# CONCENTRATIONS OF SELECTED HEAVY METALS IN SOILS AROUND REFUSE DUMPSITES IN SOME TOWNS IN DELTA STATE

BY

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AUGUST, 2016.

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**AUGUST, 2016.**

# CERTIFICATION

This is to certify that this research work was carried out by Ojegu, Joshua in the Department of Chemistry, Faculty of Science, Delta State University, Abraka, under the supervision of:

_____                                        _____
**Dr. S.O. Akporido**                                                      **Date**
*Supervisor*


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

## DEDICATION

This research work is dedicated to God Almighty for His mercies toward me.

# ACKNOWLEDGEMENT

Firstly, I am very grateful to God Almighty for being with me through the ages past and who has brought me thus far in my educational pursuit. Thank you Lord for giving me the wisdom, knowledge, grace and strength to put this work together.

Special thanks goes to my supervisor and Head of Department, Dr. S.O. Akporido for his moral support, encouragements, constructive criticism and thorough supervision.

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My heartfelt gratitude goes to all my friends.

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# LIST OF ACRONYMS

| ACRONYM | MEANING |
| --- | --- |
| AAS | Atomic Absorption Spectrophotometry |
| ANOVA | Analysis of Variance |
| ATSDR | Agency for Toxic Substance and Disease Registry |
| BCR | Community Bureau of Reference |
| CCME | Canadian Council of Ministers of the Environment |
| CEC | Cation Exchange Capacity |
| CPI | Contamination Pollution Index |
| DPR | Department of Petroleum Resources |
| EC | Electrical  Conductivity |
| ECDGE | European Commission Director General Environment |
| EDC | Endocrine disrupting chemical |
| EF | Enrichment factor |
| FOEFL | Swiss Federal Office of Environment, Forests and Landscape |
| Igeo | Index of geoaccumulation |
| NSC | National Safety Council |
| PCA | Principal Component  Analysis |
| RI | Potential Ecological Risk |
| SAP | Sapele |
| TOC | Total Organic Carbon |
| UGH | Ughelli |
| USDHHS | United States Department of Human Health Services |
| USEPA | United States Environmental Protection Agency |
| VCI | Van Commodities Incorporated |
| WHO | World Health Organization |

# ABSTRACT

Refuse dumpsites often contain material which are capable of polluting surrounding soils especially if the dumpsites are not adequately shielded from the surrounding area. This study examined levels of selected heavy metals and physicochemical parameters of soils around nine dumpsites. Soil samples were collected from nine dumpsites at 0-15 cm, 15-30 cm and 30-45 cm depths.  Some physicochemical properties of the soil profiles such as pH, conductivity and total organic carbon were determined. The concentrations of metals were determined using atomic absorption spectrometry (AAS) after digestion with aqua regia. The chemical speciation of the metal in the soil were determined using the sequential extraction procedure. The result of the pH of the soils in this study ranged between 4.64 and 7.85, electrical conductivity ranged from 60.8 to 451.2 $\mu\int$ cm$^{-1}$ and total organic carbon ranged from 0.06 to 1.49 % for all sites and depth. The concentrations of metals ranged from 0.05 to 4.5 mg kg$^{-1}$ for Cd, 9.0 to 149 mg kg$^{-1}$ for Pb, 4.20 to 15.4 mg kg$^{-1}$ for Cr, 1.0 – 14.5 mgkg$^{-1}$ for Ni, 1.0 to 124 mgkg$^{-1}$ for Cu, 20 to 510 mg kg$^{-1}$ for Zn and 1650 to 11865 mg kg$^{-1}$ for Fe. The potential ecological risk of the metals is in the order of Cd > Pb > Cu > Zn > Cr > Ni. The speciation result showed that the residual fraction was the predominant fraction of all the metals except Lead. The average values of pH in two sites were acidic. The average concentrations of Cd in majority of sites were above the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria target value, Canadian soil guideline values for Agricultural landuse, Norway and Germany soil guideline values as well as the Switzerland soil guideline value.

# CHAPTER ONE
# INTRODUCTION

## 1.1    Background of the study

Nigeria's population has increased greatly over the years; this consequently has led to the increase in human practices responsible for waste generation.  Although solid waste can be an asset when properly managed, it poses the greatest threat to life amongst all the classes of waste.  It has the potential of polluting the terrestrial, aquatic and aerial environments (Bishop, 2000).  The Nigerian Government at all levels through their agencies has invested much in waste management and enforcement of sanitation laws  but little  has  been achieved  so far.  Furthermore, the erratic growth of housing units in the urban cities, has made monitoring and management of waste difficult (Ogbemudia and Mbong, 2013). These have led to indiscriminate dumping of waste at every nook  and cranny  of major  cities  in  Nigeria.

Urbanization gives rise to a lot of industrial, commercial and agricultural activities. Wastes emanating from these activities are co-deposited on every available space indiscriminately. A typical refuse dump  consists  of  organic  wastes  such  as  poultry litter,  waste  clothing  and  paper,  wood waste  and  furniture,  corn  cob  and  chaff, vegetable  residues,  left over  foods  etc,  inorganic  wastes,  glass, discarded battery cells, ceramics, acid wastes, metals automobile parts, broken pots,  stoves, cans,  tins,  pipes, other  waste  metallic  containers,  polymeric  materials plastics,  foam, polythene bags, hair  weavon  etc,  electrical  and  electronic  wastes refrigerators,  damaged  phones  and accessories, damaged computers and accessories, damaged fans and electric irons, waste bulbs  and  sockets  and  sundry  wastes  such  as  pharmaceuticals,  paint  products  and containers (Nduka *et al.,* 2010). There is no doubt that these dumps contribute significant amounts of heavy metals migrating to the soil. Surface run offs from such refuse dumpsites

also end up in the ground water or in the surface water, thereby increasing the metal burden of the aquatic ecosystem (Osakwe, 2012).

Some heavy metals have bio-importance as trace elements but, the biotoxic effects of many of them in human biochemistry are of great concern. The term "heavy metal" refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lissy and Madhu, 2010). To a small extent, they enter the body system through food, air, and water and bioaccumulate over a period of time (Athalye *et al*., 2001). Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), manganese (Mn), Cobalt (Co), Nickel (Ni), silver (Ag), Arsenic (As), chromium (Cr), copper (Cu), Iron (Fe) and the platinum group elements (Upadhyay *et al*., 2007).

Cadmium has no beneficial biological importance in the human body and it is a pollutant of global concern (European Commission, 2002). Acute cadmium poisoning systems are similar to those of food poisoning. It is associated with kidney disease and linked to hypertension. There is also some evidence that cadmium can replaces zinc in zinc containing enzymes, which causes itai-itai disease with lethal consequences and binds calcium out of bones to cause osteoporosis (European Commission, 2002). In addition, it has cancinogenic, mutagenic and teratogenic effects (Vukojevic *et al*., 2006). The primary adverse health effects observed are lung cancer and kidney damage. In extreme exposure cases pulmonary oedema may develop and cause death. Severe cadmium induced renal damage may develop into chronic renal failure at which point some form of dialysis or kidney operation will be needed (Lenntech, 2008). Also cadmium has the ability to alter the rate of ovarian and placental steroidogenesis, thereby adversely affecting normal reproduction in both humans and animals; therefore, cadmium has been added to the list of acknowlededged endocrine disrupting chemicals (ECDs) (Chedrese *et al*., 2006). In plants (cultivated or wild), cadmium is accumulated in high quantities. The roots and leaves

suffer most from accumulation of cadmium, which causes abnormal development, necrosis and death (Vukojevic et al., 2006).

Chromium is a naturally occurring element found in rocks, animals and plants. It is usually present in several forms, the most common of which are hexavalent chromium (extremely toxic) and chromium (III) (non-toxic). Chromium (III) is essential for breaking down sugar, fat and protein inside an animal's body, thus making it vital for good health (Keith, 2004). In contrast, chromium (VI) can be detrimental to the health of anyone exposed over long period of time. Inhaling or ingesting chromium (VI) overtime can cause nose bleed, ulcers, convulsion, kidney and liver damage, various cancers and/or death (Agency for Toxic Substance and Disease Registry (ATSDR), 2006).

Lead, one of the earliest metals recognized and used by humans, has a long history of beneficial use to humankinds, but now been recognized as toxic and as posing a widespread threat to humans and wildlife (Rashed, 2003). Lead influences the nervous system, slowing down nerval response (ATSDR, 2006). Lead toxicity has also been linked with reduced intelligence and lowered school achievement scores as well as juvenile delinquency and violent behaviour (European Commission, 2002). Similar toxic effects are seen in animals and lead is also toxic to all aquatic life (Brigden et al., 2008).

Copper, a metal that occurs naturally in rocks, soil, water and air throughout the environment, is an essential element in plants and animals (including humans). Therefore, plants and animals must absorb some copper from eating, drinking and breathing (ATSDR, 2006). The most common symptom of copper toxicity is injury to red blood cells and lungs as well as damage to liver and pancreatic functions (Ontario, 2006). Long-term exposure to copper can also cause irritation of the nose, mouth, and eyes as well as headaches, stomach aches, dizziness, vomiting and diarrhea (Lenntech, 2006).

Electroplating is one important process involved in surface finishing and metal deposition for better life of articles and for decoration. Nickel, copper, zinc and chromium

are the most commonly used metals, among several metals that can be used for electroplating. The choice for this purpose depends upon the specific requirement of the articles. During washing of the electroplating tanks, considerable amounts of the metal ions find their way into the effluent. Ni (II) is present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries (Anonymous, 2007). Higher concentrations of nickel cause cancer of lungs, nose and bone. Dermatitis (Ni itch) is the most frequent effect of exposure to Ni, such as coins and jewellery. Acute poisoning of Ni (II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness (Kadirvelu, 2000).

Soils contaminated with heavy metals are not only a problem with respect to plant nutrition and food chain, they may constitute a direct health hazard as well. Since protection of both terrestrial and aquatic ecosystem from contamination as a result of anthropogenic activities is a global concern, monitoring the concentration, phase association and mobility of metals in the environment that has significant anthropogenic activities, is therefore necessary. Like other urban centres, where the demand for suitable land for development exceeds the availability, such contaminated sites may be used in the future for residential, industrial, recreational or educational purposes. If these sites are cleared for redevelopment project without any form of assessment, people using such lands may be faced with environmental hazards. Monitoring the concentrations of heavy metals in the soil is important since knowledge of the heavy metal levels in soil give vital information regarding their sources, distribution and degree of pollution (Odefemi *et al.,* 2007).

## 1.2    Statement of the problem

Many studies have been carried out to determine the concentrations of heavy metals in soil around dumpsites in different parts of this country (Amos-Tautua *et al.,*

2013; Ogbemudia and Mbong, 2013; Ogundele *et al.,* 2013; Ogbeibu *et al.,* 2013; Adelekan and Alawode, 2011; Osakwe, 2010; Nduka *et al.,* 2010; Nwajei *et al.,* 2007; Amusan *et al.,* 2005). However, there is relatively little or no information regarding the physicochemical properties and heavy metal concentrations of soil around dumpsites in Warri and its environs of Delta State. It is on this basis this research was instituted.

**1.3     Objectives of the Study**

The objectives of this study include to;

1.     determine some physico-chemical properties such as pH, Total organic carbon (TOC) and electrical conductivity of the soil

2.     assess the levels of selected heavy metals (Ni, Cu, Cd, Zn, Cr, Pb) in the soil

3.     determine the chemical speciation of the metals in the soil

4.     evaluate the contamination/pollution status of the soil with respect to each metal.

# CHAPTER TWO
# REVIEW OF RELATED LITERATURE

## 2.1    Heavy Metal Concentrations on Soil of Dumpsites

The concentration of heavy metals in plants and soil of refuse dumps in Uyo, Nigeria was studied (Ogbemudia and Mbong, 2013). Soil samples were collected from two dumpsites and digested with concentrated Trioxonitrate (V) acid and Tetraoxochlorate (IV) acid. The heavy metals investigated were: lead, manganese, Iron, Chromium, Zinc and Cadmium in two vegetables *Ipomea batatas* and *Laportea ovalifolia*. The concentrations of the heavy metals in the leaves of the vegetables were determined using Atomic Absorption Spectrophotometer (AAS). Manganese (54.3±1.4) and Iron (1013.02±8.5) were the most abundant heavy metals while Cadmium (3.7±0.2) was the least abundant across the two dumpsites.  Heavy metals in plants were found to positively correlate with that present in the soil. The authors concluded that the consumption of leafy vegetables and crops produced on soils with elevated  metal  levels  pose  serious health risk to consumers.

Plant fruits and vegetables grown on mixed waste dumpsites were used as bio indicators of  heavy metal pollution of three waste dumpsites in Ilorin Kwara State Nigeria (Ogundele *et al*., 2013). The samples were digested using Wet-oxidation method and heavy metals in the digest were analyzed by Atomic Absorption Spectrophotometer Technique. *Carica papaya, Musa Spp* and *Cocorhrous olitorous* samples were collected from contaminated and uncontaminated sites.  Copper concentrations of *Carica papaya, Musa spp,* and *Cocorhrous olitorous* from the contaminated sites were found between 0.15-0.23 mg/kg in Abayawo, 0.13 mg/kg in Okolowo, and 0.10 mg/kg in Itanmo. Zinc was found between 21.25-42.75mg/kg in Abayawo, 20.00 mg/kg in Okolowo, and 11.00 mg/kg in Itanmo. Pb and Cd were found below the detection limit of the instrument. Heavy

metals in the uncontaminated site samples were found between 0.10-0.23 mg/kg Copper, 0.75-31.75 mg/kg Zinc. Cadmium and lead were found comparatively below detection limits in all the samples. Mean concentrations of metals were higher in Abayawo dumpsite than other dumpsites. The mean concentration of Cu 0.56 mg/kg and Zn 30.75mg/kg are well above the mean concentration of metals from the control site (Oloje) 0.15 mg/kg and 24.58 mg/kg Copper and Zinc respectively. Base on this study, the three waste dumpsites are polluted with heavy metals (Copper, Zinc), which can pose great health risk and hazards on food chain.

Amos-Tautua *et al*. (2013) in their study assessed the concentrations of lead, cadmium and chromium and some physicochemical properties of soils collected from an open dumpsite in Yenagoa, Nigeria. Surface soil samples at two depths (0-10 and 10-20 cm) were randomly collected at the dump field and control site, and were analyzed for physicochemical parameters and contamination by lead, chromium and cadmium using standard analytical methods. The results show that the main dumpsite had higher sand (>80.0%) and lower clay and silt contents than the control site. Soil mean pH varied between 4.89±0.05 in the control and 7.60±0.02 in the dump. Total nitrogen (N) content of the dump soils ranged from 0.06±0.07 to 0.24±0.09% and is slightly higher than that of the control soil. This is reflected in the high value of organic matter (4.71±0.85%) in dump soils. Available P was quite high ranging from 35.00±1.01 to 84.20±1.02 mg/kg. Cation exchange capacity (CEC) varied between 12.98±0.31 and 91.07±0.11 cmol kg$^{-1}$. Cation Exchange Capacity levels were moderate to high ranging from 14.10±0.10 to 91.47±0.11 cmol/kg. All the soil samples had very high base saturation (>90.0%) and exchangeable Ca, Mg, K and Na, far above the critical levels set by FAO for agricultural soil. Average levels of Pb ranged from 14.75±0.05 to 16.14±0.04 mg/kg in the dump and 8.35±0.05 to 8.78±0.07 mg/kg in the control. Mean concentration of Cr in the dump soil varied between 0.05±0.01 and 0.06±0.01 mg/kg, and is slightly higher than the control

(0.005±0.01 mg/kg), while Cd was found in trace amounts (<0.0001±0.01 mg/kg). It is suggested that the dumpsite and the control area with their adequate soil nutrients and low levels of metals should eventually be converted to agricultural farmland. No remediation is needed at this time.

Geochemical assessment of the effect of Aladimma dumpsite on the nearby soil and shallow groundwater were undertaken by Amadi (2011). A total of twenty soils and thirty groundwater samples were collected during the dry season. The concentrations of all the parameters analyzed were higher in soil than in groundwater and these may be attributed to the high affinity between organic matter content of soils and elements. The results indicate the concentrations of the cation to be in the order of Ca > Mg > Na > K in both soil and groundwater while that of anion is in the order of Cl > $NO_3$ > $SO_4$ > $HCO_3$. The heavy metals concentrations vary as follows: Fe > Zn > Cu > Mn > Cr > Pb > As. This may be attributed to high precipitation and subsequent weathering and leaching of metallic objects from the dumpsite into the shallow groundwater table. The application of Water Quality Index (WQI) shows that the groundwater around the dumpsite is poor in quality and the factor analysis revealed five sources of groundwater pollution. Factors 1 and 2 are from natural means while Factors 3, 4 and 5 are from dumpsite and other human activities in the area. Modern sanitary landfills to replace the practice of open dumping and to reduce the reliance on waste incineration were advocated.

Akpoveta *et al*. (2010) analysed some physicochemical characteristics and heavy metal levels in soil samples around metal scrap dumps at Abraka and Agbor vicinities of Delta State, Nigeria, in order to assess the effects of the dumps on the soils. The results of their physicochemical analysis showed that the pH values in all the sites ranged from 7.01 to 7.99 indicating neutrality to slight alkalinity of the soils. The Total Organic Carbon values ranged from 0.38 to 0.54% indicating presence of some organic matter and some microbiological activities in the soil samples. The high conductivity values

ranging from 165 to 201μs/cm indicated significant presence of some soluble inorganic salts in soils studied. For all the physicochemical values recorded, the soil samples at Agbor had slightly higher values than those of Abraka. The heavy metal levels for the soils in Abraka and Agbor respectively were 1.50 mg kg$^{-1}$ and 1.52 mg kg$^{-1}$ for Cd, 5.10 mg kg$^{-1}$ and 4.48 mg kg$^{-1}$ for Ni, 1431 mg kg$^{-1}$ and 1411 mg kg$^{-1}$ for Fe, 74.26 mg kg$^{-1}$ and 97.21 mg kg$^{-1}$ for Zn, 14.31 mg kg$^{-1}$ and 34.21 mg kg$^{-1}$ for Cu, 24.0 mg kg$^{-1}$ and 18 mg kg$^{-1}$ for Cr, 9.73 mg kg$^{-1}$ and 10.54 mg kg$^{-1}$ for Co, and then 12.24 mg kg$^{-1}$ and 14.47 mg kg$^{-1}$ for Pb. The levels were all higher than those recorded in the control sites. A consistent trend showing a decrease in the concentration of heavy metals was observed for soil samples at increased distances from the impact points for the two towns studied. Metal was observed for soil samples at increased distances from the impact point for the two towns studied. The results from the contamination index indicated a significant degree of soil contamination for Pd, Cd, Co, Cu and Zn in the soils studied showing a higher degree of contamination for these metals. These soils therefore constitute a major health risk to the local population. Their study successfully related and attributed the presence of heavy metals with anomalous concentration in the soils to anthropogenic inputs from the metal scrap dumps.

Adelekan and Alawode (2011) determined the concentrations of heavy metals in soil and groundwater at municipal refuse dumps in Ibadan, Nigeria. Soil and groundwater samples from 7 municipal refuse dumps and a green uncontaminated control site at the Institute of Agricultural Research and Training in Ibadan, Nigeria were analysed for Cadmium (Cd), Cobalt (Co), Lead (Pb), Chromium (Cr) and Nickel (Ni). Soil samples were obtained in triplicates and at depths of 0-15, 15-30, 30-45 and 45-60cm. Water samples were obtained from dug wells at the dump sites. The values of Cd, Co, Pb, Ni and Cr in the dumpsites soil samples ranged from 0.75-16.30 mg/kg; 3.45-21.0 mg/kg; 45.00-624.50 mg/kg; 4.35-49.80 mg/kg and 13.15-75.55mg/kg, respectively. Evidence of

contamination of these soils by Cd, Pb, Ni and Cr was obvious when compared to the control site. Ni was below detection limit in all control samples while Pb and Cd were less than 0.05mg/kg and 0.002mg/kg, respectively. Cr ranged from 6.25-19.75mg/kg. The range obtained for Co at the dumpsites was comparable to that of the control soil which was 7.22-28.15mg/kg. Compared to established limits set for soils in some countries, the values measured in this study were higher, particularly for Pb. Co conformed to the only established limit cited in Austria. Values measured in the groundwater samples were lower than the limits set by WHO for drinking water, except Cd which was detected in 3 of the samples at a concentration close to the WHO limit. This study found that there is an ongoing build- up of heavy metals in soil at the waste dumps studied and concentrations were already higher than established limits for some metals. The recommendations of the study include formulation and enforcement of a directive to prevent any form of farming on the dumpsites, relocation of the dumpsites out of the city and the enforcement of other environmental protection regulations to stop the ongoing build-up of these metals on those locations.

Osakwe (2012) studied selected heavy metals Fe, Cd, Ni, and Cr in contaminated refuse dumpsites soil samples collected from South – Eastern Nigeria, for their geochemical differentiation into different chemical fractions, using Ma and Rao six steps sequential chemical extraction procedure in order to assess the potential mobility and bioavailability of the heavy metals in the soil profiles. It is evident from the study that the residual fraction was the most important phase for the four heavy metals under study with the following average percentage values 74.43 for Fe, 37.69 for Cd, 70.11for Ni and 62.47 for Cr. The carbonate fraction contained an appreciable portion of Fe, Cd and Ni with the average percentage values of 16.29, 14.86 and 10.47 respectively, while organic fraction was of next importance for Cr with an average percentage value of 27.14. Fe – Mn oxide fraction also contained 15.86% of Cd.

Relatively low amount of the metals were associated with water soluble and exchangeable fractions. The mobility factors for the metals in all the sites ranged from 8.55 to 40.04 for Fe, 8.66 to 56.58 for Cd, 12.74 to 30.19 for Ni and 0.82 to 7.22 for Cr. The generally low values of mobility factors coupled with significantly high level of association of the metals with the residual fraction, indicate that the metals do not pose any environmental risk or hazard.

Amusan et al. (2005) determined the characteristics of soils and crops' uptake of metals in municipal waste dump sites in Nigeria. The result showed that soils in municipal waste dump sites are higher in heavy metals: Zn, 63.2-102.11 µg/g; Co, 36.0-132.14 µg/g; Cu, 36.5-72.99 µg/g; Pb, 63.58-418.58 µg/g and Cd, 17.00-47.06 µg/g and that crops growing in the dump sites bio-accumulate considerably higher metal contents than those in normal agricultural soils. It was also observed that crops differ in their ability to up-take metals. Therefore, to minimize heavy metal load of soils in dump sites, sorting of wastes at source, provision of an enabling statutory regulation on waste management, and the enforcement of the compliance of such statutory regulation to be the responsibility of a unit of the Health Department, in the Local Government Council, are suggested. Those wastes that pose greater health hazards should be properly land-filled to reduce environmental pollution and /or soil degradation.

