ASSESSMENT OF HEAVY METALS IN NIGERIAN VEGETABLES AND SOILS IN OWO AND EDO AXES USING X-RAY FLUORESCENCE (XRF) TECHNIQUE

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CERTIFICATION

This is to certify that this research project was carried out by **OLADEBEYE ABRAHAM OLASUPO** with Matriculation Number, **AUO15AD0221** of the Department of Chemical Sciences, College of Natural and Applied Sciences, Achievers University, Owo, Ondo State in partial fulfilment of the requirements for the award of Bachelor of Science (B.Sc Honours) in Industrial Chemistry.

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DEDICATION

This research is dedicated to the Almighty God, who has always been there for me and my family.

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ABSTRACT

The soils and leaves of fluted pumpkin (*Telfairia occidentalis*), African spinach, "Green" (*Amaranthus hybridus*) and water leaf (*Talinum* triangulare) were collected as randomly composite samples from four (4) different study locations of two (2) each from Owo Local Government Area and Etsako-West Local Government Area. The samples were examined for heavy metal concentrations, using X-ray fluorescence (XRF) technique. Chromium (Cr), zinc (Zn), manganese (Mn), iron (Fe), titanium (Ti), strontium (Sr) and aluminium (Al) of both soil and vegetable samples were detected at higher proportions than the permissible limits of WHO/FAO and EU for soils and plants. Exceptions were obtained for Cr in SL_3 (*Talinum triangulare* from St. Louis farm), and Zn in WB (soil from Water-Board farm), IY (soil from Iyerekhu farm) and IY_3 (*Talinum triangulare* from Iyerekhu farm). Toxic heavy metals, such as nickel (Ni), lead (Pb), cobalt (Co), cadmium (Cd) and copper (Cu) were not detected in both soil and vegetable samples. Generally, the concentrations of the metals in the soil and vegetable samples followed the same decreasing order: Al>Fe>Ti>Mn>Sr>Cr>Zn. The Cr concentrations varied from 54.72 to 191.52 mg/kg among the soil samples and from 0.00 to 280.44 mg/kg among the vegetable samples. The concentrations of Zn were higher in the vegetable samples than the soil samples, ranging from 0.00 to 184.74 mg/kg for soil samples and from 0.00 to 795.17 mg/kg for vegetable samples. Generally, Mn concentrations were higher in the tissues of the vegetable samples than in the soil samples except for slight deviations observed in SL_1 (*Telfairia occidentalis* from St. Louis farm), SL_2 (*Amaranthum hybridus* from St. Louis farm) and OL_2 (*Amaranthum hybridus* from Osuma Layout farm). Iron (Fe) was the most abundant nutritionally essential metal in both soil and vegetable samples, ranging from 22089.07 to 64282.61 mg/kg in the soil samples and 2354.96 to 29950.57 mg/kg in the vegetable samples. Titanium (Ti) concentrations were more predominant in the soil samples than the vegetable samples. The peak (719.10 mg/kg) and least (118.44 mg/kg) Sr concentrations were observed in the OL (Osuma Layout farm) and WB (Water-Board farm) soils respectively, which bioaccumulated, in the same trend, in their

corresponding *Telfairia occidentalis* samples. The Al concentrations ranged from 48333.29 – 75021.09 mg/kg in the soil samples and 30984.10 – 63407.34 mg/kg in the vegetable samples. All the vegetable samples had significant differences in the transfer factors of metals relative to the availability of same metals in the soil, ranging from 0.00 to 9.47. Manganese (Mn) had the peak transfer factor (9.47) in WB_3 (*Talinum triangulare* from Water-Board farm) followed by 9.33 observed in WB_1 (*Telfairia occidentalis* from Water-Board farm). The vegetable samples were recommended for possible application in phytoremediation of polluted soils.

CHAPTER ONE

1.0 INTRODUCTION

Heavy metals are generally referred to as those metals which possess a specific density of more than 5 g/cm^3 and adversely affect the environment and living organisms (Järup, 2003). They, without doubt, are important constituents for plants and humans, when present only in small amount. Some micronutrient elements may also be toxic to both animals and plants at high concentrations. For instance, copper (Cu), chromium (Cr), fluorine (F), molybdenum (Mo), nickel (Ni), selenium (Se) or zinc (Zn). Other trace elements such as arsenic (As), cadmium (Cd), mercury (Hg) and lead (Pb) are toxic even at small concentrations (Divrikli et al., 2006). Heavy metals, being persistent and non-biodegradable, can neither be removed by normal cropping nor easily leached by rain water (Khadeeja et al., 2013). They might be transported from soil to ground waters or may be taken up by plants, including agricultural crops. For this reason, the knowledge of metal plant interactions is also important for the safety of the environment (Divrikli et al., 2006).

There has been increasing interest in determining heavy metal levels in public food supplied. However, their concentration in bio-available form is not necessarily proportional to the total concentration of the metal (Opaluwa et al., 2012; Nwachukwu et al., 2010).

The quality of ecosystem becomes altered, when heavy metals find their way, somehow, into it through human and natural activities. These activities are one of the most pressing concerns of urbanization in developing countries like Nigeria, which result in the problem of solid, liquid and toxic waste management. Such waste may be toxic or radioactive (Onibokun and Kumuyi, 1996; UNDP, 2006). Such waste management problems include heaps of uncontrolled garbage, roadsides littered with refuse, streams blocked with rubbish, prevalence of automobile workshops and service stations, inappropriately disposed toxic waste and disposal sites that constitute a health hazard to residential areas (Adewole and Uchegbu, 2005; Rotich et al., 2006; Ebong et al., 2008).

Occurrence of uncontrolled urban sewage farming is a common site in African cities which exposes consumers of such produce to poisoning from heavy metals (Ebong et al., 2008). Open dumps are a source of various environmental and health hazards. The decomposition of organic materials produces methane, which may cause explosions and produce leachates, which pollute surface and ground water. It ruins the aesthetic quality of the land (Oyelola et al., 2009). Automobile wastes include solvents, paints, hydraulic fluids, lubricants and stripped oil sludge; all results of activities such as battery charging, welding and soldering, automobile body works engine servicing and combustion processes (Adewole and Uchegbu, 2005; Utang et al., 2013).

Soil is the most important component of the environment, but it is the most undervalued, misused and abused one of the earth's resources (Gokulakrishnan and Balamurugan, 2010). Soil contamination has become a serious problem in all industrialized areas of the country. Soil is equally regarded as the ultimate sink for the pollutants discharged into the environment (Shokoohi et al., 2009).

Most plants and animals depend on soil as a growth substrate for their sustained growth and development. In many instances the sustenance of life in the soil matrix is adversely affected by the presence of deleterious substances or contaminants. The entry of the organic and inorganic form of contaminants results from disposal of industrial effluents (Gowd et al., 2010). The source of the organic and inorganic elements of the soil of contaminated area was mainly from unmindful release of untreated effluent on the ground (Shetty and Rajkumar, 2009). The contamination of soils with heavy metals or micronutrients in phytotoxic concentrations generates adverse effects not only on plants but also poses risks to human health (Murugesan et al., 2008).

Afterwards, the consumption of contaminated vegetables constitutes an important route of heavy metal exposure to animals and humans (Sajjad et al., 2009; Tsafe et al., 2012). Abandoned waste dumpsites have been used extensively as fertile grounds for cultivating vegetables, though research has indicated that the vegetables are capable of accumulating high levels of heavy metals from contaminated and polluted soils (Cobb et al., 2000; Benson and Ebong, 2005).

1.1 JUSTIFICATION

World Health Organization (WHO) estimates that about a quarter of the diseases facing mankind today occur due to prolonged exposure to environmental pollution (Prüss-Üstün and Corvalán, 2006; Kimani, 2007).

Heavy metal pollution of the environment, even at low levels, and their resulting long-term cumulative health effects are among the leading health concerns all over the world. Heavy metals are known as non-biodegradable, and persist for long durations in aquatic as well as terrestrial environments. They might be transported from soil to ground waters or may be taken up by plants, including agricultural crops (Oluyemi et al., 2008).

It is well known that high industrial and traffic activities contribute high levels of heavy metals to the environments. Plants grown around such areas are likely to absorb these metals either from the soil through the roots or from atmospheric contaminants through the leaves (Fifield and Haina, 1997).

The soil contamination by heavy metals can transfer to food and ultimately to consumers. For instance, plants accumulate heavy metals from contaminated soil without physical changes or visible indication, which could cause a potential risk for human and animal (Osma et al., 2012).

Based on its persistent and cumulative nature, as well as the probability of potential toxicity effects of heavy metals as a result of consumption of leafy vegetables and fruits, there is a need to test and analyse this food item to ensure that the levels of these trace elements meet the agreed international requirements.

It is on this basis that this study was designed to determine the concentrations of heavy metals in both soils and leafy vegetables from selected vegetable plantations in Nigeria.

1.2 AIM AND OBJECTIVES

The aim of this project work is to ascertain the level of heavy metal contaminations in the soils and vegetables of some selected vegetable plantations in Owo and Edo Axes.

The objectives of this project work are to:

1. prepare soil samples from selected vegetable plantations;
2. prepare plant samples from selected vegetables, namely: fluted pumpkin leaves (*Telfairia occidentalis*), African spinach, "Green" (*Amaranthus hybridus*) and water leaf (*Talinum triangulare*);
3. determine the concentration levels of heavy metals in the soil obtained from the plantations using x-ray fluorescence (XRF) spectrometer;
4. determine the concentration levels of heavy metals in the vegetable samples obtained from the plantations using x-ray fluorescence (XRF) spectrometer;
5. compare the levels of concentration of heavy metals in the soil and plant samples obtained from the plantations; and
6. suggest the possible measures to manage the contamination to ensure safety to humans and animals.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 ECOSYSTEM

All life on Earth depends on functional ecosystems and the services they provide. An ecosystem is an ecological system which is described by a habitat, the organisms which live in it and the interactions between the two (Nebel and Wright, 1993). In other words, an ecosystem is a community of living organisms in conjunction with the non-living components (Nebel and Wright, 1993). The physical environment (light, air, water, temperature, minerals, soil and climatic aspects) constitute the non-living part. The living parts of an ecosystem are called the biotic components and the non-living parts the abiotic (not biotic) components. Abiotic factors include the soil (edaphic factors) and topography (the landscape). Biotic and non-biotic components interact to sustain the ecosystem. The word ‘environment’ refers specifically to the non-living part of the ecosystem.

Dependent on geological features, a given ecosystem may encompass different environments, micro-climates, and habitats, thus enabling complementary niches that support greater biodiversity, that is, a larger variety of interdependent species (Chapin et al., 2011).

Next to natural ecosystems such as forests, lakes, or even the bodies of animals, there are also artificial systems that either emulate the mutual dependencies of natural ecosystems (e.g. aquaria, garden ponds, sustainable gardens) or are subject to ecosystem processes e.g. transformed farmland. Ecosystem processes result from the interactions of populations of plants, animals, and microbes with the abiotic geological features and properties of their environment (Nebel and Wright, 1993).

In some ecosystems, disturbances are common that lead to a successive change in the composition of the system, which over time favours a different community of species (Chapin et al., 2011). Such ecosystem imbalance or disturbance constitutes the phenomenon called pollution.

2.2 ENVIRONMENTAL POLLUTION

Pollution is defined in various ways. It is considered as the release of unwanted substances to the environment by man in quantities that damage either the health or the resource itself (Tripati et al., 2007). Environmental pollution caused by heavy metals is increasing along with the increase in the usage of chemicals in industry and agriculture. Such pollution is apparent in streams and lakes and in ground water, which is replenished directly from surface water (Huget et al., 2009).

Environmental pollution has become a major concern of developing countries in the last few decades. There is a growing sense of global urgency regarding the pollution of our environment by an array of chemicals used in various activities (Palaniappan et al., 2009). Pollution of water and soils by heavy metals is an emerging problem in industrialized countries. Since the advent of development through mining and smelting, metallurgical industries, sewage, warfare, and tanning the survival of plants and animals are much affected (Xi et al., 2009).

Soil, water and biodiversity are fundamental elements of ecosystem and are the subject of many agrarian, ecological, biological and hydrological studies. A high percentage of ecosystems consist of arable land which is treated with agrochemical products forms the upper layer of the soil. Large quantities of chemical elements infiltrate the water running off of the cultivated soils thereby entering the animal and human food chain (Noltan et al., 2005).

