CHEMICAL SPECIATION AND BIOAVAILABILITY OF SOME SELECTED HEAVY METALS IN FARMLAND SOILS AROUND WARRI REFINERY, DELTA STATE, NIGERIA

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OBARO, Ajovi

DEPARTMENT OF CHEMISTRY,

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OBARO, Ajovi
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DELTA STATE UNIVERSTY, ABRAKA

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CERTIFICATION

This is to certify that this research work was carried out by OBARO, Ajovi in the Department of Chemistry, Faculty of Science, Delta State University, Abraka, under the supervision of Dr. S.A. Osakwe.

Dr. S.A. Osakwe **Date**
Supervisor

Dr. S.O. Akporido **Date**
Head of Department

DEDICATION

This project is dedicated to God Almighty for His mercies toward me and also to my family members.

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My profound gratitude goes to the Almighty God for provision, protection and for his grace to carry on through this programme.

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My sincere gratitude goes to my wife and children as well as my numerous friends.

TABLE OF CONTENTS

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: LITERATURE REVIEW

CHAPTER THREE: MATERIALS AND METHODS

CHAPTER FOUR: RESULTS AND DISCUSSION

CHAPTER FIVE: SUMMARY AND CONCLUSION

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The aim of this study was to investigate the chemical speciation and bioavailability of selected heavy metals in farmland soils around Warri refinery, Delta State, Nigeria. Soil samples were collected from 12 farmlands around the refinery at different depths. The concentration of heavy metals were determined using atomic absorption spectrometry (AAS) after digestion with aqua-regia. The chemical forms of the heavy metals were determined using the Tessier sequential extraction method. The results showed that the concentrations of the metals ranged from 1.02 to 11.16 mg kg^{-1}, 5.59 to 42.38 mg kg^{-1}, 11.06 to 70.08 mg kg^{-1} and 39.18 to 182.35 for As, Pb, Cr and Zn respectively. Cadmium was below the detection limit of the instrument. The chemical speciation of the heavy metals indicated that the residual and organic fractions were the predominant fractions of the heavy metals. The speciation of As and Pb followed the order residual> organic> carbonate> Fe- Mn oxide> exchangeable while that of Cr and Zn followed the order residual> organic> Fe- Mn oxide > carbonate> exchangeable. The mobility factors for the heavy metals ranged from 11.90-89.91, for As, 12.61-57 for Pb, 6.64-22.30 for Cr and 4.05-11.77 for Zn following the order As> Pb> Cr> Zn. The relatively high mobility factors observed for As and Pb indicate high mobility, lability and bioavailability for As and Pb in the soils studied. The results suggest that As and Pb in these soils pose health risk to humans through the plant uptake dietary route.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Nigeria is a major producer and exporter of crude petroleum oil and also an important agricultural nation in West African sub-region (Agbogidi *et al*., 2005). Soil is considered a critical environment as it accumulates pollutants produced by various anthropogenic activities including crude oil pollution. Soil pollution caused by crude oil and its derivatives is one of the most prevalent problems in the environment. It has a significant impact on the soil micro biota and plants (Smith *et al.,* 1989). As crude oil comes from the well, it contains mixture of hydrocarbon compounds and quantities of other materials such as oxygen, nitrogen, sulphur, salt, water and some trace metals. In the refinery, most of these non-hydrocarbon substances are removed and the oil is broken down into useful products (Nwaichi*et al*., 2011).

The soil is very important to human existence for various reasons, especially for agriculture and has been subjected to various abuses including spillage of petroleum (crude oil). The release of crude oil into the environment by oil spills calls for more attention by all and sundry in the country.

According to Hutchinson (1973), the interaction of hydrocarbons and the environment has been intensely stimulated by the release of enormous quantities of petroleum hydrocarbons into the marine and terrestrial environments as a result of petrol tanker accidents and pipeline vandalisation. These pollutants affect and alter the chemical and biological properties of soil (Ewetola, 2013). As a result of soil contamination by oil spill, hazardous chemicals can enter into the human food chain from soil or water and disturb the biochemical process and finally lead to serious effect on living organisms. It is known that some crude oil components that are toxic can directly affect soil organisms, soil properties and also make soil acidic or reduce the pH of the soil (Ewetola, 2013). Soil contamination has been a growing concern since it can be a source of ground water contamination and also reduce the usability of the land for development. Elevated levels of some heavy metals in different parts of the globe have increased the interest for environmentalists and eco-toxicologists in toxicity and environmental degradation. Human and ecosystem may be exposed to chemical hazards such as heavy metals through direct ingestion, consumption of crops and vegetables grown on the contaminated lands or drinking water that has percolated through such soils (Mclaughin *et al*., 2000). These pollutants may cause long or short term damage by changing the growth rate of plant or animal species, or by interfering with human amenities, comfort, health or property values (Tietenberg, 2006). Within the European community, eleven element of highest concern are arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin and thallium (MEPPR, 2014); the emissions of which are regulated in waste incinerators. Some of these elements are actually necessary for humans in minute amounts (cobalt, copper, chromium, manganese, nickel) while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones or teeth (nickel, cadmium, copper, chromium) (Zevenhoven and Kilpinen, 2001). Cadmium, lead and zinc are also released in tiny particulates as dust from rubber tyres on busy road surfaces; the small size allows these toxic metals to rise in the wind to be inhaled, or transported into topsoil or edible plants through precipitation of their compounds or by ion exchange into soils and muds. Heavy metals pollutions can localize and lay dormant, and this can have multiple effects on the environment.

Polycyclic aromatic hydrocarbons (PAHs) are produced from incomplete combustion of organic materials, fossil fuels, petroleum product spillage and various domestic and industrial activities (Johnsen *et al*., 2005). Based on their ecotoxicity, the United State Environmental Protection Agency has prioritized 16 PAHs as environmental pollutants (Nwaichi *et al*., 2010). Total petroleum hydrocarbons (TPS) are measurable amount of petroleum-based on hydrocarbons in an environmental media (Rauckte *et al*., 2010).

Oil exploration in Ogoni land commenced in the 1950s and extensive production facilities were established. Ogoni lands situated in an area 1,000km East of Port Harcourt in Rivers State, Nigeria. The area has a tragic history of pollution from oil spills; oil well fires, environmental incidents, such as spills and uncontrolled flares (UNEP, United Nations Environment Programme, 2011). This study therefore seeks to evaluate the distribution of some heavy metals in selected regular – consumed food and soils from an oil polluted active area in agricultural farmland and making comparisons with a view to health implications.

1.2 Justification pf Study

The quantitative data on heavy metal concentrations, their contamination levels and their pollution sources have been systematically gathered. However, studies on the speciation of these heavy metals and correlation with its physico-chemical properties have not been fully reported. Therefore, this study focuses on the heavy metal speciation and its effect on the physico-chemical properties.

1.3 Aim of the Study

The overall aim of the study is to determine the chemical speciation and bioavailability of some selected heavy metals in farmland soils around Warri Refinery, Delta State, Nigeria.

1.4 Objective of the Study

The objectives of this study are to:

1. determine some physicochemical properties of farmland soils around Warri refinery.
2. determine selected heavy metals concentrations in the soil
3. determine the chemical forms of the selected heavy metals in the soil
4. assess the bioavailability of the selected heavy metals in the soil

CHAPTER TWO
LITERATURE REVIEW

2.1 Soil

Soil is the mixture of minerals, organic matter, gases, liquids and a myriad of organisms that can support plant life. Soil is considered as the "skin of the earth" with interfaces between the lithosphere, hydrosphere, atmosphere and biosphere (Chestworth *et al.*, 2008). Soil consists of a solid phase (minerals & organic matter) as well as a porous phase that holds gases and water (Voroney *et al.*, 2006). Soil is a major component of the earth's ecosystem, from ozone depletion and global warming to rain forest destruction and water pollution; the world's ecosystems are impacted in far-reaching ways by the processes carried out in the soil. Soil is the largest surficial global carbon reservoir on earth, and it is potentially one of the most reactive to human disturbance and climate change. As the planet warms, soils will add carbon dioxide to the atmosphere due to its increased biological activity at higher temperatures. Thus, soil carbon losses likely have a huge positive feedback response to global warming. Soil acts as an engineering medium, a habitat for soil organisms, a recycling system for nutrients and organic wastes, a regulator of water quality, a modifier of atmospheric composition, and a medium for plant growth. Since soil has a tremendous range of available niches and habitats, it contains most of the earth's genetic diversity.

A handful of soil can contain billions of organisms, belonging to thousands of species. The carbon content stored in soil is eventually returned to the atmosphere through the process of respiration, which is carried out by heterotrophic organisms that feed upon the carbonaceous materials in the soil. Since plant roots need oxygen, ventilation is an important characteristic of soil, this ventilation can be accomplished via networks of soil pores, which also absorb and hold rainwater making it readily available for plant uptake. Since plants require a nearly continuous supply of water, but most regions receive sporadic rainfall, the water-holding capacity of soils is vital for plant survival.

Soils offer plants physical support, air, water, temperature moderation, nutrients, and protection from toxins. Given sufficient time, a soil will evolve into a soil profile which consists of two or more layers, referred to as soil horizons that differ in one or more properties such as in their texture, structure, density, porosity, consistency, temperature, colour, and reactivity

The soil texture is determined by the relative proportions of sand, silt, and clay in the soil. The addition of organic matter, water, gases and time causes the soil of a certain texture to develop into a larger soil structure called an aggregate. At that point, a soil can develop and can be described further in terms of colour, porosity, consistency, reaction etc. The most influential factor in stabilizing soil fertility are the soil colloidal particles, clay and humus, which behave as repositories of nutrients and moisture and so act to buffer the variations of soil solution ions and moisture. The contributions of soil colloids to soil nutrition are out of proportion to their part of the soil. Colloids act to store nutrients that might otherwise be leached from the soil or to release those ions in response to changes of soil pH, and so, to make them available to plants (Sahrawat, 1979).

The greatest influence on plant nutrient availability is soil pH, which is a measure of the hydrogen ion soil reactivity, and is the function of the soil materials, precipitation level, and plant root behaviour. Soil pH strongly affects the availability of nutrients.

2.1.1 Physical Properties of Soils

The physical properties of soils, in order of decreasing importance, are;

i. Texture

ii. Structure

iii. Density

iv. Porosity

v. Consistency

vi. Temperature and

vii. Resistivity

Soil Texture: The relative proportions of sand, silt and clay particles in a mass of soil (material less than 2mm in size). Soil characteristic is influenced by texture. Structure modifies the influence of texture in regard to moisture and air relationships, availability of plant nutrients, action of microorganisms and root growth. Silt, the intermediate size, feels smooth when dry, and slippery but not sticky when moist. Because the smaller particle size promotes smaller pore spaces between particles, silty soils have a slower water intake rate but a higher water holding capacity than sandy soils. These are difficult for storage because they often lack aggregation. This result in high density and a pore size too small for suitable water percolation and aeration. Nevertheless, silt is an essential component of the medium textured, versatile soil called loam. Clay, the finest size fraction, gives the soils a sticky or plastic feel. Clay exhibits some unusual properties, unexpected if it were merely composed of smaller particles or the same minerals that make up sand and silt. Clay is largely composed of a different set of minerals, called secondary minerals. These are weathering products of the primary minerals -- quartz, feldspar, and mica -- of which sand and silt are largely composed. Soil with large diameter particles (coarse texture) can contain less water than soil with small diameter particles. Loamy soil has about 30-50% silt and 20% less than clay particles. Sand contains rock particles with diameter in range 0.125-2.0mm. Clay has soil particles whose size is less than 2-4mm in diameter. Silt soil is composed of particles whose diameter ranges from 1/256-1/16mm. Soil texture relates primarily to particles smaller than 2 millimetres, sand, silt, and clay since these are the particles most active in soil processes which support plant growth. Coarser particles, gravel and stones, are either inert or detrimental to plant cultivation.

2.1.2 Soil pH

The pH value determines to what degree the soil environment is acidic or alkaline. The pH of a solution is the logarithm of the reciprocal of the hydrogen ion concentration where $pH = \log 1/H^+$ and H_2O is ionized as an H^+cation (acid) and an OH^- anion (base). A pH value between 6.5 and 7.5 is considered optimum for the growth of many plants. Although many plants respond to an optimum pH, this value usually covers a range from 0.5 units below to 0.5 units above the optimum level. The pH of soil influences the absorption and availability of nutrients to plants. There are two general sources of soil nutrients. Some nutrients are absorbed on colloids and some are available to plants as ions in solution. In both cases the various nutrients are present as ions. In most cases the cations (positively charged ions) are absorbed on colloids and the anions (negatively charged ions) are in solution. Soil is a highly buffered ecosystem. Hydrogen ions in the soil solution are in equilibrium with negative exchange sites on the soil particles. In cation exchange, hydrogen acts as a reserve pool which continuously supplies hydrogen ions to the soil. In areas of high rainfall, soil tends to be acidic due to the leaching effect on the exchange sites. In arid and semi-arid regions, soils tend to be basic. Basic soils have higher concentrations of calcium, magnesium, and sodium carbonates. The pH of soil varies significantly in thin soil zones. These variations in pH are due to differences in both macro and micro ecosystems. The microbial population near root surfaces is an example of such an ecosystem. The rhizosphere bacteria population significantly impacts pH this microsystem and thus affects plant growth and the progress of soil remediation. Restoring the rhizosphere bacteria population and activity significantly increases available nutrients to the soil. Since most soils in Niger Delta are basic, the addition of sulphur with fertilizer is an important part of the remediation. As pH approaches 8.7, the addition of sulphur can be justified. To lower the pH of an 8 inch deep loam soil 0.5 pH units, 1,000 lbs of sulphur per acre is required. Sulphur lowers the pH thus increases the solubility of gypsum.

2.2 Heavy Metals

Heavy metals are metals having density greater than 5g/cm^3(Ademoroti, 1996). Black cotton soil may contain various toxic heavy metals. The heavy metals apart from being hazardous for living organisms, when they exceed their specific limits, have accumulating characteristics in nature as they cannot be biodegraded. Fe, Zn, Cu, Ni, Pb and Mn, are among the most common heavy metals in black cotton soil, being in the list of priority pollutant proposed by the Environmental Protection Agency (EPA) give rise to serious poisoning cases. The main symptoms of poison are dehydration, electrolyte imbalance, stomach-ache, nausea, dizziness and in-coordination in muscles.

Absorption is an important factor governing heavy metal concentration in soil and is influenced by several factors, such as pH, clay mineral content, cation exchange capacity (CEC), soil organic matter and soil types. Clay minerals show variations in their adsorbing capacity due to their CEC, specific surface area, and basic structural make up. In calcareous and alkaline soils absorption of heavy metals is by carbonates, and precipitation of heavy metal hydroxides or carbonates metals are diverse in their chemical and physical forms which change with perturbation of the system. As such, these metals are distributed among the solid and liquid phases of the soils which determine their bioavailability or the micronutrient associated with the solid phase are not available for plant uptake. In fact, less than 10% generally are in soluble and exchangeable forms (Lake *et al*, 1987). However, the redistribution is brought about by changes in soil properties due to natural and anthropogenic causes (Shuman, 1985). The forms are classified as ion exchangeable, adsorbed, organic bound, hydrous oxide.

The fate of metals added to a soil is controlled by a number of physical and biological processes acting within the soil. Their initial mobility after addition to soil will largely depend on the form in which the metals are added which in turn depends on their source. The accumulation of heavy metals in soils, represent a potential risk to human health due to the transfer of these elements to aquatic media, uptake by plant and their subsequent introduction into the food chain. The toxicity, bioavailability and mobility of metals are related to their species. However, the determination of chemical species is difficult and sometimes impossible. Therefore, the use of sequential extraction procedure for environmental studies provides an important tool for the determination of the different chemical forms between trace metals and soil components.

Chemical extraction is employed to assess operationally defined metal fractions, which can be related to chemical species, as well as to potentially mobile, bioavailable or ecotoxic phases of a sample. It is generally accepted that the ecological effects of metals e.g. their bioavailability ecotoxicology, and risk of ground water contamination are related to such mobile fractions rather that the total concentration chemical fractionation scheme for partitioning trace metals in soils and sediments have been used extensively since the 70s and are based on three to six fractions, many of them being slightly modified Tessier's schemes.