The effects of open waste dump-site on the physico-chemical and microbiological qualities of surface water were investigated (Ogbeibu et al., 2013). Water samples were collected for monitoring at a control and two other points close to the dump-site from October 2008 - October 2009. Water analysis showed that turbidity, TDS, EC, Nitrate, Total Phosphorus DO, BOD and THC were highly significantly different ($P<0.001$) across the sampling points. 'Aposteriori' comparison using Duncan Multiple Range (DMR) test showed that the control recorded higher mean value for DO and lower mean values for turbidity, TDS, EC, Nitrate and THC. Coliform was significantly lower ($P<0.001$) at the

control point. The concentration of Fe was significantly higher ($P<0.001$) at points close to the dump-site. The rainy months of June and October recorded higher values for most parameters. The dump-site impacted its surface water heavy. Evacuation and remediation of the dump-site is recommended to salvage the environment.

Osakwe (2010) analysed soil samples around some automobile waste locations in in Agbor and its environs, Delta State, Nigeria, to assess heavy metal levels particularly with respect to depth in the soil profile and distance from pollution source. The pH of the soil samples were also determined to evaluate the effect of pH on the metal concentrations. The pH values of the soils ranged from 4.9 to 7.4 indicating near neutrality to slight acidity of the soil samples and moderate availability of the metals. The vertical distribution of the heavy metals showed that the metal levels were generally higher at top soils than the sub and bottom soils. The mean concentrations of the metals in all the sites were in the order Fe > Mn > Pb > Cu. Lateral distribution of the metals showed that the metal concentrations decreased with distance from the pollution source. The metal levels obtained in all the sites were higher than those of the control sites indicating some level of heavy metal contamination at the dump sites. The values obtained from the contamination/pollution index computation, revealed that iron was in the range of moderate contamination, while the other metals were in the range that showed very slight contamination. The enrichment coefficient values indicated minimal enrichments for all the metals while the relative pollution potential values showed that the soils were contaminated at the point of impact. All the values obtained generally indicated that the soils in all the sites were contaminated with heavy metals.  However, the metal concentration levels found in this study do not pose any health risk, since the levels were below DPR target limit, but within the ranges for agricultural soils, residential, commercial/industrial and typical ranges for food crops.

Akporido and Agbaire (2014) carried out soil and water quality assessment using integrated pollution index of roofing and ceiling sheet industry waste dumpsites and

adjoining areas in Sapele, Nigeria.  Soil and water samples  were  collected from  five selected waste dumpsites of a ceiling and roofing sheet manufacturing company and two selected residential compounds in the vicinity of the factory in Sapele, Nigeria. Samples were collected twice every season (dry and rainy seasons) for two years. Heavy metals were determined in water and soil samples using the method of atomic absorption spectrometry after appropriate digestion methods. Water and soil physicochemical parameters were analyzed for by standard methods. Important results include the following:  average concentrations in water are  Pb  (24±10  µg/L), Cd  (1.1±1.5  µg/L), Cr (80.9±110  µg/L),  Zn  (115±29  µg/L),  Ni  (1.8±1.3  µg/L),  pH  (8.0±1.0)  and BOD5,(17±11  mg/L).  Average concentrations in soil are  Pb  (452±780  mg/kg),  Cd (1.02±0.79  mg/kg),  Cr  (16.7±4.5  mg/kg),  Ni  (13.1±8.6 mg/kg) and Zn (50±23 mg/kg). Application of integrated pollution index (IPI) to the results gave priority of the pollution status of the  sampling  stations  as  follows:    Dumpsite3  (0.556),  2nd  Compound (0.524), Dumpsite4  (0.505),  dumpsite5  (0.337),  1st  Compound  (0.280),  Dumpsite2 (0.256)  and  Dumpsite1  (0.228) (IPI  values  in  parenthesis).  The ranking revealed that the residential compounds had higher pollution status than some of the waste dumpsite.

Osakwe  (2014)  investigated  heavy  metal  contamination  and  physicochemical characteristics of soils from automobile workshops in Abraka, Delta State, Nigeria. Soils samples  were  collected  from  selected  automobile  workshops  in  Abraka,  Delta  State, Nigeria, at the depths of 0 – 15cm, 15 – 30cm and 30 – 45cm representing  top,- sub- and bottom soils respectively and also from control site and 20m  away  from  the  point of  impact.  The soils were analyzed for their physicochemical characteristics and heavy metal levels. The pH values of the soils in all the sites  ranged  from  3.6  to  6.7  with mean  value  of  5.97  showing  that  the  soils  were  moderately  acidic.  The electrical conductivities of the soils ranged from (µScm$^{-1}$) 202.0 to  478.0 with  mean  value  of 306.28  indicating  significant  presence  of  soluble  inorganic  substances  with  their

corresponding ions. Total Organic Carbon content ranged from (%) 29.56 to 77.76 with mean value of 42.07 signifying presence of degradable substances and increased microbial activities in the soil. Total nitrogen contents ranged from (%) 2.03 to 9.35 with mean value of 4.19 which may be attributed to presence of some organic matters. Soil textural classification showed that the soils were sandy loamy. The heavy metal levels had the mean values of (mgkg$^{-1}$) 40.05 for Fe, 16.74 for Zn, 34.39 for Mn and 0.66 for Cu showing the abundance trend of Fe>Mn>Zn>Cu. The Relative Pollution Potential and contamination/Pollution Index values revealed that the soils were slightly contaminated by heavy metals. Although the present level of heavy metal contamination of the soils does not call for any alarm, proactive steps must be taken tominimize gradual accumulation of these metals. It is hereby recommended that a separate portion of land be set apart for automobile workshops which can be called mechanic village as it is in some cosmopolitan areas in this country.

Katana *et al*., (2013) determined concentrations of Ni and Cr in the various fractions of soils obtained from open-air garages in Ngara, Nairobi, Kenya. Soil samples were collected twice from ten sampling sites at a depth of 0 to 10 cm. The modified Community Bureau of Reference (BCR) sequential extraction method was used and metals analysed using a Flame Atomic Absorption Spectrophotometer (FAAS). The mean total concentration of Ni and Cr obtained was 487.96±12.58 mg/kg and 261.51±13. 38 mg/kg respectively. The ranges in the soils were between 401.55±58.32 mg/kg to 584.31±46.34 mg/kg and 160.77±26.42 mg/kg to 361.72±78.16 mg/kg for Ni and Cr respectively. These results show that the levels are high when compared with maximum allowed limits. The percentage of Ni in the fractions followed the order exchangeable (29.09%)>oxidisable (26.93%)>residual (23.63%)> reducible (20.35%) while percentage of Cr followed the order exchangeable= residual (25.75%) > reducible (24. 41%) >oxidisable (23. 69%). The % of non-residual Ni and Cr was 76.37 and 74.25 respectively. The mobility factors for the

heavy metals were 29.10% and 25.82% and ranged from 16.67% to 36.19% and 19.65% to 32.49% for Ni and Cr respectively. These shows that the concentration levels of the metals were not only high but substantial proportions were mobile and bioavailable. As expected from the high mobility factors obtained in the study, the concentration levels of the metals in nearby grass, water pools and run offs were found to be high. Pearson correlation of the exchangeable fraction with the total concentration showed a significantly positive correlation with Ni (r = 0.511) and Cr (r = 0.714). This indicates that high concentration levels of the metals in the soil infer increased amount of the metal in mobile fractions.

Heavy metals in surface soil under waste dumps in Onitsha metropolis was investigated (Nwajei *et al.*, 2007) seven metal, namely arsenic, barium, cadmium, chromium, manganese, lead and lithium were considered. Analytical determinations were performed by atomic absorption spectrometry after samples digestion with acid mixture. Elevated concentrations of the aforementioned metals were obtained in the study. All metals were detected except for the background soil sample from inland form where Cr and Pb were below detects limit. There were variations in the concentration of metals in soil from various locations. Metals concentrations in soils obtained from Emagba phase II, Wolino Layout, Fegge Road, Head bridge, Odoakbu layout, Awada Layout and Isiafor layout were higher than those from Ozala layout and inland from (Background soil samples). The highest concentrations of the contaminants metals found in the soil location near the head bridge of River Niger. The sources of these metals were attributed to the industrial and anthropogenic wastes in various samples locations.

## 2.2   Basic Soil Chemistry and Potential Risks of Heavy Metals

The most common heavy metals found at contaminated sites, in order of abundance are Pb, Cr, As, Zn, Cd, Cu, and Hg (USEPA, 2001). Those metals are important since they are capable of decreasing crop production due to the risk of bioaccumulation and

biomagnification in the food chain. There's also the risk of superficial and groundwater contamination. Knowledge of the basic chemistry, environmental, and associated health effects of these heavy metals is necessary in understanding their speciation, bioavailability, and remedial options. The fate and transport of a heavy metal in soil depends significantly on the chemical form and speciation of the metal. Once in the soil, heavy metals are adsorbed by initial fast reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying bioavailability, mobility, and toxicity (Shiowatana *et al.*, 2001; Buekers, 2007). This distribution is believed to be controlled by reactions of heavy metals in soils such as (i) mineral precipitation and dissolution, (ii) ion exchange, adsorption, and desorption, (iii) aqueous complex at ion, (iv) biological immobilization and mobilization, and (v) plant uptake (Wuana and Okiemen, 2011).

**Lead**

Lead is a metal belonging to group IV and period 6 of the periodic table with atomic number 82, atomic mass 207.2, density 11.4 g cm$^{-3}$, melting point 327.4 $^{\circ}$C, and boiling point 1725 $^{\circ}$C. It is a naturally occurring, bluish-gray metal usually found as a miner al combined with other elements, such as sulphur (i.e., PbS, PbSO4), or oxygen (PbCO$_3$), and ranges from 10 to 30 mg k g$^{-1}$ in the earth's crust (United States Department of Human Health Services (USDHHS), 1999). Typical mean Pb concentration for surface soils worldwide averages 32 mg kg$^{-1}$ and ranges from 10 to 67 mg kg$^{-1}$ (Kabata-Pendias and Pendias, 2001). Lead ranks fifth behind Fe, Cu, Al, and Zn in industrial production of metals. About half of the Pb used goes for the manufacture of Pb storage batteries. Other uses include solders, bearings, cable covers, ammunition, plumbing, pigments, and caulking. Metals commonly alloyed with Pb are antimony (in storage batteries), calcium (Ca) and tin (Sn) (in maintenance -free storage batteries), silver (Ag) (for solder and anodes), strontium (Sr) and Sn (as anodes in electro winning processes), tellurium (Te)

(pipe and sheet in chemical installations and nuclear shielding), Sn (solders), and antimony (Sb), and Sn (sleeve bearings, printing, and high-detail castings) (Manahan, 2003).

Ionic lead, Pb (II), lead oxides and hydroxides, and lead-metal oxyanion complexes are the general forms of Pb that are released into the soil, groundwater, and surface waters. The most stable forms of lead are Pb (II) and lead-hydroxy complexes. Lead (II) is the most common and reactive form of Pb, forming mononuclear and polynuclear oxides and hydroxides (GWRTAC, 1997). The pre-dominant insoluble Pb compounds are lead phosphates, lead carbonates (form when the pH is above 6), and lead hydroxides (Raskin and Ensley, 2000). Lead sulphide (PbS) is the most stable solid form within the soil matrix and forms under reducing conditions, when increased concentrations of sulphide are present. Under anaerobic conditions a volatile organolead (tetramethyl lead) can be formed due to microbial alkylation (GWRTAC, 1997).

Lead (II) compounds are predominantly ionic (e.g., $Pb^{2+}SO_4^{2-}$), whereas Pb(IV) compounds tend to be covalent (e.g., tetraethyl lead, $Pb(C_2H_5)_4$). Some Pb(IV) compounds, such as $PbO_2$, are strong oxidants. Lead forms several basic salts, such as $Pb(OH)_2 \cdot 2PbCO_3$, which was once the most widely used white paint pigment and the source of considerable chronic lead poisoning to children who ate peeling white paint. Many compounds of Pb (II) and a few Pb(IV) compounds are useful. The two most common of these are lead dioxide and lead sulphate, which are participants in the reversible reaction that occurs during the charge and discharge of lead storage battery.

In addition to the inorganic compounds of lead, there are a number of organolead compounds such as tetraethyl lead. The toxicities and environment al effects of organolead compound s are particularly noteworthy because of the former widespread use and distribution of tetraethyllead as a gasoline additive. Although more than 1000 organolead compounds have been synthesized, those of commercial and toxicological importance are

largely limited to the alkyl (methyl and ethyl) lead compounds and their salts (e.g., dimethyldiethyllead, trimethyllead chloride, and diethyllead dichloride).

Inhalation and ingestion are the two routes of exposure, and the effects from both are the same. Pb accumulates in the body organs (i.e., brain), which may lead to poisoning (plumbism) or even death. The gastrointestinal tract, kidneys, and central nervous system are also affected by the presence of lead. Children exposed to lead are at risk for impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration, with children under the age of six being at a more substantial risk. Adults usually experience decrease d reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to lead (NSC, 2009). Lead is not an essential element. It is well known to be toxic and its effects have been more extensively reviewed than the effects of other trace metals. Lead can cause serious injury to the brain, nervous system, red blood cells, and kidneys (Baldwin and Marshall, 1999). Exposure to lead can result in a w ide rang e of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of dose s, with the developing young and infants being more sensitive than adults. Lead poisoning, which is so severe as to cause evident illness, is now very rare. Lead performs no known essential function in the human body, it can merely do harm after uptake from food, air, or water. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains.

The most serious source of exposure to soil lead is through direct ingestion (eating) of contaminated soil or dust. In general, plants do not absorb or accumulate lead. However, in soils testing high in lead, it is possible for some lead to be taken up. Studies have shown that lead does not readily accumulate in the fruiting parts of vegetable and fruit crops (e.g., corn, beans, squash, tomatoes, strawberries, and apples). Higher concentrations are more likely to be found in leafy vegetables (e.g., lettuce) and on the surface of root crops (e.g.,

carrots). Since plant s do not take up large quantities of soil lead, the lead levels in soil considered safe for plants will be much higher than soil lead levels where eating of soil is a concern (pica). Generally, it has been considered safe to use garden produce grow n in soils with total lead levels less than 300 ppm. The risk of lead poisoning through the food chain increase s as the soil lead level rises above this concentration. Even at soil levels above 300 ppm, most of the risk is from lead contaminated soil or dust deposit s o n the plants rather than from uptake of lead by the plant (Rosen, 2002).

**Chromium**

Chromium is a first-row d-block transition metal of group VIB in the periodic table with the following properties: atomic number 24, atomic mass 52, density 7.19 g cm$^{-3}$, melting point 1875 $^{\circ}$C, and b oiling point 2665 $^{\circ}$C. It is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of the mineral chromite, $FeCr_2O_4$.Major sources of Cr- contamination include releases from electroplating processes and the disposal of Cr containing wastes (Smith $et$ $al.$, 2005). Chromium (VI) is the form of Cr commonly found at contaminated sites. Chromium can also occur in the +III oxidation state, depending on pH and redox conditions. Chromium (VI) is the dominant form of Cr in shallow aquifers where aerobic conditions exist. Chromium (VI) can be reduced to Cr(III) by soil organic matter, $S^{2-}$ and $Fe^{2+}$ ions under anaerobic conditions often encountered in deeper groundwater. Major Cr(VI) species include chromate ($CrO_4^{2-}$) and dichromate ($Cr_2O_7^{2-}$) which precipitate readily in the presence of metal cations (especially $Ba^{2+}$ ,$Pb^{2+}$, and $Ag^{+}$ ). Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminium oxides. Chromium (III) is the dominant form of Cr at low pH (< 4). $Cr^{3+}$ forms solution complexes with $NH_3$, $OH^{-}$, $Cl^{-}$, $F^{-}$, $CN^{-}$, $SO_4^{2-}$, and soluble organic ligands.

Chromium (VI) is the more toxic form of chromium and is also more mobile. Chromium (III) mobility is decrease d by adsorption to clays and ox ide minerals below pH 5 and low solubility above pH 5 due to the formation of $Cr(OH)_3$ (s) (Chrostowski *et al*.,1991). Chromium mobility depend on sorption characteristics of the soil, including clay content, iron oxide content, and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and unadsorbed chromium complexes can leach from soil into groundwater.

The leachability of Cr (VI) increases as soil pH increases. Most of Cr released into natural waters is particle associated, however, and is ultimately deposited into the sediment (Smith *et al*., 2005). Chromium is associated with allergic dermatitis in humans (Scragg, 2006).

**Zinc**

Zinc is a transition metal with the following characteristics: period 4, group IIB, atomic number 30, atomic mass 65.4, density 7.14 g $cm^{-3}$, melting point 419.5 ∘C, and boiling point 906 ˚C. Zinc occurs naturally in soil (about 70 mg $kg^{-1}$ in crustal rocks) (Davies and Jones, 2008), but Zn concentrations are rising unnaturally, due to anthropogenic additions. Most Zn is added during industrial activities, such as mining, coal, and waste combustion and steel processing. Many foodstuffs contain certain concentrations of Zn. Drinking water also contains certain amounts of Zn, which may be higher when it is stored in metal tanks. Industrial sources or toxic waste sites may cause the concentrations of Zn in drinking water to reach levels that can cause health problems (Wuana and Okiemen, 2011).

Zinc is a trace element that is essential for human health. Zinc shortages can cause birth defects. The world's Zn production is still on the rise which means that more and more Zn ends up in the environment. Water is polluted with Zn, due to the presence of large quantities present in the wastewater of industrial plants. A consequence is that Zn -

polluted sludge is continually being deposited by rivers on their banks. Zinc may also increase the acidity of waters. Some fish can accumulate Zn in their bodies, when they live in Zn-contaminated waterways. When Z n enters the bodies of these fish, it is able to biomagnify up the food chain (Wuana and Okiemen, 2011).

Water-soluble zinc that is located in soils can contaminate groundwater. Plants often have a Zn uptake that their systems cannot handle, due to the accumulation of Zn in soils. Finally, Zn can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter (Greany, 2005).

**Cadmium**

Cadmium is located at the end of the second row of transition elements with atomic number 48, atomic weight 112.4, density $8.65$ g cm$^{-3}$, melting point 320.9 $^{\circ}$C, and boiling point 765 $^{\circ}$C. Together with Hg and Pb, Cd is one of the big three heavy metal poisons and is not known for any essential biological function. In its compounds, Cd occurs as the divalent Cd(II) ion. Cadmium is directly below Zn in the periodic table and has a chemical similarity to that of Zn, an essential micronutrient for plants and animals. This may account in part for Cd's toxicity; because Zn being an essential trace element, its substitution by Cd may cause the malfunctioning of metabolic processes (Campbell, 2006).

The most significant use of Cd is in Ni / Cd batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance, and high tolerance to physical and electrical stress. Cadmium coatings provide good corrosion resistance coating to vessels and other vehicles, particularly in high-stress environments such as marine and aerospace. Other uses of cadmium are as pigments, stabilizers for polyvinyl chloride (PVC), in alloys and electronic compounds. Cadmium is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products. In addition, acid rain and the resulting acidification of soils and surface waters

have increased the geochemical mobility of Cd, and as a result its surface-water concentrations tend to increase as lake water pH decreases (Wuana and Okiemen, 2011; Campbell, 2006). Cadmium is produced as an inevitable by-product of Zn and occasionally lead re fining. The application of agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils, and the bioavailability of this Cd determines whether plant Cd uptake occurs to a significant degree (Weggler et al., 2004). Cadmium is very biopersistent but has few toxicological properties and, once absorbed by an organism, remains resident for many years.

Since the 1970s, there has been sustained interest in possible exposure of humans to Cd through their food chain, for example, through the consumption of certain species of shellfish or vegetables. Concern regarding this latter route (agricultural crops) led to research on the possible consequences of applying se wage sludge (Cd-rich biosolids) to soils u se d for crops meant for human consumption, or of using cadmium-enriched phosphate fertilizer (Campbell, 2006). This rese arch has led to the stipulation of highest permissible concentrations for a number of food crops (McLaughlin et al., 2000).

Cadmium in the body is known to affect several enzymes. It is believed that the renal damage that results in proteinuria is the result of Cd adversely affecting enzymes responsible for reabsorption of proteins in kidney tubules. Cadmium also reduces the activity of delta-aminole vulinic acid synthetase, arylsulfatase, alcohol dehydro genase, and lipoamide dehydrogenase, whereas it enhances the activity of delta-aminole vulinic acid dehydratase, pyruvate dehydrogenase, and pyruvate decarboxylase (Manahan, 2003). The most spectacular and publicized occurrence of cadmium poisoning resulted from dietary intake of cadmium by people in the Jintsu River Valley, near Fuchu, Japan. The victims were afflicted by itai itai disease, which means ouch, ouch in Japanese. The symptoms are the result of painful osteomalacia (bone disease) combined with kidney

malfunction. Cadmium poisoning in the Jintsu River Valley was attributed to irrigated rice contaminated from an upstream mine producing Pb, Zn, and Cd. The major threat to human health is chronic accumulation in the kidneys leading to kidney dysfunction. Food intake and tobacco smoking are the main route s by which Cd enters the body (Manahan, 2003).

**Copper**

Copper is a transition metal which belongs to period 4 and group IB of the periodic table with atomic number 29, atomic weight 63.5, density 8.96 g cm$^{-3}$, melting point 1083 $^{\circ}$C and boiling point 2595 $^{\circ}$C. The metal's average density and concentrations in crustal rocks are 8.1 × 103 kg m$^{-3}$ and 55 mg kg$^{-1}$, respectively (Davies and Jones, 2008).

Copper is the third most used metal in the world (VCI, 2011). Copper is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. In plants, Cu is especially important in seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. Copper normally occurs in drinking water from Cu pipes, as well as from additive s designed to control algal growth. While Cu's interaction with the environment is complex, research shows that most Cu introduced into the environment is, or rapidly becomes, stable and results in a form which does not pose a risk to the environment. Infact, unlike some man-mad e materials, Cu is not magnified in the body or bioaccumulated in the food chain. In the soil, Cu strongly complexes to the organic implying that only a small fraction of copper will be found in solution as ionic copper, Cu (II). The solubility of Cu is drastically increase d at pH 5.5 (Martınez and Motto, 2000), which is rather close to the ideal farmland pH of 6.0–6.5 (Eriksson *et al*., 2007). Copper and Zn are two important essential elements for plants, microorganisms, animals, and humans. The connection

between soil and water contamination and metal uptake by plants is determined by many chemical and physical soil factors as well as the physiological properties of the crops.

Soils contaminated with trace metals may pose both direct and indirect threats: direct, through negative effects of metals on crop growth and yield, and indirect, by entering the human food chain with a potentially negative impact on human health. Even a reduction of crop yield by a few percent could lead to a significant long-term loss in production and income. Some food importers are now specifying acceptable maximum contents of metals in food, which might limit the possibility for the farmers to export their contaminated crops (Bjuhr, 2007).

