DETERMINATION OF PHYSICOCHEMICAL AND HEAVY METAL CONTENT OF SOIL AROUND THE VICINITY OF SELECTED INDUSTRIES IN KADUNA METROPOLIS

The soaring trend of environmental contamination by heavy metals is a global issue. The continual monitoring of soils around industrial areas becomes necessary. The present study focused on the physicochemical and heavy metal concentration in soil around the vicinity of selected industries in Kaduna metropolis. The mean pH, electrical conductivity, % organic matter, % sand, % clay and % silt obtained were 7.16±0.35, 362.60 ±10.7µS/cm, 2.92±0.50, 76.50±0.81, 17.79±5.51 and 6.13±1.65 respectively. The mean concentrations of the heavy metals investigated ranged between 26.89±0.36 – 77.18±0.40 µg/g for Pb, 29.25±0.7 – 44.20±0.35µg/g for Cr, ND – 1.5±0.02µg/g for Cd, 134.63±1.10 – 217.96±0.16 µg/g for Zn, 9.58±0.7–74.45±0.20µg/g for Cu, 92.14±0.20 – 200.8±0.31 µg/g for Mn and 1185.80±4.66 – 2488.00± 2.37 µg/g for Fe respectively. The highest concentration of Cr in the sampling areas was obtained at the vicinity of textile industry. The concentration of Fe was much higher than those of other elements. Cd was not detected in some of the soil samples. The concentrations of the metals were in the order Cd<Cu<Cr<Pb<Mn<Zn<Fe. The results of geoaccumulation index and enrichment factor showed that the soils were moderately contaminated with most of the metals investigated. The concentrations of the metals examined were significantly higher than the control, which also implied contamination due to anthropogenic contribution. Inter-elemental correlation matrix showed significant positive correlation of Pb with Cr and Mn, but negative correlation with Cd. Pb, Cd and Cu also showed a significant positive correlation with total organic matter of soil. Planned monitoring of the discharge of industrial effluents into the environment as well as avoidance of agricultural activities around the vicinity of these industries was recommended.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the Study

Industrialization and urbanization have promoted socio-economic development. However they have also led to varieties of environmental hazards. This is because the soaring trend of industrialization has engendered significant environmental pollution (Ghosh and Singh, 2005; Sayyed and Sayadi, 2011).

Heavy metals are metals that are non biogradable and are widely distributed in the environment (Campbell, 2006). The fact that they are not detoxified readily or removed by natural processes once they are present in the environment makes them potential environmental pollutants. Environmental pollutions due to heavy metals is usually as a result of human activities that are associated with industrialization, fuel combustion or other reactions driven by temperature and related to vehicular performances (Eruyogho, Okuo and Ndiokwere, 2007). Various metals such as zinc, cadmium, copper, and lead used as additives in fuel are discharged into the air and are carried to soil by rainfall and wind (Kabata and Pendias, 2001). Heavy metals are naturally part of the environment, however, metals such as arsenic , nickel, mercury, cadmium, and lead do not have any known or reported biochemical importance and their appreciable concentration could constitute significant lethal hazards (Seaward, 2004).

The total content of heavy metals in the soil and plant does not necessarily correspond to their bioavailability in the environment. The bioavailability of heavy metal depends on the properties of the soil. Such soil parameters include pH, organic matter content, texture, clay content, sulphate, carbonate, and hydroxide content (Gosh and Singh, 2005). The prominent environmental issue associated with the release and dispersal of industrial wastes produced by manufacturing processes is soil pollution. Controlled and indiscriminate dispersal of wastes from industrial activities, extraction and processing of metaliferous ores, application of sewage sludge to agricultural soil are responsible for the contamination of our ecosystem (Gosh and Singh, 2005). As trace elements, trace metals such as zinc, cobalt, and copper are necessary for maintaining the body physiological processes. However, at higher concentrations, they constitute significant toxicity. Contamination of soils by metals may be wide spread in urban areas due to industrial activities and combustion of fossil fuel. Prolong and indiscriminate exposure to heavy metals such as lead, cadmium, copper, zinc and nickel can cause deleterious health effect to plants and animals (Kabata and Pendias, 2001).

Varieties of inorganic and organic compounds cause pollution of the soil, especially through the action of rainfall. Their decay results to malodorous effect thereby, constituting health hazards (Ogbonna, Igbenije and Isirimah, 2006). The major components of these compounds include heavy metals, hazardous materials and petroleum based products (Eruyogho, Okuo and Ndiokwere, 2007). Organic contaminants are readily biodegraded through soil microbial activities; trace metals on the other hand need immobilization or physical removal because metals at high chemical content are poisonous and can result to physiological damages by free radical formation (Henry, 2000). This may reduce the effectiveness of the land for the growth of plant and also constitute danger to biodiversity. Also, soil plays an indispensable role in biogradation of wastes thus acting as a natural store-house for the intake of ions and as a medium for the restoration of natural vegetation (Seaward, 2004).

Heavy metals present in the air are then transferred into the soil through precipitation and fallout (Jagrati, 2012). Soil pollution with heavy metals can bring about the bioavailability of the metals for plant uptake which can eventually cause harm to human and animals. Heavy metals are the most harmful and insidious pollutants because they are not biodegradable and have the tendency to cause harm beyond a certain level of exposure.

1.2 Statement of the Research Problem

The indispensable role played by industrialization in economic and social development of any nation cannot be overstated, hence the assertion that no nation can grow beyond the level of its industrialization (Jonathan, 2010). However this skyrocketing trend in industrialization has not left the environment unpolluted (Onianwa, 2001). Among the various pollutants that are released into the environment through industrial processes and related sources, heavy metals constitute one of the major groups of pollutants. Various researchers have reported a continuous rise in heavy metal content of soil (Iyaka and Kakulu, 2012). The continual rise in the concentration of heavy metal in the environment therefore constitutes a significant problem. From the foregoing, there is an increasing need to monitor the extent of soil contamination by these metals especially the toxic ones around industrial areas.

1.3 Justification of the Study

Kaduna has witnessed influx of people from neighbouring states as capital of Kaduna state. This is due to the concentration of industries in the metropolis. Although much study has been carried on the concentration of heavy metals in soils around industrial areas of various cities, there is still need to continually monitor heavy metal loads on these areas due to changes in production processes and use of materials which could bring about change in heavy metal loads released by these industries to the environment.

In view of this, it is necessary to investigate the concentration of heavy metals in soils around the vicinity of industries in this area. The findings from the study will no doubt provide useful information on rate of mobilization of heavy metals into the environment thus serving as a useful input into the global quantitative inventory of land-based cause of pollution by the metals. The study will accentuate the need for a more constant monitoring of the concentration around industries. It will also facilitate the formulation of more appropriate and reliable guidelines, limitation standards and other environmental management measures within feasible framework. Furthermore, findings from such quantitative study will serve as a baseline data for future monitoring of soils around industrial area of Kaduna and other areas producing similar products.

1.4.0 Aim and Objectives

The aim of this study is to determine the physicochemical properties of the soils and concentration of some heavy metals present in soil around the vicinity of some selected industries in Kaduna. The above stated aim will be achieved through the following specific objectives:

1. To determine the concentration of heavy metals in soils in the vicinity of the selected industries.
2. To compare the concentration of heavy metal in the soil of the study area with the maximum value allowed by international standards.
3. To ascertain the effect of industrial activities on the physico-chemical properties of the soil in the study area.
4. To make recommendations based on findings from the study area.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 The Concept of Heavy Metals

Generally, metals are usually identified and differentiated from non-metals by their physical properties such as: the ability to allow the passage of heat, and a resistance that is directly proportional to temperature, ductility and malleability (Housecroft and Sharpe 2008; Muller, 2007). However the physical properties are lost after the chemical transformation of the metal into a chemical compound that can be absorbed by plants (Klaus, 2000).

Defining heavy metals might look simple and straight forward on first sight: they are metals that are “heavy”. Thorough examination has revealed the difficulties associated with the definition. The definition shows the prominence of density; however, this physical property is not relevant in case of living organisms (Duffus, 2002; Klaus, 2000).

According to Lenntech (2004), heavy metal is a metallic element that is relatively dense and is poisonous even at trace concentration. “Heavy metal” is a generic concept, which refers to a group of elements (metals and metalloids) whose density is more than $4g/cm^3$. However the chemical properties are more relevant than density. Heavy metals include elements such as Mercury (Hg), Cadmium (Cd), Copper (Cu), Arsenic (As), Silver (Ag), Lead (Pb), Iron (Fe) and Chromium (Cr) (Zhang, Yan, Zheng, Devkota, Shrestha and Yao, 2012; Akbar, Hale, Headley, and Athar, 2006).

2.2 Chemistry of Heavy Metals

Proper understanding of the speciation, bioavailability and remediation options of heavy metals requires a basic knowledge of their chemistry, effect on environment and health implications (Luilo and Othman, 2006). Some properties of selected heavy metals are discussed.

2.2.1 Lead

2.2.1.1 Properties and Occurrence

Lead is a metal that belongs to the group IV and period 6 of the periodic table. Its atomic mass, atomic number and density are 207.2, 82 and 11.4g/cm^3 respectively. It also has a melting point of 327.4°C and boiling point of 1725°C.

In its natural form, it occurs as a bluish-gray metal usually in combined form with other elements like sulphur in minerals (i.e. PbS, $PbSO_4$) and ranges from 10 to 30mg/kg. Basically, the concentration of lead in surface soils globally averages 32mg/kg and it exists in various forms such as hydroxides, oxides, and ionic lead and oxylanion complexes of lead. These are the general form of leads that are discharged into the soil, surface and underground waters (Luilo and Othman, 2006). The most stable forms in which lead exist are Pb (II) and lead hydroxide complexes. Pb (II) is a very common and highly reactive form of lead. There are a number of lead based organic compounds such as tetraethylead, in addition to inorganic compounds of lead. The level of toxicity and environmental effect of organolead compound are specifically well known because of the previous wide spread distribution and utilization of tetraethyl lead as a very important additive in gasoline.

2.2.1.2 Toxic Effect of Lead

Inhalation and oral consumption are the two common pathway of exposure to lead. Both routes have similar effect. Lead accumulates in vital body organs such as kidney and brain, which can lead to poisoning (plubism) and eventually death at higher concentration. The presence of lead can also cause damage to the centranervous system and gastrointestinal tract. Exposure of children to lead causes mental deterioration, decline in IQ, poor development, hyperactivity and lower attention span, with those below six being more vulnerable to the risk. In adults, some of the effects of lead include: loss of memory; insomnia; nausea among others. Lead has no known function in the body system of living organisms. Its toxicity has been studied comprehensively than any other heavy metal (Baldwin and Marshall, 2009).

2.2.2 Copper

2.2.2.1 Properties and Occurrence

Copper is a transition metal and belongs to group IB and period 4 the periodic table. It has atomic number and atomic weight of 29 and 63.5 respectively. It has a density of 8.96g/cm^3, and melting point of 1083°C. Copper is an important material in various industrial and agricultural processes where it has several applications. It is an essential material in the manufacturing of antifouling paints, textiles, cooking utensils, pipes and many other related products (Sandra, 2011). The background content of copper in the soil is dependent on the compositions of the parent material as well as the various processes of the soil formation (Kabata and Pendias, 2001).

2.2.2.2 Toxic Effect of Copper

Copper in high concentrations can result to anaemia, irritation of the stomach and intestine as well as damage of the liver. Copper occurs normally in domestic water from copper pipes, as well as from the use of chemical for control algal growth. Though the interaction of copper with the environment is complex, findings from various studies have shown that most copper realeased into the environment is rapidly converted into stable form which does not constitute damage to the environment. In fact, unlike some materials, Cu is not magnified in the body or bioaccumulated in the food chain (Martinez and Moto, 2000).

2.2.3 Zinc

2.2.3.1 Occurrence and Properties

Zinc belongs to period 4 and group IIB. It is a transition metal with atomic number and mass number of 30 and 65.4 respectively. Zinc naturally occurs in soil, about 70mg/kg in crustal rocks (Zhuang, Lan and Shun, 2005). Zinc content in the environment is increasing unnaturally due to anthropogenic influence. Zinc is mostly released into the environment during industrial activities, such as mining, steel processing as well as combustion of fossil fuel. Many food items usually contain certain amount of zinc. Zinc is also present in drinking water and its concentration may rise due to storage in metal tank. Industrial sources or toxic waste site may cause the concentrations of the Zn in drinking water to reach level that causes health hazard. The accumulation of zinc in most soil is usually on the surface horizon, this is due to the formation of bonds with the soil organic matter in most soils (Kabata and Pendias, 2001).

2.2.3.2 Toxic Effect of Zinc

The production and use of Zn based material is still on increase globally, this implies that more Zn will end up in the environment. Water is polluted by Zinc as a result of the presence of large amount of zinc in water released from industries. The acidity of water may rise due to the presence of Zinc. Aquatic organisms could also concentrate Zn in their tissues when they live in lead contaminated water. Biomagnifications of zinc occur along the food chain when it is accumulated in the bodies of these fishes. Water soluble Zn that is found in soil can result to the pollution of ground water. Plants also absorb this zinc enriched solution. It can also interrupt with the activities of soil as it negatively affects microbial activities, thus retarding the decomposition of organic materials (Greany, 2005).

2.2.5 Chemistry of Chromium

2.2.5.1 Occurrence and Properties.

Chromium is a transition element with atomic mass of 52 and atomic number of 24. Its boiling point and specific gravity are 2672°C and 7.18-7.20 (20°C) respectively. Its shows a variable oxidation state of 2,3 or 6. It occurs in its natural form in the environment and is found in rocks, plants, animals and soil. Chromium is also found in combined form with other elements as salts, some of which are soluble in water. Metallic form of Chromium in its pure form is hardly found naturally. Chromium does not undergo evaporation, but it can be present in air as particles. Due to its elementary nature, chromium does not undergo degradation nor can it be decomposed. It is a vital element in the making of steel and other materials, for electroplating, and as an additive to minimize the corrosion of metals. Its name is from it coloured compounds. The use of Chromium for making dyes and pigments for paints, tan leather, making of bricks, and as preservative for wood is well known (Household Food Security, 2005).

2.2.5.2 Toxicity of Chromium

Chromium shows varying level of toxicity which depends on its oxidation state. Chromium in its hexavalent form is more poisonous than the trivalent form. The compounds of Cr (VI) readily penetrate the cell membranes when compared to the Cr (III). After it passage across the cellular membrane, the reduction of Cr (VI) to Cr (III) may occur through a number of hypothesized reaction mechanisms. Various reactive intermediates – chromium species (pentavalent and tetravalent), and radicals of oxygen are known to be involved in the reduction process. Such intermediates could interact with vital components of the cells, as a result of their reaction, thus causing damage. Apart from the greater level of toxicity of hexavalent compared with trivalent form of Chromium, the absorption of the former through the oral and inhalation route occurs more readily. The Environmental Protection Agency (EPA) has developed toxicity values to assess the risk of getting cancer or experiencing other adverse health effects as a result of inhaling or oral intake of chromium (Kabata, Pendias and Mukerjee, 2007).

2.2.6 Iron

2.2.6.1 Occurrence and Properties

Iron is a transition metal with atomic number of 26 and mass number of 55. It is the most abundant metal. It has a melting point of 1535°C and boiling point of 2750°C, specific gravity of 7.874 and shows valencies of 2, 3, 4 and 6. Iron is found in combined state with oxygen, chlorine and some other elements. It is found in very high abundance, being the fourth most readily available element in the earth crust. Hematite (Fe_20_3) is the most commonly available ore of iron.

