AN ASSESSMENT OF HEAVY METAL CONTAMINATION IN SOILS AND VEGETATION – A CASE STUDY OF KORLE LAGOON RECLAMATION SITE

BY

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DECLARATION

I hereby declare that except for references of other people's work which have been cited and duly acknowledge, this work is the result of my own research and initiative conducted under supervision, and that this thesis has neither in whole nor in part been presented for an award of a degree elsewhere.

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ABSTRACT

This study investigated the concentration of heavy metals and vegetation around the Korle Lagoon Reclamation site in Accra (Ghana). The dispersion of heavy metals such as Pb, Hg, Cd, As, Zn, Sn, Ni, Cu and Cr within the soil profile from a depth of 0 – 60cm (at 20cm intervals) were assessed. A total of ninety (90) soil samples were taken from the e-waste zone (EW), central gardens zone (GZ), recreational zone (KD), reclaimed zone (RZ) and estuary zone (ES) and eighteen (18) soil samples were sampled from the control zone (CZ) at the Korle-Bu flats. Ten (10) samples of forage grasses (*Panicum maxima and Imperata cylindrical*) were also taken from each of the sampling zones and ten (10) samples each of lettuce (*Latuca sativa*) and bissap (*Hibiscus sabdariffa*) were taken from central garden zone (GZ) and the control zone (CZ). At the depth of 0 – 20cm, the ranges of heavy metal concentrations recorded were Hg (<0.001 – 0.67), Pb (1.28 – 183.66), Cu (3.47 – 202.99), Zn (0.83 – 37.33), Cr (2.28 – 56.00), Cd (<0.001 – 103.66), Ni (0.91 – 72.00), Sn (8.77 – 705.32) and As (0.04 – 3.67) in mg/kg. At the depth of 20 – 40cm, Hg (<0.001 – 0.67), Pb (1.12 – 167.96), Cu (2.57 – 199.99), Zn (0.73 – 34.33), Cr (0.11 – 49.99), Cd (0.04 – 68.32), Ni (0.55 – 66.65), Sn (8.67 – 334.25) and As (0.21 – 15.66) in mg/kg. At the depth of 40 – 60cm, Hg (0.00 – 0.00), Pb (0.96 – 134.00), Cu (1.49 – 98.66), Zn (0.52 – 27.66), Cr (1.13 – 52.67), Cd (0.04 – 68.32), Ni (0.55 – 66.65), Sn (8.67 – 334.25) and As (0.21 – 10.99) in mg/kg. The levels of Pb, Cd and As analyzed from some of the zones exceeded international thresholds for agriculture lands. The ranges of heavy metal concentrations in the vegetation were: Hg (<0.001 – 0.08), Pb (<0.001 – 36.72), Cd (0.16 – 1.64), Cr (0.24 – 3.84), Cu (0.16 – 95.56), Zn (1.16 -34.92), Ni (0.40 – 7.00), As (<0.001 – 0.32) and Sn (2.52 – 28.52) in mg/kg with Cu, Pb and Cd exceeding the acceptable limits of heavy metals in plants.

The enrichment factor of the heavy metals had a general trend of Cr = Ni < Zn < Cu < Hg < As < Pb < Cd < Sn. The geoaccumaltion index also had a general trend of Cr < Ni < Zn < Cu < As < Cd < Pb < Hg < Sn. The pollution index also recorded a general trend Cr < Zn <Ni < As < Cu < Hg < Pb < Sn < Cd. The presence of heavy metals in the vegetation from the other sampling zones may probably be due to frequent dumping of solid waste. The plants sampled are shallow rooted plants that absorb nutrient from the top soil. This might have contributed to the presence of heavy metals in their leaves since most of the heavy metals were within a depth of 0 – 20cm.

The significantly high concentration of heavy metals such Cd, Pb and As in the soils and vegetation may have adverse effect on human health and grazing cattle from the Abossey Okai Zongo Community.

DEDICATION

With love to my mum **MARY QUAYE-BRUCE** and my late aunt **NAOMI TSOTSOO BRUCE**

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LIST OF ABBREVIATIONS

ATSDR	Agency for Toxic Substances and Disease Registry
CCME	Canadian Council of Ministers of the Environment
CEC	Cation Exchange Capacity
ECB	European Chemicals Bureau
FAO	Food and Agricultural organization
FIAM	Free Ion Activity Model
GPS	Global Positioning System
IPCS	International Programme on Chemical Safety
JECFA	Joint FAO/WHO Expert Committee on Food Addictives
LEAD	Lead Education and Abatement Design
NIEHS	National Institute of Environmental Health Sciences
NRC	National Research Council
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
WHO	World Health Organization

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CHAPTER ONE

INTRODUCTION

Heavy metals are found naturally in undisturbed soils and, in fact, small amounts of many metals are required by plants to remain healthy. Metals found in waste dumps exist in various forms either as the pure metal or alloyed with various other metals. Heavy metals impairing the quality of our environment come from various sources that can be categorized into urban-industrial aerosols, liquid and solid wastes from animal and man, mining and industry and agricultural chemicals (Gerard, 1996; Ideriah *et al.*, 2010). Heavy metals are largely present in e-wastes, especially Cu used for wires, and also Cr, Ni, Zn, Cd, and Hg as well as many other metals and rare-earth elements. Because of high air emissions or liquid leaking, significant amounts of metals are concentrated in landfills or dispersed in the environment despite recycling (Robinson, 2009).

The labile fraction of particle-bound metals is considered to be more readily available to environmental receptors and hence possesses greater environmental risk than the resistant fraction. (Adamson *et al.*,2000; X.D. Feng *et al.*,2009). Soil has the ability to immobilize chemicals like heavy metals in any form introduce to it. The immobilization of xenobiotics are mainly due to sorption properties which are determined by physicochemical properties of the soil such as: amount of clay and organic fraction, pH, water content, temperature of the soil and properties of the particular metal ion (Dube *et al.*,2000). The most important heavy metals with regard to potential hazards and occurrence in contaminated soils are: arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), antimony (Sb), molybdenum (Mo) and zinc (Zn) (Asio, 2007).

Asio, (2007) further stated that the sources of heavy metal pollutants are metal mining, metal smelting, metallurgical industries, and other metal-using industries, waste disposal, corrosion of metals in use, agriculture and forestry, fossil fuel combustion, and sports and leisure activities. Heavy metals may be found in water, soil, sediments and plants in divers amounts this may be as a result of natural or anthropogenic. Chemicals found in the environment may contain some amounts of heavy metals and this may be absorbed by the components of the soil profile. The mechanism by which the heavy metals are transported through the soil profile has long presented great interest to both environmental and soil scientists because of the possibility of groundwater contamination through metal leaching. The protection of soils is and should be a principal objective of environmental policy makers to prevent pollution of soils.

1.1 Background

Landfill reclamation is the process of transforming a full landfill from waste land to woodland by successfully turning garbage into resilient landscape. Landfill sites are large areas of land found near cities that in some cases have had a previous life as mine or quarry and now acts as a large garbage receptacle. In the past decades there has been an interest in reclaiming these areas for recreational purposes. The land cover around the Korle Lagoon in Accra Metropolitan Assembly has different uses. The area can be classified into four zones namely the wetland, reclaimed land, waste dump site and wildlife habitat.

This research seeks to assess the levels of heavy metals in soils of the reclaimed landfill site, e-waste dump site and central gardens site around the study area. Landfills are sources of groundwater and soil pollution due to the production of leachate and its migration through refuse.

Soon and Bates (1982) reported that high concentrations of heavy metals contamination can frequently be established in the vicinity of mining sites, public roads, smelting sites and solid waste dump sites. They can be present in soils forming chemical and physical associations of different availability:

i. Simple or complex ions in soils solution
ii. Exchangeable ions
iii. Linked to organic substances
iv. Occluded or co-precipitated with oxides, carbonates, and phosphates or other secondary minerals.
v. Ions in the crystalline lattices of primary minerals

1.2 Research Problem

An emerging environmental and human health problem in the world in the 21st century is as a result of the indiscriminate disposal of electrical and electronic waste (e-waste) (Schmidt, 2002, 2006; Asante *et al.*, 2012). Electronic waste (e-waste) can be said to be the end-of-life for electronic goods including televisions, monitors, computers, audio and stereo equipment, video cameras, fax/photocopy machines and other peripheral items (Frazzoli *et al*., 2010; Asante *et al*., 2012). According to the United Nations Environment Programme (UNEP) (2005) as reported by Asante *et al*. (2012), 20–50 million tons of e-waste is generated annually in the world. Of these quantities, significant amounts of e - waste have been exported to developing countries such as China, India, Pakistan, Vietnam, and the Philippines for disposal. The environmental problem with heavy metals is that they are unaffected during degradation of organic waste and have toxic effects on living organisms when exceeding a certain concentration. Exposure of heavy metals may cause blood and bone disorders, kidney damage and decreased mental capacity and neurological damage (NIEHS, 2002; Esakku, 2003).

In recent times, developing nations in West Africa (e.g., Ghana and Nigeria) have become major destinations for e-waste worldwide (Asante *et al.*, 2012). On the north-eastern part of the Korle lagoon lies the Agbogbloshie slum, one of Ghana's largest electronics-waste processing sites. Electronic gadgets of no value are disposed off in a large area on the edge of the e-waste market that is also used for the disposal of a wide range of other types of wastes (Brigden *et al*., 2008) which normally find their way into the Korle lagoon. Settlers burn discarded electronic gadgets at a section of the Korle lagoon reclamation area to extract copper and other valuable metals. Local manufacturers buy the commodities, offering one of the only steady income streams for most of the young men in the slum. Unfortunately, the fumes which contain heavy metals and polyaromatic compounds from the burning e-waste which eventually fall on soils and vegetation in the reclaimed area are extremely hazardous (Schmidt, 2006; Otsuma *et al*., 2011).

Herds of cattle cross from the Abossey Okai Zongo and Korle Gonno communities to graze on the vegetation at the reclaimed waste land. Just beside the reclaimed area is a former dump site which has been converted to an active vegetable garden by the urban poor in the vicinity. Ideriah *et al.* (2010) reported that concentrations of heavy metals in soil around waste dumps are predisposed by all types of wastes. If high concentrations of heavy metals are found in the vegetation, this may bioaccumulate in the herds of cattle and other animals. This will further cause health problems along the food chain. The fumes from the e-waste site may end up at the reclaimed portion (RZ) of the study area since its topography is higher. A section of the reclamation area has been turned into a recreational zone (KD) where children come to play especially on weekends and during school vacations. These children may be exposed to heavy metals which may affect their health. As reported by Ideriah *et al.* (2010), it has been shown that considerable amounts of toxic metals arising from human activities are accumulated in soil (Agirtas *et al*., 1999) and vegetation. This may have serious effect on the health of humans and animals. Although, research works have been carried out on the Korle Lagoon, the presence of heavy metals along the soil profile, forage grasses and crops grown have not been critically assessed. It is therefore highly imperative that the presence of these metals be evaluated which is the rationale for this research.

1.3 Objectives

The objectives of this project are:

- To assess the level of heavy metal pollution in soils and vegetation around the research area.
- To assess the variability in heavy metal along the soil profile from the surface of the soil to a depth of 60cm.
- To identify possible sources, and
- Risk assessment on the environment

1.4 Justification

Soils and vegetation in waste dump sites and e-waste areas are contaminated with heavy metals, persistent organic pollutants and other pollutant as well. There is visible presence of huge piles of dismantled e-waste materials some of which are frequently burnt in the study area, leading to possible release of various elements or compounds, heavy metals inclusive, originally contained in the e-waste into the immediate environment. This study sought to investigate the extent of the heavy metal contamination in soils and vegetation around the area where e-waste is dumped including around the waste dump, areas already reclaimed and an area extensively used for vegetable farming by many low income residents in the area.

CHAPTER TWO

LITERATURE REVIEW

A heavy metal is a member of an ill – defined subset of elements that exhibit metallic properties, which would mainly include the transition metals, some metalloids, lanthanides and actinides. Many different definitions have been proposed, some based on density, some on atomic weight and some on chemical properties or toxicity. Heavy metals can include elements lighter than carbon and can exclude some of the heaviest metals. The speciation and bioavailability of trace metals in water are controlled by physical and chemical interactions and equilibra. These interactions are affected by many factors, including pH, redox, temperature, hardness, carbon dioxide concentrations, the type and concentration of available ligands, chelating agents and type and concentrations of metal ions (Lente *et al.*, 2011). Beyersmann and Hartwig (2008) concluded that the toxicity of heavy metals and their compounds largely depends on their bioavailability, that is, the mechanisms of uptake through cell membranes, intracellular distribution, and binding to cellular macromolecules.

According to Baird and Cann (2008), biologically the mechanism of the toxic action of heavy metals usually arises from the strong affinity of the cations for sulphur which aid to ingest molecules that contain metals. The sulfhydryl group, -SH which occurs commonly in enzymes that control the speed of critical metabolic reactions in the human body. The resultant metal-sulphur bonding affects the functioning of the enzyme to act normally and as a result human health is adversely affected or sometimes fatal. The reaction of heavy-metal cations M^{2+} (where M is Hg, Pb, or Cd) with the sulfhydryl units of enzymes R-S-H to produce stable systems such as R-S-M-S-R (where R is an alkyl or aryl group and S is sulphur) is analogous to their reaction with the simple inorganic chemical hydrogen sulfide, H_2S, with which they yield the insoluble solid MS (Baird and Cann, 2008).

High concentration of some heavy metals has a cumulative carcinogenic health effect on human and this need to be avoided. Olawoyin *et al.*(2012) concluded that the extents of deleterious health effects are aggravated mostly for children, especially the non-carcinogenic risks. The individual heavy metals do not show significant health risk, but their combined effects are of particular concern.

2.1 Cadmium (Cd)

Cadmium (Cd) is a silvery-white metallic element that can easily be shaped. The atomic number of cadmium is 48; the element is one of the transition elements in group 12 (or IIb) of the periodic table. Cadmium melts at 321°C (610°F), boils at 767°C (1413°F), and has a specific gravity of 8.64; the atomic weight of cadmium is 112.41. When heated, cadmium burns in air with a bright light, forming the oxide CdO. Because of its high rates of soil-to-plant transfer, cadmium is a contaminant found in most human foodstuffs, which renders diet a primary source of exposure among nonsmoking, non-occupationally exposed populations (Clemens, 2006; Franz *et al.*, 2008; McLaughlin *et al.*, 2006).

2.1.1 Occurrence in environment

Cadmium occurs naturally in soils as a result of the weathering of the parent rock (Alloway, 1995; Environment Agency, 2009). Sedimentary rocks have the greatest range of cadmium concentrations with the highest values found in sedimentary phosphate deposits and black slates (Alloway, 1995; Environment Agency, 2009). Large concentrations of Cd in the soil are associated with parent material (black slates) and most are manmade (burning of fossil fuels, application of fertilizers, sewage sludge, plastic waste and e-waste) which is responsible for soil contamination and also contaminates pasture (Reis *et al.*,2010)

Anthropogenic sources of cadmium are much more significant than natural emissions and account for its ubiquitous presence in soil (Alloway, 1995; ECB, 2007; ATSDR, 2008; Environment Agency, 2009).

Atmospheric deposition is also an important source of cadmium pollution (Alloway, 1995; ECB, 2007; ATSDR, 2008; Environment Agency, 2009). The major sources of atmospheric emissions are non-ferrous metal production, fossil fuel combustion, waste incineration, and iron and steel production (Alloway, 1995; ATSDR, 2008). A representative deposition rate to agricultural land across the European Union has been estimated to be 3 g of cadmium per hectare per year (Alloway, 1995; Kabata-Pendias and Mukherjee, 2007; Environment Agency, 2009).

The primary commercial source of cadmium is as a byproduct from the processing of zinc ores including sphalerite and smithsonite (Alloway, 1995; ECB, 2007; Environment Agency, 2009a). Cadmium metal, its alloys and compounds have been used in a variety of different industrial and consumer products, although most uses are now declining due to concerns about its toxicity (ATSDR, 2008; Environment Agency, 2009a).

Adsorption of cadmium by soil depends strongly on pH, which affects mobility of cadmium but decreases with increasing alkalinity (Anderson and Christensen, 1988; Alloway, 1995; Holm *et al.*, 2003; Environment Agency, 2009) and soil organic matter (SOM) is also an important factor (Holm *et al.*, 2003; Kabata-Pendias and Mukherjee, 2007; Environment Agency, 2009c).

2.1.2 Uses

Cadmium lowers the melting point of metals with which it is alloyed; it is used with lead, tin, and bismuth in the manufacture of fusible metals for automatic sprinkler systems, fire alarms, and electric fuses. An alloy of cadmium with lead and zinc is used as a solder for iron. Cadmium salts are used in photography and in the manufacture of fireworks, rubber, fluorescent paints, glass, and porcelain. Cadmium has been used as a control or shielding material in atomic energy plants because of its high absorption of low-energy neutrons. Cadmium sulfide is employed in a type of photovoltaic cell, and nickel-cadmium batteries are in common use for specialized purposes. Cadmium (Cd) occurs in electronics both as cadmium metal, in some switches and solder joints, and as cadmium compounds in rechargeable batteries, UV stabilizers in older PVC cables and “phosphor” coatings in older cathode ray tubes.

2.1.3 Health effect

According to Olawoyin *et al.*(2012) cadmium (Cd) causes damage to the lungs, kidneys and bones, and it is a known human carcinogen. Its toxicity is linked with reproduction problem because it affects sperm and reduces birth weight. It is a potential carcinogen and seems to be a causal factor in cardiovascular diseases and hypertension

Like lead, cadmium can accumulate in the body over time, with long-term exposure causing damage to the kidneys and bone structure. Oral, dermal and inhalation exposures contribute to the same systemic effects on the kidney and bone (Environment Agency, 2009c). Cadmium and its compounds are known human carcinogens, primarily through inhalation of contaminated fumes and dusts. (Asio, 2007, http://soil-environment.blogspot.in/search/label/heavy%20metalsretrieved on the 18th February 2013).

2.2 Nickel (Ni)

The nickel institute reported that nickel is a naturally occurring element (the 24th most abundant element in the periodic table) and as a consequence of natural and man-made processes can be found ubiquitously in the air, soil, sediments and water. As with all metals and chemicals, excessive amounts of nickel in any of these environmental compartments can result in deleterious impacts on the quality of the environment for flora and fauna.

Barceloux (1999) reported that nickel is abundant in the crust of the earth, comprising about 3% of the composition of the earth. Nickel averages 50 $mgkg^{-1}$ in soils and commonly varies from 5 to 500 $mgkg^{-1}$ but ranges up to 24,000 to 53,000 $mgkg^{-1}$ in soil near metal refineries or in dried sewage sludge, respectively. Agricultural soils typically contain 3 to 1000 $mgkg^{-1}$, whereas soils derived from basic igneous rocks may contain from 2000 to 6000 $mgkg^{-1}$

2.2.1 Occurrence in the environment

Most nickel on Earth is inaccessible because it is locked away in the planet's iron-nickel molten core, which is 10 % nickel. The total amount of nickel dissolved in the sea has been calculated to be around 8 billion tons. Organic matter has a strong ability to absorb the metal which is why coal and oil contain considerable amounts. The nickel content in soil can be as low as $0.2mgkg^{-1}$ or as high as $450mgkg^{-1}$ in some clay and loamy soils. The average is around $20mgkg^{-1}$. Nickel occurs in some beans where it is an essential component of some enzymes. Another relatively rich source of nickel is tea which has 7.6 mg/kg of dried leaves. (http://www.lenntech.com/periodic/elements/ni.htm#ixzz2DiaUqP74 retrieved on 29th November 2012).

2.2.2 Uses

Humans use nickel for many applications like the use of nickel as an ingredient of steel and other metal products.

2.2.3 Health effect

Foodstuffs have low natural content of nickel but high amounts can occur in food crops growing in polluted soils. Humans may also be exposed to nickel by inhalation, drinking water, smoking, and eating contaminated food. Uptake of high quantities of nickel can cause cancer, respiratory failure, birth defects, allergies, and heart failure (www.Lenntech.com/periodic-chart-elements/Ni-en.htm retrieved on the 29th November 2012).

2.3 Chromium (Cr)

Chromium has atomic number of 24 and electronic configuration of [Ar] $4s^1 3d^5$. The stable forms of Cr in the environment are the trivalent Cr(III) and the hexavalent Cr(VI) species, although there are various other valency states that are unstable and short-lived in biological systems. Chromium(VI) exists in soils as a relatively soluble anion under most conditions (CrO_4^{2-} or $HCrO_4^-$). While sodium and potassium salts of chromates are freely soluble over the pH range 1–14, calcium chromate ($CaCrO_4$) is only moderately soluble, and lead and barium chromates ($PbCrO_4$) and ($BaCrO_4$) are only sparingly soluble at near-neutral pH values. In the absence of solubility-controlling solids, Cr(VI) aqueous concentrations under acidic to slightly alkaline conditions will primarily be controlled by adsorption/desorption reactions. Cr(VI) is adsorbed by mineral solids that have exposed inorganic hydroxyl groups on their surfaces, including iron and aluminum oxides, kaolinite, and, to a lesser extent, montmorillonite (Rai *et al.*, 1989; Zupancic *et al.*, 2008). Cr(VI) adsorption increases with decreasing pH as a result of protonation of the surface hydroxyl site ($SOH^+{}_2$) and aqueous speciation of Cr(VI). Chromium (III) is less mobile, less toxic and mainly bound to organic matter in soil and aquatic environments (Shanker *et* *al.*, 2005). Zupancic *et al.* 2008 asserted that Cr (III) in soil, is found predominantly in insoluble forms, such as sparingly soluble Cr_2O_3 and $Cr(OH)_3$.

2.3.1 Uses

Chromium and its compounds have multifarious industrial uses. They are extensively employed in leather processing and finishing, in the production of refractory steel, electroplating cleaning agents, catalytic manufacture, etc., (Shanker *et al.*, 2005). These anthropogenic activities have led to widespread contamination of the environment by Cr, as well as to deposition of Cr-contaminated waste (Zupancic *et al.*, 2008).

2.3.2 Health effect on the environment

Shanker *et al.*(2005) reported that chromium is a toxic, non-essential element to plants therefore they do not possess specific mechanisms for its uptake. This metal's toxicity in plants is observed at multiple levels, from reduced yield, through effects on leaf and root growth, to inhibition of enzymatic activities and mutagenesis. It is required for carbohydrate and lipid metabolism and the utilization of amino acids. Toxic levels are common in soils applied with sewage sludge.