**Nickel.**

Nickel is a transition element with atomic number 28 and atomic weight 58.69. In low pH regions, the metal exists in the form of the nickelous ion, Ni(II). In neutral to slightly alkaline solutions, it precipitates as nickelous hydroxide, $Ni(OH)_2$, which is a stable compound. This precipitate readily dissolves in acid solutions forming Ni(III) and in very alkaline conditions; it forms nickelite ion, $HNiO_2$, that is soluble in water. In very oxidizing and alkaline conditions, nickel exist s in form of the stable nickelo-nickelic oxide, $Ni_3O_4$, that is soluble in acid solutions. Other nickel oxides such as nickelic oxide, $Ni_2O_3$, and nickel peroxide, $NiO2$, are unstable in alkaline solutions and decompose by giving off oxygen. In acidic regions, however, these solids dissolve producing $Ni^{2+}$ (Wuana and Okiemen, 2011).

Nickel is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer on different sites within the bodies of animals, mainly of those that live near refineries. The most common application of Ni is an ingredient of steel and other metal products. The major sources of nickel contamination in the soil are metal plating industries, combustion of fossil fuels, and nickel mining and

electroplating (Khodadoust *et al*., 2004). It is released into the air by power plants and trash incinerators and settles to the ground after undergoing precipitation reactions. It usually takes a long time for nickel to be removed from air. Nickel can also end up in surface water when it is a part of waste water streams. The larger part of all Ni compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result. In acidic soils, however, Ni becomes more mobile and often leaches down to the adjacent groundwater. Microorganisms can also suffer from growth decline due to the presence of Ni, but they usually develop resistance to Ni after a while. Nickel is not known to accumulate in plant s or animals and as a result Ni has not been found to biomagnify up the food chain. For animals, Ni is an essential foodstuff in small amounts (Wuana and Okiemen, 2011).

# CHAPTER THREE
## MATERIALS AND METHODS

**3.1    Description study area**

Ughelli is the headquarter of Ughelli North Local Government Area and lies within Longitude 5.30$^o$ N and Latitude 5.59$^o$ E. The town was originally an agricultural centre but industry has now developed there. It hosts the Beta Glass factory and Shell petroleum Development Company. Ughelli has a population of 79, 986 according to the 2006 census (National Population Commission, 2006).

Sapele is the headquarter of Sapele Local Government Area and lies within Longitude 5.54$^o$ N and Latitude 5.54$^o$ E. The town has one of Nigeria's major seaports. It hosts the African Timber and Plywood Company. Sapele has a population of 142,652 according to the 2006 census (National Population Commission, 2006).

Udu is a suburb of the Warri metropolis. It lies within Longitude 5.45$^o$ N and Latitude 5.43$^o$ E. Udu is host to the Delta Steel Company, Ovwian/Aladja and Utorogun Gas Plant, Otor-udu. Udu has a population of 100,000 according to the 2006 census (National Population Commission, 2006).

The region experiences moderate rainfall and moderate humidity for most part of the year. The climate is equatorial and is marked by two distinct seasons: the dry season and the rainy season. The dry season lasts from about November to April and is significantly marked by the cool "harmarttan" dusty haze from the north-east winds. The rainy season spans May to October with a brief dry spell in August, but it frequently rains even in the dry season. The area is characterized by tropical equatorial climate with mean annual temperature of 32.8 °C and annual rainfall amount of 2673.8 mm.
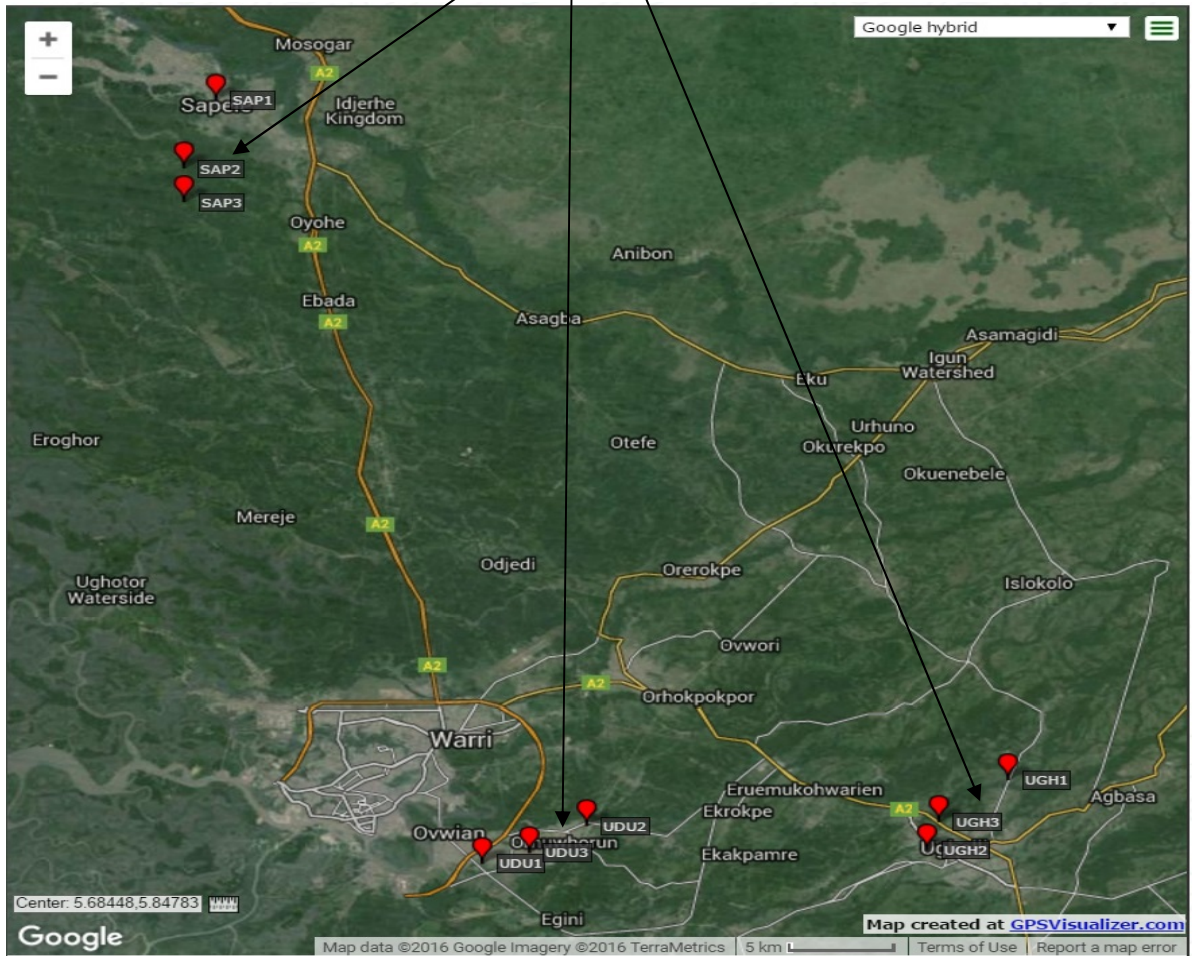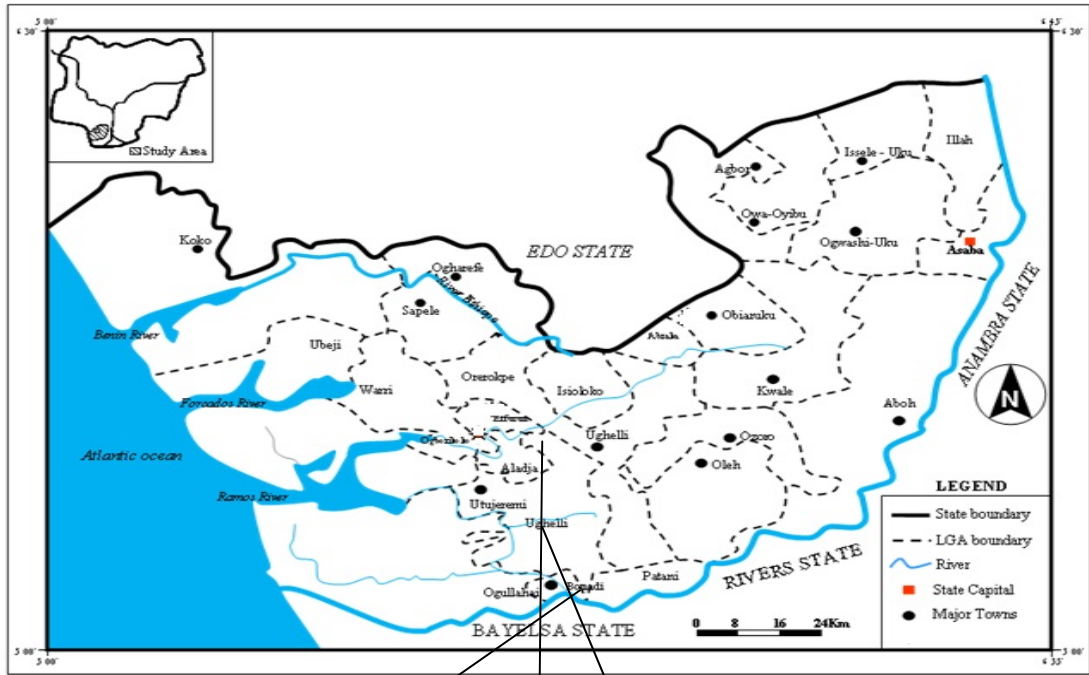
**Figure 3.1: Map of the study area**

### 3.2    Sample Collection

Soil samples were collected from 9 dumpsites from 3 towns at depth 0-15 cm, 15-30 cm and 30-45 cm. Soil samples were collected with a stainless steel auger after removal of the uppermost debris from the soil layer. Samples were stored in stainless-steel containers and immediately transferred to the laboratory. In the laboratory, the soil samples were air dried, twigs and stones removed and sieved over stainless steel sieves (< 2mm). Thereafter, they were stored in sealed stainless steel containers at $4^oC$ prior to analysis.

### 3.3    Physicochemical Characterization of Soil Samples

### 3.3.1    pH

The soil pH was determined in soil suspension (1:2 soil to water ratio) using a glass electrode pH meter and the pH read according to the method of Abollino *et al*. (2002).

### 3.3.2    Electrical conductivity

The soil electrical conductivity was determined in soil suspension (1:2 soil to water ratio) using a conductivity meter (Abollino *et al*., 2002).

### 3.3.3    Total Organic Carbon:

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

**Procedure:** 0.5 g of air-dried homogenised and sieved soil was weighed and placed in a conical refluxing flask. 10 ml of the standard $K_2Cr_2O_7$ solution was added and swirl to mix. 15 ml concentrated $H_2SO_4$ was added.Flask was connected to a condenser, placed on a hot plate and refluxed for 1 hr. The solution was cooled and 100 ml of water was added.

Solution was swirled to mix and 5 drops of ferroin indicator was added. Solution was titrated with ferrous ammonium sulphate to the end point at which the colour changes from blue-green to violet-red. In the same way, a blank consisting of all the same reagents but without the soil was carried out. The total organic carbon was calculated as:

Organic carbon (mg g$^{-1}$) = (18 × C × V) / M × (1-V$_1$/V$_2$)

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

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

## 3.4    Metals analysis

0.5g of the soil sample was placed in digestion tube followed by addition of 15 mL of aqua regia (3:1 HCl:HNO$_3$) and was swirled to wet the sample and allowed to stand overnight.  The next day, the tube was heated in a heating block of 50$^{o}$C for 30 min and raise to temperature of 120 $^{o}$C for 2 hr.  The digest was made up dissolved with 0.25 mol/L HNO$_3$ and filtered through Whatman No. 1 filter paper and made up to 25 mL with 0.25 mol/L HNO$_3$ (Radojevic and Bashkin, 1999).  The samples solution was subsequently analysed for Cd, Pb, Zn, Ni, Cu, Fe and Cr using air-acetylene atomic adsorption spectrophotometry (Perkin Elmer Analyst 200).

## 3.5    Chemical Fractionation of Heavy Metals in Soil

For the chemical fractionation of the metals under study, the procedure of Tessier *et al.,* (1979) was employed. In this method heavy metal, were separated into five operationally defined fractions:

Exchangeable (F1), bound to carbonate (F2), bound to Fe-Mn oxide (F3), bound to organic matter (F4) and residual fraction (F5).

1g of the soil sample was weighed and extracted into five fractions as follows:

1. **F1:** Exchangeable: the soil sample was extracted at room temperature for 1 hour with 8ml of 1M Magnesium Chloride solution at pH 7.0 with continuous agitation.

2. **F2:** Metals Bound to Carbonates: the residue from step (1) was extracted at room temperature with 8ml of 1M Sodium acetate solution adjusted to pH 5.0 with acetic acid. Continuous agitation was maintained.

3. **F3:** Metals Bound to Fe-Mn Oxide:the residue from step (2) was extracted with 20ml of 0.04M hydroxylamine chloride ($NH_2OH.HCl$) in 25% (v/v) acetic acid and was heated to $96^oC$ with occasional agitation for 6 hours.

4. **F4:** Metals Bound to Organic Matter: the residue from step (3) was extracted with 3ml of 0.02M nitric acid ($HNO_3$) and 5ml of 30% Hydrogen peroxide ($H_2O_2$) adjusted to pH 2.0 with nitric acid and the mixture was heated to $86^oC$ for 3 hours with intermittent agitation. The mixture was cooled and 5ml of 3.2M ammonium acetate ($NH_4OAc$) in 20% (v/v) nitric acid ($HNO_3$) wereadded and the solution was then be diluted to 20ml and agitated continuously for 30 minutes.

5. **F5:** Residual Metals: the residue from step (4) was digested with a mixture of Hydrofluoric acid, nitric acid and perchloric acid.

After each successive extraction, the supernatant solution was separated by centrifuging the suspension at 7,500 rpmfor 30 min and filtering through Whatman 42 filter paper. The concentration of Cd, Pb, Zn, Ni, Cu, Fe and Cr was determined using atomic adsorption spectrophotometer (Perkin Elmer Analyst 200).

### 3.6 Quality Assurance Programme

Sterilized and disposable rubber gloves was worn during analysis. Plastics (polypropylene) containers were used for storing samples prior to analysis. All the bottles for metal analysis were washed with metal free detergent and sterilized by soaking with 10 % $HNO_3$ analar grade overnight and then rinsed several times with distilled water. For every six samples, procedural blank and a sample spiked standard was used for monitoring

interferences and cross contaminations, all results were blank-corrected. Also, in the QA/QC programme, the instruments was calibrated with calibration standards before used. Matrix matching, standard addition and background correction was used to overcome interference in metal analysis.

## 3.7 Statistical Analysis

Two-way analysis of variance (ANOVA) wasused to determine whether the concentrations of metals varied significantly within sampling locations, with value less than 0.05 ($p < 0.05$) consider statistically significant. The Pearson's correlation coefficient was used to determine the relationship between physicochemical properties and heavy metals. The statistical analysis was performed using SPSS version 19.

## Data Treatment

### 1. Contamination/pollution index:

The contamination/pollution index will be derived by employing the contamination/pollution index as defined by Lacutusu (2002).

$$C/PI \quad = \quad \frac{Concentration\ of\ metal\ in\ soil}{Target\ value}$$

The target (reference) value of metals used in this study is the Department of Petroleum Resources of Nigeria (DPR, 2002) target value of heavy metals is soil.

C/P index value greater than unity defines a pollution range and when the values less than unity define the contamination range.

### 2. Index of geoaccumulation ($I_{geo}$):

The index of geoaccumulation enables the assessment of contamination by comparing the current and pre-industrial concentration originally used with bottom sediments (Muller, 1969). The index of geoaccumulation equation is given as follows:

$$I_{geo} \quad = \quad \log_2 \frac{Cn}{1.5\ Bn}$$

Where Cn is the measured concentration of the element in the dust fraction (<2µm) and Bn is the geochemical background value. The constant 1.5 allow us to analyse natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences.

### 3.      Enrichment Factor (EF)

Enrichment factor of metals in the soil was calculated following the equation of Reimann and De Caritat (2000).

$$EF = \frac{\frac{Cn\ (test\ element)}{Cn\ (Reference)}}{\frac{Bn\ (test\ element)}{Bn\ (Reference)}}$$

Where

Cn  = Concentration of the test metal in the sample

$Cn_{ref}$ = Concentration of the reference metal in the sample

Bn test element = background concentration of the test metal in crustal rock

$Bn_{ref}$ background concentration of the reference metal in crustal rock (Reimann and De Caritat, 2000).  In this case, Iron is chosen as the reference element because it is the most abundant element in the earth crust among those study. The crustal abundance values for the respective metals (Turiekianan and Wedepohl, 1961) were used as background concentrations for the estimation of the enrichment factors. Five contamination categories are recognized on the basis of the enrichment factor (Suntherland, 2000; Loska and Wiechula, 2003). EF<2 =Deficiency to minimal enrichment. EF=2-5 = Moderate enrichment. FE=5-20 = Significant enrichment. EF=20-40 =Very high enrichment. EF>40 =extremely high enrichment.

### 4      Ecological risk assessment metals in soils

The method of determining ecological risks of metals was originally introduced by Hakanson (1980). The index has been applied for ecological risks assessments of metals in sediments, soil and dusts (Saeedi *et al.,* 2012). The potential ecological risk index is given by the equation.

$$RI = \Sigma\ Er \qquad\qquad (10)$$

Where $Er = Tr \times CF$

$$CF = \frac{Cs}{Cn}$$

Where; Tr is the biological toxic factor of a single metal. Hekanson (1980) demonstrated Tr value for Cd, Cu, Pb, Cr, Zn and Ni to be 30, 5, 5, 2, 1, and 5 respectively. CF is contamination factor, Cs and Cn are metal concentrations for samples and background respectively. Also, the background concentrations used are the crustal abundance values of the respective metals (Turiekian and Wedepohl, 1961). These are; 0.3, 45, 20, 90, 95 and 68 for Cd, Cu, Pb, Cr, Zn and Ni respectively. Er is the ecological risk of each metal and RI shows the ecological risk of multiple metals. The Er and RI have been classified into five and four categories depending on their values respectively. Er value <40 denotes low potential ecological risk; ≥40<80 moderate potential ecological risk; ≥80<100 strong potential ecological risk; ≥100<320 very strong potential ecological risk and ≥320 extremely strong potential ecological risk. RI value <150 indicates low ecological risk; ≥150<300 moderate ecological risk; ≥300<600 strong ecological risk and ≥600 very strong ecological risk.

# CHAPTER FOUR
## RESULTS AND DISCUSSION

The individual results obtained for each physicochemical property and metal are shown in Table 4.1. Table 4.2a shows descriptive statistical data contents of the metals in the dumpsite soils and also contains the Department of Petroleum Resources target and intervention values which served as reference values (DPR, 2002). Table 4.2b shows the concentrations of metals in the dumpsite soils in this study in comparison with others in the literature. Analysis of variance showed that the concentration of metals varied significantly with depth in each site ($p<0.05$) and among the locations ($p<0.05$).

## 4.1 Physicochemical properties

### 4.1.1 pH

Soil pH is a major factor influencing the availability of element in soil (Igwe *et al*., 2005). It is well known that metal concentrations in soil solution and consequently leaching can be much enhanced in soils with low pH and/or redox potential (Adie and Osibanjo, 2009). Most metals in the pH range of 6.0 – 9.0 are not always in the free form (Adie and Osibanjo, 2009). The pH of the soils in this study ranged between 4.64 and 7.85 for all sites and depth. The highest and lowest pH values were obtained at sites SAP3 (0-15 cm depth) and UGH3 (30-45 cm depth). The pH of the soils decreased with depth in all sites. The pH of the soil samples in this study are slightly acidic to neutral. This near neutrality to slight acidic is common to anaerobic soils in the Niger Delta (Odu *et al*., 1985; Isirimah, 1987; Osakwe, 2010). The soil pH values obtained in this study were similar to the range of 5.9-6.2 reported in soils of municipal waste dumpsites at Obafemi Awolowo University, Ile-Ife (Amusan *et al*., 2005), 5.5-6.4 reported in soils of dumpsites in Portharcourt municipality and environs (Ogbonna *et al*., 2009), 4.21-7.26 for soils of refuse dumpsites in Akure (Oviasogie *et al*., 2009), 4.9-7.4 for soils around automobile dumpsites in Agbor and Environs (Osakwe, 2010), 4.17-7.4 for Aladimma dumpsite soils

(Amadi, 2011) and 5.9-6.7 for soils of dumpsites in Njoku market, Imo State, Nigeria (Ubuoh *et al*., 2012).