Some elements regarded as heavy metals are essential, in small quantities, for human health. These elements include vanadium, manganese, iron, cobalt, copper, zinc, selenium, strontium and molybdenum. (Wanklyn,1986). A deficiency of these essential metals may increase susceptibility to heavy metal poisoning (Whorton, 2011).

2.2.1 Origins of Heavy Metals in the Soil

With the increasing demand for metals and improvement in mineral extraction technology, ore bodies progressively lower metal contents are being mined. These lower great ore bodies are usually larger in extent and require a higher proportion of rock to be mined per tonne of metal extracted and consequently much greater quantities of waste are produced, especially tailing.

Modern mineral dressing techniques are generally quite efficient and so the tailing produced from them only contain relatively small concentrations of metals. However, historic mine site which operated during the nineteenth and early twentieth century have tailings with higher metals contents due to much less efficient ore separation.

Therefore, these tailings particles, which can be transported by either winds or water, constitute a significant source of metal contamination in surrounding the mines and in alluvial soil downstream.

2.2.2 Sources of heavy metals in contaminated soil

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

2.2.2.1 Atmosphere to soils pathway

Heavy metals in the atmosphere are mainly from gas and dust produced by energy, transport, metallurgy and production of construction materials. With the exception of mercury, heavy metals basically go into the atmosphere in the form of aerosol and deposit to the soil through natural sedimentation, precipitation, etc. For example, the lead pollution (Lin, 1998) in a downtown, Central Sweden, was reported mainly from the urban industrial copper plant, sulphuric acid plant, paint factory, and the large amount of waste from mining and chemical industries. Due to transporting by wind, these fine lead particles spread from industrial waste heap to surrounding areas. The superimposed chromium contamination by a heavy industrial factory producing chromium (Zhang, 1997) in Nanjing was reported more than 4.4 times of the local background value. The chromium contamination was centered on the chimney of workshop, ranging up to 1.5 km^2, and extending 1.38 km away. A sulphuric acid production plant in Russia (Meshalkina, 1996)was reported to contaminate the environment because of the discharge of sulphur and arsenic from the factory chimneys. Transport, especially the automotive transport, causes serious heavy metal contamination (Pb, Zn, Cd, Cr, Cu, etc.) of the atmosphere and soils (Falahiardakani, 1984).

2.2.2.2 Sewage to soils pathway

Wastewater can be divided into several categories: sanitary sewage, chemical wastewater, industrial mining wastewater and urban mining mixed sewage, etc. Heavy metals are brought to the soil by irrigative sewage and are fixed in the soil in different ways. It causes heavy metals (Hg, Cd, Pb, Cr, etc.) to continually accumulate in the soil year by year. Sewage irrigation is a feasible way to solve the problem of crop irrigation in the arid area. However, heavy metal contamination caused by sewage irrigation must be paid enough attention. Quality of irrigative sewage must be strictly controlled within the national quality standard for irrigation water (Ding, 2000).

2.2.2.3 Solid wastes to soils pathway

There are a variety of solid wastes which have complex composition of which mining and industrial solid waste contamination is the most serious. When these wastes are in the process of being piled or governed, heavy metals move easily due to the facilitation of sunlight, raining and washing. And they spread to the surrounding water and soils at the shape of funnel and radiation. With the development of industry and the acceleration of urban environmental construction, sewage treatment is continuing to be strengthened. China now has more than 80 sewage treatment plants, with the estimated 400 million tons of sludge production. Due to the high content of organic matter, nitrogen and phosphorus in the sludge, soils become the main places for soil sludge treatment. In general, Cr, Pb, Cu, Zn and As in the sludge will exceed the control standards easily (Ding, 2000).

2.2.2.4 Agricultural supplies to soils pathway

Fertilizers, pesticides and mulch are important agricultural inputs for agricultural production (Zhang and Zhang, 2007). Nevertheless, the long-term excessive application has resulted in the heavy metal contamination of soils. The vast majority of pesticides are organic compounds, and a few are inorganic compound or pure mineral, and some pesticides contain Hg, As, Cu, Zn and other heavy metals (Arao, *et al.*2010). Heavy metals are the most reported pollutants in fertilizers. Heavy metal content is relatively low in nitrogen and potash fertilizers, while phosphoric fertilizers usually contain considerable toxic heavy metals. Heavy metals in the compound fertilizers are mainly from master materials and manufacturing processes. The content of heavy metals in fertilizers is generally as follows: phosphoric fertilizer> compound fertilizer>potash fertilizer> nitrogen fertilizer (Boyd, 2010). Cd is an important heavy metal contaminant in the soil. Cd is brought to soils with the application of phosphoric fertilizers. Many studies showed that, with the application of a large amount of phosphate fertilizers and compound fertilizers, the available content of Cd in soils increases constantly, and Cd taken by plants increases accordingly. In recent years, the mulch has been promoted and used in large areas, which results in white pollution of soils, because the heat stabilizers, which contain Cd and Pb, are always added in the production process of mulch. This increases heavy metal contamination of soils (Satarug *et al.,* 2003).

2.3 Remediation

Soils contaminated by heavy metals can be remediated by one or more of the following technologies: isolation; immobilization; toxicity reduction; physical separation; or extraction.

a. **Isolation:** Involves the use of caps, membranes or below-ground barriers in an attempt to quarantine the contaminated soil.

b. **Immobilization:** Aims to alter the properties of the soil so as to hinder the mobility of the heavy contaminants.

c. **Toxicity Reduction:** Attempts to oxidise or reduce the heavy metal ions, via chemical or biological means into less toxic or mobile forms.

d. **Physical Separation:** Involves the removal of the contaminated soil and the separation of the metal contaminants by mechanical means.

e. **Extraction:** Is an on or off-site process that uses chemicals, high-temperature vitalization, or electrolysis to extract contaminants from soils. The process or processes used will vary according to contaminant and the characteristics of the site (Waldron,1983).

2.4 Toxicity of some selected heavy metals

The following are catalogue of some important toxic heavy metals and their toxicological effects:

Arsenic

Arsenic sprays or gases were used during World War 1 warefare, the one favoured by the British was known as “lewisite”. Arsenic can produce all three types of toxicity at different dosages, acute, sub-acute and chronic. One sign of acute exposure is edema of the eyelids and gastro intestinal irritation and both central and peripheral neuropathies frequently occur. During chronic toxication “gaslic breath”, skin sensitivity dermatitis and keratitus frequently occur. All types of arsenic exposure can cause kidney and liver damage and in the most severe exposure there is erythrocyte haemolysis (ATSDR, 2006).

Lead

Depending on one’s location on the face of the planet, the food and water supply, as well as the air we breathe exposes us to lead. Areas of particular risk are places where the drinking water is obtained from geological strata with significant lead content. Areas which have deposits of gold, zinc and other economically useful metals, also have lead as an ore contaminant and the “tailings” of the mining and purification of the ore often have a very high lead content. In old houses in which lead based paints were used, there is a risk of toddlers consuming flaking paints hips with high lead content. This was a particular problem in the “slums” of large cities in the U.S until the ecological consciousness was raised in the 60’s and 70’s. There are probably many old houses in new found lant, with lead paint in their interiors and there are many known communities with significant lead, zinc and manganese concentrations in the ground water (ATSDR, 2006).

In most individuals, there is a “lead balance”, that is, one excretes as much as he or she takes in, and the tissue levels are below the concentrations which result in pathological changes. However, an increase in the rate of intake will result in accumulation of a “positive lead balance”. Since lead is chemically very similar to calcium, it is handled by the body as if it is calcium. Thus, the first place to which it transport is to the plasma and the membrane sites where calcium plays an important role most notably in the teeth of developing children and in bone at all ages (ATSDR, 2006).

Following ingestion of a large amount of lead there will be direct tissue interaction. This includes tissue desiccation, mucosal, tissue damage and convulsion possibly resulting in death. The biosynthesis of bones in general is deranged by the presence of lead (European Commission, 2002).

With a gradual build-up of a positive lead balance, there is no sudden onset of symptoms as seen with acute poisoning. The initial symptoms include clumsiness, ataxia, vertigo, irritation and insomnia. In affected children, they are often considered "slow", the real basis for difficulty is not recognized. As lead level rises, hyper excitability is seen. Confusion delirious and convulsion may occur in some cases, while in others there is progressive lethargy leading to a comatose state (ATSDR, 2006).

Manganese

This heavy metal is often associated with iron deposits and in fact the strata underlying conception, by providing the base for the webana mines which has very rich manganese content. This metal is known to block calcium channels and with chronic intoxication result in central nervous system dopamine sepletion. This latter condition duplicates almost all the symptom logy of Parkinson's disease, and is treated with some success using typical and Parkinson drugs (Blaurock-Busch, 2009).

Cadmium

Cadmium derives its toxicology properties from its chemical similarities with zinc and essential micronutrient for plant and animal. Cadmium is biopersistent for many years (over decades for humans), although, it is eventually excreted.

In human long-term exposure is associated with renal dysfunction. High exposure can lead to obstructive lung disease and has been linked with lung cancer, although data concerning the later difficult to interpret due to compounding factors (European Commission, 2002).

Cadmium may also produce bone defects, (osteomalia, osteoporosis) in human and animal in addition, the metal can be linked to increase in blood pressure and effects on the myocardium in animals, although most human data do not support this finding.

The average daily intake for human is estimated as 0.12µg from air and 1µg from water. Smoking a packet of 20 cigarettes can lead to inhalation of around 2.4µg of cadmium, but levels may vary widely (Lenntech, 1999).

Chromium

Chromium is used in metal alloys and pigments for paints, cement, paper, rubber and other materials, low level of exposure can irritate the skin and cause laceration. Long term exposure can cause kidney and liver damage, and also can damage circulatory and nerve tissues. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high level of chromium. (http://www.lenntech.com/ heavymetals.htm).

Nickel

Small amount of nickel isneeded by the human body to produce red blood cells. However, in excess amount, it can become mildly toxic. Short-term exposure to nickel is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage and skin irritation. The Environmental Protection Agency (EPA) does not currently regulate nickel levels in aquatic life, but its presence is not magnified along food chains (Akhtar *et al*., 2004).

Zinc

Zinc is an essential trace element for all living organisms. As a constituent of more than 200 metalloenzymes and other metabolic compounds, zinc assures stability of biological molecules such as DNA and of biological structures such as membranes and ribosomes (Eisler, 2007). Plants do not grow well in zinc-depleted soils, and clinical manifestations of zinc deficiency in animals include growth retardation, testicular atrophy, skin changes, and poor appetite (ATSDR, 2006).

Zinc poisoning has been documented in dogs, cats, ferrets, birds, cattle, sheep, and horses, usually as a result of ingesting galvanized metal objects, certain paints and fertilizers, zinc-containing coins, and skin and sunblock preparations containing zinc oxide. Signs of acute poisoning include anorexia, depression, enteritis, diarrhea, decreased milk yield, excessive eating and drinking and, in severe cases, convulsions and death (Eisler, 2007).

Emissions from zinc smelters destroyed wildlife habitat; reduced prey abundance; poisoned deer, songbirds, and shrews; and eliminated terrestrial amphibians from the mountainside at Aquatic populations are frequently decimated in zinc-polluted waters. Zinc in the aquatic environment is of particular importance because the gills of fish are physically damaged by high concentrations of zinc. Zinc toxicosis in humans is not a common medical problem, although it may appear in some metal workers and others under special conditions. Industrial processes such as welding, smelting, or fabrication of molten metals can produce ultrafine metal oxides at harmful concentrations. Inhalation of these metal oxides, including oxides of zinc, causes the industrial malady known as metal fume fever (ATSDR, 2006).

Iron

Iron can be found in meat, whole meal products, potatoes and vegetables. The human body absorbs iron in animal products faster than iron in plant products. Iron is an essential part of hemoglobin; the red colouring agent of the blood that transports oxygen through our bodies (Lenntech, 1999).

Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray change. No physical impairment of lung function has been associated with siderosis. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens (Hoekmann, 2000). LD50 (oral, rat) =30 mg/kg. (LD50: Lethal dose 50. Single dose of a substance that causes the death of 50% of an animal population from exposure to the substance by any route other than inhalation. Usually expressed as milligrams or grams of material per kilogram of animal weight (mg/kg or g/kg).

A more common problem for humans is iron deficiency, which leads to anaemia. A man needs an average daily intake of 7 mg of iron and a woman 11 mg; a normal diet will generally provide all that is needed. Iron (III)-O-arsenite, pentahydrate may be hazardous to the environment; special attention should be given to plants, air and water. It is strongly advised not to let the chemical enter into the environment because it persists in the environment (ATSDR, 2006).

Copper

Copper, a metal that occurs naturally in rocks, soil, water and air throughout the environment, is an essential element in plants and animals (including humans). Therefore, plants and animals must absorb some copper from eating, drinking and breathing (ATSDR, 2006). Although, copper is not toxic as chromium (VI), it can be potentially serious if high levels are present in drinking water. The most common symptom of copper toxicity is injury to red blood cells and lungs as well as damage to liver and pancreatic functions (Ontario, 2006). Long-term exposure to copper can also cause irritation of the nose, mouth, and eyes as well as headaches, stomach aches, dizziness, vomiting and diarrhea (Lenntech, 2006).

2.5 Chemical speciation and speciation analysis of metals

There has been confusion in the use of the terms “speciation” and “speciation analysis” by researchers in the field of environmental and analytical chemistry, biology, geochemistry among others. They find it difficult to differentiate between the two concepts and thus they use them interchangeably. Many researchers have defined speciation to reflect their field. Speciation according to the International Union of Pure and Applied Chemistry (IUPAC) is the distribution of an element amongst defined chemical species as to electronic or oxidation state, complex or molecular structure and isotopic composition. While speciation analysis is an analytical activity of identifying and/or assessing the quantities of one or more individual chemical species or patterns in an environmental sample or a biosystem (Templeton et al., 2000). A good comprehension of environment-organism interactions can be gotten from the distribution patterns and bioavailability of metals in the environment. Therefore, bioactivity and bioavailability of metals is a function of their chemical co-existing forms and thus their speciation (Benson *et al.,* 2013).

2.5.1 Analytical significance of metal speciation analysis

Analytical measurements of metals expressed as total concentrations in environmental and biological samples are insufficient to assess the environmental impact of polluted soils and sediments since metals may exist in different chemical forms and only a fraction of the total metal can be remobilized (Ramirez *et al.,* 2005; Benson *et al.,* 2013). According to Benson et al. (2013), one major importance of speciation analysis is the qualitative and quantitative sign it has given to individual metal forms, which could be used in the evaluating the index of metal toxicity.

Metal distribution, mobility, bioavailability, reactivity and toxicity in environmental matrices depends strongly on the mineralogical and chemical forms in which they are present (Baeyens *et al.,* 2003; Okoro *et al.,* 2012). Thus, it is important to find out the chemical forms of metals in environmental matricesemploying speciation analysis.

Speciation analysis provides additional information on collected results through characterizing some of the most important chemical species of metals with a view to understand the transformations between species that are likely to occur and to deduce from such information the associated environmental and health effects (Benson *et al.,* 2013). Likewise, metal speciation analysis is a necessary tool in analytical and environmental chemistry for predicting the fate of metals in aquatic ecosystems and designing effective and efficient methods for water quality monitoring.

2.5.2 Techniques for the study of speciation

A broad range of sensitive and specific analytical techniques has been designed and developed for speciation studies.Among these techniques are hyphenated techniques such as GC-ICP-MS for the analysis of organometallic elements, x-ray spectroscopic techniques and sequential leaching techniques (Ohnuki *et al.,* 2005; Hirata *et al.,* 2006). Although the various techniques originated by various researchers are capable of quantifying the amount of free and bound metal, Benson et al. (2013) noted that only the most sensitive techniques are suitable for speciation analysis. For Zaporozhets and Linnik (2004), speciation techniques using inductively coupled plasma in combination with mass spectrophotometry (ICP-MS), inductively coupled plasma combined with atomic emission spectrophotometry (ICP-AES) and electrothermal technique combined with atomic absorption spectrometry (ET-AAS) are the most sensitive and selective.