2.4 Lead (Pb)

Lead(Pb) is a chemical element with symbol Pb and atomic number of 82 and it is a main group element belonging to group 4. It forms oxidation states +2 and +4, with +4 being achieved with highly electronegative elements (F, O) (Greenwood and Earnshaw, 1997). Lead has many isotopes but four (4) stable ones. The four (4) stable isotopes are ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb with ^{204}Pb regarded as primordial Pb and Pb-206, Pb-207, Pb-208 are formed from decay of Uranium(U) and Th. The one common radiogenic isotope, ^{202}Pb, has a half-life of approximately 53,000 years**.**

2.4.1 Occurrence in the environment

LEAD Group Inc.(2011) asserted that lead deposited on the ground is transferred to the upper layers of the soil surface, where it may be retained for many years (up to 2000 years). In undisturbed ecosystems, organic matter in the upper layer of soil surface retains atmospheric lead. In cultivated soils, this lead is mixed with soil to a depth of 25cm (i.e., within the root zone). Atmospheric lead in the soil will continue to move into the micro-organism and grazing food chains, until equilibrium is reached. The central nervous of animals are affected by lead and this inhibits their ability to synthesis red blood cells. Lead has been known to be toxic since the 2nd century BC in Greece according to Asio, (2007) (retrieve on the 18th February 2013 from http://soil-environment.blogspot.in/search/label/heavy%20metals). It is a widespread contaminant in soils and lead poisoning is one of the most prevalent public health problems in many parts of the world. It was the first metal to be linked with failures in reproduction.

The metal can affect all components of the environment and can move through the ecosystem until it reaches equilibrium. Lead accumulates in the environment, but in certain chemical environments it will be transformed in such a way as to increase its solubility (e.g., the formations of lead sulfate in soils), its bioavailability or its toxicity. The effects of lead at the ecosystem level are usually seen as a form of stress (US EPA, 1986).

2.4.2 Uses

LEAD Group Inc.(2011) reported from Lead action news, (1993) that lead moves into and throughout the ecosystems in different routes. Atmospheric lead is deposited in vegetation, ground and water surfaces. The chemical and physical properties of lead and the biogeochemical processes within ecosystems will influence the movement of lead through ecosystems.

The main sources of lead entering an ecosystem are atmospheric lead (primarily from automobile emissions), paint chips, used ammunition, fertilizers and pesticides and lead-acid batteries or other industrial products. The transport and distribution of lead from major emission sources, both fixed and mobile, are mainly through air (UNEP, 1991). Pb is widely used in electronic goods, as a major component of solders (as an alloy with tin) and its compounds have also been used as stabilizers in some PVC cables and other products.

2.4.3 Health effect

Lead affects the brain, causing hyperactivity and deficiency in the fine motor functions, thus, it results in damage to the brain. The nervous systems of children are especially sensitive to Pb leading to retardation. It is also cardiotoxic and contributes to cardiomyopathy (disease of the heart muscle leading to the enlargement of the heart). Lead is highly toxic to humans, as well as to animals and plants (Khan *et al*., 2008)

2.5 Zinc (Zn)

Zinc has an electron configuration of $[Ar]3d^{10}4s^2$ and is a member of the group 12 of the periodic table. Zinc is a metallic chemical element; it has the symbol Zn and atomic number 30. It is the first element in group 12 of the periodic table. According to Wikipedia zinc is, in some respects, chemically similar to magnesium, because its ion is of similar size and its only common oxidation state is +2. Zinc is the 24th most abundant element in the Earth's crust and has five stable isotopes. It is a moderately reactive metal and strong reducing agent (CRC, 2006). The surface of the pure metal tarnishes quickly, eventually forming a protective passivating layer of the basic carbonate $Zn_5(OH)_6(CO_3)_2$, by reaction with atmospheric carbon dioxide (Porter, 1994). This layer helps prevent further reaction with air and water.

Zinc burns in air with a bright bluish-green flame, giving off fumes of zinc oxide. Zinc reacts readily with acids, alkalis and other non-metals. Extremely pure zinc reacts only slowly at room temperature with acids. Strong acids, such as hydrochloric or sulfuric acid, can remove the passivating layer and subsequent reaction with water releases hydrogen gas (Holleman *et al.*, 1985).

2.5.1 Occurrence in the environment

Zinc(I) compounds

Zinc (I) compounds are rare, and requires bulky ligands to stabilize the low oxidation state. Most zinc(I) compounds contains formally the $[Zn_2]^{2+}$ core, which is analogous to the $[Hg_2]^{2+}$ dimeric cation present in mercury(I) compounds (Housecroft and Sharpe, 2008).

Zinc (II) Compounds

Binary compounds of zinc are known for most of the metalloids and all the nonmetals except the noble gases. The chemistry of zinc is dominated by the +2 oxidation state (Ritchie, 2004). The oxide ZnO is a white powder that is nearly insoluble in neutral aqueous solutions, but is amphoteric, dissolving in both strong basic and acidic solutions (Holleman *et al.*,1985).

2.5.2 Uses

Zinc oxide is widely used as a white pigment in paints, and as a catalyst in the manufacture of rubber. It is also used as a heat disperser for the rubber and acts to protect its polymers from ultraviolet radiation (the same UV protection is conferred to plastics containing zinc oxide) (Emsley, 2001).The semiconductor properties of zinc oxide make it useful in varistors and photocopying products (Zhang, 1996). Zinc sulfide (ZnS) is used in luminescent pigments such as on the hands of clocks, X-ray and television screens, and luminous paints. Crystals of ZnS are used in lasers that operate in the mid-infrared part of the spectrum (Paschotta, 2008). Zinc sulfate is a chemical in dyes and pigments. Zinc pyrithione is used in antifouling paints (Konstantinou and Albanis, 2004)

2.5.3 Health effect

Even though zinc is an essential requirement for a healthy body, excess zinc can be harmful, and cause zinc toxicity (Fosmire, 1990). Excessive absorption of zinc can suppress copper and iron absorption. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish. The Free Ion Activity Model (FIAM) is well-established in the literature, and shows that just micromolar amounts of the free ion kills some organisms. A recent example showed 6 micromolar killing 93% of all *Daphnia* in water (Muyssen, 2006).

The free zinc ion is also a powerful Lewis acid up to the point of being corrosive. Stomach acid contains hydrochloric acid, in which metallic zinc dissolves readily to give corrosive zinc chloride. Swallowing a post-1982 American one cent piece (97.5% Zinc) can cause damage to the stomach lining due to the high solubility of the zinc ion in the acidic stomach (Bothwell *et al.*, 2003).

There is also a condition called the zinc shakes or "zinc chills" that can be induced by the inhalation of freshly formed zinc oxide formed during the welding of galvanized materials (Fosmire, 1990). Soils contaminated with zinc through the mining of zinc-containing ores, refining, or where zinc-containing sludge is used as fertilizer, can contain several grams of zinc per kilogram of dry soil. Levels of zinc in excess of 500 ppm in soil interfere with the ability of plants to absorb other essential metals, such as iron and manganese. Zinc levels of 2000 ppm to 180,000 ppm (18%) have been recorded in some soil samples (Emsley, 2001).

Zinc (Zn) is an indispensable element required by the human body within an allowable daily intake of 15 mg and 5 mg for adults and children respectively. Levels of zinc above 150 mg/day are considered to have deleterious effects in humans (RAIS, 2009; Olawoyin *et al.*, 2012).

2.6 Arsenic (As)

Arsenic has atomic number of 33 and is in group 5. In its elemental form arsenic occurs in two forms under ambient conditions – a steel grey coloured brittle metallic solid or a dark grey amorphous solid (ATSDR, 2007; Environment Agency, 2009b). Although it is commonly described as a heavy metal, arsenic is a metalloid with a complex chemistry similar to phosphorous (CCME, 2001).Arsenic is a well-known poison and a carcinogen. It has an average concentration in the soil of 5 to 6 mg/kg. Its amount in the soil is related to rock type and industrial activity.

2.6.1 Occurrence in the environment

Arsenic occurs naturally in the environment although rarely in its elemental form (CCME, 2001). Over 200 arsenic-containing minerals have been identified, with approximately 60 per cent being arsenates, 20 per cent sulphides and sulphosalts, and the remaining 20 per cent including arsenides, arsenites and oxides. The most commonly occurring form is arsenopyrite, an iron arsenic sulphide associated with many types of mineral deposits and especially those including sulphide mineralisation (O’Neill, 1995; Farago *et al.*, 2003). Arsenate reportedly binds strongly to iron and manganese oxides, and therefore remains in the surface soil layer after deposition (ATSDR, 2007). Arsenic was observed to be still concentrated after 15 years in the top 20–40 cm of orchard soils treated with lead arsenate (Merwin *et al*. 1994; Environmental Agency, 2009c).

Arsenic forms organic and inorganic compounds with the most common valence states being -3, +3 or +5 (ATSDR, 2007). Arsenic trioxide is a white crystalline solid at room temperature. It is produced commercially as a by-product of the smelting of non-ferrous ores including copper and lead (IPCS, 2001; ATSDR, 2007). Most arsenic trioxide is subsequently converted to arsenic acid (H_3AsO_4), which forms arsenate salts (ATSDR, 2007; Environment Agency, 2009c).

In typical surface soils, the most important inorganic forms of arsenic are arsenite (AsO_3^{3}) and arsenate (AsO_4^{3-}), with the latter dominating under aerobic/oxidizing conditions (O’Neill, 1995; Kabata-Pendias and Mukherjee, 2007).

Anthropogenic activity has resulted in the widespread atmospheric deposition of arsenic from the burning of coal and the smelting of non-ferrous metals including copper (O’Neil, 1995; Environmental Agency, 2009c). Agricultural practice including the historical use of arsenic-based pesticides and ongoing application of fertilizers, sludges and manures containing arsenic has resulted in the accumulation of arsenic in topsoils (O’Neil, 1995; Kabata-Pendias and Mukherjee, 2007, Environment Agency, 2009c).

2.6.2 Uses

Arsenic and its inorganic compounds have also been used as a decolourizer in the manufacture of glass, in various metallurgical processes including the production of alloys, in veterinary and human medicines, and lead– acid batteries (CCME, 2001; IPCS, 2001; ATSDR, 2007; Kabata-Pendias and Mukherjee, 2007).

2.6.3 Health effect

The organs of the body that are usually affected by arsenic poisoning are the lungs, skins, kidney and liver (Mayo Medical Laboratory, 2012). Arsenic is related to heart diseases (hypertension and cardiovascular), cancer and stroke (Tseng *et al.*, 2003). The final result of arsenic poisoning is coma to death.

2.7 Copper (Cu)

Copper is a chemical element with atomic number 29 with symbol Cu. It has electronic configuration [Ar] $3d^{10}$ $4s^{1}$. It is a ductile metal with very high thermal and electrical conductivity. Pure copper is soft and malleable; a freshly exposed surface has a reddish-orange color. It is used as a conductor of heat and electricity, a building material, and a constituent of various metal alloys.

Copper (III) and Copper(IV)

Copper (III) is mostly characteristically found in oxides. A simple example is potassium cuprate, $KCuO_2$, a blue-black solid. The best studied copper (III) compounds are the cuprate superconductors. Yttrium barium copper oxide ($YBa_2Cu_3O_7$) consists of both Cu (II) and Cu (III) centres. Like oxide, fluoride is a highly basic anion and is known to stabilize metal ions in high oxidation states. Indeed, both copper (III) and even copper (IV) fluorides are known, K_3CuF_6 and Cs_2CuF_6, respectively (Holleman *et al.*, 2001).

2.7.1 Occurrence in the environment

Copper is a very common element that occurs naturally in the environment and spreads through the environment through natural phenomena. Humans widely use copper in industries and in agriculture. Globally, production of copper has increased over the years and this has increase the copper in the environment.

Rivers are depositing sludge on their banks that is contaminated with copper, due to the disposal of copper-containing wastewater. Copper evaporate into the air, mainly through release during the combustion of fossil fuels. Copper in air will remain there for an eminent period of time, before it settles when it starts to rain. It will then end up mainly in soils. As a result soils may also contain large quantities of copper after copper resulting in absorption or uptake by some plants.

2.7.2 Uses

Most copper is used for electrical equipment (60%); construction, such as roofing and plumbing (20%); industrial machinery, such as heat exchangers (15%) and alloys (5%). The main long established copper alloys are bronze, brass, copper-tin-zinc, which is strong enough to make guns and cannons, and is known as gun metal. Copper and nickel is known as cupronickel, which is the preferred metal for low-denomination coins(Emsley, 2003). Copper is ideal for electrical wiring because it is easily worked, can be drawn into fine wire and has a high electrical conductivity.

2.7.3 Health effect

Copper is an essential micronutrient required by plants, animals, and human health. It is also required for the normal functioning of aerobic microorganisms. Soils that are naturally deficient in copper often require copper supplements before agricultural crops, such as cereals, can be grown.

Copper deficiencies in soil can lead to crop failure. Copper deficiency is a major issue in global food production, resulting in losses in yield and reduced quality of output. Nitrogen fertilizers can worsen copper deficiency in agricultural soils.

The most effective strategy to counter copper deficiency is to supplement the soil with copper, usually in the form of copper sulfate. Sewage sludge is also used in some areas to replenish agricultural land with organics and trace metals, including copper.

In livestock, cattle and sheep commonly show indications when they are copper deficient. Swayback, a sheep disease associated with copper deficiency, imposes enormous costs on farmers in many tropical countries.

Toxicity from copper deficiency can be treated with a balanced diet or supplementation under the supervision of a doctor. On the contrary, like all substances, excess copper intake at levels far above World Health Organization limits can become toxic (http://www.copperinfo.com/health/facts.html retrieved on the 13th March 2013)

2.8 Mercury (Hg)

Mercury is a chemical element with atomic number of 80 and symbol Hg. It has electronic configuration of [Xe] $4f^{14}5d^{10}6S^{2}$. Mercury exists in two main oxidation states, I and II. Higher oxidation states are unimportant, but have been detected, e.g., mercury(IV) fluoride (HgF_4) but only under extraordinary conditions (Wang *et al*, 2007). Azevedo *et al.*(2012) quoted in a review of phytotoxicity of mercury in plants that among metals, Hg is unique as it is found in the environment in several physical and chemical forms: for example, elemental Hg(Hg^0), inorganic Hg (Hg^{2+}), associated with ions (SHg), mercurous chloride or calomel (Hg_2Cl_2), and organic Hg (e.g. CH_3-Hg) (Boening, 2000; Zahir *et al.*, 2005; Clarkson *et al.*, 2007).

According to Environment Agency (2009) mercury is most commonly encountered in the environment in elemental form, as inorganic mercuric (Hg^2) compounds, or as monomethylmercury compounds with the general formula, CH_3HgX_2.The most important source of mercury is the naturally occurring mineral, cinnabar (HgS).

In its elemental form, mercury is a dense, silvery white metal, which is a volatile liquid at room temperature (ATSDR, 1999). Mercury readily forms amalgams with a variety of other metals including sodium and zinc, although not with the lighter transition metals such as iron (Greenwood and Earnshaw, 1997; Environment Agency, 2009b).

Mercury(II) oxide, the main oxide of mercury, arises when the metal is exposed to air for long periods at elevated temperatures. It reverts to the elements upon heating near 400 °C, as was demonstrated by Priestly in an early synthesis of pure oxygen (Greenwood and Earnshaw, 1997).

Being a soft metal, mercury forms very stable derivatives with the heavier chalcogens. Preeminent is mercury(II) sulfide, HgS, which occurs in nature as the ore cinnabar and is the brilliant pigment vermillion. Like ZnS, HgS crystallizes in two forms, the reddish cubic form and the black zinc blend form (Hammond, 2005). Mercury(II) selenide (HgSe) and mercury(II) telluride (HgTe) are also known, these as well as various derivatives, e.g. mercury cadmium telluride and mercury zinc telluride being semiconductors useful as infrared detector materials (Rogalski, 2000).

Hammond (2005) reported that mercury(II) salts form a variety of complex derivatives with ammonia. These include Millon's base (Hg_2N^+), the one-dimensional polymer (salts of $HgNH^+{}_2$)n, and "fusible white precipitate" or $[Hg(NH_3)_2]Cl_2$. Known as Nessler's reagent, potassium tetraiodomercurate(II)($HgI^{2-}{}_4$) is still occasionally used to test for ammonia owing to its tendency to form the deeply colored iodide salt of Millon's base. Mercury fulminate is a detonator widely used in explosives.

Organic mercury usually have the formula HgR_2, which are often volatile, or HgRX, which are often solids, where R is aryl or alkyl and X is usually halide or acetate. Methylmercury, a generic term for compounds with the formula CH_3HgX, is a dangerous family of compounds that are often found in polluted water (National Research Council, 2000).

2.8.1 Occurrence in the environment

Almost all commercial production of mercury comes from the sulphide ore, cinnabar, which results from hydrothermal mineralization associated with volcanic activity (Steinnes, 1995; Kabata-Pendias and Mukherjee, 2007; Environment Agency, 2009c). Anthropogenic activity is a major source of aerial emissions of mercury and a significant contributor to soil contamination (Steinnes, 1995; ATSDR, 1999). Most of the mercury in air is present as elemental mercury vapour: 90–99% according to European Commission (2001); over 95% according to ATSDR (1999); and 75% according to IPCS (1990), which assumed 5% occurred as inorganic mercury and 20% as methylmercury (Environment Agency, 2009b). The main sources of contamination have been mining and smelting, burning of fossil fuels, industrial production of sodium hydroxide and chloride, and waste incineration although mercury also occurs in trace amounts in fertilizers used on farmland (Steinnes, 1995).

2.8.2. Uses

Elemental mercury was employed in hundreds of applications, many of which (e.g., electrical switches) took advantage of the unusual property that it is a liquid that conducts electricity well (US EPA, 2005).

Mercury is still used in some batteries and lighting components for flat screen electronic displays, and was formerly used also in switches and relays. Mercury can also be used in the preservation of wood.

2.8.3 Health effect

Mercury is the most volatile of metals, and its vapor is highly toxic as asserted by Colin Baird. Mercury and most of its compounds are extremely toxic and must be handled with care; in cases of spills involving mercury (such as from certain thermometers or fluorescent light bulbs), specific cleaning procedures are used to avoid exposure and contain the spill (US EPA, 2005).This heavy metal is toxic even at low concentrations to a wide range of organisms including humans. Mercury and its compounds are highly toxic, causing damage to the central nervous system and kidneys. Once in the environment, mercury can be converted to its organic methylated form by bacterial activity, a form, which is highly bio-accumulative, as well as being toxic.

The organic form of mercury can be particularly toxic, and the methyl-and ethyl-forms have been the cause of several major epidemics of poisoning in humans resulting from the ingestion of contaminated food, e.g. fish. Two major epidemics in Japan were caused by the release of methyl and other mercury compounds from an industrial site followed by accumulation of the chemicals in edible fish. The poisoning became well-known as Minamata disease (Posted by Victor B. Asio (2007), http://soil-environment.blogspot.in/search/label/heavy%20metals; retrieved on 18th February 2013).

2.9 Tin (Sn)

Tin has atomic number 50 and electronic configuration [Kr] $4d^{10}$ $5s^2$ $5p^2$. It is in group 14 of the periodic table with symbol Sn. Tin shows chemical similarity to both neighboring group 14 elements, germanium and lead and has two possible oxidation states, +2 and the slightly more stable +4. Tin is the 49th most abundant element and has 10 stable isotopes, the largest number of stable isotopes in the periodic table. Tin is obtained chiefly from the mineral cassiterite, where it occurs as tin dioxide, SnO_2.

2.9.1 Occurrence in the environment

Tin is a natural element in the earth's crust. It is a soft, white, silvery metal that does not dissolve in water. It is present in brass, bronze, pewter, and some soldering materials. Tin metal is used to line cans for food, beverages, and aerosols. Tin is a component of many soils. Tin may be released in dusts from wind storms, roads, and farming activities. Gases, dusts, and fumes containing tin may be released from smelting and refining processes, burning of waste, and burning of fossil fuels (coal or oil). Tin binds to soils and to sediments in water and is generally regarded as being relatively immobile in the environment. Tin cannot be destroyed in the environment. It can only change its form or become attached or separated from particles in soil, sediment, and water (ATSDR, 2005)

2.9.2 Uses

Tin can combine with other chemicals to form compounds. Combinations with chemicals like chlorine, sulfur, or oxygen are called inorganic tin compounds (i.e., stannous chloride, stannous sulfide, stannic oxide). These are used in toothpaste, perfumes, soaps, food additives and dyes. Tin also can combine with carbon to form organotin compounds (i.e., dibutyltin, tributyltin, triphenyltin) (Hon and Shiraishi, 2001). These compounds are used to make plastics, food packages, plastic pipes, pesticides, paints, and pest repellents.

2.9.3 Health effect

Draggan, 2012, published an article on http://www.eoearth.org (Retrieved December 5, 2012) titled "Health effects of tin" wrote that tin is present in the air, water, soil, and landfills and is normally found in plants and animals. Tin is therefore found in human tissues even though there is no evidence that tin is an essential element for a healthy body.

Tin concentrations in vegetables, fruits and fruit juices, nuts, dairy products, meat, fish, poultry, eggs, beverages, and other foods not packaged in metal cans are generally less than 2ppm. Humans exposed to tin when contaminated food or juice are eaten or taken. Canned food from lacquered tin-lined cans contains less than 25 ppm of tin since the lacquer prevents the food from reacting with the tin. Food from unlacquered tin-lined cans contains up to 100 ppm of tin since the reaction of the food with the can causes some of the tin to dissolve in the contents of the can.

Humans are usually exposed to tin at far less than 1 ppm from air and water. The amounts in air and water near hazardous waste sites could be higher. Young children sometimes eat soil during play. While most soil contains about 1 ppm tin, some soils may contain as much as 200 ppm tin (http://www.eoearth.org/article/Health_effects_of_tin.html retrieved on 5th December 2012).

2.10 Physicochemical analysis of soils

2.10.1Total organic carbon / total organic matter

Total organic carbon (TOC) is the carbon (C) stored in soil organic matter (SOM). Organic carbon (OC) enters the soil through the decomposition of plant and animal residues, root exudates, living and dead microorganisms, and soil biota. SOM is the organic fraction of soil exclusive of non-decomposed plant and animal residues. Nevertheless, most analytical methods do not distinguish between decomposed and non-decomposed residues. SOM is a heterogeneous, dynamic substance that varies in particle size, Carbon content, decomposition rate, and turnover time.

Soil Organic Carbon (SOC) is the main source of energy for soil microorganisms. The ease and speed with which SOC becomes available is related to the SOM fraction in which it resides. In this respect, SOC can be partitioned into fractions based on the size and breakdown rates of the SOM in which it is contained.