**Table 4.1: Physicochemical properties and metal concentrations (mg kg$^{-1}$) of soils in sampled dumpsites**

| DEPTH | SITES | pH | EC (µ∫/cm) | TOC (%) | Cd | Pb | Cr | Ni | Cu | Zn | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0-15 cm | SAP1 | 7.57 | 188 | 0.54 | 1.50 | 16.5 | 10.2 | 2.50 | 4.00 | 408 | 3900 |
| | SAP2 | 7.60 | 212 | 0.85 | ND | 35.5 | 7.20 | 6.00 | 68.5 | 300 | 5535 |
| | SAP3 | 7.85 | 214 | 0.37 | 1.50 | 10.0 | 7.60 | 1.00 | ND | 53.5 | 3360 |
| | UDU1 | 7.10 | 173 | 1.49 | ND | 45.0 | 6.50 | 1.00 | 66.0 | 29.5 | 3437 |
| | UDU2 | 7.60 | 145 | 0.26 | ND | 12.0 | 7.90 | 1.50 | 1.00 | 165 | 2790 |
| | UDU3 | 7.13 | 411 | 0.06 | ND | 54.0 | 4.60 | 1.00 | 2.00 | 71 | 4430 |
| | UGH1 | 7.46 | 170 | 0.61 | 2.00 | 70.0 | 10.1 | 3.00 | 25.0 | 285 | 2810 |
| | UGH2 | 7.11 | 245 | 0.92 | 3.00 | 112 | 14.9 | 14.5 | 66.5 | 505 | 11865 |
| | UGH3 | 6.25 | 84.9 | 0.21 | 1.00 | 149 | 8.50 | 7.50 | 40.0 | 338 | 5260 |
| 15-30 cm | SAP1 | 7.50 | 126 | 1.25 | ND | 15.0 | 6.85 | 1.00 | 3.00 | 39.5 | 5055 |
| | SAP2 | 7.73 | 192 | 0.14 | 1.00 | 22.0 | 5.70 | 3.00 | 11.0 | 64.5 | 3990 |
| | SAP3 | 7.70 | 189 | 0.73 | ND | 12.0 | 4.40 | 1.50 | ND | 35.5 | 4210 |
| | UDU1 | 7.10 | 139 | 0.35 | ND | 21.0 | 13.4 | 1.50 | 1.00 | 33 | 5110 |
| | UDU2 | 6.45 | 67.3 | 0.23 | 0.50 | 16.0 | 9.70 | 2.00 | ND | 50 | 3370 |
| | UDU3 | 6.64 | 451 | 0.11 | 1.50 | 15.0 | 15.4 | 3.00 | ND | 55.5 | 6820 |
| | UGH1 | 5.33 | 90.6 | 0.49 | 2.50 | 131 | 9.90 | 6.00 | 124 | 330 | 10050 |
| | UGH2 | 6.90 | 173 | 0.46 | 0.50 | 17.5 | 7.10 | 1.50 | 1.00 | 29 | 4580 |
| | UGH3 | 4.95 | 64.1 | 0.16 | 3.00 | 131 | 10.0 | 9.50 | 19.0 | 273 | 4160 |
| 30-45 cm | SAP1 | 7.53 | 134 | 0.21 | ND | 10.0 | 8.60 | 3.00 | 4.50 | 23.5 | 4860 |
| | SAP2 | 7.56 | 164 | 0.06 | ND | 18.5 | 4.20 | 1.00 | 2.50 | 18.5 | 2850 |
| | SAP3 | 7.70 | 211 | 0.45 | ND | 9.0 | 7.40 | ND | ND | 27.5 | 1650 |
| | UDU1 | 6.15 | 125 | 0.28 | 1.00 | 31.5 | 14.2 | 5.00 | 2.50 | 133 | 8750 |
| | UDU2 | 6.00 | 70.6 | 0.61 | ND | 16.5 | 10.6 | 1.50 | ND | 36 | 3030 |
| | UDU3 | 6.93 | 417 | 0.37 | 2.50 | 17.0 | 10.8 | 1.50 | ND | 21 | 4640 |
| | UGH1 | 5.14 | 60.8 | 0.23 | 3.00 | 60.5 | 14.2 | 7.50 | 74.0 | 375 | 9660 |
| | UGH2 | 6.82 | 162 | 0.38 | ND | 21.0 | 11.5 | 7.00 | 9.50 | 20 | 5790 |
| | UGH3 | 4.64 | 61.8 | 0.45 | 4.50 | 134 | 8.20 | 4.00 | 12.5 | 510 | 3340 |

**ND = Below detection limit**

**Table 4.2a: Descriptive statistics of metal concentrations in dumpsite soils and DPR target values (mg kg$^{-1}$)**

| Parameters | Cd | Pb | Cr | Ni | Cu | Zn | Fe |
|---|---|---|---|---|---|---|---|
| Minimum | ND | 9.00 | 4.20 | 1.00 | 1.00 | 18.5 | 1650 |
| Maximum | 4.50 | 149 | 15.4 | 14.5 | 124 | 510 | 11865 |
| Mean | 1.93 | 44.5 | 9.25 | 3.75 | 26.9 | 157 | 5011 |
| SD | 1.09 | 44.4 | 3.12 | 3.25 | 33.8 | 161 | 2410 |
| Kurtosis | 0.14 | 0.40 | -0.56 | 3.14 | 1.70 | -0.51 | 1.64 |
| Skewness | 0.63 | 1.29 | 0.36 | 1.59 | 1.38 | 0.91 | 1.35 |
| DPR target value | 0.8 | 85 | 100 | 35 | 36 | 140 | - |
| DPR intervention value | 17.0 | 530 | 380 | 210 | 190 | 720 | - |

**SD = standard deviation**

### 4.1.2 Electrical Conductivity

The electrical conductivity of the dumpsite soils in this study ranged from 60.8 to 451.2 $\mu s\ cm^{-1}$ for all sites and depth. The highest and lowest EC were observed at sites UDU3 (15-30 cm depth) and UGH1 (30-45 cm depth) respectively. Electrical conductivity decreased with depth in all sites except at site UDU3. Higher EC was obtained at site UDU3 relative to other sites. These values were comparable to those reported by Akpoveta et al. (2010), Osakwe (2010) and Amadi (2011) for dumpsites soils. For example, Akpoveta et al. (2010) reported EC values in the range of 165-201 $\mu s\ cm^{-1}$, Osakwe (2010) reported EC values in the range of 202-478 $\mu s\ cm^{-1}$ while Amadi reportedEC values in the range of 38.0-198 $\mu s\ cm^{-1}$.The high conductivity values obtained in this study might be due to the presence of scraps in these dumpsites. The implication of these high values of EC is that there is significant presence of trace metal ions or ionisable materials in the soil (Arias et al., 2005).

### 4.1.3 Total Organic Carbon

The total organic carbon (TOC) of these soil profiles ranged from 0.06 to 1.49 %. The highest TOC value was obtained at site UDU1. There was no regular trend in the values of TOC in these soil profiles. The values of TOC obtained in this study were lower than 0.08-3.41 %, 0.85-6.04 % and 29.6-77.8 % reported by Ogbonna et al. (2009), Ubuohet al. (2012) and Osakwe (2014). While soil organic carbon is not a requirement for plant growth, the levels of organic matter in soils influence a number of soils influence a number of chemical and physical processes and it is an important indicator of the soil as a rooting environment (Okalebo et al., 1993).

### 4.2 Metal concentrations in soils

### 4.2.1 Cadmium

Cadmium was detected in 56% of these soil samples at concentrations ranging from 0.05 to 4.5 mg kg$^{-1}$. The highest concentration of Cd was found at site UGH 3 (30 – 45cm depth). Cd was found majorly in the soil samples of UGH 1, UGH2 and UGH3. The concentrations of Cd obtained in this study were higher than the Department of Petroleum Resources (DPR) target value of 0.8 mgkg$^{-1}$ stipulated for Nigerian soils but were lower than the Department of Petroleum Resources (DPR) intervention value of 17 mg kg$^{-1}$. Various concentration of Cd in dumpsites soils have been reported in literature. The concentration of Cd obtained in this study were comparable to some reported in the literature (Odukoya *et al.*, 2011; Ogbemudia, and Mbong, 2013) (Table 4.2b). The concentration of Cd in these soil profiles were higher than concentrations reported by Nwajei *et al.* (2007) in soil around refuse dumpsites in Onitsha, Oviasogie *et al.* (2009) for dumpsites in Akure and Akpoveta *et al.* (2010) for soil around scrap dumpsites (Table 4.2b). However, higher concentrations of Cd have been reported in the literature. For instance, Amusan *et al.* (2005) reported Cd concentration ranging from 17. 0 to 47.06 mg kg$^{-1}$ in refuse dump sites soils in the Obafemi Awolowo University, Ile-Ife (Table 4.2b). Also, Ogbonna *et al.* (2009) reported Cd concentration of 1. 28 to 21.31 mgkg$^{-1}$ dumpsite soil in Port Harcourt municipality.

### 4.2.2 Lead

In this study, Lead was detected in all sites and depth. The concentration of Pb in these soil profiles ranged from 9.0 to 149 mg kg$^{-1}$. The highest and lowest concentrations of Pb were observed at sites UGH3 (0 – 15 cm depth) and SAP3 (30 – 45 cm depth) respectively. The concentration of Pb decreased with depth at all sites except site UDU2. The Department of Petroleum Resources (DPR) target value for Pb is 85 mg kg$^{-1}$. The concentration of Pb obtained in site UGH3 (0-15cm, 15-30 cm and 30-45 cm) and UGH2 (0-15 cm) were higher than the DPR target value. The concentration of Pb obtained in this study were below the Department of Petroleum Resources (DPR) intervention value 530 mg kg$^{-1}$ for Pb. The concentration of Pb obtained in this study were higher than those reported by

Nwajei *et al*. (2007), Ogboma *et al*. (2009), Oviasogie *et al*., (2009), Amadi (2011), Osakwe (2011) and Ogbemudia and Mbong (2013) (Table 4.2b). However, the concentration of Pb in this study were lower than others reported in the literature (Amusan *et al*., 2005; Adefemi and Awokumi, 2009; Adelekan and Alawode, 2011; Odukoya *et al*., 2011) (Table 4.2b).

**Table 4.2b: Metal concentrations (mg kg$^{-1}$) in dumpsite soils in comparison with others in the literature**

| Location | Cd | Pb | Cr | Ni | Cu | Zn | Fe | Reference |
|---|---|---|---|---|---|---|---|---|
| Sapele, Udu and Ughelli | 0.5-4.5 | 9.0-148.5 | 4.2-15.4 | 1.0-14.5 | 1.0-124 | 18.5-510 | 1650-11865 | This study |
| Uyo municipality | 3.7-4.4 | 16.1-17.8 | 13.9-15.8 | | | 16.4-24.4 | 143-1013 | Ogbemudia and Mbong (2013) |
| Aladimma | | 0.28-26.5 | 1.56-5.28 | | 5.2-58.6 | 68.3-291 | 26.1-264 | Amadi (2011) |
| Ibadan | <0.002-8.85 | 45.0-625 | 6.25-62.8 | 4.35-49.8 | | | | Adelekan and Alawode (2011) |
| Onitsha | 0.40-1.60 | ND-1.00 | ND-0.96 | | | | | Nwajei *et al*. (2007) |
| Ife | 17.0-47.1 | 63.6-418 | | | 36.5-73.0 | 63.2-102 | 926-2527 | Amusan *et al*. (2005) |
| Abraka | | | | | 0.25-1.10 | 4.00-25.8 | 12.2-50.0 | Osakwe (2014) |
| Agbor | | 1.36-3.76 | | | 0.59-2.85 | | 768-2897 | Osakwe (2011) |
| Ado-Ekiti | | 51.9-313 | 5.55-22.2 | ND-2.36 | 3.64-67.8 | 72.5-202 | 208-359 | Adefemi and Awokunmi |

| Location | | | | | | | | Reference |
|---|---|---|---|---|---|---|---|---|
| Port-harcourt | 1.28-21.3 | 3.81-46.2 | | | 1.38-76.2 | 10.3-128 | 20.1-280 | Ogbonna et al.(2009) |
| Akure | ND-2.91 | ND-23.0 | ND-9.0 | ND-17.0 | | | | Oviasogie et al. (2009) |
| Abraka and Agbor | 1.50-1.65 | 12.2-14.5 | 18.7-22.4 | 4.48-5.10 | 14.3-34.2 | 74.3-97.2 | 1327-1431 | Akpoveta et al. (2010) |
| Warri | ND-6.8 | 19.1-110 | 0.4-26.0 | 0.06-21.5 | 2.5-82.1 | 4.64-40.6 | 2311-7130 | Iwegbue et al. (2010) |
| Lagos | | ND-4.9 | 34.0-1057 | 41.0-125 | | 13.0-498 | 25.0-1625 | Odukoya et al.(2011) |
| Ngara, Nairobi | | | 161-362 | 402-584 | | | | Chengo et al. (2013) |

### 4.2.3 Chromium

The concentration of chromium in these soil samples ranged from 4.20 mg kg$^{-1}$ (at 30 – 45 cm depth of site SAP2) to 15.4 mg kg$^{-1}$ (at 15 – 30 cm depth of site UDU3) in all sites and depth. The concentrations of Cr decreased with depth except at sites UDU1, UDU2, UDU3 and UGH1. The concentration of Cr obtained in this study were lower than the DPR target and intervention values of 100 mg kg$^{-1}$ and 380 mg kg$^{-1}$ respectively (DPR, 2002) and also comparable to values reported by Adefemi and Awokunmi (2009) and Ogbemudia and Alawode (2011) (Table 4.2b). Lower concentration of Cr in dumpsites soils have been reported in the literature. For instance, Amadi (2011) reported Cr concentrations ranging from 1.56 to 5.28 mgkg$^{-1}$ in Aladima dumpsites soils. Furthermore, Nwajei *et al*. (2007) and Oviasogie *et al*. (2011) reported Cr concentrations in the ranged of ND – 0.96 and ND – 9.0 mgkg$^{-1}$ respectively in dumpsites soil in Onitsha and Akure respectively.

### 4.2.4 Nickel

Nickel was detected at concentrations ranging from 1.0 – 14.5 mgkg$^{-1}$ in these soil profiles. The highest concentration of Ni was found at 0 – 15 cm depth of the site UGH2. Ni was not detected at site SAP3 (30-45cm depth). In these soil profiles, the concentration of Ni increased with depth except at sites SAP1, UDU3, UGH2 and UGH3. The concentration of Ni in these dumpsites soils were lower than the DPR target and intervention values of 35 mg kg$^{-1}$ and 210 mg kg$^{-1}$ in soils respectively (DPR, 2002). The concentrations of Ni obtained in this study were lower than those reported in the literature (Adelekun and Alomode, 2011; Chengo *et al*., 2013) (Table 4.2b). The concentration of Ni in this study were however higher than those reported by some researcher (Adefemi and Awokunmi, 2009; Oviasogie *et al*., 2009; Akpoveta *et al*., 2010) (Table 4.2b).

### 4.2.5   Copper

In this study, Cu was detected at concentrations ranging from 1.0 to 124 mgkg$^{-1}$. The highest concentration of Cu was found at site UGH1 (15–30 cm depth). Copper was not detected at site SAP3 while it was detected only at the surface soil (0 – 15 cm depth) of sites UDU2 and UDU3. The DPR target value for Cu in soil is 36 mgkg$^{-1}$. Copper concentration in 19% of these soil samples were higher than the DPR target value. The concentration of Cu in these soil was however lower than the DPR intervention value of 190 mgkg$^{-1}$. The concentration of Cu in these soil profiles were comparable to Cu concentrations reported in dumpsite soils in the literature (Amusan *et al*., 2005; Adefemi and Awokunmi, 2009; Ogboma *et al*., 2009, Akpoveta *et al*., 2009; Iwegbue *et al*., 2010; Amadi *et al*., 2011) (Table 4.2b).

### 4.2.6   Zinc

The concentration of Zn in these soil profiles ranged from 20 to 510 mg kg$^{-1}$ . The highest and lowest concentration of Zn were observed at the 30 – 45 cm depth of sites UGH2 and UGH3 respectively. The concentration of Zn in these soil profiles decreased with depth except at site UDU1 and UGH1 and UGH3. The concentration of Zn in 41% of these soil samples was higher than the 140 mgkg$^{-1}$ DPR target value for Zn in soils but Zn concentrations in all samples were lower than the DPR intervention value of 720 mgkg$^{-1}$. A wide range of Zn concentration have been reported inTable 4.2b (Amusan *et al*., 2005; Akpoveta *et al*., 2010; Iwegbue *et al*., 2010; Amadi, 2011; Ogbemudia and Mbong, 2013). Amusan *et al*. (2005) reported concentration of Zn ranging from 63.2 to 102 .11 mgkg$^{-1}$ in soils of dumpsites in Ile-Ife, Nigeria while Amadi (2011) reported Zn concentration ranging from 68.3 to 290 mgkg$^{-1}$ in soil Aladinma dumpsite. Also, Adefemi and Awokunmi (2009) reported Zn concentration of 72.47 to 201.6 mgkg$^{-1}$in dumpsites of Ado-Ekiti.

**4.2.7 Iron**

The concentration of Fe in these soils ranged from 1650 to 11865 mgkg$^{-1}$ in all sites and depth. The highest and lowest concentration of Fe were observed at sites UGH2 (0 – 15 cm depth) and SAP3 (30 – 45 cm depth) respectively. The concentration of Fe decreased with depth at sites SAP2, SAP3 UGH2 and UGH4. There is no DPR target value for Fe in Nigeria. However, the values of Fe obtained in this study were lower than 4.7% crustal abundance values of Fe (Tunekien and Wedepohl, 1960). The concentration of Fe obtained in this study were higher than those reported in the literature (Amusan *et al*., 2005; Adefemi and Awokunmi, 2009; Ogbonna *et al*., 2009; Akpoveta *et al*. 2009; Amadi, 2011; Osakwe, 2011; Ogbemudia and Mbong, 2013) but comparable to those reported by Iwegbue *et al*. (2010) (Table 4.2b).

**4.3     Comparison with Canadian Soil Quality Guidelinesand other countries guidelines**

Table 4.3 gives a comparison of average concentration of each metal in the study area with the Canadian Soil Quality Guidelines for the Protection of Environmental and Human health for different land uses(Agricultural, Residential/parkland, commercial and industrial land uses) and other countries guidelines.

From Table 4.3, the average values of pH in all the studied sites except sites UGH1 and UGH3 were within the pH values (6.0 to 8.0) recommended by the Canadian Soil Quality Guidelines for all types of land uses (CCME, 1999). Soils at sites UGH1 and UGH3 were acidic indicating high tendency of heavy metal mobility in the two sites.

The average concentrations of Cd in sites SAP1, SAP3, UDU3, UGH1, UGH2 and UGH3 were above the Canadian soil quality guideline for Agricultural soil (1.4 mg kg$^{-1}$), Norway and Germany guideline value (1.0 mgkg$^{-1}$) as well as the Switzerland guideline value of 0.8 mg kg$^{-1}$. The average concentrations of Cd at UGH1 and UGH3 were higher

than the guideline value (2.0 mg kg$^{-1}$) for France.

**Table 4.3: Comparison of average pH and metals concentrations (mg kg$^{-1}$) in the study area with guideline values of different countries**

| Sample sites/Guideline | pH | Cd | Pb | Cr | Ni | Cu | Zn | Fe | References |
|---|---|---|---|---|---|---|---|---|---|
| SAP1 | 7.53 | 1.5 | 13.8 | 8.55 | 2.17 | 3.83 | 157 | 4605 | This study |
| SAP2 | 7.63 | 1.0 | 25.3 | 5.70 | 3.33 | 27.3 | 128 | 4125 | This study |
| SAP3 | 7.75 | 1.5 | 10.3 | 6.47 | 1.25 | ND | 38.8 | 3073 | This study |
| UDU1 | 6.78 | 1.0 | 32.5 | 11.4 | 2.50 | 23.2 | 65.2 | 5766 | This study |
| UDU2 | 6.68 | 0.5 | 14.8 | 9.4 | 1.67 | 1.0 | 83.7 | 3063 | This study |
| UDU3 | 6.90 | 2.0 | 28.7 | 10.3 | 1.83 | 2.0 | 49.2 | 5297 | This study |
| UGH1 | 5.98 | 2.5 | 87.2 | 11.4 | 5.50 | 74.3 | 330 | 7507 | This study |
| UGH2 | 6.94 | 1.8 | 50.2 | 11.2 | 7.67 | 25.7 | 185 | 7412 | This study |
| UGH3 | 5.28 | 2.8 | 138 | 8.9 | 7.00 | 23.8 | 374 | 4253 | This study |
| Canada (Agricultural) | 6.0-8.0 | 1.4 | 70 | 64 | 50 | 63 | 200 | - | CCME, 1999 |
| Canada (Residential/Parkland) | 6.0-8.0 | 10 | 140 | 64 | 50 | 63 | 200 | - | CCME, 1999 |
| Canada (Commercial) | 6.0-8.0 | 22 | 260 | 87 | 599 | 91 | 360 | - | CCME, 1999 |
| Canada (Industrial) | 6.0-8.0 | 22 | 600 | 87 | 599 | 91 | 360 | - | CCME, 1999 |
| Norway | - | 1.0 | 50.0 | 100 | 30 | 100 | 150 | - | Reinmann *et al*. (1997) |
| Netherland (Action level) | - | 12.0 | 530 | 380 | 210 | 190 | - | - | Reinmann *et al*. (1997) |
| Switzerland (guide values) | - | 0.8 | 50.0 | - | | 50 | 200 | - | FOEFL, 1987 |
| Germany | - | 1.0 | 70 | 60 | 50 | 40 | - | - | ECDGE (2010) |
| United Kingdom | - | 3.0 | 300 | 400 | 75 | 135 | - | - | ECDGE (2010) |
| France | - | 2.0 | 100 | 150 | 50 | 40 | - | - | ECDGE (2010) |

However, the average Cd concentration in other sites were below the Canadian soil quality guideline for Residential, Industrial and Commercial soil, Netherland action level value (12.0 mg kg$^{-1}$) and United Kingdom guideline value (3.0 mg kg$^{-1}$).

The average concentrations of Pb at sites UGH1 (87.2 mg kg$^{-1}$) and UGH3 (138 mg kg$^{-1}$) were higher than the Canadian soil quality guideline for Agricultural soil (70 mg kg$^{-1}$), Norway guideline value (50 mg kg$^{-1}$), Switzerland (50 mg kg$^{-1}$) and Germany guideline value (70 mg kg$^{-1}$). Other sites had average Pb concentrations below the guideline values of the different countries.

The average concentrations of Cr and Ni in all the sites studied were below the guideline values of all the various countries.

The average concentrations of Cu at site UGH1 (74.3 mg kg$^{-1}$) was above the Canadian soil quality guideline value (63 mg kg$^{-1}$) for Residential and Agricultural soils. It was also higher than guideline values of 40mg kg$^{-1}$, 50mg kg$^{-1}$ and 40 mg kg$^{-1}$ for Germany, Switzerland and France respectively. Other sites had average Cu concentrations lower than the various countries guideline values.

 The concentrations of Zn at sites SAP1 (157 mg kg$^{-1}$) and UGH2 (185 mg kg$^{-1}$) were higher than Norway guideline value of 150 mg kg$^{-1}$ while the concentration of Zn at sites UGH1 (330 mg kg$^{-1}$) and UGH3 (374 mg kg$^{-1}$) were higher than the Canadian guideline value of 200 mg kg$^{-1}$ for Agricultural soils as well as the Switzerland guideline value. Only site UGH3 had concentration higher than the Canadian guideline value of 360 mg kg$^{-1}$ for Commercial and Industrial soils. Sites SAP2, SAP3, UDU1, UDU2 and UDU3 were below the guideline values of the different countries.

## 4.4 Contamination/pollution Index (CPI)

The significance of interval of contamination/pollution index is shown in Table 4.4a while the contamination/pollution index and the multiple pollution index (MPI) of the soil samples in this study are displayed in Table 4.4b.