Initial speciation analysis on environmental matrices were directed mainly on separation of specific elemental species (Adamu *et al.,* 2013). Species were separated using the observing techniques; liquid chromatography (LC), gas chromatography (GC), capillary electrophoresis (CE) and gel electrophoresis (GE) (Rosen and Hieftje *et al.*, 2004; Adamu et al., 2013). In recent times, separation methods have been incorporated with highly sensitive and powerful detection methods for reliable quantitative measurements (Benson *et al.,* 2013). High performance liquid chromatography (HPLC) is one major and readily available methods utilized in separating non-volatile species of interest and has been widely coupled to atomic spectroscopy for quantification. A long list of resin supports have been utilized as the stationary phase with size exclusion, cation exchange, chelating, anion exchange, and reversed phase (Adamu et al., 2013). In this way, analytes with different oxidation states e.g. Cr^{3+} and Cr^{6+} are separated and qualified. Other suitable techniques for on-line coupling are inductively coupled plasma combined with atomic emission spectrometry (ICP-AES) and inductively coupled plasma with mass spectrometry (ICP-MS). ICP-MS has helped greatly in multi-element determinations, isotopic discernment with very high sensitivity. In the same vein, electroanalytical techniques such as anodic stripping voltammetry (ASV), amperometry and potentiometry have also been utilized for determination of the various oxidation states of metals, metals' organometallic species and their complexes (Adamu *et al.,* 2013).

Mathematical models and computer assisted programs have likewise been designed for speciation analysis. The Free Ionic Activity Model (FIAM) has been employed to determine metal speciation in soil, which involves the uptake of metal by target organisms (Campbell, 1995). The FIAM was later changed into the Biotic Ligand Model (BLM) so as to admit the influence of completing cations like Ca^{2+} and H^+ (Di-Toro et al., 2001).Continuing development in this regard, Donnan Membrane Technique (DMT) Diffusive Gradient in Thin films (DGTs) have been designed and successfully used in speciation analysis.The Windermere Humic Aqueous Model (WHAM VII) is the latest variant of the mathematical model and computer assisted program developed and generally accepted worldwide (Adamu *et al*., 2013). According to Adamu et al. (2013), the WHAM VII model contains a database for cation binding to humic and fulvic acids, including all rare earth elements and silver; and also mimics the precipitation of iron (III) and aluminium hydroxides, and binding of irons to precipitate. The binding activity of dissolved organic matter is used to generate distributions of predicted free ions concentrations (Lofts and Tipping, 2011).

2.5.3 Speciation studies in soils

To understand metal speciation in soils several approaches involving multi steps extraction procedures have been employed (Tessier *et al.,* 1979; Barnah *et al.,* 1996; Okoro *et al.,* 2012; Benson *et al.,* 2013). The number of steps in these extraction procedures varies from 3 to 8 steps. For example, Li and Thornton (2000) (3 steps), Tessier et al. (1979) (5 steps), Kersten and Fronstier (1986) (6 steps) and Krishnamauti et al. (1995) (8 steps). These extraction procedures vary in their extraction reagent, types and experimental conditions. The 5-step Tessier et al. (1979) is one of the widely utilized sequential extraction procedure. This sequential extraction procedure demarcates the metal forms sequentially as exchangeable, carbonate-bound, iron and manganese oxide-bound, organically-bound and residual. However, following this basic procedure, a number of modified procedures have been developed which uses different reagents or experimental conditions to separate individual fractions (Gomez-Ariza *et al.,* 2000; Ma and Rao, 1997; Zdenek, 1996; Camparella *et al.,* 1995). The type of reagents used in extracting when it comes to speciation analysis is based on selectivity and specificity towards a particular physicochemical form of metals (Gitari *et al.,* 2010). According to Benson et al. (2013), the reagent cocktail for respective extraction steps are capable of disrupting the binding agents between individual elements and the sediment/soil thereby enabling the release of the metal species into the solution. Since sequential extraction procedures were not standardized, researchers use schemes developed by themselves.

However, in an effort to harmonized and standardized the extraction procedures the Community Bureau of Reference (BCR) (now Standards, Measurement and Testing Programme (SMTP) sequential extraction method was developed (Moc'ko and Waclawek, 2004; Jung *et al.,* 2010; Okoro *et al.,* 2012). The BCR method is a 3-step method which delineate metals into exchangeable, reducible and oxidizable fractions which are extracted with reagents. A summary of this approach is displayed in Table 2.1.

Table 2.1: Three-step sequential extraction procedure developed by BCR

Species	**Regent**	**Extraction time/temp.**
Exchangeable, Water- and acid-soluble	40 cm^3 11 M CH_3 COOH per 1.0 g of sample	Shake using mechanical shaker overnight at 25°C
Reducible species (metal oxides- and hydroxides-bound)	40 cm^3 0.1 M $NH_2OH.HCl$ (adjusted to pH = 2 with HNO_3) added to residue.	300 min at 25°C
Oxidisable species (organic matter and suphides-bound)	10 cm^3 5.8 M H_2O_2 added to residue in water bath. Evaporate solution to few cm_3. After cooling, add 50 cm^3 1 M CH_3COONH_5 (adjusted to pH = 2 with HNO_3) to residue.	60 min at room temperature 60 min at 85° C 360 min (25° C)

A sediment certified reference material BCR-701 was used to validate this method employing certified and indicative extractable concentration of Cd, Cr, Cu, Ni, Pb and Zn (Rauret and Lopez-Sanchez, 2001; Okoro *et al.,* 2013). This method was applied and taken over by a large group of scientists, despite some shortcomings in the sequential extraction steps (Usero et al., 1998; Ho and Evans 1997; Agnieszka and Wieslaw, 2002).

The application of sequential extraction procedures abound in the literature. For instance, Iwegbue (2007) in investigating the chemical speciation and likely mobility of Cd, Cu, Pb, Zn, Cr and Ni in the soils of automobile mechanic waste dumps in Port-Harcourt, Nigeria uses a sequential fractionation protocol that generated six different fractions into which soil metal could partition. The author found out that for surface soil, Cd was partitioned among all the fractions except residual fraction, Cu was dominant in the organic fraction, Zn and Pb were predominant in the reducible fraction while Cr and Ni were associated with the residual fraction.

Osakwe (2012) studied selected heavy metals Fe, Cd, Ni, and Cr in contaminated refuse dumpsites soil samples collected from South – Eastern Nigeria, for their geochemicaldifferentiation into different chemical fractions, using Ma and Rao six steps sequential chemical extraction. The author found that the residual fraction was the most important phase for the four heavy metals under study with the following average percentage values 74.43 for Fe, 37.69 for Cd, 70.11 for Ni and 62.47 for Cr.

Shasheen et al. (2013) studied the fractionation of metals in floodplain soils from Egypt, Germany and Greece using sequential extraction to delineate Cd, Cu, Ni, Pb and Zn into five phases. The authors reported that the predominant phase of the metals is the residual phase for Egyptian and Greek soils while for the German soil non-residual phase predominated for all metals. Katana et al., (2013) carried out a speciation analysis utilizing the modified Community Bureau of Reference (BCR) sequential extraction procedure for Ni and Cr in soils of open-air garages in Ngara, Nairobi, Kenya. The authors found that the metals partitioned in the order of; exchangeable >oxidisable >residual > reducible for Ni and exchangeable= residual > reducible > oxidisable for Cr. The % of non-residual Ni and Cr was 76.37 and 74.25 respectively while the mobility factors for the heavy metals were 29.10% and 25.82% respectively.

Ajala et al. (2014) evaluated the chemical fractionation of iron, manganese, copper, zinc, nickel, lead, cadmium and chromium in soils of Eke-Mgbom, Afikpo Nigeria the authors employed the sequential extraction procedure of Horowitz (1991). The authors reported that the metal fractions is are in the order of Oxidizable >> Exchangeable >> Carbonate > Residual > Reducible.

The principle of operation of atomic absorption spectrophotometer (AAS)

The sample solution is aspirated into a flame (introduction of the sample into the flame as a fine spray to obtain atomic vapour). In the flame, the element of the atoms in the flame remains in the ground state and it is these ground state atoms that are measured in atomic absorption. As the name implies, this is accomplished by measuring the amount of radiation from the lamp source, with a line spectrum of characteristics wave-length absorbed by atom.

The absorption follows beer lambert law, that is, the absorbance is directly proportional to the path length, length in the flame, but these variables is difficult to qualify, however path length is held constant and the concentration of atomic vapour is directly proportional to the concentration of the analyte in the solution being aspirated. The procedure used is to prepare a calibration of the analyte in the sample to be analyzed (Warri, 2008).

The operation of the AAS proceeds as follows: A light beam hollow cathode lamp (the cathode contains the elements to be analyzed) is directed through the flame into a monochromator, then onto a detector that measures the amount of light absorbed. Absorption depends on the presence of free unexcited ground state atom in the flame.

Since the wavelength of the light beam is characterized by the metal being determined, the light energy absorbed by the flame is a measure of the concentration of the metal in the sample. (Warri, 2008).

CHAPTER THREE
MATERIALS AND METHODS

3.1 Description of the study area

Warriis a commercial city in Delta State, Nigeria. It is one of the hubs of petroleum related businesses in the southern Nigeria. It lies between latitude 5^o 31 N and longitude 5^o 45 E with a population of over 311,970 people according to the national population census figures for 2006. TheWarri Refinery and Petrochemicals arelocated at Ekpan, Ubeji and Ifie-Kporo where majority of international and local oil companies operating in Nigeria have their operational offices. One of the nation major sea ports is sited within Ugbuwangue, Warri. The map of the study area showing the sampling sites is shown in Figure 3.1.

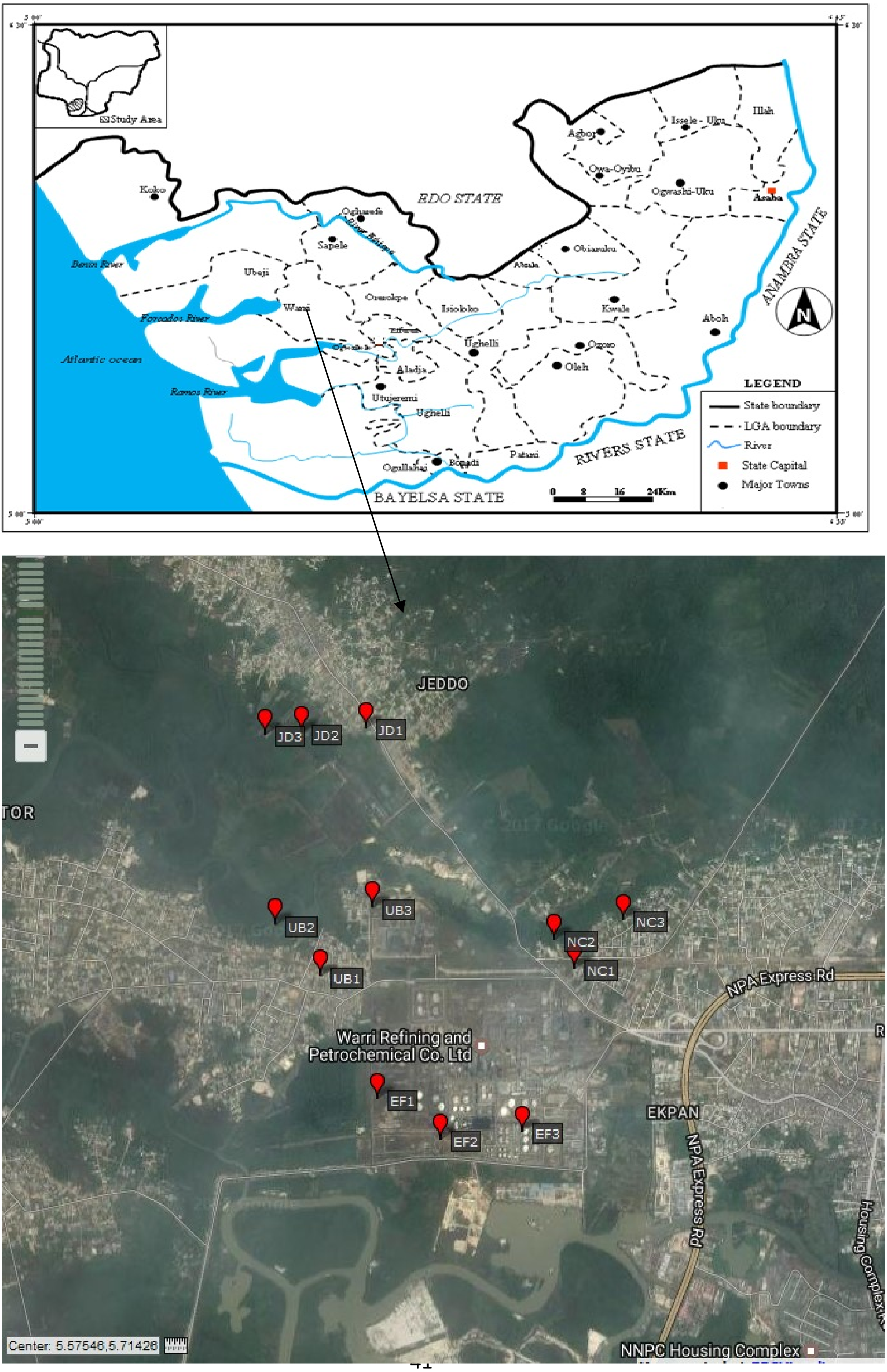
Study Area
EDO STATE
ANAMBRA STATE
RIVERS STATE
BAYELSA STATE
Atlantic ocean
Benin River
Forcados River
Ramos River
River Ethiope
Koko
Ogharefe
Sapele
Ubeji
Warri
Orerokpe
Isiokolo
Effurun
Ovwian
Aladja
Ughelli
Utujeremi
Ughelli
Ogulahai
Bomadi
Patani
Agbor
Issele - Uku
Illah
Owa-Oyibu
Ogwashi-Uku
Asaba
Obiaruku
Abraka
Kwale
Aboh
Ozoro
Oleh
N
LEGEND
State boundary
LGA boundary
River
State Capital
Major Towns
0 8 16 24Km
JEDDO
JD3
JD2
JD1
TOR
UB2
UB3
UB1
NC2
NC3
NC1
NPA Express Rd
Warri Refining and Petrochemical Co. Ltd
EF1
EF2
EF3
EKPAN
NPA Express Rd
Housing Complex R
NNPC Housing Complex
Center: 5.57546,5.71426

Figure 3.1: Map of Study Area

3.2 Sample Collection

Soil samples were collected using a soil auger from twelve (12) farmlands around the Warri Refinery. At each farmland, soil samples were collected from three locations at depths of 0-15cm, 15-30cm and 30-45cm representing top, middle and bottom soils respectively. The soil samples for each depth from the three locations of each farmland were bulked and properly mixed using coning and quartering method to get a composite or representative sample. Control samples were also collected from a farmland which was far remote from influence of anthropogenic activities or use of agrochemicals at Orerokpe.All the samples were placed in sterile polythene bags and transported to the laboratory for analysis.

3.3 Sample Preparation

Soil samples were air dried, ground, passed through a 2mm sieve and stored in labeled plastic cans until analysis. The samples for metal analysis were digested according to the method described by Ademoroti (1996). The digested samples were analyzed for the metals using Atomic Absorption Spectrophotometer.

3.4 Determination of Physicochemical Properties of soil samples

3.4.1 Soil pH

The pH meter was calibrated with buffer solution of pH 4.0, 7.0 and 10.0 respectively. 20g of the processed soil samples were placed in a 50ml beaker. 40ml of distilled water was added to it and stirred in the beaker, allowed to stand for 30 minutes with occasional stirring with glass rod. The electrodes of the pH meter were inserted into the partly settled mixture and pH was read on the meter.

3.4.2 Total Organic Carbon

The wet oxidation digestion method of Walkley and Black (1934) as described by Radojevic and Bashkin (1999) was used. This method involves the quantification of the amount of oxidizable carbon as determined by reaction with excess dichromate and sulphuric acid. The remaining unreacted dichromate is titrated with ferrous sulphate using 1, 10- phenanthroline as indicator.