SOM contains approximately 58% C; therefore, a factor of 1.72 can be used to convert OC to SOM. There is more inorganic C than TOC in calcareous soils. TOC is expressed as percent C per 100 g of soil (Edwards *et al*., 1999; http://soilquality.org/indicators/total_organic_carbon.html retrieved on 29th November 2012)

2.10.2 Soil pH

Soil pH generally refers to the degree of soil acidity or alkalinity. Chemically, it is defined as the log10 hydrogen ions (H^+) in the soil solution. The pH scale ranges from 0 to 14; a pH of 7 is considered neutral. If pH values are greater than 7, the solution is considered basic or alkaline; if they are below 7, the solution is acidic. A few changes in the pH units can induce significant changes in the chemical environment and sensitive biological processes. For example, a soil with pH 5 is 10 or 100 times more acidic than a soil with pH 6 or 7, respectively. Sources of H^+ ions in soil solution include carbonic acid produced when carbon dioxide (CO_2) from decomposing organic matter, root respiration, and the soil atmosphere is dissolved in the soil water. Other sources of H+ ions are root release, reaction of aluminum ions (Al^{+3}) with water, nitrification of ammonium from fertilizers and organic matter mineralization, reaction of sulfur compounds, rainwater, and acid rain. Certain soils are more resistant to a drop or rise in pH (buffering capacity). Soil pH affects the soil's physical, chemical, and biological properties and processes, as well as plant growth. The nutrition, growth, and yields of most crops decrease where pH is low and increase as pH rises to an optimum level (Smith and Doran, 1996; http://soilquality.org/indicators/soil_ph.html retrieved on 29th November 2012).

2.10.3 Cation exchange capacity

The cation exchange capacity (CEC) of a soil is a measure of the quantity of negatively charged sites on soil surfaces that can retain positively charged ions (cations) such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+), by electrostatic forces.

Cation exchange sites are found primarily on clay minerals and organic matter (OM) surfaces. Soil OM will develop a greater CEC at near-neutral pH than under acidic conditions (pH-dependent CEC). Thus, addition of an organic material will likely increase a soil's CEC over time. On the other hand, a soil's CEC can decrease with time as well, through e.g. natural or fertilizer-induced acidification and/or OM decomposition. Soil CEC is normally expressed in one of two numerically equivalent sets of units: meq/100 g (milliequivalents of charge per 100 g of dry soil) or $cmol_c$/kg (centimoles of charge per kilogram of dry soil) (Ross and Kettering, 2011).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study site

A general site survey was done prior to the main sampling. This was done for effective sampling and reduces major obstacles during sampling. Mock sampling points were taken using the GPS in each case. The Korle Lagoon is a coastal wetland comprising beautiful sand dunes, open lagoon, salt pans, marsh and scrubs, which provide extensive suitable feeding, roosting and nesting grounds for various species of seabirds and it used to be a haven for bird-watchers.

Located in the south-west of the central business district of Accra, it is the major basin into which the greater proportion of the floodwaters from metropolitan Accra flows before finally entering the sea.

The lagoon covers a total surface area of about 0.6 km^2 and drains a total catchment area of about 400 km^2.The major inlets into the lagoon are the Odaw River with its major tributary, River Onyasia, which drains the northern parts of Accra including Haatso, Papao and Agbogba.

The research area, Korle Lagoon Reclamation Area is separated from the densely populated Old Fadama slum (Sodom and Gomorrah slum) by the Korle Lagoon. The research area covers the popular E-waste area (EW) where burning of electronic waste collected along the length and breadth of the capital is brought for burning, in order for the essential components taken for onward sale abroad. The Garden area (GZ) is behind the International Central Gospel Church, where growing of vegetables is on the increase. Farmers keep expanding their farms at this area which used to be a waste dumping area for the Abossey Okai zongo community. The reclaimed waste dump site (RZ) opposite the

Ghana Revenue Authority office for the Ablekuma District use to be one of the waste dumping sites in the Accra metropolis. The recreational site (KD) created during the Korle lagoon reclamation project (even though not complete) which is almost opposite the Accra waste treatment site which has some see-saws and a well-planned football field where children normally comes to play from Korle Gonno and the Agbogbloshie communities through to the land area at the estuary area (ES) end of the Korle Lagoon just behind the Ablekumah district Assembly office.

Source: Centre for Remote Sensing and Geographic Information Service (CERSGIS)

Fig.3.1: A Map of Korle Lagoon reclamation area in the AMA

3.1.1 Vegetation

The dominant vegetation cover at the E-waste area (EW) is mainly turf grasses (*Panicum maximum and Imperata cylindrical)* which are mainly grazed by cattle and sheep from the Abossey Okai zongo and Old Fadama slum. The central garden area (GZ), where planting of vegetables like lettuce (*Latuca sativa*) which has very low fat and cholesterol and Bissap (*Hibiscus sabdariffa*) which is an antioxidant and anti-hyperlipidemic (Tee *et al*., 2002). More farmers are joining this activity at this area because of the income from the sale of these vegetables. So the area is rapidly changing from typical waste dumping scenery to a farming area. The reclaimed waste dump site area is dominantly covered by turf grasses (*Panicum maximum)* within well demarcated area and path ways. The recreational area has turf grasses and some trees planted by the Ghana Wildlife Society. The estuary area has turf grasses (*Panicum maximum*) grown all over that stretch of land. The control area which happens to be within the Korle-bu flats was carefully selected in order to be able to sample all the plants sampled at the other sampling sites.

Plate 3.1a: Burning of electronic waste at the Old Fadama E-waste grounds.

Plate 3.1b: Vegetation and soil after burning of electronic waste

3.2 Sampling

3.2.1 Soil sampling

Sampling was done at random in all the sampling sites. The Korle lagoon reclamation zone was divided into five sampling areas namely the e-waste zone (EW), central garden zone (GZ), reclaimed zone (RZ), recreational area (KD) and the estuary zone (ES) at almost 300m intervals and samples were taken at random in these areas. Six samples each was taken at each sampling site after the zone has been divided into different sectors using surveyors tape, stainless shovel, garden trowels, plastic sealable containers/bags and an etrex GERMIN GPS. Soil sampling depth was within 0 – 60cm (0 – 20, 20 – 40, 40 – 60).The colour, texture and soil type at the various sampling areas and depths varied. Sampling at the control area (CZ) which happens to be the Korle-bu flat was also done using the same method. Samples at the central garden zone (GZ) and the control zone (CZ) were taken specific beds. A total of one hundred and eight (108) soil samples were taken. The etrex GERMIN GPS was used to take the coordinates of the various sampling points in all the sampling zones.

Plate 3.2: Soil sampling at the central garden zone

Plate 3.3: Soil and vegetation samples taken at the Control Zone, Korle-Bu Flats

3.2.2 Plant sampling

At the Central gardens area lettuce (*Latuca sativa*) and bissap leaves (*Hibiscus sabdariffa*) were the dominant plants grown on the garden beds. Twelve samples each of medium aged lettuce (*Latuca sativa*) and bissap (*Hibiscus sabdariffa*) leaves were taken from different sampling beds and their GPS coordinate taken. Twelve samples each of medium aged green grasses (*Panicum maximum)* were also sampled at the reclaimed site, estuary site, recreational site and the e-waste burning site. At the control site, Korle-Bu flats, twelve samples each of medium aged lettuce (*Latuca sativa*) and bissap (*Hibiscus sabdariffa*) leaves were taken from different sampling position.

Plate 3.4: Plant samples being taken at the Control Zone, Korle-Bu Flats.

Plate 3.5: Cattle grazing at the e-waste zone, Old Fadama.

3.3 Sample treatment

Soil and vegetation samples were kept in zip-locked plastic bags and labeled. The samples were then carried in cardboard boxes to the laboratory for further analysis.

Soil samples were air dried and cleaned off any stones and plants materials. Soil samples were ground in a mortar, pass through a 2mm sieve and were stored in sealable plastic bags.

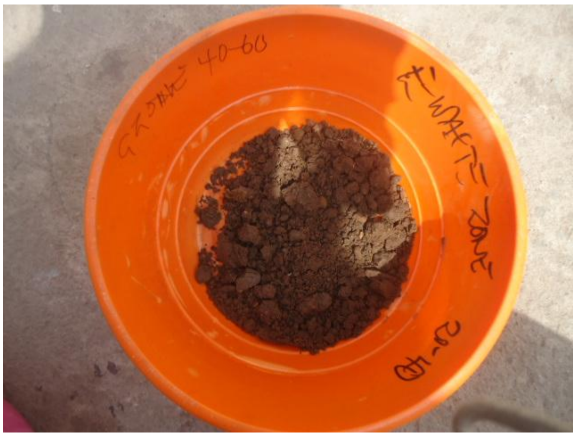

Plate 3.6: Soil being dried after sampling

3.4 Precautions taken during sampling

Gloves were worn during the sampling to prevent further contamination and the GPS equipment was thoroughly checked to be in good condition. Samples were then kept in sealable plastic bags to avoid contamination.

3.5 Preparation of soil for AAS analysis

3.5.1 Soil Sample

Soil samples were air-dried for two days and then cleaned off stones and plant residues after they have been grounded and passed through a 2mm sieve. Equal volumes of dried soil samples from the same depth were then thoroughly mixed to ensure that the sample is as representative as possible in a composite manner for each sampling site. They were adequately mixed by stirring the material in a circular fashion, reversing directions, and occasionally turning the material over (SESD Operating Procedure Soil Sampling, 2011). The sieved soil samples and the composites soil samples at the various sampling zones were then collected and stored in zip-locked plastic bags and then taken to the laboratory for analysis.

3.5.2 Preparation of Plants for AAS Analysis

Samples were taken from the various sampling sites and their GPS coordinates taken. The samples were kept in zip-locked plastic bags and labeled. Samples were washed thoroughly with water and cut into pieces using a stainless steel knife. They were then fridge dried using the CHRIST Getriertrocknugsanlagen GmbH Freeze dryer at a temperature of 17˚C with a vacuum mbar of 6.110. After two days of drying in the freeze dryer, the vegetation samples were blended into powdery forms using a stainless steel blade blender and the various heavy metal analyses done on them.

Plate 3.7: Freeze drying of plants samples

3.6 Determination of organic carbon

Walkley-Black Method (Walkley and Black, 1934) was used during the determination of the organic carbon. Recommended Soil Testing Procedures for the Northeastern United States, Last Revised 10/2009

3.6.1 Reagents Preparation:

H_3PO_4, 85%, H_2SO_4, concentrated (96%) and NaF solid.

Standard 0.167M $K_2Cr_2O_7$ was prepared by dissolving 49.04g of dried (105˚C) $K_2Cr_2O_7$ in water and dilute to 1L.

A 0.5M Fe^{2+} solution: Prepared by dissolving 196.1g of $Fe(NH_4)_2(SO_4)$.6H2O in 800ml of water containing 20ml of concentrated H_2SO_4 and dilute to 1L. The Fe^{2+} in the solution oxidizes slowly on exposure to air so it was standardized against dichromate.

Ferroin indicator: Prepared by dissolving 3.71g of o-phenanthroline and 1.74g of $FeSO_4{\cdot}7H_2O$ in 250ml of water.

3.6.2 Procedure

A 0.10 to 2.00g of dried soil (ground to <60 mesh) was weighed and transferred to a 500ml Erlenmeyer flask. A 10ml of 0.167M $K_2Cr_2O_7$ was added by means pipette.20ml of concentrated H_2SO_4 was then added by means of a dispenser and swirled gently to mix. Excessive swirling was avoided to prevent organic particles adhering to the sides of the flask.

The suspension was allowed to stand an insulating pad (asbestos) for 30 minutes. This was done to avoid rapid heat loss. The suspension was diluted with 200ml of water to provide a clearer suspension when viewing the endpoint.

A 10ml of 85% H_3PO_4 was added, using a suitable dispenser, and 0.2g of NaF was then added. The H_3PO_4 and NaF were added to complex the Fe^{3+}which would interfere with the titration endpoint.10drops of ferroin indicator was added. The indicator was added prior to the titration to avoid deactivation by adsorption onto clay surfaces.

The titration was done with 0.5M Fe^{2+} to a burgundy endpoint. The colour of the solution at the beginning was yellow-orange to dark green, depending on $Cr_2O_7^{2-}$ remaining , which shifts to a turbid gray before the endpoint and then changes sharply to a wine red at the endpoint. A magnetic stirrer was use to stir the solution during the titration.

A reagent blank was run using the above procedure without soil. The blank was used to standardize the Fe^{2+} solution daily.

The %C and %organic matter were then calculated.

% Easily oxidizable Organic C

$$\%C = \frac{(B - S) \times M \text{ of } Fe^{2+} \times 12 \times 100}{G \text{ of soil} \times 4000}$$

Where:

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

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

12/4000 = milli-equivalent weight of C in g

To convert easily oxidizable organic C to total C, divided by 0.77(or multiply by 1.30) or other experimentally determined correction factor. Total organic C is converted to organic matter using the following equation:

% Organic Matter(OM)

%OM = % total organic carbon x 1.72

3.7 Determination of pH

A 10g of soil samples was weighed into a beaker and 20ml distilled water added. The suspension was stirred for 15minutes using a glass rod and allowed to settle for 20minutes. A buffer solution of pH 4 and pH 7 was used to standardize the pH meter. The electrodes of the pH meter were inserted into supernatant and the pH of the samples was measured to the nearest 0.10. The electrodes of the pH were rinsed with distilled water before each reading. The pH of the various suspensions was recorded digitally by the pH meter. pH meter used was the Wissenschaftlich-Technische Werkstatten 8120 Weilheim i. OB.

3.8 Digestion of soil and plants

3.8.1 Acid digestion of soil

A 1.5g of soil sample was weighed into a previously acid washed labeled 100ml polytetraflouroethylene (PTFE) Teflon bombs.6ml of concentrated nitric acid (HNO_3, 65%), 3ml of concentrated hydrochloric acid (HCl,35%) and 0.25ml of hydrogen peroxide (H_2O_2,30%) was added to each sample in a fume chamber. The samples were then loaded on the microwave carousel. The vessel caps were secured tightly using a wrench. The complete assembly was microwave irradiated for 26minutes using milestone microwave labstation ETHOS 900, INSTR: MLS-1200 MEGA.

3.8.2. Acid digestion for plants

A 0.5g of vegetable sample was weighed into a previously acid washed labeled 100ml polytetraflouroethylene (PTFE) Teflon bombs.6ml of concentrated nitric acid (HNO_3, 65%), and 1ml of hydrogen peroxide (H_2O_2,30%) was added to each sample in a fume chamber. The samples were then loaded on the microwave carousel. The vessel caps were secured tightly using a wrench. The complete assembly was microwave irradiated for 25minutes using milestone microwave labstation ETHOS 900, INSTR: MLS-1200 MEGA.

3.9 Determination of heavy metals

After digestion the Teflon bombs mounted on the microwave carousel were cooled in a water bath to reduce internal pressure and allowed volatilized material to re- stabilize. The digestate was made up to 20ml with double distilled water and an analytical blank was prepared for each sample. A series of calibration solutions (standard) containing known amounts of analyte elements were also prepared and used to calibrate the VARIAN AA 240FS- Atomic Absorption Spectrometer AA240FS. Blanks were atomized followed by the standards and calibration graphs plotted showing response from the ASS. The concentrations were then calculated based on the absorbance obtained using the Beer Lambert law. Responses of standard were used to establish accurate performance of machine and accurate concentration values of elements. The machine was calibrated after every three analysis.

Light was generated from a hollow cathode lamp at wavelength characteristic to each analyte.

Each analyte were then atomized using an atomizer to create free atoms from the samples. Air-acetylene gas was used as the source of energy for the production of free atoms for the elements Zinc (Zn), Lead (Pb), Copper (Cu), Nickel (Ni), Chromium (Cr), Cadmium (Cd), and argon-acetylene gas for Mercury (Hg) and Arsenic (As) and nitrous oxide-acetylene for Tin(Sn). The sample was introduced as an aerosol into the flame and the burner aligned in the optical path to allow the light beam pass through the flame where the light was absorbed. The light was then directed into a monochromator which then isolates the specific analytical wavelength of the light emitted by the hollow cathode lamp from the non-analytical. The sensitive light detector then measures the light and translates the response into the analytical measurements.

Calculation of concentration of heavy metals were done using

$$\text{Final conc. (mg/L or mg/kg)} = \frac{\text{Conc.(analytical measurement)} \times \text{Nominal volume}}{\text{Sample weight in gramme}}$$

Where conc. = instrumental measurement
Nominal volume = final volume of digestate sample solution

Conc. (mg/kg) = concentration of metals in soil and plants.

3.9.1 Quality control and quality assurance

The following Quality Control and Quality Assurance techniques were used during the analysis.

Blanks: They were to check contamination during sample preparation.

Duplicates: To check the reproducibility of the method used.

Standards: To check the efficiency of the equipments being used.

Reference standards used for the elements of interest, blanks and duplicates of samples were digested the same conditions as the samples. These served as internal positive controls.

Reference standards used are from FLUKA ANALYTICAL, Sigma-Aldrich Chemie GmbH, product of Switzerland. Before the analysis, equipment were calibrated using the appropriate standards.

3.10 Geoaccumulation Index (Igeo)

The index of geoaccumulation (Igeo) is widely used in the evaluation of contamination by comparing the levels of heavy metal obtained to a background levels originally used with bottom sediments (Muller, 1969; Atiemo, 2011). It is calculated using the equation:

$\text{Igeo} = \log_2(\text{Cn} / 1.5\text{Bn})$

where Cn is the measured concentration of the heavy metal in soil being studied and Bn is the geochemical background concentration of the heavy metal (crustal average) (Taylor and Meclenan, 1985). The constant 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments (Lu *et al.,* 2009; Atiemo, 2011).

The following classification is given for geoaccumulation index (Muller, 1969; Huu *et al.*, 2010; Atiemo, 2011).

<0 = practically unpolluted, 0-1 = unpolluted to moderately polluted, 1-2 = moderately polluted,

2-3 = moderately to strongly polluted, 3-4 = strongly polluted, 4-5 = strongly to extremely polluted and >5 = extremely polluted.

3.11 Enrichment factor (EF)

Enrichment Factor (EF) of an element in the studied samples is based on the standardization of a measured element against a reference element. A reference element is often the one characterized by low occurrence variability such as Al, Fe, Ti, Si, Sr, K, Sn, etc. (Li *et al.*, 2001; Sezgin *et al.*, 2003, Duzgoren-Aydin, 2007, Ahiamadjie *et al.*, 2011). It is used to differentiate heavy metals originating from human activities and those of natural sources. This is determined by the relation:

$$EF = \frac{[C_x/C_{ref}]_{sample}}{[C_x/C_{ref}]_{background}}$$

Where C_x is the element of interest

C_{ref} is the concentration of reference element for normalization.

Values of EF above 5 are considered significant because EF below 5 may arise from difference in soil composition of local soil material and reference soil used in EF calculation (Sezgin *et al.*, 2003; Ahiamedjie *et al.*, 2011).

Five contamination categories are recognized on the basis of the enrichment factor: EF < 2 states deficiency to minimal enrichment, EF = 2-5 moderate enrichment, EF = 5-20 significant enrichment, EF = 20-40 very high enrichment and EF > 40 extremely high enrichment (Sezgin *et al.*, 2003; Duzgoren-Aydin *et al.*, 2006; Ahiamedjie *et al.*, 2011).

3.12 Pollution index (PI)

Pollution index and integrated pollution index are also commonly used to assess the environment quality (dos Anjos *et al.*, 2000). The PI is defined as the ratio of element concentration in the study to the background content of the abundance of chemical elements in the continental crust. The PI of each element is and classified as either low ($PI \leq 1$), middle ($1 < PI \leq 3$) or high ($PI > 3$).

3.13 Data Analysis

The data obtained was subjected to SPSS 16.0 and XLSTAT-2012 analysis. Correlation analysis was done to determine the association between soil heavy metals, pH, percentage Organic matter content, percentage organic carbon, K^+, Na^+, Ca^{2+} and Mg^{2+},

CHAPTER FOUR

RESULTS

4.1 Physicochemical Properties

4.1.1 pH of soils

The pH of the study site ranged from 3.21 to 8.26 as shown in fig. 4.1. The pH of the reclaimed zone (RZ) showed a declining pH with depth ranging from 3.21(RZ3) to 4.67 (RZ1) which corresponds to increasing acidity. The pH at the e-waste area shows an increasing pH with values ranging from 6.72 (EW1) to 7.18 (EW3) which represent a near acidic soil to neutral with depths. The Central gardens zone pH values ranges from 7.27 (GZ3) to 7.69 (GZ1) while the recreational area also showed a neutral to near basic soil with pH values ranging from 7.47 (KD1) to 7.80 (KD2). The Estuary and the control zone (CZ) ranged from 7.75 (ES1) to 8.26 (ES3) and 7.27 (CZ1) to 7.38 (CZ3) respectively.

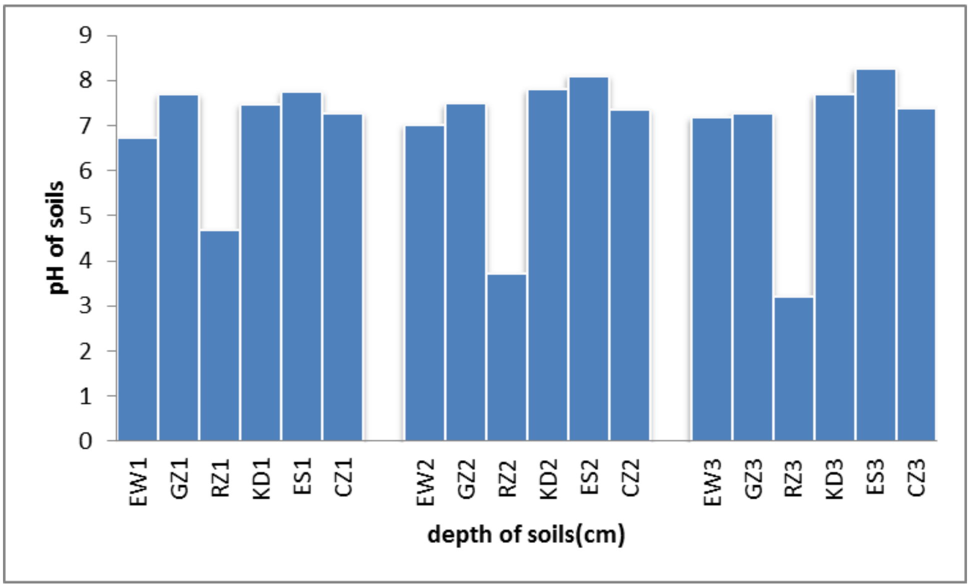

Fig.4.1: pH of soils at 0 – 60cm depth

4.1.2 Percentage organic matter

From the graph in fig. 4.1it can be observed that the general organic matter percentage recorded was low. The mean organic matter content recorded in the reclaimed area ranged from 0.63% (RZ3) to 1.40% (RZ1) which shows a decreasing pattern as the depth increases for all sites. The garden zone soil had low organic matter with values ranging from GZ3 (0.75%) to GZ1 (1.42%). In the EW site the organic matter ranged from 1.33% (EW2) to 2.51% (EW1) this show that the depth of 0 – 20 contains more organic matter and it drastically reduces with depth. The KD site recorded the lowest values ranging from 0.13% (KD1) to 0.40% (KD3).The LS site showed decreasing levels of OM with increasing depth ranging from 0.61% (ES3) to 1.13% (ES1) while the control area CZ showed the same pattern with values ranging from 0.75% (CZ3) to 1.25% (CZ1).From the results organic matter decreases with increasing depth, however the KD zone is an exception as it showed a different pattern .It can also be seen that the EW1 has the highest organic matter (OM) content whilst KD2 had the lowest.