**Table 4.4a: Significance of intervals of contamination/pollution index (C/PI)**

| C/PI | Significance |
|------|--------------|
| <0.1 | Very slight contamination |
| 0.10-0.25 | Slight contamination |
| 0.26-0.5 | Moderate contamination |
| 0.51-0.75 | Severe contamination |
| 0.76-1.00 | Very severe contamination |
| 1.1-2.0 | Slight pollution |
| 2.1-4.0 | Moderate pollution |
| 4.1-8.0 | Severe pollution |
| 8.1-16.0 | Very severe pollution |
| >16.0 | Excessive pollution |

**Table 4.4b: Contamination/pollution index of metals in sampled dumpsite soils**

| DEPTH | SITES | Cd | Pb | Cr | Ni | Cu | Zn | MPI |
|---|---|---|---|---|---|---|---|---|
| 0-15 cm | SAP1 | 1.88 | 0.19 | 0.10 | 0.07 | 0.11 | 2.91 | 4.79 |
| | SAP2 | | 0.42 | 0.07 | 0.17 | 1.90 | 2.14 | 4.05 |
| | SAP3 | 1.88 | 0.12 | 0.08 | 0.03 | | 0.38 | 1.88 |
| | UDU1 | | 0.53 | 0.07 | 0.03 | 1.83 | 0.21 | 1.83 |
| | UDU2 | | 0.14 | 0.08 | 0.04 | 0.03 | 1.18 | 1.18 |
| | UDU3 | | 0.64 | 0.05 | 0.03 | 0.06 | 0.51 | |
| | UGH1 | 2.50 | 0.82 | 0.10 | 0.09 | 0.69 | 2.04 | 4.54 |
| | UGH2 | 3.75 | 1.32 | 0.15 | 0.41 | 1.85 | 3.61 | 10.52 |
| | UGH3 | 1.25 | 1.75 | 0.09 | 0.21 | 1.11 | 2.41 | 6.52 |
| 15-30 cm | SAP1 | | 0.18 | 0.07 | 0.03 | 0.08 | 0.28 | |
| | SAP2 | 1.25 | 0.26 | 0.06 | 0.09 | 0.31 | 0.46 | 1.25 |
| | SAP3 | | 0.14 | 0.04 | 0.04 | | 0.25 | |
| | UDU1 | | 0.25 | 0.13 | 0.04 | 0.03 | 0.24 | |
| | UDU2 | 0.63 | 0.19 | 0.10 | 0.06 | | 0.36 | |
| | UDU3 | 1.88 | 0.18 | 0.15 | 0.09 | | 0.40 | 1.88 |
| | UGH1 | 3.13 | 1.54 | 0.10 | 0.17 | 3.44 | 2.36 | 10.47 |
| | UGH2 | 0.63 | 0.21 | 0.07 | 0.04 | 0.03 | 0.21 | |
| | UGH3 | 3.75 | 1.54 | 0.10 | 0.27 | 0.53 | 1.95 | 7.24 |
| 30-45 cm | SAP1 | | 0.12 | 0.09 | 0.09 | 0.13 | 0.17 | |
| | SAP2 | | 0.22 | 0.04 | 0.03 | 0.07 | 0.13 | |
| | SAP3 | | 0.11 | 0.07 | | | 0.20 | |
| | UDU1 | 1.25 | 0.37 | 0.14 | 0.14 | 0.07 | 0.95 | 1.25 |
| | UDU2 | | 0.19 | 0.11 | 0.04 | | 0.26 | |
| | UDU3 | 3.13 | 0.20 | 0.11 | 0.04 | | 0.15 | 3.13 |
| | UGH1 | 3.75 | 0.71 | 0.14 | 0.21 | 2.06 | 2.68 | 8.48 |
| | UGH2 | | 0.25 | 0.12 | 0.20 | 0.26 | 0.14 | |
| | UGH3 | 5.63 | 1.58 | 0.08 | 0.11 | 0.35 | 3.64 | 10.84 |

The contamination/pollution index of the metals for all sites and depth ranged from 0.63 to 5.63 for Cd, 0.12 to 1.75 for Pb, 0.04 to 0.15 for Cu and 0.14 to 3.64 for Zn. For Cd, 7% of the sample fall within the severe contamination range, 22% each falls within slight pollution and moderate pollution while only one sample falls within the severe pollution range. For Pb, 19% of the samples falls within the slight pollution ranged while others fall within the contamination ranged. The index of Cr and Ni falls within the contamination range. 22% of samples falls into the contamination range while 37% of samples falls into the pollution range with respect to Zn. The multiple pollution index for all sites and depth ranged from 1.18 at site UDU 2 to 10.84 at site UGH2.

## 4.5    Geoaccumulaton Index

The significance of interval of geoaccumulation index are displayed in Table 4.5a while the geoaccumulation index of these soil profiles from the dumpsites are displayed in Table 4.5b.

The geoaccumulation index of Cd ranged from 0.15 to 3.32. Based on the Muller (1969) classification, 7% of the samples falls into unpolluted to moderately polluted (class 2), 22% falls into moderately polluted (class 3), 22% falls into moderately polluted to strongly polluted (class 4) and 4% falls into strongly polluted (class 5). For Pb, only 41% of the samples have different degree of pollution. For instance, 15%, 11% and 4% of the samples falls into class 2, class 3 and class 4 respectively. Cr, Ni and Fe have geoaccumulation index values < 0. Thus, they fall into unpolluted class (class 1). For Cu, 11% fall into class 1 i.e unpolluted to moderately polluted. For Zn, 11% and 26% falls into class 1 and class 2 respectively.

## 4.6    Enrichment Factor (EF)

The significance of interval of enrichment factor are displayed in Table 4.6a while the enrichment factor of metals in the soils of the dumpsites in this study are shown in

Table 4.6b.

**Table 4.5a: Significance of intervals of Geoaccumulation index**

| Igeo Values | Significance |
| --- | --- |
| <0 | Practically unpolluted (Class 1) |
| 0-1 | Unpolluted to moderately polluted (Class 2) |
| 1-2 | Moderately polluted (Class 3) |
| 2-3 | Moderately to strongly polluted (Class 4) |
| 3-4 | Strongly polluted (Class 5) |
| 4-5 | Strongly polluted to very polluted (Class 6) |
| >5 | Extremely polluted(Class 7) |

**Table 4.5b: Geoaccumulation index of metals in sampled dumpsite soils**

| DEPTH | SITES | Cd | Pb | Cr | Ni | Cu | Zn | Fe |
|---|---|---|---|---|---|---|---|---|
| 0-15 cm | SAP1 | 1.74 | -0.86 | -3.73 | -5.35 | -4.08 | 1.52 | -4.18 |
| | SAP2 | 0.00 | 0.24 | -4.23 | -4.09 | 0.02 | 1.07 | -3.67 |
| | SAP3 | 1.74 | -1.59 | -4.15 | -6.67 | 0.00 | -1.41 | -4.39 |
| | UDU1 | 0.00 | 0.59 | -4.38 | -6.67 | -0.03 | -2.27 | -4.36 |
| | UDU2 | 0.00 | -1.32 | -4.10 | -6.09 | -6.08 | 0.21 | -4.66 |
| | UDU3 | 0.00 | 0.85 | -4.88 | -6.67 | -5.08 | -1.01 | -3.99 |
| | UGH1 | 2.15 | 1.22 | -3.74 | -5.09 | -1.43 | 1.00 | -4.65 |
| | UGH2 | 2.74 | 1.90 | -3.18 | -2.81 | -0.02 | 1.83 | -2.57 |
| | UGH3 | 1.15 | 2.31 | -3.99 | -3.77 | -0.75 | 1.24 | -3.74 |
| 15-30 cm | SAP1 | 0.00 | -1.00 | -4.30 | -6.67 | -4.49 | -1.85 | -3.80 |
| | SAP2 | 1.15 | -0.45 | -4.57 | -5.09 | -2.62 | -1.14 | -4.14 |
| | SAP3 | 0.00 | -1.32 | -4.94 | -6.09 | 0.00 | -2.01 | -4.07 |
| | UDU1 | 0.00 | -0.51 | -3.33 | -6.09 | -6.08 | -2.11 | -3.79 |
| | UDU2 | 0.15 | -0.91 | -3.80 | -5.67 | 0.00 | -1.51 | -4.39 |
| | UDU3 | 1.74 | -1.00 | -3.13 | -5.09 | 0.00 | -1.36 | -3.37 |
| | UGH1 | 2.47 | 2.13 | -3.77 | -4.09 | 0.88 | 1.21 | -2.81 |
| | UGH2 | 0.15 | -0.78 | -4.25 | -6.09 | -6.08 | -2.30 | -3.94 |
| | UGH3 | 2.74 | 2.13 | -3.76 | -3.42 | -1.83 | 0.94 | -4.08 |
| 30-45 cm | SAP1 | 0.00 | -1.59 | -3.97 | -5.09 | -3.91 | -2.60 | -3.86 |
| | SAP2 | 0.00 | -0.70 | -5.01 | -6.67 | -4.76 | -2.95 | -4.63 |
| | SAP3 | 0.00 | -1.74 | -4.19 | 0.00 | 0.00 | -2.37 | -5.42 |
| | UDU1 | 1.15 | 0.07 | -3.25 | -4.35 | -4.76 | -0.10 | -3.01 |
| | UDU2 | 0.00 | -0.86 | -3.67 | -6.09 | 0.00 | -1.99 | -4.54 |
| | UDU3 | 2.47 | -0.82 | -3.64 | -6.09 | 0.00 | -2.76 | -3.93 |
| | UGH1 | 2.74 | 1.01 | -3.25 | -3.77 | 0.13 | 1.40 | -2.87 |
| | UGH2 | 0.00 | -0.51 | -3.55 | -3.87 | -2.83 | -2.83 | -3.61 |
| | UGH3 | 3.32 | 2.16 | -4.04 | -4.67 | -2.43 | 1.84 | -4.40 |

**Table 4.6a: Significance of intervals of**

| | EF Values | Significance |
|---|---|---|
| | <2 | Deficiency to minimal enrichment |
| | 2-5 | Moderate enrichment |
| | 5-20 | Significant enrichment |
| | 20-40 | Very high enrichment |
| >40 | >40 | Extremely high enrichment |

**Table 4.6b: Enrichment factor of metals in sampled dumpsite soils**

| DEPTH | SITES | Cd | Pb | Cr | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|
| 0-15 cm | SAP1 | 6.03 | 0.99 | 0.14 | 0.04 | 0.11 | 5.17 |
| | SAP2 | 0.00 | 1.51 | 0.07 | 0.07 | 1.29 | 2.68 |
| | SAP3 | 6.99 | 0.70 | 0.12 | 0.02 | 0.00 | 0.79 |
| | UDU1 | 0.00 | 3.08 | 0.10 | 0.02 | 1.99 | 0.42 |
| | UDU2 | 0.00 | 1.01 | 0.15 | 0.04 | 0.04 | 2.93 |
| | UDU3 | 0.00 | 2.86 | 0.05 | 0.02 | 0.05 | 0.79 |
| | UGH1 | 11.15 | 5.85 | 0.19 | 0.07 | 0.93 | 5.02 |
| | UGH2 | 3.96 | 2.22 | 0.07 | 0.08 | 0.59 | 2.11 |
| | UGH3 | 2.98 | 6.63 | 0.08 | 0.10 | 0.79 | 3.17 |
| 15-30 cm | SAP1 | 0.00 | 0.70 | 0.07 | 0.01 | 0.06 | 0.39 |
| | SAP2 | 3.93 | 1.30 | 0.07 | 0.05 | 0.29 | 0.80 |
| | SAP3 | 0.00 | 0.67 | 0.05 | 0.02 | 0.00 | 0.42 |
| | UDU1 | 0.00 | 0.97 | 0.14 | 0.02 | 0.02 | 0.32 |
| | UDU2 | 2.32 | 1.12 | 0.15 | 0.04 | 0.00 | 0.73 |
| | UDU3 | 3.45 | 0.52 | 0.12 | 0.03 | 0.00 | 0.40 |
| | UGH1 | 3.90 | 3.06 | 0.05 | 0.04 | 1.29 | 1.62 |
| | UGH2 | 1.71 | 0.90 | 0.08 | 0.02 | 0.02 | 0.31 |
| | UGH3 | 11.30 | 7.40 | 0.13 | 0.16 | 0.48 | 3.24 |
| 30-45 cm | SAP1 | 0.00 | 0.48 | 0.09 | 0.04 | 0.10 | 0.24 |
| | SAP2 | 0.00 | 1.53 | 0.08 | 0.02 | 0.09 | 0.32 |
| | SAP3 | 0.00 | 1.28 | 0.23 | 0.00 | 0.00 | 0.82 |
| | UDU1 | 1.79 | 0.85 | 0.08 | 0.04 | 0.03 | 0.75 |
| | UDU2 | 0.00 | 1.28 | 0.18 | 0.03 | 0.00 | 0.59 |
| | UDU3 | 8.44 | 0.86 | 0.12 | 0.02 | 0.00 | 0.22 |
| | UGH1 | 4.87 | 1.47 | 0.08 | 0.05 | 0.80 | 1.92 |
| | UGH2 | 0.00 | 0.85 | 0.10 | 0.08 | 0.17 | 0.17 |
| | UGH3 | 21.11 | 9.43 | 0.13 | 0.08 | 0.39 | 7.55 |

From the Table 4.6b the EF values ranged from 1.71 to 21.11, 0.52 to 7.40, 0.05 to 0.23, 0.01 to 0.01, 0.02 o 2.01 and 0.22 to 7.5 for Cd, Pb, Cr, Ni, Cu and Zn respectively. All the EF values are less than 10 except at site UGH1 (0-15 cm), UGH3 (30–45 cm depth). Thus, this indicate that all the metals originate from natural or crustal origin (Northing *et al*., 1999).However, for cadmium 48 %, 26 %, 22 % and 4 % of the samples falls into the deficiency to minimal enrichment, moderate enrichment, significant enrichment and very high enrichment respectively. For Pb, 70 %, 4 % and 4 % of the samples falls into the deficiency to minimal enrichment, moderate enrichment and significant enrichment respectively while for Zn, 70 %, 19 % and 3 % of the samples falls into the deficiency to minimal enrichment, moderate enrichment and significant enrichment respectively.  Chromium, Ni and Cu have enrichment factors that fall into deficiency to minimal enrichment category for all samples.

## 4.7    Ecological Risk of metals

The potential ecological risk of metals are shown in Table 4.7. The potential ecological risk of the metals is in the order of Cd> Pb > Cu > Zn > Cr > Ni. The potential ecological risk of the metals except Cd were in the low potential ecological risk categories (i. e. < 80). However, Cd have a strong potential ecological risk (> 80) in 48% of the samples.

The RI values of these soil profiles ranged from 3.0 to 491. The highest and lowest values were observed at the 30 – 45 cm depth of sites UGH3 and SAP3 respectively. Low ecological risk of metals (RI value < 150), moderate ecological risk of metals (RI values $\geq$ 150 < 300) and strong ecological risk of metal (RI value $\geq$ 300 < 600), were associated with 63%, 19% and 19 % of these soils samples respectively with significant contribution from Cd pollution.

**Table 4.7: Ecological risk of metals in sampled dumpsite soils**

| DEPTH | SITES | Cd | Pb | Cr | Ni | Cu | Zn | RI |
|---|---|---|---|---|---|---|---|---|
| 0-15 cm | SAP1 | 150 | 4.1 | 0.2 | 0.2 | 0.4 | 4.3 | 159 |
| | SAP2 | 0 | 8.9 | 0.2 | 0.4 | 7.6 | 3.2 | 20 |
| | SAP3 | 150 | 2.5 | 0.2 | 0.1 | 0.0 | 0.6 | 153 |
| | UDU1 | 0 | 11.3 | 0.1 | 0.1 | 7.3 | 0.3 | 19 |
| | UDU2 | 0 | 3.0 | 0.2 | 0.1 | 0.1 | 1.7 | 5 |
| | UDU3 | 0 | 13.5 | 0.1 | 0.1 | 0.2 | 0.7 | 15 |
| | UGH1 | 200 | 17.5 | 0.2 | 0.2 | 2.8 | 3.0 | 224 |
| | UGH2 | 300 | 28.0 | 0.3 | 1.1 | 7.4 | 5.3 | 342 |
| | UGH3 | 100 | 37.1 | 0.2 | 0.6 | 4.4 | 3.6 | 146 |
| 15-30 cm | SAP1 | 0 | 3.8 | 0.2 | 0.1 | 0.3 | 0.4 | 5 |
| | SAP2 | 100 | 5.5 | 0.1 | 0.2 | 1.2 | 0.7 | 108 |
| | SAP3 | 0 | 3.0 | 0.1 | 0.1 | 0.0 | 0.4 | 4 |
| | UDU1 | 0 | 5.3 | 0.3 | 0.1 | 0.1 | 0.3 | 6 |
| | UDU2 | 50 | 4.0 | 0.2 | 0.1 | 0.0 | 0.5 | 55 |
| | UDU3 | 150 | 3.8 | 0.3 | 0.2 | 0.0 | 0.6 | 155 |
| | UGH1 | 250 | 32.8 | 0.2 | 0.4 | 13.8 | 3.5 | 301 |
| | UGH2 | 50 | 4.4 | 0.2 | 0.1 | 0.1 | 0.3 | 55 |
| | UGH3 | 300 | 32.8 | 0.2 | 0.7 | 2.1 | 2.9 | 339 |
| 30-45 cm | SAP1 | 0 | 2.5 | 0.2 | 0.2 | 0.5 | 0.2 | 4 |
| | SAP2 | 0 | 4.6 | 0.1 | 0.1 | 0.3 | 0.2 | 5 |
| | SAP3 | 0 | 2.3 | 0.2 | 0.0 | 0.0 | 0.3 | 3 |
| | UDU1 | 100 | 7.9 | 0.3 | 0.4 | 0.3 | 1.4 | 110 |
| | UDU2 | 0 | 4.1 | 0.2 | 0.1 | 0.0 | 0.4 | 5 |
| | UDU3 | 250 | 4.3 | 0.2 | 0.1 | 0.0 | 0.2 | 255 |
| | UGH1 | 300 | 15.1 | 0.3 | 0.6 | 8.2 | 3.9 | 328 |
| | UGH2 | 0 | 5.3 | 0.3 | 0.5 | 1.1 | 0.2 | 7 |
| | UGH3 | 450 | 33.5 | 0.2 | 0.3 | 1.4 | 5.4 | 491 |

## 4.8    Correlation analysis

Pearson correlation coefficients of metals in the dumpsites soils are summarized in Table 4.8. At the 0 – 15 cm depth in Table 4.8, significant positive correlation ($r^2 > 0.50$) at 0.01 and 0.05 level of significance were observed between Cr/Cd, Ni/Cd, Pb and Cr, Cu/TOC, Cu/Ni, Zn/Cd, Cr, and Ni, Fe/Cd, Pb, Cr, Ni, Cu and Zn which may suggest a common origin. At the 15 – 30 cm depth, Pb correlated with Cd, Ni correlated with Cd and Pb, Cu correlated with Cd and Pb, while Zn correlated with Cd, Pb, Ni and Cu. Meanwhile, Fe correlated with Pb, Cu and Zn. Similarly, at 30 – 45 cm depth, EC correlated with pH, Pb correlated with Cd, Ni correlated with Cr, Cu correlated with Ni, Zn correlated with Cd, Pb and Cu while Fe correlated with Cr, Ni and Cu.

## 4.9    Principal Component Analysis (PCA)

PCA was applied to assist in the identification of sources of the metals. The result of the PCA analysis is are shown in Table 4.9 and Figures 4.1-4.3

At the 0-15 cm depth (Table 4.9 and Figure 4.1) four factors were obtained accounting for 93.07% of the total variance. Factor 1 is dominated by Cd, Cr, Ni, Zn and Fe, accounting for 48.95% of the total variance. This suggest that Cd, Cr, Ni and Zn may be present in the Fe - Mn oxide phase.  Factor 2 accounts for 17.09% of the total variance and was dominated by Pb. In this factor there is moderate loading of Ni. Factor 3 account for 15.37% of the total variance and was dominated by TOC and Cu while factor which account for 11.66% of the total variance have high loading of electrical conductivity (EC) and moderate loading of Fe.

At the 15–30 cm depth (Table 4.9b and Figure 4.2), three component factors accounting for 87.88% of the total variance were observed. Factor 1 which account for 57.30% of the total variance was dominated by Cd, Pb, Ni Cu and Zn. Factors 2 which

accounts for 18.79% of total variance high loading of Cu and Fe and a moderate loading of

Zn. Factor 3 accounting for 13.79% of the total variance was dominated by EC and Cr.

**Table 4.8: Correlation analysis of metals in sampled dumpsite soils**

| | EC (μʃ/cm) | TOC (%) | Cd | Pb | Cr | Ni | Cu | Zn | Fe |
|---|---|---|---|---|---|---|---|---|---|
| **0-15 cm depth** | | | | | | | | | |
| EC (μʃ/cm) | 1.000 | -0.186 | -0.101 | -0.195 | -0.260 | -0.100 | -0.197 | -0.250 | 0.194 |
| TOC (%) | | 1.000 | 0.063 | -0.023 | 0.230 | 0.193 | 0.766* | 0.041 | 0.230 |
| Cd | | | 1.000 | 0.388 | 0.887* | 0.617** | 0.085 | 0.654** | 0.569** |
| Pb | | | | 1.000 | 0.394 | 0.702* | 0.471 | 0.487 | 0.561** |
| Cr | | | | | 1.000 | 0.779* | 0.298 | 0.830* | 0.701* |
| Ni | | | | | | 1.000 | 0.616** | 0.796* | 0.936* |
| Cu | | | | | | | 1.000 | 0.324 | 0.563** |
| Zn | | | | | | | | 1.000 | 0.656** |
| Fe | | | | | | | | | 1.000 |
| **15-30 cm depth** | | | | | | | | | |
| EC (μʃ/cm) | 1.000 | -0.231 | -0.080 | -0.435 | 0.401 | -0.271 | -0.292 | -0.382 | 0.174 |
| TOC (%) | | 1.000 | -0.478 | -0.198 | -0.477 | -0.415 | 0.005 | -0.190 | 0.057 |
| Cd | | | 1.000 | 0.890* | 0.296 | 0.950* | 0.607** | 0.895* | 0.463 |
| Pb | | | | 1.000 | 0.134 | 0.921* | 0.757* | 0.987* | 0.507** |
| Cr | | | | | 1.000 | 0.195 | 0.056 | 0.134 | 0.375 |
| Ni | | | | | | 1.000 | 0.499 | 0.888* | 0.270 |
| Cu | | | | | | | 1.000 | 0.832* | 0.844* |
| Zn | | | | | | | | 1.000 | 0.596** |
| Fe | | | | | | | | | 1.000 |
| **30-45 cm depth** | | | | | | | | | |
| EC (μʃ/cm) | 1.000 | -0.045 | -0.061 | -0.447 | -0.123 | -0.424 | -0.397 | -0.519 | -0.217 |
| TOC (%) | | 1.000 | 0.093 | 0.138 | 0.203 | -0.160 | -0.246 | 0.065 | -0.335 |
| Cd | | | 1.000 | 0.862* | 0.251 | 0.329 | 0.470 | 0.872* | 0.268 |
| Pb | | | | 1.000 | 0.063 | 0.367 | 0.366 | 0.951* | 0.114 |
| Cr | | | | | 1.000 | 0.704* | 0.480 | 0.232 | 0.843* |
| Ni | | | | | | 1.000 | 0.673** | 0.477 | 0.825 |
| Cu | | | | | | | 1.000 | 0.604** | 0.658 |
| Zn | | | | | | | | 1.000 | 0.314 |
| Fe | | | | | | | | | 1.000 |

*Pearson correlation is significant at 0.01 level of significance (1 tailed)
**Pearson correlation is significant at 0.05 level of significance (1 tailed)

At the 30 – 45 cm depth (Table 4.9 and Figure 4.3), three factors were obtained accounting for 84.34% of the total and variance. Factor 1 which accounts for 51.03% of the total variance was characterized by high loadings of Cd, Pb and Zn. Factor 2 which accounts for 21.25% of the total variance was loaded with Cr, Ni, Cu and Fe while factor 3 which accounts for 12.04% of the total variance was dominated by TOC.