Procedure: 0.5 g of air-dried homogenised and sieved soil was weighed and placed in a conical refluxing flask. 10 ml of the standard $K_2Cr_2O_7$ solution was added and swirled to mix. 15 ml concentrated H_2SO_4 was added.Flask was connected to a condenser, placed on a hot plate and refluxed for 1 hr. The solution was cooled and 100 ml of water was added. Solution was swirled to mix and 5 drops of ferroin indicator was added. The solution was titrated with ferrous ammonium sulphate to the end point at which the colour changed from blue-green to violet-red. In the same way, a blank consisting of all the same reagents but without the soil was carried out. The total organic carbon was calculated as:

$$\text{Organic carbon (mg g}^{-1}\text{)} = (18 \times C \times V) / M \times (1 - V_1/V_2)$$

Where C is the concentration in mol L^{-1} of the dichromate solution (0.166M), V is the volume of dichromate solution used (10 mL), V1 is the volume of titrant used up in the sample determination (mL), V2 is the volume of titrant used up in the blank determination (mL) and M is the weight of sample used (g). Calculate organic carbon in % as:

$$\text{Organic carbon (\%)} = \text{Organic carbon (mg g}^{-1}\text{)} / 10$$

3.4.3 Exchangeable Cations (Na, K, Ca, Mg)

5g of the air dry soil samples was weighed into clean plastic bottles with stoppers. 100ml of Neutral NH_4OAc solution (pH7) was added into the bottles and the content shaken for 30 minutes. This was then filtered through Whatman No. 42 filter paper. The soil extracts were used for the determination of Na, K, Ca and Mg. l00ml of Ammonium acetate (NH_4OAc) solution without the soils put in plastic tubes represented the blank samples.

The standard working solution was measured to calibrate the instruments (Flame Photometer for Na and K, Atomic Absorption Spectrophotometer for Ca and Mg) to fall within the measurable range of the flame photometer and atomic absorption spectrophotometer. The soil extracts were diluted as required by the samples. 5ml of the soil extract solution was introduced into 50ml volumetric flask. 1ml of 2.8% lanthanum chloride solution was added and the content diluted with 1M NH_4OAc extraction solution. The solution was then aspirated into the instruments for the different determinations. Graph of absorbance versus concentration was plotted from which the slope reciprocal was calculated.

Calculations

The concentration of K, Na, C, and Mg in the soil samples expressed in mili-equivalent (meq) per l00g soil is calculated as follows:

$$\frac{A \times S_R \times V_l}{W_S}$$

Where A, S_R, V_l, W_S are as previously defined,

The cation exchange capacity expressed in milli-equivalent per 100g soil or Cmol/kg

$$= \frac{\text{Cation (meq) / 100g}}{E}$$

Where E = Equivalent weight of cation x 10

That is, Na = 22.99

K = 39. 10

Ca = 20.04

Mg = 12.1

3.4.4 Particle size distribution

Particle size distribution was determined using the hydrometer method developed by Bouyoucos (1962). 100 g of soil sample was weighed into a 1000 mL plastic beaker. 75 mL of distilled water and 15 mL of H_2O_2 (Sigma-Aldrich) were added and gently stirred with a glass rod. 200 mL of distilled water and 100 mL sodium hexametaphosphate solutions were added and the solution was stirred, covered and kept for 4 to 5 hrs. Thereafter, the solution was made up to 500 mL and stirred for 10 min. Then the whole content was quantitatively transferred to a suspension cylinder and made up to 1000 mL with distilled water. The cylinder was stoppered tightly and shaken several times to allow the soil particles to disperse completely. Then the stopper was removed and the hydrometer was immediately placed in the suspension. Hydrometer reading was recorded exactly 40 seconds after placement of hydrometer (S_1 and B_1). Thereafter, the cylinder was stoppered and inverted several times again to ensure complete dispersal of particles. Hydrometer was placed into suspension after two hours and the reading recorded (S_2 and B_2). Blank determination was simultaneously carried out and the room temperature in ^{o}F was also recorded. Particle size distribution was thus obtained using the expressions;

$$\%\ \text{Silt} = \frac{(S_1 - B_1) + CF}{Weight\ of\ sample\ (g)} \times 100$$

Where,

Contamination factor (CF) = (Room temperature in ^{o}F – 68) × 0.2

S_1 and B_1 are hydrometer reading of sample and blank taken at 40 seconds

$$\% \text{ Clay } = \frac{(S_2 - B_2) + CF}{Weight\ of\ sample\ (g)} \times 100$$

S_2 and B_2 are hydrometer reading of sample and blank taken at 2hrs

% Sand = 100 – (Silt + Clay)

3.4.5 Total Nitrogen

Regular Macro-Kjedahl, 1983 Method was used for this analysis. 0.2g of the finely-ground soil was transferred into 100ml digestion tube, one tablet of selenium catalyst and 4.0ml of concentrated H_2SO_4 was added to it. The tubes were placed on the digestion block and heated until the solution was clear. The tubes were removed from the digestion blocks and allowed to cool until just warm enough to the touch. 10ml of distilled water was introduced into the tubes. The solutions were decanted by filtration through Whatman No. 42 filter paper into a 100ml volumetric flask. 10ml of distilled water was added. This was followed by 4.5ml of alkaline phenate, stirring to ensure interaction of the reagent with sample. 3 ml of potassium sodium titrate was added stirred and finally 2.5 ml of sodium hypochlorite was added, stirred and allowed the colour to develop. This procedure was carried out for all the sample extracts with a set of working standard solutions prepared from 25mg/l ammonia solution. The absorbance of all the preparations was measured at 630nm. Graph of absorbance versus concentration was plotted from which the slope reciprocal was calculated.

Calculation

$$N\% = \frac{A \times S_R \times V_1 \times V_2 \times 100}{W_S \times V_3 \times 106}$$

Where A, S_R, V1, V_2, V_3 and W_S are as previously defined.

A = Absorbance

S_R = Slope reciprocal

V_1 = Volume of extract

V_2 = Volume of colour developed

V_3 = Aliquot used

W_S = Weight of sample

3.4.6 Phosphate

The Bray and Kurtz (l945) method was used in determining available phosphorus. 5g of processed soil was weighed into a 150 ml plastic bottle. 35ml of extracting solution (0.03 M NH_4F in 0.025 M HCl) was added and stopped. The content was shaken manually for l minute and filtered through a Whatman filter paper No. 42, 5ml of the filtrate was pipette into a 100ml polyethylene bottle, followed by the addition of 4ml of phosphorus colour developer (a combination of ammonium molybdate and ascorbic acid reagent) this was allowed to stay for l minute and then read at 882nm using Unico, UV/Visible spectrophotometer. The absorbance of standards and samples were read.

Calculation

$$\text{Phosphate (mg kg}^{-1}) = \frac{A \times S_R \times V_1 \times V_2}{Ws \times V_3}$$

A = Absorbance

S_R = Slope reciprocal

V_1 = Volume of extract

V_2 = Volume of colour developed

V_3 = Aliquot used

W_S = Weight of sample

3.5 Metals analysis

0.5 g of the soil sample was placed in digestion tube followed by addition of 15 mL of aqua regia (3:1 HCl:HNO_3) and was swirled to wet the sample and allowed to stand overnight. The next day, the tube was heated in a heating block of 50°C for 30 min and raise to temperature of 120 °C for 2 hr. The digest was made up dissolved with 0.25 mol/L HNO_3 and filtered through Whatman No. 1 filter paper and made up to 25 mL with 0.25 mol/L HNO_3 (Radojevic and Bashkin, 1999). The samples solution were subsequently analysed for Cd, As, Pb, Cr and Zn using air-acetylene atomic adsorption spectrophotometry (Perkin Elmer Analyst 200).

3.6 Sequential Extraction Procedure

The five-step extraction procedure of Tessier et al. (1979) was used in this study as shown in Table 3.1.

Table 3.1: Sequential Extraction method of Tessier et al. (1979) for Soils

Step	Fractions	Extraction
1	Exchangeable	1mol/L $MgCl_2$ (pH7), 20°C
2	Carbonate - bound	1mol/L NaOAc+ HOAc (pH 5.1), 20°C
3	Reducible (Fe/Mn Oxide bound)	0.04 mol/L $NH_2OH.HCI$ + 25% HOAc 95°C
4	Organic bound	30% H_2O_2 + 0.02 mol/L HNO_3 (pH2), 85°C; 2mol/L NH_4OAc+ 20% HNO_3
5	Residual Fraction	HF/$HCIO_4$

3.6.1 Fraction 1—Exchangeable Fraction

Soil samples were extracted at room temperature for 1 hour with 16 ml of magnesium chloride solution (1 M $MgCl_2$) at pH 7. Soil and extraction solution were thoroughly agitated throughout the extraction. This is mainly an adsorption-desorption process. Metals extracted in the exchangeable fraction include weakly adsorbed metals and can be released by ion-exchange process. Changes in the ionic composition of the water would strongly influence the ionic exchange process of metal ions with the major constituents of the samples like clays, hydrated oxides of iron, and manganese (Abu-Kukati, 2001). The extracted metals were then decanted from the residual soil.

3.6.2 Fraction 2—Bound to Carbonates

The metals bound to carbonate phase are affected by ion exchange and changes of pH. The residue of Fraction 1 was extracted with 16 ml of 1 M sodium acetate/acetic acid NaOAc buffer at pH 5 and shake for 5 hours at room temperature. Significant amount of trace metals can be co-precipitated with carbonates at the appropriate pH. The extracted metal solution was decanted from the residual soil. The residual soil was used for the next extraction.

3.6.3 Fraction 3—Bound To Fe-Mn Oxides

The residue from fraction 2 was extracted under mild reducing conditions. 13.9 g of hydroxyl amine hydrochloride ($NH_2OH·HCl$) was dissolved in 500 ml of distilled water to prepare 0.4M $NH_2OH·HCl$. The residue was extracted with 20 ml of 0.4 M $NH_2OH·HCl$ in 25% (v/v) acetic acid with agitation at 96°C in a water bath for 6 hours. Iron and manganese oxides which can be present between particles or coatings on particles are excellent substrates with large surface areas for absorbing trace metals. Under reducing conditions, Fe (III) and Mn (IV) could release adsorbed trace metals.

The extracted metal solution was decanted from the residual soil which was used for the next extraction.

3.6.4 Fraction 4—Bound to Organic Matter

The residue from fraction 3 was oxidized as follows: 3 ml of 0.02 M HNO_3 and 5 ml of 30% (v/v) hydrogen peroxide, which has been adjusted to pH 2, was added to the residue from fraction 3. The mixture was heated to 85°C in a water bath for 2 hours with occasional agitation and allowed to cool down. Another 3 ml of 30% hydrogen peroxide (H_2O_2), adjusted to pH 2 with HNO_3, was then added. The mixture was heated again at 85°C for 3 hours with occasional agitation and allowed to cool down. Then 5 ml of 3.2 M ammonium acetate (NH_4OAc) in 20% (v/v) nitric acid (HNO_3) was added, followed by dilution to a final volume of 20 ml with de-ionized water. Trace metals may be bound by various forms of organic matter, living organisms, and coating on mineral particles through complexion or bioaccumulation. These substances may be degraded by oxidation leading to a release of soluble metals. The extracted metal solution was decanted from the residual soil which was used for the next extraction.

3.6.5 Fraction 5—Residual Fraction

Residue from Fraction 4 was oven dried at 105°C. Digestion was carried out with a mixture of 5 ml conc. HNO_3 (HNO_3, 70% w/w), 10 ml of hydrofluoric acid (HF, 40% w/w) and 10 ml of perchloric acid ($HClO_4$, 60% w/w) in Teflon beakers. Fraction 5 largely consists of mineral compounds, where metals are firmly bonded within crystal structure of the minerals comprising the soil.

3.7 Quality Control and Assurance

To validate the procedure, the instrument was programmed and it carried out metal detection by displaying three absorbance readings and what was reported was the average. Blanks were also used for correction of background and other sources of error. Apart from calibration before use, quality checks were also performed on the instrument by checking the absorbance after every ten sample runs.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Physicochemical properties of soil samples

The results of the physicochemical properties of the soils in this study are presented on Table 4.1.

Table 4.1: Some physicochemical properties of the soils of the study and control areas

SITES	DEPTH	pH	TOC (%)	CEC (meg/ 100g)	CLAY (%)	SILT (%)	SAND (%)	Total Nitrogen (%)	Phosphate (mg kg^{-1})
NC1	0-15cm	6.6	1.4	4.9	4.8	2.3	92.9	0.132	22.47
	15-30cm	6.5	1.6	4.3	5.8	1.9	92.3	0.081	15.9
	30-45cm	6.4	0.9	3.0	6.8	1.2	92.0	0.069	7.68
NC2	0-15cm	6.9	1.5	6.0	3.3	2.2	94.5	0.131	18.2
	15-30cm	6.0	0.9	3.1	5.3	1.7	93.0	0.063	11.99
	30-45cm	5.5	0.8	2.6	6.3	1.2	92.5	0.047	5.47
NC3	0-15cm	7.2	1.4	15.8	2.8	3.2	94.0	0.123	23.6
	15-30cm	6.7	1.3	7.7	4.3	2.7	93.0	0.089	13.23
	30-45cm	6.0	0.9	4.5	7.3	1.7	91.0	0.067	8.12
EF1	0-15cm	4.6	1.3	3.0	4.3	3.2	92.5	0.117	10.59
	15-30cm	4.5	1.1	3.0	6.8	2.7	90.5	0.089	2.35
	30-45cm	4.3	0.9	2.6	7.3	2.0	90.7	0.061	1.68
EF2	0-15cm	4.6	1.6	4.3	4.8	3.2	92.0	0.131	11.6
	15-30cm	4.5	0.8	3.5	5.8	2.7	91.5	0.057	3.28
	30-45cm	4.3	0.7	2.8	8.3	1.7	90.0	0.043	1.58
EF3	0-15cm	4.7	1.0	5.4	7.8	3.2	89.0	0.074	3.41
	15-30cm	4.6	0.7	4.8	11.3	2.7	86.0	0.053	1.24
	30-45cm	4.5	0.5	4.6	11.8	1.9	86.3	0.037	0.64
JD1	0-15cm	4.9	1.6	4.5	4.3	3.2	92.5	0.133	8.05
	15-30cm	4.8	0.7	3.9	4.8	2.7	92.5	0.044	4.27
	30-45cm	4.6	0.5	4.0	7.8	2.0	90.2	0.032	0.96
JD2	0-15cm	4.8	1.4	5.0	4.8	3.2	92.0	0.123	13.53
	15-30cm	4.7	0.9	4.3	8.3	2.7	89.0	0.053	9.83
	30-45cm	4.5	0.3	4.4	9.3	1.7	89.0	0.021	1.04
JD3	0-15cm	4.7	1.5	4.3	6.3	2.8	90.9	0.124	15.26
	15-30cm	4.6	1.0	3.5	7.8	2.2	90.0	0.077	5.63
	30-45cm	4.5	0.6	3.5	9.8	1.7	88.5	0.032	1.88
UB1	0-15cm	6.4	1.7	6.4	3.8	3.2	93.0	0.207	8.27
	15-30cm	5.4	1.5	3.9	5.8	2.2	92.0	0.094	4.15
	30-45cm	4.7	0.8	4.3	8.8	1.2	90.0	0.053	2.3
UB2	0-15cm	5.6	1.8	6.6	2.8	3.2	94.0	0.213	12.94
	15-30cm	5.4	1.1	4.9	8.3	2.7	89.0	0.089	3.61

	30-45cm	5.0	0.6	4.6	13.3	1.7	85.0	0.037	2.01
UB3	0-15cm	5.5	1.3	4.5	5.3	2.2	92.5	0.122	13.41
	15-30cm	5.4	1.2	4.3	9.8	2.0	88.2	0.079	4.89
	30-45cm	5.3	0.7	4.7	11.3	1.7	87.0	0.048	3.38
	AVERAGE	**5.3**	**1.1**	**4.6**	**6.9**	**2.3**	**90.8**	**0.085**	**7.73**
CTR	0-15cm	5.7	1.1	4.1	3.8	2.2	94.0	0.081	22.27
	15-30cm	5.1	0.9	3.1	5.3	1.7	93.0	0.062	12.39
	30-45cm	4.8	0.6	2.8	8.3	1.0	90.7	0.039	5.06
	AVERAGE	**5.2**	**0.9**	**3.3**	**5.8**	**9.6**	**92.6**	**0.061**	**13.24**

NC = Niger Cat sites, EF = Effie sites, JD = Jeddo sites, UB = Ubeji sites, CTR = Control site

4.1.1 pH

Soil pH is a major factor influencing the availability of element in soil (Igwe *et al*., 2005). It is well known that metal concentrations in soil solution and consequently leaching can be much enhanced in soils with low pH and/or redox potential (Adie and Osibanjo, 2009). The pH of the soils in the study area ranged from 4.3 to 7.2 with an average of 5.3for all sites and depths while the pH of the control area ranged from 4.8 to 5.7 with an average of 5.2. The pH of the control site was slightly higher than that of the study area though no significant difference in the pH value of the study area and the control area was observed.The pH of the soils of the study area were moderately acidic and decreased with depth. The decreased in depth of the pH values indicate that the acidity of the soil increase with depth. The acidic pH value may be due to the application of nitrogen fertilizers. The soil pH values obtained in this study were similar to the range of 4.6-7.8 reported for farmlands in Bartin-Iskalan, Turkey (Korkanic et al., 2008), 5.08-7.5 for farmland soils in Ondo, Southwestern Nigeria (Olelade et al., 2010), 5.0-5.8 reported in Agricultural soils in Minna, Niger State, Nigeria (Ahaneku and Sadiq, 2014), 6.1-7.8 reported for farmland soils of Lunawada, Taluka District, Mahisagar (Gujarat) India (Jain et al., 2014), 4.1-6.8 reported in arable agricultural soils in southwestern Nigeria (Olatunji et al., 2015), 3.54-5.8 with an average of 5.15 for soils of farmlands along a major highway in Delta State, Nigeria (Osakwe and Okolie, 2015).