The quality of life on earth is inextractably linked to overall quality in the environment. Currently there are two fundamental pollution related problems, the disposal of large quantities of wastes that are continually being produced and the removal of toxic compounds that have been accumulating at dump sites in the soils and in water system over the last few decades (Hsua et al., 2006).

2.2.1 Types of Environmental Pollution

2.2.1.1 Air Pollution

The air we breathe is an essential ingredient for our wellbeing and a healthy life. Unfortunately, polluted air is common throughout the world (EPHA, 2009) specially in developed countries from 1960s (Kan, 2009).

Polluted air contains one, or more, hazardous substance, pollutant, or contaminant that creates a hazard to general health (Health and Energy, 2007). The main pollutants found in the air we breathe include, particulate matter, PAHs, lead, ground-level ozone, heavy metals, sulphur dioxide, benzene, carbon monoxide and nitrogen dioxide (EPHA, 2009).

According to Mishra (2003) rapid growth in urban population, increasing industrialization, and rising demands for energy and motor vehicles are the worsening air pollution levels. He added other factors, such as poor environmental regulation, less efficient technology of production, congested roads, and age and poor maintenance of vehicles, also add to the problem. He further added that air pollution is a cause of ill health and death by natural and man-made sources. Major man-made sources of ambient air pollution include tobacco smoke, combustion of solid fuels for cooking, heating, home cleaning agents, insecticides industries, automobiles, power generation, poor environmental regulation, less efficient technology of production, congested roads, and age and poor maintenance of vehicles. The natural sources include incinerators and waste disposals, forest and agricultural fires (EPHA, 2009).

2.2.1.2 Water Pollution

Water is an essential ingredient for our wellbeing and a healthy life. Unfortunately, polluted water and air are common throughout the world (EPHA, 2009). The WHO states that one sixth of the world’s population, approximately 1.1 billion people do not have access to safe water and 2.4 billion lack basic sanitation (EPHA, 2009). Polluted water consists of Industrial discharged effluents, sewage water, rain water pollution (Ashraf et al, 2010) and polluted by agriculture or households cause damage to human health or the environment (European Public Health Alliance, 2009). This water pollution affects the health and quality of soils and vegetation (Carter, 1985).

2.2.1.3 Land/Solid Waste Pollution

Improper management of solid waste is one of the main causes of environmental pollution (Kimani, 2007). Land pollution is one of the major forms of environmental catastrophe our world is facing today (Khan, 2004). Deposition of wastes from heavy metal industries into landfills without special precautions has been reported (Lenkova and Vargova, 1994). Rushbrook (1994) has reported that coal and uranium mines have produced serious pollution problems, and much of the solid industrial waste containing heavy metals is disposed of, without pretreatment, in open dumps.

2.3 HEAVY METALS

Heavy metals are generally referred to as those metals which possess a specific density of more than 5 g/cm^3 and adversely affect the environment and living organisms (Järup, 2003).

A heavy metal is not toxic per se and it is only toxic when its concentration in the plant and animal exceeds a certain threshold ("it is the dose that makes the effect"). Some elements, called trace elements or micronutrients, have essential functions in plant and animal cells. This has been shown for Co, Cu, Fe, Mn, Mo, Ni and Zn. Only when the internal concentration exceeds a certain threshold do they demonstrate toxic effects, and then they are commonly termed "heavy metals" (Klaus-J, 2010).

Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional an d environmental reasons (Jaishankar et al., 2013).

Heavy metals are one of the important types of contaminants that can be found on the surface and in the tissues of fresh vegetables. Heavy metals rank high amongst the major contaminants of leafy vegetables (Mapanda et al., 2005). Zheijazkov and Neilson (1996) found that the concentrations of heavy metals in vegetables per unit dry matter generally follow the order: leaves > fresh fruits > seeds.

The prolonged human consumption of unsafe concentrations of heavy metals in foodstuffs may lead to the disruption of numerous biological and biochemical processes in the human body. Vegetables, especially leafy vegetables grown in heavy metal-contaminated soils, accumulate higher amounts of metals than do those grown in uncontaminated soils because they absorb these metals through their leaves (Al Jassir et al., 2005).

2.4 HEAVY METAL POISONING

Metals can contaminate the general environment through many routes. Because of their stability, they may penetrate environmental compartments, in some cases, many years after the initial deposition pollution of the soil and water systems may also arise from the weathering of disposed product (Nordberg et al., 2005). Heavy metal accumulations in plant and soil from natural and artificial sources and subsequent consequences represent important environmental pollution problems. Food safety issues and potential adverse health risks make this one of the most serious environmental concerns (Cui et al., 2004).

Some heavy metals such as copper, zinc, manganese, cobalt and molybdenum act as micronutrients for the growth of animals and human beings when present in trace quantities, whereas others such as cadmium, arsenic and chromium acts as carcinogens (Trichopoulos et al., 1997). Mercury and lead are associated with the development of abnormalities in children (Gibb and Chen, 1989). Long term intake of cadmium causes renal, prostate and ovarian cancers (Hartwig, 1998).

Generally, at the biochemical levels, the toxic effects caused by excess concentrations of heavy metals include competition for sites with essential metabolites, replacement of essential ions, reactions with –SH groups, damage to cell membranes and reactions with the phosphates groups (Okoronkwo et al., 2005).

2.4.1 Routes of Heavy Metal Exposure

Heavy metals enter the human body mainly through two routes which are inhalation and ingestion. Ingestion is the main route of exposure to these elements in human population (Türkdogan et al., 2003). Absorption through the skin is another route of exposure when the metals come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure accounts for a common route of exposure for adults (Ngan, 2006).

Ingestion is the most common route of exposure in children. Children may acquire toxic levels from the normal hand-to-mouth activity with contaminated soil or by actually eating objects that are not food (Dupler, 2001). Less common routes of exposure are during a radiological procedure, from inappropriate dosing or monitoring during intravenous nutrition and from broken thermometers (Smith et al., 1997).

2.4.2 Classifications of Heavy Metal Exposure

Exposure to toxic heavy metals is generally classified as acute, 14 days or less; intermediate, 15-354 days; and chronic, more than 365 days. Heavy metals are not easily biodegradable and so they can accumulate in vital human organs. Chronic low level intakes of heavy metals have adverse effects on human beings and other animals due to the fact that there is no effective mechanism for their elimination from the body (Bahemuka and Mubofu, 1999). Metals such as lead, mercury, cadmium and copper are cumulative poisons. These metals cause environmental hazards and are reported to be exceptionally toxic (Ellen et al., 1990).

Chronic toxicity results from repeated or continuous exposure, leading to an accumulation of the toxic substance in the body. Chronic exposure may result from contaminated food, air, water, or dust; living near a hazardous waste site; spending time in areas with deteriorating lead paint; maternal transfer in the womb; or from participating in hobbies that use lead paint or solder. Chronic exposure may occur in either at home or workplace. Symptoms of chronic toxicity are often similar to many common conditions and may not be readily recognized (WHO, 1998; Dupler, 2001).

2.4.3 Mechanism of Action of Heavy Metals

The heavy metal ions form complexes with proteins, in which carboxylic acid (–COOH), amine ($–NH_2$), and thiol (–SH) groups are involved. These modified biological molecules lose their ability to function properly and result in the malfunction or death of the cells. When metals bind to these groups, they inactivate important enzyme systems, or affect protein structure, which is linked to the catalytic properties of enzymes. This type of toxin may also cause the formation of radicals, dangerous chemicals that cause the oxidation of biological molecules (Neal and Guilarte, 2012).

2.5 HEAVY METALS CONTAMINATION OF SOILS

The heavy metals essentially become contaminants in the soil environments, because:

- their rates of generation via man-made cycles are more rapid relative to natural ones;
- they become transferred from mines to random environmental locations where higher potentials of direct exposure occur;
- the concentrations of the metals in discarded products are relatively high compared to those in the receiving environment; and
- the chemical form (species) in which a metal is found in the receiving environmental system may render it more bioavailable (D'Amore et al., 2005).

A simple mass balance of the heavy metals in the soil can be expressed as follows:

$$M_{total} = (M_p + M_a + M_f + M_{ag} + M_{ow} + M_{ip}) – (M_{cr} + M_l) \qquad (1)$$

where, “M” is the heavy metal, “p” is the parent material, “a” is the atmospheric deposition, “f” is the fertilizer sources, “ag” are the agrochemical sources, “ow” are the organic waste sources, “ip” are other inorganic pollutants, “cr” is crop removal, and “l” is the losses by leaching, volatilization, and so forth (Alloway, 1995; Lombi and Gerzabek, 1998).

2.5.1 Sources of Heavy Metal Contamination of Soils

2.5.1.1 Fertilizer

Agriculture was the first major human influence on the soil (Scragg, 2006). To grow and complete the lifecycle, plants must acquire not only macronutrients (N, P, K, S, Ca, and Mg), but also essential micronutrients. Some soils are deficient in the heavy metals (such as Co, Cu, Fe, Mn, Mo, Ni, and Zn) that are essential for healthy plant growth, and crops may be supplied with these as an addition to the soil or as a foliar spray. Cereal crops grown on Cu deficient soils are occasionally treated with Cu as an addition to the soil, and Mn may similarly be supplied to cereal and root crops (Lasat, 2000).

Large quantities of fertilizers are regularly added to soils in intensive farming systems to provide adequate N, P, and K for crop growth. The compounds used to supply these elements contain trace amounts of heavy metals (e.g., Cd and Pb) as impurities, which, after continued fertilizer, application may significantly increase their content in the soil (Jones and Jarvis, 1981). Metals, such as Cd and Pb, have no known physiological activity. Application of certain phosphatic fertilizers inadvertently adds Cd and other potentially toxic elements to the soil, including F, Hg, and Pb (Jones and Jarvis, 1981).

2.5.1.2 Pesticides

Several common pesticides used fairly extensively in agriculture and horticulture in the past contained substantial concentrations of metals. For instance in the recent past, about 10% of the chemicals have approved for use as insecticides and fungicides in UK were based on compounds which contain Cu, Hg, Mn, Pb, or Zn. Examples of such pesticides are copper-containing fungicidal sprays such as

Bordeaux mixture (copper sulphate) and copper oxychloride (Jones and Jarvis, 1981).

Such contamination has the potential to cause problems, particularly if sites are redeveloped for other agricultural or non-agricultural purposes. Compared with fertilizers, the use of such materials has been more localized, being restricted to particular sites or crops (McLaughlin et al., 2000).

2.5.1.3 Biosolids and Manures

The application of numerous biosolids (e.g. livestock manures, composts, and municipal sewage sludge) to land inadvertently leads to the accumulation of heavy metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Tl, Sb, and so forth, in the soil (Basta et al., 2005). Certain animal wastes such as poultry, cattle, and pig manures produced in agriculture are commonly applied to crops and pastures either as solids or slurries (Sumner, 2000). Although most manures are seen as valuable fertilizers, in the pig and poultry industry, the Cu and Zn added to diets as growth promoters and As contained in poultry health products may also have the potential to cause metal contamination of the soil (Sumner, 2000).

The manures produced from animals on such diets contain high concentrations of As, Cu, and Zn and, if repeatedly applied to restricted areas of land, can cause considerable build-up of these metals in the soil in the long run.

Biosolids (sewage sludge) are primarily organic solid products, produced by wastewater treatment processes that can be beneficially recycled (USEPA, 1994). Land application of biosolids materials is a common practice in many countries that allow the reuse of biosolids produced by urban populations (Weggler, 2004). The term sewage sludge is used in many references because of its wide recognition and its regulatory definition.

However, the term biosolids is becoming more common as a replacement for sewage sludge because it is thought to reflect more accurately the beneficial characteristics inherent to sewage sludge (Silveira, 2003). It is estimated that in the United States, more than half of approximately 5.6 million dry tonnes of sewage sludge used or disposed of annually is land applied, and agricultural utilization of biosolids occurs in every region of the country. In the European community, over 30% of the sewage sludge is used as fertilizer in agriculture (Silveira, 2003). In Australia over 175000 tonnes of dry biosolids are produced each year by the major metropolitan authorities, and currently most biosolids applied to agricultural land are used in arable cropping situations where they can be incorporated into the soil (McLaughlin et al., 2000).