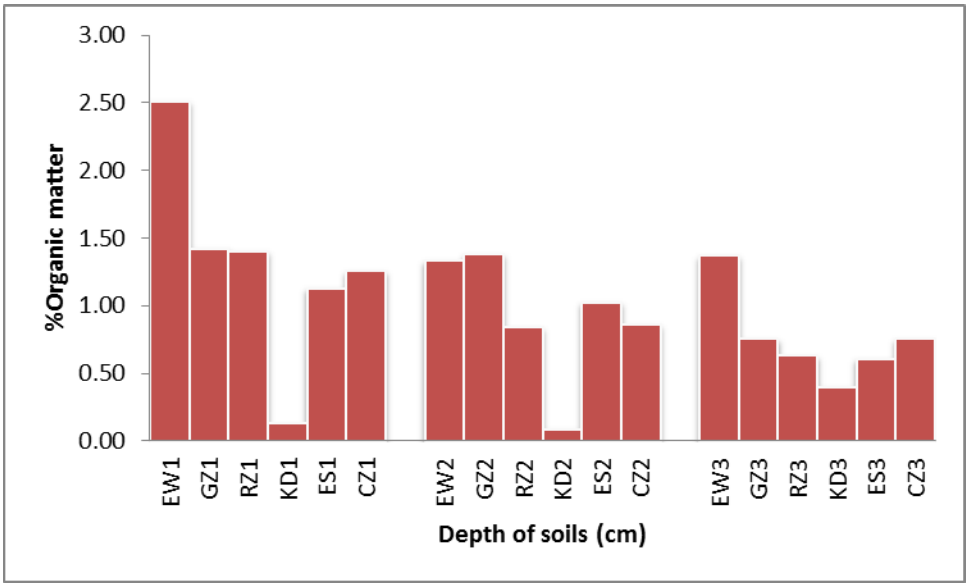

Fig. 4.2: Percentage organic matter content of soils at 0 – 60cm depth

4.1.3 Percentage organic carbon

From the graph in fig.4.3, it can be observed that at 0 – 20cm depth the EW1 recorded a mean percentage of 0.85%.The lowest mean percentage of organic carbon was recorded at ES1 zone with value of 0.38%. The mean percentage organic carbon of 0.47% was recorded at GZ2 as the highest observed and KD2 (0.03%) is the lowest for the depth of 20 – 40cm. Similarly, the mean percentage organic carbon for the 40 – 60cm depth in the sampling zones showed a lower amounts with EW3 (0.46%) and KD3 (0.13%) again being the lowest mean.

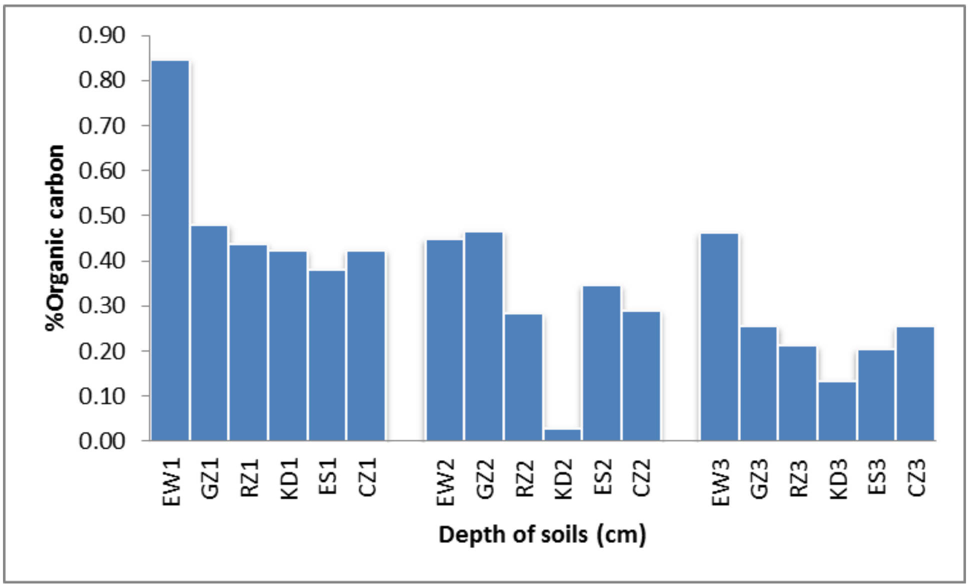

Fig. 4.3: Percentage organic carbon in soils at 0 – 60cm depth

4.2 Concentration of heavy metals at various depths at the research areas

4.2.1 Lead (Pb) concentrations in soils at various depths

In fig 4.4 it can be observed that at the depth of 0 - 20cm the concentrations recorded ranged from 1.28 to 183.66mg/kg with a mean value of 37.12mg/kg. EW1 recorded high concentration of Pb with mean value of 183.66mg/kg, followed by the KD1 with mean concentration of 17.41mg/kg. GZ1 recorded the lowest mean concentration of 1.28mg/kg. The soil texture was sandy loamy at that depth.

At 20 - 40cm depth the concentration of Pb recorded ranged from 1.12mg/kg to 167.96mg/kg with a mean value 32.13mg/kg. EW2 recorded the highest concentration of Pb with mean value of 167.96mg/kg. The estuary zone (ES2) had Pb mean concentration of 11.02mg/kg. The lowest concentration was observed at the GZ2 zone with a mean concentration of 1.12mg/kg. The soil texture at this depth is sandy loam.

At 40 - 60cm depth the overall concentrations of heavy metals in soils recorded ranged from 0.96 to 137.00mg/kg with mean value of 27.43mg/kg. The EW3 recorded the highest mean concentration of Pb with value 137.00mg/kg. ES3 also recorded Pb with mean concentration of 7.38mg/kg. The GZ3 recorded the lowest Pb concentration of with mean value of 0.96mg/kg. The control zone (CZ) also recorded the presence of this heavy metals at the various depths with mean concentrations of 4.39mg/kg, 4.88mg/kg and 4.16mg/kg corresponding to the depths of 20cm 40cm and 60cm respectively. The soil type in this zone is Sandy loamy texture.

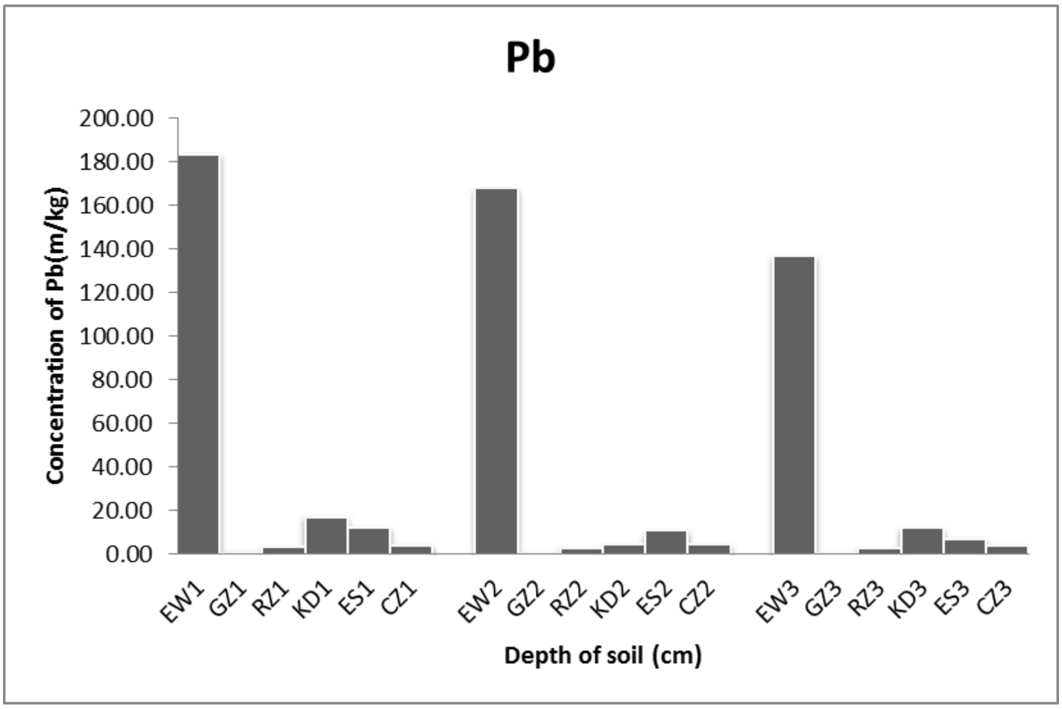

Fig.4.4: Lead (Pb) concentration (mg/kg) in soils at 0 – 60 cm depth

4.2.2 Copper (Cu) concentrations in soils at various depths

In fig.4.5 it can be observed that at0 - 20cm depth, the mean concentrations recorded ranged from 3.47 to 203.00mg/kg with a mean value of 38.80mg/kg. EW1 recorded the highest mean concentration of 203.00mg/kg. Additionally, the KD1 recorded mean concentration of 10.90 mg/kg. The lowest mean concentration of 3.47mg/kg of Cu was recorded at the GZ1. The overall concentration of Cu at the 20 - 40cm depth ranges from 2.57 to 200.00mg/kg with a mean value of 37.00mg/kg. EW2 have the highest mean concentration of 200.00mg/kg. The least mean concentration of 2.57 mg/kg was recorded at the GZ2. At depth of 40 - 60cm the overall concentration ranged from 1.49 to 98.66mg/kg with a mean value of 20.03mg/kg. EW3 recorded the highest mean concentration of 98.66mg/kg. The KD3 recorded mean concentration of 9.12mg/kg and RZ3 recorded the lowest concentration of 1.49mg/kg. The CZ recorded mean concentrations of 5.20mg/kg, 4.33mg/kg and 4.11mg/kg at depths of 20cm, 40cm and

60cm respectively and this showed that the concentrations of Cu in the soil decreased with depth.

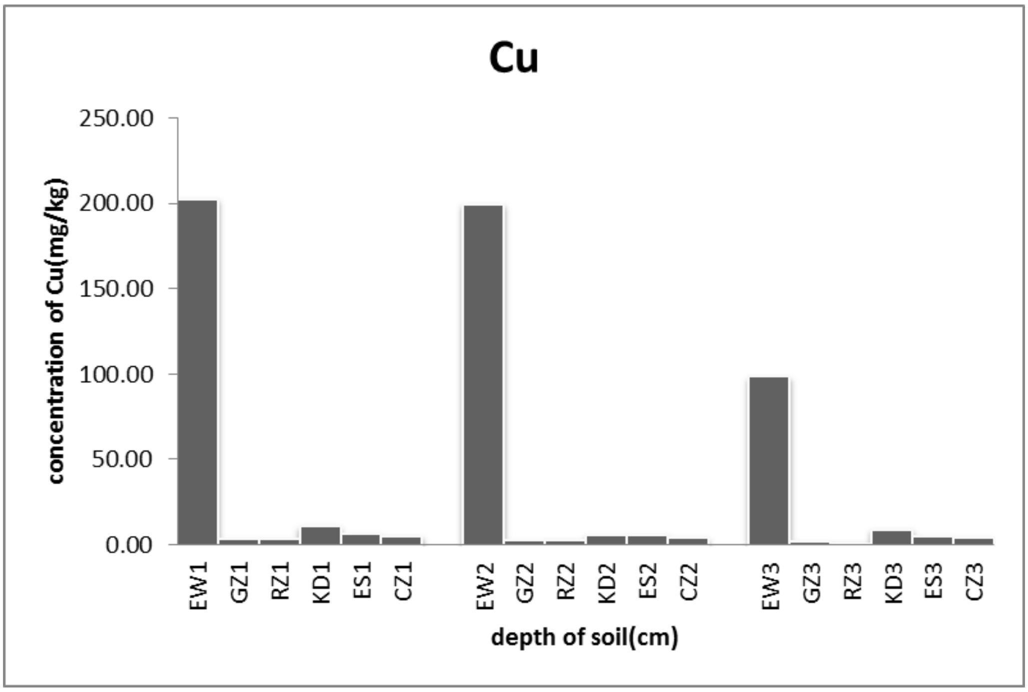

Fig. 4.5: Copper (Cu) concentration (mg/kg) in soils at 0 – 60cm depth

4.2.3 Zinc (Zn) concentrations in soils at various depths

In Fig.4.6 the graph shows that EZ had the highest Zn concentration with values ranging from 0.83 to 37.33mg/kg with a mean value of 8.68mg/kg. The corresponding exchangeable cations content were K^+(1.52), Na^+(6.15), Ca^{2+}(97.87) and Mg^{2+}(73.40).The highest percentage mean of OC and OM recorded were 3.36%and 5.78% respectively. KD1 had a mean concentration of 6.33mg/kg which also recorded high exchangeable cations values of K^+(1.33), Na^+(5.41), Ca^{2+}(17.60) and Mg^{2+}(13.20) which affects the leaching of heavy metals greatly and the OM mean percentage was also observed to be 0.38%. The lowest mean concentration of Zn was observed at the RZ1 with value of 1.03mg/kg even though it had the highest OM mean percentage of 3.13% and exchangeable cations with K^+(1.52), Na^+(6.40), Ca^{2+}(15.46) and Mg^{2+}(11.60). At the CZ1, the mean concentration of Zn of depth 20cm recorded was 2.05mg/kg which was higher than lowest mean concentration that is at the RZ1.

At the depth of 20 - 40cm the overall concentration of Zn ranges from 0.73 to 34.32mg/kg with a mean value of 7.01mg.kg. EW2 recorded the highest mean concentration of 34.32mg/kg with exchangeable cations values of K^+(1.27), Na^+(3.77), Ca^{2+}(53.86) and Mg^{2+}(40.40).High OC and OM mean percentages of 1.86 % and 3.20% respectively were recorded. KD2 zone recorded a mean concentration of 2.33mg/kg with exchangeable cations of K^+(0.96), Na^+(2.79), Ca^{2+}(26.00) and Mg^{2+}(19.50).The sandy loamy soil of the GZ2 recorded mean concentration of 0.73mg/kg with exchangeable cations of K^+(1.32), Na^+(3.69), Ca^{2+}(8.40 and Mg^{2+}(66.30) and OM mean percentage of 1.48% and OC mean percentage of 0.78%.

At the 40 - 60cm depth Zn recorded an overall concentration ranging from 0.52 to 27.66mg/kg with a mean value of 6.35mg/kg. EW3 recorded the highest mean concentration of 27.66mg/kg, KD3 also recorded a mean concentration of 4.75mg/kg and the Garden zone again having the least mean concentration of 0.52mg/kg. The concentration of Zn at the CZ3 at a depth of 20cm had a mean concentration of 2.05mg/kg which was the fourth highest concentration of Zn in all the sampling areas. Even though the values recorded were not up to the critical value the EW recorded higher concentration which may be due to the burning of electronic waste in the zone.

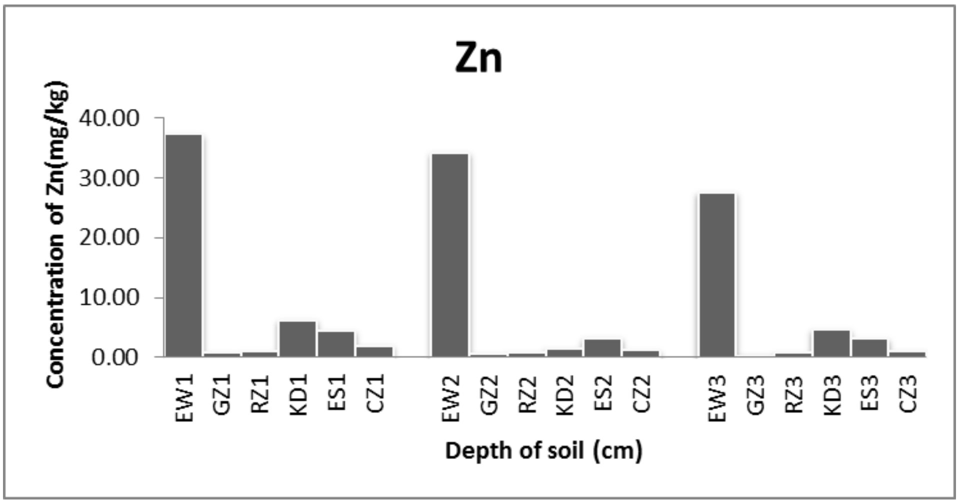

Fig. 4.6: Zinc (Zn) concentration(mg/kg) in soils at various depth

4.2.4 Chromium (Cr) concentrations in soils at various depths

In fig. 4.7 it can be observed that at the depth of 0 - 20cm the concentration of Cr ranged from 2.28 to 56.00mg/kg with a mean value of 11.55mg/kg. EW1 recorded the highest mean concentration of 56.00mg/kg and GZ1 recorded a mean concentration of 3.03mg/kg. CZ1 recorded the least with mean concentration of 2.28mg/kg.

At 20 - 40cm depth the overall concentration ranged from 0.11 to 49.99mg/kg with a mean value 10.07mg/kg. The highest mean concentration was observed at the EW2 zone with mean concentration of 49.99mg/kg and the lowest recorded at CZ2 with mean concentration of 0.11mg/kg.

The depth of 40 - 60cm also showed the presence of this element with overall concentrations ranging from 1.13 – 52.67mg/kg with mean concentration of 10.60mg/kg. EW3 recorded the highest mean concentration of 53.00mg/kg and the RZ3 had the lowest mean concentration of 1.13mg/kg. The concentration of Cr in the various depths generally increased with increasing depth. The CZ2 at the depth of 40cm had the lowest mean concentration across all the various sampling depths.

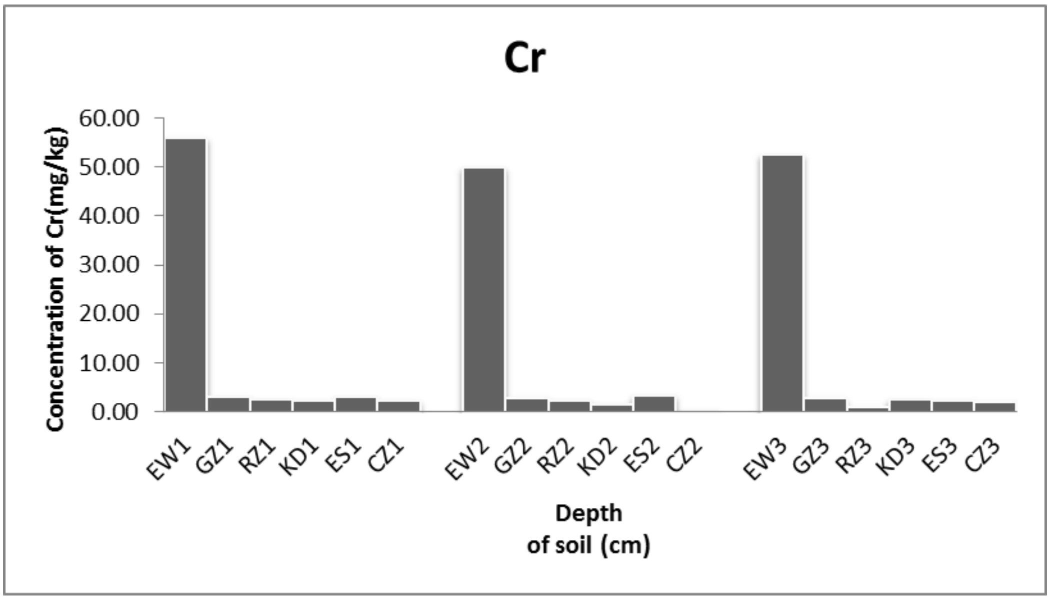

Fig. 4.7: Chromium (Cr) concentration (mg/kg) in soils at various depths.

4.2.5 Cadmium (Cd) concentrations in soil at various depths

In fig. 4.8 below, it can be observed that the overall Cd concentration at the depth of 0 - 20cm ranges from <0.001 to 103.66mg/kg with a mean value of 18.64mg/kg. It was observed from the results that the EW1 recorded the highest mean concentration of 103.66mg/kg followed by the RZ1 which recorded mean concentration of 4.35mg/kg. The lowest concentration was observed at the CZ1 with mean concentration beyond detectable limit <0.001mg/kg at the 20cm depth.

At the 20 - 40cm depth the concentration of the element ranges from 0.04 to 90.31mg/kg with a mean value of 16.22mg/kg. High concentration of the element was recorded at the EW2 with mean concentration of 90.31mg/kg and RZ2 with mean concentration of 3.77mg/kg and the least was detected at the ES1with mean concentration of 0.04mg/kg.

The 40 - 60cm depth recorded concentrations ranging from 0.04 to 68.32mg/kg with a mean value of 12.51mg/kg. The EW3 and RZ3 recorded mean concentrations of 68.32mg/kg and 3.73mg/kg respectively. The ES3 recorded the least mean concentration of 0.04mg/kg. It was further observed that the cadmium levels were very low at the KD, ES and CZ zones across the various sampling depth.