2.2.6.2 Toxicity of Iron

Iron plays a vital role in animal and plants life. In humans, it is an important component of haemoglobin. Exposure to high doses of iron can result to iron poisoning. Symptoms include stomach pain due to ulceration, nausea, vomiting. Exposure to high doses through ingestion can result in metabolic acidosis and damages to vital internal organs of the body such as liver and brain (Tenenbein, 2005).

2.2.7 Manganese

2.2.7.1 Occurrence and Properties

Manganese is a hard and grayish white metal of the transition series. It has a boiling point of 2235°C, melting point of 1517°C and density of 7.21g/cm^3. Like other transition metals it shows variable oxidation states, with 0, +2, +6 and +7 being the most common. Minerals that contain manganese are in high abundance. Rhodochrosite ($MnCO_3$) and Pyrolusite (MnO_2) are among the most common of these ores. Manganese is usually found in combined state with oxygen, sulphur or chlorine (Agency for Toxic Substances and Disease Registry, 2005).

Manganese compounds are mostly found in two forms in the environment. Inorganic compounds of Manganese are used in production of ceramics, batteries and steels. Organic manganese compounds are important component of pesticide, gasoline additives and fertilizers. Compound of manganese are found in dust particles, air, ground water and soil (Bang, 2002).

2.2.7.2 Toxicity of Manganese

Manganese is recognized as an essential trace element. Exposure to high concentration is however toxic to health. The detrimental effect of manganese to health is more targeted to the central nervous system and the brain. Prolonged exposure to high concentrations has been reported to be associated with mental and emotional abnormalities, impaired neuromuscular coordination and respiratory difficulties. High doses of the element in series of studies conducted resulted in impaired male fertility and birth defects (Sharma and Pervez, 2005).

2.3.0 Speciation and Concentration of Heavy Metals in Soil

2.3.1 Lead

The element lead (in its soluble form) when present in the soil readily reacts with compounds present in the soil such as hydroxide, organic materials, clays, carbonates and phosphates, thus reducing its solubility. At pH values higher than 6, the adsorption of lead on clay surface and the formation of its carbonate occur readily. Lead retention by soils occurs in a greater extent under well-defined sample matrices. A decreased in the sorption of lead has been reported when it is in the presence of competing cations and complexing ligands. Lead has a high affinity for organic ligands and the formation of such complexes may greatly enhance the mobility of lead in soil (Bang, 2002). Gilbert and Osibanjo (2009), reported a concentration of 35.9-306.7mg/kg of lead in soil around automobile battery manufacturing plant in Nigeria.

Yahaya, Ezeh, Musa and Mohammad (2009) reported a concentration of 35.9- 306.7µg/kg of Pb in Yauri road side soil, Nigeria, while Gilbert (2009) reported 2.5-11.0mg/kg of Pb in soil around areas polluted by slag from smelting plant which was considered to be far lower than the maximum permissible limit of 400mg/kg of lead in soil (Chen, Ma, Hoogeweg and Harris, 2001).

2.3.2 Zinc

The adsorption of Zinc by clay minerals, carbonates and hydrous oxides occurs readily, with the highest percent of total zinc being associated with manganese and iron oxides. Precipitation is not a primary mechanism of retention of zinc in soils because of the solubility of zinc compounds. Precipitation may become a significant means of zinc retention in soil-waste system. As with other cationic metals, the adsorption of Zinc rises with pH. Zinc hydrolyses at pH greater than 7.7, and these hydrolysed species are adsorbed to the soil surface strongly. Zinc forms various complexes with both organic and inorganic ligands and this affects its adsorption reactions with the surface of the soil (Asaah, Abimbola and Suh, 2006).

Bang (2002) reported 6 to 101mg/kg of Zinc in soil. Asaah *et al*. (2006) in their study of surface soil of the Bassa industrial zone reported a higher range of Zn content of 30-3782mg/kg.

2.3.4 Copper

The retention of copper in the soils occurs through specific adsorption and exchange mechanism. At concentrations typically found in natural soils, the precipitates of copper are unstable. This may not be so in waste-soil systems and precipitation may be an important mechanism of retention. The adsorption of copper by soil and soil constituents occurs to a greater extent than other metals, with the exception of lead. Copper, however, has a greater preference for organic ligands that are soluble and the formation of these complexes may greatly enhance the mobility of copper in soil (Nwegoha and Kahampa, 2010). Iyaka and Kakulu (2012) reported a mean value of 16mg/kg of Cu for soil around vicinity of pharmaceutical industry. Nwegoha and Kahampa (2010) reported a concentration range of 21.07 ± 2.88 mg/kg of Cu for heavy metal contamination in a sampling point that featured electroplating material.

2.3 Sources of Heavy Metals

Heavy metals are ubiquitous. They are found everywhere in the environment: water, land, sediments and plants. Heavy metals occur in trace amount (<1000mg/kg) in soil and are released from the weathering of the parent materials. At the naturally occurring concentration, they are non-toxic and in fact some metals are known to be useful for the physiological functioning of plants and animals (Kaba and Pendias, 2001). Toxicity of heavy metals results from their redistribution from non-toxic geochemical state to the surface of the earth where they become readily available with lethal effects. Anthropogenic inputs through industrialization, urbanization and agricultural activities have been identified as the causal factor for this shift of heavy metals to surface soil and sediment (Suciu, Cosma, Todica, Bolboaca and Jantschi, 2008; D'Amore, Al-Abed and Ryan, 2005). Heavy metals therefore occur from either pedogenic (lithorgenic) or anthropogenic sources. The pedogenic form are in the stable state hence not readily bioavailable or mobile (Kaasalainen and Tli-Halla, 2005). The various sources of heavy metals are examined below:

2.3.1 Industrial discharge

The increasing trend of industrialization in different parts of the world has not left the environment unpolluted. Pollutants are released into the environment from point or non-point sources. Point sources include waste from residential and chemical factories while non-point is source such as vehicular emission (Sayyed and Sayadi, 2011). Soils around the vicinities of industries are prone to higher level of trace metal contamination (Kharn, Hang and Zhu, 2008; Fakoyade and Onianwa, 2002).

The pollution of soil through discharge of waste from industrial activities occurs at alarming trend. Various industries such as paint, textile, pharmaceuticals, and petrochemicals all generate water that has varying composition of trace metals. Even though some of these wastes are treated prior to disposal, they still contain heavy metals in significant quantity.

2.3.2 Metal Mining

The mining and milling of metallic ores involves the removal of the trace metals from their naturally occurring state to the earth surface for industrial use. This no doubt is a direct source of the metals. Tailings (denser materials that settle at the bottom of the floatation cell during mining) are used for filling of natural depressions on the earth surface resulting to increase in trace metal concentration (Devolder, Brown and Pandya, 2003). Large scale mining of various metals such as Pb and Zn ores has resulted to the elevated contamination of soil which poses danger to life. Remediation measures for such highly contaminated areas are expensive and may not restore the productivity of the soil (Scragg, 2006).

2.3.3 Pesticide Application

Pesticides are chemical compounds used in agriculture in other to destroy pest, thus enhancing agricultural yields. Most compounds used as pesticides have heavy metal as a major component. Some chemicals approved for use as pesticides and fungicide in most countries were compounds based on metals such as copper, zinc, lead and mercury. The fungicidal spray such as Bordeaux mixture contains copper sulphate and copper oxylchloride (Sandra, 2011). Arsenic- containing compounds were used extensively in the control of various pests. Likewise the use of lead arsenate has been used in fruit orchard for killing parasitic insects (Sharma and Prasade, 2010).

2.3.4 Fertilizers Application

Man in his attempt to boost agricultural yield through fertilizer application has further increased environmental pollution by heavy metals. Fertilizer has altered the chemical composition and nature of soil. Trace metals (Co, Fe, Cu, Mo and Zn) are also required for the proper growth of plants. These are mainly applied to the soil in form of their salts. For example cereal crops grown in soil that are deficient in copper are occasionally treated with copper so as to increase their nutrient content. Various fertilizer used to supply N, P and K have been shown to contain trace metals. This becomes significant after continued application (Scragg, 2006).

2.3.5 Waste Water

The use of industrial and domestic waste water on land has long been practiced and it has been reported that over 20 million hectare of agricultural land are irrigated using waste water (Sayyed and Sayadi, 2011). Various studies carried out in African and Asian cities suggest that the agriculture based on waste water irrigation account for over 50% of vegetable consumed in the areas. The farmers tend to be more concerned with profit maximization with little consideration on health and environmental implication. Though heavy metals are present in such waste water in trace amount, long period of application could result to the build-up of trace metals in the environment (Bjurh, 2007).

2.3.6 Biosolids

The use of biosolids such as composts, livestock manures, and municipal sewage sludge in agriculture has long been known. Biosolids contain various heavy metals such Zn, Cu, Cr, Sb, As, Cd, Hg and Ni (Basta, Ruyan and Chaney, 2005). Thus the use of such biosolids on land results to the enrichment of the soil with trace metals which could constitute toxic effect on man and livestock. The metals are absorbed by plants, accumulated in all their parts and then passed across the food chain (Sumer, 2000). The repeated application of most manure to restricted land area can result in considerable accumulation of heavy metals in soil (Sharma and Prasade, 2010).

2.4 Soil as a Repository of Environmental Waste

In order to ensure proper monitoring of environmental contamination by heavy metals, due to anthropogenic activities, the soil samples are excellent media because heavy metals are frequently deposited on the top soil (Govil, Reddy and Krishna, 2001; Romic and Romic, 2003).

2.5 Forms of Heavy Metals

The form or speciation of trace metal contaminants in soil determines the extent to which the metals are available for plant uptake and the potential for ground water contamination. Thus the chemical behaviour of heavy metals in soil environments is dependent on the form in which the metal exists in soil.

The presence of a trace metal in soil may not necessarily imply toxicity. However, almost any element is poisonous beyond a certain concentration. The level of toxicity of a metal is dependent on its concentration in soil and the extent to which it is available for plant uptake (Johnson, 2010). The only forms available to plants are those in soil solution or exchangeable components.

2.5.1 Soluble Form

Soil water naturally contains salts. Almost all metals in solution form positive ions, called cations, such as (Zn^{2+}). Metals in this soluble form are readily available for plant uptake. The soil solution basically acts as source of plant nutrients (Akoji, 2010).

2.5.2 Exchangeable

Most soil particle surfaces are negatively charged, most especially clay particles and organic matter. Such places in soil are referred to as exchange sites. The number of exchange sites varies depending on the particle size distribution of the soil as well as it compositions. Trace metals being positively charged are attracted and held at these exchange sites. There is a relationship between the numbers of cations on exchange sites. Replacement of cations from the exchange sites occur when those in the solution medium are used up.

The two forms highlighted above are by far the most active biologically hence any metal must be in one of these two forms before plants can take it up. Trace metals in the other forms are not readily absorbed by plants except they are altered before plants can assimilate them (Bhattacharya, Mukhajee, Jack and Nordqvist, 2002).

2.5.3 Organically Bound

When plants and soil fauna absorb metals, they generally are incorporated into organic substances. However, metals can also form chelates with organic material in soil solution. Some of these organic materials decompose quickly, temporarily releasing metals back into the soil solution. The decomposition of others occurs slowly taking up to hundreds of years (Afshin and Farid, 2007).

2.5.4 Absorbed by Hydrous Oxides

Various metals such as manganese, copper and iron readily combine with oxygen to form solids, often coating soil surfaces. A typical example is rust; an iron oxide which gives some soils a reddish colour. Metals may form solid with these elements (co-precipitation) or become wrapped in the coating. When these happen, the metals are in stable forms that restrict change (Sharma and Prasade, 2010).

2.5.5 Bound to Carbonates

Most soils with neutral or alkaline pH usually contain large amount of calcium salts present in the form of calcium carbonate ($CaCO_3$) or calcium bicarbonate ($Ca(HCO_3)_2$). Other metals (including trace elements) can undergo precipitation by taking the place of calcium thus forming solid product. If precipitates do form, they usually contain more than one trace metal thus resulting to the formation of a mixed crystal that includes combinations of major elements, typically calcium or iron. The more crystalline and mixed the solids are, the less their tendency to go into solution. The availability of simple solids occurs as the acidity of the soil increases (Afshin and Farid, 2007).

2.6.0 Factors Affecting the Bioavalability and Mobility of Heavy Metals in Soil

The availability, retention and mobility of heavy metals in soil are determined by various factors within the soil. The major factors are total organic carbon (TOC) and pH. Others include cation exchange capacity (CEC) and particle size distribution (Bhattacharya, Mukhajee, Jack and Nordqvist, 2002; Henry, 2000 and Martinez and Motto, 2000).

2.6.1 Soil pH

The pH of a solution refers to its degree of acidity and alkalinity. It is the negative logarithm of hydrogen ion concentration. Basically, soils are grouped into acidic, neutral, or alkaline (basic), based on its value on the pH scale. The pH of soil is influenced by the presence both acid and base-forming ions present in the soil. Common cations associated with acidity are hydrogen (H^+), aluminium (Al^{3+}), and iron (Fe^{2+} or Fe^{3+}), whereas common cations that form base include potassium (K^+), sodium (Na^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}).
Soil pH is the principal factor that determines metal mobility in soil. The solubility of Metal cation generally increases with a decrease pH. As pH decreases, the solubility of the metal cation increases due to desorption from soil minerals such as carbonates, metal oxides and hydroxides. Also as organic acids are degraded, the pH rises to an almost neutral level, buffered by the bicarbonate system (Bozkurt *et al*., 2000). Thus increase in soil acidity results to an increase in solubility, mobility and concentration of heavy metals in the soil. Oxidation of pyrite (FeS_2) is recognized as a major factor responsible for the acidity of acid soil. As FeS_2 oxidizes, the soil pH decreases and the concentration of dissolved sulphate SO_4^{2-}

increases (Galceran, Companys, Puy, Cecilia and Garce, 2004). The classification of soil according to their pH range as given by the United States Department of Agriculture is shown below:

Table 2.1: Soil Classification Based on pH

Class	pH range
Ultra acid	<3.5
Extreme acid	3.5 – 3.4

Very strong acid	4.5 – 5.0
Strong acid	5.1 – 5.5
Moderate acid	5.6 – 6.0
Slight acid	6.1– 6.5
Neutral	6.6 – 7.3
Slightly alkaline	7.4 – 7.8
Moderately alkaline	7.9 – 8.4
Strongly alkaline	8.5 – 9.0
Very strongly alkaline	> 9.0

Source: (Soil Survey Manual, 1993)

Inuwa, Abdulrahman, Yuauri and Ibrahim (2013) in their study on trace elements in soil around industrial areas in northwestern Nigeria reported a mean soil pH of 6.6 around Kakuri industrial estate in Kaduna. This was attributed to industrial pollution by acidic gases and bush burning. Similarly, Gabriela, Cristina and Angela (2011) reported a pH range of 6 - 8.4 in soil around industrial area of Mare city in their study.