Heavy metals most commonly found in biosolids are Pb, Ni, Cd, Cr, Cu, and Zn, and the metal concentrations are governed by the nature and the intensity of the industrial activity, as well as the type of process employed during the biosolids treatment (Mattigod and Page, 1983). Under certain conditions, metals added to soils in applications of biosolids can be leached downwards through the soil profile and can have the potential to contaminate groundwater (McLaren et al., 2004).

2.5.1.4 Wastewater

The application of municipal and industrial wastewater and related effluents to land dates back 400 years and now is a common practice in many parts of the world (Reed et al., 1995). Worldwide, it is estimated that 20 million hectares of arable land are irrigated with waste water. In several Asian and African cities, studies suggest that agriculture based on wastewater irrigation accounts for 50% of the vegetable supply to urban areas (Bjuhr, 2007).

Farmers generally are not bothered about environmental benefits or hazards and are primarily interested in maximizing their yields and profits. Although the metal concentrations in wastewater effluents are usually relatively low, long-term irrigation of land with such can eventually result in heavy metal accumulation in the soil (Bjuhr, 2007).

2.5.1.5 Metal Mining and Milling Processes and Industrial Wastes

Mining and milling of metal ores coupled with industries have bequeathed many countries, the legacy of wide distribution of metal contaminants in soil. During mining, tailings (heavier and larger particles settled at the bottom of the flotation cell during mining) are directly discharged into natural depressions, including onsite wetlands resulting in elevated concentrations (DeVolder et al., 2003). Extensive Pb and Zn ore mining and smelting have resulted in contamination of soil that poses risk to human and ecological health. Many reclamation methods used for these sites are lengthy and expensive and may not restore soil productivity. Soil heavy metal environmental risk to humans is related to bioavailability. Assimilation pathways include the ingestion of plant material grown in (food chain), or the direct ingestion (oral bioavailability) of, contaminated soil (Basta and Gradwohl, 1998).

Other materials are generated by a variety of industries such as textile, tanning, petrochemicals from accidental oil spills or utilization of petroleum-based products, pesticides, and pharmaceutical facilities and are highly variable in composition. Although some are disposed of on land, few have benefits to agriculture or forestry. In addition, many are potentially hazardous because of their contents of heavy metals (Cr, Pb, and Zn) or toxic organic compounds and are seldom, if ever, applied to land. Others are very low in plant nutrients or have no soil conditioning properties (Sumner, 2000).

2.5.1.6 Air-Borne Sources

Airborne sources of metals include stack or duct emissions of air, gas, or vapour streams, and fugitive emissions such as dust from storage areas or waste piles. Metals from airborne sources are generally released as particulates contained in the gas stream. Some metals such as As, Cd, and Pb can also volatilize during high-temperature processing. These metals will convert to oxides and condense as fine particulates unless a reducing atmosphere is maintained (Smith et al., 1995).

2.6 HEAVY METAL CONTAMINATION OF VEGETABLES

Vegetables are an important part of a human beings diet because they are a source of nutrients. Vegetables constitute important functional food components by contributing protein, vitamins, iron, calcium and other nutrients which have marked health effects (Arai, 2002). There is an inherent tendency of plants to take up toxic substances including heavy metals that are subsequently transferred along the food chain (Singh et al., 2010). And as such, heavy metal contamination in vegetables cannot be underestimated as food stuffs are important components of human diet. Heavy metal contamination of the food items is one of the most important aspects of food quality assurance (Khan et al., 2008).

Contamination of foods by heavy metals has become a challenge for producers and consumers. The main sources of heavy metals to vegetable crops are their growth media (soil, air, nutrient solutions) from which these heavy metals are taken up by the roots or foliage (Lokeshwari and Chandrappa, 2006). The toxic and detrimental impacts of heavy metals become apparent only when long-term consumption of contaminated vegetables occurs. Regular monitoring of heavy metals in vegetables and other food items should be performed in order to prevent excessive build up of these heavy metals in the human food chain (Khanna and Khanna, 2011).

Vegetables can take up and accumulate heavy metals in quantities high enough to cause clinical problems to humans (Alam et al., 2003). Daily metal intake estimate does not take into account the possible metabolic ejection of the metals but can easily tell the possible ingestion rate of a particular metal. Leafy vegetables grown on heavy metal contaminated soils accumulate higher amounts of metals than those grown in uncontaminated soils because of the fact that they absorb these metals through their roots (Sharma et al., 2007; Marshall et al., 2007). Heavy metals are persistent in the environment and are subject to bioaccumulation in food-chains. They are easily accumulated in the edible parts of leafy vegetables, as compared to grain or fruit crops (Mapanda et al., 2005).

2.7 SELECTED HEAVY METALS

2.7.1 Zinc (Zn)

Zinc is an essential nutrient in humans and animals and is necessary for the function of a large number of metallo-enzymes. These enzymes include alcohol dehydrogenase, alkaline phosphatase, carbonic anhydrase, leucine aminopeptidase, superoxide dismutase, and deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) polymerase. An acute oral dose of zinc may cause symptoms such as tachycardia, vascular shock, dyspeptic nausea, vomiting, diarrhoea, pancreatitis and damage of hepatic parenchyma (Salgueiro et al., 2000).

When high levels of zinc are ingested inhibition of copper absorption through interaction with metallothionein at the brush border of the intestinal lumen occurs. Both copper and zinc appear to bind to the same metallothionein protein; however, copper has a higher affinity for metallothionein than zinc and displaces zinc from metallothionein protein. Copper complexed with metallothionein is retained in the mucosal cell, relatively unavailable for transfer to plasma, and is excreted in the feces when the mucosal cells are sloughed off. Thus, an excess of zinc can result in a decreased availability of dietary copper, and the development of copper deficiency (Gyorffy and Chan, 1992).

On the other hand zinc deficiency has been associated with dermatitis, anorexia, growth retardation, poor wound healing, hypogonadism with impaired reproductive capacity, impaired immune function, and depressed mental function; increased incidence of congenital malformations in infants has also been associated with zinc deficiency in the mothers (Sandstead, 1981).

2.7.2 Chromium (Cr)

Chromium (Cr) is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of the mineral chromite, $FeCr_2O_4$. Major sources of Chromium contamination include releases from electroplating processes and the disposal of Cr containing wastes (Smith et al., 1995).

Chromium (VI) is the form of Cr commonly found at contaminated sites. Chromium (VI) can be reduced to Cr (III) by soil organic matter, S^2- and Fe^{2+} ions under anaerobic conditions often encountered in deeper groundwater. Major Cr (VI) species include chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$). Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides (Smith et al., 1995).

Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content, and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and un-adsorbed chromium complexes can leach from soil into groundwater. Chromium is associated with allergic dermatitis in humans (Scragg, 2006).

2.7.3 Cobalt (Co)

As a component of cyanocobalmin (vitamin B12), cobalt is essential in the body; the cobalt has been identified in most tissues of the body, with the highest concentrations found in the liver (ATSDR, 2004). Cobalt enters the air through burning of oil and cobalt compounds that are used as colorants in glass, ceramics, and paints, as catalysts, and as paint driers. Cobalt compounds are also used as trace element additives in agriculture and medicine (ATSDR, 2004). After it enters the air cobalt is associated with particles which will settle to the ground within few days. Some of the compounds may then settle in water, food and drinking water and these are the largest sources of exposure to the general population (Udeh, 2004).

2.7.4 Lead (Pb)

Lead is a toxic element that can be harmful to plants, although plants usually show ability to accumulate large amounts of lead without visible changes in their appearance or yield. Lead is a well-known neurotoxin. Impairment of neurodevelopment in children is the most critical effect. Exposure in uterus, during breastfeeding and in early childhood may all be responsible for the effects. Lead accumulates in the skeleton and its mobilization from bones during pregnancy and lactation causes exposure to fetuses and breastfed infants (ATSDR, 2007). In many plants, lead accumulation can exceed several hundred times the threshold of maximum level permissible for human (Wierzbicka, 1995). It has been suggested that lead on a cellular and molecular level may permit or enhance carcinogenic events involved in DNA damage, DNA repair, and regulation of tumour suppressor and promoter genes (Silbergeld, 2003).

Plants grown in lead-contaminated soils accumulate low levels of lead in the edible portions of the plant from adherence of dusts and translocation into the tissues (Finster et al., 2004).

2.7.5 Cadmium (Cd)

Cadmium is one of the big three heavy metal poisons and is not known for any essential biological function. In its compounds, Cd occurs as the divalent Cd (II) ion. Cadmium is directly below Zn in the periodic table and has a chemical similarity to that of Zn, an essential micronutrient for plants and animals. This may account in part for Cd’s toxicity; because Zn being an essential trace element, its substitution by Cd may cause the malfunctioning of metabolic processes (Campbell, 2006).

Cadmium is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products. In addition, acid rain and the resulting acidification of soils and surface waters have increased the geochemical mobility of Cd, and as a result its surface-water concentrations tend to increase as lake water pH decreases (Campbell, 2006).

Cadmium is produced as an inevitable by-product of Zn and occasionally lead refining. The application of agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils, and the bioavailability of this Cd determines whether plant Cd uptake occurs to a significant degree. Cadmium is very biopersistent, but has few toxicological properties and, once absorbed by an organism, remains resident for many years (Weggler et al., 2004).

Since the 1970s, there has been sustained interest in possible exposure of humans to Cd through their food chain, for example, through the consumption of certain species of shellfish or vegetables. Concern regarding this latter route (agricultural crops) led to research on the possible consequences of applying sewage sludge (Cd-rich biosolids) to soils used for crops meant for human consumption, or of using cadmium-enriched phosphate fertilizer (Campbell, 2006).

Cadmium in the body is known to affect several enzymes. It is believed that the renal damage that results in proteinuria is the result of Cd adversely affecting enzymes responsible for reabsorption of proteins in kidney tubules. Cadmium also reduces the activity of delta-aminolevulinic acid synthetase, arylsulfatase, alcohol dehydrogenase, and lipoamide dehydrogenase, whereas it enhances the activity of deltaaminolevulinic acid dehydratase, pyruvate dehydrogenase, and pyruvate decarboxylase (Manahan, 2003). The most spectacular and publicized occurrence of cadmium poisoning resulted from dietary intake of cadmium by people in the Jintsu River Valley, near Fuchu, Japan. The victims were afflicted by itai itai disease, which means ouch, ouch in Japanese. The symptoms are the result of painful osteomalacia (bone disease) combined with kidney malfunction. Cadmium poisoning in the Jintsu River Valley was attributed to irrigated rice contaminated from an upstream mine producing Pb, Zn, and Cd. The major threat to human health is chronic accumulation in the kidneys leading to kidney dysfunction. Food intake and tobacco smoking are the main routes by which Cd enters the body (Manahan, 2003).

2.7.6 Copper (Cu)

Copper is an essential nutrient that is incorporated into a number of metalloenzymes involved in haemoglobin formation, drug/xenobiotic metabolism, carbohydrate metabolism, catecholamine biosynthesis, the crosslinking of collagen, elastin, and hair keratin, and the antioxidant defense mechanism. Copper-dependent enzymes, such as cytochrome C oxidase, superoxide dismutase, ferroxidases, monoamine oxidase, and dopamine β- monooxygenase, function to reduce activated oxygen species or molecular oxygen. Symptoms associated with copper deficiency in humans include normocytic, hypochromic anaemia, leukopenia, and osteoporosis (ATSDR, 2004).

Although copper homeostasis plays an important role in the prevention of copper toxicity, exposure to excessive levels of copper can result in a number of adverse health effects including liver and kidney damage, anaemia, immunotoxicity, and developmental toxicity. Many of these effects are consistent with oxidative damage to membranes or macromolecules. Copper can bind to the sulfhydryl groups of several enzymes, such as glucose-6- phosphatase and glutathione reductase, thus interfering with their protection of cells from free radical damage (ATSDR, 2004).

2.7.7 Iron (Fe)

An elevated dietary iron intake enhances the incidence of carcinogen-induced mammary tumors in rats and estrogen-induced kidney tumors in Syrian hamsters. Estrogen administration increases iron accumulation in hamsters and facilitates iron uptake by cells in culture. In humans, increased body stores of iron have been shown to increase the risk of several estrogen-induced cancers (Liehr and Jones, 2001).