## 4.10    Chemical speciation of metals

**Cadmium**

Cadmium was present mostly in the residual fraction (Figure 4.4). The percentage of Cd in the residual fraction in these soil profiles ranged from 21.1 to 100 %. According to Osakwe (2012) a relatively high percentage of Cd in the residual fraction suggests lithogenous origin and cannot be mobilized. Similar results have been reported by other researchers in literatures (Osakwe, 2012, Iwegbue, 2007; Horsfall and Spiff, 2005; Kotoky *et al*., 2003). The next important fraction for Cd was Fe–Mn oxide fraction. The percentage of Cd in the Fe–Mn oxide fraction ranged from 6.8 to 45.5%. This is expected as Cd correlated well with Fe. The presence of Cd in this fraction may be due to the fact that Fe–Mn oxide control the fixation fraction is relatively stable but could change with variation in redox condition (Horsfall and Spiff, 2005; Osakwe, 2012).   Cd in the Fe-Mn oxide fraction have also been reported by Suayah *et al*., (2004), Hosfall and Spiff, (2005) and Osakwe, 2012). The percentage of Cd in the carbonate and organic fractions ranged from 0.4 to 41.1 % and 5.3 to 25.2 % respectively, while the percentage of Cd in the exchangeable fraction ranged from 0.1 to 13.3 %. This result is similar to others in the literature (Li *et al*., 2001; Osakwe, 2012). The percentage of Cd in the exchangeable fraction indicates that Cd is potentially available to some extent in these soil profiles.

**Table 4.9: PCA factor loadings after varimax with Kaiser Normalization Rotation for metals and some physicochemical properties of dumpsite soils**

| | 0-15 cm depth | | | | 15-30 cm depth | | | 30-45 cm depth | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Component | | | | Component | | | Component | | |
| | Factor 1 | Factor 2 | Factor 3 | Factor 4 | Factor 1 | Factor 2 | Factor 3 | Factor 1 | Factor 2 | Factor 3 |
| pH | | -.971 | | | -.910 | | | -.855 | -.388 | |
| EC | | | | .959 | -.415 | | .786 | -.505 | | |
| TOC | | | .949 | | -.485 | .380 | -.642 | | | .963 |
| Cd | .908 | | | | .913 | | | .857 | | |
| Pb | .368 | .902 | | | .917 | .357 | | .980 | | |
| Cr | .964 | | | | | | .829 | | .928 | .329 |
| Ni | .786 | .468 | .310 | | .967 | | | .339 | .839 | |
| Cu | | .373 | .892 | | .523 | .791 | | .481 | .634 | -.329 |
| Zn | .860 | | | | .883 | .452 | | .973 | | |
| Fe | .727 | .357 | .343 | .421 | | .939 | | | .943 | |
| % Varia | **48.95** | **17.09** | **15.37** | **11.66** | **57.30** | **18.79** | **13.79** | **51.05** | **21.25** | **12.04** |

nce
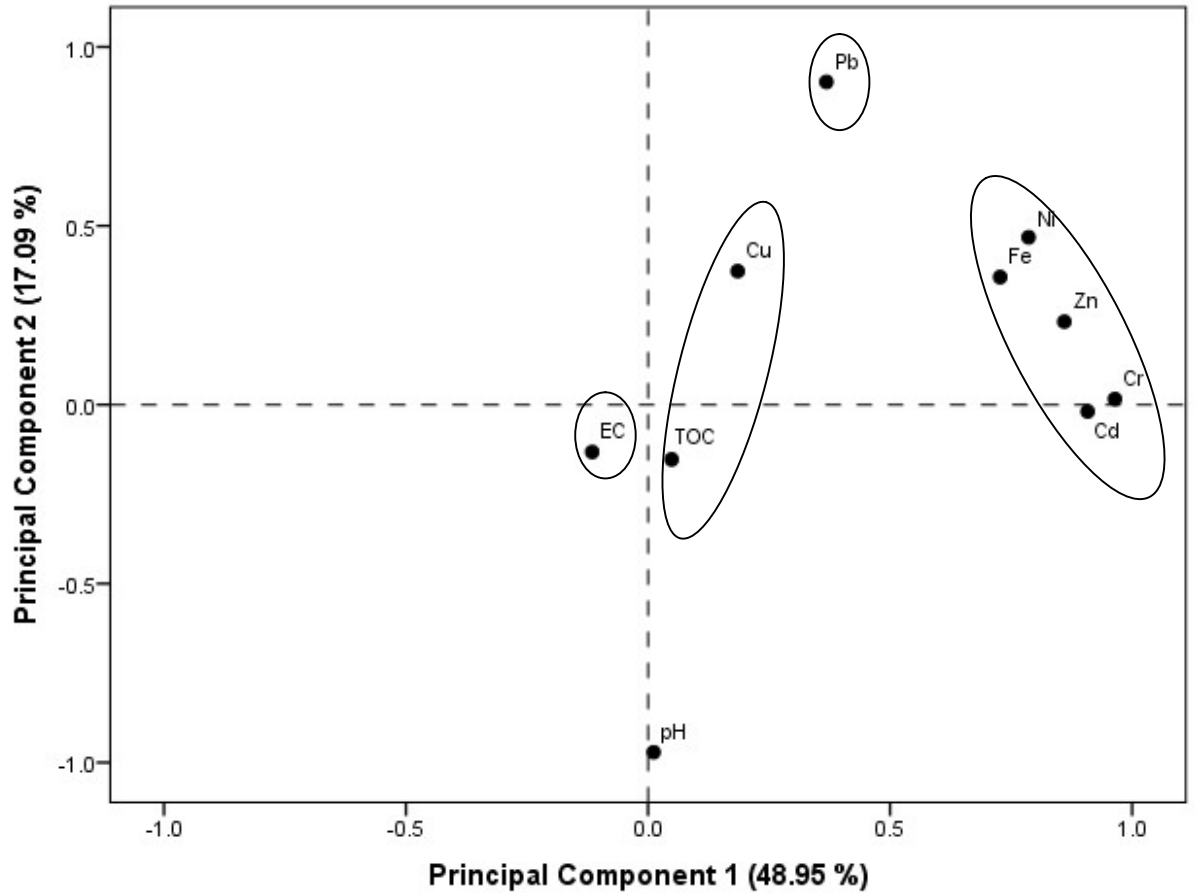
Figure 4.1: The loading plot of PCA of heavy metals and some physicochemical properties at depth 0-15 cm.
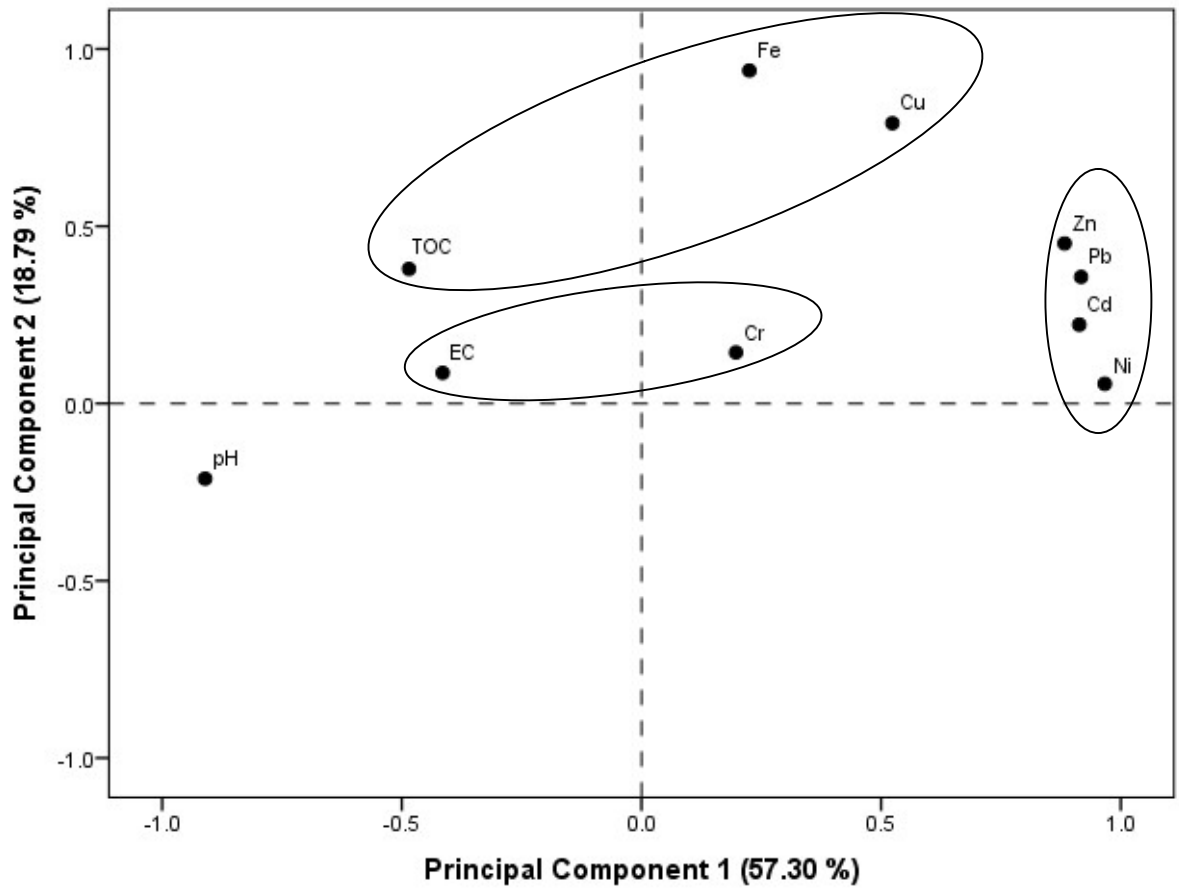
Figure 4.2: The loading plot of PCA of heavy metals and some physicochemical properties at depth 15-30 cm.
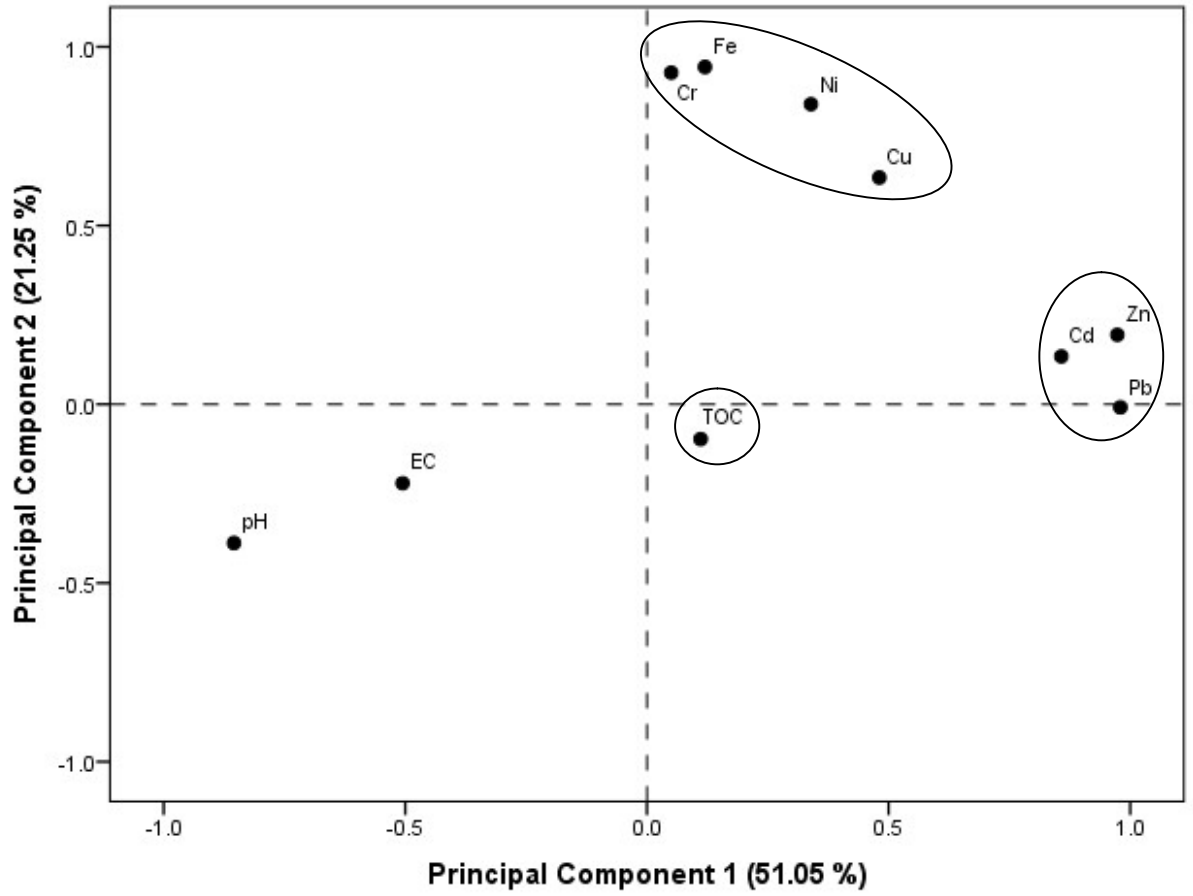
Figure 4.3: The loading plot of PCA of heavy metals and some physicochemical properties at depth 30-45 cm.
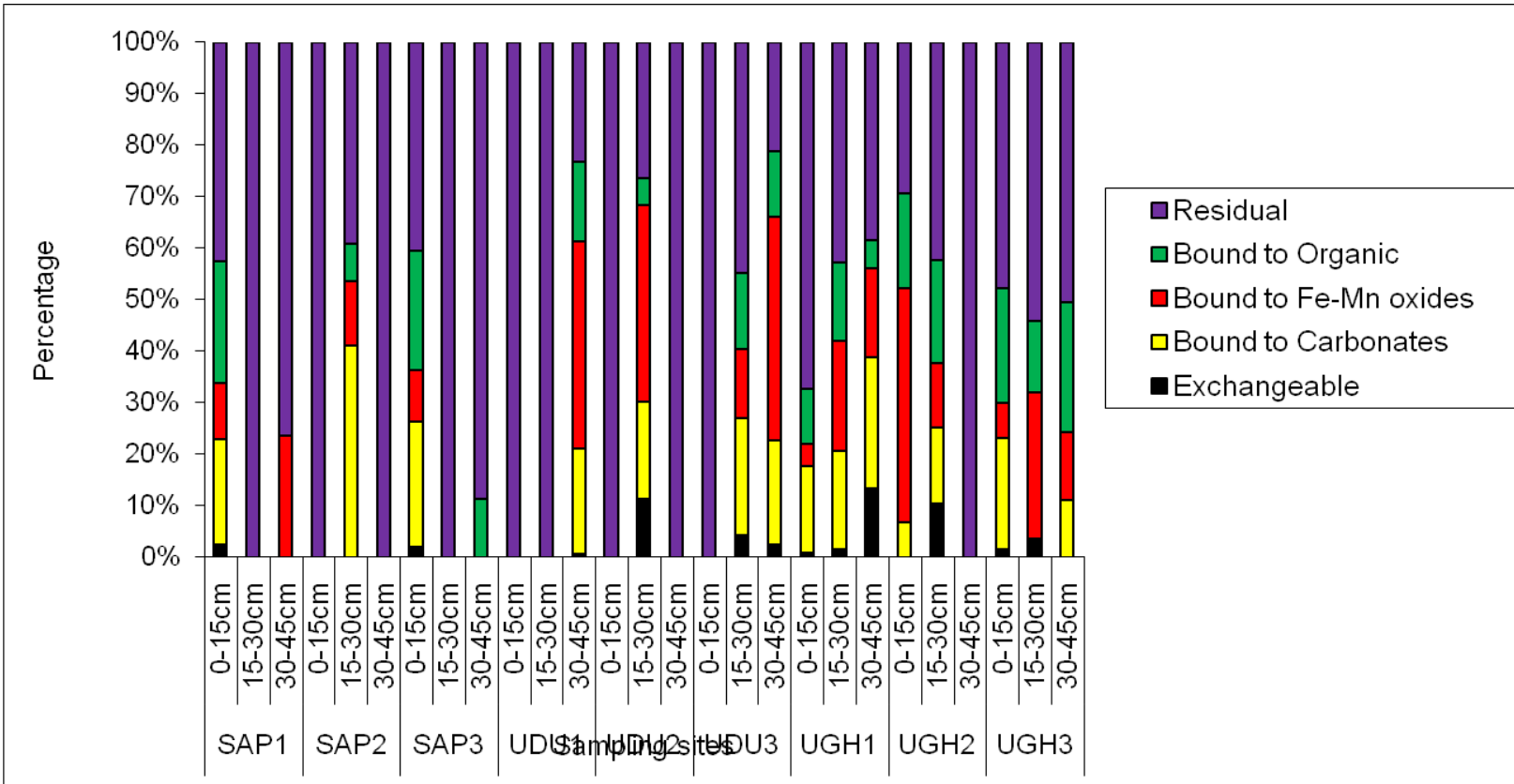
**Figure 4.4: Speciation pattern of Cadmium in the dumpsite soils**

**Lead**

Lead partition predominantly in the organic bound fraction (Figure 4.5). The percentage of Pb in the organic fraction ranged from 17.4 to 55.5%. The high distribution of Pb in this fraction is as a result of the strong complexes lead formed with humic minerals (Ajala *et al*., 2014). The next dominant fraction of Pb in these soil profiles is Fe–Mn oxide fraction. The percentage of Pb in the Fe–Mn oxide fraction range from 14.1 to 41.6%. Higher amount of Pb in the Fe–Mn oxide fraction was also reported by Iwegbue *et al*. (2007) and Iwegbue (2011). The exchangeable form of Pb was the next important fraction with a range of 11.2 to 28.4 % of Pb. Metals in this fraction are soluble and easily released into biota. The accumulation of Pb in this fraction call for concern as Pb is one of the metal that constitutes the widest possible health risk to humans through the plant uptake dietary route (Papafilippaki *et al*., 2008; Ajala *et al*., 2014). The percentage of lead in the residual and carbonate fraction ranged from 1.4 to 33.9 % and 0.3 to 30. 1% respectively.

**Chromium**

In these soil profiles, the dominant species of Cr is the residual fraction (Figure 4.6). The percentage of Cr in the residual fraction ranged from 16.6 to 83.6%. This is similar to the report of other researchers (Ebony *et al*., 2014; Osakwe, 2012; Iwegbue *et al*., 2007; Kotoky *et al*., 2003). The amount of Cr in the residual fraction indicates that Cr is not available for plant uptakes or biota in these soil (Iwegbue *et al*., 2007; Osakwe, 2012). The organic bound fraction followed the residual fraction with a range of 7.6 to 52.3%. Cr in the organic bound fraction might be due to its strong affinity for organic matter. However, according to Kotoky *et al*. (2003) the existence of Cr in the organic bound fraction results from the existing physiochemical conditions which include the pH and total organic carbons. The percentage of Cr in the Fe–Mn oxide ranged from 6.1 to

43.2%. The carbonates and exchangeable fractions constituted 0.2 to 26.2 % and 0.2 to 21.6 % respectively.
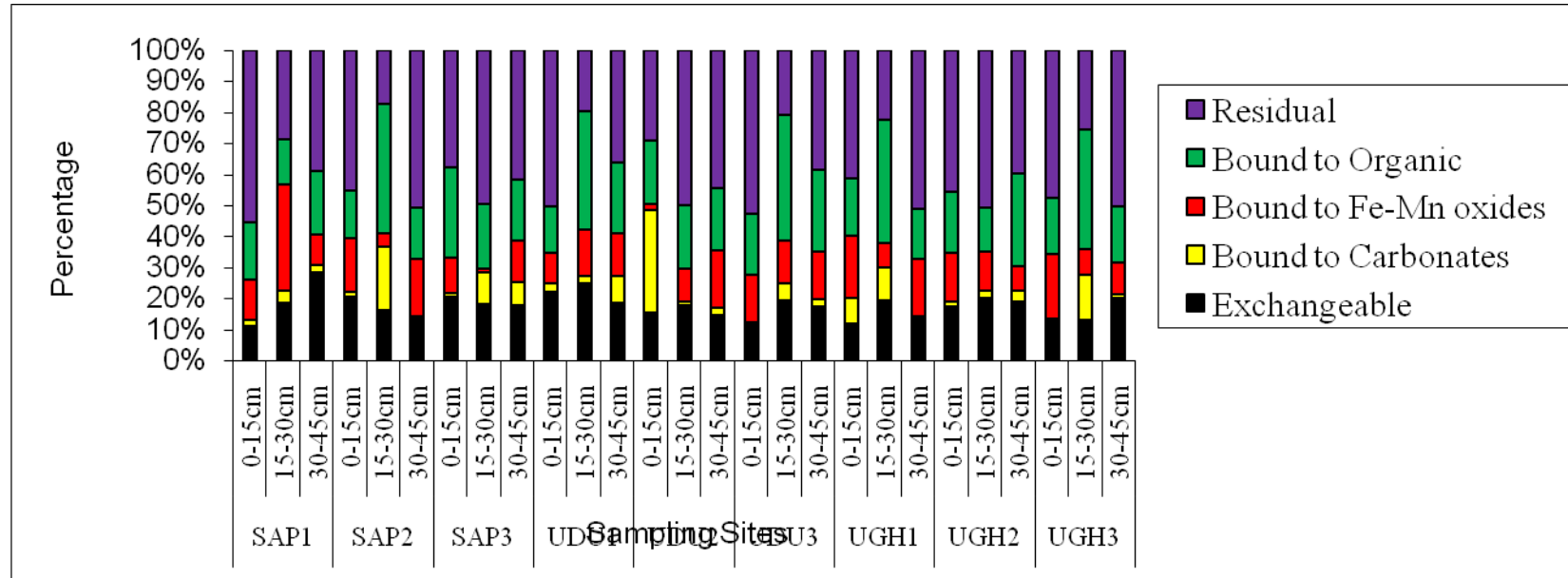
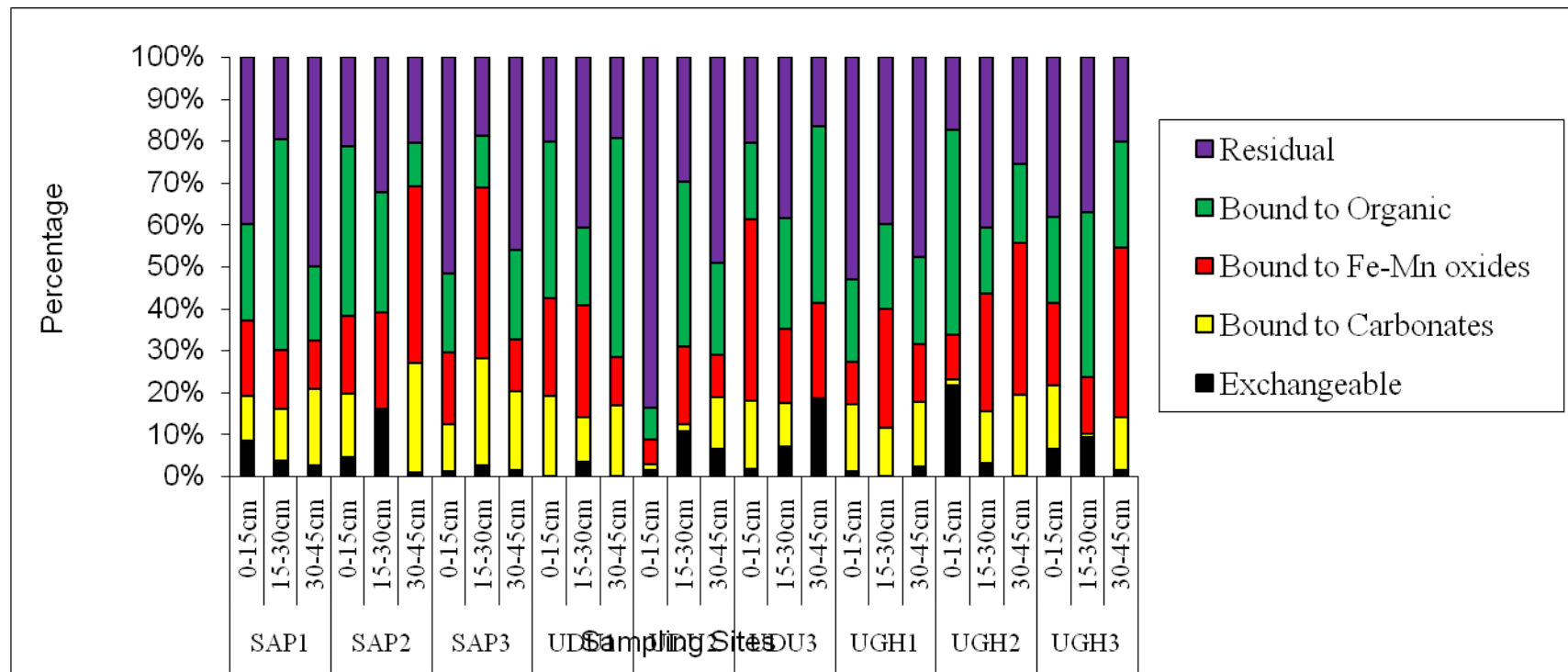**Figure 4.5: Speciation pattern of Lead in the dumpsite soils**

**Figure 4.6: Speciation pattern of Chromium in the dumpsite soils**

**Nickel**

The speciation of Ni follows the order residual > Fe–Mn oxides > organic > carbonate > exchangeable (Figure 4.7). The percentage of Ni in the different fractions ranged from 20.2 to 76.1 %, 11.2 to 50.8 %, 7.1 to 47.8 %, 0.8 to 25.9 % and 0.1 to 12.4 % for residual, Fe-Mn oxides, organic, carbonates and exchangeable fractions respectively. The dominance of the residual fraction is an indication that Ni is controlled by parent materials in these soil profiles (Moral *et al*., 2005; Iwegbue *et al*., 2007). This results is in agreement with the result of other researchers (Osakwe, 2012; Iwegbue *et al*., 2007; Moral *et al*., 2005).