2.6.2 Soil Organic Matter

Soil organic matter refers to plant and animal materials present in their varying stage of decomposition, cells and tissues of soil organisms, and decomposed materials (Brady and Weil, 2008). Although the definition above does not include living organisms, their presence is important in the formation of soil organic matter. The roots of plant and fauna such as rodents, mites and earthworms all contribute to the movement and breakdown of soil organic material. Four major processes are involved in the cycling of soil organic materials: decomposition of organic substances; mineralization of nutrient; transfer of organic carbon and nutrients from a soil organic matter reservoir to another; and continual discharge of carbon dioxide (CO_2) through microbial activities (Jones, Jacobsen and Lorbeer, 2002). Soil organic matter is a principal variable that affects the differential distribution of heavy metals in soil (Afshin and Farid, 2007). Increase in soil organic matter content lead to elevation of soil adsorption capacity hence enhancing trace metal accumulation and storage. Organic matter can therefore be considered as an important medium through which heavy metals are incorporated and reserved in the soil.

The formation of complexes with organic matter in the soil tend to occur and this differ for each metal. Organic matter also retains these metals in exchangeable form (Jones, Jacobsen and Lorbeer, 2002). With increasing organic matter content, soil heavy metal retention capacity increases hence an increase in metal concentrations, especially Cu^{2+}, Hg^{2+} and Pb^{2+}. These metal ions become strongly bound to organic matter. Organic matter forms complexes with heavy metals cations by ion exchange and chemisorption reaction.

Thus, the determination of the organic matter content of soil and predicting its relationship with the concentration of heavy metals in soil can be a strong tool for assessing heavy metal contamination in soil (Afshin, 2007). Iyaka and Kakulu (2012) in their study had TOC of 0.42 to 2.7% in soil around the vicinity of pharmaceutical industry in Niger state. Oyedele, Gasu and Awotoye (2008) reported a soil organic matter content of 2.7 to 4.2% in soil around waste dump site.

2.6.3 Soil Electrical Conductivity

The electrical conductivity of soil is a measure of the ability of soil to conduct electrical current and it is expressed mostly in units of MilliSiemens per meter (mS/m). Also, electrical conductivity measurements can be expressed in unit such as DeciSiemens per meter (dS/m), which is 100 times greater than MilliSiemens per meter (Sudduth, Kitchen, Wiebold and Thelen, 2005).

Soil electrical conductivity is an indirect measurement that is strongly associated with several physical and chemical properties of soil.

2.6.4 Soil Particle Sizes

Trace metals are mainly found adsorbed in clay and silt fraction of soil (Sayyed and Sayadi, 2011). Generally, the concentration of heavy metal in soil increases with decrease in the sizes of the soil particles. This is because finer particles have larger surface area. Thus there is a higher concentration of metal such as lead in fine silt and clay soils than with coarse soil (Momani, 2006).

2.7.0 Remediation of Soil Heavy Metals

Remediation is a scientific approach to environmental decontamination. It involves the removal of pollutants from the environment so as to ensure its safety for man, livestock and plants (Finzgar and Lestan, 2006). Various methods of remediation of polluted soils have been developed: physical, chemical and biological. Some of the currently applied methods of remediation are highlighted as follows:

2.7.1 Contaminant Immobilization Technique

This involves the use of various materials (organic and inorganic) to restrict the mobility of trace metals in soil. The focus of this technique is to ensure the geochemical stability of the contaminants through complexation and sorption phenomena (Anoduadi, Okenwa and Okieimen, 2009). Various naturally occurring materials have found use as amendment substances: zeolites, red mud, and termitarium, organic compost among others (Anoduadi, Okenwa and Okieimen, 2009; Finzgar and Lestan, 2006).

2.7. 2 High Temperature Vitrification

This is a thermal driven process of remediation that modifies the contaminated area into a granular, hard and non-leachable substance through the application of heat. The mobility of the metal contaminants is reduced. This approach is applicable to various organic and inorganic contaminants. It can be carried out ex situ or in situ.

2.7.3 Stabilization Technique

This is similar to vitrification in that contaminants are immobilized. Stabilization technique is the application of stabilizers (binding materials) to the polluted soil so as to control its movement and access by external agents through various chemical processes. This is an established remediation technology that is adopted for hazardous waste treatment in some countries of the world (Finzgar and Lestan, 2006).

2.7.4 Bio-enhancement Technique

This is the additive assistance of indigenous microbes by the introduction of other microorganisms with the contaminant degradative potential into the environment. Physical and chemical processes like adsorption, mineralization and enzymatic modification occur (Agamuthu, Abioye and Abdulaziz, 2010).

2.7.5 Phytoremediation

Phytoremediation is the decontamination of soil through the effective utilization of plants. It is also known as botanoremediation or green remediation. Phytoremediation has found relevance in the treatment of soil contaminated with heavy metals, crude oil, aromatic hydrocarbons and pesticides. The use of contaminant-accumulating plants to remove soil pollutants has been practiced for long and the concept has been employed for the past three hundred years for treating waste water discharge. In some of the mechanisms employed in phytoremediation, plants are grown in the contaminated soil. The plants absorb the toxic metals through their root and then translocate them to other parts of the plants. The plants are later harvested and incinerated or composted to recycle the metals. This method is known for its high public acceptance due to its cheap cost, easier implementation and significant aesthetic impact (Gerhardt, Huang, Glick and Greenberg, 2009).

2.8.0 Enrichment Factor

The extent of soil contamination and accumulation by a given metal can be established through comparism of the concentrations of the metal with that of a reference element. The result obtained is expressed as Enrichment factor (EF), given by the following equation:

$$EF = (C_n/C_{ref}) / (B_n/B_{ref})$$

In which Cn is concentration of the investigated element in the soil, C_{ref} is concentration of the investigated element in the earth's crust, B_n is concentration of the reference element in the soil, and B_{ref} is content of the reference element in the earth's crust. A reference element is 'pedogenic' that is, one in which is conservative, and whose content is basically from the earth's crust with negligible anthropogenic impact. The most commonly used referenced elements in literature include: aluminum (Al), zirconium (Zr), iron (Fe), scandium (Sc), and titanium (Ti), although several attempts have been made to use other elements such as manganese (Mn), chromium (Cr) and lithium (Li). Generally, the enrichment factor is used to assess soil contamination (enrichment) and its interpretation is as follows:

Table 2.2 Classes of Soil Enrichment

EF Range	Class
< 2	depletion to minimal enrichment;
2–5	moderate enrichment

5–20	significant enrichment
20–40	very high enrichment
> 40	extremely high enrichment

Source: (Sutherland, 2000).

EF is also employed in assessing soil elemental depletion (Blaser, Zimmermann, Luster and Sbotyk, 2000). All EF values less than 1 may indicate that leaching and consumption of an element take precedence over its accumulation in soil. Fergusson (1990) also used Fe as reference element for the normalization of elements, because Fe content is unrelated to that of other metals.

2.8.1 Index of Geo-accumulation

Geo-accumulation index (I_{geo}) as soil heavy metal assessment index was first employed by Müller in 1969, in order to express and define trace metal pollution in sediment by comparing present concentrations with pre-industrial era. I_{geo} is calculated using the following equation:

$I_{geo} = \log_2 [C_n / (1.5B_n)]$

Where Cn is the measured concentration of the metal in the enriched soil sample and Bn is the concentration of the metal in the unpolluted samples or control (geochemical background concentration). The factor 1.5 is used to account for natural fluctuations in the content of a given metal in the environment as well as very small anthropogenic influences.

The geo-accumulation index (I_{geo}) was classified into seven groups.

Table 2.3 Soil Classes Based on I-geo

I geo range	**Class**	**Description**
$I_{geo} \leq 0$	class 0	unpolluted
$0 < I_{geo} \leq 1$	class 1	from unpolluted to moderately polluted
$1 < I_{geo} \leq 2$	class 2	moderately polluted

$2<I_{geo}\leq3$	class 3	from moderately to strongly polluted
$3<I_{geo}\leq4$	class 4	strongly polluted
$4<I_{geo}\leq5$	class 5	from strongly to extremely polluted
$I_{geo}>5$	class 6	extremely polluted

Source: (Buccolieri *et al*., 2006)

2.9.0 Atomic Absorption Spectroscopy

2.9.1 Principle

Atomic absorption spectroscopy (AAS) is an analytical technique that is used in determining the concentrations of elements. The sensitivity of this technique makes it possible for it to measure concentrations as low as parts per billion of a gram in a sample. The technique makes use of the wavelengths of light specifically absorbed by an element which is characteristic of the element. They correspond to the energies needed to promote electrons from one energy level to another. This technique has found practical relevance as analytical tool in various aspects of chemistry.

Characteristic wavelengths of light are absorbed by atoms of different elements. Analysing a sample to see if it contains a particular element means using the specific light from that element. For example with lead, a lamp containing lead emits light from excited lead atoms that produce the right mix of wavelengths to be absorbed by any lead atoms from the sample. In AAS, the sample is atomized: it is converted into ground state free atoms in the vapour state and a beam of electromagnetic radiation emitted from excited lead atoms is passed through the vaporized sample.

Some of the radiation is absorbed by the lead atoms in the sample. The amount of light absorbed is proportional to the number of lead atoms. A calibration curve is constructed by running several samples of known lead concentration under the same conditions as the unknown. The amount the standard absorbs is compared with the calibration curve and this enables the calculation of the lead concentration in the unknown sample.

2.9.2 The Atomic Absorption Spectrometer

The device has four major components:

i. **Light source** (Hollow Cathode Lamp);

The hollow cathode lamp which is the usual light source is made from the element being analysed. The anode is made of tungsten while the cathode is cylindrical and made from the element to be measured. These are assembled in a glass tube filled with argon or neon (noble gases) and kept tight.

2. **Atomizer**: Prior to the analysis, the element of concern must be in atomic state. This is achieved using an atomizer or atom cell. Atomization involves the thermal conversion of the analyte into their free gaseous atom by the use of flame or graphite furnace. The gaseous atoms in their ground state are then available for the absorption of radiation from the light source. On absorption, they generate signal that is directly proportional to the concentration of the analyte. Atomization can be achieved using either flame or graphite furnace atomization.

3. **Monochromator**: This component of the spectrometer is used for the selection of specific wavelength of light absorbed by the analyte, leaving out other wavelength. The wavelength selected is characteristic of the analyte thus allowing the determination of the selected element in the presence of others.

4. **Detector**: this is an important component of the spectrometer. It is typically a photomultiplier tube were light selected by the monochromator is passed into. The processing of electrical signal is achieved by a signal amplifier. The signal can be fed into data station for printout format.

2.9.3 Calibration Curve

This is a curve used for the determination of the unknown concentration of an element in the solution. The absorbance of each is measured and then a calibration curve of concentration vs. absorbance is plotted.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials / Equipment

1. Analytical Balance

2. Atomic Absorption Spectrometer (Model: AA240FS)
3. Beaker (250ml)
4. Burette (50ml)
5. Conductivity Meter (Model: Kent EIL5013)
6. Dispenser (10 and 20ml)
7. Dispersing Cup
8. Electric Mixer
9. Erlenmeyer Flask
10. Filter Paper (whatman No.42)
11. Glass Cylinders (1000 ml)
13. Glass Rod
14. Hot Plate
15. Hydrometer
16. Magnetic Stirrer
17. Measuring Cylinder (10, 20 and 1000ml)
18. pH Meter (Model : pHep H196107)
19. Pipette (10ml)
20. Plunger
21. Sieve (0.5mm and 2mm)
22. Soil Auger
23. Thermometer
24. Volumetric Flask
25. Watch glass

3.2 Reagents

1. Conc. H_2SO_4
2. Conc. HNO_3
3. Fe^{2+} solution (0.5M)
4. Ferroin Indicator
5. $HClO_4$ (70%)
6. H_3PO_3 (85%)
7. NaF, solid
8. Sodium Hexametaphosphate Solution (5%)
9. Standard Buffer Solution (pH 4 and pH 9)
10. Standard 0.167M $K_2Cr_20_7$

3.3 Study Area

The present study focused on selected industries in Kaduna metropolis. Kaduna is the capital of Kaduna state. It derived its name from the Hausa word 'Kaduna' meaning 'crocodiles' due to the large number of crocodiles in river Kaduna. The state occupies an area of approximately 48,473.2 square kilometres with a population of more than 6 million (2006 census). It lies along the Kaduna River, which is a tributary of the River Niger (Jonathan, 2010).

Kaduna is recognized as one of the major industrial and commercial center of northern Nigeria. Most of the industries are located in the south of Kaduna River near the main railway junction. The major industries in the area include textile industries, steel rolling plants, pharmaceutical industries, plastic industries, ceramic industries, paint industries, food industries among others. Most of the industries are in active state of production while a few are dormant.

The industries selected for this study include Power Seal Paint Industry, Chilox Paint Limited, United Nigeria Textile, Kaduna textile limited, Abumec Pharmaceuticals and Arewa Pharmaceutical Industry, all located in the industrial area of Kaduna(Kakuri, Sabon tasha and Nasarawa).

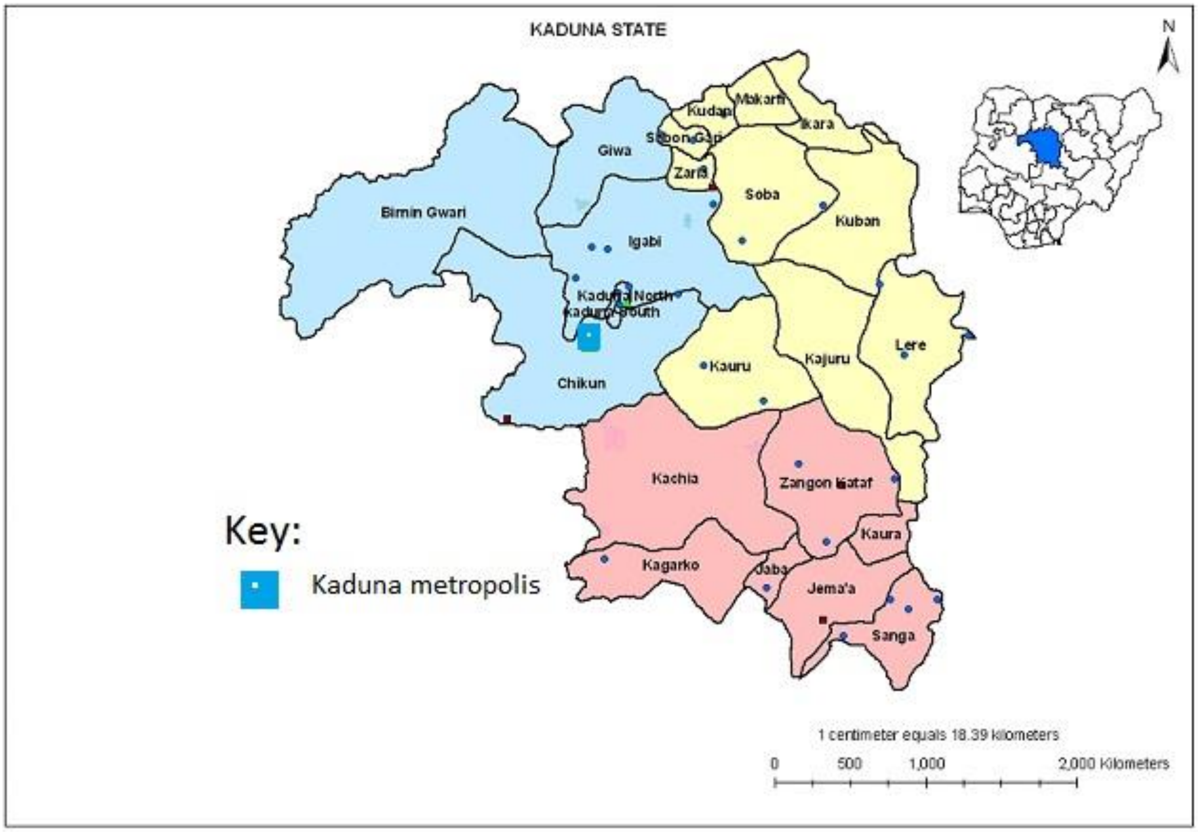

Plate I: Map of the Study Area (Kaduna)

3.4 Methods

3.4.1 Sampling Method

The soil samples were collected around the industrial areas in a systematic random pattern using a soil auger. Control samples were also collected from an uncontaminated site, about four kilometres away from the industries in line with method described by Gilbert and Osibanjo (2009).