Iron acts as a catalytic centre for a broad spectrum of metabolic functions. Iron is also a component of various tissue enzymes, such as the cytochromes, that are critical for energy production, and enzymes necessary for immune system functioning. The fact that serum copper has been found to be low in some cases of iron deficiency anemia suggests that iron status has an effect on copper metabolism (Michael et al., 2009).

Iron deficiency includes symptoms such as reduced resistance to infection, reduced work productivity, reduced physical fitness, weakness, fatigue, impaired cognitive function, and reduced learning ability, increased distractibility, impaired reactivity and coordination, itching, inability to regulate body temperature and eating pica (Beard, 2001).

2.7.8 Mercury (Hg)

Mercury is a ubiquitous environmental toxin that produces a wide range of adverse health effects in humans (Guzzi and La Porta, 2008). The most common natural forms of mercury found in the environment are metallic mercury, mercuric sulfide (cinnabar ore, mercuric chloride, and methylmercury). Each of them has its own profile of toxicity (ATSDR, 1999).

Methylmercury is of particular concern because it can build up in certain edible freshwater and saltwater fish and marine mammals to levels that are many times greater than levels in the surrounding water. Metallic and inorganic mercury enters the air from mining deposits of ores that contain mercury, from the emissions of coal fired power plants, from burning municipal and medical waste, from the production of cement, and from uncontrolled releases in factories that use mercury. Metallic mercury is a liquid at room temperature, but some of the metal will evaporate into the air and can be carried long distances. In air, the mercury vapour can be changed into other forms of mercury, and can be further transported to water or soil in rain or snow (Wiwanitkit, 2009).

Inorganic mercury may also enter water or soil from the weathering of rocks that contain mercury, from factories or water treatment facilities that release water contaminated with mercury, and from incineration of municipal garbage that contains mercury (for example, in thermometers, electrical switches, or batteries that have been thrown away (Balshaw et al., 2007). Mercury can enter and accumulate in the food chain. The form of mercury that accumulates in the food chain is methylmercury (Balshaw et al., 2007; Wiwanitkit, 2009).

Symptoms of mercury poisoning include permanent damage to the brain and kidneys, personality changes (irritability, shyness, and nervousness), tremors, changes in vision, deafness, muscle incoordination, loss of sensation, and difficulties with memory (ATSDR, 1999).

2.7.9 Manganese

Manganese (Mn) is an essential plant mineral nutrient, playing a key role in several physiological processes, particularly photosynthesis. Manganese deficiency is a widespread problem, most often occurring in sandy soils, organic soils with a pH above 6 and heavily weathered, tropical soils. Mn is readily transported from root to shoot through the transpiration stream, but not readily remobilized through phloem to other organs after reaching the leaves (Loneragan, 1988).

Necrotic brown spotting on leaves, petioles and stems is a common symptom of Mn toxicity (Wu, 1988). This spotting starts on the lower leaves and progresses with time toward the upper leaves (Horiguchi, 1988). With time, the speckles can increase in both number and size resulting in necrotic lesions, leaf browning and death. Another common symptom is known as ‘‘crinkle leaf’’, and it occurs in the youngest leaf, stem and petiole tissue. It is also associated with chlorosis and browning of these tissues (Loneragan, 1988). Manganese toxicity in some species starts with chlorosis of older leaves moving toward the younger leaves with time. This symptom starts at the leaf margins progressing to the interveinal areas and if the toxicity is acute, the symptom progresses to marginal and interveinal necrosis of leaves (Bachman and Miller, 1995).

2.7.10 Aluminium

Aluminium is primary among the factors that reduce plant growth on acid soils. Although it is generally harmless to plant growth in pH-neutral soils, the concentration in acid soils of toxic Al^{3+} cations increases and disturbs root growth and function (Ma et al., 2001).

Most acid soils are saturated with aluminium rather than hydrogen ions. The acidity of the soil is therefore, a result of hydrolysis of aluminium compounds. The concept of "corrected lime potential” is now used to define the degree of base saturation in soil testing to determine the "lime requirement" (Turner and Clark, 1966).

While aluminium can be toxic at higher levels, it is considerably less toxic than either mercury or lead. In fact, aluminium is found at easily measurable levels in various biological fluids and tissues. However, at high levels aluminum has the potential to cause a number of health problems such as anaemia and other blood disorders, colic, fatigue, dental caries, dementia dialactica, kidney and liver dysfunctions, neuromuscular disorders, osteomalacia and Parkinson's disease (NAS/NRC, 1999).

Wheat has developed a tolerance to aluminium, releasing organic compounds that bind to harmful aluminium cations. Sorghum is believed to have the same tolerance mechanism. The first gene for aluminium tolerance has been identified in wheat. It was shown that sorghum's aluminium tolerance is controlled by a single gene, as for wheat. This adaptation is not found in all plants (Turner, 1965).

2.7.11 Titanium

Potential anthropogenic sources of Ti in the environment include paint pigments (TiO_2 pigment accounts for the largest use of the element) and its alloys with Al, Mo, Mn and Fe, which are used extensively in aircraft, ship and missile manufacture. Cooper and Thornton (1994) have reported that anthropogenic anomalies in drainage are rarely recorded for Ti, which is not surprising, given the general background levels for this element in the environment and its aqueous chemistry.

There is no evidence to suggest that Ti performs any necessary role in the human body (Mertz, 1987). Titanium is considered to be nontoxic, because of its poor absorption and retention in living organisms (Mertz, 1987). No environmental effects have been reported.

TiO_2 nanoparticles are approved by the FDA and European Food Safety Authority (EFSA) TiO_2 (E171) is approved by the FDA as a food additive to a level of up to 1% by weight, and up to 358 mg per dosage in drug tablets (Kumpel and Ruder, 2006).

2.7.12 Strontium

Strontium is "natural" in the sense that it is an element commonly found in soil and water. Non-radioactive strontium, while of low toxicity, is generally considered a food contaminant and has no currently known biological role (ASTDR, 2007).

The effect of strontium on bone is likely related to its similarity to calcium, a mineral with a known biological value. Strontium is structurally similar to calcium and can replace calcium in the bone mineral matrix. A key difference is that calcium, as an essential nutrient, is homeostatically controlled, while strontium is not. Strontium is not alone as a mineral with "bone seeking" activity. Lead is well absorbed from the gut, is incorporated into bone, and increases bone density (Campbell et al., 2004). Lead, of course, is also a natural element found in the soil, yet does not have a biological role in human health.

As an element found in water and soil, strontium is a trace mineral in the diet. The average total body store (primarily in bone) for strontium in humans is estimated to be 300 to 400 mg. The average daily intake of strontium from the diet is estimated at only 1 to 5 mg. In contrast, calcium accounts for approximately 2% to 4% of body weight. The average female body contains about 1,000 to 1,200 grams of calcium, 99% of which is found in bones and teeth. Calcium intake data taken from the National Health and Nutrition Examination Survey (NHANES) indicate that the mean dietary calcium intake among adults in the U.S. is 800 mg/day, well below the recommended intake for adults of 1,000 to 1,200 mg/day. Calcium deficiency is also a common concern worldwide. For example, Pasco et al. (2000) have reported that 76% of Australian women aged 20 to 54 years, 87% of older women, and 82% of lactating women had total daily calcium intakes that were below the recommended dietary intake (RDI) even when calcium supplements were included.

2.8 SELECTED VEGETABLES

2.8.1 Fluted Pumpkin (*Telfairia occidentalis*)

Fluted Pumpkin (*Telfairia occidentalis*) is a species of cucurbitaceace family in the tropics largely consumed in Nigeria, Ghana, and Sierra Leone. The common names for fluted pumpkin include Ubong in Ibibio and Ugu in Igbo. It is a creeping vegetable that spreads low across the ground with lobed leaves and long twisting tendrils. It is a warm weather crop that grows well in low lands and tolerates elevation of some few meters above the ground. It thrives best in soils rich in organic matter (Uboh et al., 2011). Fluted pumpkin plays important role in human and livestock nutrition. It is a source of protein, oil, minerals, and vitamins. The leaves are low in crude fibre, but a rich source of folic acid, calcium, zinc, potassium, cobalt, copper, iron, and vitamins A, C, and K. It also has medicinal values as fluted pumpkin leaves and seeds could be used to increase hematological indices, improve sperm quality, and reduce blood glucose. It is rich in antioxidants, thiamin, riboflavin, and ascorbic acid. The young shoots and leaves of this vegetable are used in preparation of several delicacies in southern Nigeria, including Edikang Ikong Soup, a popular delicacy of the Efiks and Ibibios in Cross River and Akwa Ibom States, Nigeria. It thrives better in the early part of the rainy season, planted between August and October, and can be grown in a garden. It can survive 3-4 years if there is moisture in the soil (Idodo-Umeh and Ogbeibu, 2010).

***Figure 2.1: Typical fluted pumpkin leaves* (*Telfairia occidentalis*)**

2.8.2 African Spinach (*Amaranthus hybridus*)

Amaranthus hybridus is an annual herbaceous plant of 1- 6 feet high. The leaves are alternate petioled, 3 – 6 inches long, dull green, and rough, hairy, ovate or rhombic with wavy margins. The flowers are small, with greenish or red terminal panicles. Taproot is long, fleshy red or pink. The seeds are small and lenticellular in shape; with each seed averaging 1 – 1.5 mm in diameter and 1000 seeds weighing 0.6 – 1.2 g. It is rather a common species in waste places, cultivated fields and barnyards. In Nigeria, *Amaranthus hybridus* leaves combined with condiments are used to prepare soup (Oke, 1983; Mepha et al., 2007). In Congo, their leaves are eaten as spinach or green vegetables (Dhellot et al., 2006). These leaves boiled and mixed with a groundnut sauce are eaten as salad in Mozambique and in West Africa (Oliveria and DeCarvalho, 1975). *Amaranthus hybridus* has been shown to contain large amount of squalene, a compound that has both health and industrial benefits (He and Corke, 2003).

***Figure 2.2: Typical African spinach* Spinach (*Amaranthus hybridus*)**

2.8.3 Waterleaf (*Talinum triangulare*)

Waterleaf (*Talinum triangulare*) is a non-conventional vegetable crop of the portulacea family which originated from tropical Africa and is widely grown in West Africa, Asia, and South America. Waterleaf as a vegetable has some inherent characteristics which makes it attractive to small-holder farmers and consumers (Schippers, 2000).

Nutritionally, waterleaf has been proven to be high in crude-protein (22.1%), ash (33.98%), and crude fibre (11.12%). It also has some medicinal values in humans and acts as green forage for rabbit feed management (Ekpenyong, 1986; Aduku and Olukosi, 1990). In addition, waterleaf production provides a complementary source of income to small-scale farming households (Udoh, 2005).

Figure 2.3: Typical waterleaf (Talimun triangulare)

2.9 REMEDIATION OF HEAVY METAL CONTAMINATION

At present, there are varieties of approaches for heavy metal remediation (USEPA, 2007; Grupta et al., 2000).

The key factors that may influence the applicability and selection of any of the available remediation technologies are:

- cost,
- long-term effectiveness/permanence,
- commercial availability,
- general acceptance,
- applicability to high metal concentrations,
- applicability to mixed wastes (heavy metals and organics),
- toxicity reduction,
- mobility reduction, and
- volume reduction.

2.9.1 Immobilization Techniques

Ex situ and *in situ* immobilization techniques are practical approaches to remediation of metal-contaminated soils. The ex situ technique is applied in areas where highly contaminated soil must be removed from its place of origin, and its storage is connected with a high ecological risk (e.g., in the case of radio nuclides).

The advantages of this method are:

- fast and easy applicability and
- relatively low costs of investment and operation.

The disadvantages of this method include:

- high invasivity to the environment,
- generation of a significant amount of solid wastes (twice as large as volume after processing),
- the by-product must be stored on a special landfill site, (iv) in the case of changing of the physicochemical condition in the side product or its surroundings, there is serious danger of the release of additional contaminants to the environment, and
- permanent control of the stored wastes is required.