4.1.2 Total Organic Carbon

The total organic carbon (TOC) of the soil of the study area ranged from 0.50 to 1.80 % with an average of 1.1 % while the TOC of the control site ranged from 0.6 to 1.1 with an average of 0.9 %. The highest and lowest TOC values in the study area were observed at sites UB2 (0-15 cm depth) and EF3 (30-45 cm depth respectively). The TOC values was obtained in this study decrease with depth at all sites. While soil organic carbon is not a requirement for plant growth, the levels of organic matter in soils influence a number of soils chemical and physical processes and it is an important indicator of the soil as a rooting environment (Okalebo *et al*., 1993). The low total organic carbon obtained in this study may be due to factors which includes conversion of grassland, forest and natural vegetation to arable land, deep ploughing of arable soils; drainage, liming; application of nitrogen fertilizer; tillage of peat soils and crop rotation (Banwart, 2010).The soil TOC values obtained in this study were similar to the range reported for farmland soils in Ondo, Southwestern Nigeria (Olelade et al., 2010), farmland soils of Lunawada, Taluka District, Mahisagar (Gujarat) India (Jain et al., 2014), arable agricultural soils in southwestern Nigeria (Olatunji et al., 2015), soils of farmlands along a major highway in Delta State, Nigeria (Osakwe and Okolie, 2015).

4.1.3 Cation Exchange Capacity

The cation exchange capacity (CEC) of the soils of the study area ranged from 2.6 to 15.8 meg/100g with an average of 4.6 meg/100g for all sites and depth with sites NC3 (0-15 cm depth) and EF1 (30-45 cm depth) having the highest and lowest values respectively. The CEC values of the soil of control area ranged from 2.8 to 4.1meg/100gwith an average of 3.3meg/100g. The average CEC value of the soil of the study area was slightly higher than that of the control area. In this study, the CEC values decrease with depth. Thecationexchangecapacityisdirectlyrelatedtosoilcapacityofadsorbingheavymetals.ThegreatertheCECvalues,themoreexchangesiteonthesoilmineralswillbeavailableformetalretention (Osakwe and Okolie, 2015). Surfaceandsubsurfacesoilsamplesofthesamesoilcanexhibitdifferentcapacitiesofheavy metaladsorption, sincetheadsorption behavior dependsonthecombinationofsoilpropertiesandthespecificcharacteristicsofthemetal(Barry etal.,1995). Similar CEC values have also been reported for farmland soils in Ondo, Southwestern Nigeria (Olelade *et al*., 2010),

4.1.4 Particle size distribution

The particle size distribution followed the order; Sand > Clay > Silt. The percent fraction of sand in these soil profiles ranged from 85.0 to 94.5 %for all sites and depth with an average of 90.8 % whereas that of the control area ranged from 90.7 to 94.0 % with an average of 92.6 %. The highest and lowest sand fraction in soil of the study area were observed at sites NC1 (0-15 cm depth) and UB2 (30-45 cm depth) respectively. The percent sand fraction decrease with depth in all sites. The percentage of sand fraction indicate that the soil of the study area is predominantly sandy in texture and this implies that heavy metals mobility may be enhanced in these soils. The percent silt fraction in the soil of the study area ranged from 1.2 to 3.2%for all sites and depth with an average of 2.3 % whereas that of the control area ranged from 1.0 to 2.2 % with an average of 1.6 %. The percent silt fraction also decreases with depth. The percent clay fraction ranged from 2.8 to 13.3 % for all sites and depth an average of 6.9 % whereas that of the control area ranged from 3.8 to 8.3 % with an average of 5.8 %.

Clay content increased with depth at all sites. Increased clay minerals enhanced the retention of contaminants in soil and thereby decreasing contaminants mobility. The clay content in the soil of the study area was low compared to sand. Hence, there is potential tendency for contaminants mobility in these soil profiles. Similar particle size distribution were also reported by Olelade et al. (2010) and Osakwe and Okolie (2015).

4.1.5 Total Nitrogen

The values of total nitrogen in the soil of the study area ranged from 0.021 to 0.213 % with an average of 0.085 % for all sites and depth while that of the control site ranged from 0.039 to 0.081 % with an average of 0.061 %. The soil total nitrogen values obtained in this study were similar to those reported by Osakwe (2009), Jain et al. (2014) and Osakwe and Okolie (2015). Nitrogen can be introducedinto the soils by natural processes such as lightening, decay of plant tissues (Eddy et al, 2006; Osakwe and Okolie, 2015).

4.1.6 Phosphate

The phosphate values in soil of the study area ranged from 0.64 to 23.6 mg kg^{-1} for all sites and depth with an average of 7.73mg kg^{-1} while that of the control site ranged from 5.06 to 22.27 mg kg^{-1} with an average of 13.24 mg kg^{-1}. The values of phosphate obtained in this study are similar to those reported by Jain et al. (2014) and Osakwe and Okolie (2015) but higher than those reported byIwegbue *et al.* (2006) and Chaudhare (2013). Cassava tuberis a rich source of phosphorus (Jung et al, 2002), therefore the level of phosphate recorded in this study could be attributed to some decayed cassava tubers in the farmlands.

4.2 Metal concentrations in the soils

The results of the heavy metal concentrations in soils of this study are presented on Table 4.2.

Table 4.2: Heavy metal concentrations (mg kg^{-1}) in soil samples

SITES	DEPTH	Cd	As	Pb	Cr	Zn
NC1	0-15cm	ND	6.51	18.10	56.10	169.79
	15-30cm	ND	3.26	11.85	42.06	131.71
	30-45cm	ND	1.09	7.08	28.37	64.85
NC2	0-15cm	ND	6.99	16.11	44.76	161.00
	15-30cm	ND	2.40	10.81	20.52	110.83
	30-45cm	ND	1.21	7.14	13.94	66.24
NC3	0-15cm	ND	4.13	14.02	54.88	149.63
	15-30cm	ND	1.26	10.95	33.04	116.36
	30-45cm	ND	1.02	9.45	20.50	61.02
EF1	0-15cm	ND	5.48	20.40	60.00	156.34
	15-30cm	ND	4.03	17.31	33.82	117.20
	30-45cm	ND	3.20	11.64	24.07	79.04
EF2	0-15cm	ND	5.01	28.05	40.99	143.89
	15-30cm	ND	2.96	12.98	28.86	110.14
	30-45cm	ND	1.56	7.47	19.05	72.04
EF3	0-15cm	ND	11.16	40.08	33.01	163.12
	15-30cm	ND	10.84	24.01	22.46	94.96
	30-45cm	ND	7.15	11.92	13.44	56.85
JD1	0-15cm	ND	10.04	23.69	70.08	104.28
	15-30cm	ND	6.18	21.04	47.86	66.01
	30-45cm	ND	3.98	11.89	13.93	39.18
JD2	0-15cm	ND	8.86	26.45	64.76	142.48
	15-30cm	ND	5.62	14.62	44.02	98.40
	30-45cm	ND	4.67	7.08	18.36	51.06
JD3	0-15cm	ND	9.79	42.38	30.67	99.17
	15-30cm	ND	7.56	22.01	24.74	70.32
	30-45cm	ND	3.68	7.31	16.03	52.54
UB1	0-15cm	ND	11.14	23.28	43.42	209.98
	15-30cm	ND	4.98	15.12	29.08	123.16
	30-45cm	ND	4.00	5.59	18.89	47.23
UB2	0-15cm	ND	11.11	25.03	38.84	282.35
	15-30cm	ND	6.04	17.81	28.38	157.28
	30-45cm	ND	4.00	9.44	11.06	62.84
UB3	0-15cm	ND	8.99	26.08	63.08	230.06
	15-30cm	ND	6.08	15.12	31.75	150.43
	30-45cm	ND	2.54	10.04	18.59	51.82
	AVERAGE	**ND**	**5.51**	**16.76**	**33.43**	**112.88**
CTR	0-15cm	ND	0.05	0.17	0.22	0.58
	15-30cm	ND	0.04	0.15	0.19	0.31
	30-45cm	ND	0.01	0.13	0.11	0.27
	AVERAGE	**ND**	**0.03**	**0.15**	**0.17**	**0.35**

4.2.1 Cadmium (Cd)

The concentration of Cd in the soils of this study were below the limitof detection of the instrument used in this study.

4.2.2 Arsenic (As)

The concentrations of Arsenic in these soil samples ranged from 1.02 to 11.16 mg kg^{-1} for all sites and depth with an average of 5.51 mg kg^{-1} while that of the control site ranged from 0.01 to 0.05 mg kg^{-1} with an average of 0.03 mg kg^{-1}.The highest concentration of As was found at site EF3 (0-15 depth) while the lowest concentration was observed at site NC3 (30-45 cm depth). The concentrations of As obtained in this study decrease with depth at all sites. The concentrations of As obtained in this study were higher than the Department of Petroleum Resources (DPR) target value of 1.0 mg kg^{-1} stipulated for Nigerian soils(DPR, 2002). The concentrations of As recorded in this study were higher than the range of not detected to 0.011 mg kg^{-1}reported by Ahaneku and Sadiq (2014) for Agricultural soils in Minna, Niger State Nigeria.

4.2.3 Lead (Pb)

In this study, lead was detected in all sites and depth at concentrations in the range of 5.59 to 42.38 mg kg^{-1} with an average of 16.76 mg kg^{-1}while that of the control site ranged from 0.13 to 0.17 mg kg^{-1} with an average of 0.15 mg kg^{-1}. The highest and lowest concentrations of Pb were observed at sites UB3 (0 – 15 cm depth) and UB1 (30 – 45 cm depth) respectively. The concentrations of Pb decreased with depth at all sites. The Department of Petroleum Resources (DPR) target value for Pb is 85 mg kg^{-1} (DPR, 2002). The concentration of Pb obtained in this study were lower than the DPR target value. The concentrations of Pb obtained in this study were similar to those reported for

Agricultural soils in Minna, Niger State, Nigeria (Ahaneku and Sadiq, 2014), farmland soils in urban fringe environment in Asaba, Delta State (Bassey et al., 2014), for soils of farmlands along a major highway in Delta State, Nigeria (Osakwe and Okolie, 2015) and tropical gricultural soils of Ago-Iwoye, Southwest, Nigeria (Adewuyi and Osobamiro, 2016). However, the concentrations of Pb obtained in this study were higher than those reported by Mohammed and Folorunsho (2015) and Olatunji et al. (2015) for farmlands in Makera area of Kaduna and arable agricultural soils in southwestern Nigeriarespectively.

4.2.4 Chromium

The concentrations of chromium in these soil samples ranged from 11.06 to 70.08 mg kg^{-1} with an average of 33.43 mg kg^{-1} at all sites and depth while that of the control site ranged from 0.11 to 0.22 mg kg^{-1} with an average of 0.17 mg kg^{-1}.. The highest concentration of Cr was found at site JD1 (0-15 cm depth) while the lowest concentration was found at site JD3 (30-45 cm depth). The concentrations of Cr decreased with depth at all sites. The concentrations of Cr obtained in this study were lower than the DPR target value of 100 mg kg^{-1} **(**DPR, 2002) and are comparable to values reported by Mohammed and Florunsho (2015) and Osakwe and Okolie (2015). The concentrations of Cr obtained in this study were however higher than those reported by Ahaneku and Sadiq (2014) and Bassey et al. (2014).

4.2.5 Zinc

The concentrations of Zn in these soils ranged from 39.18 to 282.35 mg kg^{-1} - with an average of 112.88 mg kg^{-1} while that of the control site ranged from 0.27 to 0.58 mg kg^{-1} with an average of 0.35 mg kg^{-1}. The highest and lowest concentrations of Zn were observed at the 0-15 cm depth of site UB2 and 30-45 cm depth of site JD130 respectively. The concentration of Zn in these soils decreased with depth. The concentration of Zn in 31% of these soil samples was higher than the 140 mgkg^{-1} DPR target value for Zn in soils (DPR, 2002). Similar concentrations of Zn in farmland soils have also been reported by Mohammed and Florunsho (2015) and Osakwe and Okolie (2015) while lower concentrations were reported by Ahaneku and Sadiq (2014), Bassey et al. (2014) and Olatunji et al. (2015).

4.3 Chemical Speciation of heavy metals in soil samples

4.3.1 Arsenic

The results of the speciation analysis of As are shown on Table 4.3 while the percentage of As in the various fractions as a function of the sum of As in the soil are shown in Figure 4.1.

Table 4.3: Concentrations (mg kg^{-1})and percentage of As in the different fractions