**Copper**

Copper also existed mainly in the residual fraction in the soil profiles in this study (Figure 4.8). The percentage of Cu in the residual fraction ranged from 30.3 to 100%. This is in agreement with the results reported by Ebony *et al*. (2001) and Kin and Kin (2010). The next predominant species of Cu is the organic bound fraction. The percentage of Cu in the organic bound fraction ranged from 12.4 to 47.6 % in these soil profiles. High percentage of Cu in the organic bond fraction have also been reported by Iwegbue *et al*. (2007) and Iwegbue (2011). Cu in the organic fraction might be as a result of the high formation constant of the Cu-organic complex (Abollino *et al*., 2012).

Significant amount of Cu was found in the Fe-Mn oxide fraction (10.2 to 34.9%). The significant amount of Cu in the Fe–Mn oxide fraction suggest that Cu in these soil profiles is controlled by adsorption that Cu may be immobilized under reducing condition (Iwegbue *et al*., 2007; Boyle, 2001). The result of this study is similar to that of Ebony *et al*., (2004) and Iwegbue *et al*. (2007). The amount of Cu in the carbonate and exchangeable fractions ranged from 0.1 to 23.0% and 0.1 to 5.4% respectively. The low percentage of Cu in the exchangeable fraction might be as a result of complex formation with organic matter and low precipitation with hydrous Fe–Mn oxides.
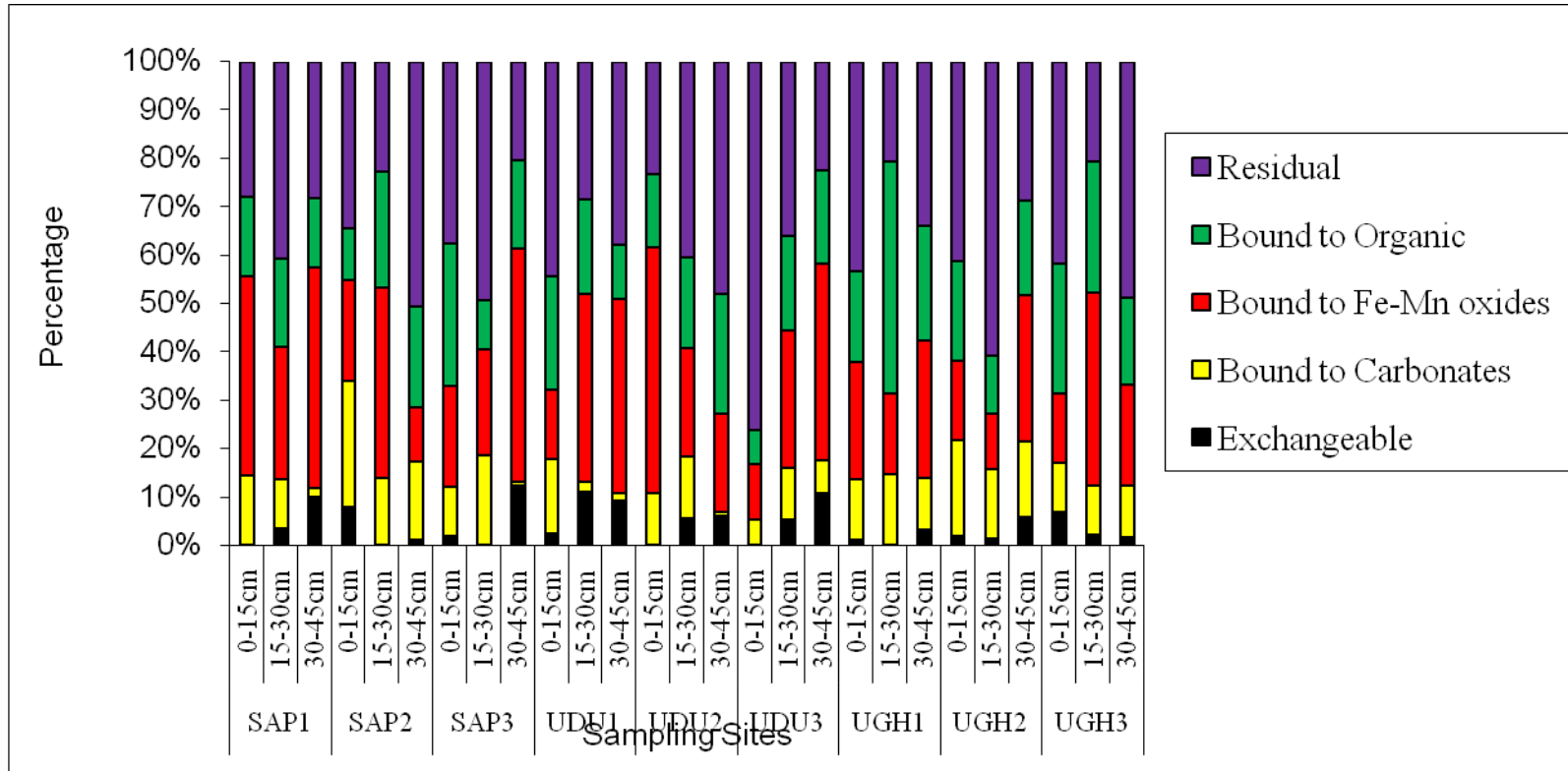
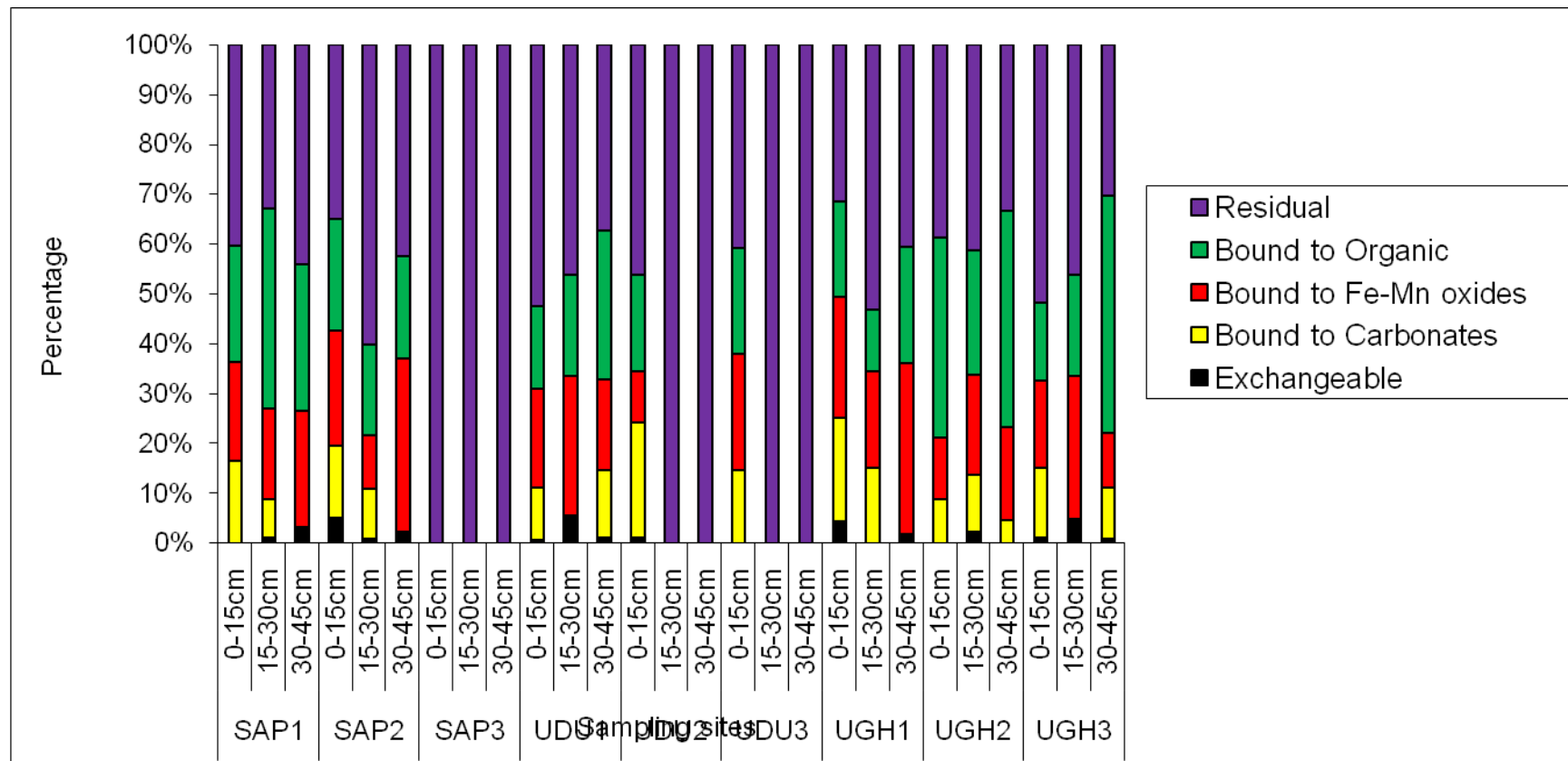**Figure 4.7: Speciation pattern of Nickel in the dumpsite soils**

**Figure 4.8: Speciation pattern of copper in the dumpsite soils**

**Zinc**

The speciation of Zn follows the order residual > Fe–Mn oxides > carbonate > exchangeable > organic (Figure 4.9). The percentage of Zn in the different fractions ranged from 10.2 to 30.5 %, 10.1 to 40.2 %, 10.3 to 40.5%, 10.1 to30.8 % and 16.6 to50.5 % for exchangeable, carbonates, Fe-Mn, organic and residual fractions respectively. The dominance of the residual fraction is an indication that Zn is controlled by parent materials in these soil profiles (Moral *et al*., 2005; Iwegbue *et al*., 2007). This results is in agreement with the result of other researchers (Osakwe, 2012; Moral *et al*., 2005).

**Iron**

The speciation of Fe follows the order Residual > Carbonate > Fe–Mn oxide > organic > exchangeable (Figure 4.10). The residual fraction is the dominant fraction of Fe in these soil profiles. It ranged from 20.7 to 52.5%. The presence of Fe in the residual fraction may be due to its association with silicate minerals (Osakwe, 2012). Fe have been reported in the residual fraction in a number of studies (Horsfall and Spiff, 2005; Abeh *et al*., 2007). The carbonate fraction ranged from 10.4 to 48.5%. The high percentage of Fe in this fraction indicate that Fe is not readily available due to the relative stability of this fraction. Fe in the carbonate fraction have also been reported by Abeh *et al*. (2007), Urunmatsoma *et al*. (2005) and Osakwe (2012).

Significant fraction of Fe was found in the Fe-Mn oxide fraction. The Fe-Mn oxide fraction in these soils profiles ranged from 10.7 to 41.6%. The percentage of Fe in the organic fraction ranged from 0.3 to 28.2%. Iwegbue (2007) also reported significant fraction of Fe in the organic phase. The percentage Fe in the exchangeable fraction ranged from 0.2 to 16.1%. The low percentage of Fe in the exchangeable fraction may be due to the easy utilization of Fe by plants and other organisms in the soil.
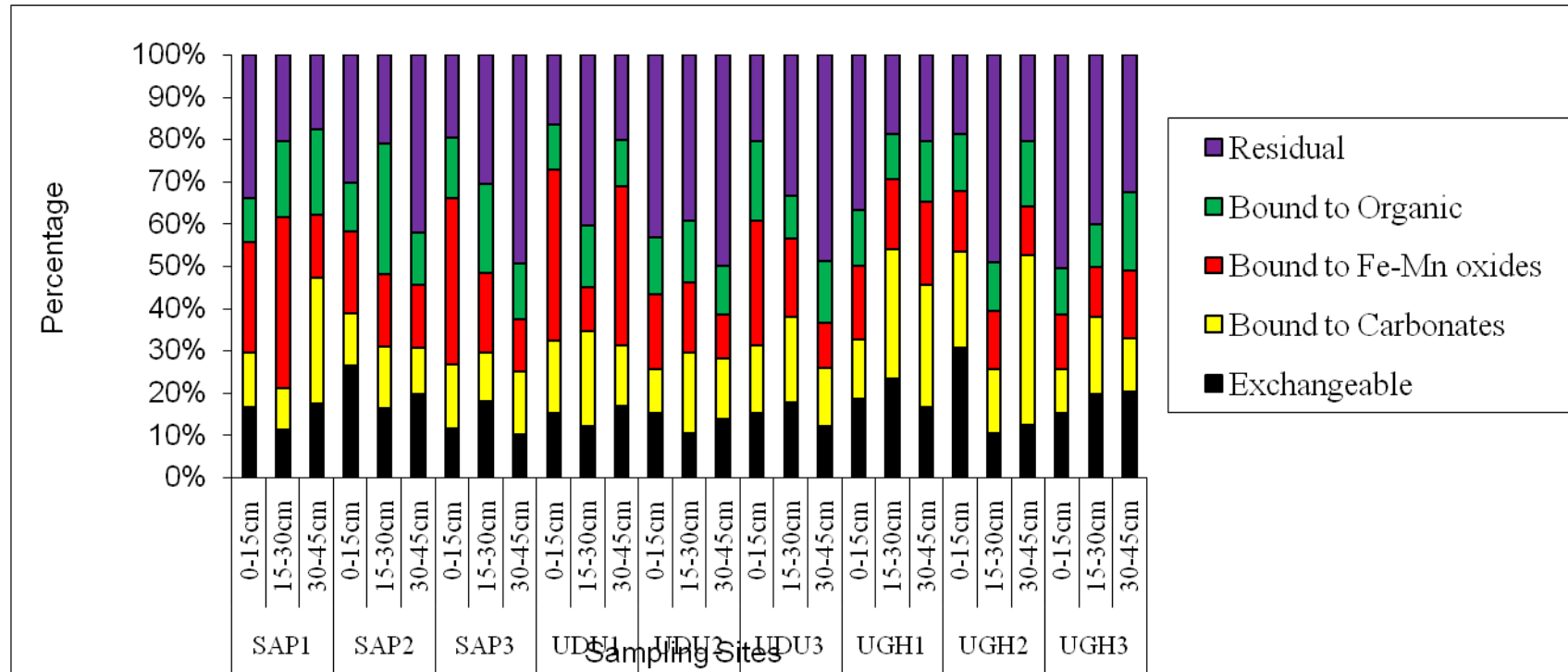
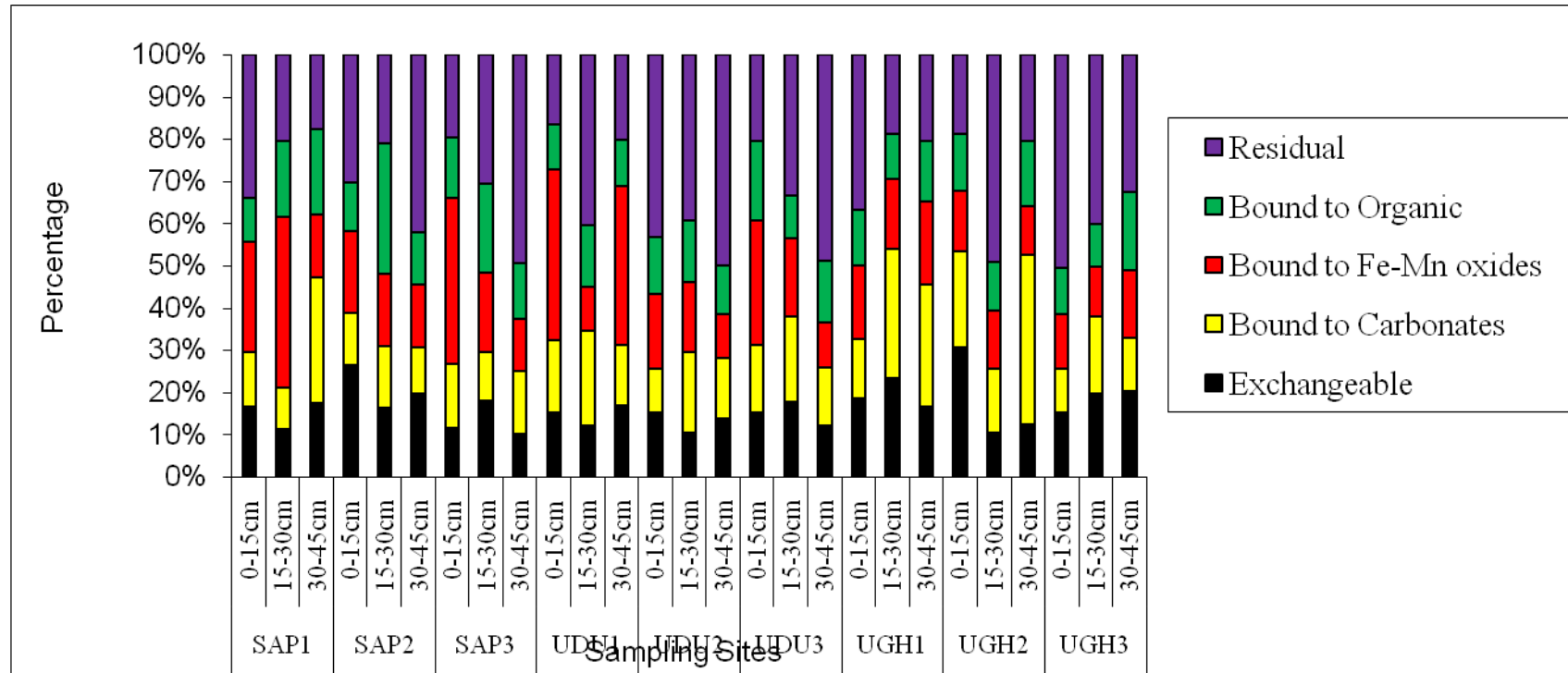**Figure 4.9: Speciation pattern of Zinc in the dumpsite soils**

**Figure 4.10: Speciation pattern of Iron in the dumpsite soils**

# CHAPTER FIVE
## SUMMARY, CONCLUSION AND RECOMMENDATION

**5.1    Summary of major findings**

1.    The concentrations of metals ranged from 0.05 to 4.5 mg kg$^{-1}$ for Cd, 9.0 to 149 mg kg$^{-1}$ for Pb, 4.20 to 15.4 mg kg$^{-1}$for Cr, 1.0 – 14.5 mgkg$^{-1}$ for Ni, 1.0 to 124 mgkg$^{-1}$ for Cu, 20 to 510 mg kg$^{-1}$ for Zn and 1650 to 11865 mgkg$^{-1}$ for Fe.

2.    The dumpsite soils were contaminated with Pb, Cr, Ni, Cu, Zn and Fe but were polluted with Cadmium.

3.    The average values of pH in two dumpsites (UGH1and UGH3)indicated that the soils were acidic.

4.    The average concentrations of Cd in sites SAP1, SAP3, UDU3, UGH1, UGH2 and UGH3 were above the Canadian soil quality guideline for Agricultural soil (1.4 mg kg$^{-1}$), Norway and Germany guideline value (1.0 mgkg$^{-1}$) as well as the Switzerland guideline value of 0.8 mg kg$^{-1}$.

5.    The average concentrations of Cr and Ni in all the sites studied were below the guideline values of all the various countries.

6.    The residual fraction was the predominant fraction of all the metals except Lead.

7.    The enrichment values showed that all the metals originate from natural or crustal origin

**5.4    Conclusion and Recommendation**

This study have demonstrated the potential accumulation of heavy metals in the soils of the studied dumpsites. Thus, sorting and recycling of wastes especially electronic and metallic wastes should be intensified to reduce the levels of these toxic metals in these dumpsites.

**5.5    Contributions to knowledge**

The contribution to knowledge of this study are that the study have;

1.  showed that the average values of pH in all the studied sites except UGH1and UGH3 were within the pH values (6.0 to 8.0) recommended by the Canadian Soil Quality Guidelines for all types of land uses.

2.  showed that the dumpsites were polluted with Cd as most sites has average concentrations of Cd higher than the guideline values of different countries.

3.  revealed that the potential ecological risk of the metals is in the order of Cd> Pb > Cu > Zn > Cr > Ni.

**REFERENCES**

Abeh, T., Gungshik, J and Adamu, M.M (2007), Speciation studies of trace element in sediment from Zaramagada Stream in Jos. *Journal of Chemical Society of Nigeria,* 32(2): 218-225.

Abollino, O.M., Malandrino, M., Menstasti, E. and Petrella, F. (2002). Heavy metals in Agricultural soils from Piedmount, Italy: distribution, speciation and chemometric data treatment. *Chemosphere*, 49**:** 545-557.