In the *in situ* technique, the fixing agents amendments are applied on the unexcavated soil. The technique's advantages are:

- its low invasivity,
- simplicity and rapidity,
- relatively inexpensive, and
- small amount of wastes are produced,
- high public acceptability,
- covers a broad spectrum of inorganic pollutants.

The disadvantages of in situ immobilization are:

- its only a temporary solution (contaminants are still in the environment),
- the activation of pollutants may occur when soil physicochemical properties change,
- the reclamation process is applied only to the surface layer of soil (30–50cm), and
- permanent monitoring is necessary (Martins and Ruby, 2004; USEPA, 1997).

Immobilization technology often uses organic and inorganic amendment to accelerate the attenuation of metal mobility and toxicity in soils. The primary role of immobilizing amendments is to alter the original soil metals to more geochemically stable phases via sorption, precipitation, and complexation processes (Hashimoto et al., 2009).

2.9.2 Soil Washing

Soil washing is essentially a volume reduction/waste minimization treatment process. It is done on the excavated (physically removed) soil (ex situ) or on-site (in situ). Soil washing as discussed in this review refers to ex situ techniques that employ physical and/or chemical procedures to extract metal contaminants from soils.

During soil washing, (i) those soil particles which host the majority of the contamination are separated from the bulk soil fractions (physical separation), (ii) contaminants are removed from the soil by aqueous chemicals and recovered from solution on a solid substrate (chemical extraction), or (iii) a combination of both. In all cases, the separated contaminants then go to hazardous waste landfill (or occasionally are further treated by chemical, thermal, or biological processes (Dermont, 2008).

2.9.3 Phytoremediation

Phytoremediation, also called green remediation, botanoremediation, agroremediation, or vegetative remediation, can be defined as an in situ remediation strategy that uses vegetation and associated microbiota, soil amendments, and agronomic techniques to remove, contain, or render environmental contaminants harmless (Cunningham and Ow, 1996; Helmisaar, et al., 2007). The idea of using metal accumulating plants to remove heavy metals and other compounds was first introduced in 1983, but the concept has actually been implemented for the past 300 years on wastewater discharges (Chaney et al., 1997; Henry, 2000).

2.10 X-RAY FLUORESCENCE TECHNIQUE

Earlier, X-ray fluorescence (XRF) analysis was used in quantitative elemental analysis of a wide range of organic and inorganic samples. The basis of the technique is that all elements emit secondary (fluorescent) X-rays of characteristic energy when exposed to X-rays of appropriate higher energy. Energy and intensity of emitted X-rays are used to determine elemental composition. In general, heavier the element being analysed, higher the energy of X-rays required to elicit fluorescence, higher the energy of fluorescence, then it is easier to detect fluorescence (Fig. 2.4 – 2.5). The lightest elements exist in biological samples (e.g. H, B, C, N, O) are not generally detectable by XRF, while the elements such as Na, Mg, P, S, Cl, K, Ca are detectable only at higher concentrations or under highly specialized conditions, and heavier elements namely Mn, Fe, Cu and Zn (trace metals) or toxic heavy metals are readily analysed, even at trace levels (Arai, 2006; West et al., 2010).

Major advantages of XRF over other analytical methods are that analyses are non-destructive, simultaneous multi-element analysis, use no noxious chemicals and produce no toxic wastes, losses that encounter in chemical methods during dry ashing and acid extractions are avoided and can be made on solid samples. Since XRF signal is obtained from transitions among inner shell electrons, not bonding electrons, XRF also has the advantage that signals are independent of chemical form.

Of the various types of X-ray spectrometry available, laboratory ‘bench-top‘ Energy-Dispersive X-ray Fluorescence (EDXRF) is the foremost commonly used for routine analysis of large number of samples (Gezahegn et al., 2017; Arai, 2006; West et al., 2010).

The wavelength dispersive X-ray fluorescence (WDXRF) spectrometer, which is the second type of X-ray fluorescence (XRF) technique, is different from EDXRF spectrometer only in the aspect of X-ray sources and optics and detector technologies. EDXRF technique depends on semiconductor-type detectors such as Si(Li) or lithium-drifted silicon detector. WDXRF technique uses analysing crystals to disperse the emitted photons based on their wavelength and place the detector at the fixed angular locations in order to analyse the elements. Such detectors are NaI(Tl) scintillation detector (Jenkins, 1995).

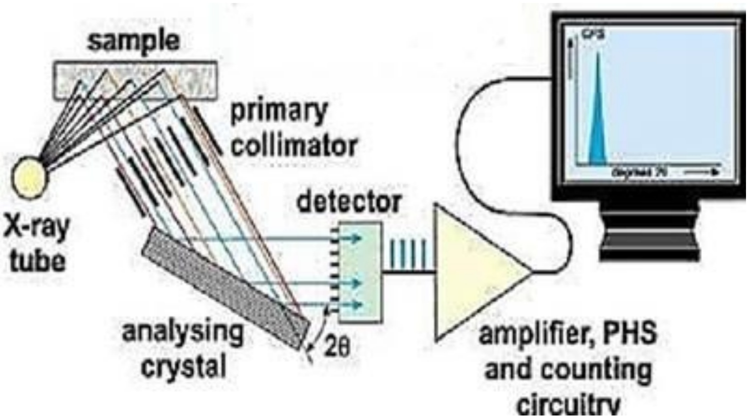

Figure 2.4: Schematic Diagram of X-ray Fluorescence (XRF) Spectrometer

Figure 2.5: Typical X-ray Fluorescence (XRF) Spectrometer

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 Study Locations

Four (4) different study locations were chosen in the South-West Geopolitical Region of the Federal Republic of Nigeria, two (2) each from Owo Local Government Areas of Ondo State and Etsako-West Local Government Areas of Edo State. Owo, situated halfway between the towns of Ile-Ife and Benin-City, is located on Latitude 7.1989° N and Longitude 5.5932° E with a population of 222,262, based on 2006 population census (Figure 3.1). Etsako-West Local Government Area has an area of 660 km^2 on Latitude 7.0878° N and Longitude 6.5010° E with the headquarters in Auchi, comprising Auchi, Uzairue, South Ibie, Agbede and The Anwain Clan (Figure 3.2). The population grew to 42,638 by 1952, including people from many Nigerian tribes, and as of 2005–2006, the population was 152,652.

The study locations in Owo Local Government Area were farmlands at St. Louis and Osuma Layout. The farmland at St. Louis was behind St. Louis Nursery and Primary School, close to Okosi Spring, flowing through Sadibo, Ijasun and Ajaka areas. The farmland at Osuma Layout was located close to Adedewe Nursery School along old Owo-Akure Road with a spring, Agunka Spring flowing through it. The locations in Etsako-West Local Government Area were Water-Board, Auchi and Iyerekhu, South-Ibie, Edo State. The farmland in Water-Board, called Peter Farm was located on a slope of a hill, flanked with River Orle, running through Warrake and Iyamho. The farmland in Iyerekhu, called Oloyede-Ogunbodede Farm was a piece out of many farmlands in the location without any sight of water body or refuse disposal site. Majority were into sustenance farming with the use of fertilizers to enhance the soil fertility.

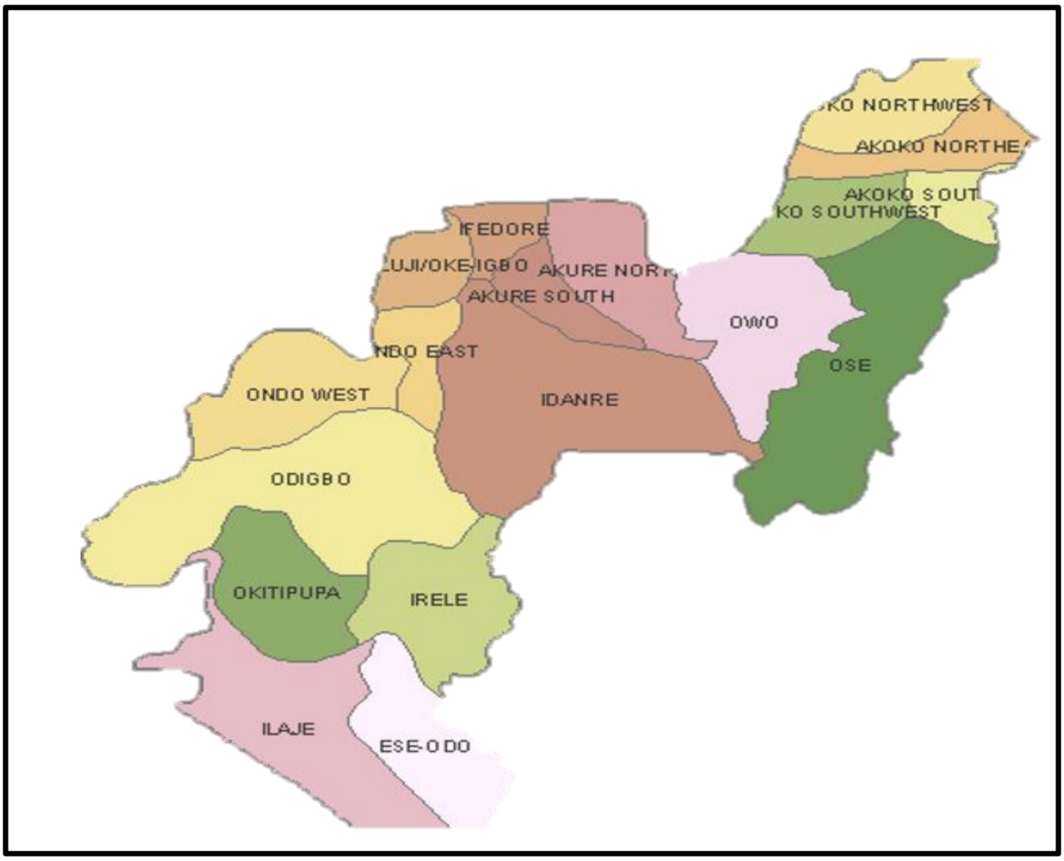

Figure 3.1: Map of Ondo State showing Owo Local Government Area

(Source: Google Map data, 2017a)

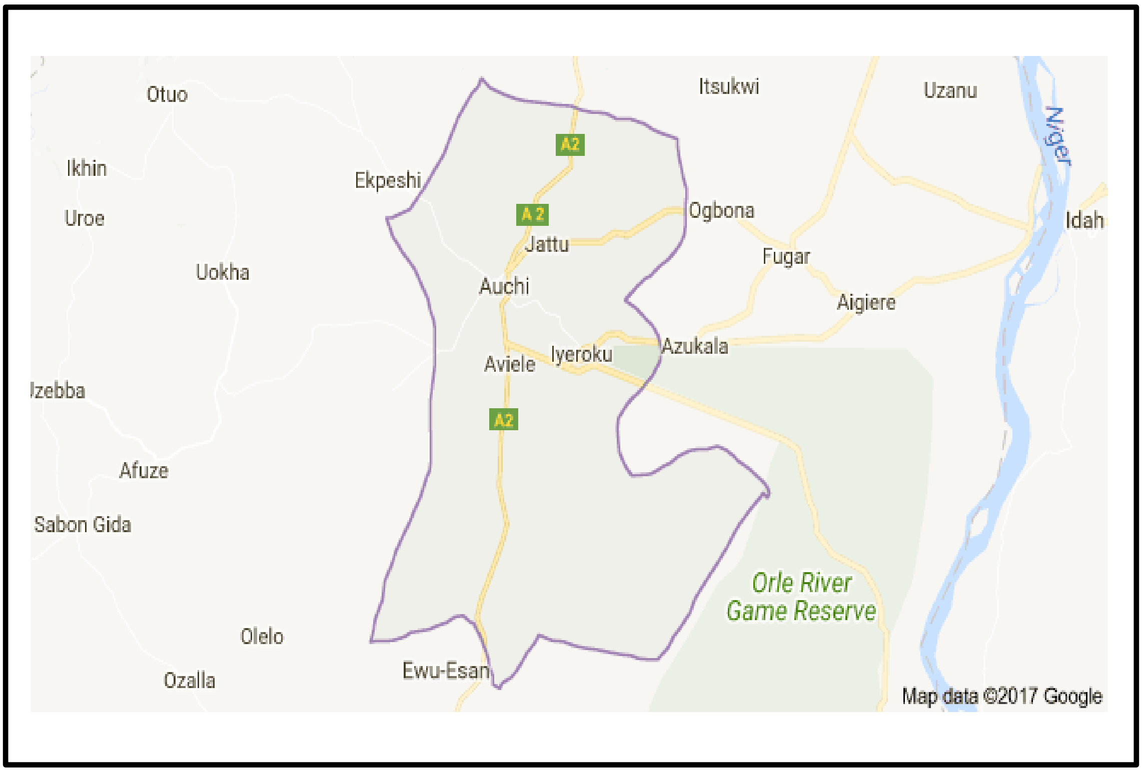

Figure 3.2: Map of Edo State showing Etsako-West Local Government Area

(Source: Google Map data, 2017b)

3.1.2 Vegetable Samples

Random sampling technique was employed to collect the vegetable samples of fluted pumpkin leaves (*Telfairia occidentali*s), African spinach, "Green" (*Amaranthus hybridus*) and waterleaf (*Talinum* triangulare) at St. Louis farm, Osuma Layout farm, Water-Board farm and Iyerekhu farm to obtain composite samples. The leaves of vegetable samples were separated from the whole plants with the aid of a stainless steel knife and labelled.