		Concentration (mg kg^{-1})							Percentage (%)					
SITES	DEPTH	F1	F2	F3	F4	F5	SUM	TM	F1	F2	F3	F4	F5	RECOVERY
NC1	0-15cm	0.32	0.57	1.10	1.84	2.48	6.31	6.51	5.07	9.03	17.43	29.16	39.30	96.93
	15-30cm	0.22	0.35	0.59	0.87	1.32	3.35	3.26	6.57	10.45	17.61	25.97	39.40	102.76
	30-45cm	0.11	0.22	0.13	0.25	0.46	1.17	1.09	9.40	18.80	11.11	21.37	39.32	107.34
NC2	0-15cm	0.86	1.50	1.15	1.73	2.07	7.31	6.99	11.76	20.52	15.73	23.67	28.32	104.58
	15-30cm	0.71	1.06	0.09	0.13	0.17	2.16	2.40	32.87	49.07	4.17	6.02	7.87	90.00
	30-45cm	0.24	0.74	0.02	0.03	0.06	1.09	1.21	22.02	67.89	1.83	2.75	5.50	90.08
NC3	0-15cm	0.49	0.82	0.57	0.84	1.10	3.82	4.13	12.83	21.47	14.92	21.99	28.80	92.49
	15-30cm	0.22	0.66	0.10	0.17	0.23	1.38	1.26	15.94	47.83	7.25	12.32	16.67	109.52
	30-45cm	0.18	0.57	0.03	0.05	0.09	0.92	1.02	19.57	61.96	3.26	5.43	9.78	90.20
EF1	0-15cm	0.34	0.88	0.86	1.07	2.56	5.71	5.48	5.95	15.41	15.06	18.74	44.83	104.20
	15-30cm	0.27	0.72	0.74	0.98	1.14	3.85	4.03	7.01	18.70	19.22	25.45	29.61	95.53
	30-45cm	0.15	0.53	0.51	0.97	0.95	3.11	3.20	4.82	17.04	16.40	31.19	30.55	97.19
EF2	0-15cm	0.54	0.93	0.39	0.83	1.92	4.61	5.01	11.71	20.17	8.46	18.00	41.65	92.02
	15-30cm	0.32	0.71	0.54	0.77	0.64	2.98	2.96	10.74	23.83	18.12	25.84	21.48	100.68
	30-45cm	0.18	0.54	0.36	0.44	0.15	1.67	1.56	10.78	32.34	21.56	26.35	8.98	107.05
EF3	0-15cm	0.54	0.89	2.15	4.11	4.33	12.02	11.16	4.49	7.40	17.89	34.19	36.02	107.71
	15-30cm	3.36	0.77	1.76	3.06	2.76	11.71	10.84	28.69	6.58	15.03	26.13	23.57	108.03
	30-45cm	1.59	0.44	1.09	1.84	1.89	6.85	7.15	23.21	6.42	15.91	26.86	27.59	95.80
JD1	0-15cm	0.81	1.77	1.74	2.98	2.62	9.92	10.04	8.17	17.84	17.54	30.04	26.41	98.80
	15-30cm	0.32	0.86	0.95	2.02	1.96	6.11	6.18	5.24	14.08	15.55	33.06	32.08	98.87
	30-45cm	0.21	0.62	0.66	1.25	1.35	4.09	3.98	5.13	15.16	16.14	30.56	33.01	102.76
JD2	0-15cm	1.07	1.33	1.58	2.01	2.62	8.61	8.86	12.43	15.45	18.35	23.34	30.43	97.18
	15-30cm	0.84	1.14	1.07	1.56	1.96	6.57	5.62	12.79	17.35	16.29	23.74	29.83	116.90
	30-45cm	0.32	0.73	0.86	1.01	1.35	4.27	4.67	7.49	17.10	20.14	23.65	31.62	91.43
JD3	0-15cm	0.91	1.30	0.86	3.47	3.54	10.08	9.79	9.03	12.90	8.53	34.42	35.12	102.96
	15-30cm	0.45	0.93	1.78	2.64	1.51	7.31	7.56	6.16	12.72	24.35	36.11	20.66	96.69
	30-45cm	0.21	0.48	1.07	1.07	0.96	3.79	3.68	5.54	12.66	28.23	28.23	25.33	102.99
UB1	0-15cm	0.93	1.53	1.97	3.83	2.58	10.84	11.14	8.58	14.11	18.17	35.33	23.80	97.31
	15-30cm	0.33	0.64	1.27	1.79	1.58	5.61	4.98	5.88	11.41	22.64	31.91	28.16	112.65
	30-45cm	0.23	0.52	0.85	1.08	1.30	3.98	4.00	5.78	13.07	21.36	27.14	32.66	99.50
UB2	0-15cm	0.84	1.09	1.86	3.91	3.07	10.77	11.11	7.80	10.12	17.27	36.30	28.51	96.94
	15-30cm	0.35	0.62	1.04	2.67	2.19	6.87	6.04	5.09	9.02	15.14	38.86	31.88	113.74
	30-45cm	0.24	0.45	0.93	1.28	0.98	3.88	4.00	6.19	11.60	23.97	32.99	25.26	97.00
UB3	0-15cm	0.43	0.78	1.54	2.69	3.50	8.94	8.99	4.81	8.72	17.23	30.09	39.15	99.44
	15-30cm	0.21	0.55	1.03	2.47	1.34	5.60	6.08	3.75	9.82	18.39	44.11	23.93	92.11
	30-45cm	0.14	0.34	1.17	0.39	0.69	2.73	2.54	5.13	12.45	42.86	14.29	25.27	107.48
	Min	0.11	0.22	0.02	0.03	0.06	0.92	1.02	3.75	6.42	1.83	2.75	5.50	90.00
	Max	3.36	1.77	2.15	4.11	4.33	12.02	11.16	32.87	67.89	42.86	44.11	44.83	116.90
	Average	0.54	0.79	0.96	1.61	1.65	5.56	5.51	10.23	19.18	16.75	25.99	27.84	100.47

F1 = Exchangeable fraction; F2 = Carbonates fraction; F3 = Fe-Mn oxide fraction; F4 = Organic fraction; F5 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil

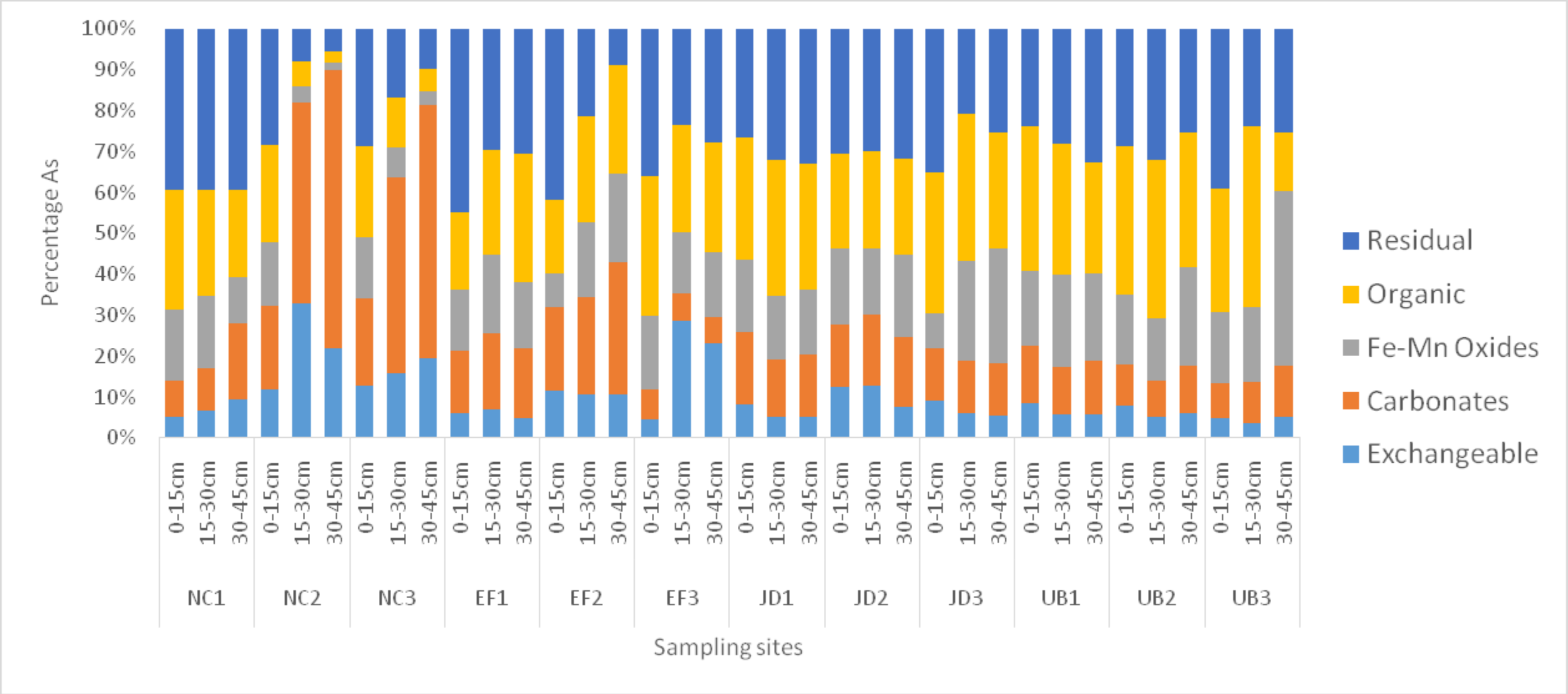

Figure 4.1: Percentage of As in the various fractions as a function of the sum of As concentration in the soils

Arsenic existed mainly in the residual and organic fractions in the soil samples in this study. The percentage of As in the residual fraction ranged from 5.50 to 44.83 % with an average of 27.84 % while the percentage of As in the organic fraction ranged from 2.75 to 44.11 % with an average of 25.99 %. This results corroborates the findings of Ashraf et al. (2012). The next predominant species of As is the carbonate fraction. The percentage of As in the carbonate fraction ranged from 6.42 to 67.89 % with an average of 19.18 %. The significant amount of As in the carbonate fraction suggest that As in these soils may be immobilized under reducing condition. High percentage of As in the carbonate fraction have also been reported in literatures (Ashraf et al., 2012; Yang et al., 2016). The percentage of As in the Fe-Mn oxide fraction ranged from 1.83 to 42.86 % with an average of 16.75 %. The result of this study is also similar to that of Ashraf et al. (2012) and Yang et al. (2016). Significant amount of As was found in the exchangeable fraction considering the toxicity of As.The percentage of As in the exchangeable fractions ranged from 3.75 to 32.87 % with an average of 10.23 %. This result implies that a significant amount of As in these soils will be readily mobile which may pose human health risk. Similar result were also reported in literatures (Ashraf *et al.*, 2012; Yang *et al.*, 2016).

4.3.2 Lead

The results of the speciation analysis of Pb are shown on Table 4.4while the percentage of Pb in the various fractions as a function of the sum of Pb in the soil are shown in Figure 4.2.

Table 4.4: Concentrations (mg kg^{-1}) and percentage of Pb in the different fractions

		Concentration (mg kg^{-1})							Percentage (%)					
SITES	DEPTH	F1	F2	F3	F4	F5	SUM	TM	F1	F2	F3	F4	F5	RECOVERY
NC1	0-15cm	2.13	3.43	2.63	3.74	4.96	16.89	18.10	12.61	20.31	15.57	22.14	29.37	93.31
	15-30cm	1.37	2.44	1.56	2.37	3.71	11.45	11.85	11.97	21.31	13.62	20.70	32.40	96.62
	30-45cm	0.91	1.75	1.09	1.95	2.07	7.77	7.08	11.71	22.52	14.03	25.10	26.64	109.75
NC2	0-15cm	1.86	3.93	2.19	3.27	4.48	15.73	16.11	11.82	24.98	13.92	20.79	28.48	97.64
	15-30cm	1.19	2.66	1.57	2.18	3.43	11.03	10.81	10.79	24.12	14.23	19.76	31.10	102.04
	30-45cm	0.89	1.06	1.06	1.75	2.91	7.67	7.14	11.60	13.82	13.82	22.82	37.94	107.42
NC3	0-15cm	1.54	2.24	2.11	3.27	5.66	14.82	14.02	10.39	15.11	14.24	22.06	38.19	105.71
	15-30cm	1.09	2.12	1.55	2.15	4.72	11.63	10.95	9.37	18.23	13.33	18.49	40.58	106.21
	30-45cm	0.83	1.25	1.09	1.86	3.58	8.61	9.45	9.64	14.52	12.66	21.60	41.58	91.11
EF1	0-15cm	2.13	4.47	2.95	5.47	7.78	22.80	20.40	9.34	19.61	12.94	23.99	34.12	111.76
	15-30cm	1.37	3.67	2.07	4.26	6.14	17.51	17.31	7.82	20.96	11.82	24.33	35.07	101.16
	30-45cm	0.98	2.55	0.88	2.75	4.55	11.71	11.64	8.37	21.78	7.51	23.48	38.86	100.60
EF2	0-15cm	3.47	5.98	3.13	6.39	8.97	27.94	28.05	12.42	21.40	11.20	22.87	32.10	99.61
	15-30cm	2.14	5.29	0.97	1.95	2.60	12.95	12.98	16.53	40.85	7.49	15.06	20.08	99.77
	30-45cm	1.23	2.85	0.87	1.26	1.94	8.15	7.47	15.09	34.97	10.67	15.46	23.80	109.10
EF3	0-15cm	2.17	3.32	5.74	11.47	16.51	39.21	40.08	5.53	8.47	14.64	29.25	42.11	97.83
	15-30cm	1.28	2.50	2.98	6.32	9.20	22.28	24.01	5.75	11.22	13.38	28.37	41.29	92.79
	30-45cm	0.93	1.56	1.39	3.41	5.26	12.55	11.92	7.41	12.43	11.08	27.17	41.91	105.29
JD1	0-15cm	1.97	3.74	4.25	7.65	10.62	28.23	23.69	6.98	13.25	15.05	27.10	37.62	119.16
	15-30cm	1.09	2.08	2.63	4.75	9.67	20.22	21.04	5.39	10.29	13.01	23.49	47.82	96.10
	30-45cm	0.09	1.46	1.74	3.21	5.79	12.29	11.89	0.73	11.88	14.16	26.12	47.11	103.36
JD2	0-15cm	2.45	5.59	2.59	6.78	9.44	26.85	26.45	9.12	20.82	9.65	25.25	35.16	101.51
	15-30cm	1.38	2.81	1.67	3.38	5.66	14.90	14.62	9.26	18.86	11.21	22.68	37.99	101.92
	30-45cm	0.95	1.62	0.89	1.39	2.12	6.97	7.08	13.63	23.24	12.77	19.94	30.42	98.45
JD3	0-15cm	2.19	4.32	5.57	12.74	17.46	42.28	42.38	5.18	10.22	13.17	30.13	41.30	99.76
	15-30cm	1.56	2.85	2.29	5.19	8.26	20.15	22.01	7.74	14.14	11.36	25.76	40.99	91.55
	30-45cm	1.01	1.85	1.07	2.03	2.36	8.32	7.31	12.14	22.24	12.86	24.40	28.37	113.82
UB1	0-15cm	2.08	4.09	3.49	6.87	8.73	25.26	23.28	8.23	16.19	13.82	27.20	34.56	108.51
	15-30cm	1.47	2.23	1.87	3.24	5.32	14.13	15.12	10.40	15.78	13.23	22.93	37.65	93.45
	30-45cm	1.05	1.58	0.94	1.05	1.47	6.09	5.59	17.24	25.94	15.44	17.24	24.14	108.94
UB2	0-15cm	2.85	5.05	2.77	5.91	8.73	25.31	25.03	11.26	19.95	10.94	23.35	34.49	101.12
	15-30cm	1.27	2.47	2.13	4.26	7.70	17.83	17.81	7.12	13.85	11.95	23.89	43.19	100.11
	30-45cm	0.98	1.62	0.85	2.17	4.25	9.87	9.44	9.93	16.41	8.61	21.99	43.06	104.56
UB3	0-15cm	2.14	4.82	2.74	6.29	9.93	25.92	26.08	8.26	18.60	10.57	24.27	38.31	99.39
	15-30cm	1.25	3.05	1.86	3.47	5.55	15.18	15.12	8.23	20.09	12.25	22.86	36.56	100.40
	30-45cm	0.86	1.77	1.05	2.74	3.30	9.72	10.04	8.85	18.21	10.80	28.19	33.95	96.81
	Min	0.09	1.06	0.85	1.05	1.47	6.09	5.59	0.73	8.47	7.49	15.06	20.08	91.11
	Max	3.47	5.98	5.74	12.74	17.46	42.28	42.38	17.24	40.85	15.57	30.13	47.82	119.16
	Average	1.50	2.95	2.12	4.14	6.25	16.95	16.76	9.66	18.79	12.42	23.34	35.79	101.85

F1 = Exchangeable fraction; F2 = Carbonates fraction; F3 = Fe-Mn oxide fraction; F4 = Organic fraction; F5 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil

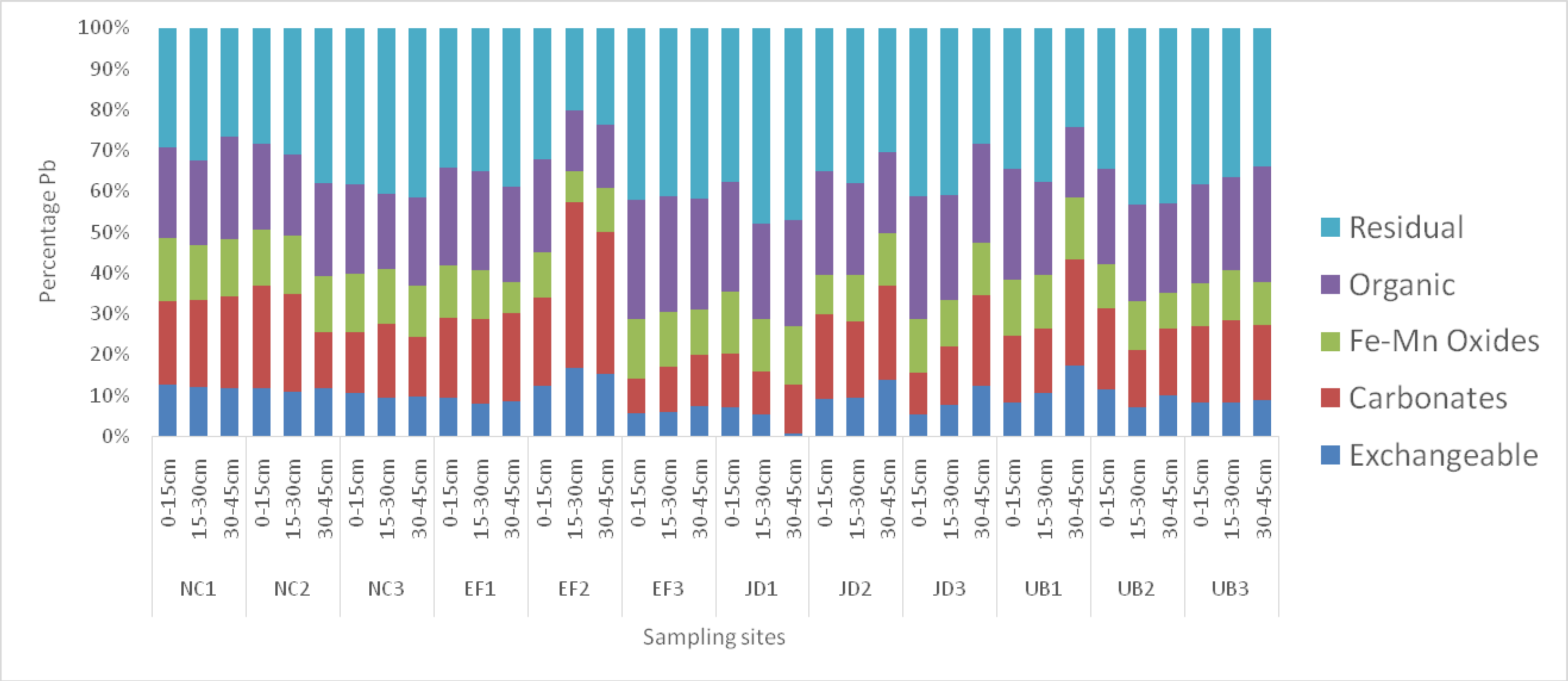

Figure 4.2: Percentage of Pb in the various fractions as a function of the sum of Pb concentration in the soils