Four samples were collected from the vicinity of each of the industry. At each sampling point, four sub-samples were taken at a depth of 0-15cm. They were then mixed thoroughly in order to ensure a representative sample from each sampling location. The soil samples were then packed in a clean polythene bag. The sampling equipment was decontaminated between sites by washing and rinsing with distilled water, and allowing to air dry between each industrial location.

3.4.2 Sample Pre-treatment

The soil samples were air-dried for 48 hours. They were then ground using agate mortar and sieved using a 2mm sieve initially, and further pulverized and sieved with a 0.5mm sieve.

3.4.3 Preparation of Reagents

i. Sodium hexametaphosphate solution (5%): This was prepared by dissolving 50g of sodium hexametaphosphate ($Na_6 (P0_4)_6$) in deionized water and diluted to 1 litre.

ii. Standard 0.167M $K_2Cr_20_7$: 49.04g of dried $K_2Cr_20_7$ was dissolved in water and diluted to 1L.

iii. 0.5M Fe^{2+} solution: 196.1g of $FeSO_4.7H_20$ was dissolved in water and then 20ml of conc. H_2SO_4 added. The solution was then cooled and diluted to 1L. The Fe^{2+} in this solution oxidizes slowly on exposure to air so it was standardized against dichromate daily.

iv. Ferroin indicator: 3.71g of O-phenanthroline and 1.74g of $FeSO_4.7H_2O$ were slowly dissolved in 250ml of water.

v. 1000 ppm Pb(II) solution: this was prepared by dissolving 1.5986g of lead(II) trioxonitrate (V) ($Pb(NO_3)_2$) in 200ml of distilled deionized water in a beaker. Then 1.5ml of conc. HNO_3 was added. This was then quantitatively transferred into a 1 litre flask and diluted to the mark with distilled deionized water.

vi. 1000 pm Cd (II) solution: this was prepared by dissolving 2.7442g of cadmium trioxonitrate (V) tetrahydrate ($Cd(NO_3)_2.4H_2O$) in 200ml of distilled deionized water in a beaker, then 1.5ml conc. HNO_3 added. This was then quantitatively transferred into a 1-litre flask and diluted to the mark with distilled deionized water.

vii.1000 ppm Cr (VI) solution: this was prepared by dissolving 2.828g of potassium heptaoxodichromate (VI) ($K_2Cr_2O_7$) in 200ml of distilled deionized water in a beaker. Then 1.5 ml of conc. HNO_3 was added. This was then quantitatively transferred into a 1-litre flask and diluted to the mark with distilled deionized water.

viii. 1000 ppm Zn (II) stock solution: this was prepared by dissolving 1g of analar grade Zn dust in about 20ml of conc. HCl in a fume cupboard until effervescence stopped. The resulting solution was dissolved in about 200ml of distilled deionized water. This was then quantitatively transferred in a 1-liter flask and diluted to the mark with distilled deionized water.

ix. 1000ppm Mn (II) stock solution: 3.6077g of manganese chloride ($MnCl_2.4H_20$) was dissolved in 50ml conc. hydrochloric acid and diluted to 1 litre in a volumetric flask with deionised water.

x. 1000ppm Cu(II) stock solution: 3.7980g of ($Cu(NO_3)_2.3H_2O$) was dissolved in 250ml of deionised water and diluted to 1 litre in a volumetric flask with deionized water.

xi. 1000ppm Fe(III) stock solution: 4.8400g of iron (III) chloride ($FeCl_3.6H_2O$) was dissolved in 200ml of deionised water and diluted to 1 litre in a volumetric flask with deionized water.

3.4.3. Determination of Soil pH

20 gram of soil sample was taken into a 100ml beaker to which 40ml of distilled water was added. The suspension was stirred at regular interval for 30 minutes to ensure effective dispersal and dissolution of all soluble compounds. The pH meter was calibrated with two buffers, one on the acidic side and other alkaline. The pH was then recorded using a pH meter. The electrodes were rinsed with distilled water after each use.

3.4.3.2 Particle Size Determination

The percentage of sand, silt and clay in the inorganic fraction of soil was measured using hydrometer method (IITA, 1979).

100ml of the 5% dispersing solution was mixed with 880ml of deionized water in 1000ml cylinder. This mixture was the blank. The blank was not diluted to 1000ml the other 20ml is the volume occupied by 50g of soil. 50grams of soil (<2mm) was weighed and transferred into a dispersing cup. 50ml of 5% dispersing solution was added followed by 100ml of distilled water. This was then stirred and the mixture was allowed to stand for 30 minutes. The dispersing cup was attached to the mixer and the sample stirred for 1 hour using a mechanical shaker and then quantitatively transferred into a 1000ml measuring cylinder. This was then filled to 1000ml and allowed to stand overnight to equilibrate. At the beginning of each set, the temperature and hydrometer reading of the blank was recorded. To determine the density, the plunger was inserted into the suspension, and carefully mixed for 30sec, until a uniform suspension was obtained. The plunger was removed and the hydrometer gently inserted into the suspension. The hydrometer reading was recorded at 40sec. This is the amount of silt plus clay suspended. Two hours after the sand had settled to the bottom of the cylinder, the reading was taken again. The reading obtained at this time was the amount of clay in the suspension. At this time, the silt had settled to the bottom of the cylinder by that time.

Calculation

i. Temperature and density correction

0.2 units were added to the reading of samples for every 1F (-17◦C) above 67F (19.5 ◦C), and 0.2 units were also subtracted for every 1F below 67F.

ii. Percentage (%) silt and clay = (R-RL + (0.36T1)

R= hydrometer reading of sample

RL= hydrometer reading of blank

T1= temperature taken during plunging

% Clay = R2-RL2 + (0.36T)

% Silt = % silt and clay - %clay

% sand = 100 -% silt and clay

R2 =hydrometer sample reading after 2 hours

RL2 =hydrometer blank reading after 2 hours

3.4.3.3 Determination of Electrical Conductivity of Soil

The electrical conductivity of the soil was determined using electrical conductivity meter. Soil-water suspension in the ratio of 1:5 was prepared by weighing 10gram of air-dried soil (<2mm) into a 250ml beaker and 50ml of deionized water added. The mixture was shaken mechanically at 15rpm for 1 hour to dissolve soluble salts. The conductivity was then measured and recorded (Akoji, 2010).

3.4.3.4 Determination of Organic carbon by Walkey-Black Method (Luilo and Othman, 2010)

1g of dried soil sample (<0.5mm) was weighed and transferred into a 500ml Erlenmeyer flask. 10ml of 0.167M $K_2Cr_2O_7$ was then added by means of pipette followed by the addition of 20ml of conc. H_2SO_4 added by means of dispenser and the mixture was swirled gently to mix. The suspension was then allowed to stand for 30 minute and diluted with 200ml of distilled water. 10ml of 85% H_3PO_4 was then added using a suitable dispenser, then 0.2g of NaF. The H_3PO_4 and NaF were added to complex Fe^{3+} which could interfere with the titration endpoint. This was then followed by 10 drops of ferroin indicator. The mixture was titrated with 0.5M Fe^{2+} solution. The color at the beginning was yellow-orange to dark green, which shifted to a turbid gray before the end point. A blank titration was also run using the same procedure but without soil. The blank was used to standardize the Fe^{2+} solution daily.

Calculation

i. Percentage (%) Easily oxidizable organic carbon

$$\%C = \frac{(B-S)\times M\ of\ Fe2+ \times 12}{g\ of\ soil\ \times 4000} \times 100$$

Where:

B = ml of Fe^{2+} solution used to titrate blank.

S= ml of Fe^{2+} solution used to titrate sample.

$\frac{12}{4000}$ = milli equivalent weight of Carbon in gram.

The easily oxidizeable organic carbon was then converted to total carbon, multiplying by 1.30. The total organic carbon was converted to organic matter using the equation:

ii. % organic matter = $\frac{\%\ total\ C \times\ 1.72}{0.58}$

3.4.4 Total Metal Analysis

The soil heavy metal determination was carried out after digestion with perchloric, sulphuric and nitric acid mixture (Zheng, 2003). The concentration of heavy metal was determined using Fast Sequential Atomic Absorption Spectrometer (AA240FS).

1g of the soil sample was weighed into 250ml digestion flask and 10ml of conc. HNO_3 was added. The mixture was boiled gently for 30-45 min to oxidize all easily oxidizeable matter. After cooling, 5ml of 70% $HClO_4$ was added and the mixture was boiled gently until dense white fumes appeared. After cooling, 20ml of distilled water was added and the mixture was digested further to release any fumes. The solution was cooled, and then filtered using whatman No.42 filter paper and then quantitatively transferred to a 250ml volumetric flask and made up to the mark with distilled water.

A blank was run for the digestion procedure to correct for reagent impurities and other environmental contaminations during analysis. The analysis was duplicated in order to ensure precision in the digestion procedure and analytical instrument. The digested sample solution was analyzed for Pb, Cr, Mn, Zn, Fe, Cd and Cu. Analysis of blank was also done.

3.5 Data Analysis

In order to quantitatively analyze and confirm the relationship among soil physico-chemical properties and heavy metal contents the data obtained were subjected to analysis using statistical SPSS 16.0.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Results

4.1.1 Physicochemical Properties of the Soil

Table 4.1 gives the results of the physicochemical parameters of the soil samples from the study area. The pH range of the soil is from 6.64±0.46 to 7.35±0.22. The mean pH value from the study is 7.16. The mean value for the total organic matter (TOM) content for all the soil samples is 2.92±0.50% with minimum and maximum values of 2.46% and 3.56% respectively. The range for electrical conductivity (EC) is 275.13±0.78 µS/cm to 506.60±0.44µS/cm respectively. The mean EC is 362.6±0.67µS/cm. Particle size analysis shows that silt has the lowest composition in all the samples (6.13±3.65%) with minimum and maximum values of 1.50±0.07% and 9.50±0.17 % respectively. The clay component ranged from 13.25±0.14 to 27.0±0.36%, with a mean value of 17.79±0.17%. Sand had the highest percentage composition with a mean value of 76.50±0.45% and a range of 64.50±0.92% to 86.01±0.79%.

Table 4.1 Physico-chemical Properties of Soil Samples Around the Selected Industrial Areas

Sampling Areas	pH	EC(µS/cm)	TOM (%)	% Sand	% Clay	% Silt
Ph1	6.64 ± 0.46^{a}	275.13 ± 0.78^{b}	3.56 ± 0.11^{c}	72.25 ± 0.13^{b}	20.75 ± 0.13^{f}	9.50 ± 0.17^{c}
Ph2	7.22 ± 0.62^{abc}	407.20 ± 0.92^{e}	2.68 ± 0.76^{b}	85.25 ± 0.13^{e}	13.25 ± 0.14^{b}	1.50 ± 0.07^{a}
Pt1	7.35 ± 0.22^{c}	467.30 ± 0.10^{f}	2.46 ± 0.53^{a}	64.50 ± 0.92^{a}	27.00±0.36g	8.50 ± 0.09^{c}
Pt2	7.08 ± 0.76^{bc}	357.30 ± 0.56^{d}	2.57 ± 0.61^{ab}	86.01 ± 0.79^{e}	12.50 ± 0.87^{a}	1.50 ± 0.62^{a}
Te1	7.12 ± 0.17^{bc}	506.60 ± 0.44^{g}	2.69 ± 0.86^{b}	76.75 ± 0.27^{d}	14.75 ± 0.13^{c}	8.50 ± 0.95^{c}
Te2	7.25 ± 0.44^{cd}	288.20 ± 0.13^{c}	3.53 ± 0.36^{c}	75.25 ± 1.60^{c}	18.50 ± 0.26^{d}	7.25 ± 0.70^{bc}
C	7.09 ± 0.21^{b}	208.23 ± 0.20^{a}	2.47 ± 0.61^{a}	74.23 ± 0.29^{c}	20.25 ± 0.13^{e}	5.50 ± 0.16^{b}
Mean	7.16	362.60	2.92	76.50	17.79	6.13

Ph_1: Abumec Pharmaceutical Industry EC: Electrical Conductivity TOM: Total Organic Matter

Ph_2:Arewa Pharmaceutical Industry Pt_1: Chilox Paint Industry Pt_2: Power Seal Paint industry

Te_1: Kaduna textile industry Te_2: United Nigeria Textile Industry C: control

Values are expressed as mean±SD for triplicate determinations. Values with the same subscripts down a column do not differ significantly from each other at $P< 0.05$

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4.1.2 Total Heavy Metal Concentration in the Soil

Table 4.3 shows the statistical result of the total concentrations of the metals investigated in the study. The mean concentration of Pb in the studied area ranged from 20.01±0.85 – 77.18±0.40µg/g. The concentration of Pb at Te$_1$ (77.18±0.40 µg/g) was higher than that of Te$_2$ (61.74±0.40µg/g). The concentration of Pb at Pt$_1$ and Pt$_2$ were 45.91 ±0.26µg/g and 55.29±0.10µg/g respectively. The concentrations at Ph$_1$ (29.35±0.44µg/g) and Ph$_2$ (26.89±0.36 µg/g) were significantly different.

The concentration of Zn ranged from 88.90±0.46 to 217.96±0.16µg/g. The highest concentration of Zn (217.86±0.16 µg/g) was obtained at Pt$_1$ while the concentration of Zn at Pt$_2$ was 205.60±0.46 µg/g. Te$_1$ had a concentration of 191.15±0.98 µg/g while that at Te$_2$ was 134.63±1.10 µg/g. The concentrations of Zn at the various industrial areas were higher than that of the control (88.90±0.46 µg/g). There was a significant difference ($P<0.05$) in the concentration of Zn at the various industrial areas.

Cd was not detected in most of the soil samples analysed. It had a concentration ranging from ND to 1.5±0.02 µg/g with Pt$_2$ having the highest. The concentration of Cd at Te$_1$ was 0.12±0.10 µg/g while that at Te$_2$ was 0.13±0.06 µg/g. There was no significant difference

(P<0.05) in the concentration of Cd at Te_1 and Te_2. Cd concentration at Ph_2 (1.30±0.26µg/g) was also higher than Ph_1 (0.13±0.06 µg/g).

The concentration of Cr ranged from 29.25±0.70 µg/g to 41.25± 0.14 µg/g. Te_1 had the highest concentration of Cr (44.20±0.35µg/g) while that at Te_2 was 41.25±0.14 µg/g. The concentration of Cr at Ph_1 (34.25±0.70 µg/g) was higher than that at Ph_2 (29.25± 0.70 µg/g), while those at Pt_1 and Pt_2 were not significantly different (P<0.05). There was a significant difference in the concentrations of Cr between Ph_1 and Ph_2.