3.1.3 Soil Samples

Random samples of soils from St. Louis farm, Osuma Layout farm, Water-Board farm and Iyerekhu farm were taken at uniform depth of 15 cm with the aid of a hand trowel that had been pre-cleaned with concentrated nitric acid in order to prevent heavy metal contamination prior to analysis.

3.2 METHODS

3.2.1 Preparation of Vegetable Samples

The vegetable samples were washed with tap water and de-ionized water to remove air pollutants, followed by oven drying at 105 ^{o}C 48 h to remove moisture. The dried samples were pulverized, using agate pestle and mortar, followed by sieving through a 0.5 mm mesh size sieve to obtain a uniform particle size. Each vegetable sample was labelled and stored in a dry plastic container that had been pre-cleaned with concentrated nitric acid to prevent heavy metal contamination prior to analysis with x-ray fluorescence (XRF) spectrometer.

3.2.2 Preparation of Soil Samples

The soil samples were air dried for 48 hours, ground and sieved using 0.5 mm mesh size sieve to have uniform particle size. Each sample was labelled and stored in a dry plastic container that had been pre-cleaned with concentrated nitric acid prior to analysis with X-ray fluorescence (XRF) spectrometer.

3.2.3 Determination of Heavy Metals

Experimental studies of both soil and vegetable samples were carried out at Ahmadu Bello University, Department of Chemical Engineering, Zaria, Nigeria, using a wavelength dispersive X-ray fluorescence (WDXRF) spectrometer (Oxford Instrument, X-MET8000 series). Samples were oven-dried at 80°C for 18-20 hours. Each sample was repeatedly fine-ground to less than 50 μm sieve-size, weighed to between 100 - 200 mg from which pellets of 2.5 cm diameter were made in a pellet-pressing machine under 10-15 ton of pressure. The pellets were subjected to XRF spectroscopic analysis according to the protocols described in Sparks (1975). Each pellet was irradiated with a primary radiation from a Cd-109 radioactive source for a period of 2500 seconds. For each pellet, two irradiations were done; sample alone and sample with a molybdenum target on top. These two measurements were then used to calculate the absorption corrections. The characteristic X-rays emitted by the elements in the sample were detected NaI(Tl) detector. The measurements were performed in vacuum using different filters (between the source and sample) for optimum detection of elements. A 0.05-mm-thick Ti filter was used in front of the source for Cr, Mn, Fe, Co, Ni, Cu and Zn with an applied voltage of 14 kV and a current 900 mA. For higher Z elements such as Pb, Bi, Ag and As, a Fe filter of 0.05 mm thickness was used at a voltage of 37 kV and 45 mA current. The X-ray fluorescence spectra were quantitatively analysed by the 'nEXt', system software runs under the Windows NTTM operating system integrated with the system. Acquiring spectra was the first and one of the most important steps performed in both qualitative and quantitative analysis. Acquisition parameters were used in the spectrum capture process to determine the spectrum profile and parameters. They were chosen to enhance the number of counts obtained for the elements of interest.

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CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 RESULTS

Table 4.1: Heavy metals of soil and vegetable samples from Saint Louis Farm, Owo Local Government Area

Sample	Mineral (mg/kg)										
	Cr	Zn	Mn	Fe	Ti	Sr	Al	Pb	Co	Cd	Cu
SL	191.52	184.74	1642.32	64282.61	16687.72	516.06	75021.09	ND	ND	ND	ND
SL_1	88.92	578.30	793.33	10265.37	3079.89	152.28	54312.12	ND	ND	ND	ND
SL_2	136.80	385.54	869.88	27399.95	4098.53	321.48	63407.34	ND	ND	ND	ND
SL_3	0.00	722.88	1391.80	29950.57	7100.52	482.22	61534.33	ND	ND	ND	ND

SL = soil sample from St. Louis; SL_1 = *Telfairia occidentalis* from St. Louis
SL_2 = *Amaranthum hybridus* from St. Louis; SL_3 = *Talinum triangulare* from St. Louis
ND = Not detected

Table 4.2: Heavy metals of soil and vegetable samples from Osuma Layout Farm, Owo Local Government Area

Sample	Mineral (mg/kg)										
	Cr	Zn	Mn	Fe	Ti	Sr	Al	Pb	Co	Cd	Cu
OL	109.44	80.32	1363.96	35736.63	10935.40	719.10	64407.34	ND	ND	ND	ND
OL_1	47.88	40.16	1579.69	25820.66	13134.46	676.80	46407.36	ND	ND	ND	ND
OL_2	27.36	72.29	772.45	21795.57	8958.04	516.06	50359.74	ND	ND	ND	ND
OL_3	150.48	377.50	3931.84	8406.56	2690.41	609.12	38290.97	ND	ND	ND	ND

OL = soil sample from Osuma Layout; OL_1 = *Telfairia occidentalis* from Osuma Layout
OL_2 = *Amaranthum hybridus* from Osuma Layout; OL_3 = *Talinum triangulare* from Osuma Layout
ND = Not detected

Table 4.3: Heavy metals of soil and vegetable samples from Water-Board Farm, Etsako-West Local Government Area

Sample	Mineral (mg/kg)									
	Cr	Zn	Mn	Fe	Ti	Sr	Al	Pb	Co	Cd	Cu
WB	61.56	0.00	104.39	23186.18	9754.98	118.44	68296.23	ND	ND	ND	ND
WB_1	123.12	441.76	974.26	2354.96	611.18	93.06	35227.48	ND	ND	ND	ND
WB_2	82.08	377.50	480.17	11704.90	5662.44	363.78	60079.31	ND	ND	ND	ND
WB_3	136.80	514.05	988.18	4661.00	1671.77	194.58	40322.71	ND	ND	ND	ND

WB = soil sample from Water-Board; WB_1 = *Telfairia occidentalis* from Water-Board
WB_2 = *Amaranthum hybridus* from Water-Board; WB_3 = *Talinum triangulare* from Water-Board
ND = Not detected

Table 4.4: Heavy metals of soil and vegetable samples from Iyerekhu Farm, Etsako-West Local Government Area

Sample	Mineral (mg/kg)										
	Cr	Zn	Mn	Fe	Ti	Sr	Al	Pb	Co	Cd	Cu
IY	54.72	0.00	807.24	22089.07	13595.85	186.12	48333.29	ND	ND	ND	ND
IY_1	164.16	795.17	1635.37	7295.47	3139.81	177.66	30984.10	ND	ND	ND	ND
IY_2	61.56	506.02	960.34	8588.25	5986.01	355.32	42984.08	ND	ND	ND	ND
IY_3	280.44	0.00	2776.64	2250.14	1264.31	186.12	42365.04	ND	ND	ND	ND

IY = soil sample from Iyerekhu; IY_1 = *Telfairia occidentalis* from Iyerekhu
IY_2 = *Amaranthum hybridus* from Iyerekhu; IY_3 = *Talinum triangulare* from Iyerekhu
ND = Not detected

Table 4.5: Transfer factor of the vegetable samples relative to their soil sources

Sample	Transfer Factor*						
	Cr	Zn	Mn	Fe	Ti	Sr	Al
SL_1	0.46	3.13	0.48	0.16	0.18	0.30	0.72
SL_2	0.71	2.09	0.53	0.43	0.25	0.62	0.85
SL_3	0.00	3.91	0.85	0.47	0.43	0.93	0.82
OL_1	0.44	0.50	1.16	0.72	1.20	0.94	0.72
OL_2	0.25	0.90	0.57	0.61	0.82	0.72	0.78
OL_3	1.38	4.70	2.88	0.24	0.25	0.85	0.59
WB_1	2.00	0.00	9.33	0.10	0.06	0.79	0.52
WB_2	1.33	0.00	4.60	0.50	0.58	3.07	0.88
WB_3	2.22	0.00	9.47	0.20	0.17	1.64	0.59
IY_1	3.00	0.00	2.03	0.33	0.23	0.95	0.64
IY_2	1.13	0.00	1.19	0.39	0.44	1.91	0.89
IY_3	5.13	0.00	3.44	0.10	0.09	1.00	0.88

SL_1 = *Telfairia occidentalis* from St. Louis;
SL_2 = *Amaranthum hybridus* from St. Louis;
SL_3 = *Talinum triangulare* from St. Louis
OL_1 = *Telfairia occidentalis* from Osuma Layout;
OL_2 = *Amaranthum hybridus* from Osuma Layout;
OL_3 = *Talinum triangulare* from Osuma Layout
WB_1 = *Telfairia occidentalis* from Water-Board;
WB_2 = *Amaranthum hybridus* from Water-Board;
WB_3 = *Talinum triangulare* from Water-Board
IY_1 = *Telfairia occidentalis* from Iyerekhu;
IY_2 = *Amaranthum hybridus* from Iyerekhu;
IY_3 = *Talinum triangulare* from Iyerekhu
*Transfer factor = $\frac{\text{concentration of metal in plant}}{\text{concentration of metal in soil}}$