Lead partitioned predominantly in the residual fraction (Figure 4.2). The percentage of Pb in the residual fraction ranged from 20.08 to 47.82 % with an average of 35.79 %. The high value may not pose any threat to human and his environment considering the fact that metals in this form are not readily released into solution but incorporated in the crystal lattices of clay minerals and silicate (Ajala and Onwukeme, 2012). The association of Pb with the residual fraction have been reported in the literature (Iwegbue *et al*., 2009; Ajala and Onwukeme, 2012; Shaheen et al., 2013). The next predominant fraction was the organic fraction. The percentage of Pb in the organic fraction ranged from 15.06 to 30.13 % with an average of 23.34 %. The high distribution of Pb in this fraction is as a result of the strong complexes lead formed with humic minerals (Ajala *et al*., 2014). The carbonate fraction followed the organic fraction. The percentage of lead in the carbonate fraction ranged from 8.47 to 40.85 % with an average of 18.79 %. Similar results have been reported by Ajala and Onwukeme (2012). The next dominant fraction of Pb in these soil profiles is Fe–Mn oxide fraction. The percentage of Pb in the Fe–Mn oxide fraction range from 7.49 to 15.57 % with an average of 12.42 %. Higher amount of Pb in the Fe–Mn oxide fraction was also reported by Iwegbue (2007) and Iwegbue (2011). The exchangeable form of Pb was the next important fraction with a range of 0.73 to 17.24 % with an average of 9.66 % of Pb. Metals in this fraction are soluble and easily released into biota. The accumulation of Pb in the exchangeable and carbonate fractions which are known as the major contributors to the mobility and bioavaiability of metals in soil call for concern as Pb is one of the metal that constitutes the widest possible health risk to humans through the plant uptake dietary route (Papafilippaki *et al*., 2008; Ajala *et al*., 2014).

4.3.3 Chromium

The results of the speciation analysis of Cr are shown on Table 4.5while the percentage of Cr in the various fractions as a function of the sum of Cr in the soil are shown in Figure 4.3.

Table 4.5: Concentrations (mg kg^{-1}) and percentage of Cr in the different fractions

		Concentration (mg kg^{-1})							Percentage (%)					
SITES	**DEPTH**	**F1**	**F2**	**F3**	**F4**	**F5**	**SUM**	**TM**	**F1**	**F2**	**F3**	**F4**	**F5**	**RECOVERY**
NC1	0-15cm	1.74	2.98	9.89	17.54	23.01	55.16	56.1	3.15	5.40	17.93	31.80	41.72	98.32
	15-30cm	1.22	2.32	5.74	13.38	18.92	41.58	42.06	2.93	5.58	13.80	32.18	45.50	98.86
	30-45cm	0.96	1.12	2.86	9.71	15.1	29.75	28.37	3.23	3.76	9.61	32.64	50.76	104.86
NC2	0-15cm	1.15	1.88	8.54	14.54	19.55	45.66	44.76	2.52	4.12	18.70	31.84	42.82	102.01
	15-30cm	0.97	1.72	2.78	6.98	9.87	22.32	20.52	4.35	7.71	12.46	31.27	44.22	108.77
	30-45cm	0.83	1.25	1.35	3.27	7.19	13.89	13.94	5.98	9.00	9.72	23.54	51.76	99.64
NC3	0-15cm	2.35	4.7	10.56	16.49	20.38	54.48	54.88	4.31	8.63	19.38	30.27	37.41	99.27
	15-30cm	1.19	3.14	5.48	9.72	13.59	33.12	33.04	3.59	9.48	16.55	29.35	41.03	100.24
	30-45cm	0.89	1.96	2.76	5.74	10.9	22.25	20.5	4.00	8.81	12.40	25.80	48.99	108.54
EF1	0-15cm	1.99	3.27	9.59	17.87	21.96	54.68	60	3.64	5.98	17.54	32.68	40.16	91.13
	15-30cm	1.18	1.56	3.76	10.39	16.73	33.62	33.82	3.51	4.64	11.18	30.90	49.76	99.41
	30-45cm	1.01	1.38	2.18	7.24	10.96	22.77	24.07	4.44	6.06	9.57	31.80	48.13	94.60
EF2	0-15cm	1.98	2.88	8.12	14.98	18.3	46.26	40.99	4.28	6.23	17.55	32.38	39.56	112.86
	15-30cm	1.21	1.47	4.21	9.63	12.55	29.07	28.86	4.16	5.06	14.48	33.13	43.17	100.73
	30-45cm	0.87	1.23	2.37	5.28	9.46	19.21	19.05	4.53	6.40	12.34	27.49	49.25	100.84
EF3	0-15cm	1.23	1.72	6.52	10.75	12.57	32.79	33.01	3.75	5.25	19.88	32.78	38.33	99.33
	15-30cm	1.01	1.25	2.97	6.38	10.46	22.07	22.46	4.58	5.66	13.46	28.91	47.39	98.26
	30-45cm	0.89	1.06	1.78	3.57	6.43	13.73	13.44	6.48	7.72	12.96	26.00	46.83	102.16
JD1	0-15cm	3.78	6.63	11.75	21.27	25.62	69.05	70.08	5.47	9.60	17.02	30.80	37.10	98.53
	15-30cm	1.86	4.55	5.96	15.85	21.67	49.89	47.86	3.73	9.12	11.95	31.77	43.44	104.24
	30-45cm	1.07	2.19	1.87	3.87	5.62	14.62	13.93	7.32	14.98	12.79	26.47	38.44	104.95
JD2	0-15cm	3.89	5.94	10.54	19.48	26.15	66	64.76	5.89	9.00	15.97	29.52	39.62	101.91
	15-30cm	1.87	3.06	6.39	13.74	18.36	43.42	44.02	4.31	7.05	14.72	31.64	42.28	98.64
	30-45cm	1.08	1.94	2.18	4.96	8.37	18.53	18.36	5.83	10.47	11.76	26.77	45.17	100.93
JD3	0-15cm	1.19	1.56	6.79	11.58	14.64	35.76	30.67	3.33	4.36	18.99	32.38	40.94	116.60
	15-30cm	0.98	1.09	3.58	7.57	10.69	23.91	24.74	4.10	4.56	14.97	31.66	44.71	96.65
	30-45cm	0.74	0.94	1.97	4.38	7.16	15.19	16.03	4.87	6.19	12.97	28.83	47.14	94.76
UB1	0-15cm	3.16	5.33	5.48	11.75	16.73	42.45	43.42	7.44	12.56	12.91	27.68	39.41	97.77
	15-30cm	1.18	1.72	3.26	8.63	13.3	28.09	29.08	4.20	6.12	11.61	30.72	47.35	96.60
	30-45cm	0.86	1.25	2.17	5.54	9.21	19.03	18.89	4.52	6.57	11.40	29.11	48.40	100.74
UB2	0-15cm	1.57	2.19	7.63	11.18	16.21	38.78	38.84	4.05	5.65	19.68	28.83	41.80	99.85
	15-30cm	1.11	1.94	3.47	7.39	11.92	25.83	28.38	4.30	7.51	13.43	28.61	46.15	91.01
	30-45cm	0.87	1.41	1.19	2.48	4.7	10.65	11.06	8.17	13.24	11.17	23.29	44.13	96.29
UB3	0-15cm	1.36	2.72	11.38	19.74	25.63	60.83	63.08	2.24	4.47	18.71	32.45	42.13	96.43
	15-30cm	1.09	1.88	6.37	11.75	14.62	35.71	31.75	3.05	5.26	17.84	32.90	40.94	112.47
	30-45cm	0.86	1.03	2.73	5.37	9.16	19.15	18.59	4.49	5.38	14.26	28.04	47.83	103.01
	Min	0.74	0.94	1.19	2.48	4.7	10.65	11.06	2.24	3.76	9.57	23.29	37.10	91.01
	Max	3.89	6.63	11.75	21.27	26.15	69.05	70.08	8.17	14.98	19.88	33.13	51.76	116.60
	Average	1.42	2.34	5.17	10.28	14.38	33.59	33.43	4.46	7.15	14.49	29.90	43.99	100.87

F1 = Exchangeable fraction; F2 = Carbonates fraction; F3 = Fe-Mn oxide fraction; F4 = Organic fraction; F5 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil

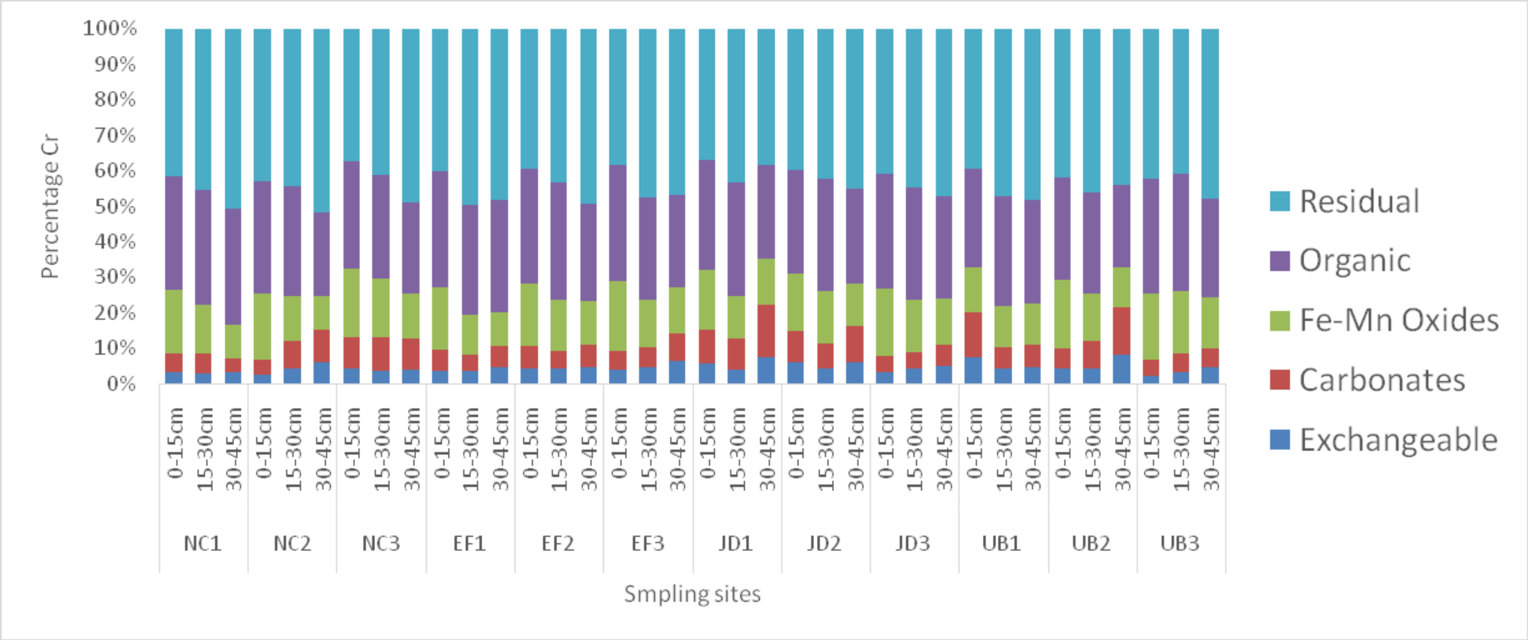

Figure 4.3: Percentage of Cr in the various fractions as a function of the sum of Cr concentration in the soils

In these soil profiles, the dominant species of Cr is the residual fraction (Figure 4.3). The percentage of Cr in the residual fraction ranged from 37.10 to 51.76% with an average of 43.99 %. This is similar to the report of other researchers (Osakwe, 2012; Iwegbue, 2007; Kotoky *et al.*, 2003). The amount of Cr in the residual fraction indicates that Cr is not available for plant uptakes or biota in these soil (Iwegbue, 2007; Osakwe, 2012). The low solubility of chromium in these soils may be attributed to the poorly soluble hydroxo complexes where Cr (iv) forms oxyanion such as CrO_4^{2-} and $Cr_2O_7^{2-}$ and are adsorbed minimally to negatively charged soil particles (Iwegbue, 2011; Osakwe, 2012). The organic bound fraction followed the residual fraction with a range of 23.29 to 33.13% with an average of 29.9 %. Cr in the organic bound fraction might be due to its strong affinity for organic matter. However, according to Kotoky *et al.* (2003) the existence of Cr in the organic bound fraction results from the existing physiochemical conditions which include the pH and total organic carbons. The percentage of Cr in the Fe–Mn oxide ranged from 9.57 to 19.88 % with an average of 14.49 %. This result is in agreement with those reported by Kotoky *et al.* (2003). The carbonates fraction ranged from 3.76 to 14.98 % with an average of 7.15 % while the exchangeable fraction constituted 2.24 to 8.17% with an average of 4.46 %. Similar results of Cr in carbonates and exchangeable fractions have also been reported in literatures (Kotoky *et al.*, 2003; Iwegbue, 2011; Osakwe, 2012).

4.3.4 Zinc

The resultsof the speciation analysis of Zn are shown on Table 4.6while the percentage of Zn in the various fractions as a function of the sum of Zn in the soil are shown in Figure 4.4.

