. N. (2001). Heavy metal contamination of topsoil in the vicinities of auto-repair workshops, gas stations and motor parks in a Nigerian city Toxicol. *Environ. Chem.,* 84 (1-4):33-39

Onweremadu, E. U.; Doruigbo, C. I. (2007). Assessment of Cd concentration of crude oil arable soil *Int. J. Environ. Sci. Tech.,* 4 (3): 409-412

Papp, C.S.E., Filipek, L.H and Smith, K.S. (1991). Selectivity and effectiveness of extractants used to release metals associated with organic matter. *Applied Geochemistry* 6: 349-353

Patterson, J. W. and Passino, R. (1990). Metal Speciation, Separation, and Recovery, Lewis Publishers INC. Michigan, USA.

Peijnenburg, W. J. G. M., and Jager, T. (2003). 'MonitoringApproaches to Assess bioaccessibility and Bioavailability of Metals: Matrix Issues', *Ecotoxicology and Environmental Safety,* 56: 63-77

Pichhode, M. and Nikhil, K. (2015). “Effect of copper dust on photosynthesis pigments concentrations in plants species,” *International Journal of Engineering Research and Management* (IJERM), 02: 63-66

Ramos, l., Hermandez, L.M. and Gonzalez, M.J. (1994). Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Donnal Park. *J. Environ. Qual.,* (23): 50–57

Rauret, G. (1998). Extraction procedures for the determination of heavy metals in contaminated soil and sediment. *Talanta* 46: 449-455

Reeves, R.D and Baker, A.J.M (2000). Metal –accumulating plants in Raskin I, Ensley BD (eds) *phytoremediation of toxic metals: using plants to clean up the environment.* Wiley, New York, 193-229.

Remigijus, C., Jolita, R. and Bronislovas, M. (2009). The concept of sustainable development and its uses for for sustainability scenario, Kaunas University of Technology.

Roberts, G.P., Sollins, P., Ellis, B. G. and Lajtha, K. (1999). Exchangeable ions, Ph, and Cation Exchange Capacity. In Robertson, G.P., Coleman, D.C., Beldsoe, C. S. and Sollins, P. (Ed.) New York: Oxford University Press.

Ros, U., Joergensen, R. G. and Chander, K. (2001). Effect of zinc enriched sewage sludge on microbial activities and biomass in soil, *soil, biology and biochemistry,* 33: 633-638

Ross, S. M., (1994). `Retention, Transformation of mobility of toxic metal in soils, in Ross,S. M.,(Ed) toxic metal in soil plant system. Chichester: Jonh wiley and sons.

Rowell, D. J. (1994), *Soil Science, Methods and Applications,* Longman, Essex, England, UK.,

Saldana, A., Stein, A. and Zinck, J.A. (1998). spatial variability of soil properties at different scales within three terrace of the Henares River. *catena*, 33: 139-153

Sanchez, P.A. (1979). *Properties and management of soils in the tropics,* john Willey and Sons Inc, New York

Sanghoon, L. (2006). Geochemistry and partitioning of trace metals in paddy soils affected by metal mine tailings in Korea. *Geoderma,* 135: 26–37

Sarah, P. (1999). Temporal and spatial variability of pedo-geomorphic processes as a response to changing climatic condition along a Topo-climatic transect between the Judean Mountains and the Dead Sea, Ph.D. Thesis, Bar-Ilan University, Isreal.

Sauve, S. (2003).The role of chemical speciation in bioavailability. bioavailability, toxicity and risk *Relationships in Ecosystem*: 59-82

Schaecke, W., Tanneberg, H., and Schilling, G. (1991). Plant, Element and Soil Properties Governing Uptake and Availability of Heavy Metals Derived from Sewage Sludge, Water, Air abd Soil Pollution, 57-58, 227-237

Schaller, A. and Diez, T. (1991). *"Plant specific aspects of heavy metal uptake and comparison with quality standards for food and forage crops,"* in Der Einflub von festen Abfallen¨ auf Boden,¨ Pflanzen, D. Sauerbeck and Lubben,¨ Eds., 92–125. KFA, Julich, ¨ Germany, (German).

Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M. (1993). *Environmental organic chemistry,* p. 259–261. John Wiley and Sons, Inc., New York.