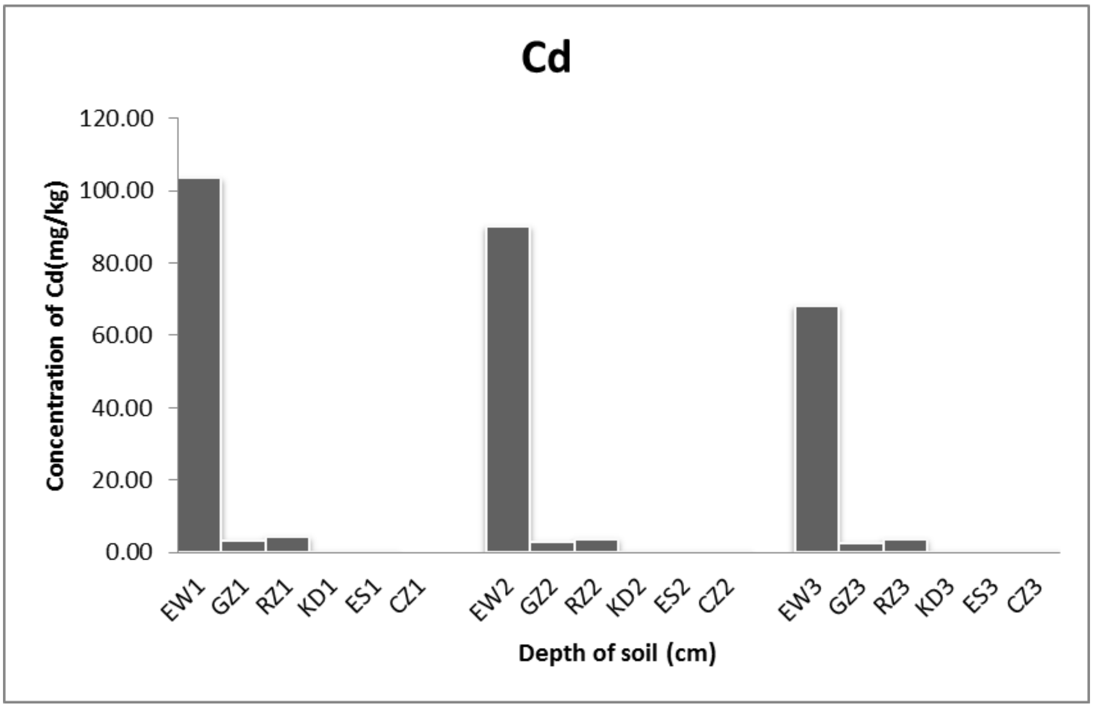

Fig. 4.8: Cadmium (Cd) concentration in soils from 0 – 60cm depth

4.2.6 Arsenic (As) concentrations in soils at various depths

In fig. 4.9 below, it can be observed that the depth 0 - 20cm at all sites recorded concentrations ranging from 0.04 to 3.67mg/kg with mean value of 1.09mg/kg. The highest As mean concentration was recorded at the EW1 with a value of 3.67mg//kg followed by the KD1 with a mean concentration of 1.41mg/kg. The least was recorded at RZ1 with a mean concentration of 0.04mg/kg.

At the depth of 20 - 40cm the concentration of As at all sites ranged from 0.21 to 15.66mg/kg with mean value of 2.97mg/kg. The highest value was recorded at the EW2 with a mean concentration of 15.66mg/kg followed by the KD2 with mean concentration of 0.85mg/kg. The least value recorded was at the ES2 zone with a mean concentration of 0.21mg/kg.

Similarly, 40 - 60cm depth, concentrations at all sites ranged from 0.21 to 11.00mg/kg with mean concentration of 2.26mg/kg. EW3 again showed a higher presence of the heavy metal with a mean concentration of 11.00mg/kg followed by KD3 recording a mean concentration of 1.08mg/kg and the least was recorded at RZ3 with mean concentration of 0.21mg/kg. The control zone also recorded 0.49mg/kg at depths 40 - 60cm.

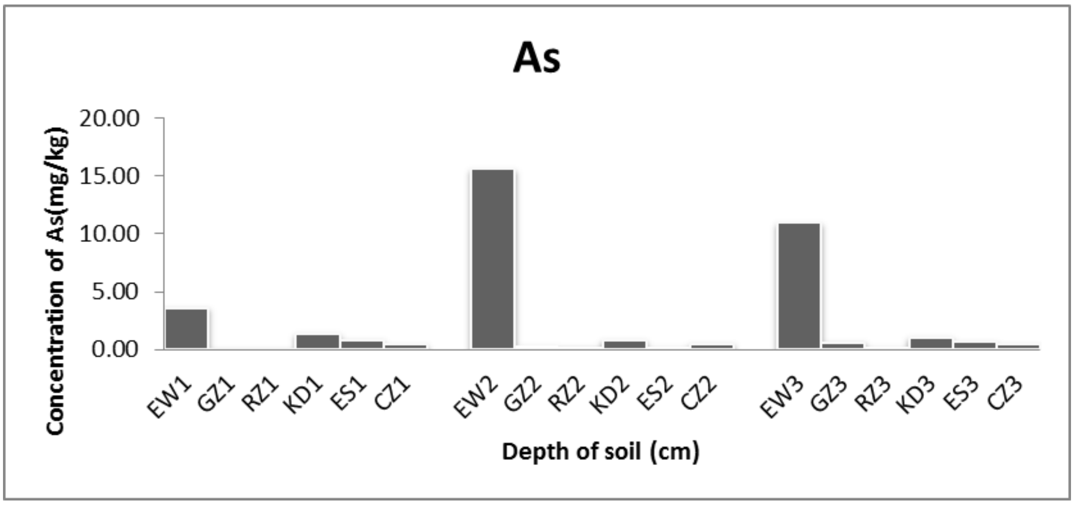

Fig.4.9: Arsenic (As) concentration (mg/kg) in soils from 0 – 60cm depths

4.2.7 Nickel (Ni) concentrations in soil at various depths

In figure 4.10 below, it can be observed that at 0 - 20cm depth the concentrations recorded ranged from 0.91mg/kg to 72.00mg/kg with a mean value of 13.60mg/kg. EW1 recorded the highest concentration of Ni with mean concentration of 72.00mg/kg followed by the KD1 with concentration of 4.56mg/kg. The least mean concentration was recorded at GZ1 with mean concentration of 0.91mg/kg.

At the depth of 20 - 40cm the recorded concentration at all sites ranged from 0.84 to 67.32mg/kg. The highest mean concentration of Ni recorded was 67.32mg/kg at the EW2 followed by the KD2 with a mean concentration of 2.15mg/kg. The least recorded value was 0.84mg/kg at the GZ2. At the depth of 40 - 60cm, Ni recorded concentrations ranging from 0.55 to 66.65mg/kg with the highest mean concentration 66.65mg/kg recorded at EW3 followed by KD3 with a mean value of 4.37mg/kg. The least mean concentration of 0.55mg/kg was recorded at the GZ3. The GZ zone recorded the lowest concentrations of Ni in all the various depth and consistently showed a decreasing amount with increasing depth. The control zone showed an increasing concentration of Ni with increasing depth. The mean concentrations of 1.09mg/kg, 1.20mg/kg and 1.59mg/kg at depths of 20cm, 40cm and 60cm respectively were recorded.

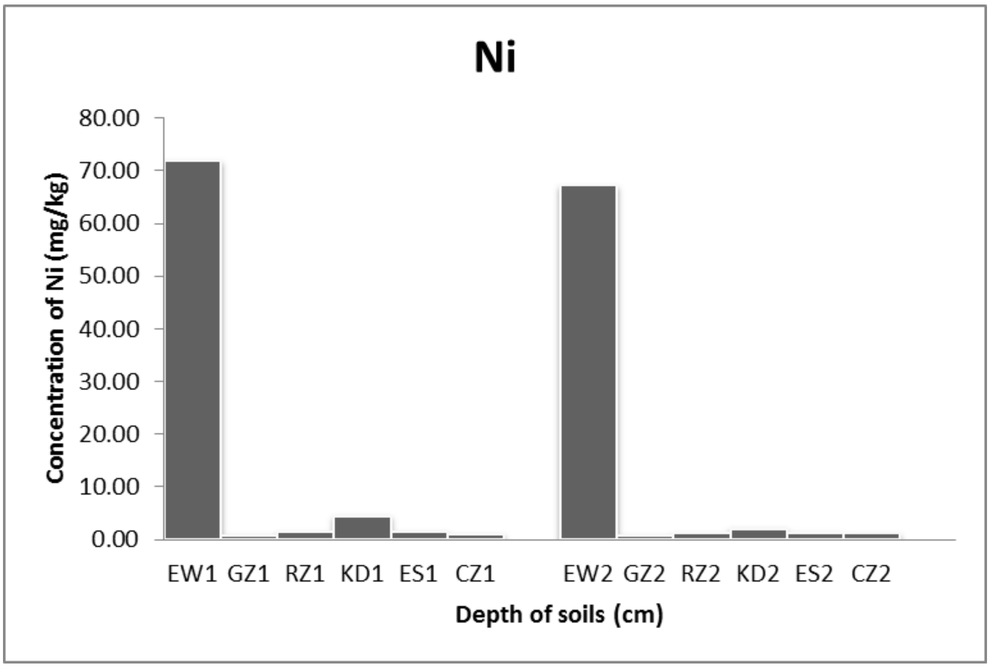

Fig.4.10: Nickel (Ni) concentration (mg/kg) in soils at depth 0 – 60cm

4.2.8 Mercury (Hg) concentrations in soil at various depths

Figure 4.11 presents Hg concentrations for all depths at all sites. From the graph, it can be observed that at the depth 0- 20cm, the concentration of Hg ranged from <0.001 – 0.667.

The EW1 recorded the highest mean concentration of 0.667 followed by the KD1 zone with mean concentration of 0.04mg/kg. The rest recording values below detectable figures.

At 20 - 40cm depth, the concentration of Hg ranges from <0.001 – 0.667 mg/kg with a mean value of 0.25mg/kg. The highest mean concentration 0.667mg/kg was at EW2 followed by GZ2 with mean concentration of 0.04mg/kg. RZ2 recorded the least value of 0.01mg/kg. No Hg was detected at the sampling depth 60cm at all sites.

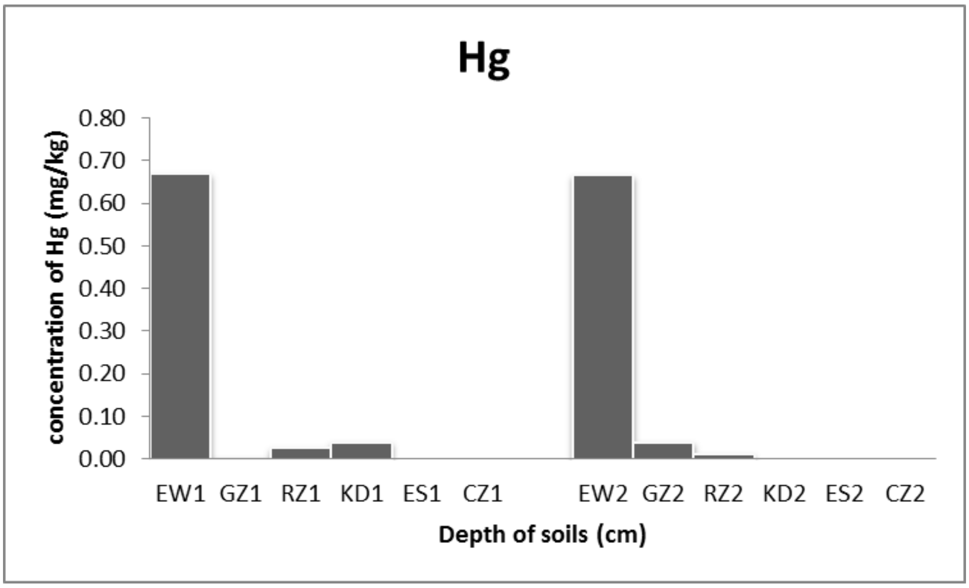

Fig. 4.11: Mercury (Hg) concentration (mg/kg) in soils at depths 0 – 60cm

4.2.9 Tin (Sn) concentrations in soils at various depths

In fig. 4.12 below, it can be observe that at the 0 - 20cm depth the concentration of Sn ranged from 8.77 to 705.32mg/kg with a mean value of 132.86mg/kg. The EW1 recorded the highest mean concentration of 705.32mg/kg and the lowest recorded at the CZ1 with a mean concentration of 8.77mg/kg.

At 20 - 40cm depth, the concentration of Sn ranged from 9.04 to 695.16 mg/kg. EW2 zone again recorded the highest mean concentration of 695.16mg/kg followed by GZ2 with mean concentration of 26.72mg/kg with CZ2 area recording the least mean concentration value of 9.04mg/kg.

The 40 - 60cm depth recorded concentrations ranging from 8.67 to 334.25mg/kg.EW3 recorded the highest mean concentration of 332.25mg/kg. GZ3 recorded a mean concentration of 16.73mg/kg followed by 15.13mg/kg representing the RZ3 and the lowest mean concentration of 9.04mg/kg was recorded at the control zone.

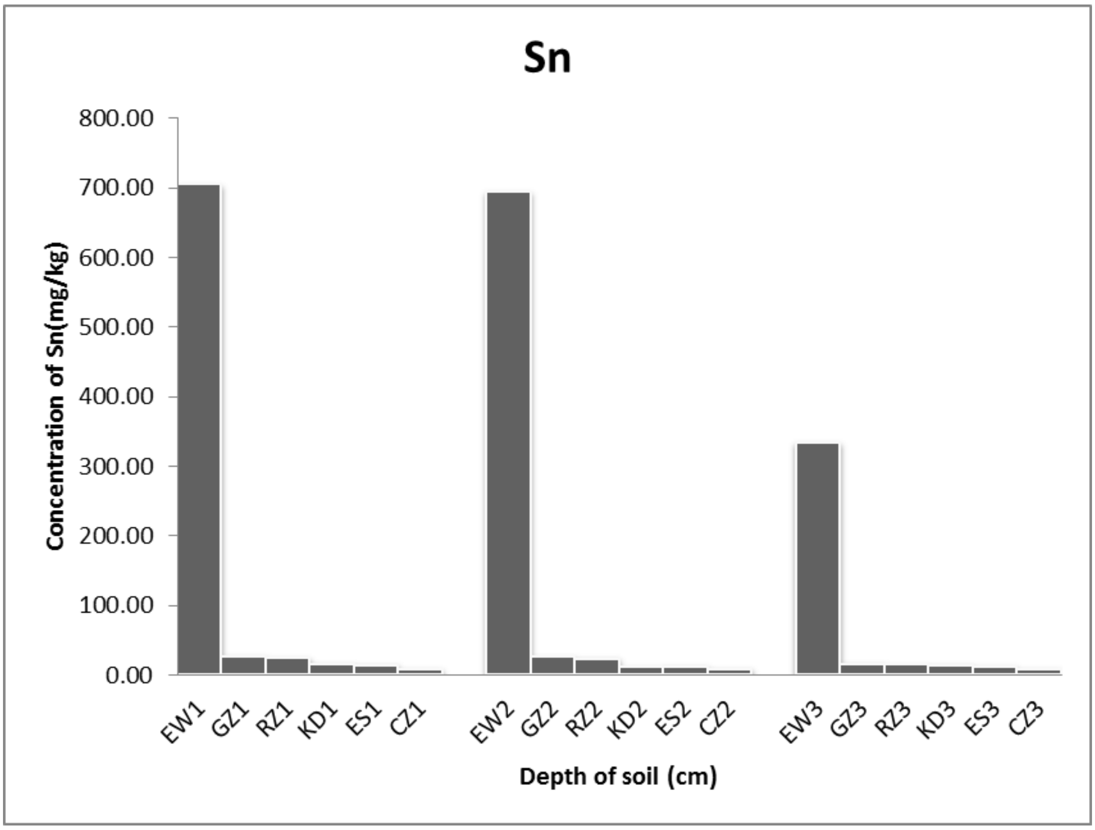

Fig.4.12: Tin (Sn) concentrations (mg/kg) in soils at various depth

4.3 Geoaccumulation Index (Igeo)

In appendix 8 it can be observed that the Igeo values recorded at a depth of 0 - 20cm for Hg ranges from -5.322 to 2.474 with a mean value of -1.100. Lead value ranges from -3.873 to 3.292 while Cu values ranged from -4.573 to 1.299.Similarly, Zn recorded values ranging from -6.989 to -1.492 and Cr values ranging from -6.040 to -1.421. Cadmium values ranges from -2.907 to 8.433 while Ni values ranges from -6.955 to -0.644.The values for Tin ranges from 1.548 to 7.877 with As values ranging from -6.077 to 0.441.The mean values of Igeo increases in the order of Cr < Ni < Zn < Cu < As < Cd < Pb < Hg < Sn.

It can be observed from appendix 9, that at depth 20 - 40cm Hg Igeo values ranges from -3.170 to 2.474 while that of Pb ranges from -4.065 to 3.163. Copper had values ranging from -5.003 to 1.277 with Zn recording values ranging from -7.162 to -1.613.Cadmium had values ranging from -10.458 to -1.585 with Cd values ranging from -2.907 to 8.234.Nickel values ranges from -7.065 to -0.741 with Sn values ranging from 1.591 to 7.856 while As had values ranging from -3.662 to 2.536.The mean values of Igeo increase in the order of Zn < Ni < Cu < As < Pb < Hg < Cr < Sn < Cd.

In appendix 10, it can be observed at depth of 40 - 60cm that Hg recorded no value for Igeo. Lead had values ranging from -4.288 to 2.887 while Cu recorded values ranging from -5.788 to 0.258 with Zn values ranging from -7.658 to -1.925.Chromium values ranges from -7.048 to -1.510 with Cd values ranging from -2.907 to 7.831.Similarly, Ni values ranges from -7.685 to -0.755Sn values ranging from 1.530 to 6.800. The Igeo values for As ranges from -3.662 to 2.026.The mean values of Igeo increases in order of Zn < Cr < Ni < Cu < As < Pb < Hg < Sn < Cd.

4.4 Enrichment factor (EF)

The EF values recorded at a depth of 0 - 20cm in appendix 8 shows that for Hg values range from 0.000 to 0.061 with a mean value of 0.019.Lead values ranges from 0.008 to 0.169 with a mean value of 0.076while Cu values ranging from 0.005 to 0.024 with a mean value of 0.014.Zinc values ranges from 0.001 to 0.011 with mean values 0.005. Cr values ranges from 0.002 to 0.005 with mean value of 0.003. Cd values ranges from 0.000 to 1.759 with a mean value of 0.784. Ni values ranges from 0.001 to 0.007 with mean value of 0.003. Sn values ranges from 1.000 to 1.000 with a mean value 1.000 and As values ranges from 0.002 to 0.095 with a mean value of 0.039. The mean EF values increases in the order of Cr = Ni < Zn < Cu<Hg< As < Pb < Cd < Sn.

At a depth of 20 - 40cm EF values recorded in the appendix 9 shows that Hg ranges from 0.000 to 0.030 with a value 0.013, Pb ranges 0.007 to 0.136 with a mean value of 0.059. Cu ranges from 0.004 to 0.018 with a mean of 0.012. Zn ranges from 0.001 to 0.007 with a mean value of 0.003. Cr ranges from 0.000 to 0.005 with a mean value of 0.002. Cd ranges from 0.031 to 1.567 with a mean value 0.696. Ni ranges from 0.001 to 0.005 with a mean value of 0.003. Sn ranges from 1.000 to 1.000 with a mean value of 1.000 and As ranges from 0.012 to 0.081 with a mean value of 0.036. The mean EF values increases in the order of Cr < Ni = Zn < Cu < Hg < As < Pb < Cd < Sn. The mean EF values falls within the deficiency to minimal enrichment category since all the mean values have EF < 2.

From appendix 10, 40 - 60cm depth recorded EF values for Hg ranges from 0.000 to 0.000 with mean of 0.000. Pb values ranges from 0.009 to 0.133 with mean value of 0.069. Cu values range from 0.004 to 0.023 with mea value of 0.012. Zn values ranges from 0.001 to 0.009 with mean value of 0.004. Cr values ranges from 0.001 to 0.005 with a mean value of 0.003. Cd values ranges from 0.033 to 2.467 with mean value of 1.060. Ni values ranges from 0.001 to 0.008 with a mean value of 0.004. Sn values ranges from 1.000 to

1.000 with a mean value of 1.000 and As values ranges from 0.016 to 0.082 with a mean value of 0.051. The mean EF values increases in the order of Hg < Cr < Zn < Ni < Cu < As < Pb < Sn < Cd.

4.5 Pollution Index (PI)

It can be observed from appendix 8 that at the depth of 0 - 20cm PI values ranges from 0.000 to 8.333 with mean value of 1.534 for Hg and Pb values ranging from0.102 to 14.693.Copper values ranges from 0.063 to 3.691 with mean value of 0.705 while Zn values ranges from 0.012 to 0.533 with mean value of 0.124. Chromium values ranges from 0.023 to 0.560 with mean values of 0.115. Cd values ranges from 0.000 to 518.320 with mean value of 93.187. Ni values ranges from 0.012 to 0.960 with mean values of 0.181. Sn values ranges from 4.386 to 352.658 with mean values of 66.432 and As values ranges from 0.022 to 2.037 with mean value of 0.691. The PI values increase in the order Cr < Zn <Ni < As < Cu < Hg < Pb < Sn < Cd.

At a depth of 20 - 40cm it can be observed from appendix 9 that PI values for Hg ranges from 0.000 to 8.331 with mean value of 1.500. Pb values ranges from 0.090 to 13.437 with mean value of 2.571. Cu values ranged from 0.047 to 3.636 with mean value of 0.673. Zn values ranges from 0.010 to 0.490 with mean value of 0.100. Cr values ranges from 0.001 to 0.500 with mean values of 0.101. Cd values ranged from 0.200 to 451.554 with mean value of 81.114 and Ni values ranged from 0.011 to 0.898 with mean values of 0.165. Sn values ranges from 4.519 to 347.580 with mean values of 64.974 and As values ranged from 0.118 to 8.702 with mean value of 1.650. The PI values increase in the order Zn < Cr < Ni < Cu < Hg < As < Pb < Sn < Cd.

At a depth of 40 - 60cm it can be observed from appendix 10, that PI values for Hg ranges from 0.000 to 0.000 with mean value of 0.000. Pb values ranged from0.077 to 10.960 with mean value of 2.195and Cu values ranged from 0.027 to 1.794 with mean value of 0.364. Zn values ranged from 0.007 to 0.395 with mean value of 0.091 and Cr values ranged from 0.011 to 0.527 with mean values of 0.106. Cd values ranged from 0.200 to 341.581 with mean value of 62.530 and Ni values ranged from 0.001 to 0.889 with mean values of 0.169. Sn values ranges from 4.332 to 167.125 with mean values of 33.464 and As values ranged from 0.119 to 6.110 with mean value of 1.312. The PI values increase in the order Hg < Zn < Cr < Ni < Cu < As < Pb < Sn < Cd.