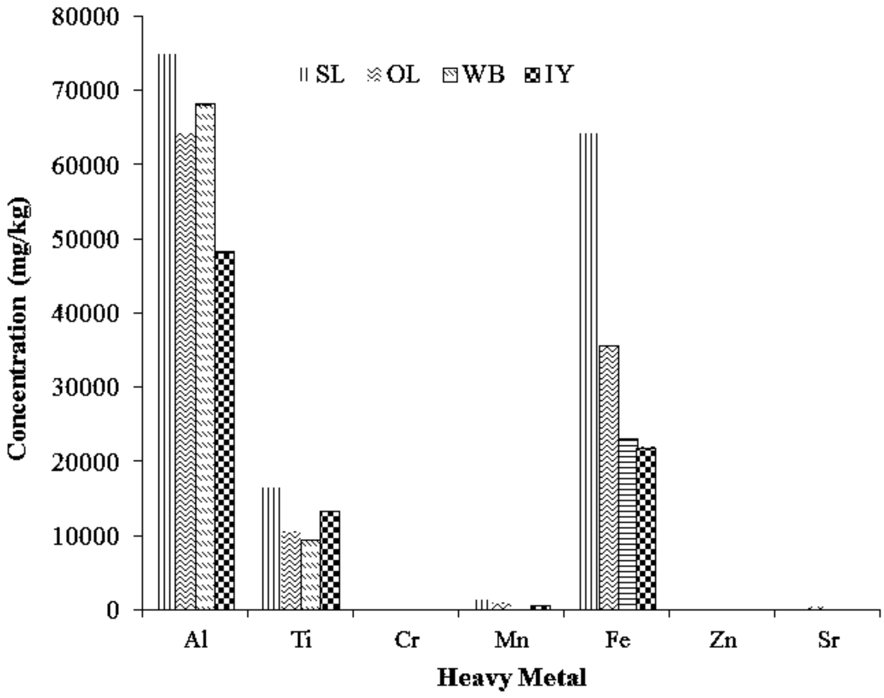

Figure 4.1: Bioavailability of heavy metals in the soil samples

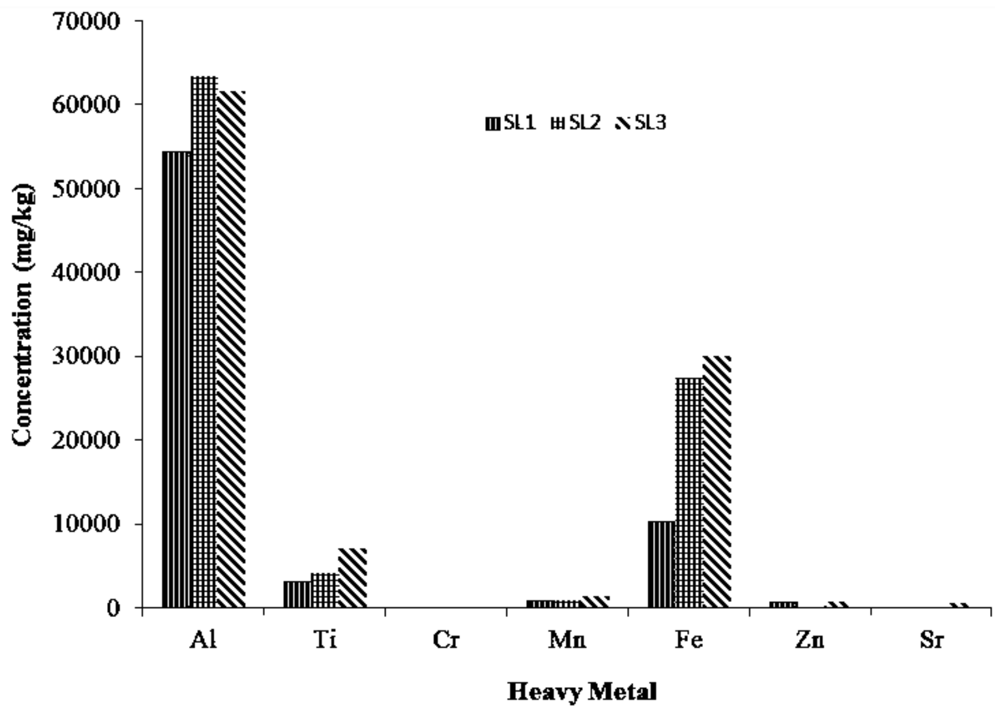

Figure 4.2: Bioaccumulation of heavy metals in the vegetable samples obtained from St. Louis Farm

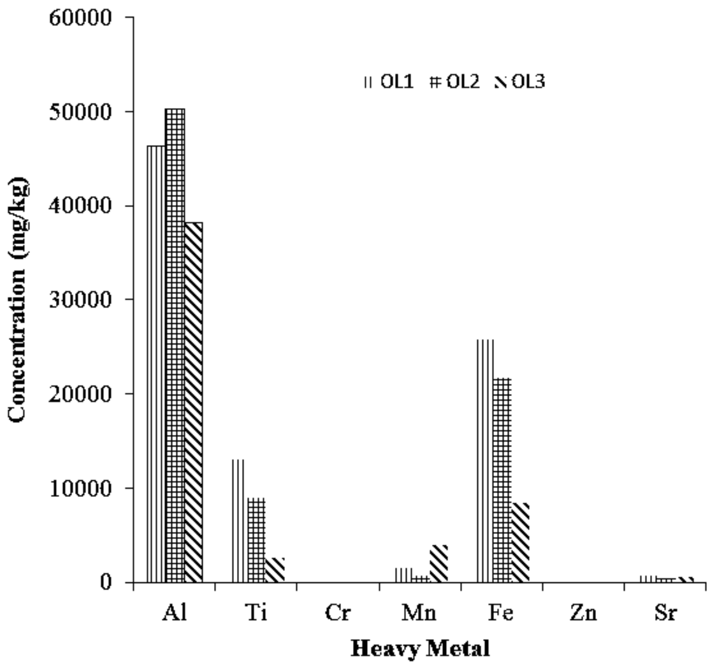

Figure 4.3: Bioaccumulation of heavy metals in the vegetable samples obtained from Osuma Layout Farm

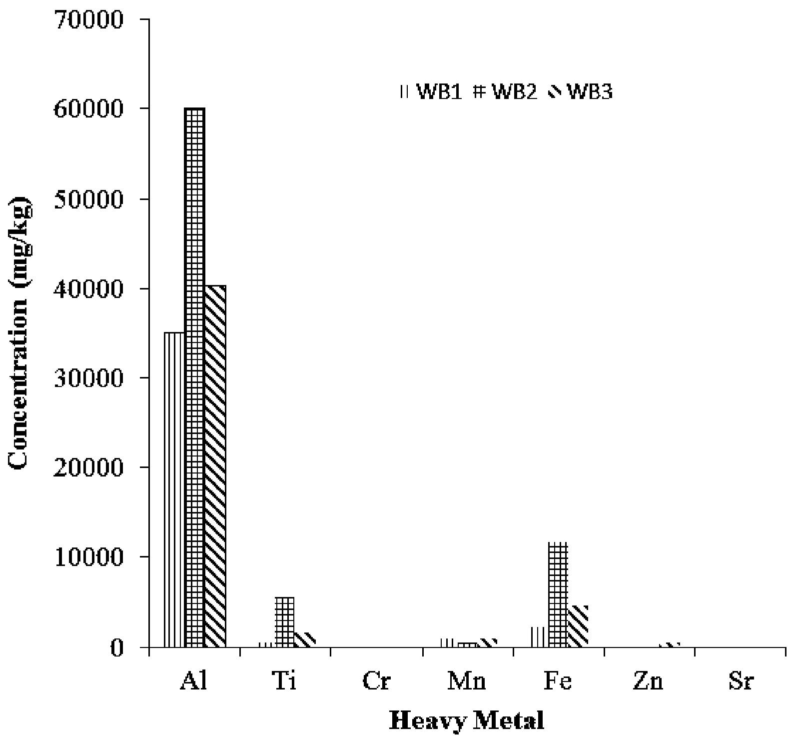

Figure 4.4: Bioaccumulation of heavy metals in the vegetable samples obtained from Water-Board Farm

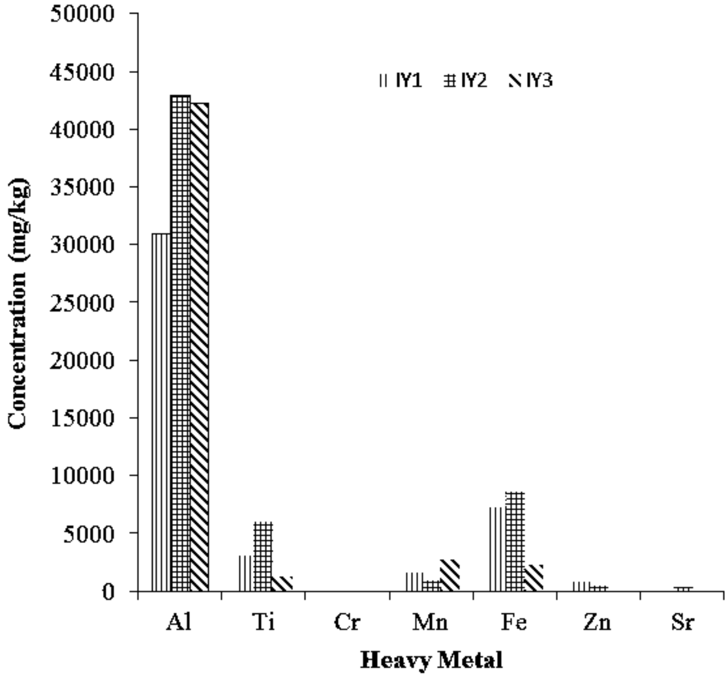

Figure 4.5: Bioaccumulation of heavy metals in the vegetable samples obtained from Iyerekhu Farm

4.2 DISCUSSION

4.2.1 Heavy Metal Concentrations

The concentrations (mg/kg) of chromium (Cr), zinc (Zn), manganese (Mn), iron (Fe), titanium (Ti), strontium (Sr) and aluminium (Al) of both soil and vegetable samples are depicted in Tables 4.1 – 4.4. However, toxic heavy metals, such as nickel (Ni), lead (Pb), cobalt (Co), cadmium (Cd) and copper (Cu) are not detected in both soil and vegetable samples. Generally, the concentrations of the metals in the soil samples are in the decreasing order: Al>Fe>Ti>Mn>Sr>Cr>Zn. A similar trend is observed for the decreasing order of concentrations of metals in the vegetable samples. A comparative bioavailability of the heavy metals among the soils samples obtained from four different farms, SL, OL, WB and IY is displayed in Figure 4.1. In addition, comparative bioaccumulations of the heavy metals among the vegetable samples, *Telfairia occidentalis*, *Amaranthus hybridus* and *Talinum triangulare* obtained from the different farms are displayed in Figures 4.2 – 4.5.

4.2.1.1 Chromium

Chromium (Cr) plays a vital role in the metabolism of cholesterol, fat, and glucose. Its deficiency causes hyperglycemia, elevated body fat, and decreased sperm count, while at high concentration it is toxic and carcinogenic (Chishti et al., 2011). Chromium (Cr) is more available in the soils than the vegetable samples obtained from both St. Louis and Osuma Layout farms, Owo LGA while an opposite trend is observed in the soil and vegetable samples obtained from Water-Board and Iyerekhu farms, Etsako-West LGA. These differences may be adduced to the varying abilities of plants to absorb minerals from the soils on which they grow. These varying abilities, according to Morgan and Connolly (2013) depend on: (i) root architecture induction of root-based transport systems; (ii) adaptation to changes in the climate and atmosphere; and (iii) enhanced absorption associated with beneficial soil microorganisms.

The Cr concentrations vary from 54.72 to 191.52 mg/kg among the soil samples and from 0.00 to 280.44 mg/kg among the vegetable samples. While there are relatively high transfer factors among the vegetable samples collected from Water-Board and Iyerekhu farms, there are relatively low transfer factors among the vegetable samples collected from St. Louis and Osuma Layout farms. The peak Cr (280.44 mg/kg) is observed in IY_3 (*Talinum triangulare* from Iyerekhu farm), followed by 150.48 mg/kg in OL_3 (*Talinum triangulare* from Osuma Layout farm) while SL_3 (*Talinum triangulare* from St. Louis farm) is exceptional with a nil value of Cr. This observation is a way to confirm that the same plant behaves differently on different soils and climatic conditions.

Adah et al. (2013) have reported low Cr concentrations of 0.1444, 0.1146, and 0.1184 mg/kg for the soils and 0.0268, 0.0090 and 0.0172 mg/kg for the leaves of *T. occidentalis, T. triangulare* and *A. hybridus* respectively. Anwanghe et al. (2013) have reported a range of values for chromium concentration in *T. occidentalis* (0.06-0.14 mg/kg), and *A. hybridus* (0.02-0.44 mg/kg). The EU Standards for the metal in soils and vegetables are 150 and 0.3 mg/kg, respectively (EU, 2006). All the samples (soils and vegetables) investigated in this study exceed the EU permissible limits for Cr except SL_3 (*Talinum triangulare* from St. Louis farm).

4.2.1.2 Zinc

After chromium (Cr), zinc (Zn) is the second least available metal in the soil and vegetable samples studied in this research work. Generally, Zn concentrations are higher in the vegetable samples than the soil with a slight deviation observed in OL_1 (*Telfairia occidentalis* from Osuma Layout farm) and OL_2 (*Amaranthum hybridus* from Osuma Layout farm). The Zn concentrations range from 0.00 to 184.74 mg/kg for soil samples and from 0.00 to 795.17 mg/kg for vegetable samples. Although the soils obtained from Water-Board and Iyerekhu farms do not possess Zn metal or its ore, the bioaccumulation of Zn in the tissues of the crop may be as a result of high uptake of Zn by the roots and its transportation to the leaves through transpiration process without the metal being remobilized through phloem. Due to their high absorption and bioaccumulation of Zn in the leaves, these vegetable samples can possible be applied in the phytoremediation of polluted soils.

Concentrations of Zn found in contaminated soils frequently exceed to those required as nutrients and may cause phytotoxicity. Zn concentrations in the range of 150–300 mg/kg have been measured in polluted soils (Devries et al., 2002). High levels of Zn in soil inhibit many plant metabolic functions; result in retarded growth and cause senescence. Zinc toxicity in plants limited the growth of both root and shoot (Choi et al., 1996).