Segarra, M.J.B., Prego, R., Wilson, M.J., Bacon, J. and SantosEcheandia, J.S. (2008). *Sci.Mar. ,* 72(1): 119-126

Shanker, A.K., Cervantes, C., Loza-Tavera, H. and Avudainayagam, S. (2005). Chromium toxicity in plants. *Environ. Int.,* 31(5): 739–753

Shuman, L. M. (1983). Sodium hypochlorite methods for extracting microelements associated with soil organic matter. *Soil Science Society of America Journal* 47: 656-660

Silveira, M. L. A., Alleoni, L. R. F. and Guilherme, L. R. G.(2003). Biosoilds and Heavy Metals in Soils, Scientia Agricola, 60:793-806

Simon T. (1999): The effect of increasing rates of nickel and arsenic on the growth of radish and soil microflora. Rostlinná výroba, 45: 421–430

Stumn, W. and Morgan, J.J. (1981) *Aquatic chemistry; chemical equilibra and rates in natural water,* p.1022. John Wiley and Sons Inc. New York.

Surthland, R. A., Tolosa, C.A., Tack, F. M. G and Verloo, M. Verloo, M. G.,(2000).Characterization of selected element concentration and enrichment ratios in background and anthropogenically impacted roadside area. *Archives of Environmental Contamination and Toxicology* 38: 428-438

Tack F.M.G. and Verloo, M. G. (1995). "Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review," *International Journal of Environmental Analytical Chemistry,* 59 (2): 225–238

Tahar, K. and Keltoum, B. (2011). Effect of heavy metals pollution in soil and plant in industrial areas, west Algeria, *journal of Korean chemical society ,* 55 (6): 23-40.

Tan K. H., (2009). *Environmental soil science,* 3rd edition, C.R.C Press, Francis nd Tailor Group, 6 : 93-430

Tanko, A. T. (2004). An Introduction to Water Evalution. B.Sc. Lecture Series, Department of Geography, Bayero University, Kano, Nigeria, (2003/2004 Session)

Tessier, A., Campbell, P. G. C. and Benon, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem.,* 51: 844–851

Udousoro II, Umoren IU, Asuquo EO (2010). Survey of some heavy metal concentrations in selected soils in South Eastern parts of Nigeria. *World J. Appl. Sci. Technol.* 2(2):139 - 14

UK Food Standards Agency (2003). 'Safe Upper Levels for Vitamins and Minerals', Expert Group on Vitamins and minerals. Available at: http://WWW.foodgov.uK/multimedia/pdfs/vitmin2003.pdf (Accessed: 15 January 2007).

Virkutyte, J. and Sillanpaa, M. (2006). Chemical Evaluation of Potable Water in Eastern Qinghai Province, China. Hum Health Aspects *Environ. Int.,* 32 (1):80-86

Wang, C.X., Mo, Z., Wang, H., Wang, Z. J. and Cao, Z. H. (2003).The transport, time-dependent distribution of heavy metals in paddy crops.*Chemosphere* 50: 717-723

Watanabe, M. A. (1997). 'Phytoremediation on the Brink of Commercialization', *Environmental Science and Technology,* 31: 182A-186A

Wolnik, K. A., Fricke, F. L., Capar, S.G., Braude, G. L., M. W., Satzger, R. D. and Bonnin, E. (1983).'Elements in Major Raw Agricultural Crops in the United State. 1.Cadmium and Lead in Lettuce, Pwanuts, Potatoes, Soyabeans, Sweet Corn, and Wheat', *Journal of Agriculture and Food Chemistry,* 31:12490-1244

World Health Organization, (2006). Elemental speciation in human health risk assessment Environmental Health Criteria 234 Geneva Switzerland: World Health Organization. Accessed from http://www.who.int/ipcs/publications/ ehc/ehc234.pdf March 18, 2007

World Health Organization, (2001). 'Environmental Health Criteria for Zinc', Available at http://WWW.inchem.org/documents/ehc/ehc221.htm (Accesssed: 1 February 2007).

World Development Report (1992): *Development and the Environment* International Bank For Reconstruction And Development The World Bank

Wufem, M. B, Ibrahim, A. Q., Maina, M. H.and Nangbes, J. (2013). speciation of some heavy metals around A Cement Factory in Gombe State. *IJES.,* 2 (9) : 110-115

Yusuf, K.A. (2007). Sequential Extraction of Lead, copper, Cadmium and Zinc in soils near Ojota Waste Site. *J.Argon.,* 6 (2) : 331-337

Appendix I Correlation between Heavy Metals and pH

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	10.03155	1.222099	8.208459	0.000176	7.041178	13.02191	7.041178	13.02191
Cd	8.201893	4.509313	1.818879	0.118805	-2.832	19.23578	-2.832	19.23578

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	12.08483	1.322717	9.136372	9.67E-05	8.84826	15.3214	8.84826	15.3214
Cu	-0.57513	7.580069	-0.07587	0.941986	-19.1229	17.97264	-19.1229	17.97264