Cu had a minimum and maximum concentration of 9.58±0.70 µg/g and 74.45±0.20 µg/g respectively. The highest concentration of Cu was at Te_1 (74.40±0.20 µg/g) while Te_2 had 34.37±0.16 µg/g. Cu was present in a higher concentration at Ph_2 (14.87±0.85 µg/g) than Ph_1 (9.58±0.70 µg/g). The concentration of Cu at Pt_1 and Pt_2 were not significantly different (P<0.05).

Mn had a concentration ranging from 48.85±0.38 µg/g to 200.00±0.31 µg/g. The maximum concentration was obtained at Pt_1 (200.00±0.31 µg/g). The concentrations of Mn at the various industrial areas were significantly different. The control had the lowest concentration of Mn (48.85±0.38 µg/g).

The concentration of Fe was the highest among the various metals analysed. It concentration was several times greater than those of other metals. The mean concentration of Fe was from 1185.8±4.66 µg/g to 2488±1.37 µg/g. Fe was higher at Pt_2 than Pt_1. Its concentrations at Te_1 and Te_2 were 1240±2.69 µg/g and 1185±4.66 µg/g respectively. There was a significant difference (P<0.05) in the concentration of Fe among the various industrial areas.

Table 4.2 Concentration of Heavy Metals in Soil (μg/g)

Sampling Area	Pb	Zn	Cd	Cr	Cu	Mn	Fe
Ph$_1$	$29.35\pm0.44^{\mathbf{c}}$	$168.54\pm0.44^{\mathbf{d}}$	$0.13\pm0.06^{\mathbf{d}}$	$34.25\pm0.70^{\mathbf{b}}$	$9.58\pm0.70^{\mathbf{b}}$	$92.14\pm0.20^{\mathbf{d}}$	1351±1.
Ph$_2$	$26.89\pm0.36^{\mathbf{b}}$	$141.43\pm0.95^{\mathbf{c}}$	$0.09\pm0.26^{\mathbf{c}}$	$29.25\pm0.70^{\mathbf{b}}$	$14.87\pm0.85^{\mathbf{c}}$	$124.00\pm0.10^{\mathbf{e}}$	1978±2.
Pt$_1$	$44.91\pm0.26^{\mathbf{d}}$	$217.96\pm0.16^{\mathbf{f}}$	ND$^{\mathbf{a}}$	$36.75\pm0.50^{\mathbf{c}}$	$22.40\pm0.26^{\mathbf{d}}$	$200.00\pm0.31^{\mathbf{f}}$	2100±1.
Pt$_2$	$55.29\pm0.10^{\mathbf{e}}$	$205.6\pm0.46^{\mathbf{f}}$	$1.50\pm0.02^{\mathbf{e}}$	$36.38\pm0.69^{\mathbf{c}}$	$22.95\pm0.46^{\mathbf{d}}$	$190.00\pm0.46^{\mathbf{f}}$	2488±1.
Te$_1$	$77.18\pm0.40^{\mathbf{g}}$	$191.15\pm0.98^{\mathbf{e}}$	$0.12\pm0.10^{\mathbf{d}}$	$44.20\pm0.35^{\mathbf{e}}$	$74.40\pm0.20^{\mathbf{f}}$	$87.42\pm0.26^{\mathbf{c}}$	1200±2.
Te$_2$	$61.74\pm0.33^{\mathbf{f}}$	$134.63\pm1.10^{\mathbf{b}}$	$0.13\pm0.06^{\mathbf{d}}$	$41.25\pm0.14^{\mathbf{d}}$	$34.37\pm0.16^{\mathbf{e}}$	$81.15\pm0.44^{\mathbf{b}}$	1185±4.
C	$20.01\pm0.85^{\mathbf{a}}$	$88.90\pm0.46^{\mathbf{a}}$	$0.05\pm0.06^{\mathbf{b}}$	$12.75\pm0.40^{\mathbf{a}}$	$8.32\pm0.26^{\mathbf{a}}$	$48.85\pm0.38^{\mathbf{a}}$	721±1.6

Values are expressed as mean±SD for triplicate determinations. Values with the same subscripts down a column do not differ significantly from each other at $P< 0.05$

4.1.3 Geoaccumulation Index (I-geo) of the Metals

The result of the geoaccumulation index (I-geo) of the heavy metals in the study area is presented in the table 4.4. The geoaccumulation index (I-geo) of Pb, Zn, Cd, Cr, Cu, Mn and Fe ranged from 1.12-2.62, 0.01-0.71, 0.00-1.20, 0.61 -1.20, -0.38 – 2.57, 0.18 -1.45, and 0.21 – 1.20 respectively. The highest I-geo of Pb (2.62) was obtained in samples from textile industry (Te_1) while the least was obtained in samples from pharmaceutical industry, Ph_2 (1.12). The I-geo of Zn was generally <1. Cd had a maximum I-geo of 1.20 which was at Pt_2. The I-geo of Cr were general <1 except at Te_1 and Te_2, with I-geo of 1.20 and 1.11 respectively. Cu had a maximum I-geo of 2.57 at Te_1 while Mn had a maximum of 1.45. The I-geo of Fe was generally <1, except at Pt_2. The result shows that some of the sampling areas were moderately polluted with the metals.

Table 4.3 Geoaccumulation Index(I-geo) of Heavy Metals

Industry	Pb	Zn	Cd	Cr	Cu	Mn	Fe
Ph_1	1.23	0.34	0.56	0.84	-0.38	0.33	0.32
Ph_2	1.12	0.08	1.10	0.61	0.25	0.76	0.87
Pt_1	2.00	0.71	0.00	0.94	0.86	1.45	0.96
Pt_2	2.15	0.61	1.20	0.93	0.88	1.22	1.20
Te_1	2.62	0.52	0.71	1.20	2.57	0.25	0.29
Te_2	2.30	0.01	0.74	1.11	1.46	0.18	0.21

4.1.4 Enrichment Factor (EF) of the Metals

The result of enrichment factor (EF) of the investigated metals (Pb, Zn, Cd, Cr, Cu, Mn and Fe) is presented in table 4.5. The enrichment factor was based on the standardization of the element investigated against a selected reference metal. EF<2 implies a deficiency to minimal enrichment of the metal tested; 2-5 indicates moderate enrichment and 5-20 significant enrichment due to anthropogenic input. The EF of Pb in all the areas ranged from 0.49 to 2.24, with a mean of 1.40. The EF of Zn in all the areas was <2.2. Zn had a maximum EF of 1.3, at Te_1. The EF of Cd was from 0.00 to 8.7, with the highest enrichment being at Pt_2(1.20). The EF of Cr was < 2 except at Te_1 (2.01) which imply moderate enrichment. The EF of Zn and Fe in all the areas was less than 2. Cu and Mn have EF values ranging from 0.63 to 5.2 and 0.92 to 1.41 respectively. The EF of Cu in most of the studied area was < 1, except at Te_1 and Te_2 with a maximum of 5.2 and 2.5 respectively. The EF of Fe ranged from 0.95 to 1.11 with Ph_2 and Te_1 having the highest and lowest respectively.

Table 4.4 Enrichment Factor (EF) of Heavy Metals in Soil

Industry	Pb	Zn	Cd	Cr	Cu	Mn	Fe
Ph_1	0.80	1.01	0.92	1.43	0.63	1.01	1.01
Ph_2	0.49	0.58	1.20	0.84	0.98	0.92	0.95
Pt_1	2.16	0.84	0.00	0.99	0.92	1.41	1.04
Pt_2	2.00	0.72	2.70	1.70	0.79	1.20	1.02
Te_1	2.24	1.30	1.43	2.01	5.20	1.04	1.11
Te_2	1.89	0.92	1.52	1.97	2.50	1.01	0.97

4.1.5 Correlation Analysis Among Soil Physicochemical Properties and Heavy Metals

Table 4.6 shows the result of Pearson correlation analysis among various physicochemical properties of the soil. The result shows a significant positive correlation of Zn with soil pH and EC. Inter-elemental analysis also indicates a significant correlation of Zn with Cr and Mn. Zn was however negatively correlated with Cd. Pb was positively correlated with soil pH and EC. There was a strong positive correlation of Pb with Cr and Cu. The correlation between Cd and TOM was significantly positive. Cd significantly positively correlated with Fe. Cr significantly positively correlated with soil EC, while Mn positively correlated with pH, clay and silt components of soil. Fe significantly positively correlated with Cd and Mn but negatively with silt component of the soil.

Table 4.6 Correlation Analysis Among Soil Physicochemical Properties

	pH	EC	TOM	Sand	Silt	Clay	Pb	Zn	Cd	Cr	Cu	Mn	Fe
pH	1												
EC	0.27	1											
TOM	-0.48	0.25	1										
Sand	-0.30	0.53	-0.15	1									
Silt	-0.05	0.73*	0.43	-0.85	1								
Clay	0.34	0.33	0.05	-0.95	0.67*	1							
Pb	0.31	0.57	0.04	0.06	0.18	-0.27	1						
Zn	0.61	0.76*	-0.24	-0.23	0.21	0.17	0.48	1					
Cd	-0.60	-0.20	0.29	0.36	-0.18	-0.30	-0.06	-0.16	1				
Cr	0.37	0.69*	0.21	0.10	0.11	-0.25	0.84*	0.71*	0.03	1			
Cu	0.11	0.68*	0.03	-0.05	0.39	-0.23	0.89*	0.43	-0.08	0.69*	1		
Mn	0.48	0.42	-0.16	-0.37	0.16	0.46	0.12	0.72*	0.27	0.36	-0.08	1	
Fe	0.07	0.16	-0.01	0.05	-0.10	0.04	0.13	0.45	0.72*	0.35	-0.12	0.84*	1

*correlation is significant at 0.05 level (2-tailed).

4.2 DISCUSSION

4.2.1 Physicochemical Properties of the Soil

Table 4.1 shows the physicochemical properties of the soil samples analysed. The soil pH ranged from 6.64±0.46 to 7.35±0.22. This implies that the soil in the study area is neutral to slightly alkaline. The value obtained is lower than the pH range of 6.22-8.40 documented by Okunola (2007). It is however close to that reported by Umoru (2013) in a similar study. The least pH value was obtained at the vicinity of pharmaceutical industry (Ph_1). This may be attributed to the acidic waste discharged into the soil from the manufacturing process of drugs. The pH values are characteristic of areas were rainfall is low thus reducing leaching of cations and resulting to the accumulation of base forming cations on the soil surface (Akoji, 2010). Alkaline soil condition will result to increase in heavy metal concentration in the soil (Nath, 2013; Bansal, 2004).

The electrical conductivity (EC) of the soil sample fluctuates within 287.5±0.13 to 506.3±0.44. The mean value obtained was 362.6±0.56. The variation in EC values of the samples show the differences in the dissolved salt content of the studied soils. The mean organic matter content obtained in the study is 2.92 %. Such low organic matter content would affect the ability of the soil to absorb heavy metals through cation exchange and chelate formation. Thus, heavy metal would be poorly binded to the soil surface and made readily mobile and available for plant uptake and underground water contamination (Nath, 2013). The high percentage composition of sand implies that such soil would enhance the leaching of soil heavy metals from soil surface. Generally, the concentration of heavy metal in soil increases with decrease in the sizes of the soil particles (Sayyed and Sayadi, 2011).

4.2.2 Total Heavy Metal Concentration of the Soil

The result in table 4.3 shows a significant variation in the heavy metal content of the soil investigated. Such differences are apparent and could be attributed to the differing activities; raw materials and consequently effluents discharged into the environment (Ogbemudia and Mbong, 2013).

4.2.2.1 Lead

Pb was present in appreciable amount in all the soil samples analysed. The mean concentration ranged from 20.01±0.85 µg/g to 77.18±0.40 µg/g. The concentration of Pb at the vicinity of Te_1 (77.18±0.40 µg/g) was higher than that of Te_2 (61.74±0.40 µg/g). The elevated concentration obtained might be due to presence of mechanic workshops, garbage disposal sites and commercial roads along this area, thus making the soil to be relatively prone to Pb from vehicular discharge, garbages and other Pb bearing materials (Yahaya, Ezeh, Musa and Mohammad, 2010 ; Gilbert *et al.*, 2009). The concentration of Pb at Ph_1 (29.35±0.44 µg/g) was slightly higher compared to that at Ph_2 (26.89±0.36 µg/g). The disparity in concentration was small thus suggesting a common origin. The concentration of Pb at Ph_2 was the least among all the industrial areas. The source of Pb in this area could be attributed to leaching and runoff of the metal from sources around the vicinity as well as traffic in the area. There was a significant difference in the concentration of Pb at Pt_2 (55.29±0.10 µg/g) and Pt_1 (44.91±0.26 µg/g). The difference in the metal content may be due to the higher organic matter content of the soil in this area. Higher organic matter enhances the adsorptive capacity of the soil thus favouring the accumulation of heavy metals (Afshin and Farid, 2007). The presence of large traffic in this area is also a contributing factor. The mean concentration of Pb obtained in this study is higher than Soil quality criteria of 55µg/g reported by Cheng for soil in South Africa. The result was however lower than 151.5 – 540 µg/g reported by Inuwa *et al.* (2013) in a similar study. The concentration of Pb is also lower than the European Union (EU) upper limit of 300 µg/g reported by European Commission (2000). The concentration of Pb obtained was however higher than the background concentration of 25 µg/g of Pb in soil (Canadian Environmental Quality, 1992). It is also within the range of 2 - 200 µg/g documented by the United State Environmental Protection Agency (USEPA, 1991) as the permissible limit of Pb in soil. The concentration of Pb in the sampling area where generally higher than the control.

4.2.2.2 Zinc

The concentration of Zn obtained ranged from 134.63±86.30 µg/g to 217.96±38 µg/g. The concentration at Pt_1 (217.96±0.16 µg/g) was higher when compared to Pt_2 (205±0.46 µg/g) which might be due to the preferential accumulation of Zn in the clay and silt components of the soil. However the difference at Pt_1 and Pt_2 was not significant at $P<0.05$. Reduced soil particle sizes favour higher metal concentration due to enhance surface interaction (Sayyed and Sayadi, 2011). The generally higher concentration of Zn in vicinities of paint industries is because Zn is widely used to make paint and dye (David and Stokes, 2008). The concentration at Te_1 (191.15±0.98 µg/g) was higher than Te_2 (134.63±1.10 µg/g). Te_2 has been in a state of dormancy for many years, this no doubt might have contributed to the decrease in the extent of soil contamination by Zn in this area. Soils in area with longer history of industrial activities tend to show higher contamination by trace metals (Afshin and Farid, 2007). The concentration of Zn in the study area was three times higher than that of the control. The result of Zn concentration in the area studied is higher than 36 - 113 µg/g reported by Shamah and Prasade (2009) and 121 µg/g reported by Shivah *et al.* (2012). It is lower than the WHO (2000) standard of 300 µg/g maximum permissible limit of Zn in soil. It is however within the range of 10 - 300 µg/g allowable limit of Zinc in soil (USEPA, 1991). Zn is an essential trace metal in soil, however at high concentration, it may be toxic to plants and animals. It also has high tendency to bind to soil organic matter and has higher availability at lower pH.