4.6 Correlation of heavy metals concentration and physicochemical properties

From the correlation of heavy metals concentration (mg/kg) at depth 0 – 20 cm in the appendix 5, it was observed that all the heavy metals (Cu and Ni, Cr and Sn, and Cd and Sn) recorded had strong positive correlation at this depth as all recording a near perfect correlation (0.995). Arsenic and Cadmium recorded a very strong positive correlation with a value of 0.911. This value was however the least recorded amongst the heavy metals. The heavy metals and the pH recorded weak positive correlation with Hg and pH (0.462), Pb and pH(0.453), Cd and pH(0.444),As and pH(0.499). Sn and pH(0.448), pH and %OM(0.012), pH and K^+(0.917), pH and Na^+(0.775), pH and Ca^{2+}(0.343) and pH and Mg^{2+}(0.342). All the metals recorded negative values for their correlation with %OC. Mercury and %OC (-0.187), Pb and %OC(-0.222), Cu and %OC(-0.190), Zn and %OC(-0.258), Cr and %OC(-0.165), Cd and %OC(-0.144), Ni and %OC(-0.190), Sn and %OC(-0.155), As and %OC(-0.374).The Correlation between %OC and physicochemical parameters recorded strong positive correlation with the exception of %OC and pH(0.403); %OC and %OM(0.794), %OC and K^+(0.524), %OC and Na^+(0.582), %OC and Ca^{2+} (0.930) and %OC and Mg^{2+}(0.929). %OM and Hg(0.022), %OM and Pb(-0.014), %OM and Cu(0.031), %OM and Zn(-0.070), %OM and Cr(-0.070), %OM and

Cd(0.090), %OM and Ni(0.021), %OM and Sn (0.074), %OM and As(-0.271), %OM and K^+(0.211), %OM and Na^+(0.453), %OM and Ca^{2+}(0.723) and %OM and Mg^{2+}(0.721). K^+ and the heavy metals recorded significant positive correlation, K^+ and Hg(0.528), K^+ and Pb(0.514), K^+ and Cu(0.517), K^+ and Zn(0.517), K^+ and Cr(0.515), K^+ and Cd(0.523), K^+ and Ni(0.525), K^+ and Sn(0.524) and K^+ and As(0.503), K^+ and Na^+(0.921), K^+ and Ca^{2+}(0.498) and K^+ and Mg^{2+}(0.497). Na^+ recorded significant positive correlation with the heavy and the physicochemical parameters. Na^+ and Hg(0.577), Na^+ and Pb(0.573), Na^+ and Cu(0.582), Na^+ and Zn(0.566), Na^+ and Cr(0.592), Na^+ and Cd(0.595), Na^+ and Ni(0.583), Na^+ and Sn(0.596), Na^+ and As (0.511), Na^+ and Ca^{2+}(0.620) and Na^+ and Mg^{2+}(0.620). Ca^{2+} recorded weak negative correlation with all the heavy metals but had strong positive correlation with the physicochemical parameters with the exception of K^+.Ca^{2+} and Hg(-0.243), Ca^{2+} and Pb(-0.253), Ca^{2+} and Cu(-0.233), Ca^{2+} and Zn(-0.273), Ca^{2+} and Cr(-0.211), Ca^{2+} and Cd(-0.202), Ca^{2+} and Ni(-0.236), Ca^{2+} and Sn(-0.206), Ca^{2+} and As(-0.340) and Ca^{2+} and Mg^{2+}(0.995). Mg^{2+} recorded weak negative correlation with all the heavy metals but had strong positive correlation with the physicochemical parameters with the exception of K^+. Mg^{2+} and Hg(-0.244), Mg^{2+} and Pb(-0.254), Mg^{2+} and Cu(-0.235), Mg^{2+} and Zn(-0.274), Mg^{2+} and Cr(-0.212), Mg^{2+} and Cd(-0.204), Mg^{2+} and Ni(-0.238), Mg^{2+} and Sn(-0.208), Mg^{2+} and As(-0.341).

From the correlation of heavy metal concentration (mg/kg) at the depth 20 – 40 cm in appendix 6, it can be observed that all the heavy metals recorded strong positive correlation above 0.994 among themselves with Ni and Cu, Ni and As, Cd and Sn and Zn and Pb recording near perfect positive correlation (0.995). pH recorded significant positive correlation with the heavy metals, K^+ and Na^+ , the rest of the physicochemical parameters recorded were negative and weak positive correlated. pH and Hg(0.606), pH and Pb(0.583), pH and Cu(0.595), pH and Zn(0.586), pH and Cr(0.607), pH and Cd(0.593), pH and Ni(0.599), pH and Sn(0.597), pH and As(0.608),pH and %OC(-0.457), pH and %OM(-0.457), pH and K^+(0.530), pH and Na^+(0.924), pH and Ca^{2+}(0.277), pH and Mg^{2+}(0.277). Percentage OC and the heavy metals recorded a negative correlation, perfect positive correlation with %OM(0.995) and weak positive correlation with the physicochemical parameters with the exception of Na^+(-0.426). Percentage OC and heavy metals were, % OC and Hg(-0.051), %OC and Pb(-0.096), %OC and Cu(-0.098), %OC and Zn(-0.098), %OC and Cr(-0.062), %OC and Cd(-0.053), %OC and Ni(-0.100), %OC and Sn(-0.068), %OC and As(-0.121),%OC and K^+(0.249), %OC and Na^+(-0.426), %OC and Ca^{2+}(0.308), %OC and Mg^{2+}(0.308). The correlation between the heavy metals and the physicochemical parameters recorded same values as recorded in the case of the %OC. K^+ and the heavy metals recorded weak positive correlation and weak positive correlation with the physicochemical parameters with the exception of pH(0.530) and Na^+(0.568). K^+ and Hg(0.183), K^+ and Pb(0.128), K^+ and Cu(0.143), K^+ and Zn(0.130), K^+ and Cr(0.188), K^+ and Cd(0.183), K^+ and Ni(0.150), K^+ and Sn(0.170), K^+ and As(0.141), K^+ and N^+(0.568), K^+ and Ca^{2+}(0.352) and K^+ and Mg^{2+}(0.352). Na^+ and heavy metals recorded strong positive correlations and the physicochemical parameters recorded weak negative correlation with the exception of K^+ (0.568). Na^+ and Hg(0.723), Na^+ and Pb(0.707), Na^+ and Cu(0.720), Na^+ and Zn(0.7060, Na^+ and Cr(0.726), Na^+ and Cd(0.723), Na^+ and Ni (0.726), Na^+ and Sn(0.723), Na^+ and As(0.733), Na^+ and Ca^{2+}(-0.055), Na^+ and Mag^{2+}(-0.055). Ca^{2+} and the heavy metals recorded weak negative correlation and weak positive correlation with the physicochemical parameters with the exceptions of Mg^{2+} which recorded a perfect correlation (0.995). Mg^{2+} and Hg(-0.169), Mg^{2+} and Pb(-0.227), Mg^{2+} and Cu(-0.221), Mg^{2+} and Zn(-0.219), Mg^{2+} and Cr(-0.183), Mg^{2+} and Cd(-0.202), Mg^{2+} and Ni(-0.222), Mg^{2+} and Sn(-0.201), Mg^{2+} and As(-0.226).

From the correlation of heavy metal concentration (mg/kg) at the depth 40 – 60 cm in appendix 7, it can be observed that all the heavy metals recorded almost near perfect correlation with the exception of Hg which recorded values beyond detectable limit at that depth, therefore had no correlation with the other heavy metals and the physicochemical parameters. Zn and Pb(0.997), Sn and Cr(0.995), Pb and Cu(0.995) and Ni and Cu(0.995). pH recorded weak negative correlation with the heavy metals and physicochemical parameters with the exception of K+(0.202), Ca^{2+}(-0.774) and Mg^{2+}(0.775). pH and Pb(-0.095), pH and Cu(-0.091), pH and Zn(-0.134), pH and Cr(-0.095), pH and Cd(-0.088), pH and Ni(-0.083), pH and Sn(-0.097), pH and As(-0.115), pH and %OC(-0.115), pH and %OM(-0.155), pH and Na^+(-0.242). %OM recorded weak negative correlation with the heavy metals and strong positive correlation with the physicochemical parameters with the exception Na+(-0.024). %OM and Pb(-0.244), %OM and Cu(-0.235), %OM and Zn(-0.300), %OM and Cr(-0.176), %OM and Cd(-0.149), %OM and Ni(-0.221), %OM and Sn(-0.175), %OM and As(-0.203), %OM and K+(0.672), %OM and Ca^{2+}(0.539) and %OM and Mg^{2+}(0.537). K^+ recorded weak negative correlation with the heavy metals and positive correlations with the physicochemical parameters with the exception of N^+(0.291). K^+ and Pb(-0.458), K^+ and Cu(-0.441), K^+ and Zn(-0.485), K^+ and Cr(-0.415), K^+ and Cd(-0.432), K^+ and Ni(-0.443), K^+ and Sn(-0.432), K^+ and As(-0.422), K^+ and Ca^{2+}(0.316) and K^+ and Mg^{2+}(0.314). Na+ recorded almost near perfect correlation with the heavy metals and weak negative correlation with the physicochemical parameters with the exception of Ca^{2+}(0.053) and Mg^{2+}(0.052). Na^+ and Pb(0.959), Na^+ and Cu(0.962), Na^+ and Zn(0.952), Na^+ and Cr(0.969), Na^+ and Cd(0.967), Na^+ and Ni(0.963), Na^+ and Sn(0.968), Na^+ and As(0.971). Ca^{2+} recorded weak negative correlation with the heavy metals but recorded a near perfect correlation with Mg^{2+}(0.995). Ca^{2+} and Pb(-0.124), Ca^{2+} and Cu(-0.120), Ca^{2+} and Zn(-0.111), Ca^{2+} and Cr(-0.093), Ca^{2+} and Cd(-0.114),

$Ca^{2+}$and Ni(-0.130), Ca^{2+} and Sn(-0.105), Ca^{2+} and As(-0.087). Mg^{2+} recorded weak negative correlation with the heavy metals but recorded positive correlation with the physicochemical parameters. Mg^{2+} and Pb(-0.124), Mg^{2+} and Cu(-0.120), Mg^{2+} and Zn(-0.111), Mg^{2+} and Cr(-0.093), Mg^{2+} and Cd(-0.155), Mg^{2+} and Ni(-0.131), Mg^{2+} and Sn(-0.105), Mg^{2+} and As(-0.088).

4.7 Concentration of heavy metals in vegetation

4.7.1 Forage grasses (*Imperata maximum and Panicum maximum*)

Forage grasses in all sampling zones recorded all the heavy metals under study with different concentrations as shown in fig. 4.13 with the exception of Hg which was below detectable limits. Forage grasses had roots which did not go beyond 20cm depth.

The EW forage grasses recorded the highest concentration of heavy metals due to the constant exposure of these grasses to the smoke that emanates from the burning of the electronic gadgets. The KD section has been corded off and some plants grown on them. The ES zone is currently not exposed to lot of insanitary activity. The control zone recorded the least concentration of this element with mean concentration of 0.16mg/kg. Forage grasses at the recreational zone (KD) recorded the highest mean concentration of 3.84mg/kg for Cr. The Estuary zone recorded a mean concentration of 3.52mg/kg and forage grasses at EW site recorded mean concentration of 1.56mg/kg. The control zones recorded concentration higher than that of the EW zone with a mean concentration of 2.20mg/kg.

The e-waste zone (EW) recorded the highest concentration (95.56mg/kg) of Cu in the forage grasses. This was followed by the KD with a mean concentration of 6.92mg/kg while mean concentration of 5.48mg/kg was recorded in forage grasses at ES. The elevated RZ zone recorded a mean concentration of 2.68mg/kg and the control zone recording the least exposure or presence of Cu in the forage with a mean concentration of 0.26mg/kg. The EW zone again recorded the highest concentration of Zn with mean concentration of 34.92mg/kg followed by the RZ zone with a mean concentration of 14.84mg/kg. The KD and ES recorded mean concentrations of 7.88mg/kg and 7.36mg/kg respectively. The control zone recorded the least concentration of Zn in the forage grasses with a mean concentration of 1.56mg/kg. The EW zone recorded the highest concentration of Pb in the forage grasses with mean concentration of 36.72mg/kg. This was followed by the ES zone forage grasses with a concentration 3.64mg/kg. The RZ recorded a mean concentration of 0.48mg/kg whilst the concentration of Pb at the KD zone was beyond detectable limit. The control zone recorded a mean concentration of 0.80mg/kg in the forage grasses and which can be attributed to the soil or running water used in watering the plants grown in the sampling zone.

The various sampling areas recorded some concentration of Ni in the forage grasses. The EW, KD and RZ recorded relatively equal mean concentration of Ni with values 2.00mg/kg, 2.20mg/kg and 2.28mg/kg respectively. The highest mean concentration was recorded at the ES zone with mean concentration of 6.80mg/kg. The control zone recorded the least mean concentration of 0.80mg/kg. Arsenic (As) concentration in the EW zone forage grasses was recorded as the highest with mean concentration of 0.32mg/kg followed by the ES zone forage grasses and the control zone all recording a mean concentration 0.16mg/kg each. The RZ zone recorded a mean concentration of 0.12mg/kg whilst the KD zone recorded the least mean concentration of 0.08mg/kg. Tin (Sn) in the forage grasses recorded showed that the EW zone recorded the highest with mean concentration of 22.00mg/kg and the minimum was recorded at the KD zone with a mean concentration of 2.52mg/kg. The concentration of Hg in the forage grasses was beyond detectable limits <0.001mg/kg.

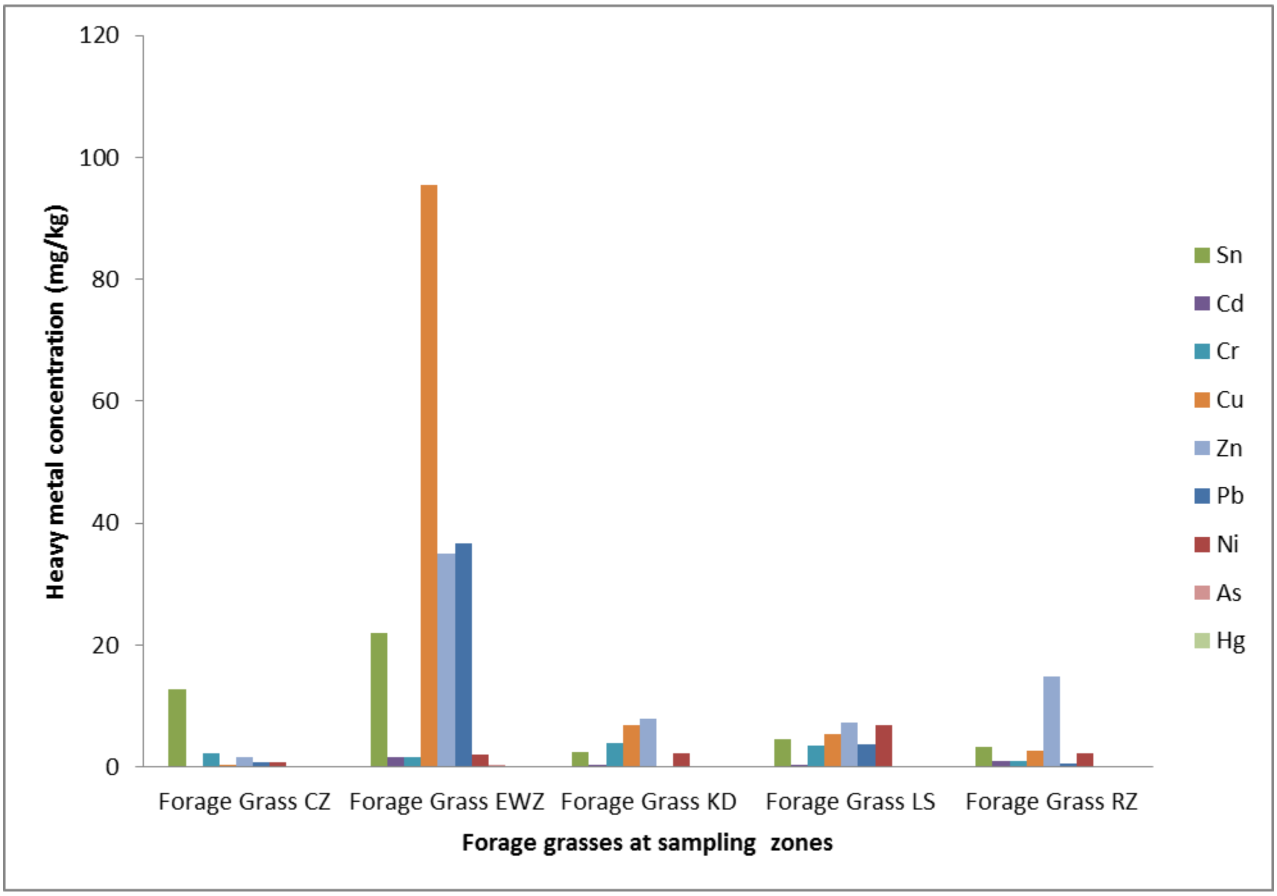

Fig. 4.13 Heavy metal concentration (mg/kg) in Forage grasses

4.7.2 Bissap (*Hibiscus sabdariffa*)

Bissap was analyzed from the Central garden zone (GZ) and the control zone (CZ). The concentrations of heavy metals recorded in Bissap from the central garden zone as shown in fig. 4.14were higher than those in the control zone with the exception of Pb and As which recorded values of 0.20mg/kg each. The central gardens zones recorded values below detectable limits. The mean concentration of heavy metals recorded at the GZ area are as follows Cd (0.64mg/kg), Cr(0.98mg/kg), Cu(4.40mg/kg), Zn (7.64mg.kg), Ni(1.84mg/kg), Sn(14.24mg/kg) and Hg(<0.001mg/kg) and the mean concentration of heavy metals at the CZ recorded were Cd(0.36mg/kg), Cr(0.24mg/kg), Cu(0.20mg/kg), Zn(1.16mg/kg), Ni(0.46mg/kg) and Hg(<0.001mg/kg). Mean concentrations of heavy metals recorded in forage grasses at the control zone were Sn(28.52mg/kg), Cd(0.36mg/kg), Cr(0.24mg/kg), Cu(0.20mg/kg), Zn(1.16mg/kg), Pb(0.20mg/kg), Ni(0.46mg/kg), As(0.20mg/kg) and Hg(0.08mg/kg).

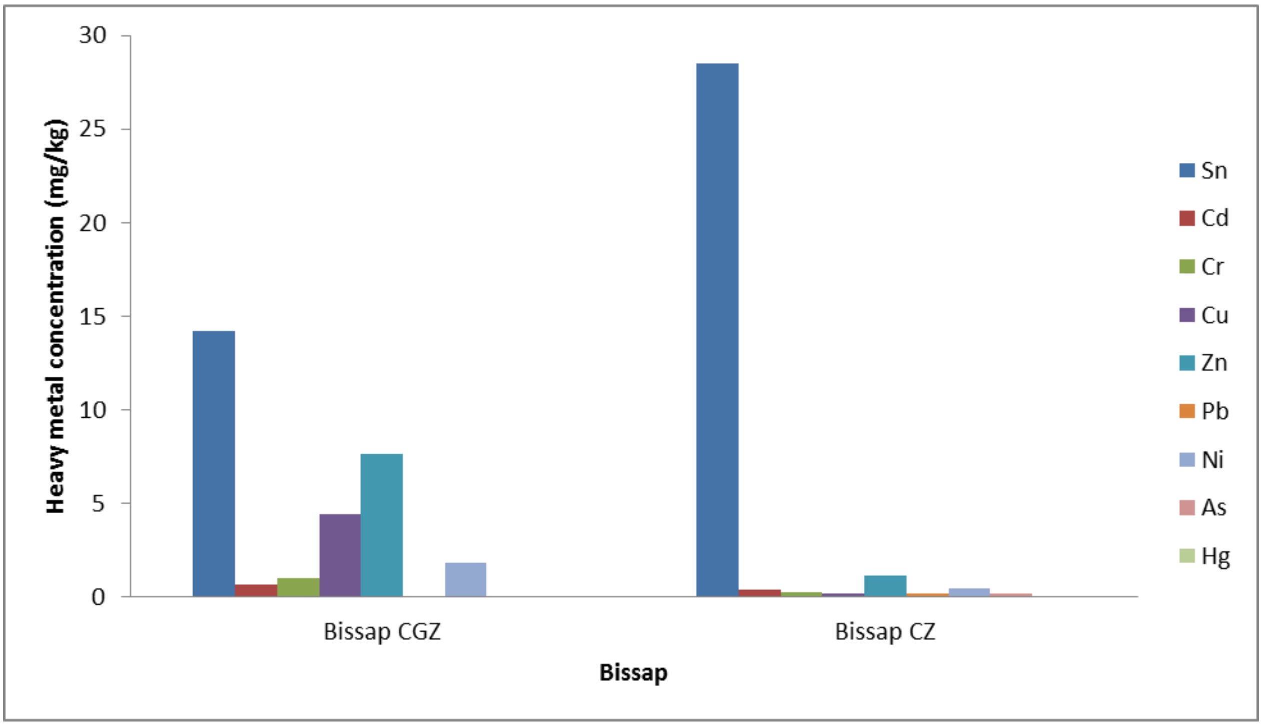

Fig. 4.14: Heavy metal concentration (mg/kg) in Bissap

4.7.3 Lettuce (*Latuca sativa*)

Lettuce was analyzed from the central garden zone (GZ) and the control zone (CZ). The concentrations of heavy metals recorded in lettuce from the central garden zone are shown in fig.4.15. Tin was the highest found heavy metal in lettuce with concentration value of 25.72mg/kg and 18.64mg/kg in the control zone (CZ) and garden zone (GZ) respectively. Mean concentrations of heavy metals in lettuce at the Central garden zone were Cd(0.92mg/kg), Cr(1.32mg/kg), Cu(13.00mg/kg), Zn(8.24mg/kg), Pb(1.04mg/kg), Ni(4.80mg/kg), As and Hg <0.001mg/kg respectively. The mean heavy metals concentrations recorded in lettuce at the control area are Cd(0.24mg/kg), Cr(1.24mg/kg), Cu(0.16mg/kg), Zn(1.26mg/kg), Pb(0.64mg/kg), Ni(0.50mg/kg), As(0.20mg/kg) and Hg(<0.001mg/kg).