Adelekan, B.A. and Alawode, A.O. (2011). Contributions of municipal refuse dumps to heavy metals concentrations in soil profile and groundwater in Ibadan Nigeria. *Journal of Applied Biosciences*, 40: 2727 - 2737

Adie, G.U. and Osibanjo, O.O. (2009). Assessment of Soil Pollution by Slag from an automobile battery manufacturing Plantin Nigeria. *African Journal of Environmental Science and Technology,* 3(9): 239 – 250.

Akporido S. O. and Agbaire P. O. (2014). Soil and water quality assessment using integrated pollution index of roofing and ceiling sheet industry waste dumpsites and adjoining areas in Sapele, Nigeria. *Research Journal of Physical and Applied Sciences,* 3(1): 015 – 032.

Akpoveta, O.V., Osakwe, S.A., Okoh, B.E. Otuya, B.O. (2010). Physicochemical characteristics and levels of some heavy metals in soils around metal scrap dumps in some parts of Delta State, Nigeria. *Journal of Applied Sciences and Environmental Management,* 14(4): 57– 60

Amadi, A.N.  (2011). Assessing the effects of Aladimma dumpsite on soil and groundwater using water quality index and factor analysis. *Australian Journal of Basic and Applied Sciences,* 5(11): 763-770.

Lissy, M. P. N. and Madhu, G. (2010):  Removal of heavy metals form waste water using water hyacinth.  Proc. Of Int. Conf. on Advances in Civil Engineering.

Athalye, R. P., Mishra, V., Quadios, G., Ullal, V., and Gokhale, K. S. (2001):  heavy metals in the abiotic and biotic components of Thane Creek, India. *Pollut. Res.,* 18(3): 329 – 333.

Amos-Tautua, B.M.W., Onigbinde, A.O. and Ere, D. (2013). Assessment of some heavy metals and physicochemical properties in surface soils of municipal open waste dumpsite in Yenagoa, Nigeria. *African Journal of Environmental Science and Technology,* 8(1): 41-47

Amusan, A.A., Ige, D.V. and Olawale, R. (2005). Characteristics of Soil and Crop uptake of metals in municipal waste dumpsites in Nigeria.  *Journal of Human and Ecology,* 1(2): 167-171.

Arias, M.E., Gonzalez-Perez, J.A., Gonzalez-villa, F.J. and Ball, A.S. (2005). Soil Helath: A new challenge for microbiologists and chemists. *International Microbiology*, 8: 13-21.

Asaah. V.A., Abimbola, A.F. and Such, C.E. (2005). Heavy metal concentrations and distribution in surface soils of the Bassa industrial zone 1, Douala, Cameroon. *Arabian Journal for Science and Engineering,* 31(2A): 147-158.

ATSDR (2006). TOXFAQs for copper. Retrieved from http://www.atsdr.cdc.gov/tfacts/32.html

Baldwin, D.R. and Marshall, W.J. (1999). Heavy metal poisoning and its laboratory investigation. *Annals of Clinical Biochemistry,* 36(3): 267–300.

Bishop, P.L. (2000). Pollution Prevention: Fundamentals and Practice. McGraw-Hill, Companies Inc., U.S.A., pp. 67-89.

Brigden, K., Labunska, I., Santillo, D. and Johnston P. (2008). Chemical contamination at e-waste recycling and disposal sites in Accra and Korforidua, Ghana. Greenpeace Research Laboratories Technical Note 10/2008, Publ. Greenpeace International 24pp.

Buekers, J. (2007). Fixation of cadmium, copper, nickel and zinc in soil: kinetics, mechanisms and its effect on metal bioavailability. Ph.D thesis, Katholieke Universiteit Lueven, Dissertationes De Agricultura, Doctoraatsprooefs chrift nr.

Campbell, P.G.C. (2006). Cadmium: A priority pollutant. *Environmental Chemistry,* 3(6): 387–388.

Chedrese, P. J., Piasek, M., Henson, M. C. (2006). Cadmium as an endocrine disruptor in the reproductive system. *Medicinal chemistry*, 6(9): 27 – 35.

Chengo, K., Murungi, J. and Mbuvi, H. (2013). Speciation of chromium and nickel in open-air automobile mechanic workshop soils in Ngara, Nairobi, Kenya. *World Environment*, 3(5): 143-154

Chrostowski, P., Durda, J.L. and Edelmann, K.G. (1991). The use of natural processes for the control of chromium migration. *Remediation,* 2(3): 341–351.

Davies, D.E. and Jones, L.H.P. (2008). Micronutrients and toxic elements. In Wild, A. (Ed) (11th edition). Russell's Soil Conditions and Plant Growth. John Wiley & Sons; Interscience, NewYork, NY, USA, pp. 781–814

DPR (Department of petroleum resources) (2002). *Environmental guidelines and standards for the petroleum industry in Nigeria (revised edition).* Department of Petroleum Resources, Ministry of Petroleum and Natural Resources, Abuja, Nigeria.

Eriksson, J., Andersson, A. and Andersson, R. (2007). The state of Swedish farmlands. Tech. Rep. 4778, Swedish Environmental Protection Agency, Stockholm, Sweden.

European Commission (2002). Heavy metals in waste. Project Env. E. 3/ETU.2000/0058. Final Report.

Greany, K.M. (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.

GWRTAC (1997). Remediation of metals-contaminated soils and groundwater. Tech. Rep. TE-97-01, GWRTAC, Pittsburgh, Pa, USA, GWRTACE Series.

Horsfall, M. (Jnr.) and Spiff, A. (2005). Speciation and bioavailability of heavy metals in sediment of Diobu River, Port-Harcourt, Nigeria. *EuropeanJournal of Scientific Research,* 6(3): 20-36

Horsfall, M. Jnr., and Spiff I. A. (2005). Effects of temperature on the sorption of $Pb^{2+}$ and $Cd^{2+}$ from aqueous solution by *Caladium bicolor* (Wild cocoyam) biomass. *Electronic Journal of Biotechnology* [online] 8(2). Available from internet: http//www.ejbiotechnology.info/content/10/8/issue2/full/4/index.html.

Igwe, J.C. Nnorom, I.C. and Gbaruko, B.C. (2005). Kinetics of radionuclides and heavy metals behaviour in soils: Implications for Plant growth. *African Journal of Biotechnology*, 4(13): 1541-1547.

Iwegbue, C.M.A. (2007) Metal Fractionation in Soil Profiles at Automobile Mechanic Waste Dumps. *Waste Management Research,* 25: 1-9

Iwegbue, C.M.A. (2011). Assessment of Heavy Metal Speciation in Soils Impacted with Crude Oil in Niger delta, Nigeria. *Chemical Speciation and Bioavailability,* 23(1): 7-15

Kabala, C. and Singh, B.R. (2001). Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter. *Journal of Environmental Quality,* 30: 485 – 495

Kabata-Pendias, A. and Pendias, H. (2001). Trace metals in soils and plants, CRC Press, Boca Raton, Fla, USA, 2nd edition.

Kadirvelu, K., Namasivayam, C. and Thamaraiselve, K. (2001). Removal of heavy metal from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresource Technology,* 76: 63 – 65.

Katana, C., Murungi, J. and Mbuvi, H. (2013). Speciation of chromium and nickel in open-air automobile mechanic workshop soils in Ngara, Nairobi, Kenya. *World Environment,* 3(5): 143-154

Keith, C., Borazjani, H., Diehl, S. V., Su, Y. and Baldwin, B. S. (2004). Removal of Cu, Cr and As by water hyacinth. Retrieved on 21st march, 2011 from http//www.fwrc.msstate.edu/pubs/keith.pdf

Kotoky, P., Bora, B.J., Baruah, N.K., Baruah, P. and Borah, G.C.(2003). Chemical fractionation of heavy metals in soils around oil installation, Assam. *Chemical Speciation and Bioavailability,* 15(4): 115-125

Lacutusu, R. (1998). Appraising levels of soil contamination and pollution with heavy metalsIn Heinike H. J.,.Eckselman W., Thomasson A.J., Jones R.J.A, Montanarella L. and Buckeley B.(eds.). *Land information systems for planning the sustainable use of land resources.*European Soil Bureau Research Report No. 4. Office of Official Publication of the European Communities, Luxembourg, pp 393-402.

Lenntech (2008). Toxicological effects of copper. Retrieved from http://www.lenntech.con/ periodic-chart-elements/Cu-en.htm

Manahan, S.E. (2003). Toxicological Chemistry and Biochemistry (3rd edition). CRC Press, Limited Liabiliy Company (LLC).

Martınez, C.E. and Motto, L.H. (2000). Solubility of lead, zinc and copper added to mineral soils. Environmental Pollution, 107(1): 153–158.

McLaughlin, M.J., Hamon, R.E., McLaren, R.G., Speir, T.W. and Rogers, S.L. (2000). Review: a bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. *Australian Journal of Soil Research,* 38(6): 1037–1086.

Moral, R., Gilkes R.J. and Jordan M.M. (2005). Chemical fractionation of Cd, Cu, Ni and Zn in contaminated soils. *Journal of Environmental Quality,* 26: 259-264 (2005)

Muller, G. (1969). Index of geoaccumulation in sediment of the Rhine River. *Geological Journal,*2:108-118.

Nduka, J.K., Anyakora, C., Obi, E., Obumselu, F.O., Ezenwa, T.E. and Ngozi-Olehi, L.C. (2010). Polyaromatic hydrocarbons (PAHs) and inorganic chemical contaminants at refuse dumpsites in Awka, South Eastern Nigeria: A public health implication

NSC (National Safety Council) (2009). Lead poisoning. Retrieved on August 1, 2014 from http://www.ns c.org/news resources/Resources/Documents/LeadPoisoning.pdf.

Nwajei, G.E., Iwegbue, C.M.A. and Okafor, M.I. (2007). Heavy metals in surface soils under waste dumps from Onitsha, Nigeria. *Journal of Biological Sciences,* 7(2): 405-408.

Obasi, N.A. Akubugwo, E.I. Ugbogu, O.C. and Otuchistian, G. (2010). Assessment of Physiochemical properties and heavy metals bioavailability in dumpsites along Enugu-Port-Harcourt Express way, Sout-East, Nigeria. Retrieved from http://www.google.com on 25th May, 2012.

Odefemi, O.S., Olaofe, O. and Asaolu S.S. (2007). Seasonal variation in heavy metal distribution in sediment of major dams in Ekiti State. *Pakistan Journal of Nutrition,* 6(6): 705-707.

Odu, CTI., Esurosu, O F., Nwaboshi, I C., Ogunwale, J A. (1985) Environmental study(Soil and Vegetation) of NigeriaAgip Oil Company Operation Area. A report submitted to Nigeria Agip Oil Company Limited, Lagos, Nigeria. Pp 102-107

Odukoya, A.M., Abimbola, A.F. and Lawal, O. (2011). Potential Soil Contiamination with toxic metals in the vicinity of active and abandoned dumpsites. *Agriculture and Biology Journal of North America,* 2(5): 785 – 790.

Ogbeibu, A.E., Chukwurah, N.A. and Oboh, I.P.(2013). Effects of Open Waste Dump-site on its Surrounding Surface Water Quality in Ekurede-urhobo, Warri, Delta State, Nigeria. *Natural Environment,* 1: 1-16.

Ogbemudia, F. O. and Mbong, E. O. (2013). Soil reaction (pH) and heavy metal index of dumpsites within Uyo municipality. *Merit Research Journal of Environmental Science and Toxicology,* 1(4): 082-085.

Ogbonna, D.N. Kii, B.L. and Youdeowei, P.O. (2009). Some physicochemical and heavy metal levels in soils of waste dumpsites in Port-Harcourt Municipality and crunons. *Journal of Applied Sciences and Environmental Management,* 13(4): 65-70.

Ogundele, D.T., Bodunde, V.T. and Bale, A.T. (2013). Assessment of heavy metal pollution of waste dump sites in Kwara State using *Carica Papaya, Musa Spp* and *Cocorhrous Olitorous* as indicators. *IOSR Journal of Environmental Science, Toxicology and Food Technology,* 6(2): 01-04.

Okalebo, J.R., Gathma, K.W. and Woomer, P.L. (1993). Laboratory methods of soil and plant analysis: A Working Manual Tropical Soil Biology and Fertility Program. TSBF Institute, Nairobi, Kenya.

Onianwa, P.C. and Essien, C.A. (1999). Petroleum hydrocarbon levels in sediments of streams and river within Ibadan City, Nigeria. *Bulletin of Chemical Society of Ethiopia,* 13: 83-85.

Ontario (OR) (2006). Copper in the environment. Retrieved from http://www.ene.Gov.on.ca/ cons/4141e.htm.

Osakwe S.A. (2012). Chemical partitioning of Iron, Cadmium, Nickel and Chromium in contaminated soils of South-Eastern Nigeria. *Research Journal of Chemical Sciences,* 2(5): 1-9

Osakwe, S.A. (2010). Distribution of heavy metals in soils around automobile dumpsites in Agbor and environs, Delta State. *Journal of Chemical Society of Ethiopia,* 35(1): 53-60

Osakwe, S.A. (2014). Heavy metal contamination and physicochemical characteristics of soils from automobile workshops in Abraka, Delta State, Nigeria. *International Journal of Natural Sciences Research,* 2(4): 48-58

Oviasogie, P.O. and Ndiokwere, C.L. (2011). Fractionation of lead and cadmium in refuse dump soil treated with cassava milling effluent. *The Journal of Agriculture and Environment*, 9: 234-245

Oviasogie, P.O., Omoruyi, O., Okoro, D. and Ndiokwere, C.L. (2009). Evaluation of physicochemical properties and distribution of Pb, Cd, Cr and Ni in soils and growing plants around refuse dumpsites in Akure, Nigeria. *African Journal of Biotechnology*, 8 (12): 2757-2762

Radojevic, M. and Bashkin, V. N. (1999). Practical environmental analysis. Royal Society of Chemistry, Cambridge UK.

Rashed, M. N. (2003). Fruits stones as adsorbents for the removal of lead ion from polluted water. Retrieved on February 20th, 2011 from http://www.eeaa.gov.eg/english/ main/env2003/day2/water/rashed.uniaswan.

Raskin, I. and Ensley, B.D. (2000). Phytoremediation of Toxic Metals: Using Plants to Clean Up the Environment, John Wiley & Sons, New York, NY, USA.

Rosen, C.J. (2002). Lead in the home garden and urban soil environment, communication and Educational Technology Services, University of Minnesota Extension.
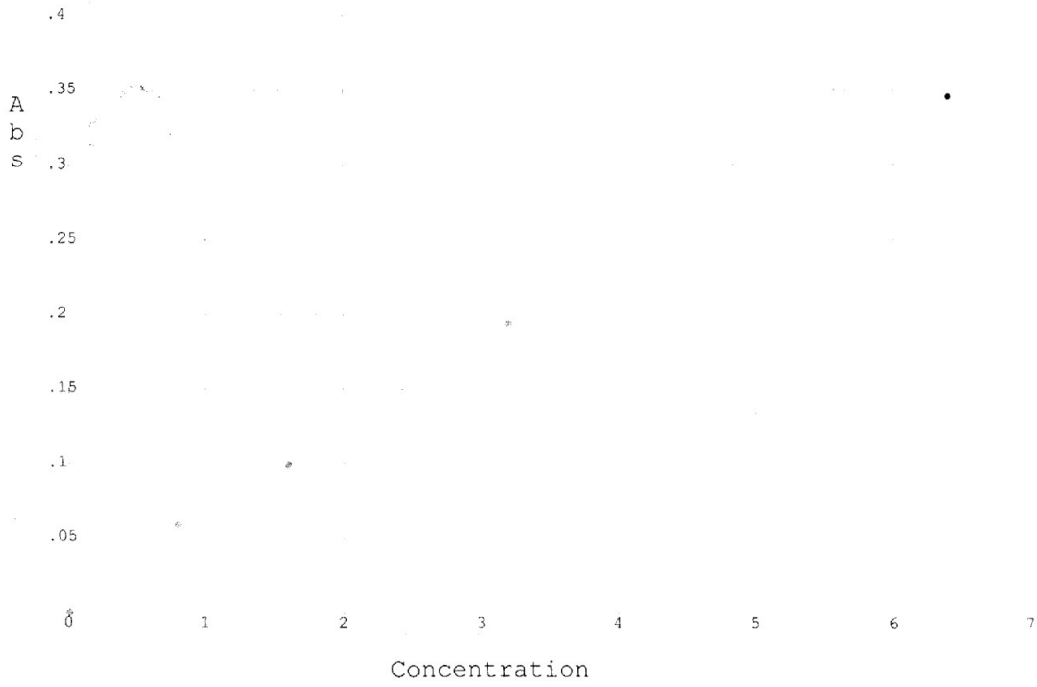
Scragg, A. (2006). Environmental Biotechnology. Oxford University Press, Oxford, UK, 2nd edition.

Shiowatana, J., McLaren, R.G., Chanmekha, N and Samphao, A. (2001). Fractionation of arsenic in soil by a continuous-flow sequential extraction method. *Journal of Environmental Quality,* 30(6): 1940–1949.

Smith, L.A., Means, J.L. and Chen, A. (2005). Remedial options for metals - Contaminated Sites. Lewis Publishers, Boca Raton, Fla, USA.

Tessier, A., Campbell, P.G.C. and Bison, M. (1979). Sequential extraction procedure for the separation, particulate trace metals. *Analytical Chemistry,* 51: 844-851.

Uba, S., Uzairu, A., Harrison, G.F.S., Balarabe, M.L. and Okunola, O.J. (2008). Assessment of heavy metals bioavailability in dumpsites of Zaira metropolis, Nigeria. *African Journal of Biotechnology,* 7: 122-130.

Ubuoh, E.A., Akande, S.O.C. and Akhionbare, S.M.O. (2012). Assessment of wood waste dumpsite on dynamics of soil physiochemical characteristics in Njoku Timber Market, Imo State, Nigeria. *International Journal of Multidisciplinary Science and Engineering,* 3(2): 1-4.

Upadhyay, A. R., and Tripathi, B. D. (2007). Principle and process of biofiltration of Cd, Cr, Co, Ni, and Pb from tropical opencast coalmine effluent. *Water, Air and Soil Pollution* (Springer), 180(1-4): 213 – 223.

Urunmatsoma , S.O. and Ikhouria E.U. (2005). Effect of leachates (heavy metal content) from solid waste at "Effurun roundabout dumpsite" Warri, Nigeria, *Chemical Technology Journal,* 1: 195-202

USDHHS (United States Department of Health and Human Services) (1999). Toxicological profile for lead. Atlanta, USA.

USEPA (U.S. Environmental Protection Agency) (2001). Report on recent developments for in situ treatment of metals contaminated soils. Office of Solid Waste and Emergency Response.

VCI (Van Commodities Inc.) (2011). Copper history/Future. Retrieved on July 25, 2014 from http://tr ademetalfutures.com/copperhistory.html

Vukojevic, V., Sabovljevic, M., Sabovljevic, A., Mihajlovic, N., Dragzic, G. and Vucinic, Z. (2006). Determination of heavy metal deposition in the county of Obrenovac (Serbia) using mosses as bio-indicators II:  Cadmium (Cd), Cobalt (Co), and Chromium (Cr). *Archives of Biological Science,* 58(2):  95 – 104.

Weggler, K., McLaughlin, M.J. and Graham, R.D. (2004). Effect of chloride in soil solution on the plant availability of biosolid-borne cadmium. *Journal of Environmental Quality,* 33(2): 496–504.

Wuana, R.A. and Okieimen, F.E. (2011). Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. *International Scholarly Research Network Ecology,* 10: 1-20.

Zuayah S., Julian B., Noorhafiza H.R., Fauziah C.L. and Rosenanic A.B., Concentration and Speciation of Heavy Metal in Some Cultivated and Uncultivated Utisols and Inceptisols in Peninsular Malaysia, In Proc. Super Soil 2004 3rd Australian New Zwaland Soil Conference, 5-9 December 2004, University of Sydney, Australia, (2004)
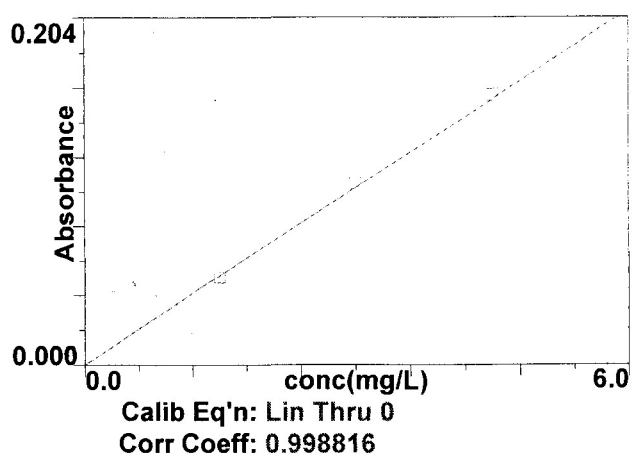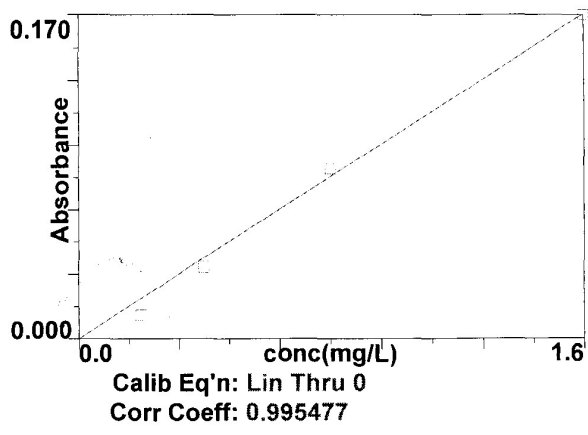
**APPENDIXES**

# Calibration Report

| Statistics | | | | | Standards | |
|---|---|---|---|---|---|---|
| Data Source: | MCRL, U.I0742.brf | | 151 | Std1-Blank | 0.00000 | 0.000000 |
| File Date: | 2:01:51 | Power-up # 118 | 152 | Std2-Max | 6.40000 | 0.345667 |
| Method: | Air/Acet Abs | | 153 | Std3 | 3.20000 | 0.193695 |
| Anl: | Cr-D2-357.9-1ib3 | | 154 | Std4 | 1.60000 | 0.099104 |
| Max Conc: | 6.4 ppm | | 155 | Std5 | 0.80000 | 0.058808 |
| Conc Coeff: | 16.1291 | | | | | |
| R Squared | 0.94699 | | | | | |

```
     .4

     .35
A
b
s    .3

     .25

     .2

     .15

     .1

     .05

      0      1        2        3        4        5        6        7
```

Concentration

X

Cu 324.75



Calib Eq'n: Lin Thru 0
Corr Coeff: 0.998816

Zn 213.86



Calib Eq'n: Lin Thru 0
Corr Coeff: 0.995477

Fe 248.33



Calib Eq'n: Lin Thru 0
Corr Coeff: 0.998850

Pb 283.31



Calib Eq'n: Lin Thru 0
Corr Coeff: 0.996879

**Cd 228.80**



Calib Eq'n: Lin Thru 0
Corr Coeff: 0.997188

**Calib Eq'n: Lin Thru 0**
**Corr Coeff: 0.989265**