4.2.2.3 Cadmium

Cd was not detected in most of the soil samples. The concentration of Cd obtained in some of the industrial areas was on average comparable to the background concentration of Cd in soil. It can therefore be inferred that the source of the element in such areas could partly be due to anthropogenic contribution and the gradual disintegration of the parent rock that formed the soil. However, appreciable concentrations of Cd were also obtained in some of the study area. The highest concentration of Cd (1.5±0.02 µg/g) was obtained at the vicinity of paint industry (Pt_2), While Cd was not detected at Pt_1. This could be due to the proximity of Pt_2 to an electroplating and alloying company. Cd is known to be a major component in the manufacture of anticorrosive coatings for metals, solders and bearing alloys (David, 2008). The concentration of Cd obtained at Te_1 and Te_2 did not differ significantly which point to a common source. The result obtained is higher than 0.1 – 0.7 µg/g reported by Inuwa *et al.* (2013) and the permissible limit of 0.1 – 1.0 µg/g reported by Fabis (1987). It is however lower than the concentration range of 0.14 to 7.0 µg/g reported by Yahaya *et al.* (2010) and the permissible limit of 22 µg/g as soil quality criteria for industrial soil in Canada (Oniawa, 2001). Cd in soil is readily absorbed by plants and thus accumulates and passes along the food chain. Consumption of plants containing 3.0 ppm Cd can poison man and animals. It interferes with enzymes and other proteins and causes damages to body organs (David, 2008).

4.2.2.4 Chromium

The mean range of Cr obtained was from 29.25±0.70 µg/g – 41.25±0.14 µg/g. The highest concentration of this metal was obtained at the vicinity of textile industry, Te_1 (44.20±0.35 µg/g). Chromium containing compounds are major raw materials used in textile industries and some other industries. Chromium compound are used as colouring agents for textiles and mordant; leather tanning and emerald green glass (David, 2008). The concentration of Cr at Te_1 was however higher than that at Te_2. The concentration of Cr at Pt_1 and Pt_2 did not differ much. Cr concentration at Ph_1 (34.25±0.70 µg/g) was higher than Ph_2 (29.25±0.70 µg/g), which could be due to the higher clay and silt content of soil at Ph_1. Heavy metals are found mainly in the clay and silt fractions than sand. Trace metal concentrations increase with decrease in particle sizes (Amusan, Bada and Salami, 2000). The concentration of Cr from the soil of textile industry is higher than 6.6 to 22 µg/g reported by Shiva (2012) in his study on heavy metal pollution in industrial area in India as well as 0.5 µg/g reported by Nwajei (2002) in a similar study. It is however lower than 14.2 – 92.7 µg/g reported by Inuwa *et al.*

*(*2013). The concentration of Cr obtained is also lower than the soil quality criteria of 87 µg/g for Canadia (industrial) soil (Onianwa, 2001).

4.2.2.5 Copper

Data on the concentration of Cu in the soil samples analysed are shown on the table. Cu was present in the various samples analysed. The concentration of copper ranged from 8.32±0.26 – 54.40±0.20 µg/g. With the exception of soil samples from the vicinity of paint and textile industries, most of the soils investigated have Cu content close to that of the control (8.32±0.26 µg/g). The concentration of Cu at Te_1 (74.40±0.20 µg/g) was higher than 34.37±0.16 µg/g obtained at Te_2. The elevated concentration of Cu at Te_1 suggests additive input from agricultural activities in the vicinity. Copper is a component of fabrics and leather, electrical wiring and some agricultural fungicides (David, 2008). The concentration of Cu at Ph_2 (14.87±0.85) was almost twice that recorded at Ph_1 (9.58±0.70). This may be due to runoff and mobility of various copper- containing metallic wastes discharged from the neighbouring metallic industries in its vicinity.

The Cu content at Pt_1 (22.40±0.26 µg/g) and Pt_2 (22.95±0.46 µg/g) were not significantly different. The concentration of Cu obtained is lower than 100 µg/g reported by Reimann *et al.* (2000) as soil quality criteria for Norway soil; 5.34 – 198.23 µg/g by Abida *et al.* (2009) for India soil and 467 µg/g by Iyaka and Kakulu (2012) for Nigeria soil.

4.2.2.6 Manganese

On average, soil contains 600 µg/g of Mn and a concentration range of 200 – 3000 µg/g (Akoji, 2010). The concentration of Mn in this study ranged from 81.15±0.44 µg/g to 200.0±0.31 µg/g. The lowest and highest concentrations were obtained at textile (Te_1) and paint industry (Pt_1) respectively. Comparisons of the result obtained with the normal background concentration of cupper in soil shows less contamination. There was no significant difference in the concentration of Mn at Pt_1 and Pt_2. This could be as a result of similarity of the industrial processes. It also points to a common source of the metals. The concentrations of Mn obtained in this study is within the range of 600 µg/g documented by USEPA (1991) as the background concentration of Mn in soil.

4.2.2.7 Iron

Fe was observed to be largely present in all the soil samples analysed. It has a mean concentration ranging from 1185.8±4.66 - 2488±1.37 µg/g. The highest concentration was obtained from paint industry, Pt_2 (2488±1.37 µg/g) while the lowest from textile industry, Te_2 (1186±4.66 µg/g). The concentration of Fe obtained was several times higher than those of other elements. Various researchers have reported the higher abundance of Fe on the earth crust in relation to most other trace metals (Adebiyi *et al.*, 2007; Fagbote, 2010). The Fe content of soil at Pt_2 (2488±1.37 µg/g) was relatively higher when compared to that at Pt_1 (2100±1.49 µg/g). The concentration of Fe at Ph_2 (1978±2.47 µg/g) was also higher than that at Ph_1 (1351± 1.69 µg/g) which implies a different extent of soil contamination by the metal. This may be due to the Fe content of the parent material. There was no significant difference in the concentration of Fe at Te_1 (1200±2.69 µg/g) and Te_2 (1185±4.66 µg/g). The concentration of Iron in various soil samples differ depending on their origin and mineralogical content of the parent material (Abida *et al.*, 2009). The presence of neighbouring metal industries that manufacture iron-containing products could have contributed to the enriched content of Fe in this area. Trace elements are readily leached and washed away to other areas. Mobility of trace metals occur more readily at lower pH (Bozkurt *et al*., 2000). The concentration of Fe obtained in this study is small when compared to the tolerable limit of 26,000 µg/g of Fe in soils (USEPA, 2004). The mean concentration of Fe in most of the site is within the range of 6761-6234 µg/g reported by Abida *et al.* (2009) for Indian soil. The concentration of Fe obtained is lower than the maximum value of 6000 µg/g reported by Yahaya *et al.* (2013).

4.2.3 Geoaccumulation Index (I-geo) of Heavy Metals in the Soil.

The background concentration of the metal in soil was used as a basis of ascertaining the degree of pollution. The result of I-geo is shown in table 4.5. It was observed that the soil was moderately to heavily polluted with Pb, most especially the soil at the vicinity of textile industries (Te_1 and Te_2). The highest contamination of soil by Zn occurred at Pt_1 (0.71). The I-geo of Zn obtained showed that the soil was unpolluted to moderately polluted with Zn. The mean I-geo of Cd in the study area also indicates moderate pollution with the element. With the highest level of pollution at Pt_2 (2.70). Most of the soils studied were unpolluted to moderately pollute with Cr, Cu and Mn. The soil at Te_1 has the highest pollution by Cr (I-geo= 1.2).

The I-geo of Fe in most of the samples was <1, thus implying uncontaminated to moderate contaminated soil, while that at Pt_2 was < 2, suggesting moderate pollution. The mean I-geo of most of the metals investigated therefore showed uncontaminated to moderate contamination of the soil. Thus Cd, Pb , Fe and Cr have the highest degree of pollution.

4.2.4 Enrichment Factor (EF) of Heavy Metals

Table 4.6 gives the enrichment factor (EF) of the metals investigated in the soil. EF values that are less than or equal to 1, generally indicate that the element is from lithogenic origin, while EF > 1 suggests that the metals are from anthropogenic contribution (Akoji, 2010). The EF of Pb obtained was generally <2 except at Pt_1 and Te_1 with 2.16 and 2.24 respectively. This implies that soil at Te_1 and Pt_1 are moderately enriched with Pb. The soil samples had a depletion to minimal enrichment with Zn (EF<2). The EF of Cd indicates a depletion or moderate enrichment. Its maximum EF of 2.7 at Pt_2 however shows an enrichment of the metal due to anthropogenic input. The maximum EF of Cr obtained is 2.01. This value shows a moderate pollution by this metal. Its mean value of 1.49 indicates deficiency to minimal enrichment. With the exception of Te_1 and Te_2 which show significant pollution and moderate pollution respectively by Cu in some sites, the EF of Cu in all the samples indicates deficiency to minimal enrichment. The EF of Mn which was generally <2 in all the areas also showed a minimal enrichment. Based on the result from EF. The pollution of the soil by the metals can be arranged in the increasing order: Zn<Fe<Mn<Pb<Cr<Cd<Cu.

4.2.5 Correlation Analysis

The result of correlation analysis shows that Zn is significantly positively correlated with pH and electrical conductivity of the soil. Soil pH is the major factor that controls metal mobility in soil. Metal cation solubility typically increase with a decrease pH. As pH decreases, the solubility of the metal cation increases due to desorption from soil minerals such as metal oxides, hydroxides and carbonates (Bozkurt *et al*., 2000). The significant positive correlation of Zn with Cr and Mn suggests the close association between the origin of these metals in the soil. The positive correlation between Pb and the pH and EC of the soil also indicates the significant role of such soil parameters in determining the solubility and mobility of the metals in soil. Pb also correlated positively with Cd and Cu thus suggesting the similarity in the source of these metals due to their close association. The positive correlation of Cd with total organic matter highlights the influence of total organic matter in soil metal concentration. Soil organic matter is a principal variable that affects the spatial distribution of heavy metals in soil (Afshin, 2007). Increase in soil organic matter content lead to elevation of soil adsorption capacity hence enhancing the accumulation of trace metals. The significant correlation of Cr with soil EC may be due to increase in the level of exchangeable Cr in the soil. The level of Cr in the soil is also controlled by the exchangeable Cr in response to pH (Akoji, 2010).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The research done within the framework of this thesis has highlighted the physicochemical and heavy metal concentration in the studied areas. It has also portrayed the need for a continuous monitoring of heavy metals in soil, most especially in industrial areas due to their tendency to bioaccumulate in plants and animals. Results from enrichment factor and geoaccumulation index have also shown the extent of soil contamination by these metals.

5.2 Recommendations

Sequel to above, the following recommendations are put forward in order to reduce the risk associated with these metals and ensure environmental protection:

i. There should be constant treatment of waste by industries before discharge to the environment.
ii. Environmental protection agencies should ensure thorough and constant monitoring of industrial activities in these areas alongside the treatment and discharge of effluents.

iii. Other researches should be carried out in this area with emphasis on the speciation of these metals.

REFERENCES

Abida, K., Akedia, B., & Jones, A. (2009). Heavy metal content of soil around industrial areas. *Journal of Applied Geology*, 3,23-35.

Adebiyi, F. & Moodle, A. (2007). Chemical and elemental characterization of components of Nigerian bitumen sands. *Energy Sources*, 29(8), 669-676.

Afshin, K. & Farid, D.(2007). Statistical analysis of accumulation and sources of heavy metals occurrence in agricultural soil of Khoshk River banks, Shiraz Iran. *American –Eurasian Journal of Agriculture and Environment.*2(5), 565-573.

Agamuthu, P., Abioye, O.P., & Abdulaziz, A. (2010). Phytoremediation of soil contaminated with used lubricating oil using *Jatrophacurcas*. *Journal of Hazardous Materials* 179:891 – 894.

Agency for Toxic Substances and Disease Registry (2005). *Toxicological profile of nickel*. Atlanta, GA: Agency for Toxic Substances and Disease Registry.

Akbar, K., Hale, W., Headley, A.,& Athar, M. (2006). Heavy metal contamination of roadside soils. *Soil Water Res*earch 1(4),158-163.

Akoji, J. (2010). Physicochemical analysis and chemical speciation of lead, copper, manganese and iron in Abuja Street Soil. Unpublished Master Thesis, Federal University of Technology, Minna.

Amusan, A.A.,Bada, S.B., & Salami,A (2000) Effect of traffic density on heavy metal content of soil and vegetation along road side in Osun state, Nigeria. *West African Journal of Applied Geology*, 4,112-120.

Anoduadi, C., Okenwa, L. & Okieimen,F. (2009). Metal immobilization of contaminated soil using laterite and termite mound soil: Evaluation by chemical fractionation, *Nigerian Journal of Applied Science,* 27:77-87.

Asaah,V., Abimbola,A.F.,& Suh,C.D. (2006). Heavy metal concentration and distribution in surface soils of the Bassa Industrial Zone 1, Douala, Cameroon. *Arabian Journal of Science,* 31 (2A), 147-158.

Baldwin, D. R. & Marshall, W.J. (1999). Heavy metal poisoning and its laboratory investigation. *Annuals of Clinical Biochemistry*, 36, 267-300.

Bansal, O.P. (2004). Uptake of heavy metals by crops plants. *Polland Research Journal* 23(3), 501-506.

Basta, N.T., Ryan, J.A & Chaney, R.L. (2005). Trace element chemistry in residual-treated soil: Key concepts and metal bioavailability. *Journal Environmental Quality,* 34(1), 49-63.

Bang, J. (2002). Dissolution of soil heavy metal contaminants as affected by pH and redox potential, Master Thesis, Carolina University Raleigh.

Bhattacharya, A.,Mukhajee, A. & Nordqvist, S. (2002). Metal contamination experimental studies on remediation. *The Science Total Environmental Journal* 2, 190-195.

Bjuhr, J. (2007).*Trace Metals in Soils Irrigated with Waste Water in a per urban Area Downstream Hanoi City*, Vietnam, Seminar Paper, Uppsala Sweden.

Blaser,P., Zimmermann, S., Luster,J. & Sbotyk, W. (2000). Critical examination of trace elements enrichments and depletions in soils: As, Cr, Cu, Ni, Pb and Zn in Swiss Forest Soils. *Science Total Environment*, 249,257-280.

.

Bozkurt, S., Moreno, L., Neretnieks, I. (2002). Long-term processes in waste deposits. *Sci.ence Total Environment.* 250, 101-121.

Brady, N.C.& Weil, R.R. (2008). *The Nature and Properties of Soils*. Pearson Education Inc; Upper Saddle River, New Jersey, 65.

Buccolieri, A., Buccolieri, G., Cardellicchio, N., Dell'Atti, A.,Di Leo, A. & Maci, A. (2006). Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, Southern Italy). *Marine Chemistry Journal*, 99, 227–235.

Canada Council of Ministers of Environment. (1992). Canadian Environmental Quality for Contaminated Sites. Report CCME EPC, Winnipeg, Miannitoba.

Campbell, G.C. (2006). Cadmium-A priority pollutant. *Environmental Chemistry*, 3(6), 49- 63.

Chen, M., Ma, L.Q., Hoogeweg, C. & Harris, W. (2001). Arsenic background concentration in Florida, USA surface soils: Determination and interpretation. *Environmental Forensics*,2,141-153.

David, D. & Stokes, C. (2008). Heavy metals in North Carolina soil: Occurrence and Significance. *Department of Agriculture and Consumers Service Publication*.

D'Amore, J.J.,Al-Abed,S.R., & Ryan, A.(2005).Methods for speciation of metals in soils: a review. *Journal of Environmental Quality,* 34(5),1707-1745.