The Zn concentrations in this study exceed the permissible limits of 60 mg/kg (WHO/FAO, 2007) with exceptions in WB (soil from Water-Board farm), IY (soil from Iyerekhu farm) and IY_3 (*Talinum triangulare* from Iyerekhu farm). Zn concentrations lower than the permissible limits of WHO/FAO (2007) have been reported for bitter leaf, water leaf and cabbage (Sobukola et al., 2010), although with a technique different from XRF used in this present research.

Zn is the least toxic and an essential element in human diet as it is required to maintain the functioning of the immune system. Zn deficiency in the diet may be highly detrimental to human health than too much Zn in the diet. The recommended dietary allowance for Zn is 15 mg/day for men and 12 mg/day for women Agency for Toxic Substances and Disease Registry, but high concentration of Zn in vegetables may cause vomiting, renal damage, cramps, etc (ATSDR, 2007).

4.2.1.3 Manganese

Manganese is a very essential trace heavy metal for plants and animals growth. Its deficiency produces severe skeletal and reproductive abnormalities in mammals. High concentration of manganese (Mn) causes hazardous effects on lungs and brains of humans (Jarup, 2003). The range of Manganese (Mn) concentrations in the soil samples is between 104.39 and 1642.32 mg/kg while in the vegetable samples is between 480.17 and 2776.64 mg/kg. Generally, Mn concentrations are higher in the tissues of the vegetable samples than in the soil samples except for slight deviations observed in SL_1 (*Telfairia occidentalis* from St. Louis farm), SL_2 (*Amaranthum hybridus* from St. Louis farm) and OL_2 (*Amaranthum hybridus* from Osuma Layout farm).

Higher proportions of Mn in the vegetable samples are another confirmation of high absorption of Mn by the tissues from the soils on which they grow and other non-anthropogenic sources. The high absorption rate of Mn by the tissue is coupled with low re-mobility of Mn through phloem to other organs after reaching the leaves. Excess Mn has been reported to inhibit synthesis of chlorophyll by blocking iron (Fe) process (Clarimont et al., 1986). Manganese toxicity is a relatively common problem compared to other micronutrient toxicity. It normally is associated with soils of pH 5.5 or lower, but can occur whenever the soil pH is below 6.0. Possible symptoms include chlorosis and necrotic lesions on old leaves, dark brown or red necrotic spots, accumulation of small particles of MnO_2 in epidermal cells of leaves or stems, often referred to as "measles", drying leaf tips, and stunted roots.

4.2.1.4 Iron

It is the most abundant and an essential constituent for all plants and animals. On the other hand, at high concentration, it causes tissues damage and some other diseases in humans. It is also responsible for anaemia and neurodegenerative conditions in human being (Fuortes and Schenck, 2000). The results show that iron (Fe) is the most abundant nutritionally essential metal in both soil and vegetable samples, ranging from 22089.07 to 64282.61 mg/kg in the soil samples and 2354.96 to 29950.57 mg/kg in the vegetable samples (Tables 4.1 – 4.4). The variations in the absorption of Fe from the soil by the plant's tissues are evident in the low Fe contents in the vegetable samples. These variations, from the present research work, are as low as one-tenth, one-sixth, one-fifth and one quarter of the original concentrations of Fe found in the soils for vegetable samples of *Talinum triangulare* from Iyerekhu farm (IY_3), *Telfairia occidentalis* from St. Louis farm (SL_1), *Talinum triangulare* in Water-Board (WB_3) and *Talinum triangulare* from Osuma Layout farm (OL_3) respectively.

The high concentrations of Fe in the soil samples may suggest a very rich anthropogenic source of Fe, which allows the percolation of Fe to the soil depths rather the surfaces. The low concentrations of Fe in the vegetable samples relative to its abundant availability in the soils, can be attributed to: (i) low absorption of Fe by the tissues of the vegetable samples, (ii) possible leaching of Fe from the soil surface and runoff during rainfall.

Fe is essential for the synthesis of chlorophyll and activates a number of respiratory enzymes in plants. The deficiency of Fe results in severe chlorosis of leaves in plants. High levels of exposure to iron dust may cause respiratory diseases such as chronic bronchitis and ventilation difficulties. The Fe contents of the vegetable samples and the soils on which they grow are higher than the FAO/WHO (2001) safe limit of 425.00 mg/kg.

4.2.1.5 Titanium

Next to the relative abundance of Fe in the soil and vegetable samples under investigation, titanium concentrations are more predominant in the soil samples than the vegetable samples except for a slight deviation observed in the samples collected from Osuma Layout farmland. This slight deviation, without doubt, might support two (2) postulations: (i) that the bioavailability of a metal in a soil does not determine its bioaccumulation in the tissues of the plants, and (ii) that soil is not the only source of metals available for plants. Other sources include the atmosphere, fertilizers and agrochemicals. The results obtained show that among the soil samples, the peak Ti (16687.72 mg/kg) and least Ti (9754.98 mg/kg) are observed in the soil samples collected from St. Louis farm and Water-Board farm respectively. Likewise, *Telfairia occidentalis* leaves collected from Osuma Layout farm and Water-Board farm possess the highest Ti (13134.46 mg/kg) and lowest Ti (611.18 mg/kg) respectively.

4.2.1.6 Strontium

Strontium concentrations in SL and OL (soils collected from St. Louis and Osuma Layout, Owo LGA) are generally higher than the concentrations in their vegetable samples (SL_1, SL_2, SL_3, OL_1, OL_2 and OL_3) whereas an opposite trend is observed between the soil and vegetable samples collected from Water-Board and Iyerekhu, Etsako-West LGA. Among the soil samples, the peak Sr concentration (719.10 mg/kg) is observed in the soil collected from the farm Osuma Layout farmland while the least concentration (118.44 mg/kg) in Water-Board farm. *Telfairia occidentalis* collected from Osuma Layout shows the highest bioaccumulation of Sr (676.80 mg/kg), followed by 609.12 mg/kg in *Talinum triangulare* from Osuma Layout while the least (93.06 mg/kg) in *Telfairia occidentalis* in Water-Board farmland. These differences can be attributed to the differences in soil properties, climatic changes, adaption to climatic changes and presence or absence of other plants.

Strontium (Sr), although considered as a food contaminant, it has no currently known biological role (ASTDR, 2007). The effect of strontium on bone is likely related to its similarity to calcium, a mineral with a known biological value. The average daily intake of strontium from the diet is estimated at only 1 to 5 mg (Pasco et al., 2000).

4.2.1.7 Aluminium

Aluminium (Al) is a toxic heavy metal, which finds its way into food chains through anthropogenic activities and sources. From Tables 4.1 – 4.4, the soil samples, SL, OL, WB and IY exhibit high content of Al, ranging from 48333.29 mg/kg in IY (soil from Iyerekhu farm) to 75021.09 mg/kg in SL (soil from St. Louis farm). Generally, the vegetable samples are lower in Al concentration than the soils on which they grow. The low transfer factor of Al (Table 4.5) is an indication of the low absorption of Al ions by the roots and mobility to the tissues. This, without doubt, suggests that bioaccumulation of Al in the *Telfairia occidefntalis*, *Amaranthus hybridus* and *Talinium triangulare* studied is mainly from anthropogenic sources. The least Al concentration (30984.10 mg/kg) is observed in IY_1 (*Telfairia occidefntalis* from Iyerekhu farm) while the peak concentration (63407.34 mg/kg) in SL_2 (*Amaranthus hybridus* from St. Louis farm).

4.2.2 Transfer Factors

Generally, transfer factor expresses the bioavailability of a metal at a particular position on a species of plant and it is calculated by dividing the concentration of metal in the vegetable by the metal concentration in soil (Kachenko *et al.*, 2006; Tsafe *et al.,* 2012). All the samples have significant differences in the transfer factors of metals relative to the availability of same metals in the soil (Table 4.5). The transfer factor ranges from 0.00 to 9.47. The peak transfer factor (9.47) of manganese (Mn) is observed in WB_3 (*Talinum triangulare* from Water-Board farm) followed by 9.33 observed in WB_1 (*Telfairia occidentalis* from Water-Board farm) and the least (0.00) is observed for Zn in vegetable samples of WB_1, WB_2, WB_3 (Water-Board farm) and IY_1, IY_2, IY_3 (Iyerekhu farm).

When transfer factor is less than one, it may be a probability that soil is the main source of metal bioaccumulation in plants. However, it is more revealing that, when the value is higher than one, the total concentrations of metals in soil do not necessary correspond to the metal bioavailability in plants. The bioavailability of heavy metals depends on a number of physicochemical properties such as pH, organic matter contents, cation exchange capacity, redox potential, soil texture and clay contents (Mwegoha and Kihampa, 2010).

The absorption of zinc (Zn) is completely null for all the vegetable samples obtained from Water-Board (WB_1, WB_2 and WB_3) and Iyerekhu (IY_1, IY_2 and IY_3), because zinc is not bio-available in their soil samples. The same phenomenon is observed in the uptake of chromium (Cr) by *Talinum triangulare* from Saint Louis farm (OL_3), Owo LGA.

Surprisingly, iron (Fe), which is the most abundant metal in both soil and vegetable samples, has transfer factor lower than one. Transfer factor of Fe is the highest (0.72) in *Telfairia occidentalis* from Osuma Layout farm (SL_1) and least (0.10) in both WB_1 (*Telfairia occidentalis* from Water-Board farm) and IY_3 (*Talinum triangulare* from Iyerekhu farm). This might be an indication of leaching or runoff during rainfall, which is an index of soil texture and erosion susceptibility.

Adah et al. (2013) have reported high transfer factors of heavy metals for *Talinum triangulare* and *Amaranthus hybridus* and low transfer factor for *Telfairia occidentalis*. Higher transfer coefficients reflect high soil contents or greater potentials of plants to absorb metals and bio-accumulate into tissues (Abah *et al.*, 2012). However, low transfer coefficients have been reported to indicate strong sorption of the metals to soil colloids (Kachenko *et al.*, 2006).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The concentrations of heavy metals in the leaves of pumpkin (*Telfairia occidentalis*), African spinach (*Amaranthus hybridus*) and waterleaf (*Talinum triangulare*) obtained from different farms in Owo (St. Louis farm and Osuma Layout farm) and Edo (Water-Board farm and Iyerekhu farm) axes have been studied in comparison with the soils on which they grow, using X-ray fluorescence (XRF) technique. The concentrations of chromium (Cr), manganese (Mn), iron (Fe), zinc (Zn), titanium (Ti), strontium (Sr) and aluminium (Al) in both soil and vegetable samples are quite higher than the permissible limits of WHO/FAO for soils and plants, except for Cr in SL_3 (*Talinum triangulare* from St. Louis farm), and Zn in WB (soil from Water-Board farm), IY (soil from Iyerekhu farm) and IY_3 (*Talinum triangulare* from Iyerekhu farm).

However, toxic heavy metals such as lead (Pb), cobalt (Co), copper (Cu), nickel (Ni) and cadmium (Cd) are not detected in both the soil and vegetable samples. Generally, the concentrations of the metals in the soil samples are in the decreasing order, Al>Fe>Ti>Mn>Sr>Cr>Zn. The vegetable samples show the same trend of metal concentrations.

In addition, the transfer factors of the vegetable samples are more pronounced than those of the soil samples. This suggests that the absorption and retention of metals by the tissues are very high, and that there are other non-anthropogenic sources of heavy metal contamination in the plants. In other words, bioaccumulation of metals in plants is, sometimes, independent of their bioavailability in the soil. The high transfer factors of pumpkin (*Telfairia occidentalis*), African spinach (*Amaranthus hybridus*) and waterleaf (*Talinum triangulare*) investigated in this research work can possibly be applied in phytoremediation of polluted soils.

5.2 RECOMMENDATIONS

Based on the findings from this research work, it is recommended that:

i. other methods of analysis of metals in soil and vegetable should be adopted for the same soil and vegetable samples;

ii. the eaters of these leafy vegetables should screened be for any incident of heavy metal contamination in the food chain;

iii. the vegetables studied in this research work could be applied for phytoremediation of polluted soils; and

iv. permissible limits by WHO/FAO be reviewed, using XRF technique as a means of comparing with the previous limits obtained with AAS technique.

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