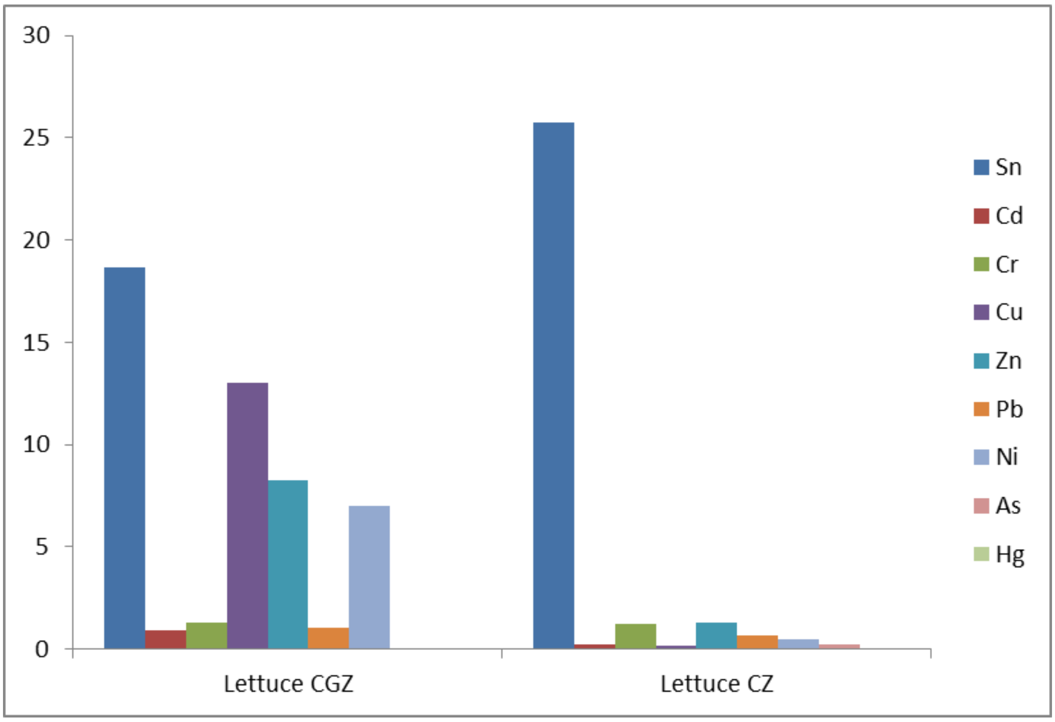

Fig.4.15: Heavy metal concentration (mg/kg) in Lettuce

CHAPTER FIVE

DISCUSSION

5.1. Heavy metals concentration in Soils

The presence of heavy metals in soils is as a result of absorption of the metals from anthropogenic sources, adsorption, and the natural occurrence of heavy metals in some soils. The mobility of heavy metals depends on soil properties, metal properties and environmental factors (Fagbote *et al.*, 2010).

The study revealed that soil depth of 20cm recorded higher concentrations of the heavy metals especially at the e-waste zone followed by the recreational zone (KD) and the reclaimed zone (RZ). Li *et al.*, (2011), reported that high concentrations of heavy metals are recorded at the pollution source instead of the expected diffusion into the surrounding environment. It was observed that the concentration of the heavy metals in the soils of these zones recorded higher concentrations as a result of continuous burning of electronic waste and other anthropogenic activities. The Accra Metropolitan Assembly (A.M.A) placed a ban on dumping of refuse at the reclaimed (RZ) and recreational (KD) zones but some residents continue to dump various kinds of refuse in these areas. The Ghana Wildlife Society (GWS) has planted some trees on the KD zone and some parts of the RZ zone in other to revegetate the land but encroachment in these areas is very extensive.

The concentration of the heavy metals at soil depth of 20cm was generally high. Singh *et al*. (2010) reported that at lower concentrations, some heavy metals act as micro-nutrients but they become toxic at higher concentrations.

The maximum Cd mean concentration of 103.66mg/kg was recorded at the e-waste zone (EW1). This was far above the WHO/FAO (2001) permissible limit of 3.00mg/kg in soils for cultivating plants. The minimum mean concentration recorded was <0.001mg/kg at the control zone (CZ1). Zhang *et al.* (2009) reported that Cd and Cu are very much connected with non-residual fractions and thus makes them mobile and potentially bio-available for uptake by plants. The higher concentration of Cd in the e-waste zone (EW1) can be attributed to continuous burning of electronic gadgets at the burning site. The soil in this area is clayey with high percentage organic matter and carbon content which reduce mobility of heavy metals thereby aiding in adsorption of these heavy metals on the surfaces of soil particles.

The maximum mean concentration of Cu recorded at the e-waste zone (EW1) was 202.99mg/kg and this was above the WHO/FAO (2001) permissible limit of 100.00mg/kg. Zhang *et al.(*2012) recorded extremely high concentrations of Cu in e-waste soils, which are beyond the acceptable agricultural soils limits of 50.00mg/kg in China. The high concentration of Cu recorded can be attributed to the burning of coppers wires into ashes during the burning of the electronic gadgets at the e-waste zone (EW1).The maximum mean concentration of Pb recorded was 183.66mg/kg at the e-waste zone (EW1) which is above the WHO/FAO(2001) permissible limit of 50.00mg/kg for soils. High concentration of the metal was also recorded at the EW2 and EW3 with values of 167.96mg/kg and 137.00mg/kg respectively. Pendias and Pendias (1989) recorded a value of 100.00mg/kg as reported by Agyarko *et al.*(2010)who recorded a value of 59.20mg/kg for a refuse dump soil in Accra. The high concentration of Pb recorded can be attributed to the use of tyres of vehicles in burning the electronic waste. Some parts of the electric gadgets may contain batteries made of Pb. Lead is known to cause lead poisoning in humans as well as chronic neurological disorders especially in foetuses and children (Opaluwa *et al.*, 2012).

The maximum mean concentration of Zn recorded at the e-waste zone (EZ1)was 37.33mg/kg which is below the WHO/FAO(2001) permissible limit of 300.00mg/kg. The minimum mean concentration of 0.82mg/kg was recorded at the garden zone (GZ1).

Agyarko *et al.*(2010) recorded a value of 297.10mg/kg on a waste dump soil in Accra. The 40cm and 60cm depths had maximum mean concentrations of 1.23mg/kg and 1.15mg/kg respectively. According to Knezevic *et al.*(2009) as reported from Adriano (1986) an average range of 50.00 – 100.00mg/kg was recommended. Wietes (1966) suggested that the critical value for zinc in soil is 170.00mg/kg and Pendias and Pendias (1989) define 70.00mg/kg as the lower "toxic" limit. Zinc is an essential microelement and plays a very essential catalytic role in enzyme reactions but its content varies with the type of soil (Knezevic *et al.*, 2009). High Zn concentration can be attributed to dry cells in municipal waste and zinc containing pesticides (Thorpe and Harrison, 2008).

The maximum mean concentration of Hg obtained was 0.66mg/kg at e-waste zone (EZ1). This was below the acceptable WHO/FAO (2001) limit of 2.00mg/kg. Agyarko *et al.*(2010) recorded a value of 0.04mg/kg on a waste dump soil in Accra. The low concentration can be attributed to the fact that Hg easily evaporates into its organo-mercury forms. Available mercury in soil is affected by the amounts which are absorbed by plants. Soil adsorption of Hg may decrease above pH 5 and therefore there is a potential that more Hg will be available for plant uptake (Environment Agency, 2009b).The main sources of the contamination were burning of electronic waste and waste incineration. Mercury also occurs in trace amounts in fertilizers used on farmland (Steinnes, 1995).

The maximum mean concentration of Ni obtained was 72.00mg/kg at the EW1. This value was above WHO/FAO (2001) acceptable value of 50.00mg/kg. The maximum mean concentration of Sn obtained was 705.32mg/kg at the EW1. The value is far above WHO/FAO(1984) permissible value of Sn. Tin may be released to soils from landfills of tin-containing wastes, including used cans (IPCS, 1980). There are no data to indicate any adverse effects in organisms associated with chronic exposure to tin (JECFA, 1989; 2000).

Maximum mean concentration of As obtained was 3.67mg/kg at the EW1. This value is below the WHO/FAO(2001) permissible limit of 20.00mg/kg. Arsenic occurs naturally in the earth's crust, with levels ranging between 2.00mg/kg and 5.00mg/kg (ATSDR, 2000). The maximum mean concentration of As recorded for the depths of 40cm and 60cm were 15.66mg/kg and 11.00mg/kg respectively. Arsenate is reported to bind strongly to iron and manganese oxides, and therefore remains in the surface soil layer after deposition (ATSDR, 2007). Arsenic was observed to be still concentrated after 15 years in the top 20–40 cm of orchard soils treated with lead arsenate (Merwin *et al*., 1994; Environmental Agency, 2009).Arsenic is related to heart diseases (hypertension and cardiovascular), cancer and stroke (Tseng *et al.*, 2003). The final result of arsenic poisoning is coma or death.

The study revealed that at depths of 40cm and 60cm, the heavy metal concentrations recorded in table 4.1, were within the WHO/FAO (2001) permissible limit. However, Cd recorded concentration of 90.31mg/kg and 68.32mg/kg respectively in the e-waste zone (EW2 and EW3 respectively) which were beyond the WHO/FAO (2001).

5.2 Organic Matter Content

The organic matter contents analyzed were generally below 2.00% with the exception of the EW1 which recorded a value of 2.51%. Odai *et al*. (2008) described organic matter content as the levels of mineral elements for plants development and growth. Odai *et al.* (2008) reported from Enwezor *et al*, (1988) who classified organic matter for cultivation as follows: values less than 2.00% as low, being values below critical limits. 2.10 – 3.00% as medium, values above the critical levels and values greater than 3.10% as high, and above the critical levels.

5.3 Geoaccumulation Index(Igeo)

Across the depth of 0 - 20cm in the research area, the mean Igeo values in appendix 8 shows that Sn and Cd are the heavy metals which falls within the category of moderately polluted. The rest falls within the category of practically unpolluted (this is with respect to using the mean Igeo values). The maximum Igeo Hg recorded was 2.474 which fall within the category of moderately polluted. The maximum Igeo of Pb recorded was 3.292 which fall with the category of moderately to strongly polluted. Tin and Cd are within the category of extremely polluted with a recorded maximum Igeo values of 7.877 and 8.433 respectively.

From the depth of 20 – 40cm the mean Igeo values recorded in appendix 9showsthat Sn and Cd are the heavy metals that falls within the category of moderately polluted with the rest within the category of practically unpolluted (this is with respect to their mean Igeo values). The maximum values of Hg, As, Pb, Sn and Cd recorded were 2.474, 2.536, 3.163, 7.856 and 8.234 respectively. These falls within the categories of moderately to strongly polluted for Hg and As, strongly polluted for Pb, and extremely polluted for Sn and Cd.

For the depth of 40 – 60cm the mean Igeo values recorded in appendix 10 shows that Sn and Cd are the heavy metals that falls within the category of moderately polluted and the rest with the category of practically unpolluted (with respect to the use of their mean Igeo values). The maximum values of As recorded was 2.026 which fall within the category of moderately polluted. The Sn value recorded was 6.800 which fall within the extremely polluted category and Cd recorded a value of 7.831 which fall within the extremely polluted category.

5.4 Enrichment factor (EF)

Along the soil profile 0 - 60cmin the study area the mean EF values in appendices 8, 9 and 10, fall within the deficiency to minimal enrichment category since all the mean values have EF < 2. The low EF value can be attributed to the fact that, it is only the e-waste zone (EZ) which churns out most of the heavy metals in the soils. The other zones and the control zone recorded low concentrations of heavy metals. This may probably originate from natural sources or the anthropogenic activities going on there, which are not intensive to churn out high volumes of these heavy metals.

5.5 Pollution Index (PI)

Along the depth of 0 - 20cm in the study area the mean PI values in appendix 8shows that the following heavy metals Cu, Zn, Cr, As and Ni falls within the PI ≤ 1 category. This means that the presence of these heavy metals in the earth crust is low and their pollution in the soil is very minimal. Hg and Pb belong to 1 < PI ≤ 3 category which means that their PI values falls within the middle category. This means that their presence in the study area falls between low to high pollutants in the soil. Cd and Sn are within the high category with PI > 3. This means that their presence is high in the earth crust and therefore they are high risk pollutant in the soil.

Along the depth of 20 - 40cm in the study area the mean PI values in appendix 9shows that the following heavy metals Cu, Zn, Cr and Ni falls within the PI ≤ 1 category. This means that the presence of these heavy metals in the earth crust is low and their pollution in the soil is very minimal. Pb, Hg and As belong to 1 < PI ≤ 3 which means that the PI values falls with the middle category. The presence of these metals in the study area fall between low to high pollutants in the soil. Cadmium and Sn are within the high category with PI > 3.This means their presence is high in the earth crust and therefore they are high risk pollutant in the soil.

At the depth of 40 – 60cm,the mean PI values in appendix 10 shows that the following heavy metals Hg, Cu, Zn, Cr and Ni falls within the PI ≤ 1 category. This means that the presence of these heavy metals in the earth crust is low and their pollution in the soil is very minimal at these depths. Lead and As belong to 1 < PI ≤ 3 category. This means that their presence in the study area fall between low to high pollutants in the soil. Cadmium and Sn are within the high category with PI > 3.This means that their presence is high in the earth crust and therefore they are high risk pollutant in the soil at the study area.

5.6 Heavy Metals In Plants

5.6.1 Heavy metals in forage grasses

Heavy metal accumulates in plants and also in herbivorous animals along the food chain. Cadmium concentration recorded ranged between 0.16 - 1.64 mg/kg, with mean value of 0.63mg/kg which was far above the WHO/FAO (1989) permissible limit of 0.20mg/kg for edible plants. This result is in line with the finding of Odai *et al.* (2008) who reported values ranging between 0.68 – 1.78mg/kg on urban waste dumpsites in Kumasi. The high concentration of Cd recorded at the EW zone might be as a result of the burning of e-waste containing cadmium-nickel batteries and pigments and paints. Significant concentrations of Cd may have gastrointestinal effect and reproductive effect on livestock (Maobe *et al.,* 2012).

Copper concentrations ranged between 0.16 - 95.56mg/kg, with value of 14.23mg/kg which was above the WHO/FAO(1984) permissible limit of 3.00mg/kg for edible plants occurring at the EW zone. This could be attributed to continuous dumping of copper-containing electrical gadgets. Agyarko *et al.*(2010) recorded mean concentrations of

10.80mg/kg for copper (Cu) in *Eleusine indica* (*L.*) *Gaertn* on waste dump site in Accra, whilst Odai *et al.*(2008) recorded a range between 16.17 – 90.33mg/kg in vegetables grown on urban waste dumpsites in Kumasi. High concentrations of Cu may cause liver disorders in livestock especially in cattle.

Zinc recorded was within the range of 1.16 - 34.92mg/kg, with a mean value of 9.43mg/kg which was below the WHO/FAO (1984) permissible limit of 27.3mg/kg. Odai *et al.* (2008) recorded values ranging between 26.77 – 106.83mg/kg in vegetables grown on waste dump soil in Kumasi. Opaluwa *et al.* (2012) recorded a value of 0.03mg/kg for spinach planted on waste dump soils in Lafia, Nasarawa State in Nigeria. Zn is also phytotoxic and high concentrations in forage grasses may result in adverse health effect in livestock.

Lead (Pb) concentrations recorded ranged from <0.001 to 36.72mg/kg, with mean value of 4.84mg/kg which was beyond the WHO/FAO (1984) acceptable value of 0.43mg/kg in edible plants. This can be attributed to the burning of lead containing products like scrap metals and batteries in the e-waste. Livestock that graze in the e-waste area stand a high risk with regards to lead toxicity through the consumption of forage grasses growing in this area.

The Tin recorded ranged from 2.52 - 22.00mg/kg, with mean value of 14.68mg/kg and this is below the recommended WHO/FAO (1984) permissible limit of 200.00mg/kg in edible plants. There is no data to indicate any adverse effects in humans associated with chronic exposure to tin (JECFA, 1989).

Chromium recorded was within the range of 1.08 – 3.84mg/kg, with mean value of 1.78mg/kg this falls below the critical range of 5.00 - 30.00mg/kg given by Radojevic and Bushkin (2008) as reported by Agyarko *et al*. (2010).

Nickel concentrations recorded ranged from 0.80 - 6.86mg/kg, with mean value of 2.65mg/kg which was lower than the value of 23.65mg/kg recorded by Singh *et al.* (2010) and attributed it to the use of sewage sludge. However, the maximum concentration was higher than the WHO/FAO permissible limit of 1.63mg/kg. The Ni concentrations in the forage grasses can be attributed to Cadmium-Nickel batteries in the electrical gadgets and some paints used to polish the surfaces of the gadgets. Arsenic concentrations recorded ranged from 0.16 - 0.32mg/kg with mean value of 0.14mg/kg. Agyarko *et al*.(2010) recorded mean concentrations of 0.13mg/kg for Arsenic (As)in the leaves *of Eleusine indica* (*L.*) *Gaertn* on a waste dump site in Accra. The presence of these heavy metals in the soils might be due to the fact that the research area used to be a waste dumpsite and the result of continuous burning of e-waste from the e-waste zone (EW).

5.6.2 Heavy metals in Bissap and Lettuce

The mean heavy metal concentration recorded in Bissap and Lettuce at the central garden zone (GZ) and control zone (CZ) recorded values were generally within the WHO/FAO (1984) permissible limits with the exception of Cadmium (Cd), Lead (Pb), Mercury (Hg).

Bissap recorded mean concentrations of 0.64mg/kg for the central garden zone (GZ) and the control zone (CZ) recorded a value of 0.36mg/kg for Cd. Lettuce recorded mean concentration of 0.92mg/kg at the central garden zone and the control zone recorded a value of 0.24mg/kg for Cd. The values recorded were above the WHO/FAO (1984) permissible limit 0.20mg/kg for edible plants. Odai *et al.* (2008) recorded values ranging between 0.68 – 1.78mg/kg in edible plants grown on urban waste dumpsites in Kumasi. Jabeen *et al*. (2010) reported that cadmium causes both acute and chronic poisoning, adverse effect on kidney, liver, vascular and the immune system.

Bissap mean concentrations of <0.001mg/kg and 0.08mg/kg were recorded for the central garden zone (GZ) and the control zone(CZ) respectively for Hg. Lettuce mean concentration of <0.001mg/kg and <0.001mg/kg were recorded at the central garden (GZ) and control (CZ) zones These values were below the WHO/FAO(1984) permissible limit of 0.02mg/kg in edible plants as reported by Jabeen *et al.*(2010) with the exception of the Bissap at the control zone. Maobe *et al.*(2012) reported a value of 0.00572mg/kg for *Physalis peruviana*. The lower concentrations recorded can be attributed to the minimal or no usage of mercury in the activities undertaken at these zones. It might also be the fact that Hg can easily transform into other organic forms which are more poisonous. Exposures to high levels of metallic, inorganic, or organic mercury can permanently damage the brain, kidneys and developing foetus. The effects of mercury on brain functioning result in irritability, changes in vision or hearing and memory problems (Vaikosen and Alade, 2011).

Bissap mean concentration of <0.001 was recorded at the central garden zone (CZ) and 0.20mg/kg at the control zone for Pb. Lettuce mean concentration 1.04mg/kg and 0.64mg/kg were recorded at the garden zone (GZ) and control zone (CZ) respectively for Pb. The permissible limit set by WHO/ FAO (1984) as reported by Jabeen *et al.*(2010) is 0.43mg/kg in edible plants. Bissap values are within WHO/FAO (1984) whilst the lettuce values were above the acceptable limit. This can be attributed to the burning of refuse and e-waste close to the garden zone. The zone use to be an active waste dumpsite and therefore the zone might be polluted with Pb containing substances like batteries and electrical gadgets. Agyarko *et al.* (2010) recorded value of 1.00mg/kg for *Eleusine indica* (*L.*) *Gaertn leaves* and 1.43mg/kg *Sida acuta* (*F.*) leaves on refuse dump soils in Accra for Pb. Odai *et al.* (2008) recorded Pb values ranging between 2.42 – 13.50mg/kg in vegetables grown from waste dump soils in Kumasi. The relatively lower concentrations of lead recorded can be attributed to reduce levels of it usage in the zone and it can also be that Pb might have formed organic compounds with other elements in the soil. Khan *et al.*(2008) reported that lead causes both acute and chronic poisoning and also poses adverse effects on kidney, liver, vascular and immune system. Lead is a non-essential trace element in humans and plants.

Bissap mean concentrations of 4.40mg/kg was recorded for Cu at the central garden zone(CZ) and the control zone recorded 0.20mg/kg. Lettuces mean concentrations of 13.00mg/kg and 0.16mg/kg of Cu at the garden zone (GZ) and control zone respectively. The permissible limit set by WHO/FAO(1984) in edible plants is 3.00mg/kg as reported by Jabeen *et al.*(2010). The recorded values at the garden zone were above the threshold limit and this can be attributed to the area been a refuse dump site. Maobe *et al.* (2012) recorded copper concentration of 1.44mg/kg in *Physalis peruviana*a malaria curing plant in Kisii region, Southwest Kenya. Moabe *et al.*(2012) reported from Ullah *et al.*(2012) that the high levels of copper may cause metal fumes fever with flue like symptoms, hair and skin decolouration, dermatitis, irritation of the upper respiratory tract, metallic taste in the mouth and nausea. Copper deficiency results in anaemia and congenital inability.

Mean concentrations of Zn recorded at the central garden zone was 7.64mg/kg and the control zone recorded 1.16mg/kg in Bissap. Whilst lettuce recorded a mean concentration 8.24mg/kg and 1.26mg/kg at the garden zone (GZ) and control zone (CZ) respectively. The permissible limit set by WHO/FAO (1984) as reported by Jabeen *et al.* (2010) is 27.30mg/kg. Whilst Opaluwa *et al.* (2012) recorded a value of 0.03mg/kg for spinach planted on waste dump soils in Lafia, Nasarawa State in Nigeria. Moabe *et al.* (2012) reported from Jabeen *et al*. (2010) that zinc is an essential trace element and plays an important role in various cell processes including normal growth, brain development, behavioural response, bone formation and wound healing. Zinc deficient diabetics fail to improve their power of sensitivity and cause loss of sense of touch and smell.

Nickel mean concentration recorded at the central garden zone (GZ) was 1.84mg/kg and 0.46mg/kg at the control zone (CZ) in Bissap. Lettuce recorded mean concentrations of 7.00mg/kg and 0.50 mg/kg for the garden and control zones. The permissible limit as set by WHO/FAO(1984) as reported by Jabeen *et al.* (2010) is 1.63mg/kg. The mean value of lettuce is beyond the permissible limit. Agyarko *et al.* (2010) recorded Ni concentrations of 8.10 mg/kg in *Eleusine indica* (*L.*) *Gaertn leaves* and 6.10 mg/kg in *Sidaacuta Burm*(*F.*) leaves from refuse dump soils in Accra. Although nickel is required in minute quantities for the body, it is mostly present in the pancreas and hence plays an important role in the production of insulin. Its deficiency results in liver disorder (Khan *et al.*, 2008).