Table 4.6: Concentrations (mg kg^{-1})and percentage of Zn in the different fractions

		Concentration (mg kg^{-1})							Percentage (%)					
SITES	DEPTH	F1	F2	F3	F4	F5	SUM	TM	F1	F2	F3	F4	F5	RECOVERY
NC1	0-15cm	3.29	5.37	21.27	39.16	104.88	173.97	169.79	1.89	3.09	12.23	22.51	60.29	102.46
	15-30cm	1.86	3.29	13.45	21.74	86.87	127.21	131.71	1.46	2.59	10.57	17.09	68.29	96.58
	30-45cm	1.03	1.58	4.95	13.64	39.47	60.67	64.85	1.70	2.60	8.16	22.48	65.06	93.55
NC2	0-15cm	4.19	6.74	17.86	28.39	89.9	147.08	161.00	2.85	4.58	12.14	19.30	61.12	91.35
	15-30cm	1.87	3.91	12.71	19.86	77.83	116.18	110.83	1.61	3.37	10.94	17.09	66.99	104.83
	30-45cm	1.06	2.15	5.38	14.34	44.89	67.82	66.24	1.56	3.17	7.93	21.14	66.19	102.39
NC3	0-15cm	4.79	7.36	21.5	32.78	89.9	156.33	149.63	3.06	4.71	13.75	20.97	57.51	104.48
	15-30cm	2.32	4.71	13.71	23.45	68.97	113.16	116.36	2.05	4.16	12.12	20.72	60.95	97.25
	30-45cm	1.09	2.82	5.89	15.26	34.3	59.36	61.02	1.84	4.75	9.92	25.71	57.78	97.28
EF1	0-15cm	5.38	8.74	23.96	41.83	74.92	154.83	156.34	3.47	5.64	15.48	27.02	48.39	99.03
	15-30cm	3.26	5.82	11.87	32.44	59.93	113.32	117.20	2.88	5.14	10.47	28.63	52.89	96.69
	30-45cm	1.19	2.44	5.95	21.48	44.64	75.7	79.04	1.57	3.22	7.86	28.38	58.97	95.77
EF2	0-15cm	5.76	7.94	19.76	43.49	74.98	151.93	143.89	3.79	5.23	13.01	28.63	49.35	105.59
	15-30cm	2.85	4.76	13.58	33.76	59.93	114.88	110.14	2.48	4.14	11.82	29.39	52.17	104.30
	30-45cm	1.17	2.67	8.78	20.54	39.74	72.9	72.04	1.60	3.66	12.04	28.18	54.51	101.19
EF3	0-15cm	5.95	8.56	23.86	45.89	74.95	159.21	163.12	3.74	5.38	14.99	28.82	47.08	97.60
	15-30cm	3.36	5.72	12.35	29.89	44.97	96.29	94.96	3.49	5.94	12.83	31.04	46.70	101.40
	30-45cm	1.59	2.38	5.72	18.63	29.96	58.28	56.85	2.73	4.08	9.81	31.97	51.41	102.52
JD1	0-15cm	4.73	7.82	17.64	31.48	44.95	106.62	104.28	4.44	7.33	16.54	29.53	42.16	102.24
	15-30cm	1.86	3.93	9.78	18.66	29.96	64.19	66.01	2.90	6.12	15.24	29.07	46.67	97.24
	30-45cm	1.21	2.17	4.59	13.56	18.79	40.32	39.18	3.00	5.38	11.38	33.63	46.60	102.91
JD2	0-15cm	4.56	6.94	22.17	41.29	59.92	134.88	142.48	3.38	5.15	16.44	30.61	44.42	94.67
	15-30cm	2.28	3.47	14.38	28.66	44.95	93.74	98.40	2.43	3.70	15.34	30.57	47.95	95.26
	30-45cm	1.12	2.29	6.85	14.58	26.74	51.58	51.06	2.17	4.44	13.28	28.27	51.84	101.02
JD3	0-15cm	3.77	5.84	10.73	28.4	44.95	93.69	99.17	4.02	6.23	11.45	30.31	47.98	94.47
	15-30cm	2.12	3.63	8.65	21.76	35.65	71.81	70.32	2.95	5.06	12.05	30.30	49.64	102.12
	30-45cm	1.34	2.17	6.38	15.67	29.86	55.42	52.54	2.42	3.92	11.51	28.27	53.88	105.48
UB1	0-15cm	5.48	7.21	27.63	58.97	164.82	264.11	209.98	2.07	2.73	10.46	22.33	62.41	125.78
	15-30cm	3.27	5.44	18.76	31.74	59.92	119.13	123.16	2.74	4.57	15.75	26.64	50.30	96.73
	30-45cm	1.54	3.26	7.29	13.92	26.82	52.83	47.23	2.92	6.17	13.80	26.35	50.77	111.86
UB2	0-15cm	4.76	6.98	25.97	59.68	164.54	261.93	282.35	1.82	2.66	9.91	22.78	62.82	92.77
	15-30cm	2.18	4.37	16.85	38.74	88.64	150.78	157.28	1.45	2.90	11.18	25.69	58.79	95.87
	30-45cm	1.15	2.19	7.93	18.27	37.48	67.02	62.84	1.72	3.27	11.83	27.26	55.92	106.65
UB3	0-15cm	5.37	8.47	21.86	43.74	134.85	214.29	230.06	2.51	3.95	10.20	20.41	62.93	93.15
	15-30cm	2.49	4.59	17.55	29.64	95.79	150.06	150.43	1.66	3.06	11.70	19.75	63.83	99.75
	30-45cm	1.21	2.38	6.67	14.74	29.79	54.79	51.82	2.21	4.34	12.17	26.90	54.37	105.73
	Min	1.03	1.58	4.59	13.56	18.79	40.32	39.18	1.45	2.59	7.86	17.09	42.16	91.35
	Max	5.95	8.74	27.63	59.68	164.82	264.11	282.35	4.44	7.33	16.54	33.63	68.29	125.78
	Average	2.85	4.73	13.73	28.34	63.32	112.95	112.88	2.52	4.35	12.12	26.05	54.97	100.50

F1 = Exchangeable fraction; F2 = Carbonates fraction; F3 = Fe-Mn oxide fraction; F4 = Organic fraction; F5 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil

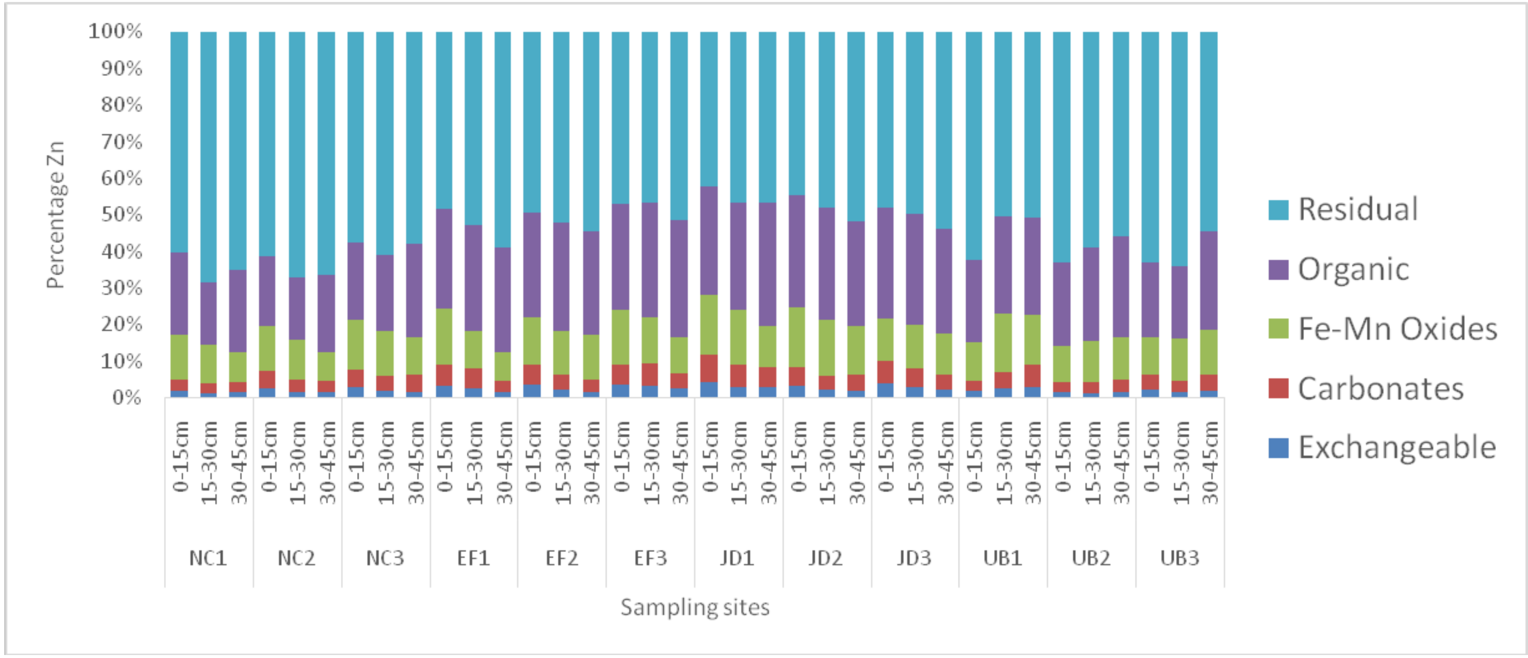

Figure 4.4: Percentage of Zn in the various fractions as a function of the sum of Zn concentration in the soils

The speciation of Zn followed the order Residual >Organic > Fe–Mn oxides > Carbonate >Exchangeable (Figure 4.4). The percentage of Zn in the residual fraction ranged from 42. 16 to 68.29 % with an average of 54.97 %. The dominance of the residual fraction is an indication that Zn is controlled by parent materials in these soil profiles (Moral *et al.*, 2005; Iwegbue, 2007). This results is in agreement with the result of other researchers (Osakwe, 2012; Moral *et al.*, 2005). The percentage of Zn in the organic fraction ranged from 17.09 to 33.63 % with an average of 26.05 %.This may be due to relatively strong co-ordination of zinc to organic matter. Zinc constituted 7.86 to 16.54 % of the Fe-Mn fraction with an average of 12.12 % while the percentage of Zn in the carbonate fraction ranged from 2.59 to 7.33 % with an average of 4.35 %. The carbonate-associated zinc is due to the relatively high stability constant of $ZnCO_3$ as well as its characteristic co-precipitation with $CaCO_3$ (Iwegbue, 2007; Iwegbue, 2011). The association of zinc with the Fe–Mn and carbonate fractions implies that zinc can be easily mobilized and is bioavailable to the biotic community when the pH and redox conditions of the soil changes (Liet al., 2001; Iwegbue, 2011). The percentage of Zn in the exchangeable fraction ranged from 1.45 to 4.44 % with an average of 2.52 %.Relatively low percentages of zinc were observed in the exchangeable fraction in the soils. The low percentages of zinc in the exchangeable fraction may be due to the fact that zinc can be easily absorbed and utilized by organisms in the environment. These results are similar to those reported by Iwegbue (2011).

4.4 Heavy metals mobility in the soils

In any sequential extraction procedure The early fractions are the most mobile and bioavailable fractions in a sequential extraction procedure. Therefore, the mobility factor value gives the relative mobility and biological availability of metals in soil. In this study, the mobility factor of the heavy metals was calculated using the equation;

$$Mobility\ Factor = \frac{F1 + F2}{F1 + F2 + F3 + F4 + F5} \times 100$$

Where, F1 = Exchangeable fraction; F2 = Carbonates fraction; F3 = Fe-Mn oxide fraction; F4 = Organic fraction; F5 = Residual fraction

High mobility factor values have been interpreted as evidence of relatively high reactivity, high lability and high biological availability of heavy metals in soil (Kabala and Singh, 2001; Osakwe, 2012). The results of the mobility factor of heavy metals in this study are showed on Table4.7.

Table 4.7: Mobility factor of heavy metals in soil samples

SITES	DEPTH	As	Pb	Cr	Zn
NC1	0-15cm	14.10	32.92	8.56	4.98
	15-30cm	17.01	33.28	8.51	4.05
	30-45cm	28.21	34.23	6.99	4.30
NC2	0-15cm	32.28	36.81	6.64	7.43
	15-30cm	81.94	34.90	12.05	4.98
	30-45cm	89.91	25.42	14.97	4.73
NC3	0-15cm	34.29	25.51	12.94	7.77
	15-30cm	63.77	27.60	13.07	6.21
	30-45cm	81.52	24.16	12.81	6.59
EF1	0-15cm	21.37	28.95	9.62	9.12
	15-30cm	25.71	28.78	8.15	8.01
	30-45cm	21.86	30.15	10.50	4.80
EF2	0-15cm	31.89	33.82	10.51	9.02
	15-30cm	34.56	57.37	9.22	6.62
	30-45cm	43.11	50.06	10.93	5.27
EF3	0-15cm	11.90	14.00	9.00	9.11
	15-30cm	35.27	16.97	10.24	9.43
	30-45cm	29.64	19.84	14.20	6.81
JD1	0-15cm	26.01	20.23	15.08	11.77
	15-30cm	19.31	15.68	12.85	9.02
	30-45cm	20.29	12.61	22.30	8.38
JD2	0-15cm	27.87	29.94	14.89	8.53
	15-30cm	30.14	28.12	11.35	6.13
	30-45cm	24.59	36.87	16.30	6.61
JD3	0-15cm	21.92	15.40	7.69	10.26
	15-30cm	18.88	21.89	8.66	8.01
	30-45cm	18.21	34.38	11.06	6.33
UB1	0-15cm	22.69	24.43	20.00	4.80
	15-30cm	17.29	26.19	10.32	7.31
	30-45cm	18.84	43.19	11.09	9.09
UB2	0-15cm	17.92	31.21	9.70	4.48
	15-30cm	14.12	20.98	11.81	4.34
	30-45cm	17.78	26.34	21.41	4.98
UB3	0-15cm	13.53	26.85	6.71	6.46
	15-30cm	13.57	28.33	8.32	4.72
	30-45cm	17.58	27.06	9.87	6.55
	Min	11.90	12.61	6.64	4.05
	Max	89.91	57.37	22.30	11.77
	Average	29.41	28.46	11.62	6.86

The potential mobility of the metals followed the order As>Pb> Cr > Zn. The mobility factor values of the heavy metals in this study ranged from 11.90 to 89.91, 12.61 to 57.37, 6.64 to 22.30 and 4.05 to 11.77 for As, Pb, Cr and Zn respectively. Similar results have be reported by Ashraf et al. (2012). The average mobility values were 29.41, 28.46, 11.62 and 6.86 for As, Pb, Cr and Zn respectively. The average mobility value of As and Pb were greater than 20 which indicates that changes in the physicochemical conditions of the soil may lead to significant remobilization of As and Pb in these soils. This is of great concern as Arsenic and Pb are very toxic and constitute the widest possible health risk to humans through the plant uptake dietary route (Papafilippaki *et al*., 2008; Ajala *et al*., 2014).

CHAPTER FIVE
SUMMARY AND CONCLUSION

5.1 Summary of major findings

1. The concentrations of metals ranged from 1.02 to 11.16mg kg^{-1}mg kg^{-1}, 5.59 to 42.38mg kg^{-1}, 11.06 to 70.08mg kg^{-1} and 39.18 to 182.35 mg kg^{-1} for As, Pb, Cr and Zn respectively while the concentration of Cd in the study area was below the detection limit of the instrument.
2. The concentrations of all the heavy metals decreased with depth in all the sites.
3. The farmland soils around the Warri Refinery were polluted with Arsenic as they had concentrations higher than the DPR target value.
4. The residual fraction was the predominant fraction of all the heavy metals.
5. The speciation of the As and Pb in the farmland soils around the Warri Refineryfollowed the order: residual fraction > organic fraction > carbonate fraction >Fe-Mn oxide fraction > exchangeable fraction while that of Cr and Zn followed the order: residual fraction > organic fraction > Fe-Mn oxide fraction > carbonate fraction > exchangeable fraction
6. The potential mobility and bioavailability of the heavy metals in these soils followed the order: As > Pb > Cr > Zn.
7. The average mobility value of As and Pb were greater than 20 which indicates that changes in the physicochemical conditions of the soil may lead to significant remobilization of As and Pb in these soils and as such pose health risk to humans through the plant uptake dietary route.

5.2 Conclusion and Recommendation

This study has demonstrated the chemical speciation and bioavailability of some selected heavy metals in farmland soils around Warri Refinery. The chemical speciation of the heavy metals indicated that residual and organic fractions were the predominant forms of the heavy metals in these soils even though the carbonate and exchangeable fractions contained an appreciable portion of As and Pb. The present study indicates that As and Pb pose an environmental and health risk considering their relatively high mobility factor values.It is however recommended that the sites be continuously monitored because of the deleterious health effects of exposure to heavy metal pollution.

5.3 Contributions to knowledge

The contributions to knowledge of this study are that the study;

1. showed that the farmland soils around the Warri Refinery are contaminated by heavy metals, with Arsenic having the highest impact since it had concentrations higher than the DPR target value.
2. identified and quantified the chemical species of the heavy metals thereby providing information on the bioavailability of the heavy metals in the soils.
3. revealed that the speciation of the As and Pb the farmland soils around the Warri Refineryfollowed the order:residual fraction > organic fraction > carbonate fraction >Fe-Mn oxide fraction > exchangeable fraction while that of Cr and Zn followed the order: residual fraction > organic fraction > Fe-Mn oxide fraction > carbonate fraction > exchangeable fraction.
4. revealed that the potential mobility and bioavailability of the heavy metals in these soils followed the order: As > Pb > Cr > Zn.
5. showed that the mobility and bioavailability of As and Pb is of great health concern as Arsenic and Pb are very toxic and constitutes the widest possible health risk to humans through the plant uptake dietary route

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