Devolder,P.S., Brown,S.L. & Pandya,K.(2003). Metal bioavailability and speciation in a wetland tailings repository amended with biosolids, compost, ash, and sulfate, *Journals of Environmental. Quality,* 32(3), 851-864.

Duffus, J.H. (2002). "Heavy metal" – a meaningless term? *Pure Applied Chemistry* 74,793–807.

European Commission (EC). (2000). European Commision, Office of official publication of the European communities, Luxembourg. Council, directive on protection of environment, in particular soil.

Eruyogho F.I, Okuo J.M & Ndiokwere C.I (2007). A Survey of Levels of some Heavy Metals in Scalp Hair of Urban dwellers: A Case Study. *Journal Applied Science*, 7(3), 465-470.

Fabis, W. (1987). Determination of heavy metal concentrations in street dusts in Istabul E-5 highway. *Environment International*, 29,979-985.

Fagbote, E. & Olanipekun, E. (2010). Speciation of heavy metals in sediment of Agbabu Bitumen deposit area, Nigeria. *Journal Applied Science and Environmental Management*, 14 (4), 47 – 51.

Fakoyade,S.O. & Onianwa,P. (2002). Heavy metal contamination of soil and bioaccumulation in Guinea grass panicumacium around Ikeja Industrial estate, Lagos, Nigeria. *Environmental Geology*, 43, 45-100.

Fergusson, J.E. (1990). *The heavy elements, chemistry, Environmental impact and health effects.* Pregamon Press, Oxford.

Finzgar, B. & Lestan, D. (2006). Bioavailability and mobility of Pb after soil treatment with different remediation methods, *Plant, Soil and Environment*, 52(1), 25–34.

Gabriela, O., Cristina, M., and Angela, M. (2011). Assessment of lead and cadmium content in the soils and plants in industrial area of Mare, Romania. *American Journal of Environmental Sciences.* (5), 402-408.

Galceran,J., Company, E., Puy,J., Cecilia, J. & Garces, J.L.(2004). A New Electroanalytical Technique for Measuring Free Metal Ion in Concentration. *Journal of Electroanalytical Chemistry*. 566, 95-109.

Gerhardt, K. E., Huang, X. D., Glick, B. R., &Greenberg, B. M. (2009). Phytoremediation and rhizoremediation of organic soil contaminants: Potential and challenges. *Plant Science*, 176, 20 – 30.

Ghosh, M., & Singh, S.P. (2005). Review of phytoremediation of heavy metals and utilization of its by-products. *Applied Ecology and Environmental Research.*3 (9), 239-250

Gilbert, O. & Osibanjo, O. (2009). Assessment of Soil Pollution by Slag from an Automobile Battery Manufacturing Plant in Nigeria. *African Journal of Environmental Science and Technology* 3 (9), 239-250.

Govil, P.K, & Reddy,G.L,(2001). Contamination of soil due to heavy metals in Pantecheru Industrial Development Area,Andra, India. *Environmental Geology*, 41,461-489.

Greany, K. (2005*). An assessment of heavy metal contamination in the marine sediments of Las Perlas Archipelago, Gulf of Panama,* M.S. thesis, School of Life Sciences Heriot-Watt University, Edinburgh, Scotland.

Henry, J.R. (2000). *An Overview of Phytoremediation of Lead and Mercury*- NNEMS Report, Washington,D.C 3-9.

Housecroft, C.E. & Sharpe, A.G. (2008). *Inorganic Chemistry* (3rd), Prentice Hall, Harlow.

IITA (1979). *Selected methods for soil and plant analysis.* Manual series No. 1, Ibadan. 2-53.

Inuwa. M., Abdulrahman.F, Yuauri, B. & Ibrahim, S.A. (2013). Analytical assesment of some trace metal in soils around the major Industrial Areas of North western Nigeria. *Trend in Applied Sciences Research*. 2,515-521.

Iyaka, Y.A. and Kakulu, S.E. (2012). Heavy metal concentration in top agricultural soils around ceramic and pharmaceutical industrial sites. *Journal of Emerging Trend in Engineering and Applied Science, Sc*. 2(5):754-758.

Jagrati, A. (2012). Determination of levels of uptake of few heavy metals to the leaves of *Menthe arvensis* Atomic absorption spectrometrically. *International Journal of Research in Chemistry* 2: 63-67.

Johnson, S. (2010). *Heavy metals speciation in street soil*. Masters Thesis, Lagos state University.

Jonathan,I(2010). *The incidence of Cerebrospinal Meningitis in Zaria.* Masters Thesis, Ahmadu Bello University, Zaria.

Jonathan, I. (2010). *The role of Industrialization in the economic growth of a nation*. Kerling Press, Kaduna.

Jones, C.A., Jacobsen J., & Lorbeer S. (2002). Metal concentrations in three Montana soils following 20 years of fertilization and cropping. *Community Soil Science Plant Anal*ysis, 33(9&10), 1401-1414.

Kaasalainen, M. & Yli-Halla, M. (2005). Uses of sequential extraction to assess metal in soils, *Environmental Pollution Journal*, 126(2), 225-258.

Kabata, A. & Pendias, H. (2001*). Trace Metals in Soils and Plants*, USA, CRS Press.

Kabata A & Mukherjee A.B (2007). *Trace elements from Soil to Human*. Berlin: Springer Verlag.

Khan.S, Haug, B. & Zhu G., (2008). Health risk of heavy metals in contaminated soils and food crops Irrigated with waste water Beijing, China, *Environmental Pollution*, 152,686-831.

Klaus. A (2000). Definition of "Heavy Metals" and Their Role in Biological Systems

Lenntech Water Treatment and Air Purification (2004). *Water Treatment*, Published by Lenntech, Rotteerdamseweg, Netherlands.

Loska, K., Wiechula, D., Barska. B., Cebula, E. & Chojnecka,A.(2003). Assessment of arseni enrichment of cultivated soils in Southern Poland. *Poland Journal of Environmental Science*. 12,187-192.

Luilo,G.B & Othman, O.C. (2006). Lead pollution in urban roadside environments of Dares Salaam city. *Tanzania Journal of Science,* 32(2),61-67.

Martin,J.A., Arias,M.L. & Corbi,J.M.(2006). Heavy metals content in the Ebro Basin (Spain); Application of the multivariate geostatistical methods to study spartial variations. *Environmental pollution,* 144,1001-1012.

Martinez, E., & Motto, E. (2000) Solubility of lead, zinc and copper added to mineral soils. *Environmental Pollution*, 107,153-158.

Muller, G. (1969). Index of geoaccumulation in sediments of the Rhine River, *Geographical Journal* 2, 109-118.

Momani, K.A. (2006). Partitioning of lead in urban street dust based on the particle size distribution and chemical environments. *Soil and Sediment Contamination,* 15, 131- 146.

Mwegoha, W. & Kihampa, C. (2010): Heavy metal contamination in agricultural soils and water in Dar es Salaam City, Tanzania. *Africa Journal of Environment Science and Technology*, 4 (11), 763-769.

Nath, T. (2013). Determination of heavy metals and its impact on tea cultivated soil and tea leaf in Dibrugarh district of Assam, India. *International Journal of Advanced Research*, 1(9), 561-567.

Nwajei, G. E. (2002). Trace Metals distribution in synodontismembranous sediment *Asyustasiagangetica* and *Platostomaafricanium* from Ofuafor River around glass factory in Ughelli North Local Government Area Delta State Nigeria. *Journal of Environmental Science*, 14,79-82.

Ogbemudia,F. & Mbong, E. (2013). Soil reaction and heavy metal index of dump site in

Uyo Municipality. *Research Journal of Environmental Science and Toxicology*, 1 (4), 82- 85.

Ogbonna, D., Igbenijie, M. & Isirimah, N. (2006). Microbiological and physicochemical characteristics of the soils of waste collection sites in Port Harcourt City, Nigeria. *Nigeria Journal Soil Science*, 16,162-167.

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

Onianwa, P.C. (2001). Monitoring atmospheric metal pollution: A review of the use of mosses as indicators, *Environment Monitoring and Assessment*, 71, 13-50.

Oyedele,D., Gasu,M. & Awotoye,O.(2008). Changes in soil properties and plant uptake of heavy metals on selected municipal solid waste dump. *Science Total Environment*, 244-269.

Reimann, C., Sieweb, U., Tarvainen,T., Bityukova,L., Erikson,J.& Giluas, A.(2000). Baltic soil survey: Total concentration of major and selected elements in arable soils from ten countries around the Baltic Sea. *Science Total Environment,* 257-270.

Romic, M. & Romic,D. (2003). Heavy metal distribution in agricultural top soil in urban area. *Environmental Geology*. 43,975-805.

Sandra, H.M. (2011).*Community garden heavy metal study*. Canada, Ecology action centre.

Sayyed, M.R. & Sayadi,M.H. (2011). *Variations in the heavy metal accumulation within the surface soils from the Chitgar Industrial Area of Tehran*. Proceedings of the International Academy of Ecology and Environmental Science 1(1), 36-46.

Scragg, A. (2006). *Environmental Biotechnology,* Oxford, Oxford University Press, 2nd edition.

Seaward, M.R, (2004). The use of lichens in environmental impact assessment. *Symbiosis*, 37,293-305.

Sharma, R. & Pervez, S.P. (2005) Toxic metal status in the blood and breast milk samples in an integrated steel plant environment in Central India. *Environment Gochemistry Health*, 27:39-45.

Sharma, S., & Prasade, F.M. (2010). Accumulation of Lead and Cadmium in Soil and Vegetable Crops along Major Highways in Agra (India). *Journal of Chemistry* 7(4), 1174-1183.

Shivah, K. (2009). *Heavy metal composition of previous industrial sites in Iran*. Proceedings of the International Academy of Ecology and Environmental Science, 1(2):34-40.

Soil Survey Manual (1993). *Soil conservation service*. U.S. Department of Agriculture Handbook No.18.

Suciu, C., Cosma, M., Todica, S.D., Bolboaca,K. & Jantschi,P. (2008). Analysis of soil heavy metal pollution and pattern in Central Transylvania, *International Journal of Molecular Sciences*, 9(4), 434–453.

Sudduth, K.A., Kitchen, N.R., Wiebold, W.J., &Thelen, K.D. (2005). Relating apparent soil electrical conductivity to soil properties across the North-Central USA. *Computers and Electronics in Agriculture,* 46(2005), 263-283.

Sutherland, R.A., (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology, 39, 611-37.*

Tenenbein, M. (2005). Unit-Dose packaging of Iron supplements and reduction of Iron poisoning in young children. *Pediatry Adolescence Medical*, 159,557-560.

Umoru,P.(2013).Concentration of heavy metals in soil from an irrigated farmland in Kaduna Metropolis, Nigeria. *International Journal of Advancements in Research & Technology*, 2(1), 123-134.

United States Environmental Protection Agency (USEPA). (1991). *Ground water issue: Behavior of metals in soil.* USEPA, EPA/5-92.

United States Environmental Protection Agency (USEPA).(2004). *Child Specific exposure factor handbook*, EPA/600/P-00. National Centre for Environmental Assessment, Washington, DC. 40.

World Health Organization (WHO). (2000). *Lead, Cadmium, Mercury and Arsenic – Environmental Health Criteria, Geneva*: World Health Organization, 165.

Yahaya, M., Ezeh, G., Musa, F., & Mohammad, S.Y. (2010). Analysis of heavy metals concentration in road sides soil in Yauri,Nigeria. *African Journal of Pure and Applied Chemistry*.4 (3), 22-30.

Zhang, F., Yan, X., Zheng, C., Zhang M, Shrestha S, Devkota L.P, & Yao, T. (2012). Influence of traffic activity on heavy metal concentrations of roadside farmland soil in mountainous areas. *International Journal Environmental Research Public Health* 9(5), 1715-1731.

Zheng,N., Qichao, W., Zhomgzhu, L. & Dongmei, Z. (2003). Characterization of heavy metal concentrations in the sediment of three freshwater river in the Hisludao city, North east, China. *Environmental Pollution*, 7(2), 234 – 239.

Zhuang, Z., Lan, Z., & Shu, W., (2005). Chemically assisted phytoextraction of heavy metal contaminated soils using three plant species, *Plant and Soil*, 276(1-2), 153–162.