The heavy metals may have entered the plants through adsorption, which refers to the binding of materials or the heavy metals onto the surface or absorption which implies penetration of the trace metals into the inner matrix of the plants. The uptake of heavy metals by plants occurs always during their vegetative period and the highest values are obtained at the end of the vegetation period (Krstic *et al.*, 2007; Stankovic, 2006; Milan Knezevic *et al.*, 2009).Toxic heavy metals will bio-accumulate and lead to bio-magnification. These metals get accumulated in soils and plants and have negative impact on physicochemical of soils and activities of plants (Suciu *et al.*, 2008; Fagbote *et al.*, 2010).

CHAPTER SIX

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

Significantly high contents of heavy metals in soils and vegetation around the Korle lagoon reclamation area were recorded, especially at the e-waste zone. The heavy metal concentrations of the soils were used to calculate enrichment factor (EF), index of geoaccummulation (Igeo) and pollution index (PI). The results of the heavy metals were then compared with the WHO/FAO acceptable values. Heavy metal analysis was then assessed in the dominant plant species in the reclamation area. Three species of plants were analyzed for these heavy metals.

The elemental analysis at the e-waste zone recorded significantly high concentrations of Cd, Pb, Cu, Ni and Sn across the various depths with all recording values above the WHO/FAO acceptable limit for soils whilst concentration of Hg, Zn, As and Cr were within the permissible limit. The concentrations of the heavy metals recorded at the control zone were within the WHO/FAO acceptable limits for soils. The soils at the garden zone (GZ), reclaimed zone (RZ), recreational zone (KD) and the estuary zone (EZ) all recorded values within the WHO/FAO acceptable limits of soils. The high concentration of the heavy metals in the soil at the e-waste zone is probably due to the burning of e-waste by the urban poor in the community and the dumping of solid waste.

The heavy metals concentrations recorded within the depth of 0 – 20 cm were significantly higher concentrations across the soil profile. Plants roots can take up these heavy metals during nutrient uptake and accumulate them in their tissues. Heavy metals like cadmium and lead can cause both acute and chronic poisoning, adverse effect on the kidney, liver, vascular and the immune system.

The forage grass cover at the various zones analyzed recorded concentrations of heavy metals, with the e-waste zone recording the highest concentrations. The concentrations of Hg in the grasses were below detectable limit. Lead (Pb), Cd, Ni, As and Cu recorded concentrations above the WHO/FAO permissible limits whilst Zn, Sn and Cr however recorded concentrations within the permissible limit. The lettuce and bissap grown at the garden zone (GZ) had higher concentrations of heavy metals than those from the control zone (CZ).

The levels of heavy metals in plants were relatively lower when compared to the soil. This may be influenced by the plant species and the form of the elements and the physicochemical properties of the soil. The burning of e-waste may have resulted in the significantly high concentrations of heavy metals in soil, forage grasses, bissap and lettuce sampled in the EW zone.

The presence of heavy metals in the vegetation from the other sampling zones may be due to frequent dumping of solid waste. The plants sampled are shallow rooted plants that absorb nutrient from the top soil. This might have contributed to the presence of heavy metals in their leaves since most of the heavy metals were within a depth of 0 – 20cm.

Consumption of lettuce and bissap from the zones where significantly high concentrations of Cd, Pb and Cu were detected poses a threat to human health. The high concentrations of heavy metals detected in the forage grasses from the EW zone may also pose health threat to herds of cattle and sheep grazing on the grasses.

6.2 Recommendation

- The management of e-waste must be given the utmost priority due to the health effect if not properly separated from solid waste materials.

- The Accra Metropolitan Assembly must enforce the law on open air burning and fast track the Korle Lagoon Reclamation Project in order to curtail the activities of these e-waste dealers and the burning of e-waste at the reclamation area. These electronic waste, ends up in the lagoon, thereby polluting it and hence making dredging cost intensive. The e-waste may end in the sea affecting the marine environment and therefore marine life can be compromised.
- The fumes generated during the burning of the electronic waste are toxic and may end up in foods or drinking water within the neighborhood. Environmental and sanitation officers should educate food vendors on proper handling of food and the health effect of consumption of polluted food from fumes from burning e-waste.
- Herds of cattle crossing from the Abossey Okai Zongo should be banned from grazing on the forage grasses on the reclamation site since most of them contain high concentrations of heavy metals due to the activities of the e-waste dealers.
- The Environmental Protection Agency and the Ghana Immigration Service should collaborate to educate importers on e-waste separation at the various entry points. E-waste dealers must be educated occasionally to create awareness on the potential health risks they are exposed to.
- Farmers cultivating along the borders of the reclamation zones should be educated to cultivate deep rooted crops since the heavy metals were found to accumulate within 0 -10 cm of the soil layer to avoid transfer of heavy metals along the food chain.
- Children must be restricted from playing within the recreational zone since it contains some hazardous chemicals.

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APPENDICES

Appendix 1.Heavy metal concentration and physicochemical parameters of soils in the reclamation area and the control area

SAMPLE ID	Hg	Pb	Cu	Zn	Cr	Cd	Ni	Sn	As	pH	%OC	%OM	K+	Na+	Ca2+	Mg2+
	mg/kg												cmol/kg			
EW1	0.67	183.66	202.99	37.33	56.00	103.66	72.00	705.32	3.67	6.72	0.85	2.51	1.52	6.15	97.87	73.4
GZ1	0.00	1.28	3.47	0.83	3.03	3.55	0.91	27.08	0.08	7.69	0.48	1.42	0.78	2.13	11.7	8.8
RZ1	0.03	3.33	3.84	1.03	2.63	4.35	1.48	24.71	0.04	4.67	0.44	1.40	1.52	6.07	15.46	11.6
KD1	0.04	17.41	10.90	6.33	2.36	0.23	4.56	16.48	1.41	7.47	0.42	0.13	1.32	3.69	18.45	14.00
ES1	0.00	12.65	6.39	4.51	2.99	0.04	1.59	14.84	0.88	7.75	0.38	1.13	0.71	3.12	30.31	23.0
CZ1	0.00	4.39	5.20	2.05	2.28	0.00	1.09	8.77	0.47	7.27	0.42	1.25	0.58	2.01	10.13	7.60
EW2	0.67	167.96	200.00	34.32	49.99	90.31	67.32	695.16	15.66	7.02	0.45	1.33	1.27	3.77	53.86	40.4
GZ2	0.04	1.12	2.57	0.73	2.84	3.08	0.84	26.72	0.29	7.48	0.47	1.38	1.32	3.69	8.4	6.30
RZ2	0.01	3.08	3.25	0.93	2.44	3.77	1.33	24.08	0.27	3.7	0.28	0.84	1.15	6.4	13.88	10.40
KD2	0.00	4.75	5.73	1.52	1.64	0.08	2.15	11.74	0.85	7.8	0.03	0.08	1.13	5.41	17.6	13.20
ES2	0.00	11.02	6.07	3.33	3.40	0.04	1.37	12.94	0.21	8.1	0.35	1.02	0.96	2.79	26	19.50
CZ2	0.00	4.88	4.33	1.23	0.11	0.05	1.20	9.04	0.53	7.35	0.29	0.86	0.57	2.05	8.68	6.50
EW3	0.00	137.00	98.66	27.66	52.67	68.32	66.65	334.25	11.00	7.18	0.46	1.37	1.86	5.41	28.25	21.20
GZ3	0.00	0.96	1.84	0.52	2.81	2.77	0.55	16.73	0.68	7.27	0.25	0.75	0.88	2.54	6.7	5.00
RZ3	0.00	2.93	1.49	0.81	1.13	3.73	1.33	15.13	0.21	3.21	0.21	0.63	0.86	14.1	13.74	10.3
KD3	0.00	12.17	9.12	4.75	2.53	0.09	4.37	14.64	1.08	7.68	0.13	0.40	1.2	4.02	12.66	9.50
ES3	0.00	7.38	4.99	3.19	2.33	0.04	1.51	12.16	0.71	8.26	0.20	0.61	0.96	2.54	24.57	18.50
CZ3	0.00	4.16	4.11	1.15	2.15	0.08	1.59	8.66	0.49	7.38	0.25	0.75	1.71	2.21	8.55	6.40

Appendix 2. Summary of heavy metal concentration (mg/kg) at depth of 0 - 20cm

Statistic	Hg	Pb	Cu	Zn	Cr	Cd	Ni	Sn	As
Minimum	0	1.28	3.467	0.827	2.279	0	0.907	8.771	0.04
Maximum	0.667	183.66	203	37.332	56	103.66	71.998	705.32	3.666
Mean	0.123	37.12	38.798	8.679	11.55	18.637	13.604	132.86	1.091
Standard deviation (n)	0.244	65.777	73.472	12.962	19.88	38.065	26.143	256.08	1.245

Appendix 3. Summary of heavy metal concentration (mg/kg) at depth of 20 - 40

Statistic	Hg	Pb	Cu	Zn	Cr	Cd	Ni	Sn	As
Minimum	0	1.12	2.573	0.733	0.107	0.04	0.84	9.038	0.213
Maximum	0.667	167.96	200	34.325	49.99	90.311	67.317	695.16	15.66
Mean	0.12	32.134	36.992	7.012	10.07	16.223	12.368	129.95	2.97
Standard deviation (n)	0.245	60.818	72.908	12.244	17.88	33.168	24.577	252.85	5.68

Appendix 4. Summary of heavy metals concentration (mg/kg) at depth of 40 - 60

Statistic	Hg	Pb	Cu	Zn	Cr	Cd	Ni	Sn	As
Minimum	0	0.96	1.493	0.52	1.133	0.04	0.547	8.665	0.213
Maximum	0	137	98.664	27.66	52.67	68.316	66.65	334.25	11
Mean	0	27.434	20.034	6.345	10.6	12.506	12.666	66.929	2.362
Standard deviation (n)	0	49.129	35.253	9.647	18.82	25.001	24.172	119.58	3.871

Appendix 5. Correlation of heavy metal concentration(mg/kg) at a depth of 0 - 20

Variables	Hg	Pb	Cu	Zn	Cr	Cd	Ni	Sn	As	pH	%O/C	%O/M	K+	Na+	Ca2+	Mg2+
Hg	1															
Pb	0.997	1														
Cu	0.995	0.998	1													
Zn	0.991	0.998	0.993	1												
Cr	0.998	0.996	0.999	0.988	1											
Cd	0.997	0.993	0.997	0.982	0.995	1										
Ni	0.995	0.995	0.995	0.993	0.995	0.997	1									
Sn	0.998	0.995	0.999	0.987	0.995	0.995	0.998	1								
As	0.933	0.953	0.937	0.971	0.923	0.911	0.939	0.920	1							
pH	0.462	0.453	0.454	0.466	0.441	0.444	0.463	0.448	0.499	1						
%O/C	-0.187	-0.224	-0.190	-0.258	-0.165	-0.144	-0.190	-0.155	-0.374	0.403	1					
%O/M	0.022	-0.014	0.031	-0.070	0.070	0.090	0.021	0.074	-0.271	0.012	0.794	1				
K^+	0.528	0.514	0.517	0.517	0.515	0.523	0.525	0.524	0.503	0.917	0.524	0.211	1			
Na^+	0.577	0.573	0.582	0.566	0.592	0.595	0.583	0.596	0.511	0.775	0.582	0.453	0.921	1		
Ca^{2+}	-0.243	-0.253	-0.233	-0.273	-0.211	-0.202	-0.236	-0.206	-0.340	0.343	0.930	0.723	0.498	0.620	1	
Mg^{2+}	-0.244	-0.254	-0.235	-0.274	-0.212	-0.204	-0.238	-0.208	-0.341	0.342	0.929	0.721	0.497	0.620	0.995	1

Appendix 6.Correlation of heavy metals concentration (mg/kg) at a depth of 20 - 40cm

Variables	Hg	Pb	Cu	Zn	Cr	Cd	Ni	Sn	As	pH	%OC	%OM	K^+	Na^+	Ca^{2+}	Mg^{2+}
Hg	1															
Pb	0.995	1														
Cu	0.997	0.995	1													
Zn	0.994	0.995	0.998	1												
Cr	0.998	0.998	0.998	0.998	1											
Cd	0.999	0.996	0.998	0.995	0.998	1										
Ni	0.998	0.999	0.995	0.998	0.998	0.998	1									
Sn	0.999	0.998	0.995	0.996	0.995	0.995	0.995	1								
As	0.997	0.998	0.995	0.996	0.996	0.997	0.995	0.998	1							
pH	0.606	0.583	0.595	0.586	0.607	0.593	0.599	0.597	0.608	1						
%O/C	-0.051	-0.096	-0.098	-0.098	-0.062	-0.053	-0.100	-0.068	-0.121	-0.457	1					
%O/M	-0.051	-0.096	-0.098	-0.098	-0.062	-0.053	-0.100	-0.068	-0.121	-0.457	0.995	1				
K^+	0.183	0.128	0.143	0.130	0.188	0.183	0.150	0.170	0.141	0.530	0.249	0.249	1			
Na^+	0.723	0.707	0.720	0.706	0.726	0.723	0.726	0.723	0.733	0.924	-0.426	-0.426	0.568	1		
Ca^{2+}	-0.169	-0.227	-0.220	-0.219	-0.183	-0.202	-0.222	-0.201	-0.226	0.277	0.308	0.308	0.352	-0.055	1	
Mg^{2+}	-0.169	-0.227	-0.221	-0.219	-0.183	-0.202	-0.222	-0.201	-0.226	0.277	0.308	0.308	0.352	-0.055	0.995	1

Appendix 7. Correlation of heavy metals concentration (mg/kg) at a depth of 40 -60cm

Variables	Hg	Pb	Cu	Zn	Cr	Cd	Ni	Sn	As	pH	%O/C	%O/M	K^+	Na^+	Ca^{2+}	Mg^{2+}
Hg																
Pb		1														
Cu		0.995	1													
Zn		0.997	0.996	1												
Cr		0.997	0.998	0.989	1											
Cd		0.993	0.993	0.980	0.997	1										
Ni		0.995	0.995	0.994	0.995	0.996	1									
Sn		0.997	0.997	0.988	0.995	0.999	0.995	1								
As		0.995	0.995	0.994	0.995	0.994	0.995	0.998	1							
pH		-0.095	-0.091	-0.134	-0.095	-0.088	-0.083	-0.097	-0.115	1						
%O/C		-0.245	-0.236	-0.301	-0.177	-0.150	-0.221	-0.175	-0.204	-0.155	1					
%O/M		-0.244	-0.235	-0.300	-0.176	-0.149	-0.221	-0.175	-0.203	-0.155	0.995	1				
K^+		-0.458	-0.441	-0.485	-0.415	-0.432	-0.443	-0.432	-0.422	0.208	0.672	0.672	1			
Na^+		0.959	0.962	0.952	0.969	0.967	0.963	0.968	0.971	-0.242	-0.024	-0.024	-0.291	1		
Ca^{2+}		-0.124	-0.120	-0.111	-0.093	-0.114	-0.130	-0.105	-0.087	-0.774	0.539	0.539	0.316	0.053	1	
Mg^{2+}		-0.124	-0.120	-0.111	-0.093	-0.115	-0.131	-0.105	-0.088	-0.775	0.536	0.537	0.314	0.052	0.995	1

Appendix 8. Summary of Igeo, EF and PI values at the depth of 0 - 20 (cm)

	Hg			Pb			Cu			Zn		
Statistic	Igeo	EF	PI	Igeo	EF	PI	Igeo	EF	PI	Igeo	EF	PI
Minimum	-5.322	0.000	0.000	-3.873	0.008	0.102	-4.573	0.005	0.063	-6.989	0.001	0.012
Maximum	2.474	0.061	8.333	3.292	0.169	14.693	1.299	0.024	3.691	-1.492	0.011	0.533
Mean	-1.100	0.019	1.534	-0.974	0.076	2.970	-3.050	0.014	0.705	-4.905	0.005	0.124
Standard deviation (n)	2.394	0.022	3.046	2.276	0.059	5.262	2.018	0.007	1.336	1.852	0.004	0.185

conti. of summary of Igeo, EF and PI values at the depth of 0 - 20 (cm)

	Cr			Cd			Ni			Sn			As		
Statistic	Igeo	EF	PI	Igeo	EF	Pi	Igeo	EF	PI	Igeo	EF	PI	Igeo	EF	PI
Minimum	-6.040	0.002	0.023	-2.907	0.000	0.000	-6.955	0.001	0.012	1.548	1.000	4.386	-6.077	0.002	0.022
Maximum	-1.421	0.005	0.560	8.433	1.759	518.320	-0.644	0.007	0.960	7.877	1.000	352.658	0.441	0.095	2.037
Mean	-5.095	0.003	0.115	2.090	0.784	93.187	-5.218	0.003	0.181	3.401	1.000	66.432	-2.633	0.039	0.606
Standard deviation (n)	1.650	0.001	0.199	3.676	0.742	190.325	2.175	0.002	0.349	2.071	0.000	128.041	2.281	0.037	0.691

Appendix 9. Summary of Igeo, EF and PI values at the depth of 20 - 40 (cm)

	Hg			Pb			Cu			Zn		
Statistic	Igeo	EF	PI	Igeo	EF	PI	Igeo	EF	PI	Igeo	EF	PI
Minimum	-3.170	0.000	0.000	-4.065	0.007	0.090	-5.003	0.004	0.047	-7.162	0.001	0.010
Maximum	2.474	0.037	8.331	3.163	0.136	13.437	1.277	0.018	3.636	-1.613	0.007	0.490
Mean	-0.380	0.013	1.500	-1.366	0.059	2.571	-3.376	0.012	0.673	-5.516	0.003	0.100
Standard deviation (n)	1.723	0.014	3.060	2.251	0.044	4.865	2.125	0.006	1.326	1.875	0.002	0.175

conti of summary of Igeo, EF and PI values at the depth of 20 - 40 (cm)

	Cr			Cd			Ni			Sn			As		
Statistic	Igeo	EF	PI	Igeo	EF	Pi	Igeo	EF	PI	Igeo	EF	PI	Igeo	EF	PI
Minimum	-10.458	0.000	0.001	-2.907	0.031	0.200	-7.065	0.001	0.011	1.591	1.000	4.519	-3.662	0.012	0.118
Maximum	-1.585	0.005	0.500	8.234	1.567	451.554	-0.741	0.005	0.898	7.856	1.000	347.580	2.536	0.081	8.702
Mean	0.000	0.002	0.101	1.323	0.696	81.114	-5.471	0.003	0.165	3.281	1.000	64.974	-1.945	0.036	1.650
Standard deviation (n)	2.581	0.002	0.179	4.087	0.655	165.840	2.152	0.001	0.328	2.120	0.000	126.427	2.113	0.027	3.156

Appendix 10. Summary of Igeo, EF, and PI values at the depth of 40 - 60 (cm)

	Hg			Pb			Cu			Zn		
Statistic	Igeo	EF	PI	Igeo	EF	PI	Igeo	EF	PI	Igeo	EF	PI
Minimum	0.000	0.000	0.000	-4.288	0.009	0.077	-5.788	0.004	0.027	-7.658	0.001	0.007
Maximum	0.000	0.000	0.000	2.869	0.133	10.960	0.258	0.023	1.794	-1.925	0.009	0.395
Mean	0.000	0.000	0.000	-1.373	0.069	2.195	-3.762	0.012	0.364	-5.437	0.004	0.091
Standard deviation (n)	0.000	0.000	0.000	2.213	0.041	3.930	1.999	0.007	0.641	1.915	0.003	0.138

conti. of summary of Igeo, EF and PI values at the depth of 40 - 60 (cm)

	Cr			Cd			Ni			Sn			As		
Statistic	Igeo	EF	PI	Igeo	EF	Pi	Igeo	EF	PI	Igeo	EF	PI	Igeo	EF	PI
Minimum	-7.048	0.001	0.011	-2.907	0.033	0.200	-7.685	0.001	0.007	1.530	1.000	4.332	-3.662	0.016	0.11
Maximum	-1.510	0.005	0.527	7.831	2.467	341.581	-0.755	0.008	0.889	6.800	1.000	167.125	2.026	0.082	6.11
Mean	-5.386	0.003	0.106	1.363	1.060	62.530	-5.316	0.004	0.169	2.908	1.000	33.464	-1.556	0.051	1.31
Standard deviation (n)	1.784	0.001	0.188	3.843	1.024	125.006	2.217	0.002	0.322	1.767	0.000	59.789	1.754	0.022	2.15

Appendix 11. Concentration of heavy metals (mg/kg) in vegetation.

ID	Botenica name	Sn	Cd	Cr	Cu	Zn	Pb	Ni	As	Hg
						mg/kg				
Bissap CGZ	*Hibiscus sabdariffa*	14.24	0.64	0.98	4.40	7.64	<0.001	1.84	<0.001	<0.001
Bissap CZ	*Hibiscus sabdariffa*	28.52	0.36	0.24	0.20	1.16	0.20	0.46	0.20	0.08
Forage Grass CZ	*Imperata cylindrica*	12.64	0.16	2.20	0.26	1.56	0.80	0.80	0.16	<0.001
Forage Grass EWZ	*Imperata cylindrica*	22.00	1.64	1.56	95.56	34.92	36.72	2.00	0.32	<0.001
Forage Grass KD	*Panicum maximum*	2.52	0.44	3.84	6.92	7.88	<0.001	2.20	0.08	<0.001
Forage Grass ES	*Panicum maximum*	4.64	0.32	3.52	5.48	7.36	3.64	6.80	0.16	<0.001
Forage Grass RZ	*Imperata cylindrica*	3.23	0.92	1.08	2.68	14.84	0.48	2.25	0.12	<0.001
Lettuce CGZ	*Latuca sativa*	18.64	0.92	1.32	13.00	8.24	1.04	7.00	0	0
Lettuce CZ	*latuca sativa*	25.72	0.24	1.24	0.16	1.26	0.64	0.500	0.2	<0.001

Appendix 12. Summary of concentration of heavy metals (mg/kg) in vegetation.

Statistic	Sn	Cd	Cr	Cu	Zn	Pb	Ni	As	Hg
Minimum	2.52	0.16	0.24	0.16	1.16	<0.001	0.46	<0.001	<0.001
Maximum	28.52	1.64	3.84	95.56	34.92	36.72	7.00	0.32	0.08
Mean	14.68	0.63	1.78	14.29	9.43	4.84	2.65	0.14	0.01
Standard deviation (n)	9.23	0.44	1.13	28.99	9.93	11.32	2.37	0.10	0.03