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	12.64728	1.127257	11.21952	2.99E-05	9.888982	15.40558	9.888982	15.40558
Zn	-0.7212	1.003017	-0.71903	0.499154	-3.1755	1.733091	-3.1755	1.733091

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	12.66779	0.983726	12.87736	1.35E-05	10.2607	15.07488	10.2607	.07488
Pb	-0.07128	0.077654	-0.91791	0.394068	-0.26129	0.118733	-0.26129	0.118733

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	12.83881	1.064275	12.06344	1.97E-05	10.23463	15.443	10.23463	15.443
Cr	-1.42776	1.428235	-0.99967	0.356065	-4.92253	2.067001	-4.92253	2.067001

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	14.19533	1.552941	9.140932	9.64E-05	10.39542	17.99524	10.39542	17.99524
Ni	-4.8921	3.19237	-1.53243	0.176302	-12.7035	2.919348	-12.7035	2.919348

Appendix II Correlation between Heavy Metals and Clay

Cd

	Coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	-0.28	0.288853	-0.96935	0.369806	-0.9868	0.426798
Clay	0.043333	0.023824	1.818879	0.118805	-0.01496	0.101629

Cu

	Coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	0.1675	0.266329	0.628922	0.552575	-0.48418	0.819183
Clay	-0.00167	0.021966	-0.07587	0.941986	-0.05542	0.052083

Zn

	coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	2.2175	1.854821	1.195533	0.276982	-2.32108	6.756084
Clay	-0.11	0.152983	-0.71903	0.499154	-0.48434	0.264336

Pb

	coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	30.09875	22.81802	1.319078	0.235247	-25.7349	85.93243
Clay	-1.7275	1.881998	-0.91791	0.394068	-6.33258	2.877584

Cr

	coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	1.7875	1.212835	1.473819	0.190966	-1.1802	4.755201
Clay	-0.1	0.100033	-0.99967	0.356065	-0.34477	0.144772

Ni

	coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	1.13875	0.45493	2.503133	0.046331	0.025577	2.251923
Clay	-0.0575	0.037522	-1.53243	0.176302	-0.14931	0.034313

Appendix III Correlation between Heavy metals and Organic Carbon

Cd

	coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	0.217963	0.147438	1.478331	0.189798	-0.14281	0.578732
OC	0.020571	0.129036	0.159424	0.878566	-0.29517	0.336312

Cu

	coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	0.222914	0.104382	2.135565	0.076618	-0.0325	0.478326
OC	-0.0704	0.091353	-0.77061	0.470184	-0.29393	0.153136

Cr

	coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	1.122643	0.484867	2.315365	0.059828	-0.06378	2.309069
OC	-0.49955	0.424349	-1.17721	0.283688	-1.5379	0.538795

Pb

	coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	20.40944	8.776477	2.325471	0.059005	-1.06582	41.88471
OC	-10.3064	7.681064	-1.34179	0.228213	-29.1013	8.48852

Ni

	coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	0.727594	0.183907	3.956319	0.007483	0.27759	1.177598
OC	-0.2603	0.160953	-1.61723	0.156956	-0.65414	0.13354

Appendix IV Correlation between Heavy Metals and CEC

Cd

	coeff	*std err*	*t stat*	*p-value*	*lower*	*Upper*
Intercept	-0.05769	0.31242	-0.18467	0.859572	-0.82216	0.706769
CEC	0.017889	0.018553	0.964232	0.372167	-0.02751	0.063285

Cu

	coeff	*std err*	*t stat*	*p-value*	*lower*	*Upper*
Intercept	-0.00583	*0.240459	-0.02425	0.981438	-0.59421	0.582551
CEC	0.009214	0.014279	0.645267	0.542626	-0.02573	0.044154

Zn

	coeff	*std err*	*t stat*	*p-value*	*lower*	*Upper*
Intercept	0.170379	1.778808	0.095782	0.926812	-4.18221	4.522965
CEC	0.043694	0.105632	0.413644	0.693513	-0.21478	0.302165

Pb

	coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	3.68425	22.61869	0.162885	0.875956	-51.6617	59.03018
CEC	0.341591	1.343174	0.254316	0.807743	-2.94504	3.62822

Cr

	coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	0.159951	1.209645	0.13223	0.899125	-2.79994	3.119846
CEC	0.025692	0.071833	0.357665	0.732839	-0.15008	0.201461

Ni

	coeff	*std err*	*t stat*	*p-value*	*lower*	*upper*
Intercept	0.447682	0.500787	0.893956	0.405774	-0.7777	1.673064
CEC	6.42E-05	0.029738	0.002159	0.998348	-0.0727	0.072832

***significant at $p<0.05$**