APPENDICES

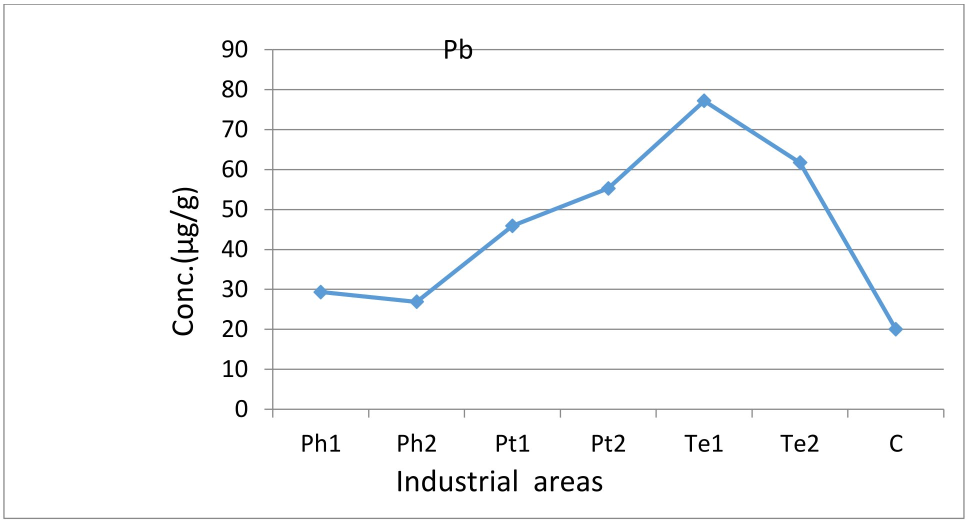


Fig. 1: Concentration of Pb in various industrial areas

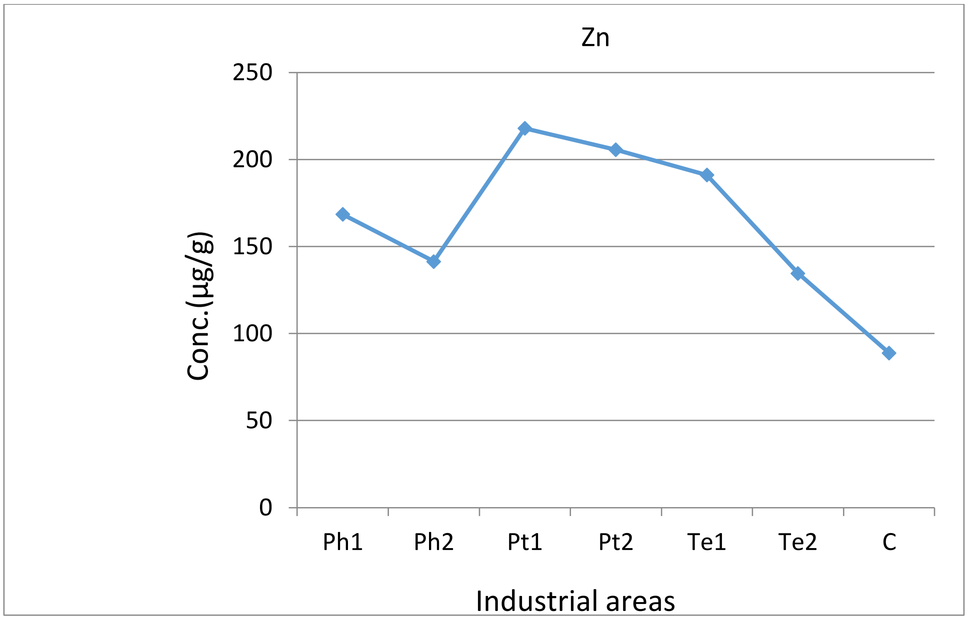
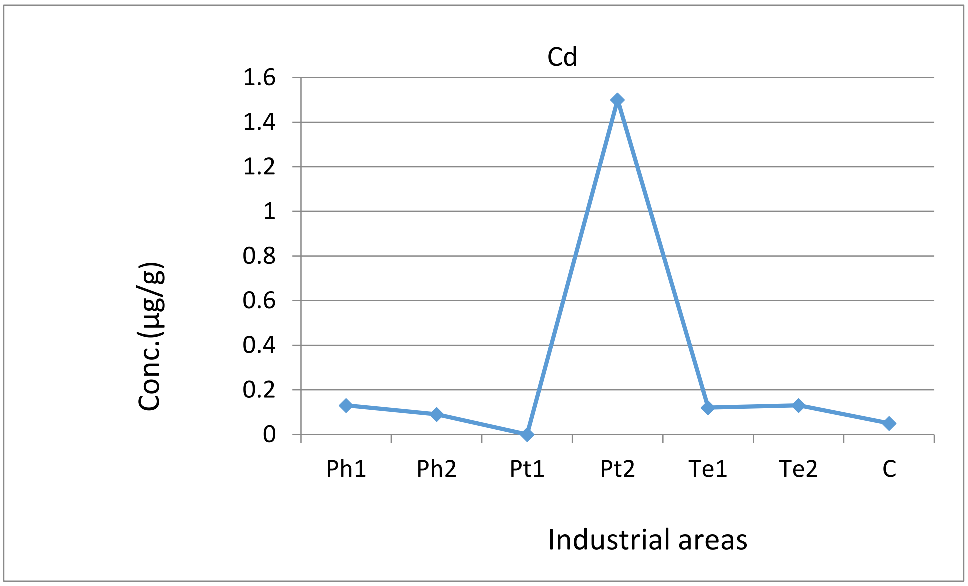


Fig. 2: Concentration of Zn in various industrial areas



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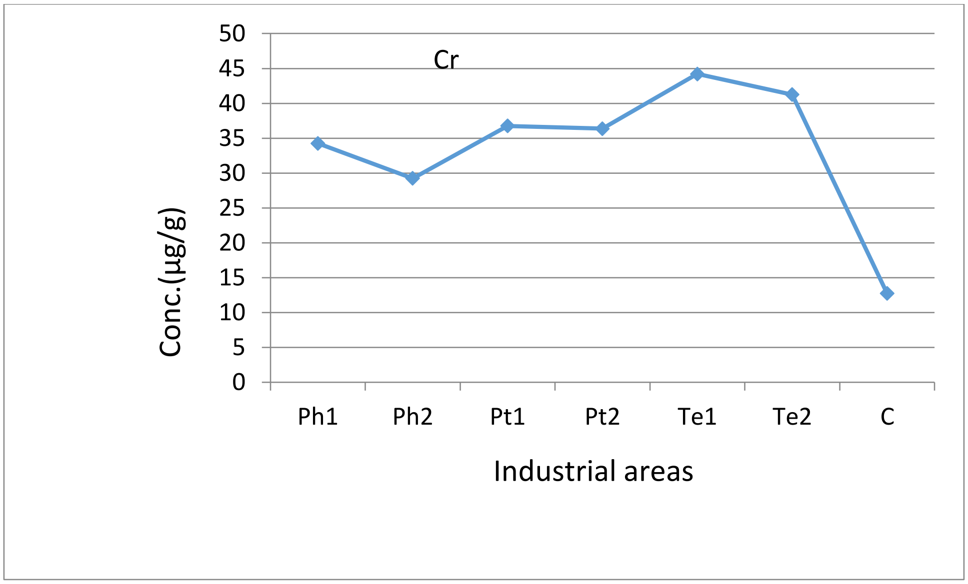

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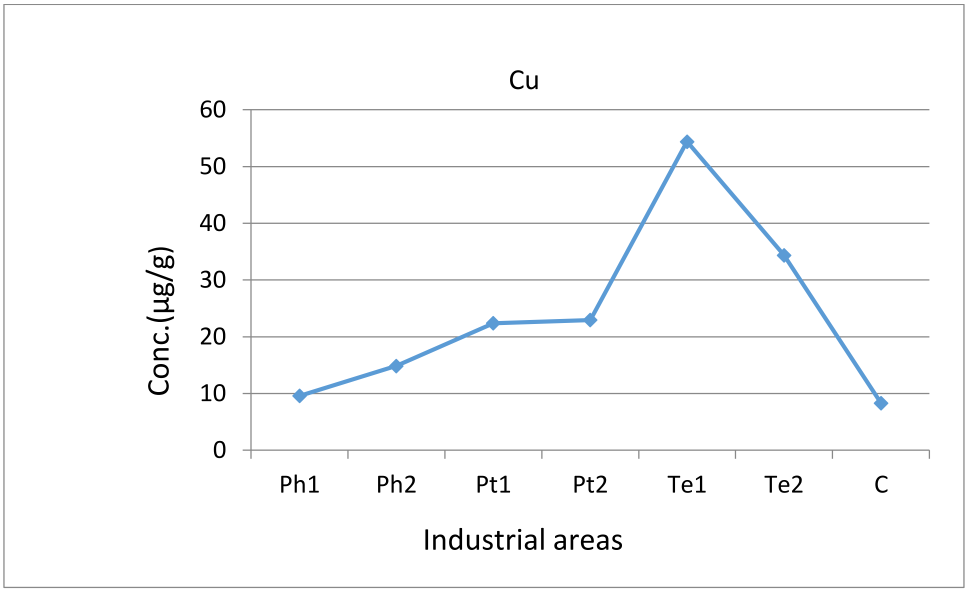

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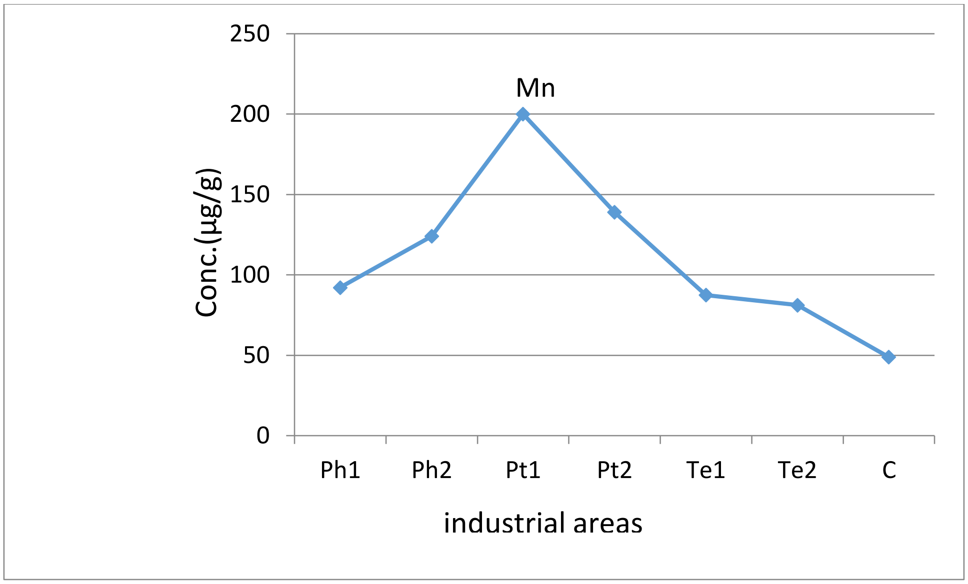

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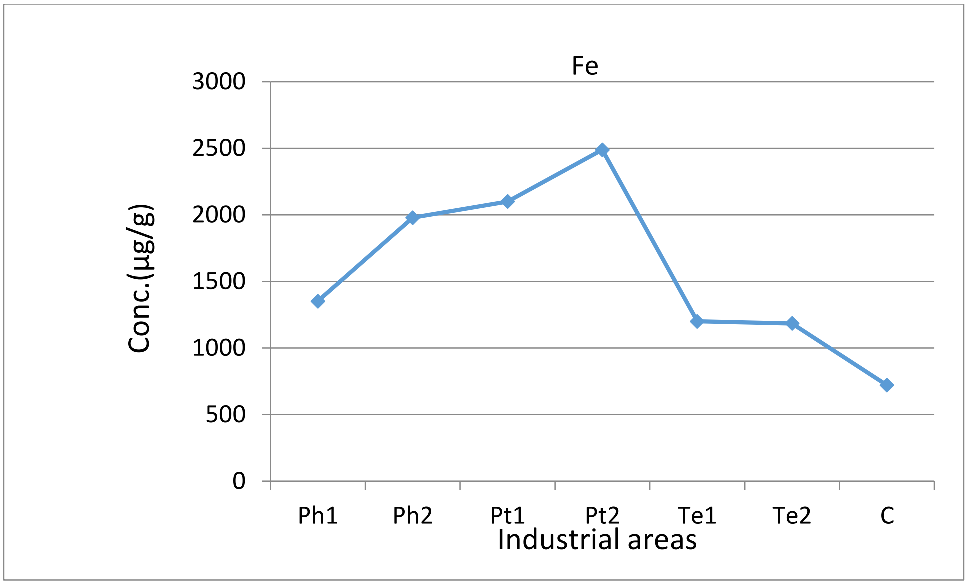

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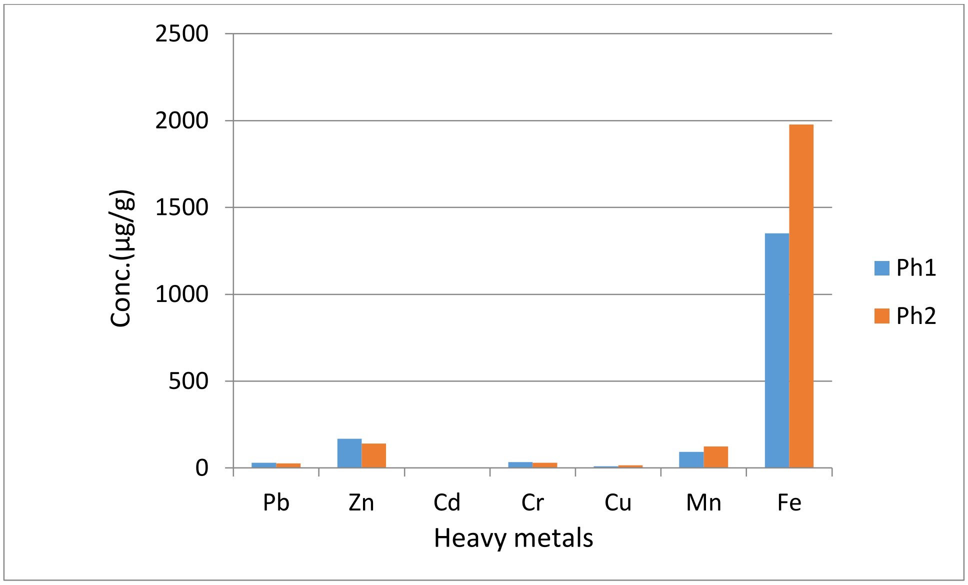

Fig. 8: Concentration of heavy metals in pharmaceutical industries

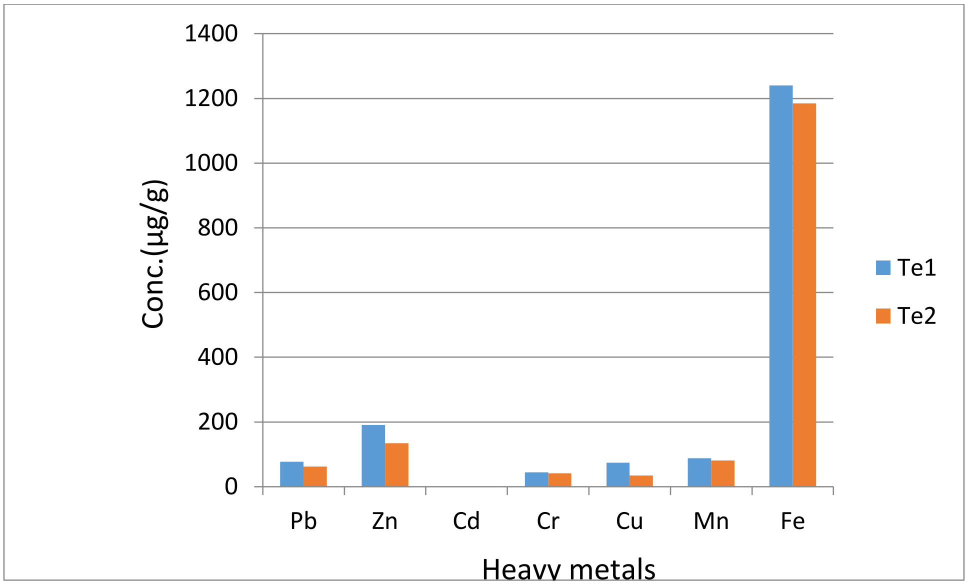

Fig. 9: Concentration of heavy metals in textile industries

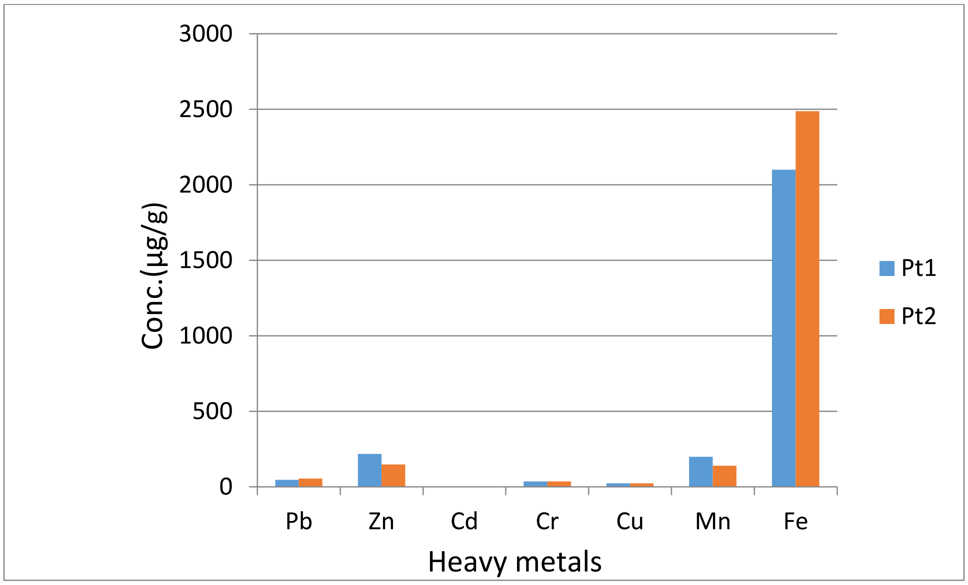

Fig. 10: Concentration of heavy metals in paint industries